III. Conclusions

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De la recerca sobre la síntesi i caracterització de complexos de Rh(I) i Ru(II) amb lligands amino- i fosfinoalquilpirazole que s'ha portat a terme, se'n poden deduir les conclusions que s'exposen a continuació i que s'agrupen d'acord amb els diferents apartats del capítol II.

Articles 1 i 2:

La síntesi dels lligands 3,5-dimetil-4-(etilamino)metilpirazole (HL^1) i 3,5-dimetil-4-(isopropilamino)metilpirazole (HL^2) amb un grup amino en posició 4 de l'anell pirazòlic, aporta uns nous lligands capaços de coordinar de forma exodidentada, i amb la qualitat de formar espècies "*zwitteriòniques*" pirazolat-amoni que proporcionen una important solubilitat en dissolvents polars als complexos dels que formen part. L'estudi de la seva complexació amb Rh(I) posa de manifest ambdues propietats, donant lloc als complexos dinuclears $[Rh(HL^1)(COD)]_2Cl_2$ (**1**) i $[Rh(HL^2)(COD)]_2Cl_2$ (**2**). Les estructures cristal·lines d'aquests dos complexos dinuclears permeten afirmar que els metalls presenten una geometria plano-quadrada, coordinant-se al lligand COD i a dues molècules de lligand pirazolat pont, formant un cicle de 6 membres Rh-N-N-Rh-N-N, en conformació de nau.

La reacció de complexació amb Rh(I) dels lligands prèviament desprotonats (L^1 i L^2), porta a la formació dels complexos neutres $[Rh(L^1)(COD)]_2$ (**5**) i $[Rh(L^2)(COD)]_2$ (**6**).

Tant els complexos iònics com els neutres, reaccionen amb monòxid de carboni per donar els complexos $[Rh(HL^1)(CO)_2]_2Cl_2$ (**3**), $[Rh(HL^2)(CO)_2]_2Cl_2$ (**4**), $[Rh(L^1)(CO)_2]_2$ (**7**) i $[Rh(L^2)(CO)_2]_2$ (**8**).

Tots els complexos presenten una solubilitat notable en dissolvents polars i, fins i tot, en aigua, essent insolubles en hidrocarburs saturats.

Els assaigs de catàlisi bifàsica amb el complex $[Rh(HL^2)(COD)]_2Cl_2$ (**2**), indiquen que aquest no és un bon catalitzador d'hidroformilació de l'1-octè, ja que tant els valors de conversió total com els de químio- i regioselectivitat són discrets.

Articles 3 i 4:

Tant els lligands 1-aminoalquilpirazole potencialment didentats (NN') com els potencialment tridentats (NN'N), reaccionen amb el dímer $[RhCl(COD)]_2$ per donar lloc a les espècies $Rh_2Cl_2(L)(COD)_2$ (L=NN' o NN'N). Les dades d'RMN indiquen que en aquests complexos, els lligands es troben coordinats de forma didentada. Els valors de conductivitat molar depenen del dissolvent, en solucions en MeCN són coherents amb una formulació no iònica dels complexos, mentre que en solucions en MeOH, se situen entre valors d'electròlits 1:1 i d'espècies no conductores. Totes aquestes dades són coherents amb l'existència d'un equilibri en solució entre la forma iònica $[Rh(L)(COD)]^+$ $[RhCl_2(COD)]^-$ i una forma neutra [Rh(COD)Cl][μ-(L)][Rh(COD)Cl]. Els espectres de masses d'Electroesprai i d'Ionització Química a Pressió Atmosfèrica confirmen la presència de les espècies iòniques $[Rh(L)(COD)]^+[RhCl_2(COD)]^-$ en solució, però el fet de no poder detectar l'espècie neutra, fa que l'equilibri proposat quedi només com a hipòtesi.

Per reacció del lligand bis[(3,5-dimetil-1-pirazolil)metil]etilamina (**1**) amb $[Rh(COD)(THF)_2][BF_4]$ s'obté el complex $[Rh(COD)(\mathbf{1})][BF_4]$ ([**2**][BF_4]), que per posterior tractament amb CO, es transforma en els complexos $[Rh(CO)_2(\mathbf{1})][BF_4]$ ([**3**][BF_4]) i $[Rh(CO)(\mathbf{1})][BF_4]$ ([**4**][BF_4]). Tant les dades estructurals obtingudes per difracció de Raigs X, com les d'RMN de tots aquests compostos, donen evidència de la flexibilitat del lligand (**1**) que adapta la seva forma de coordinació a la situació electrònica i estèrica al voltant de l'àtom de Rh(I). Així, en el complex [**2**][BF_4] en solució, el lligand **1** prefereix una forma d'enllaç didentada ([**2a**][BF_4]) per compensar l'efecte estèric del COD, mentre que en estat sòlid opta per una coordinació tridentada ([**2b**][BF_4]), minimitzant l'impediment estèric en el pla quadrat amb petites variacions de la distància d'enllaç Rh-N(pirazole). En presència d'un grup menys voluminós que el COD, els complexos [**3**][BF_4] i [**4**][BF_4] contenen el lligand **1** coordinat de forma tridentada, tant en solució com en estat sòlid, presentant configuració *fac* en el complex [**3**][BF_4] amb geometria de piràmide de base quadrada al voltant del Rh(I), i configuració *mer* en el complex [**4**][BF_4] de geometria plano-quadrada entorn del metall.

Els primers assaigs de l'activitat catalítica del complex [**2**][BF_4] en la reacció d'hidroformilació homogènia de l'estirè són poc positius, ja que tot i obtenir l'aldehid ramificat com a únic producte de la reacció, les conversions són molt baixes.

Article 5:

La síntesi del lligand N-P, 1-[(P-difenil)-2-fosfinoetil]-3,5-dimetilpirazole (**2**), aporta un nou component a la família de lligands de tipus fosfinopirazole potencialment hemilàbils. La reacció del lligand **2** i el lligand anàleg N-N' 1-[(N-etil)-2-aminoetil]-3,5-dimetilpirazole (**1**) amb $[Rh(COD)(THF)_2][BF_4]$, dóna lloc als complexos $[Rh(COD)(\mathbf{2})][BF_4]$ (**4**) i $[Rh(COD)(\mathbf{1})][BF_4]$ (**3**) caracteritzats estructuralment per difracció de Raigs X. De la comparació de la capacitat coordinativa dels lligands **1** i **2** amb Rh(I), s'observa que ambdós complexos presenten un procés fluxional en solució, que s'interpreta com a un comportament hemilàbil del lligand **1** en el complex **3** i com a una inversió nau-nau de l'anell de 6 membres format per la coordinació del lligand **2**, en el complex **4**.

La substitució del lligand COD en els complexos **3** i **4**, per CO dóna lloc als complexos $[Rh(CO)_2(\mathbf{1})][BF_4]$ (**5**) i $[Rh(CO)_2(\mathbf{2})][BF_4]$ (**6**).

En el cas del lligand **1** N-N', quan la reacció amb $[Rh(COD)(THF)_2][BF_4]$ es porta a terme en la proporció M/L 1/2, la segona molècula de lligand no és capaç de desplaçar el lligand COD per tal de coordinar-se al centre metàl·lic. Mentre que el lligand **2** N-P ho fa fàcilment, donant lloc al complex $[Rh(\mathbf{2})_2][BF_4]$ (**7**) que presenta les dues molècules del lligand en disposició *cis* en una geometria plano-quadrada al voltant del Rh(I).

En bombollejar CO en una solució del complex (**7**), s'obté el complex $[Rh(CO)(\mathbf{2})_2][BF_4]$ (**8**) que consisteix en un àtom de Rh(I) amb un entorn plano-quadrat amb els dos àtoms de fòsfor en disposició *trans*, on un dels lligands **2** està coordinat de forma didentada, mentre que l'altre ho està de forma monodentada. El procés fluxional observat per ^{1}H-RMN entre els modes d'enllaç k^2 i k^1 de les dues molècules del lligand **2**, posa de manifest el comportament hemilàbil d'aquest lligand.

De l'avaluació de l'activitat catalítica dels complexos (**4**) i (**7**), es conclou que aquests compostos no són bons catalitzadors de la reacció d'hidroformilació homogènia de l'estirè pel que fa a la conversió, però s'obté només l'aldehid ramificat com a producte de la reacció.

Article 6:

El lligand N-P, 1-[(P-difenil)-2-fosfinoetil]-3,5-dimetilpirazole (**1**), desplaça la trifenilfosfina del complex $[RuCl_2(PPh_3)_3]$ per donar lloc als complexos $[RuCl_2(PPh_3)(\mathbf{1})]$ (**2**) o $[RuCl_2(\mathbf{1})_2]$ (**3**), depenent de si es treballa en proporció M/L 1/1 o 1/2 respectivament. El complex **2** presenta una estructura amb una geometria entorn del Ru(II) de piràmide de base quadrada amb un 19% de distorsió cap a piràmide trigonal. El complex **3** presenta una geometria octaèdrica amb un eix de simetria C_2 que fa que les dues molècules de lligand **1** en disposició *cis*, siguin equivalents.

Quan es fa reaccionar el complex **2** de $16e^-$ amb acetilens, aquest descompon. Mentre que quan es porta a terme la mateixa reacció però amb el complex **3** de $18e^-$, s'obtenen nous metal·locumulens: el complex amb lligand vinilidè $[RuCl(\mathbf{1})_2(C{=}CHPh)][PF_6]$ (**6**) i els dos complexos amb lligands al·lenilidens $[RuCl(\mathbf{1})_2(C{=}C{=}CPhCH_3)][BF_4]$ (**4**) i $[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BF_4]$ (**5**). De la resolució de l'estructura cristal·lina per difracció de Raigs X del complex **5**, s'obté una cel·la unitat que consisteix en dos parells iònics independents, els cations dels quals corresponen a dos isòmers diferents. Cada un dels cations presenta una geometria octaèdrica distorsionada entorn del metall, on el lligand al·lenilidè i l'àtom de clor estan situats en disposició *trans*. La principal diferència entre els dos isòmers és la orientació de les cadenes etilèniques.

Com a conclusions generals del treball es pot dir que:

- Els lligands 4- i 1-aminoalquilpirazole i 1-fosfinoalquilpirazole es coordinen al Rh(I) de forma didentada, excepte en el cas dels lligands 1-aminoalquilpirazole de tipus NN'N que ho fan de forma di- o tridentada, depenent dels lligands que completen la coordinació del metall. Els lligands 4-aminoalquilpirazole es coordinen de forma exodidentada formant dímers de Rh(I), mentre que els lligands 1-amino- i 1-fosfinoalquilpirazole es coordinen pels diferents àtoms donadors (N o P) a un sol àtom de Rh(I) formant quelats. El lligand 1-[(P-difenil)-2-fosfinoetil]-3,5-dimetilpirazole es coordina al Ru(II) també de forma didentada.
- Tots els complexos de Rh(I) reaccionen amb CO donant lloc a complexos que contenen una o dues molècules d'aquest lligand. El complex $[RuCl_2(NP)_2]$, on NP=1-[(P-difenil)-2-fosfinoetil]-3,5-dimetilpirazole, reacciona amb acetilens per donar complexos amb lligands vinilidè i al·lenilidè.
- Els lligands 1-amino- i 1-fosfinoalquilpirazole presenten un cert caràcter hemilàbil en alguns dels complexos de Rh(I).
- Els estudis de l'activitat catalítica dels diferents complexos de Rh(I) en la reacció d'hidroformilació d'olefines en sistema bifàsic o en fase homogènia, donen uns resultats poc esperançadors.

IV. Articles

Article 1: Esquius, G.; Pons, J.; Yáñez, R.; Ros, J.; Solans, X.; Font-Bardía, M. *J. Organomet. Chem.* **2000**, *605*, 226.

Article 2: Esquius, G.; Pons, J.; Yáñez, R.; Ros, J.; Solans, X.; Font-Bardia, M. *Acta Cryst.* **2002**, *C58*, m133.

Article 3: Esquius, G.; Pons, J.; Yáñez, R.; Ros, J. *J. Organomet. Chem.* **2001**, *619*, 14.

Article 4: Mathieu, R.; Esquius, G.; Lugan, N.; Pons, J.; Ros, J. *Eur. J. Inorg. Chem.* **2001**, 2683.

Article 5: Esquius, G.; Pons, J.; Yáñez, R.; Ros, J.; Mathieu, R.; Donnadieu, B.; Lugan, N. *Eur. J. Inorg. Chem.* Acceptat per a la seva publicació (Ref. I02215).

Article 6: Esquius, G.; Pons, J.; Yáñez, R.; Ros, J.; Mathieu, R.; Donnadieu, B.; Lugan, N. *J. Chem. Soc., Dalton Trans.* En preparació.

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Synthesis and reactivity of 3,5-dimethyl-4-aminomethylpyrazole ligands. An entry to new water-soluble pyrazolate rhodium(I) complexes

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Abstract

The new pyrazoles 3,5-dimethyl-4-(ethylamino)methylpyrazole (HL^1) and 3,5-dimethyl-4-(isopropylamino)methylpyrazole (HL^2), both containing aminoalkyl groups at position 4 have been prepared by aminoalkylation of 3,5-dimethylpyrazole and by the reaction between 1-chloromethyl-3,5-dimethylpyrazolium chloride and NH_2R amines. The reaction between HL^1, HL^2 and $[RhCl(COD)]_2$ resulted in complexes of formula $[Rh_2(HL^1)_2(COD)_2]Cl_2$ (**1**) and $[Rh_2(HL^2)_2(COD)_2]Cl_2$ (**2**), which contained the pyrazole ligands in the 'zwitterionic' pyrazolate-ammonium forms. The X-ray structure analysis of **2** confirmed the neutral nature of bridging-pyrazolate ligands and revealed that **1** and **2** belonged to the $[Rh_2(Pz)_2L_2]$ family of compounds. The same reaction with two equivalents of NaOMe resulted in neutral pyrazolate complexes $[Rh_2(L^1)_2(COD)_2]$ (**5**) and $[Rh_2(L^2)_2(COD)_2]$ (**6**). The reaction between both cationic and neutral pyrazolate complexes and a 1:1 $CO–H_2$ mixture (20 atm) led to the dinuclear pyrazolate-bridged tetracarbonyl compounds **3**, **4**, **7** and **8** in good yields. Tetracarbonyl complexes **3** and **4** were not isolated in pure state. All the complexes synthesized are soluble in polar solvents such as water.

Keywords: Rhodium complexes; Pyrazolate complexes; Rhodium-pyrazolate complexes; Pyrazoles; Aminoalkylation of pyrazoles

1. Introduction

The pyrazolyl group is a remarkable versatile source of coordination ligands [1]. While monodentate pyrazole ligands are common, anionic pyrazolates frequently act as bridges between two metals [2]. Research on pyrazole-derived ligands, which has rapidly increased in the last years, has focused on the design of models of metalloproteins and the application of pyrazolylborates as organometallic ligands [3]. Both areas of research have shown the immense possibilities of pyrazole-based polydentate ligands. Aminoalkylpyrazoles have also been studied and several transition metal complexes have been prepared. So far, two families of aminoalkylpyrazole derivatives have been synthesized: *N*-aminoalkylpyrazoles [4] and 3,5-bis(aminomethyl)-pyrazoles [5]. The former are neutral polydentate ligands [4] and the later behave as tetradentate anionic bridging ligands [5], but, to our knowledge 4-alkylaminopyrazoles have not been reported. Related 4-hydroxymethylpyrazoles have been previously described and applied as intermediates in photographic couplers [6].

Pons et al. reported the synthesis of transition metal complexes with the dinucleating 3,5-bis(2-pyridyl)-pyrazole ligand [7]. Our aim is to perform the design and synthesis of new organometallic ligands based on pyrazoles and the preparation of water-soluble organometallic complexes. Whereas water-soluble P-ligand containing catalysts are well known, water-soluble systems with N-ligands are uncommon [8]. Moreover, pyrazole-derived ligands have attracted

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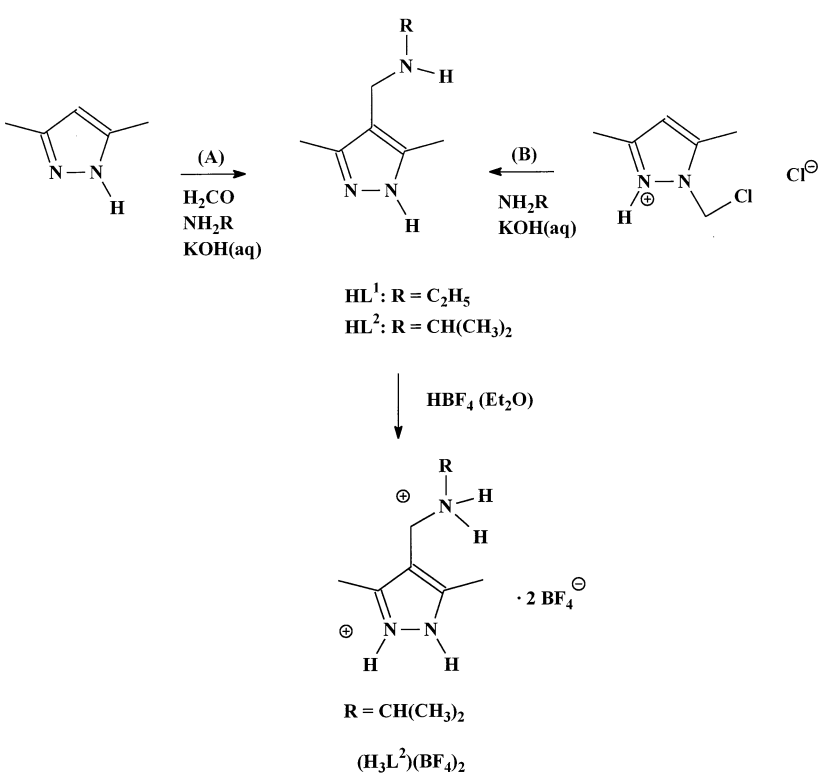
considerable interest thanks to their catalytic activity [9]. Here, we report the synthesis of new pyrazoles with an aminomethyl group at the position 4: 3,5-dimethyl-4-(ethylamino)methylpyrazole (HL^1) and 3,5-dimethyl-4-(isopropylamino)methylpyrazole (HL^2). These ligands have two main properties: they can be deprotonated so that they can bridge two metal centers and they have an amino group which can make complexes soluble in water. We also report the study of their reactivity with $[RhCl(COD)]_2$, which results in water-soluble pyrazolate rhodium(I) complexes.

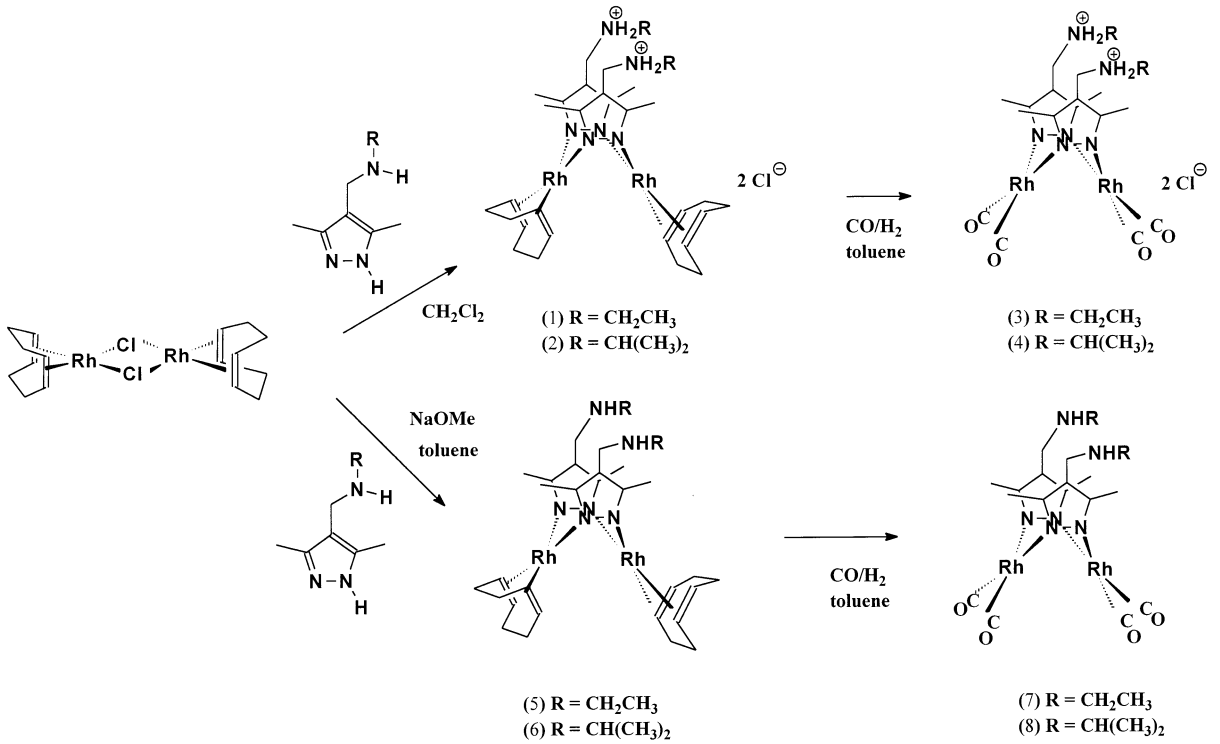
2. Results and discussion

The new pyrazole ligands (HL^1) and (HL^2) were prepared through two different routes (A and B) which involve the alkylaminoalkylation of the dimethylpyrazole at position 4 (Scheme 1). Once a mixture of 3,5-dimethylpyrazole, paraformaldehyde, NH_2R (R = Et and *i*-Pr) and KOH in water had been refluxed for 48 h, extracted with $CHCl_3$ and evaporated to dryness, pyrazoles HL^1 and HL^2 were obtained in 75% yield (route A). A more efficient method was the reaction between 1-chloromethyl-3,5-dimethylpyrazolium chloride, excess of NH_2R (R = Et and *i*-Pr) and KOH in water, at reflux for 12 h. The mixture was extracted with $CHCl_3$ and evaporated to dryness to give products in 90% yield (route B). The reaction between 2-hydroxymethyl-3,5-dimethylpyrazole and NH_2R amines, previously reported by Driessen et al. [4], yields 2-alkylaminomethyl-3,5-dimethylpyrazoles, which are the result of the amino-dehydroxylation of the hydroxymethyl group. Synthesis of HL^1 and HL^2 are particular examples of the Mannich reaction, which involves the alkylaminomethylation of the dimethylpyrazole at position 4 [10]. Via B, formaldehyde comes from 1-chloromethyl-3,5-dimethylpyrazolium chloride, which is probably transformed to 2-hydroxymethyl-3,5-dimethylpyrazole in a basic medium. The hydroxymethylpyrazole derivative is the adduct of pyrazole with formaldehyde [11] and, in reflux conditions, presumably decomposes into those molecules. The formaldehyde–amine mixture at reaction conditions should lead to the aminomethylation of pyrazole in position 4, resulting HL^1 and HL^2, which are the thermodynamically stable products of the reaction.

HL^1, isolated as a white solid and HL^2 as an oil, were characterized by spectroscopic methods. C, H, N elemental analyses of HL^1 were consistent with the formation of 3,5-dimethyl-4-(ethylamino)methylpyrazole, whereas C, H, N elemental analyses of HL^2 showed a significant presence of water. The CH_2NHR signals at 3.54 (s) and 3.39 (s) ppm in the ^{1}H-NMR spectra of HL^1 and HL^2, respectively are spectroscopic evidences of the formation of new pyrazoles. Signals of the methylenic CH_2NHR carbon at 43.4 and 39.4 ppm in the ^{13}C-NMR spectra of HL^1 and HL^2 lead to the same



Scheme 1.



Scheme 2.

conclusion. Mass spectra of HL^1 and HL^2 showed the molecular peaks at m/z: 153 $[HL^1]^+$ and 167 $[HL^2]^+$, respectively, together with other fragments of pyrazoles. Reaction between HL^2 and an excess of HBF_4 in Et_2O yielded $[H_3L^2][BF_4]_2$ as a white solid whose C, H, N and spectroscopic data were consistent with the formation of 3,5-dimethyl-4-(isopropylammonium)methylpyrazolium tetrafluoroborate salt.

The reaction between HL^1, HL^2 and an equimolar amount of $[RhCl(COD)]_2$ in CH_2Cl_2 at room temperature resulted in $[Rh(HL^1)(COD)]_2Cl_2$ (**1**) and $[Rh(HL^2)(COD)]_2Cl_2$ (**2**), respectively in quantitative yields (Scheme 2). The orange complexes **1** and **2** are very soluble in chlorinated hydrocarbons, moderately soluble in alcohols and water and insoluble in hydrocarbons. Elemental analyses and spectroscopic data of **1** and **2** revealed the neutral 'zwitterionic' pyrazolate-ammonium form of ligands. The neutral nature of pyrazole ligands involves the presence of two chlorides per molecule as counterions. Complexes **1** and **2** belong to the $[Rh(Pz)L_2]_2$ (Pz = pyrazolate anion, L = alkene, CO or PR_3 ligand) family of compounds [12] with Rh(I) atoms coordinated with terminal two-electron neutral ligands and to two bridging pyrazolate anions in square-planar environments [13]. IR spectra of compounds **1** and **2** displayed representative bands of pyrazolate-ammonium ligands, together with the expected COD absorptions [14]. The ^{1}H-NMR spectra of **1** and **2** showed signals of ligands, with the significant CH_2NH_2R protons at 3.48 and 3.49 ppm, respectively. The CH_2NH_2R carbon was observed at 42.9 and 36.3 ppm in the ^{13}C-NMR spectra of **1** and **2**.

Orange crystals of **2**, suitable for an X-ray study, were obtained from a dichloromethane–hexane mixture. The crystal structure of complex **2** contains dinuclear $[Rh_2(HL^2)_2(COD)_2]^{2+}$ (Fig. 1). Selected bond lengths and angles for compound **2** are shown in Table 1. Each rhodium center is coordinated with two pyrazolate ligands and with a chelated COD ligand in a η^4 form. The Rh–N(pyrazolate) bond distances average is 2.066(3) Å, whereas the mean distance of Rh–C(COD) bond lengths is 2.104(4) Å. A Rh–Rh distance of 3.116(3) Å can be compared to the one found in other dinuclear rhodium(I) compounds such as $[Rh_2(DMPz)_2(COD)_2]$ (DMPz = 3,5-dimethylpyrazolate) (1.15 Å) [15] but is shorter than the one found in the $[Rh_2(Pz)_2(COD)_2]$ (Pz = pyrazolate ligand) complex (3.267 Å) [16]. This metal–metal length is consistent with the usual non-bonded dinuclear Rh(I) system bridged by three-electron ligands. The N1–Rh1–N2 and N2–Rh2–N5 angles, 82.2(2) and 82.3(1)°, respectively, are smaller than those of the related compound $[Rh_2(DMPz)_2(COD)_2]$ (84.4 and 85.0°) [15] and significantly smaller than those found in $[Rh_2(Pz)_2(COD)_2]$ (88.4°) [16]. According to the coordination of metals to N(pyrazolates) atoms and to the midpoints (Mp) of olefinic C=C bonds of COD ligands, Rh1 and Rh2 atoms display a square-planar geometry. Thus, Rh1

and Rh2 deviate from its NN′MpM′p mean coordination plane (formed by the donor N atoms of pyrazolate ligands and by the midpoints of the olefinic C=C bonds of the COD ligands) in 0.34 and 0.15 Å, respectively. COD ligands are orthogonal to these planes. Finally, pyrazolate ligands bear methyl groups at position 3 and position 5 and an (isopropylammonium)methyl group at position 4. N–N bond lengths are of 1.354(4) and 1.362(4) Å, respectively. These values are lower than those found in other μ-pyrazolate rhodium(I) compounds (1.37 Å) [15]. The (ammonium)methyl group shows characteristic bond lengths: C12(pyrazole)–C15, 1.478(5); C15–N6, 1.485(5); and N6–C16(isopropyl): 1.490(5) Å. The C15–N6–C16 angle is 112.8(3)°, which is consistent with a distorted tetrahedral geometry of the N6(ammonium) atom. Two types of chloride anions Cl1 and Cl2 are found in the structure. Cl1 shows N3–Cl1 and N6–Cl1 distances of 3.17 and 3.10 Å, respectively, which suggests the presence of hydrogen bonds with ammonium NH_2R groups. Cl2 does not interact with the molecular structure of the rhodium complex.

The reaction between the compounds **1** and **2** and bubbling CO in CH_2Cl_2 at room temperature resulted in $[Rh_2(HL^1)_2(CO)_4]$ (**3**) and $[Rh_2(HL^2)_2(CO)_4]$ (**4**) solutions, which reverted to reactants if the solvent was evaporated in vacuo. When the CH_2Cl_2 solutions of **1** and **2** were placed in an autoclave pressurized with 20 atm of a 1:1 $CO–H_2$ mixture for 15 h at room temperature, orange–yellow compounds **3** and **4** were obtained in 65% yield (from ^{1}H-NMR spectra). These compounds are very soluble in chlorinated hydrocarbons, alcohols and water, but insoluble in hexane. The IR spectra of compounds **3** and **4** display sets of ν(CO) bands with the characteristic pattern of a $Rh_2(L)_2(CO)_4$ (L = three-electron bridging ligand) [17]. The ^{1}H- and ^{13}C-NMR spectra of products **3** and **4** show duplicity of signals (65:35 ratio) which indicate the presence of non reacted compounds **1** and **2**. ^{1}H-NMR spectra display signals of alkylammonium-pyrazolate hydrogens with CH_2NHR resonances at 3.58 and 3.61 ppm, respectively. ^{13}C-NMR spectra of compounds **3** and **4** show doublets of CO ligands at 185.5 and 185.8 ppm with $J_{C–Rh}$ of 69.2 Hz [12] and representative resonances of bridging ligands. The CH_2NHR signals are observed at 42.8 and 36.4 ppm, respectively.

The reaction between HL^1 and equimolar amounts of $[RhCl(COD)]_2$ and NaOMe in refluxing toluene for 1.5 h resulted in orange–yellow compounds **5** and **6** in quantitative yield (Scheme 2). Elemental C, H, N analyses and spectroscopic data support the formation of the products $[Rh_2(L^1)_2(COD)_2]$ and $[Rh_2(L^2)_2(COD)_2]$ which denote the presence of the 3,5-dimethyl-4-(ethylamino)methylpyrazolate and 3,5-dimethyl-4-(isopropylamino)methylpyrazolate as bridging anions. Compounds **5** and **6** are very soluble in chlorinated hydrocarbons and alcohols, moderately soluble in water and insoluble in hexane The IR spectra of **5** and **6** show patterns of bands in the ν(NH) region, which are consistent with the presence of secondary aminomethyl groups [18]. H- and ^{13}C-NMR spectra display the expected signals of pyrazolate and COD ligands supporting the dinuclear nature of **5** and **6** [14]. The reaction between **5** and **6** and a 1:1 $CO–H_2$ mixture at 20 atm resulted in orange–yellow compounds $[Rh_2(L^1)_2(CO)_4]$ (**7**) and $[Rh_2(L^2)_2(CO)_4]$ (**8**) in quantitative yields. Complexes **7** and **8** are very soluble in chlorinated hydrocarbons, moderately soluble in alcohols and water and

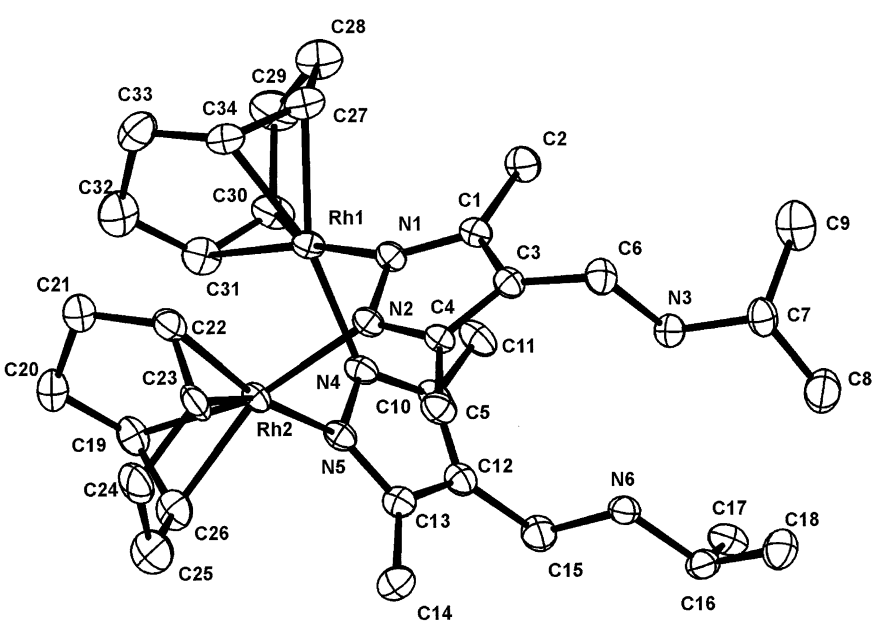


Fig. 1. Molecular structure of the cation complex in **2**.

Table 1
Selected distances (Å) and angles (°) of compound **2**

Rh1–N4	2.060(3)
Rh1–N1	2.065(3)
Rh1–C30	2.097(4)
Rh1–C34	2.105(4)
Rh1–C27	2.109(4)
Rh1–C3	2.112(4)
Rh1–Rh2	3.116(3)
Rh2–N5	2.067(3)
Rh2–N2	2.067(3)
Rh2–C23	2.087(4)
Rh2–C22	2.105(4)
Rh2–C19	2.106(4)
Rh2–C26	2.107(4)
N1–C1	1.331(5)
N1–N2	1.354(4)
N2–C4	1.319(5)
N3–C7	1.484(5)
N3–C6	1.487(6)
N4–C10	1.321(4)
N4–N5	1.362(4)
N5–C13	1.319(4)
N6–C15	1.485(5)
N6–C16	1.490(5)
C1–C3	1.372(6)
C3–C4	1.381(5)
C3–C6	1.478(6)
C10–C12	1.375(5)
C12–C13	1.378(5)
C12–C15	1.478(5)
N4–Rh1–N1	82.2(2)
N5–Rh2–N2	82.30(14)
C1–N1–N2	107.8(3)
N2–N1–Rh1	114.8(2)
C4–N2–N1	109.2(3)
C4–N2–Rh2	131.7(3)
N1–N2–Rh2	115.7(2)
C7–N3–C6	113.9(3)
C10–N4–N5	108.3(3)
C10–N4–Rh1	132.0(2)
N5–N4–Rh1	116.4(2)
C13–N5–N4	108.5(3)
C13–N5–Rh2	133.3(2)
N4–N5–Rh2	113.8(2)
C15–N6–C16	112.8(3)
N1–C1–C3	108.9(3)
C1–C3–C4	105.8(3)
C1–C3–C6	127.1(4)
C4–C3–C6	127.1(4)
N2–C4–C3	108.4(3)
C3–C6–N3	113.5(3)
N4–C10–C12	108.7(3)
C10–C12–C13	105.9(3)
C10–C12–C15	126.6(3)
C13–C12–C15	127.5(4)
N5–C13–C12	108.6(3)
C12–C15–N6	114.0(3)

insoluble in hexane. Elemental C, H, N analyses and IR, ^{1}H- and ^{13}C-NMR spectroscopies identified the compounds **7** and **8**, whose IR spectra in the ν(CO) region show absorptions with the same pattern as complexes **3** and **4** [17]. Unlike the NMR spectra of compounds **3** and **4**, the H- and ^{13}C-NMR spectra of **7** and **8** only show the signals of the carbonyl derivatives $[Rh_2(L^1)_2(CO)_4]$ and $[Rh_2(L^2)_2(CO)_4]$. Characteristic ^{1}H-NMR signals for **7** and **8** are: 9.18 and 8.92 (N*H*R) ppm and 3.58 and 3.58 (CH_2NHR) ppm, respectively. On the other hand, the ^{13}C-NMR spectrum of **7** and **8** show signals of *C*O ligands at 185.6 (d, $J_{C-Rh} = 66.0$ Hz) ppm and of the *C*H_2NHR group at 42.9 and 36.4 ppm, respectively.

3. Conclusion

The aim of this work was the synthesis of the new pyrazoles (HL^1) and (HL^2), which contain an aminomethyl group in position 4, and the study of their coordination to rhodium(I) centers. The new ligands form dinuclear rodium(I) complexes bridged by anionic pyrazolate ligands. Aminomethyl groups of pyrazoles (HL^1) and (HL^2) do not interact with metals and they can be found as ammonium cations or in a neutral form. The resulting complexes show remarkable solubility in polar solvents and in water but are insoluble in saturated hydrocarbons. These results raise new possibilities of pyrazol based ligands incorporating water-soluble aminomethyl groups as coordinating ligands. The synthesis, structural studies and research on the applications of new transition-metal complexes with pyrazole-based ligands are in course.

3.1. Experimental

All the reactions were performed in dinitrogen following standard Schlenck techniques. Solvents were dried and stored in dinitrogen. IR spectra were recorded on Perkin–Elmer models 1710-FT and 2000 spectrophotometers with KBr pellets or in CH_2Cl_2 solutions. The ^{1}H-NMR spectra were measured on a Bruker AC 250 spectrometer in $CDCl_3$ solutions at room temperature (r.t.) (^{1}H, 250 MHz; ^{13}C, 62 MHz). ^{1}H chemical shifts were referenced to the residual signals of the protons of the solvents and were quoted in ppm downfield from TMS. ^{13}C chemical shifts were calibrated against the deuterated solvent multiplet and referenced to TMS. Mass spectra were measured on a Hewlett–Packard HP-5989 A apparatus. Elemental analyses were performed by the staff of the Chemical Analysis Service at the Universitat Autònoma de Barcelona. $[RhCl(COD)]_2$ [19], and 2-chloromethyl-3,5-pyrazolium chloride [20] were prepared according to literature methods.

3.2. 3,5-dimethyl-4-(ethylamino)methylpyrazole (HL^1) and 3,5-dimethyl-4-(isopropylamino)methylpyrazole (HL^2)

Method A: 3,5-dimethylpyrazole (1.00 g, 16 mmol), paraformaldehyde (0.48 g, 16 mmol), KOH (0.9 g, 16 mmol) and amine (ethylamine 70% in water, 1.20 g, 20 mmol; isopropylamine, 1.3 g, 20 mmol) were dissolved in 50 ml of water and refluxed for 48 h. The mixture was extracted with $CHCl_3$ and dried with anhydrous $MgSO_4$. The solid was separated by filtration and the colorless filtrate was concentrated to dryness in vacuo. HL^1 was isolated as a white solid and HL^2 as an oil. Yields were ca 75%.

Method B: A mixture of 1-chloromethyl-3,5-dimethylpyrazolium chloride (1.26 g, 7 mmol) and KOH (0.45 g, 8 mmol), dissolved in 15 ml of water, was added to a 60 ml of water containing the amine (ethylamine 70% in water, 2.70 g, 42 mmol; isopropylamine, 2.48 g, 42 mmol) and KOH (2.36 g, 42 mmol). The resulting mixture was refluxed for 15 h and then extracted with $CHCl_3$. The solution was dried with anhidrous $MgSO_4$ and filtered off. The filtrate was evaporated to dryness in vacuo. HL^1 was isolated as a white solid and HL^2 as an oil. Yields were ca 90%.

(HL^1): IR (KBr): 3222 (ν_{NH}), 2975–2816 (ν_{NH}) + (ν_{CH}), 1592 cm^{-1} (ν_{CN}). ^{1}H-NMR ($CDCl_3$): $\delta = 6.90$ (br, 1H, N*H*Et), 3.54 (br s, 2H, CH_2NHEt), 2.62 (q, $^3J_{HH} = 7.3$ Hz, 2H, NCH_2CH$_3$), 2.21 (s, 6H, CH_3), 1.11 (t, $^3J_{HH} = 7.3$ Hz, 3H, NCH$_2$CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 142.6$ (C(CH$_3$)), 114.1 (C(CH$_2$NHEt)), 43.4 (CH_2NHEt), 42.1 (CH_2CH$_3$), 15.1 (CH$_2$CH$_3$), 10.7 (C(CH_3)). $C_8H_{15}N_3$ (153.22): Calc.: C, 62.74; H, 9.80; N, 27.45. Found: C, 62.03; H, 9.32; N, 27.07. EI-MS (70 eV); m/z: 153 $[HL^1]^+$.

(HL^2): IR (KBr): 3231 (ν_{NH}), 2973–2817 (ν_{NH}) + (ν_{CH}), 1594 cm^{-1} (ν_{CN}). ^{1}H-NMR ($CDCl_3$): $\delta = 6.50$ (br, 1H, N*H*i-Pr), 3.39 (br s, 2H, CH_2NHi-Pr), 2.69 (sp, $^3J_{HH} = 6.2$ Hz, 1H, NCH(CH$_3$)$_2$), 2.04 (s, 6H, CH_3), 0.93 (d, $^3J_{HH} = 6.2$ Hz, 6H, NCH(CH_3)$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 141.8$ (C(CH$_3$)), 113.2 (C(CH$_2$NHi-Pr)), 47.6 (CH(CH$_3$)$_2$), 39.2 (CH_2NHi-Pr), 22.2 (CH(CH_3)$_2$), 10.1 (C(CH_3)). EI-MS (70 eV); m/z: 167 $[HL^2]^+$.

3.3. 3,5-dimethyl-4-(isopropylammonium)methylpyrazolium tetrafluoroborate $[H_3L^2][BF_4]_2$

HBF_4 (0.36 ml, 4 mmol, 54% in Et_2O) was slowly added to a solution of HL^2 (0.50 g, 3 mmol) in 20 ml of CH_2Cl_2 with stirring at r.t.. The mixture was stirred for 1 h and the white precipitate was filtered off, washed with Et_2O and dried in vacuo. Yield was 95%. IR (KBr): 2982 (ν_{NH}), 2679 (ν_{NH}), 1594 (ν_{CN}), 1036 (ν_{BF}) cm^{-1}. ^{1}H-NMR (CD_3OD): $\delta = 7.59$ (br, NH^+), 3.87 (br s, 2H, CH_2NHi-Pr), 3.16 (sp, $^3J_{HH} = 6.5$ Hz, 1H, NCH(CH$_3$)$_2$), 2.07 (s, 6H, CH_3), 1.09 (d, $^3J_{HH} = 6.2$ Hz, 6H, NCH(CH_3)$_2$). ^{13}C{^{1}H}-NMR (CD_3OD): $\delta = 147.7$ (C(CH$_3$)), 110.5 (C(CH$_2$NHi-Pr)), 52.7 (CH(CH$_3$)$_2$), 37.4 (CH_2NHi-Pr), 18.9 (CH(CH_3)$_2$), 9.6 (C(CH_3)). $C_9H_{17}N_3 \cdot 2HBF_4$ (342.88): Calc.: C, 31.53; H, 5.59; N 12.26. Found: C, 32.71; H, 5.89; N, 12.64.

3.4. $[Rh(HL^1)(COD)]_2Cl_2$ (**1**) and $[Rh(HL^2)(COD)]_2Cl_2$ (**2**)

A total of 0.08 g (0.16 mmol) of [RhCl(COD)]$_2$, dissolved in 5 ml of CH_2Cl_2, was added to a solution of 0.32 mmol of the corresponding aminomethylpyrazole (0.08 g of HL^1 or 0.09 g of HL^2) in 5 ml of CH_2Cl_2 and the mixture was stirred for 15 h. The solvent was evaporated to dryness in vacuo and the residue was washed with Et_2O and dissolved in a minimum amount of CH_2Cl_2. Compounds **1** and **2** were precipitated by adding hexane to the solution. Yellow–orange solids were filtered off and dried in vacuo. Yields were 99%.

1: IR (KBr): 2916 (ν_{NH}) + (ν_{CH}), 1598 (ν_{CN}), 1299 (β_{CH}) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 8.96$ (br, 2H, NH_2Et), 4.48–4.42 (m, 4H, CH (COD)), 3.48 (br s, 2H, CH_2NH$_2$Et), 3.00–2.86, 2.12–1.99 (m, 8H, CH_2 (COD)), 2.61 (br, 8H, NCH_2CH$_3$ + CH_3),. 1.45 (t, $^3J_{HH} = 7.3$ Hz, 3H, NCH$_2$CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 149.4$ (C(CH$_3$)), 105.4 (C(CH$_2$NH$_2$Et)), 81.6, 81.4, 80.1, 79.9 (CH (COD)), 42.9 (CH_2NH$_2$Et), 40.3 (CH_2CH$_3$), 31.5, 30.7 (CH_2 (COD)), 13.3 (CH$_2$CH$_3$), 10.7 (C(CH_3)). $C_{32}H_{54}Cl_2N_6Rh_2$ (799.53): Calc.: C, 48.07; H, 6.81; N, 10.51. Found: C, 47.73; H, 6.67; N, 11.30.

2: IR (KBr): 2917 (ν_{NH}), 1595 (ν_{CN}), 1036 (β_{CH}) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 8.86$ (br, 2H, NH_2i-Pr), 4.50 –4.42 (m, 4H, CH (COD)), 3.49 (br s, 2H, CH_2NH$_2$i-Pr), 3.37 (sp, $^3J_{HH} = 6.6$ Hz, 1H, NCH(CH$_3$)$_2$), 2.89, 2.12–1.98 (m, 8H, CH_2 (COD)), 2.60 (s, 6H, CH_3), 1.47 (d, $^3J_{HH} = 6.6$ Hz, 6H, NCH(CH_3)$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 149.5$ (C(CH$_3$)), 105.0 (C(CH$_2$NH$_2$i-Pr)), 81.5, 81.3, 80.0, 79.9 (CH (COD)), 50.2 (CH(CH$_3$)$_2$), 36.3 (CH_2NH$_2$i-Pr), 31.5, 30.7 (CH_2 (COD)), 18.6 (CH(CH_3)$_2$), 13.3 (C(CH_3)). $C_{34}H_{58}Cl_2N_6Rh_2 \cdot CH_2Cl_2$ (912.5): Calc.: C, 46.07; H, 6.63; N, 9.21. Found: C, 46.18; H, 6.74; N, 9.67.

3.5. $[Rh(HL^1)(CO)_2]_2Cl_2$ (3) and $[Rh(HL^2)(CO)_2)]_2Cl_2$ (**4**)

A total of 20 ml of a CH_2Cl_2 solution of 0.04 g of the compounds **1** (0.05 mmol) or **2** (0.05 mmol) was placed in a 100 ml home-built stainless steel autoclave equipped with gas inlet and magnetic stirrer. The autoclave was pressurized with 20 atm of a 1:1 CO–H_2 mixture at r.t. with stirring for 15 h. The resulting solution was placed in a flask and evaporated to dry-

ness in vacuo. The orange–yellow residue was dissolved in 20 ml of CH_2Cl_2 and precipitated with hexane. 35:65 mixtures (from ^{1}H-NMR spectra) of compounds **1**–**3** and **2**–**4** were obtained in ca. 99% yield.

3: IR (CH_2Cl_2): 2093, 2075, 2022, 1975 (sh) (ν_{CO}) cm^{-1}. IR (KBr): 2088, 2070, 2024 cm^{-1} (ν_{CO}), 2956 (ν_{NH}) + (ν_{CH}), 1619 (ν_{CN}) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 9.01 (br, 2H, NH_2Et), 3.58 (br s, 2H, CH_2NH$_2$Et), 3.00 (q, $^3J_{HH}$ = 7.3 Hz, 2H, NCH_2CH$_3$), 2.41 (s, 6H, CH_3), 1.46 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH$_2$CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 185.5 (d, $^1J_{CRh}$ = 69.2 Hz, *C*O), 151.0 (*C*(CH$_3$)), 106.3 (*C*(CH$_2$NH$_2$Et)), 42.8 (*C*H$_2$NH$_2$Et), 40.2 (*C*H$_2$CH$_3$), 13.7 (CH$_2$*C*H$_3$), 10.7 (C(*C*H$_3$)).

4: IR (CH_2Cl_2): 2091, 2075, 2021, 1970 (sh) (ν_{CO}) cm^{-1}. IR (KBr): 2087, 2072, 2023 (ν_{CO}), 2929 (ν_{NH}) + (ν_{CH}), 1600 (ν_{CN}) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 8.89 (br, 2H, NH_2*i*-Pr), 3.61 (br s, 2H, CH_2NH$_2$*i*-Pr), 3.38 (sp, $^3J_{HH}$ = 6.6 Hz, 1H, NC*H*(CH$_3$)$_2$), 2.41 (s, 6H, CH_3), 1.48 (d, $^3J_{HH}$ = 6.6 Hz, 6H, NCH(CH_3)$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 185.8 (d, $^1J_{CRh}$ = 69.2 Hz, *C*O), 151.1 (*C*(CH$_3$)), 105.9 (*C*(CH$_2$NH$_2$*i*-Pr)), 50.3 (*C*H(CH$_3$)$_2$), 36.4 (*C*H$_2$NH$_2$*i*-Pr), 18.7 (CH(*C*H$_3$)$_2$), 13.6 (C(*C*H$_3$)).

3.6. [Rh(L^1)(COD)]$_2$ (**5**) and [Rh(L^2)(COD)]$_2$ (**6**)

A total of 0.93 mmol of an aminomethyl pyrazole (0.14 g of HL^1 or 0.16 g of HL^2) dissolved in 5 ml of toluene were added to a suspension of NaOMe (0.05 g, 0.93 mmol) in 20 ml of toluene. The mixture was stirred for 1.5 h after which 0.23 g of [RhCl(COD)]$_2$ (0.46 mmol) was added. The yellow solution was stirred for 15 h and the solvent was evaporated in vacuo. The solid was dissolved in 5 ml of $CHCl_3$ and the resulting mixture was filtered off. The addition of hexane to the filtrate resulted in the products **5** and **6** in 90% yield.

5: IR (KBr): 2960 (ν_{NH}) + (ν_{CH}), 1616 (ν_{CN}), 1261 (β_{CH}) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 9.35 (br, 1H, N*H*Et), 4.49–4.41 (m, 4H, C*H* (COD)), 3.48 (br s, 2H, CH_2NHEt), 2.97–2.88, 2.11–1.99 (m, 8H, CH_2 (COD)), 2.54 (br, 8H, NCH_2CH$_3$ + *C*H$_3$), 1.38 (t, $^3J_{HH}$ = 6.4 Hz, 3H, NCH$_2$CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 149.2 (*C*(CH$_3$)), 105.9 (*C*(CH$_2$NHEt)), 81.5, 81.3, 80.1, 79.9 (*C*H (COD)), 42.9 (*C*H$_2$NHEt), 40.5 (*C*H$_2$CH$_3$), 31.5, 30.7 (*C*H$_2$ (COD)), 12.9 (CH$_2$*C*H$_3$), 10.8 (C(*C*H$_3$)). $C_{32}H_{52}N_6Rh_2{\cdot}CHCl_3$ (845.98): Calc.: C, 46.85; H, 6.31; N, 9.93. Found: C, 46.59; H, 6.56; N, 9.37.

6: IR (KBr): 2950 (ν_{NH}), 1593 (ν_{CN}), 1254 (β_{CH}) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 8.92 (br, 1H, NH_2*i*-Pr), 4.50 – 4.42 (m, 4H, C*H* (COD)), 3.49 (br s, 2H, CH_2NH*i*-Pr), 3.37 (sp, $^3J_{HH}$ = 6.6 Hz, 1H, NC*H*(CH$_3$)$_2$), 2.88–2.86, 2.12–1.99 (m, 8H, CH_2 (COD)), 2.60 (s, 6H, CH_3), 1.48 (d, $^3J_{HH}$ = 6.6 Hz, 6H, NCH(CH_3)$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 149.5 (*C*(CH$_3$)), 105.1 (*C*(CH$_2$NH*i*-Pr)), 81.5, 81.3, 80.0, 79.9 (*C*H (COD)), 50.1 (*C*H(CH$_3$)$_2$), 36.3 (*C*H$_2$NH*i*-Pr), 31.5, 30.8 (*C*H$_2$ (COD)), 18.7 (CH(*C*H$_3$)$_2$), 13.3 (C(*C*H$_3$)). $C_{34}H_{56}N_6Rh_2{\cdot}0.5CHCl_3$ (814.35): Calc.: C, 50.88; H, 6.99; N, 10.32. Found: C, 51.10; H, 7.02; N, 10.01.

3.7. [Rh(L^1)(CO)$_2$]$_2$ (**7**) and [Rh(L^2)(CO)$_2$]$_2$ (**8**)

A total of 0.04 g of the compounds **5** (0.06 mmol) or **6** (0.05 mmol), dissolved in 20 ml of CH_2Cl_2, was placed in a 100 ml home-built stainless steel autoclave equipped with gas inlet and magnetic stirrer. The autoclave was pressurized with 20 atm of a 1:1 CO–H_2 mixture at r.t. with stirring for 15 h. The solution was placed in a flask and evaporated to dryness in vacuo. The orange–yellow residue was dissolved in 15 ml of CH_2Cl_2 and precipitated with hexane. Compound **7** was obtained as a pure product in 98% yield, whereas complex **8** was precipitated with 10% of compound **6** (from ^{1}H-NMR) in 99% yield.

7: IR (CH_2Cl_2): 2091, 2075, 2021, 1975 (sh) (ν_{CO}) cm^{-1}. IR (KBr): 2088, 2071, 2025 (ν_{CO}), 2961 (ν_{NH}) + (ν_{CH}) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 9.18 (br, 1H, N*H*Et), 3.58 (br s, 2H, CH_2NHEt), 2.99 (q, $^3J_{HH}$ = 6.6 Hz, 2H, NCH_2CH$_3$), 2.41 (s, 6H, CH_3), 1.45 (t, $^3J_{HH}$ = 6.6 Hz, 3H, NCH$_2$CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 185.6 (d, $^1J_{CRh}$ = 66.0 Hz, *C*O), 151.0 (*C*(CH$_3$)), 106.2 (*C*(CH$_2$NHEt)), 42.9 (*C*H$_2$NHEt), 40.2 (*C*H$_2$CH$_3$), 13.6 (CH$_2$*C*H$_3$), 10.7 (C(*C*H$_3$)). $C_{20}H_{28}N_6O_4Rh_2{\cdot}CH_2Cl_2$ (707.22): Calc.: C, 35.66; H, 4.28; N, 11.88. Found: C, 36.06; H, 4.98; N, 10.36.

8: IR (CH_2Cl_2): 2091, 2075, 2021, 1975 (sh) (ν_{CO}) cm^{-1}. IR (KBr): 2088, 2071, 2018 (ν_{CO}), 2930 (ν_{NH}) + (ν_{CH}) cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 8.92 (br, 1H, N*H*i-Pr), 3.58 (br s, 2H, CH_2NH*i*-Pr), 3.35 (sp, $^3J_{HH}$ = 6.6 Hz, 1H, NC*H*(CH$_3$)$_2$), 2.40 (s, 6H, CH_3), 1.47 (d, $^3J_{HH}$ = 6.6 Hz, 6H, NCH(CH_3)$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ = 185.6 (d, $^1J_{CRh}$ = 66.6 Hz, *C*O), 151.1 (*C*(CH$_3$)), 105.9 (*C*(CH$_2$NH*i*-Pr)), 50.3 (*C*H(CH$_3$)$_2$), 36.4 (*C*H$_2$NH*i*-Pr), 18.7 (CH(*C*H$_3$)$_2$), 13.7 (C(*C*H$_3$)).

4. X-ray crystallographic study of 2

A prismatic crystal (0.1 × 0.1 × 0.2 mm) of **2** was selected and mounted on a Enraf–Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from the automatic centering of 25 reflections ($12 < \theta < 21°$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo–K_α radiation, using the $\omega/2\theta$ scan-technique. 9549 reflections were measured in the range $2.12 \leq \theta \leq 29.98$, 9274 of which were non-equivalent by symmetry (R_{int}(on I) = 0.036). 8452 reflections were assumed as observed applying the condition $I > 2\sigma(I)$. Three reflec-tions were measured every 2 h as orientation and intensity control and significant intensity decay was not observed. The Lorentz-polarization was applied but no absorption corrections were made. The structure was

Table 2
Crystal data and structure refinement for **2**

Empirical formula	$C_{35}H_{60}Cl_4N_6Rh_2$
Formula weight	912.5
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	$P21/c$
Space group	Monoclinic
Unit cell dimensions	
a (Å)	13.600(4)
b (Å)	13.94(2)
c (Å)	21.32(2)
α (°)	90
β (°)	103.55(4)
γ (°)	90°
Volume (Å^3)	3928(7)
Z	4
D_{calc} (g cm^{-3})	1.540
Absorption coefficient (mm^{-1})	1.145
$F(000)$	1872
Crystal size (mm)	$0.1 \times 0.1 \times 0.2$
Theta range for data collection (°)	2.12–29.98
Reflections collected	9549
Independent reflections	9274 [$R_{int} = 0.0369$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9224/8/585
Goodness-of-fit on F^2	1.068
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0533$, $wR_2 = 0.1383$
R indices (all data)	$R_1 = 0.0598$, $wR_2 = 0.1572$
Extinction coefficient	0.0049(4)
Largest difference peak and hole (e Å^{-3})	0.672 and −0.647

solved by direct methods, using the SHELXS computer program [21] and refined by the full-matrix least-squares method with a SHELX-93 computer program [22], using 9224 reflections (very negative intensities were not considered). The minimized function was $\Sigma\, w|F_o|^2 - |F_c|^2$, where $w = [\sigma^2(I) + (0.0978P)^2 + 2.44414P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$, f, f' and f'' were taken from the International Tables of X-ray Crystallography [23]. The extinction coefficient was 0.0049(4). 34 H atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and 24 H atoms were computed and refined with an overall isotropic temperature factor, using a riding model. The final R (on F) factor was 0.053, wR (on $|F|^2$) = 0.138 and goodness of fit = 1.084 for all the observed reflections. The number of refined parameters was 585. Maximum shift/estimated S.D. = 0.0, mean shift/estimated S.D. = 0.00. Maximum and minimum peaks in final difference synthesis were 0.672 and −0.647 e Å^{-3}, respectively. The crystallographic data selected are summarized in Table 2.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 128224. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Bis[μ-4-(ethylammoniomethyl)-3,5-dimethylpyrazolato-κ^2N^1:N^2]bis[(η^4-1,5-cyclooctadiene)rhodium(I)] dichloride dichloromethane methanol solvate

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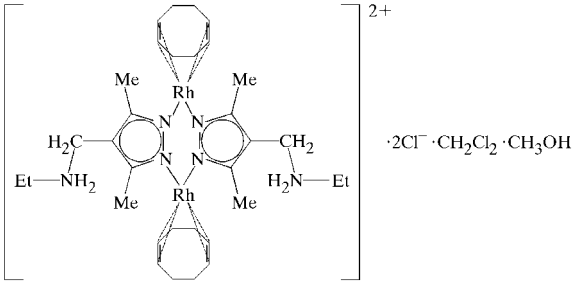
In the title compound, $[Rh_2(C_8H_{15}N_3)_2(C_8H_{12})_2]Cl_2\cdot CH_2Cl_2\cdot CH_3OH$, the dinuclear Rh^I complex has C_2 symmetry and the two pyrazolato ligands act as μ-bridges. The coordination of each Rh^I cation is completed by one cyclooctadiene (COD) ligand. It is shown that the average Rh—C(COD) distance is linearly dependent on the Rh—N(pyrazole) distance in this type of compound, and this is ascribed to the steric hindrance produced by the packing.

Comment

Research into the coordination chemistry of pyrazole-derived ligands has progressed rapidly over the last two decades. Mukherjee (2000) published an extensive review, completing those presented by La Monica & Ardizzoia (1997) and Trofimenko (1972, 1986, 1993). Only four structures of dinuclear rhodium(I) complexes with pyrazole bridges and



(I)

cyclooctadiene ligands (cod) (Louie *et al.*, 1984; Cano *et al.*, 1997; Esquius *et al.*, 2000) are present in the Cambridge Structural Database (CSD, release of November 2001; Allen & Kennard, 1993). A feature of these compounds is the variation of the Rh—C and Rh—N bond distances without a clear reason. In order to increase understanding of this distance variation, the title compound, (I), was prepared, which is similar to those previously published by Esquius *et al.* (2000).

The molecular structure of (I) is shown in Fig. 1 and selected geometric details are given in Table 1. The structure of (I) consists of discrete molecules separated by van der Waals interactions and weak hydrogen bonds (Table 2).

The methanol molecules were located as disordered, and atom O1 seems to form a hydrogen bond with a Cl^- anion [$O1\cdots Cl1^i$ 3.118 (4) Å; symmetry code (i) $\frac{1}{2}-x,\frac{1}{2}-y,1-z$]. Each Rh atom is linked to four C atoms of a cyclooctadiene ligand and two N atoms of two different pyrazole units. The pyrazole acts as a μ-*N*,*N*′-bridge between two Rh atoms. The

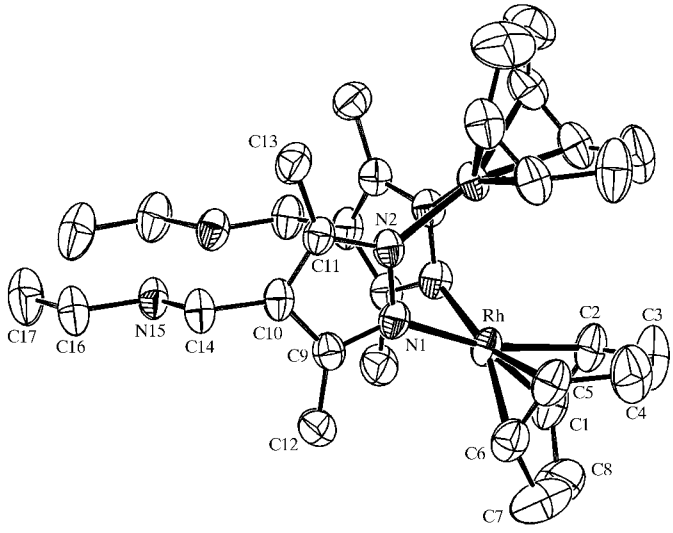


Figure 1
A view of the molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. The H atoms, the Cl^- anions and the dichloromethane and methanol solvent molecules have been omitted for clarity.

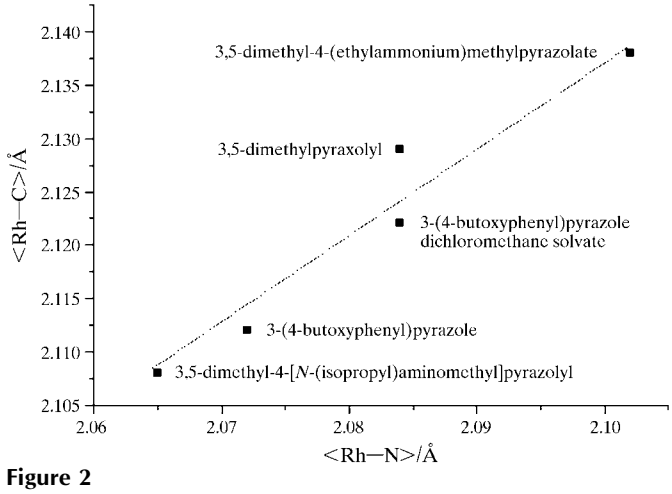


Figure 2
A graph of average Rh—C *versus* average Rh—N bond lengths in μ-pyrazole-[Rh(COD)]$_2$ units.

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Rh—N1—N2—Rh^{i} torsion angle is 2.43 (19)°. The planarity of this moiety is similar to that observed when the pyrazole lacks a bulky substituent in position 4 (Louie *et al.*, 1984; Esquius *et al.*, 2000). The dihedral angle between the Rh/N1/N2/Rh^{i} and pyrazole planes is 20.17 (10)°. The ethylammoniomethyl moiety is planar and twisted by 87.0 (2)° with respect to the pyrazole plane.

If the average Rh—C(COD) and Rh—N(pyrazole) lengths are compared, it is observed that <Rh—C> increases when <Rh—N> increases (Fig. 2), while the N—N and C—C lengths remain practically constant [average values in the five structures are 1.360 (7) and 1.375 (12) Å, respectively]. This suggests that the bond lengths involving the Rh atom are more affected by the steric hindrance of the packing than by electronic effects. This is corroborated by the two electronically more similar pyrazole ligands, 3,5-dimethyl-4-[*N*-(isopropyl)-aminomethyl]pyrazolyl and 3,5-dimethyl-4-(ethylammonium)methylpyrazolate, presenting the upper and lower limiting values.

Experimental

To prepare (I), $[RhCl(COD)]_2$ (0.08 g, 0.16 mmol) dissolved in CH_2Cl_2 (5 ml) was added to a solution of 3,5-dimethyl-4-(ethylamino)methylpyrazole (0.08 g, 0.32 mmol) in CH_2Cl_2 (5 ml) and the mixture stirred for 15 h. The solvent was evaporated to dryness *in vacuo* and the residue was washed with Et_2O and dissolved in a minimum amount of CH_2Cl_2. The title complex was precipitated by adding hexane to the solution. A yellow–orange solid was filtered off and dried *in vacuo*. Crystals of (I) were obtained by evaporation of a methanol solution.

Crystal data

$[Rh_2(C_8H_{15}N_3)_2(C_8H_{12})_2]Cl_2\cdot CH_2Cl_2\cdot CH_4O$
M_r = 916.52
Monoclinic, $C2/c$
a = 12.587 (3) Å
b = 25.762 (9) Å
c = 13.240 (13) Å
β = 108.24 (3)°
V = 4078 (4) Å^3
Z = 4
D_x = 1.492 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 12–21°
μ = 1.11 mm^{-1}
T = 293 (2) K
Prism, yellow–orange
0.2 × 0.1 × 0.1 mm

Table 1
Selected geometric parameters (Å, °).

Rh—N2^{i}	2.095 (2)	Rh—C1	2.142 (3)
Rh—N1	2.104 (2)	Rh—C5	2.144 (3)
Rh—C6	2.129 (3)	Rh—Rh^{i}	3.1579 (9)
Rh—C2	2.137 (2)	N1—N2	1.377 (3)
N2^{i}—Rh—N1	83.15 (9)	N2^{i}—Rh—C5	161.91 (10)
N2^{i}—Rh—C6	160.26 (10)	N1—Rh—C5	94.84 (10)
N1—Rh—C6	92.33 (10)	C6—Rh—C5	37.37 (11)
N2^{i}—Rh—C2	95.28 (11)	C2—Rh—C5	81.97 (12)
N1—Rh—C2	164.91 (10)	C1—Rh—C5	94.66 (12)
C6—Rh—C2	93.91 (12)	C9—N1—Rh	130.93 (15)
N2^{i}—Rh—C1	93.74 (11)	N2—N1—Rh	116.59 (13)
N1—Rh—C1	157.72 (10)	C11—N2—Rh^{i}	133.54 (16)
C6—Rh—C1	83.17 (13)	N1—N2—Rh^{i}	113.59 (13)
C2—Rh—C1	37.17 (11)		

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N15—H15···Cl1	0.90 (2)	2.45 (2)	3.286 (4)	154 (3)
N15—H15A···Cl1^{i}	0.90 (2)	2.29 (2)	3.188 (4)	175 (2)

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
6120 measured reflections
5860 independent reflections
4234 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 30°
$h = -17 \rightarrow 16$
$k = 0 \rightarrow 36$
$l = 0 \rightarrow 18$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.079
S = 0.98
5860 reflections
222 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Methanol atoms O1 and C19 were located from a difference Fourier synthesis. Their occupancy factor of 0.5 was assigned according to the peak heights. The molar ratio with respect to the remaining formula was confirmed by elemental analysis. The H atoms on N15 were refined freely. The positions of 27 H atoms were geometrically computed (C—H = 0.93–0.97 Å) and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(C). Dichloromethane H atoms were located from a difference Fourier synthesis, while methanol H atoms were not located.

Data collection: *CAD*-4/*PC* (Kretschmar, 1996); cell refinement: *CAD*-4/*PC*; data reduction: *CFEO* (Solans, 1978); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*3.2 (Brueggemann & Schmid, 1990); software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1049). Services for accessing these data are described at the back of the journal.

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Organometallic rhodium (I) complexes with 1-alkylaminopyrazole ligands

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Abstract

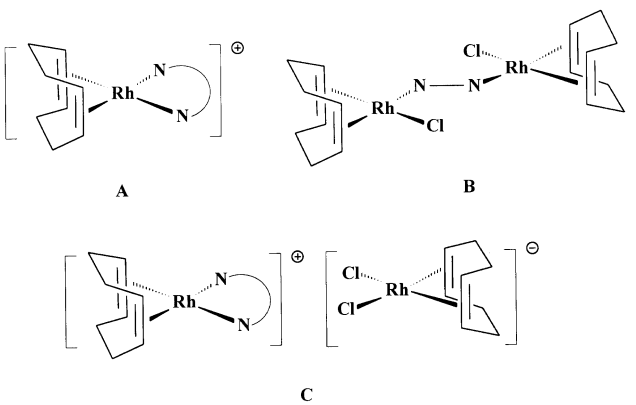
New bidentate *NN′* and tridentate *NN′N* 1-alkylaminopyrazoles were synthesized and characterized by elemental analyses and spectroscopic methods. The reaction of $[RhCl(cod)_2]$ (cod = cycloocta-1,5-diene) with one equivalent of L 1-alkylaminopyrazoles afforded $Rh_2Cl_2(L)(cod)_2$ complexes (L = *NN′* and *NN′N*). These rhodium (I) compounds were studied by IR, ^{1}H- and ^{13}C-NMR and liquid mass (with electrospray and APCI interfaces) spectrometries. The ^{1}H-NMR spectra and molar conductances of these complexes suggested the presence of 1:1 electrolyte species, $[Rh(L)cod]^+$ $[RhCl_2(cod)]^-$, in solution. A combined electrospray and APCI liquid mass spectroscopy study confirmed the presence of both $[Rh(L)cod]^+$ and $[RhCl_2(cod)]^-$ species in solution but the existence of a neutral molecular form of complexes in solution could not be demonstrated.

Keywords: Rhodium complexes; Rhodium–amine complexes; 1-Alkylaminopyrazoles; Electrospray mass spectra

1. Introduction

The coordination chemistry of pyrazoles is an active field of interest which has been extensively reviewed by Trofimenko [1–3] and more recently by La Monica et al. [4]. Pyrazoles can bear donating groups attached to any position of the aromatic ring affording a large family of polydentate ligands. Studies of the coordination chemistry of these ligands include modeling of metalloenzymes and organometallic chemistry of polypyrazolylborate ligands [4].

The synthesis of bi (*NN′*) and tridentate (*NN′N*) 1-alkylaminopyrazole ligands was developed by Driessen et al. and, so far, the study of their coordinating ability has been mainly focused on the design of chelating systems to mimic metalloenzymes [5–10]. Recently, tridentate ligands bearing three *N* atoms have been shown to stabilize unsaturated ruthenium (II) complexes which made them interesting from the viewpoint of potential application in homogeneous catalysis [11]. Reactions of $[RhCl(cod)]_2$ with polydentate *N*-donor ligands leading to different types of compounds have been previously described in the literature. Chelating bidentate *N*-donor ligands as phenantrolines [12–15], α-diimines [16], aminomethylpyridynes [17], aliphatic diamines [14] and bis(pyrazolyl)methane [18,19] form three types of rhodium (I) complexes depending on the ligand to metal ratio L:M of the reaction (Fig. 1): mononuclear with a η^2-coordinated ligand (A), dinuclear bridged by the diamino ligands (B) and



A B C

Fig. 1.

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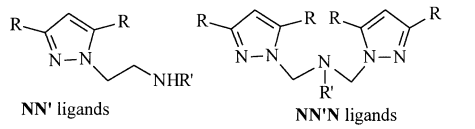


R = R = Me; R' = Et **(deae)**
R = R = Me; R' = i-Pr **(deai)**
R = R = H; R' = Et **(eae)**
R = R = H; R' = i-Pr **(eai)**

R = R = Me; R' = Et **(bdmae)**
R = R = Me; R' = i-Pr **(bdmai)**
R = R = Me; R' = Ph **(bdmab)**
R = R = H; R' = Et **(bmae)**
R = R = H; R' = i-Pr **(bmai)**
R = R = H; R' = Ph **(bmab)**

Fig. 2.

ionic compounds $[RhL_2(NN)]^+[RhCl_2L_2]$ ($L_2 = cod$) (C). Non chelating bidentate N-donor ligands have been also described for aminopyridynes [17], pyrazine [20], pyrimidyne [21], 4-4′-bipyrazoles [22], benzotriazole [23] and imidazole [24]. They form complexes of the type (B) from a 2:1 L:M ratio, and mononuclear compounds with a terminal *N*-bonded ligand from a 1:1 L:M ratio [25]. Some authors have suggested the existence of an equilibrium between forms B and C in solution [16,26,27].

In a previous study we reported the synthesis and coordination chemistry of pyridyl–pyrazole ligands [28,29]. Our present research interest is the design and synthesis of new organometallic compounds containing polydentate pyrazole-based ligands with two purposes: potential applications in catalysis and the synthesis of water-soluble complexes. This paper deals with our first results about the synthesis of new rhodium (I) complexes with bidentate *NN′* and tridentate *NN′N* ligands (Fig. 2). Some of ligands are new (deai, eae, eai, bdmai and bmaib) so we describe here their synthesis and characterization.

2. Experimental

2.1. General procedures

All reactions were carried out with the use of vacuum line and Schlenk techniques. All solvents were dried and distilled prior to use, according to standard procedures. Samples of $[Rh(cod)Cl]_2$ [30] (cod = cycloocta-1,5-diene) were prepared as described in the literature.

The elemental analyses were carried out by the staff of the Chemical Analysis Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 apparatus. IR spectra were obtained on a Perkin–Elmer 2000 spectrometer with NaCl discs or in KBr pellets. The conductivity measures were taken with a Crison, micro CM 2200 conductimeter. ^{1}H- and $^{13}C\{^1H\}$-NMR spectra were recorded on a RMN-FT Bruker AC-250 spectrometer in $CDCl_3$ solutions (^{1}H, 250 MHz; ^{13}C, 62 MHz). Electronic impact and chemical ionization mass spectra were measured on a HP 5989, mass extend to 2000 uma, GC/MS. The chemical ionization mass spectra were recorded with NH_3 as the reacting gas.

Liquid chromatography mass spectrometry experiments were performed on a Platform II instrument (Micromass, Manchester, UK) by using a Phoenix 20 syringe pump (C.E. Instruments, Milan, Italy) as an infusion pump. The carrier was NCMe at a 50 μl min^{-1} flow rate. The samples were dissolved in NCMe at a concentration of 2.0 mg ml^{-1} and 20 μl of each solution injected on line by means of a Rheodyne 7125 valve (Rheodyne, Cotati, CA, USA). In the case of electrospray interface, whole flow was introduced in the capillary of the source and nebulized with a 20 l h^{-1} nitrogen flow. The courtain gas was nitrogen at 400 l h^{-1} flow rate.

The main electrical conditions were: (a) positive electrospray: capillary at 3500 V; counter-electrode at 500 V, sampling cone was ranged between 50 and 100 V and the source temperature was 80°C; (b) negative electrospray: capillary at 3000 V, counter-electrode at 0 V, sampling cone was ranged between 25 and 100 V.

In the case of APCI interface the flow was 1000 μl min^{-1} and sample injected volume was 10 μl. The nebulizer gas was nitrogen set at 200 l h^{-1} and the courtain gas was nitrogen at 400 l h^{-1}. The main electrical conditions were: a) positive APCI: needle at 3000 V; counter-electrode at 500 V, sampling cone was ranged between 15 and 50 V, the tip temperature was 400°C and the source temperature was 80°C; b) negative APCI: needle at 4000 V; counter-electrode at 0 V, sampling cone was ranged between 15 and 50 V, the tip temperature was 400°C and the source temperature was 80°C.

2.2. Ligands

Among studied bidentate *NN′* ligands, only the 1-[(*N*-ethyl)-2-aminoethyl]-3,5-dimethylpyrazole (deae) [5] was previously described. The rest of the *NN′* ligands were synthesized for the first time following an analogous method which consists of adding a solution of 10 mmol of tosylates 1-(2-toluene-parasulfonyloxyethyl)-3,5-dimethylpyrazole [5,31] or 1-(2-toluene-parasulfonyloxyethyl)pyrazole [32] in 16 ml of THF dropwise to a stirred mixture of 2.30 g (58 mmol) NaOH in 60 ml H_2O and 66 mmol of the corresponding primary amine. The temperature was kept at about 50°C. After the addition, which was completed in 1.5 h, the temperature was raised to 70°C and the stirring was continued for 4 h. Then, the mixture was allowed to cool to room temperature (r.t.). The ligands were extracted with three portions of 25 ml $CHCl_3$ and dried overnight with $MgSO_4$. The $CHCl_3$ was removed at low pressure and products were isolated as yellow oils (Table 1).

Table 1
Starting compounds, yield, elemental analyses and MS molecular peak of ligands of the type *NN′*

Ligand	Tosylate	Weight (g)	Primary amine	Weight (g)	Yield (%)	Anal. Found (%)	Anal. Calc. (%)	MS (*m*/*e*)
deai	1-(2-Toluene-*p*-sulfonyloxyethyl)-3,5-dimethylpyrazole	2.94	Isopropylamine	4.02	80	C, 66.18; H, 10.23; N, 22.88	C, 66.26; H, 10.57; N, 23.18	182 [M^+]
eae	1-(2-Toluenen-*p*-sulfonyloxyethyl)pyrazole	2.64	Ethylamine (70% weight H_2O)	4.28	81	C, 60.07; H, 9.33; N, 30.34	C, 60.40; H, 9.41; N, 30.19	137 [M^+]
eai	1-(2-Toluenen-*p*-sulfonyloxyethyl)pyrazole	2.64	Isopropylamine	4.02	79	C, 62.08; H, 9.83; N, 27.05	C, 62.71; H, 9.87; N, 27.42	152 [M^+]

Table 2
Starting compounds, yield, elemental analyses and MS molecular peak of ligands of the type *NN′N*

Ligand	Alcohol	Weight (g)	Primary amine	Weight (g)	Yield (%)	Anal. Found (%)	Anal. Calc. (%)	MS (*m*/*e*)
Bdmai	1-(Hydroxymethyl)3,5-dimethylpyrazole	1.99	Isopropylamine	0.47	89	C, 65.18; H, 9.32; N, 25.68	C, 65.54; H, 9.17; N, 25.43	276 [M^+]
bmai	1-(Hydroxymethyl)pyrazole	1.55	Isopropylamine	0.47	86	C, 59.99; H, 7.82; N, 32.03	C, 60.23; H, 7.83; N, 31.94	151 [$M^+ - pz$]

The new 1-alkylamino ligands of the type *NN′N*: bis[(3,5-dimethyl-1-pyrazolyl)methyl]-1-methylethylamine (bdmai) and bis[(1-pyrazolyl)methyl]-1-methyl ethylamine (bmai) were synthesized following previously described methods [6,7,33]. The bdmai and bmai ligands were prepared by mixing 8 mmol of the appropriate primary amine with 16 mmol of alcohols 1-(hydroxymethyl)pyrazole [33] or 1-(hydroxymethyl)-3,5-dimethylpyrazole [33,34] in 15 ml of dichloroethane with stirring at r.t. for 24 h. The mixture was dried overnight with $MgSO_4$. The solvent was then removed at low pressure and products were isolated as a solid (bdmai) or as an oil (bmai) (Table 2).

2.3. Complexes

Rh_2Cl_2(deae)$(cod)_2$ (**1**), Rh_2Cl_2(deai)$(cod)_2$ (**2**), Rh_2Cl_2(eae)$(cod)_2$ (**3**), Rh_2Cl_2(eai)$(cod)_2$ (**4**), Rh_2Cl_2(bdmae)$(cod)_2$ (**5**), Rh_2Cl_2((bdmai)$(cod)_2$ (**6**), Rh_2Cl_2(bmae)$(cod)_2$ (**7**), Rh_2Cl_2(bmai)$(cod)_2$ (**8**).

A solution of 0.079 g (0.160 mmol) of $[RhCl(cod)]_2$ in CH_2Cl_2 was treated with a solution of 0.320 mmol of the corresponding ligand in 5 ml of CH_2Cl_2. After 6 h of stirring, the CH_2Cl_2 was evaporated and the remaining solid was washed with cold Et_2O. The addition of hexane to a solution of the solid in a minimum amount of CH_2Cl_2 gave yellow–orange complexes, which were filtered off, and vacuum dried (Table 3).

3. Results and discussion

3.1. Synthesis of ligands

All ligands were synthesized following previously described Driessen procedures [5,31,33]. New *NN′* aminoethylpyrazoles deai, eae and eai were readily prepared from tosylates 1-(2-toluene-*p*-sulfonyloxoethyl)-3,5-dimethylpyrazole and 1-(2-toluene-*p*-sulfonyloxoethyl)pyrazole and the corresponding primary amine. Yellow oily products were extracted with $CHCl_3$ and isolated in 80% yield. *NN′N* tridentate ligands, bdmai and bmab, were synthesized from the direct reaction of 1-(hydroxymethyl)-3,5-dimethylpyrazole and 1-(hydroxymethyl)pyrazole and the corresponding primary amine. Colourless oily ligands were obtained by evaporating the solvent in vacuo after drying with anhydrous $MgSO_4$. Yields were of 89 and 86%, respectively. The new ligands were obtained as pure products and were characterized unambigously by C, H, and N elemental analyses (Tables 1 and 2), IR, ^{1}H- and ^{13}C-NMR spectroscopies and by Electronic Impact or Chemical Ionisation Mass Spectra (Tables 4 and 5). Assignment of RMN signals were assigned by reference to the literature [31–34] and from DEPT, NOEDIFF and HETCORR RMN experiments (for bdmai).

3.2. Reaction of 1-alkylaminopyrazoles with $[RhCl(cod)]_2$

The reaction of the rhodium (I) $[RhCl(cod)]_2$ complex with 1-alkylaminopyrazoles (*NN′* and *NN′N*) in a 1:2 molar ratio in CH_2Cl_2 solution led to Rh_2Cl_2(*NN′*)$(cod)_2$ and Rh_2Cl_2(*NN′N*)$(cod)_2$ complexes, respectively (*NN′* = deae (**1**), deai (**2**), eae (**3**), eai (**4**) and *NN′N* = bdmae (**5**), bdmai (**6**), bmae (**7**) and bmai (**8**)) (Scheme 1). Compounds were characterized by elemental analyses, IR and ^{1}H- and ^{13}C-NMR spectroscopies and conductivity measurements. Table 3 displays yields, C, H and N elemental analyses and molar conductances of complexes in MeOH and NCMe. Tables 6 and 7 display spectroscopic data of complexes. IR spectra of

Table 3
Ligand weigths, yield, elemental analyses and molar conductances of complexes (**1–8**)

Complexes	Ligand	Weight (g)	Yield (%)	Anal. Found (%)	Anal. Calc. (%)	Λ_M (Ω^{-1} cm^2 mol^{-1}) 10^{-3} M	
						MeOH	NCMe
Rh_2Cl_2(deae)$(cod)_2$ (**1**)	Deae	0.054	85	C, 45.14; H, 6.44; N, 6.01	C, 45.47; H, 6.26; N, 6.36	78.1	59.5
Rh_2Cl_2(deai)$(cod)_2$ (**2**)	Deai	0.058	74	C, 46.37; H, 6.50; N, 6.28	C, 46.31; H, 6.43; N, 6.23	77.9	56.1
Rh_2Cl_2(eae)$(cod)_2$ (**3**)	Eae	0.044	76	C, 43.48; H, 5.89; N, 6.42	C, 43.69; H, 5.91; N, 6.65	81.6	58.2
Rh_2Cl_2(eai)$(cod)_2$ (**4**)	eai	0.048	81	C, 44.78;H, 5.89; N, 6.23	C, 44.60; H, 6.09; N, 6.50	91.7	59.0
Rh_2Cl_2(bdmae)$(cod)_2$ (**5**)	bdmae	0.084	71	C, 47.47; H, 6.23; N, 9.23	C, 47.75; H, 6.29; N, 9.28	80.1	54.2
Rh_2Cl_2(bdmai)$(cod)_2$ (**6**)	bdmai	0.088	78	C, 48.25; H, 6.27; N, 9.26	C, 48.45; H, 6.43; N, 9.11	81.2	55.0
Rh_2Cl_2(bmae)$(cod)_2$ (**7**)	bmae	0.066	80	C, 44.09; H, 5.13; N, 10.49	C, 44.71; H, 5.64; N, 10.03	79.6	54.5
Rh_2Cl_2(bmai)$(cod)_2$ (**8**)	bmai	0.070	73	C, 45.19; H, 5.66; N, 10.05	C, 45.51; H, 5.81; N, 9.83	77.8	46.9

Table 4
IR [a], ^{1}H- and ^{13}C-NMR data of ligands of the type *NN′*

Ligand	IR (NaCl) ν (cm^{-1})	^{1}H-NMR 250 MHz $CDCl_3$ δ (ppm)	$^{13}C\{^{1}H\}$-NMR 62 MHz $CDCl_3$ δ (ppm)
deai	3303 (νN–H), 2963 ($\nu C–H_{al}$), 1647 (δ N–H), 1553 ($\nu C{=}C_{ar}$, $\nu C{=}N_{ar}$), 1463 (δ CH_{3as}), 1433 (δ $C{=}C_{ar}$, $\delta C{=}N_{ar}$), 1385–1121 (νC–N), 773 (δ $C–H_{oop}$)	5.59 [s, 1H,C*H* pyrazole], 3.88 [t, $^{3}J_{H–H} = 6.2$ Hz, 2H, $CH_2CH_2NH^{i}Pr$], 2.83 [t, $^{3}J_{H–H} = 6.2$ Hz, 2H, $CH_2CH_2NH^{i}Pr$], 2.64 [septd, $^{3}J_{H–H} = 6.0$ Hz, 1H, $CH(CH_3)_2$], 2.06 [s, 3H, CH_3 pyrazole], 2.03 [s, 3H, CH_3 pyrazole], 0.87 [d, $^{3}J_{H–H} = 6.0$ Hz, 6H, $CH(CH_3)_2$]	146.9 [CCH_3], 138.6 [CCH_3], 104.4 [*C*H pyrazole], 48.0–46.4 [$CH_2CH_2NHCH(CH_3)_2$], 22.3 [$CH(CH_3)_2$], 13.0–10.6 [CCH_3]
eae	3302 (νN–H), 3106 ($\nu C–H_{ar}$), 2967 ($\nu C–H_{al}$), 1653 (δ N–H), 1514 ($\nu C{=}C_{ar}$, $\nu C{=}N_{ar}$), 1445 (δ $C{=}C_{ar}$, δ $C{=}N_{ar}$), 1399–1121 (νC–N), 756 (δ $C–H_{oop}$)	7.50 [d, $^{3}J_{H–H} = 1.9$ Hz, 1H, C*H* pyrazole], 7.41 [d, $^{3}J_{H–H} = 1.9$ Hz, 1H, C*H* pyrazole], 6.22 [t, $^{3}J_{H–H} = 1.9$ Hz, 1H, C*H* middle pyrazole], 4.22 [t, $^{3}J_{H–H} = 6.0$ Hz, 2H, CH_2CH_2NHEt], 3.03 [t, $^{3}J_{H–H} = 6.0$ Hz, 2H, CH_2CH_2NHEt], 2.62 [q, $^{3}J_{H–H} = 7.2$ Hz, 2H, CH_2CH_3], 1.83 [s, 1H, NH], 1.05 [t, $^{3}J_{H–H} = 7.2$ Hz, 3H, CH_2CH_3]	138.9 [*C*H pyrazole], 129.1 [*C*H pyrazole], 104.7 [*C*H middle pyrazole], 51.4–43.1 [$CH_2CH_2NHCH_2CH_3$], 14.6 [CH_2CH_3]
eai	3299 (νN–H), 3104 ($\nu C–H_{ar}$), 2964 ($\nu C–H_{al}$), 1654 (δ N–H), 1513 ($\nu C{=}C_{ar}$, $\nu C{=}N_{ar}$), 1444 ($\delta C{=}C_{ar}$, δ $C{=}N_{ar}$), 1396–1173 (νC–N), 752 (δ $C–H_{oop}$)	7.38 [d, $^{3}J_{H–H} = 1.8$ Hz, 1H, C*H* pyrazole], 7.31 [d, $^{3}J_{H–H} = 1.8$ Hz, 1H, C*H* pyrazole], 6.10 [t, $^{3}J_{H–H} = 1.8$ Hz, 1H, C*H* middle pyrazole], 4.10 [t, $^{3}J_{H–H} = 5.9$ Hz, 2H, $CH_2CH_2NH^{i}Pr$], 2.91 [t, $^{3}J_{H–H} = 5.9$ Hz, 2H, $CH_2CH_2NH^{i}Pr$], 2.65 [septd, $^{3}J_{H–H} = 6.3$ Hz, 1H, $CH(CH_3)_2$], 1.97 [s, 1H, NH], 0.90 [d, $^{3}J_{H–H} = 6.3$ Hz, 6H, $CH(CH_3)_2$]	139.2 [*C*H pyrazole], 129.4 [*C*H pyrazole], 105.0 [*C*H middle pyrazole], 51.9–46.6 [$CH_2CH_2NHCH(CH_3)_2$], 22.5 [$CH(CH_3)_2$]

[a] al = aliphatic, ar = aromatic, as = asymmetric, oop = out of plane, s = singlet, d = doublet, t = triplet, q = quadruplet, septd = septuplet.

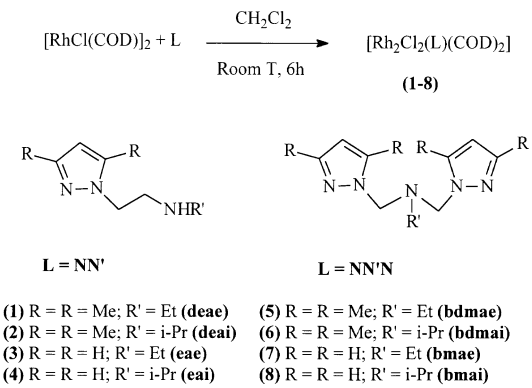
Table 5
IR [a], ^{1}H- and ^{13}C-NMR data of ligands of the type *NN′N*

Ligand	IR (NaCl–KBr) ν (cm^{-1})	^{1}H-NMR 250 MHz $CDCl_3$ δ (ppm)	$^{13}C\{^1H\}$-NMR 62 MHz $CDCl_3$ δ (ppm)
bdmai	2967–2919 (νC–H_{al}), 1558 (νC=C_{ar}, νC=N_{ar}), 1460 (δ CH_{3as}), 1422–1404 (δC=C_{ar}, δC=N_{ar}), 1379–1150 (νC–N), 776 (δ C–H_{oop})	5.68 [s, 2H,C*H* pyrazole], 4.78 [s, 4H, CH_2], 3.06 [septd, $^3J_{H-H}$ = 6.7 Hz, 1H, CH(CH_3)$_2$], 2.09 [s, 6H, CH_3 pyrazole], 1.97 [s, 6H, CH_3 pyrazole], 0.94 [d, $^3J_{H-H}$ = 6.7 Hz, 6H, CH(CH_3)$_2$]	146.8 [*C*CH_3], 139.2 [*C*CH_3], 105.6 [*C*H pyrazole], 61.8 [*C*H_2], 47.9 [*C*H(CH_3)$_2$], 18.2 [CH(*C*H_3)$_2$], 13.2–10.4 [*C*CH_3]
bmai	3105 (νC–H_{ar}), 2967 (νC–H_{al}), 1512 (νC=C_{ar}, νC=N_{ar}), 1465–1443 (δ C=C_{ar}, δ C=N_{ar}), 1395–1119 (νC–N), 751 (δ C–H_{oop})	7.35 [d, $^3J_{H-H}$ = 2.2 Hz, 2H, C*H* pyrazole], 7.34 [d, $^3J_{H-H}$ = 2.2 Hz, 2H, C*H* pyrazole], 6.08 [t, $^3J_{H-H}$ = 2.2 Hz, 2H, C*H* middle pyrazole], 4.90 [s, 4H, CH_2], 3.09 [septd, $^3J_{H-H}$ = 6.7 Hz, 1H, CH(CH_3)$_2$], 0.79 [d, $^3J_{H-H}$ = 6.7 Hz, 6H, CH(CH_3)$_2$]	138.7 [*C*H pyrazole], 128.6 [*C*H pyrazole], 105.3 [*C*H middle pyrazole], 64.9 [*C*H_2], 50.2 [*C*H(CH_3)$_2$], 19.5 [CH(*C*H_3)$_2$]

[a] al = aliphatic, ar = aromatic, as = asymmetric, oop = out of plane, s = singlet, d = doublet, t = triplet, septd = septuplet.

of complexes in KBr pellets display absorptions of both 1-alkylaminopyrazole and cod ligands. IR spectra of complexes **1**–**4** show moderated shifts of the ν(NH) band (3200–3150 cm^{-1}) to lower energies than in the free ligands (3300 cm^{-1}) whereas the δ (NH) band is observed at 1677–1654 cm^{-1} [35]. The characteristic ν(CN) + ν(C=C) absorption for the pyrazolyl group appears at 1595–1512 cm^{-1} [28,29]. The ^{1}H-NMR spectra of complexes are in accordance with the presence of 1-alkylaminopyrazoles [33] and cod [36] ligands. Most of the signals of 1-alkylaminopyrazole ligands shifted downfield by coordination. On the other hand, the corresponding signal of the N*H* hydrogen for complexes **1**–**4** could not be assigned. These data are in agreement with a bidentate coordination of *NN′* ligands. The ^{1}H-NMR signals of complexes **5**–**8** indicate that pyrazolyl groups in *NN′N* coordinated ligands are equivalents. This fact suggests also a bidentate coordination of these ligands by means of *N* (pyrazolyl) donor atoms. The cod resonances appear as broad signals, which could not be resolved at low temperatures. This can be attributed to the existence of different 'Rh(cod)' forms in solution or a possible reorientation of the coordinated cod ligand, as it has been established in pyrazolato rhodium (I) complexes [36]. The ^{13}C-NMR spectra of complexes show resonances for the carbon atoms of the 1-alkylaminopyrazole and cod ligands. No significant differences between ^{13}C-NMR spectra of free and coordinated 1-alkylaminopyrazole ligands were observed. The corresponding signals of the diolefinic ligand show the expected ^{13}C chemical shifts [36]. Molar conductances of complexes measured in MeOH are between neutral molecules and 1:1 electrolytes. Measurements in NCMe give values, which would be concordant with a neutral formulation of compounds [27,37].

The broad signals observed in the ^{1}H-NMR spectra of the synthesized $Rh_2Cl_2(L)(cod)_2$ complexes (L = *NN′* and *NN′N*) are consistent with the presence of both ionic forms $[Rh(L)(cod)]^+$ $[RhCl_2(cod)]^-$ in solution. The existence of an equilibrium between binuclear neutral and ionic forms which was suggested for related *NN′* bidentate ligands (Scheme 2) could not be proved from NMR data of products. Since efforts to grow crystals from solutions of complexes were unsuccessful, we recorded electrospray mass spectra of complexes **2** (deai; *NN′* type ligand) and **6** (bdmai; *NN′N* type ligand) in NCMe in order to confirm the presence of those ions in solution. This technique is effective for the study of inorganic complexes in solution, allowing ions present in solution to be observed in the mass spectra [38,39]. The positive ionization spectrum of **2** measured at + 50 V cone voltage gave peaks with m/z values of 339 $[Rh(L)(cod) + H]^+$ (molecular peak of the cation), 304 $[Rh(cod)(C_5H_{13}N)]^+$, 211 $[Rh(cod)]^+$ and 182 $[L + H]^+$ (100%). The negative ionization spectrum of **2** at + 50 V cone voltage gave peaks at m/z 281 $[RhCl_2(cod)–H]^-$ (molecular peak of the anion), 171 $[RhC_5H_8]^-$ (100%) and 113 $[C_8H_{17}]^-$. The ESMS spectra of **6** are similar to those of complex **2**. The positive spectrum (+ 50 V) gave peaks at m/z 487 $[Rh(L)(cod) + H]^+$ (molecular peak of the cation), 307 $[Rh(cod)(C_5H_8N_2)]^+$ and 211 $[Rh(cod)–H]^+$ (100%).



Scheme 1.

Table 6
IR [a], ^{1}H- and ^{13}C-NMR data of ligands of complexes with ligands of the type *NN′* (**1**–**4**)

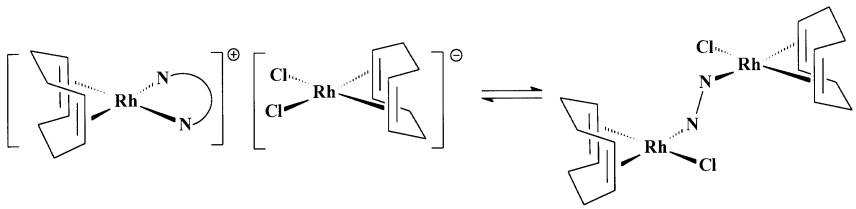
Complex	IR (KBr) ν (cm^{-1})	^{1}H-NMR 250 MHz $CDCl_3$ δ (ppm)	$^{13}C\{^1H\}$-NMR 62 MHz $CDCl_3$ δ (ppm)
Rh_2Cl_2(deae)(cod)$_2$ (**1**)	3161 (νN–H), 2928–2834 (νC–H_{al} ligand+cod), 1677 (δ N–H), 1595–1556 (νC=C_{ar}, νC=N_{ar}), 1452 (δ CH_{3as} ligand/δ CH_2 cod), 1423 (δ C=C_{ar} ligand+cod, δ C=N_{ar}), 1386–1124 (νC–N), 1036–966 (δ C–H_{ip} ligand+cod), 818 (δ CH_{oop} cod), 776 (δ C–H_{oop} ligand+cod)	5.82 [s, 1H,C*H* pyrazole], 4.69 [b, 2H, CH_2CH$_2$NHEt],4.15 [s, 8H,=C*H* cod], 3.25 [b, 2H, CH$_2$CH_2NHEt], 2.59 [b, 2H, CH_2CH$_3$], 2.38 [b, 8H, CHH_{exo} cod], 2.28 [s, 6H, CH_3 pyrazole], 1.73 [b, 8H, CHH_{endo} cod], 1.46 [t, $^3J_{H-H}=6.2$ Hz, 3H, CH$_2$CH_3]	128.5 [*C*CH$_3$], 126.0 [*C*CH$_3$], 106.5 [*C*H middle pyrazole], 79,3 [=*C*H cod], 49.8–47.1 [*C*H$_2$*C*H$_2$NH*C*H$_2$CH$_3$], 30.8 [*C*H$_2$ cod], 15.0 [CH$_2$*C*H$_3$], 15.0–11.3 [C*C*H$_3$]
Rh_2Cl_2(deai)(cod)$_2$ (**2**)	3178 (νN–H), 2917–2831 (νC–H_{al} ligand+cod), 1637 (δ N–H), 1554 (νC=C_{ar}, νC=N_{ar}), 1463 (δ CH_{3as} ligand/δ CH_2 cod), 1431 (δ C=C_{ar} ligand+cod, δ C=N_{ar}), 1385–1122 (νC–N), 1080–966 (δ C–H_{ip} ligand+cod), 818 (δ CH_{oop} cod), 777 (δ C–H_{oop} ligand+cod)	5.81 [s, 1H,C*H* pyrazole], 4.60 [b, 2H, CH_2CH$_2$NH^{i}Pr], 4.18 [s, 8H,=C*H* cod], 3.27 [b, 2H, CH$_2$CH_2NH^{i}Pr], 2.62 [b, 1H, C*H*(CH$_3$)$_2$], 2.39 [b, 8H, CHH_{exo} cod], 2.29 [s, 6H, CH_3 pyrazole], 1.74 [b, 8H, CHH_{endo} cod], 1.29 [b, 6H, CH(CH_3)$_2$]	128.4 [*C*CH$_3$], 126.0 [*C*CH$_3$], 106.8 [*C*H pyrazole], 78.4 [=*C*H cod], 49.4–46.5 [*C*H$_2$*C*H$_2$NH*C*H(CH$_3$)$_2$], 30.7 [*C*H$_2$ cod], 22.5 [CH(*C*H$_3$)$_2$], 14.0–11.4 [C*C*H$_3$]
Rh_2Cl_2(eae)(cod)$_2$ (**3**)	3191 (νN–H), 3091 (νC–H_{ar}), 2934–2827 (νC–H_{al} ligand+cod), 1636 (δ N–H), 1516 (νC=C_{ar}, νC=N_{ar}), 1467 (δ CH_{3as} ligand/δ CH_2 cod), 1431–1417 (δ C=C_{ar} ligand+cod, δ C=N_{ar}), 1384–1198 (νC–N), 1101–968 (δ C–H_{ip} ligand+cod), 815 (δ CH_{oop} cod), 752 (δ C–H_{oop} ligand+cod)	7.68 [d, $^3J_{H-H}=2.2$ Hz, 1H, C*H* pyrazole], 7.32 [b, 1H, C*H* pyrazole], 6.30 [t, $^3J_{H-H}=2.2$ Hz, 1H, C*H* middle pyrazole], 4.81 [b, 2H, CH_2CH$_2$NHEt], 4.21 [s, 8H, =C*H* cod], 3.09 [t, $^3J_{H-H}=9.9$ Hz, 2H, CH$_2$CH_2NHEt], 2.56 [b, 2H, CH_2CH$_3$], 2.41 [m, 8H, CHH_{exo} cod], 1.73 [b, 8H, CHH_{endo} cod], 1.38 [t, $^3J_{H-H}=6.2$ Hz, 3H, CH$_2$CH_3]	139.6 [*C*H pyrazole], 132.2 [*C*H pyrazole], 107.0 [*C*H middle pyrazole], 79.4 [=*C*H cod], 52.2–47.7 [*C*H$_2$*C*H$_2$NH*C*H$_2$CH$_3$], 30.7 [*C*H$_2$ cod], 14.7 [CH$_2$*C*H$_3$]
[Rh_2Cl_2(eai)(cod)$_2$ (**4**)	3153 (νN–H), 3094 (νC–H_{ar}), 2920–2829 (νC–H_{al} ligand+cod), 1654 (δ N–H), 1512 (νC=C_{ar}, νC=N_{ar}), 1468 (δ CH_{3as} ligand/δ CH_2 cod), 1433 (δ C=C_{ar} ligand+cod, δ C=N_{ar}), 1389–1136 (νC–N), 1100–955 (δ C–H_{ip} ligand+cod), 816 (δ CH_{oop} cod), 764 (δ C–H_{oop} ligand+cod)	7.60 [b, 1H, C*H* pyrazole], 7.38 [b, 1H, C*H* pyrazole], 6.29 [b, 1H, C*H* middle pyrazole], 4.84 [b, 2H, CH_2CH$_2$NH^{i}Pr], 4.23 [s, 8H, =C*H* cod], 3.17 [b, 2H, CH$_2$CH_2NH^{i}Pr], 2.91 [b, 1H, C*H*(CH$_3$)$_2$], 2.42 [m, 8H, CHH_{exo} cod], 1.75 [b, 8H, CHH_{endo} cod], 1.21 [d, $^3J_{H-H}=5.1$ Hz, 6H, CH(CH_3)$_2$]	139.5 [*C*H pyrazole], 131.5 [*C*H pyrazole], 106.7 [*C*H middle pyrazole], 79.5 [=*C*H cod], 52.5–45.4 [*C*H$_2$*C*H$_2$NH*C*H(CH$_3$)$_2$], 30.8 [*C*H$_2$ cod], 22.1 [CH(*C*H$_3$)$_2$]

[a] al = aliphatic, ar = aromatic, as = asymmetric, oop = out of plane, ip = in plane, s = singlet, d = doublet, t = triplet, q = quadruplet, septd = septuplet, b = broad signal, m = multiplet.

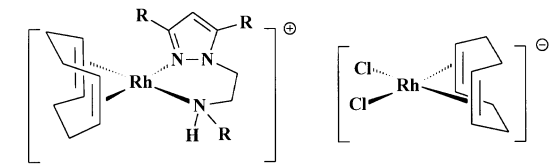
Table 7
IR [a], ^{1}H- and ^{13}C-NMR data of ligands of complexes with ligands of the type *NN′N* (**5**–**8**)

Complex	IR (KBr) ν (cm^{-1})	^{1}H-NMR 250 MHz $CDCl_3$ δ (ppm)	$^{13}C\{^1H\}$-NMR 62 MHz $CDCl_3$ δ (ppm)
Rh_2Cl_2(bdmae) $(cod)_2$ (**5**)	3139 (νC–H_{ar}), 2917–2830 (νC–H_{al} ligand+cod), 1556 (νC=C_{ar}, νC=N_{ar}), 1464–1430 (δ CH_{3as} ligand/δ CH_2 cod), 1423 (δC=C_{ar} ligand+cod, δC=N_{ar}), 1396–1117 (νC–N), 1052–965 (δC–H_{ip} ligand+cod), 818 (δ CH_{oop} cod), 778 (δ C–H_{oop} ligand+cod)	5.83 [s, 2H,C*H* pyrazole], 4.44 [b, 4H, CH_2], 3.53 [b, 8H, =C*H* cod], 2.59 [b, 2H, C$H_2$$CH_3$], 2.38 [b, 8H, CH$H_{exo}$ cod], 2.23 [s, 12H, CH_3 pyrazole], 1.72 [b, 8H, CHH_{endo} cod], 1.45 [b, 3H, CH_2CH_3]	148.4 [*C*CH_3], 140.6 [*C*CH_3], 105.6 [*C*H middle pyrazole], 78,4 [=*C*H cod], 65.3 [*C*H_2], 44.6 [*C*$H_2$$CH_3$], 29.3 [*C*$H_2$ cod], 18.7 [CH_2*C*H_3], 12.9–10.3 [C*C*H_3]
Rh_2Cl_2(bdmai) $(cod)_2$ (**6**)	3117 (νC–H_{ar}), 2917–2830 (νC–H_{al} ligand+cod), 1559 (νC=C_{ar}, νC=N_{ar}), 1464 (δ CH_{3as} ligand/δ CH_2 cod), 1431 (δ C=C_{ar} ligand+cod, δ C=N_{ar}), 1381–1142 (νC–N), 1060–966 (δ C–H_{ip} ligand+cod), 806 (δ CH_{oop} cod), 778 (δ C–H_{oop} ligand+cod)	5.83 [s, 2H,C*H* pyrazole], 5.26 [s, 4H, CH_2], 4.31 [b, 8H, =C*H* cod], 3.58 [b, 1H, C*H*$(CH_3)_2$], 2.44 [b, 8H, CHH_{exo} cod], 2.28 [s, 12H, CH_3 pyrazole], 1.77 [b, 8H, CHH_{endoo} cod], 1.15 [d, $^3J_{H-H}$ = 5.8 Hz, 6H, CH(CH_3)$_2$]	147.0 [*C*CH_3], 139.6 [*C*CH_3], 105.8 [*C*H middle pyrazole], 80.3 [=*C*H cod], 61.0 [*C*H_2], 51.0 [*C*H$(CH_3)_2$], 30.7 [*C*H_2 cod], 22.4 [CH(*C*H_3)$_2$], 14.7–11.0 [C*C*H_3]
Rh_2Cl_2(bmae) $(cod)_2$ (**7**)	3004 (νC–H_{ar}), 2943–2836 (νC–H_{al} ligand-cod), 1554 (νC=C_{ar}, νC=N_{ar}), 1473 (δ CH_{3as} ligand/δ CH_2 cod), 1420 (δ C=C_{ar} ligand+cod, δ C=N_{ar}), 1376–1172 (νC–N), 1049–952 (δ C–H_{ip} ligand+cod), 816 (δ CH_{oop} cod), 735 (δ C–H_{oop} ligand+cod)	7.55 [s, 2H, C*H* pyrazole], 7.49 [s, 2H, C*H* pyrazole], 6.30 [b, 2H,C*H* middle pyrazole], 5.30 [b, 4H, CH_2], 4.21 [b, 8H, =C*H* cod], 2.83 [b, 2H, C$H_2$$CH_3$], 2.42 [m, 8H, CH$H_{exo}$ cod], 1.75 [d, $^3J_{H-H}$ = 8.0 Hz, 8H, CHH_{endo} cod], 1.13 [t, $^3J_{H-H}$ = 6.9 Hz, 3H, CH_2CH_3]	139.8 [*C*H pyrazole], 130.0 [*C*H pyrazole], 106.0 [*C*H middle pyrazole], 79.6 [=*C*H cod], 67.6 [*C*H_2], 44.4 [*C*$H_2$$CH_3$], 30.7 [*C*$H_2$ cod], 12.8 [CH_2*C*H_3]
Rh_2Cl_2(bmai)$(cod)_2$ (**8**)	3098 (νC–H_{ar}), 2936–2831 (νC–H_{al} ligand–cod), 1513 (νC=C_{ar}, νC=N_{ar}), 1470 (δ CH_3 ligand/δ CH_2 cod), 1433 (δ C=C_{ar} ligand+cod, δ C=N_{ar}), 1394–1173 (νC–N), 1087–960 (δ C–H_{ip} ligand+cod), 814 (δ CH_{oop} cod), 756 (δ C–H_{oop} ligand+cod)	7.53 [b, 2H, C*H* pyrazole], 7.51 [b, 2H, C*H* pyrazole], 6.24 [b, 2H, C*H* middle pyrazole], 5.22 [b, 4H, CH_2], 4.26 [b, 8H, =C*H* cod], 3.30 [b, 1H, C*H*$(CH_3)_2$], 2.45 [m, 8H, CHH_{exo} cod], 1.80 [d, $^3J_{H-H}$ = 8.8 Hz, 8H, CHH_{endo} cod], 1.00 [d, $^3J_{H-H}$ = 6.8 Hz, 6H, CH(CH_3)$_2$]	139.5 [*C*H pyrazole], 129.4 [*C*H pyrazole], 106.1 [*C*H middle pyrazole], 79.8 [=*C*H cod], 66.0 [*C*H_2], 50.9 [*C*H$(CH_3)_2$], 30.8 [*C*H_2 cod], 20.2 [CH(*C*H_3)$_2$]

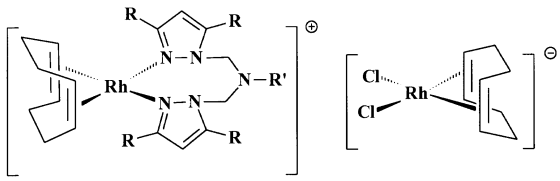
[a] al = aliphatic, ar = aromatic, as = asymmetric, oop = out of plane, ip = in plane, s = singlet, d = doublet, t = triplet, q = quadruplet, septd = septuplet, b = broad signal, m = multiplet.



Scheme 2.



Complexes 1-4



Complexes 5-8

Fig. 3.

The negative electrospray spectrum (-50 V) shows peaks at m/z 283 $[RhCl_2(cod)+2H]^-$ (molecular peak of the anion), 281 $[RhCl_2(cod)–H]^-$, 171 $[Rh(C_5H_9)]^-$ and 113 $[C_8H_{17}]^-$ (100%). In order to identify the molecular complexes of the type $Rh_2(L)Cl_2(cod)_2$ (L = deai NN' and bdmai $NN'N$) we also recorded the APCI (atmospheric pressure chemical ionization) mass spectra of complexes **2** and **6**. This technique shows a different fragmentation pattern but peaks of some cationic and anionic species can be observed. APCI(+) spectra displays m/z peaks:(**2**) 25 V, 392 $[Rh(L)(cod)]^+$ and 182 $[L+H]^+$ (100%); (**6**) 50 V, 211 $[Rh(cod)]^+$ (100%). APCI(−) spectra of complexes **2** and **6** show identical patterns with a m/z peak at 381 $[RhCl_2(cod)]^-$. Neither mass spectrum spectroscopy shows peaks corresponding to the molecular complex $Rh_2Cl_2(L)(cod)_2$.

4. Conclusions

We have synthesized new rhodium (I) complexes containing a 1-aminomethylpyrazole ligand. These complexes were characterized as $Rh_2Cl_2(L)(cod)_2$ complexes (L = NN' and $NN'N$ 1-alkylaminopyrazoles) by elemental analyses, IR and NMR spectroscopies. Molar conductivity values for complexes suggest that complexes are in an 1:1 electrolyte form in solution and NMR data agree with a bidentate coordination of ligands (Fig. 3). To confirm the existence of those ionic species we registered positive and negative electrospray mass spectra of compounds. The results confirmed our hypothesis and cationic $[Rh(L)(cod)]^+$ and anionic $[RhCl_2(cod)]^-$ species have been detected in the ES mass spectra. In addition, the atmospheric pressure chemical ionization mass spectra of some complexes were also registered to detect the molecular form of complexes but only ionic species were found.

Acknowledgements

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Bis[(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine − A Versatile Ligand for Complexation in Rh^I Cationic Complexes

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Keywords: Rhodium / Aminopyrazole / Hemilabile ligands / Cationic complexes

The bis[(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine ligand (**1**) reacts with $[Rh(COD)(THF)_2][BF_4]$ leading to $[Rh(COD)(\mathbf{1})][BF_4]$ ($[\mathbf{2}][BF_4]$) in which **1** is κ^3 bonded in the solid state. Because of the steric bulk of 1,5-cyclooctadiene, it prefers the κ^2 mode of bonding in solution. Substitution of 1,5-cyclooctadiene by carbon monoxide generates $[\mathbf{3}][BF_4]$ in which **1** is κ^3 bonded in solution and solid state. Variable temperature NMR spectroscopic studies give evidence of a $\kappa^3 \rightleftarrows \kappa^2$ equilibrium in solution. $[\mathbf{3}][BF_4]$ is easily decarbonylated to $[Rh(CO)(\mathbf{1})][BF_4]$ $[\mathbf{4}][BF_4]$ in which **1** is κ^3 bonded; however on bubbling carbon monoxide through, $[\mathbf{3}][BF_4]$ is regenerated. The single-crystal X-ray structures of $[\mathbf{2}][BF_4]$, $[\mathbf{3}][BPh_4]$, and $[\mathbf{4}][BPh_4]$ are reported.

Introduction

The readily available pyrazolyl group has allowed the construction of various bi- or polydentate ligands, thus furnishing metal complexes of varying coordination geometry and nuclearity.[1−4] One of the reasons for this success arises from the ability to change the nature, number, and position of substituents in the pyrazole ring, thus allowing a fine tuning of the reactivity of the metal centre to which they are bound. For instance, the most well-developed ligands, the poly(pyrazolyl)borates and their complexes, have found interesting applications in catalysis and bioinorganic chemistry.[1,5−8]

The bonding properties of another family of pyrazole-based chelating ligands, the pyrazole derivatives of simple amines, are also well documented.[4,9,10] They are considered to be hard donor ligands, and the studies of their bonding properties have focussed on cations in high oxidation states, essentially to provide routes to a variety of bioinorganic model systems, or to evaluate their extracting properties. Prompted by the increasing success in catalysis of complexes containing amino ligands,[11−13] it was thought interesting to probe the bonding properties of aminopyrazoles toward soft cations, such as Rh^I. In contrast to the well studied tris(pyrazolyl)borate/Rh^I systems,[14−16] these ligands contain two types of donating centres with different degrees of hardness which might be expected to exhibit different types of behaviour toward the soft Rh^I centre.

We here describe the interactions of a typical aminopyrazole, bis[(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine (**1**) towards a series of cationic Rh^I complexes.

Results and Discussion

Bis[(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine (**1**) reacts with $[Rh(COD)(THF)_2][BF_4]$ − generated in situ from the reaction of $[Rh(COD)Cl]_2$ and $AgBF_4$ in THF − to give the complex $[Rh(COD)(\mathbf{1})][BF_4]$ ($[\mathbf{2}][BF_4]$) in 90% yield. At room temperature, the proton NMR spectrum of $[\mathbf{2}]^+$ shows the presence of two isomers $[\mathbf{2a}]^+$ and $[\mathbf{2b}]^+$ in a 2:1 ratio. The most salient feature of the spectra, and the most significant for probing structural differences, is provided by the NEt resonances, where the ethyl group resonances of the minor isomer are more deshielded than those of $[\mathbf{2a}]^+$. This observation suggests that in $[\mathbf{2b}]^+$ the nitrogen of the amine group is bonded to rhodium, and that the two isomers differ in their coordination to rhodium, which can be either the κ^2 or κ^3 type.

To clarify this point, $[\mathbf{2}][BF_4]$ was structurally characterised by X-ray crystallography. The complex crystallises with three independent ion pairs per unit cell. The three cations of $[\mathbf{2}]^+$ present the same geometry, with the respective distances and angles being equal within experimental errors. A view of one of the three independent cations (cation A) appears as Figure 1; selected bond length and angle data are provided in Table 1. In the solid state, only isomer $[\mathbf{2b}]^+$ is observed. The nitrogen of the amino group N3 is 2.513(7) Å from Rh1; it is longer than the other two Rh−N distances but smaller than the sum of van der Waals radii (3.4 Å). The pyrazolyl-nitrogen to Rh distances are slightly different but are in the range found for hydridotris(pyrazolyl)borate rhodium complexes.[15,16] The N4−Rh1 bond is significantly longer than the N1−Rh1 bond, and this is certainly the consequence of the steric crowding around rhodium as there are no electronic reasons to justify this differ-

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ence. This is evident if we consider the positioning of the 1,5-cyclooctadiene ligand. The atoms C15, C18, N1, and N4 lie in a plane, which is usually[16] defined by the pyrazolyl nitrogen atoms and the middle of the olefinic carbon-carbon bonds. The rhodium atom lies 0.1 Å out of that coordination plane. The position of the cyclooctadiene undoubtedly results from steric crowding attributable to the amino group. Indeed C7 is nearer to C18 carbon than to C15, and lengthening of the Rh1−N4 distance minimises the steric crowding of the ethyl group. Likewise, the C18−Rh1−N4 angle is 10° wider than that of the C15−Rh1−N1 angle. If we consider the pyrazolyl planes, the angle between the mean plane defined by the N4 pyrazolyl ring and the Rh−N4 vector is more acute (142.8°) than the angle between the Rh−N1 vector and the mean plane of the N1 pyrazolyl ring (163.9°). Because of the strain induced by the methylene bridges, the N1−Rh1−N3 and N4−Rh1−N3 angles are around 73°.

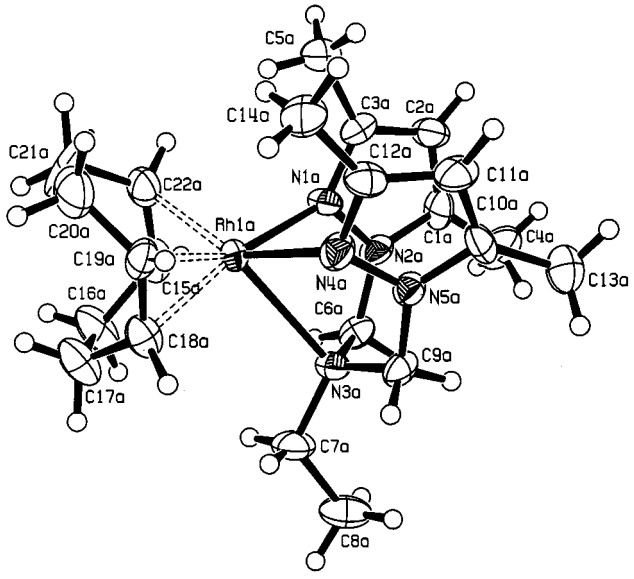


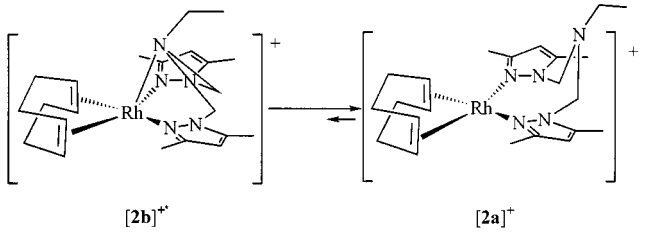
Figure 1. Structure of the cation $[\mathbf{2}]^+$ showing the numbering scheme; ellipsoids are drawn at the 50% probability level

To check whether the solid-state structure is maintained in solution, some crystals were dissolved in deuterated dichloromethane at −70 °C, and the solution was examined by ^{1}H NMR spectroscopy at this temperature. Initially, $[\mathbf{2b}]^+$ is the major component, but the concentration of $[\mathbf{2a}]^+$ slowly increases. When the temperature is raised to 20 °C, the previously observed 2:1 ratio of the isomers $[\mathbf{2a}]^+$/$[\mathbf{2b}]^+$ is rapidly restored, demonstrating the operation of a thermodynamic equilibrium which favours the less sterically encumbered isomer $[\mathbf{2a}]^+$, as summarised in Scheme 1.

We note that, as previously observed by several of the present authors, the reaction of **1** with $[Rh(COD)Cl]_2$ leads to $[Rh(COD)(\mathbf{1})]^+[Rh(COD)Cl_2]^-$.[17] However, in contrast to $[\mathbf{2}]^+$, the cationic part of this latter complex is characterised by broad ^{1}H NMR peaks assignable to ligand **1**, supporting the author's earlier hypothesis concerning the existence of an equilibrium in solution between the ionic

Table 1. Selected bond lengths [Å] and angles [°] for compounds $[\mathbf{2}][BF_4]$, $[\mathbf{3}][BPh_4]$, and $[\mathbf{4}][BPh_4]$

	$[\mathbf{2}][BF_4]$	$[\mathbf{3}][BPh_4]$	$[\mathbf{4}][BPh_4]$
C15−C22	1.403(15)		
C15−Rh1	2.091(10)		
C18−C19	1.384(14)		
C18−Rh1	2.102(10)		
C19−Rh1	2.106(9)		
C22−Rh1	2.091(10)		
N1−Rh1	2.115(7)	2.081(6)	2.015(3)
N3−Rh1	2.513(7)	2.566(5)	2.120(2)
N4−Rh1	2.216(8)	2.107(5)	2.022(3)
C15−Rh1		1.803(9)	1.809(4)
C16−Rh1		1.800(10)	
C6−N3−C9	113.4(8)	111.0(5)	111.8(2)
C6−N3−C7	111.2(8)	109.0(5)	113.2(2)
C9−N3−C7	112.2(8)	114.7(5)	113.1(2)
C6−N3−Rh1	99.7(5)	100.1(4)	105.3(2)
C9−N3−Rh1	106.9(6)	106.7(4)	103.9(2)
C7−N3−Rh1	112.8(6)	114.3(4)	108.7(2)
C15−Rh1−C18	82.6(4)		
C15−Rh1−C19	97.5(4)		
C22−Rh1−C19	81.3(4)		
C15−Rh1−N1	92.6(4)		
C22−Rh1−N1	92.4(3)		
C18−Rh1−N1	166.7(4)		
C19−Rh1−N1	154.9(4)		
C15−Rh1−N4	173.3(4)		
C22−Rh1−N4	143.9(4)		
C18−Rh1−N4	102.2(4)		
C19−Rh1−N4	89.1(3)		
N1−Rh1−N4	81.7(3)	90.4(2)	161.9(1)
C15−Rh1−N3	101.3(4)		
C22−Rh1−N3	138.3(4)		
C18−Rh1−N3	95.8(3)		
C19−Rh1−N3	126.8(3)		
N1−Rh1−N3	72.9(3)	71.7(2)	81.4(1)
N4−Rh1−N3	73.8(3)	72.4(2)	80.5(1)
C15−Rh1−N3		116.9	179.3(2)
C16−Rh1−N3		115.0(3)	
C15−Rh1−N4		89.3(3)	99.3(1)
C15−Rh1−C16		90.0(4)	
C16−Rh1−N1		89.3(3)	
C15−Rh1−N1			98.8(1)



Scheme 1

form and a neutral one [Rh(COD)Cl][μ,η^2−(**1**)]-[Rh(COD)Cl].

In order to evaluate the influence of the 1,5-cyclooctadiene on the bonding capabilities of **1**, we replaced the diene by carbon monoxide. Bubbling carbon monoxide into a solution of $[\mathbf{2}]^+$ in dichloromethane at room temperature

produces $[Rh(CO)_2(\mathbf{1})][BF_4]$ ($[\mathbf{3}][BF_4]$) which can be isolated as a yellow solid in a nearly quantitative yield. The infrared spectrum in the νCO region shows two strong absorption bands at 2080 and 2011 cm^{-1}, and two weak peaks at 2100 and 2038 cm^{-1}, suggesting the presence of two complexes. This is corroborated by the ^1H NMR spectrum that, analogously to $[\mathbf{2a}]^+$ and $[\mathbf{2b}]^+$, exhibits ethyl resonances for two isomers $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$, in the ratio 1:10. However, in contrast to $[\mathbf{2}]^+$, it is the isomer $[\mathbf{3b}]^+$, with the more deshielded ethyl resonances, that is the major compound in solution. For this complex, the methylene protons appear as a broad AB spectrum indicating the existence of a fluxional process in solution. As for $[\mathbf{2}]^+$, the NMR spectroscopic data reveals that there are two isomers where the aminopyrazole ligand can be κ^2 $[\mathbf{3a}]^+$ or κ^3 $[\mathbf{3b}]^+$ bonded. This is corroborated by the infrared data which shows that the minor isomer $[\mathbf{3a}]^+$ exhibits CO absorption at high frequencies, as expected for a 16 valence electron isomer compared to an 18 electron complex. To confirm this hypothesis an X-ray structure determination was undertaken on $[Rh(CO)_2(\mathbf{1})][BPh_4]$ ($[\mathbf{3}][BPh_4]$) obtained by metathesis with $NaBPh_4$, which was easier to crystallise than $[\mathbf{3}][BF_4]$.

Figure 2 depicts cation $[\mathbf{3}]^+$ and salient bond length and angle data are collected in Table 1. The cation has a distorted square pyramid geometry, in which the square plane is defined by the atoms C15, C16, N1, and N4, and the rhodium atom is out of that plane by 0.15 Å. As a consequence of the steric strain imposed by the methylene bridges, the N3 nitrogen atom is not perpendicular to this plane. The Rh−N3 bond is slightly longer than in $[\mathbf{2b}]^+$, but N3 remains within the bonding distance of rhodium. Thus, in the solid state, the structure corresponds to the major isomer $[\mathbf{3b}]^+$ observed in solution. The reduction of the steric crowding around rhodium induced by the replacement of 1,5-cyclooctadiene by two CO molecules is particularly evident if we consider the N1−Rh−N4 angle, which is 81.7(3)° in $[\mathbf{2b}]^+$ and 90.4(2)° in $[\mathbf{3b}]^+$. For the same reasons the Rh−N1 and Rh−N4 bond lengths are, as expected, equal within experimental error.

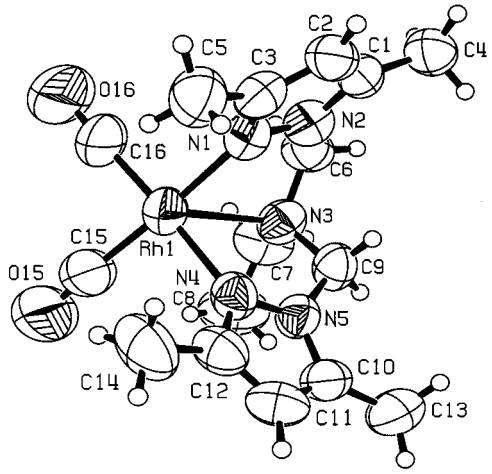
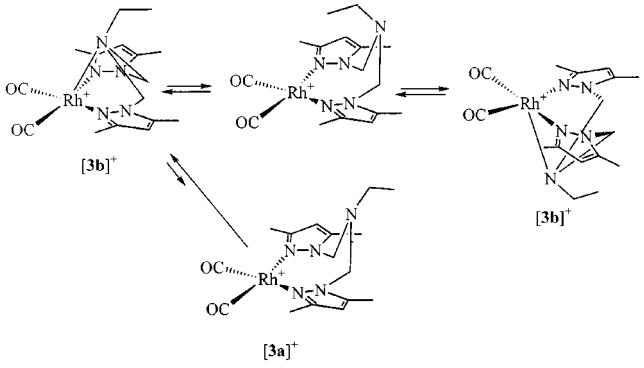


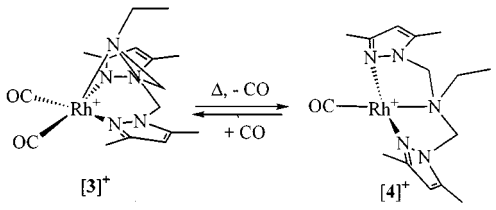
Figure 2. Structure of the cation $[\mathbf{3}]^+$ showing the numbering scheme; ellipsoids are drawn at the 30% probability level

As mentioned above, we observed a broad ^1H NMR AB spectrum for the methylene groups of the isomer $[\mathbf{3b}]^+$, indicating fluxional behaviour in solution for this complex. For this reason we have carried out a variable-temperature ^1H NMR spectroscopic study on the mixture of $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$ in $(CD_3)_2CO$ solution. For the $[\mathbf{3a}]^+$ spectrum no significant changes were observed during this study. At 253 K the methylene hydrogens of $[\mathbf{3b}]^+$ appear as a narrow AB spectrum, but lowering the temperature to 193 K induces no other significant changes, except for a slight broadening of the *N*-ethyl resonances. Raising the temperature to 333 K brings about coalescence of the AB spectrum to a broad singlet. (The solvent and the thermal stability of the complex did not allow acquisition of spectra above this temperature.) This corresponds to a $\Delta G^{\ddagger}$ value of ca. 70 $kJ \cdot mol^{-1}$, a value consistent with the mechanism proposed in Scheme 2 which implies an inversion of configuration of the nitrogen atom.[18] The initial step is the decoordination of N3, followed by inversion at the nitrogen atom, and subsequent coordination of N3 on the other face of the square plane.



Scheme 2

During the workup of $[\mathbf{3}]^+$, and especially after the evaporation of its solutions under vacuum, we observed the formation, in small quantities, of a new product characterised by a ν(CO) absorption at 1997 cm^{-1} in the infrared spectrum. This implies a decarbonylation of $[\mathbf{3}]^+$ and, indeed, refluxing a THF solution of $[\mathbf{3}]^+$ induces the nearly quantitative formation of the new complex $[Rh(CO)(\mathbf{1})][BF_4]$ ($[\mathbf{4}][BF_4]$) possessing a ν(CO) absorption at 1997 cm^{-1}. Bubbling carbon monoxide through a solution of $[\mathbf{4}]^+$ regenerates $[\mathbf{3}]^+$ immediately (Scheme 3).



Scheme 3

The ^{1}H NMR spectrum of $[\mathbf{4}]^+$ shows only the resonances of the coordinated ligand **1**. The solid-state structure of $[\mathbf{4}]^+$ was established by X-ray crystallography on the tetraphenylborate salt $[Rh(CO)(\mathbf{1})][BPh_4]$ ($[\mathbf{4}][BPh_4]$). A view of $[\mathbf{4}]^+$ is shown in Figure 3 and bond lengths and angles of interest are gathered in Table 1. The cation is square-planar, with the atoms N1, N3, N4, and C15 defining the plane, and the rhodium atom lying 0.02 Å above it. The Rh−N3 bond is longer than the other two Rh−N bonds, a consequence of the *trans* influence of the carbonyl ligand and of the different hybridisation of the nitrogen atom. Owing to the steric strain induced by the methylene bridges, the N1−Rh−N3 and the N3−Rh−N4 angles are less than 90°.

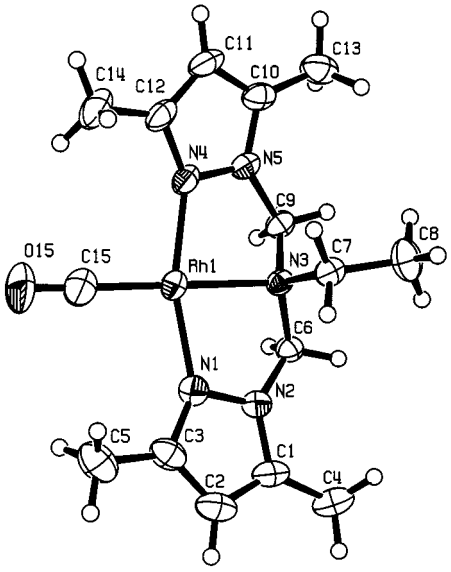


Figure 3. Structure of the cation $[\mathbf{4}]^+$ showing the numbering scheme; ellipsoids are drawn at the 50% probability level

All these structures reveal that **1** is a very flexible ligand that can accommodate, depending on the other ligands around rhodium, either a square-pyramidal geometry in a *fac* configuration or a square planar geometry in a *mer* configuration. Moreover, examination of the structures of other known complexes of bis[(3,5-dimethyl-1-pyrazolyl)methyl]-phenyl or ethylamine with Co^{II},[19,20] Ni^{II},[21] Cu^{I},[22] or Cu^{II},[19] salts shows that the most acute [81.7(3)°] N−M−N angles for the pyrazole ligands have been observed, in our case, with Rh^{I}. The smallest angle observed in the other complexes is 112.5° for the bis[(3,5-dimethyl-1-pyrazolyl)-methyl]phenylamine κ^3 bonded to the $Co(NO_3)_2$ salt[20] in a structure intermediate between a distorted trigonal bipyramid and a square pyramid. This shows that, for this family of ligands, the two pyrazolyl groups can equally adopt *cis*-positions in a square plane. In the other extreme of their bonding capabilities, i.e. in a *trans* configuration, 162° seems to be the maximum value these ligands can accommodate: 161.9(1)° for the N−M−N angle in $[\mathbf{4}]^+$ and 161.3° in an octahedral complex with the $Ni(NO_3)_2$ salt.[21]

Conclusion

This study provides further evidence of the flexibility of the ligand **1** which adapts its bonding mode to various electronic and steric situations around rhodium(I). For instance, for $[\mathbf{2}]^+$ to compensate the steric bulk of the cyclooctadiene ligand it prefers the κ^2 mode of bonding in solution. In the solid state, it adopts the κ^3 mode of bonding but minimises the steric bulk in the square plane by small variations of the length of the Rh−N (pyrazole) bonds. In the absence of steric strain, it adopts a κ^3 mode of bonding either in a *fac* (complex $[\mathbf{3}]^+$) or a *mer* (complex $[\mathbf{4}]^+$) configuration.

Experimental Section

General Remarks: All reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. Tetrahydrofuran and diethyl ether, used for the synthesis, were distilled under nitrogen from sodium benzophenone ketyl just before use. Other solvents were purified following the standard procedures and stored under nitrogen. − NMR spectra were recorded on Bruker AC 200, AC 250, or AMX 400 instruments. All chemical shift values are given in ppm and are referenced with respect to residual protons in the solvent for proton spectra, to solvent signals for ^{13}C spectra. − Elemental analyses were performed in our laboratory on a Perkin−Elmer 2400 CHN analyser. − The bis[(3,5-dimethyl-1-pyrazolyl)methyl]ethylamine[9] and $[Rh(COD)Cl]_2$[23] have been prepared according to published procedures.

Synthesis of [Rh(COD)(1)][BF$_4$] ([2][BF$_4$]): To a solution of 0.079 g (0.16 mmol) of $[Rh(COD)Cl]_2$ in 20 mL of THF was added 0.062 g (0.32 mmol) of $AgBF_4$ and the solution was stirred for half an hour at room temperature. The orange solution turned yellow and AgCl precipitated. The solution was then filtered through a pad of Celite and 0.084 g (0.32 mmol) of **1** was then added. After stirring for an hour, the solution was evaporated to dryness and the residue was crystallised in a dichloromethane/ether mixture to give 0.160 g (90%) of $[\mathbf{2}][BF_4]$ as yellow crystals. − $C_{22}H_{35}BF_4N_5Rh$ (559.3): C 47.24, H 6.32, N 12.52; found C 47.11, H 6.11, N 12.51. Isomer $[\mathbf{2a}]^+$: ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ = 6.58 (d, ^2J = 15.4 Hz, 2 H, CH_2N), 5.79 (s, 2 H, C*H* pyrazole), 5.42 (d, ^2J = 15.4 Hz, 2 H, pyrazole CH_2N), 3.99 (b, 4 H, C*H* cod), 2.76 (q, ^3J = 7.1 Hz, 2 H, CH_2CH$_3$), 2.68 (b, 4 H, CHH_{exo} cod), 2.61 (s, 6 H, CCH_3), 2.56 (b, 4 H, CHH_{endo} cod), 2.25 (s, 6 H, CCH_3), 0.64 (t, ^3J = 7.1 Hz, 3 H, CH$_2$CH_3). − ^{13}C{^{1}H} NMR ($CDCl_3$ solution, 50 MHz) δ: 150.8−137.3 (*C*CH$_3$), 107.5 (*C*H pyrazole), 85.2−83.6 (m, =*C*H cod), 69.4 (*C*H$_2$N), 44.8 (*C*H$_2$CH$_3$), 30.8−30.2 (*C*H$_2$ cod), 15.6−10.6 (CH$_2$*C*H$_3$, C*C*H$_3$). Isomer $[\mathbf{2b}]^+$: ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ = 5.68 (s, 2 H, C*H* pyrazole), 4.96 (d, ^2J = 12.2 Hz, 2 H, CH_2N), 4.87 (d, ^2J = 12.2 Hz, 2 H, CH_2N), 4.14 (q, ^3J = 7.2 Hz, 2 H, CH_2CH$_3$), 3.75 (b, 4 H, =C*H* cod), 2.68 (b, 4 H, CHH_{exo} cod), 2.60 (s, 6 H, CCH_3), 2.56 (b, 4 H, CHH_{endo} cod), 2.17 (s, 6 H, CCH_3), 1.56 (t, ^3J = 7.2 Hz, 3 H, CH$_2$CH_3);. − ^{13}C{^{1}H} NMR ($CDCl_3$ solution, 50 MHz)150.8−137.3 (*C*CH$_3$), 107.6 (*C*H pyrazole), 85.2−83.6 (m, =*C*H cod), 65.5 (*C*H$_2$N), 52.5 (*C*H$_2$CH$_3$), 30.8−30.2 (*C*H$_2$ cod), 15.6−10.6 (CH$_2$*C*H$_3$, C*C*H$_3$).

Synthesis of [Rh(CO)$_2$(1)][BF$_4$] ([3][BF$_4$]): Carbon monoxide was bubbled for 1 h through a solution of 0.168 g of $[\mathbf{2}][BF_4]$ dissolved in 20 mL of dichloromethane. The solution was then evaporated to dryness in vacuum leaving 0.124 g (80%) of **3** as a yellow powder.

− IR (CH_2Cl_2 solution) ν(CO): 2100 (w), 2080 (s), 2038 (w), 2011 (s) cm^{-1}. Isomer [**3a**]$^+$: ^1H NMR δ = 6.28 (s, 2 H, C*H*), 5.23 (AB system, ^2J = 11.7 Hz, 4 H, CH_2N), 3.79 (q, ^3J = 7.2 Hz, 2 H, CH_2CH$_3$), 2.64 (s, 6 H, CCH_3), 2.45 (s, 6 H, CCH_3), 1.61 (t, ^3J = 7.2 Hz, 3 H, CH$_2$CH_3); Isomer [**3b**]$^+$: ^1H NMR (CD_3)$_2$CO solution, 250 MHz) δ = 6.29 (s, 2 H, C*H*), 5.59 (broad AB system, ^2J = 11.8 Hz, 4 H, CH_2N), 3.16 (q, ^3J = 7.3 Hz, 2 H, CH_2CH$_3$), 2.58 (s, 6 H, CCH_3), 2.35 (s, 6 H, CCH_3), 1.17 (t, ^3J = 7.3 Hz, 3 H, CH$_2$CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 63 MHz) δ = 185 (d, ^1J = 69.0 Hz, *C*O), 151.7 (*C*CH$_3$), 144.7 (*C*CH$_3$), 108.1 (*C*H), 65.7 (*C*H$_2$N), 50.3 (*C*H$_2$CH$_3$), 16.1, 13.9.11.2 (2 C*C*H$_3$ + CH$_2$*C*H$_3$).

Synthesis of [Rh(CO)$_2$(1)][BPh$_4$] ([3][BPh$_4$]): To a solution of 0.135 g (0.32 mmol) of [**3**][BF_4] in 10 mL of methanol was added 0.110 g (0.32 mmol) of $NaBPh_4$ and the solution was stirred for 1 h. A yellow precipitate appeared which was filtered and dried under vacuum. It was recrystallised in a dichloromethane/methanol mixture under a CO atmosphere. $C_{40}H_{43}BN_5O_2Rh$ (739.5): C 64.97, H 5.86, N 9.47; found C 64.52, H 6.01, N 9.20.

Synthesis of [Rh(CO)(1)][BF$_4$] ([4][BF$_4$]): A solution of 0.12 g of [**3**][BF_4] in 20 mL of THF was refluxed for 2 h. The solvent was evaporated to dryness in vacuum leaving 0.1 g of a yellow solid. − IR (CH_2Cl_2 solution) ν(CO): 1997 cm^{-1}. − ^1H NMR ($CDCl_3$ solution, 200 MHz) δ = 5.95 (s, 2 H, C*H*), 5.28 (AB system, ^2J = 12.1 Hz, 4 H, CH_2N), 2.93 (q, ^3J = 7.4 Hz, 2 H, CH_2CH$_3$), 2.37 (s, 6 H, CCH_3), 2.18 (s, 6 H, CCH_3), 0.98 (t, ^3J = 7.4 Hz, 3 H, CH$_2$CH_3). − $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 50 MHz) δ = 188.3 (d, ^1J = 78.0 Hz, *C*O), 152.7 (*C*CH$_3$), 142.7 (*C*CH$_3$), 107.3 (*C*H), 68.7 (*C*H$_2$N), 51.6 (*C*H$_2$CH$_3$), 14.5−11.8, 11 (CH$_2$*C*H$_3$ + 2 C*C*H$_3$).

Synthesis of [Rh(CO)(1)][BPh$_4$] ([4][BPh$_4$]): To a solution of 0.1 g of [**4**][BF_4] in 10 mL of methanol was added 0.110 g (0.32 mmol) of $NaBPh_4$ and the solution was stirred for 1 h. A yellow precipitate appeared which was filtered and dried under vacuum. It was recrystallised in a dichloromethane/methanol mixture. $C_{39}H_{43}BN_5ORh$ (711.5): C 65.82, H 6.10, N 9.84; found C 65.67, H 5.79, N 9.63.

X-ray Crystallographic Study: Crystals of [**2**][BF_4], [**3**][BPh_4], and [**4**][BPh_4] suitable for X-ray diffraction were obtained through recrystallisation from a dichloromethane/ether mixture for [**2**][BF_4] and dichloromethane/methanol mixture for [**3**][BPh_4], and [**4**][BPh_4]. Data were collected on an STOE IPDS diffractometer at 160 K [**2**][BF_4] and [**4**][BPh_4], and at 298 K [**3**][BPh_4]. Full crystallographic data for the three complexes are gathered in Table 2. All calculations were performed on a PC-compatible computer using the WinGX system.[24] The structures were solved using the SIR92 program,[25] which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses by using the SHELXS97 program.[26] Phenyl ring within the tetraphenylborate counter anion in the structure of [**4**][BPh_4] have been refined as rigid groups (D_{6h} symmetry; C−C = 1.39 Å; C−H = 0.93 Å). Atomic scattering factors were taken from the usual tabulations.[27] Anomalous dispersion terms for Rh were included in F_c.[28] All non-hydrogen atoms were allowed to vibrate anisotropically. All

Table 2. Crystal data for [**2**][BF_4], [**3**][BPh_4], and [**4**][BPh_4]

compound	[**2**][BF_4]	[**3**][BPh_4]	[**4**][BPh_4]
empirical formula	$C_{66}H_{105}B_3F_{12}N_{15}Rh_3$	$C_{41}H_{45}BCl_2N_5O_2Rh$	$C_{39}H_{43}BN_5ORh$
molecular mass, g	1677.81	824.44	711.50
temperature, K	160(2)	298(2)	160(2)
wavelength, Å	0.71073		
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)
a, Å	11.958(2)	10.562(1)	10.335(1)
b, Å	15.218(2)	13.757(1)	11.549(1)
c, Å	20.010(3)	28.379(3)	15.208(2)
α, deg	85.76(2)		80.38(1)
β, deg	81.15(2)	95.93(1)	87.04(1)
γ, deg	88.24(2)		84.89(1)
volume, Å^3	3587.3(8)	4101.6(7)	1781.3(3)
Z	2	4	2
$D_{calcd.}$, g.cm^{-3}	1.553	1.335	1.327
μ, mm^{-1}	0.765	0.587	0.517
F(000)	1728	1704	740
θ range, deg	2.07−25.99	2.07−26.23	2.56−26.16
index ranges	$-14 \le h \le 14$	$-12 \le h \le 13$	$-12 \le h \le 12$
	$-18 \le k \le 18$	$-16 \le k \le 16$	$-14 \le k \le 14$
	$-24 \le l \le 24$	$-34 \le l \le 35$	$-18 \le l \le 18$
reflections collected	35478	28064	17761
independent reflections	13042 [*R*(int) = 0.0332]	7859 [*R*(int) = 0.0791]	6528 [*R*(int) = 0.0286]
completeness to θ_{max},%	92.5	95.2	90.9
refinement method	full-matrix least-squares on F^2		
data/restraints/parameters	13042/0/902	7859/0/474	6479/0/491
g.o.f. on F^2	0.823	0.856	1.043
$R[I > 2\text{sigma}(I)]$	0.0251	0.0577	0.0404
$R[I > 2\text{sigma}(I)]$	0.0687	0.1475	0.1012
R(all data)	0.0895	0.1529,	0.0466,
R(all data)	0.0909	0.2072	0.1052
residual electron density e·Å^{-3}	0.424 and −0.501	0.373 and −0.622 e	0.836 and −0.654

the hydrogen atoms were set in an idealised position (R_3CH, C−H = 0.96 Å; R_2CH_2 = 0.97 Å; $C(sp^2)$−H = 0.93 Å; U_{iso} 1.2 times greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and held fixed during refinements. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication n° CCDC 16295, CCDC 16296, CCDC 16297. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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Synthesis of the new potentially hemilabile ligand: 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole, and comparison of its bonding properties with the related 1-[(N-ethyl)-2-aminoethyl]-3,5-dimethylpyrazole ligand toward Rh(I)

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Keywords: Rhodium / Phosphinoalkylpyrazole / Aminoalkylpyrazole / hemilabile ligands/ hydroformylation.

The new ligand 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**2**) has been prepared by the reaction between 1-(chloroethyl)-3,5-dimethylpyrazole and PPh_2Li. Didentate *N*,*N* 1-[(N-ethyl)-2-aminoethyl]-3,5-dimethylpyrazole (**1**) and **2** ligands react with $[Rh(COD)(THF)_2][BF_4]$ to give $[Rh(COD)(\mathbf{1})][BF_4]$ (**3**) and $[Rh(COD)(\mathbf{2})][BF_4]$ (**4**), respectively. Substitution of 1,5-cyclooctadiene for carbon monoxide in the later complexes generates $[Rh(CO)_2(\mathbf{1})][BF_4]$ (**5**) and $[Rh(CO)_2(\mathbf{2})][BF_4]$ (**6**), respectively. The treatment of $[Rh(COD)(THF)_2][BF_4]$ by two equivalent amounts of **2** results in the $[Rh(\mathbf{2})_2][BF_4]$ complex (**7**) which converts to $[Rh(CO)(\mathbf{2})_2][BF_4]$ (**8**) upon reaction with carbon monoxide. The ligand **2** in complex **7** exhibits an hemilabile character. The single-crystal X-ray structures of **3**, **4** and **7** are reported.

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Introduction

In recent years the use of hemilabile ligands in coordination and organometallic chemistry has increased because of their potential applications in catalysis. Many didentate ligands containing two donor centres of different strength-such as mixed phosphorus-heteroatom ligands have been reviewed in recent reports and articles.[1,2,3] Their interest in catalysis arises from the easy decoordination of the weak donor centre without the displacement of the ligand, which should confer a better stability to the reaction intermediates. Mixed ligands containing phosphorus along with oxygen, nitrogen or sulphur donor atoms have been specifically designed for use in catalytic reactions such as hydrogenation,[4, 5, 6] oligomerization,[7] and hydroformylation of olefins.[8]

Pyrazole-derived molecules are good candidates in the preparation of interesting N,N' or N,P mixed ligands owing to their ease of synthesis and the possibility of electronic and steric modulation of their properties. Pyrazole-amines have been extensively studied as ligands for hard transition metal cations.[9] These studies have lead to remarkable structures for the resulting complexes, some of which can be regarded as bioinorganic models.[10,11] Some reviews about pyrazole chelating ligands in biological model systems have recently appeared.[12,13]

Pursuing investigations of pyrazole-based polydentate ligands, we have directed our efforts toward the study of their reactivity with soft transition metal ions in order to compare their behaviour with that of the well known tris(pyrazolyl)borate anion.[14] Very recently we have described the coordinating properties of Bis[(3,5-dimethylpyrazolyl)methyl]ethylamine toward Rh(I). This ligand, which contains two different N donor centres, leads to a $\kappa^2 \rightleftharpoons \kappa^3$ equilibrium in solution revealing its hemilabile character through a reversible de-coordination of the amino group. κ^3 coordination mode has been found in the solid state structure determinations.[15]

In the present paper we describe an extension of this work to a new family of N,P ligands of the type phosphinoalkylpyrazole. Prior to our investigations, in this class of ligands only the diphenylphosphinomethylpyrazole has been described.[16] We report the synthesis of 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole and the study of its bonding properties toward Rh(I). For comparative purpose, the reactivity of the related N,N' didentate ligand 1-[(N-ethyl)-2-aminoethyl]-3,5-dimethylpyrazole toward Rh(I) has also been investigated.

Results and Discussion

The 1-[(N-ethyl)-2-aminoethyl]-3,5-dimethylpyrazole (**1**) was synthesized according to a procedure previously described by Driessen.[17]

The new 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**2**) was prepared by reaction of 1-(chloroethyl)-3,5-dimethylpyrazole[18] with PPh_2Li - generated *in situ* by deprotonation of PPh_2H by n-BuLi in tetrahydrofuran - at 0ºC (Scheme 1). The new ligand, isolated in 83% yield as a colourless oil, was characterized by C, H and N elemental analyses, IR, ^{1}H-, ^{13}C and ^{31}P-NMR spectroscopies and by electron impact mass spectrometry. The diphenylphosphino moiety gives a singlet at δ = -20.9 ppm in the ^{31}P-NMR spectrum.

1-[(N-ethyl)-2-aminoethyl]-3,5-dimethylpyrazole (**1**) or 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**2**) react with one equivalent of $[Rh(COD)(THF)_2][BF_4]$ – generated *in situ* from the reaction of $[Rh(COD)Cl]_2$ and $AgBF_4$ in tetrahydrofuran – to give the complexes $[Rh(COD)(\mathbf{1})][BF_4]$ (**3**) and $[Rh(COD)(\mathbf{2})][BF_4]$ (**4**) in 89% and 94% yield, respectively (Scheme 2). Elemental analyses of both complexes were consistent with their formulation.

We were able to prepare X-ray quality crystals of complexes **3** and **4** and we undertook the crystal structure determination of both of them. The molecular structures of the complexes consist of discrete $[Rh(COD)(\mathbf{1})]^+$ and $[Rh(COD)(\mathbf{2})]^+$ cations, respectively, and BF_4^- anions. Perspective views of the cation complexes are given in Figure 1, and Figure 2, respectively. Selected bond distances and angles are provided in Table 1, and the details of data collection and crystal data are summarized in Table 2. A slightly distorted square-planar geometry is observed around Rh in both structures. Thus, in **3** Rh deviates by 0.025 Å from the mean coordination plane formed by two N donor atoms of the ligand and the centroid of the olefinic C=C bonds of the COD ligand. In **4** Rh deviates by 0.139 Å from the mean plane formed by the donor N and P atoms of the ligand and the centroid of the olefinic C=C bonds of the COD ligand. The Rh-N distances of 2.116(3) and 2.148(3) Å for **3**, and of 2.141(2) Å for **4** fall between the experimental values reported for related complexes.[15,19,21] The Rh-P bond length of 2.274(1) Å for **4** is also comparable to those found in the litterature.[19,22] Due to the different *trans* effect of the donor atoms in **4** the Rh-C bonds *trans* to phosphorus [2.236(2) and 2.216(2) Å] are longer than the Rh-C bonds *trans* to nitrogen [2.132(2) and 2.129(2) Å].[19] The N1-Rh1-N3 angle [82.90(14)º] for **3** and

the N1-Rh1-P1 angle [82.68(5)º] for **4** are smaller than 90º but consistent with the reported angles for similar complexes.[15, 19] It is worth noting that in both structures the 6-membered rings formed by the didentate ligands coordinated to rhodium adopts a boat-type conformation, the atoms Rh1 and C6 (both structures) being at the apex of the boat.

The ^{1}H-NMR spectrum for **3** recorded at 293 K (250 MHz) shows three signals of relative intensity 2:1:1 at 4.37, 4.29 and 4.21 ppm for the non equivalent olefinic protons of the 1,5-COD ligand in a *trans* position to the pyrazole ring and in a *trans* position to the amino group. This is fully consistent with the solid state structure that in fact evidences that the nitrogen atom of the amino group coordinated to rhodium constitutes a stereogenic centre. Lowering the temperature to 243K induces the splitting of the signals at 4.37 ppm. On the opposite, by increasing the temperature to 323K a general broadening of all the signals and very significantly, a coalescence of the olefinic protons of the 1,5-COD is observed at 310K to a single signal centred at 4.35 ppm. This clearly demonstrates that complex **3** executes a dynamic process in solution. The coalescence temperature corresponds to a $\Delta G^{\ddagger}$ value of 15 (±1) kcal.mol^{-1}.[20] The averaging of the olefinic protons of 1,5-COD can reasonably be interpreted in term of decoordination of one end of the ligand **1**, rotation and recoordination, thus revealing the hemilabile character of the ligand **1** in complex **3**. The experimental data don't allow, however, to determine unambiguously which end of the ligand eventually decoordinates. Indeed, except a general broadening of the signals, there are no significant changes of the chemical shifts for the protons of the methyl and ethyl groups of the ligand. We can only suspect that the harder end of the ligand, the amino group, is mainly concerned with this phenomenon as shown in Scheme 3.

In the case of complex **4** the room temperature ^{1}H NMR spectrum shows, three thin signals characteristic of the CH (δ = 5.59 ppm) and the methyl substitutents (δ = 2.34, 2.22 ppm) of the pyrazolyl group. The other resonances are broad signals centred at 5.29 ppm (4H), 3.71 ppm (2H) and a large signal between 3.2 and 1.8ppm (10H). The signals at 5.29 and 3.71 ppm are in area characteristic of the olefinic protons of 1,5-COD in a *trans* position to a phosphorus atom and in a *trans* position to a nitrogen atom.[19]. So we can deduce that the signal at 5.29 ppm is the sum of two olefinic protons of 1,5-COD and the two protons of the methylene group bonded to the nitrogen of the pyrazolyl ring. The large signal is the sum of the protons of the methylene group bonded to phosphorus and the alkyl protons of the 1,5-COD.These observations suggested that complex **4** was executing a fluxional process and variable-temperature experiments were performed at 500 MHz. By

lowering the temperature to 230 K each resonance splits into two more signals at 5.43 and 5.25 ppm for the olefinic protons in a *trans* position to the phosphorus atom and 3.85 and 3.46 ppm for the olefinic protons in a *trans* position to the nitrogen atom, leading to four signals for the non equivalent olefinic protons of the 1,5-COD. The coalescence temperature of the 5.43 and 5.25 ppm resonances occurred at 280 K while the 3.85 and 3.46 ppm resonances coalescence was observed at 290 K. This corresponds to a $\Delta G^{\ddagger}$ value of 13 (±1) kcal·mol^{-1} [20]. Raising the temperature to 333 K brought no more significant differences than the narrowing of the two signals at 5.33 and 3.68 ppm. The ^{31}P-NMR spectra, recorded in the same temperature range, show a doublet at 28.4 ppm ($^{1}J_{P,Rh}$ = 146.3 Hz) with no other changes than a slight displacement with temperature. From these observations it is clear that the fluxional process implies an exchange between the two protons of 1,5-COD which are *trans* to the phosphorus atom, and between the two protons which are *trans* to the nitrogen only. No exchange between the two groups of proton could be evidenced. All this has been corroborated by ^{1}H NMR spin transfer experiments on the olefinic proton resonances. The dynamic behaviour of complex **4** can thus be rationalised in terms of boat-boat configuration inversion of the 6-membered ring Rh1-P1-C7-C6-N2-N1 (see Figure 2) in solution. No evidence for a hemilabile behaviour of ligand **2** in complex **4** –that would have led to an averaging of *all* the olefinic proton resonances- could be obtained in the temperature range allowed by the thermal stability of the complex.

In complex **3** and **4** the 1,5-COD ligand was displaced by carbon monoxide upon bubbling the gas in dichloromethane solutions at room temperature to give [Rh(CO)$_2$(**1**)][BF$_4$] (**5**) and [Rh(CO)$_2$(**2**)][BF$_4$] (**6**) respectively (Scheme 2). Complex **6** reverted to some extent to complex **4** upon evaporation of the solvent. Thus, several cycles of bubbling of carbon monoxide and vacuum drying were necessary to eliminate free 1,5-COD in order to get complex **6** in reasonable yield.

The IR spectrum of **5** shows two strong absorption bands at 2098 and 2033 cm^{-1} due to νCO vibrations. The ^{1}H-NMR spectrum proved the absence of the 1,5-COD ligand and the appearance of two doublets at 182.5 ppm ($J_{Rh,C}$= 69.8 Hz) and 181.5 ppm ($J_{Rh,C}$= 67.3 Hz) in the ^{13}C-NMR spectrum confirmed the presence of two CO ligands coordinated to the rhodium atom.

The IR spectrum of **6** shows two strong absorption bands at 2103 and 2042 cm^{-1} in the νCO region. Its ^{1}H-NMR spectrum confirms the deco-ordination of the 1,5-COD ligand. The ^{13}C-NMR spectrum displays resonances of the two CO ligands as doublet of doublets

at 184.8 ppm ($J_{Rh,C}$= 67 Hz, $J_{P,C}$= 16 Hz) for the CO in *trans* position to nitrogen atom, and at 179.9 ppm ($J_{Rh,C}$= 60 Hz, J_{PC}= 104 Hz) for the CO in *trans* position to phosphorus atom. The ^{31}P-NMR spectrum of **6** displays a doublet at 30.2 ppm with $J_{P,Rh}$ = 120.9 Hz.

The reaction of $[Rh(COD)(THF)_2][BF_4]$, -generated *in situ* from the reaction of $[Rh(COD)Cl]_2$ and $AgBF_4$ in tetrahydrofuran- and two equivalent amounts of the ligand **1** led only to **3**. This is not a total surprise since it is known that NN ligands cannot displace 1,5-COD in $[Rh(COD)(NN)]BF_4$ complexes.[23] The same reaction conducted from **2** resulted in the formation of a yellow-orange complex **7** in 92% yield. Elemental analyses and spectroscopic data supported the formation of the $[Rh(\mathbf{2})_2][BF_4]$ complex. The ^{1}H- and ^{13}C-NMR spectra display the expected signals of the ligand whereas the ^{31}P-NMR spectrum shows a doublet at 44.9 ppm with $^1J_{P,Rh}$ = 171 Hz. This complex was also characterized by X-ray crystallography. The molecular structure **7** consists of discrete $[Rh(\mathbf{2})_2]^+$ cations and BF_4^- anions. The cation complex is shown in Figure 3, selected bond distances and angles are provided in Table 1, and the details of data collection and crystal data are summarized in Table 2. The structure shows a planar geometry around rhodium atom, the phosphorus atoms of the two ligands **2** being in a *cis* position. The metal slightly deviates from the mean coordination plane formed by the two N and the two P donor atoms by 0.031 Å. The Rh-N (2.119(2) Å and 2.113(2) Å) and the Rh-P bond distances (2.207(1) Å and 2.223(1) Å) are consistent with those found in the literature.[19,21,22] Phenyl rings are oriented face to face at a distance of 3.287 Å, suggesting a π-π stacking interaction[24]. The P1-Rh1-P2 angle [99.03(3)º] is larger than 90º and as a consequence the N3-Rh1-P2 angle [83.43(6)º] is more acute than the others [N3-Rh1-N1 = 88.37(9)º; N1-Rh1-P1 = 89.13(7)º].

To prove a hemilabile behaviour of the ligand **2** in **7**, carbon monoxide was bubbled into a solution of the complex in dichloromethane. This led to the formation of a new compound that was characterised by IR and NMR spectroscopies as $[Rh(CO)(\mathbf{2})_2][BF_4]$ (**8**). The evaporation of the solvent in vacuum or bubbling nitrogen into the solution of **8** slowly regenerated **7**. In solution **8** shows a νCO absorption band at 2014 cm^{-1}. At room temperature the ^{1}H, ^{13}C and ^{31}P-NMR spectra indicate that the two ligands **2** are equivalent, thus suggesting a fluxional process in solution. Variable temperature $^{31}P\{^1H\}$ and ^{1}H NMR experiments were performed. The most informative results were obtained from the $^{31}P\{^1H\}$ experiments in CD_2Cl_2 solution. Indeed, the room temperature spectrum shows a thin doublet at 25.8 ppm ($J_{Rh,P}$ = 122 Hz). Lowering the temperature first induces a progressive broadening of the signal to give a broad resonance centred at 23.9 ppm at

193K. At 173K, the lowest temperature we could attain, a slightly broad ABX spin system appears. The parameters of the system- δ_A = 28.1ppm, δ_B = 19.5ppm; $J_{A,B}$ = 291 Hz, $J_{A,X}$ = 120 Hz, $J_{B,X}$ = 125 Hz - are consistent with a square planar structure in which the two phosphorus atoms are in *trans* position and only one of the two ligands **2** is κ^2 coordinated the second one being κ^1 coordinated by the phosphorus atom to rhodium. At the same temperature the ^{1}H NMR spectrum shows broad resonances only. The coalescence temperature in the $^{31}P\{^1H\}$ NMR spectra lead to a $\Delta G^{\ddagger}$ value of 8 (±1) kcal.mol^{-1}.[20] The fluxionality observed for **8** likely results from an exchange between κ^2 and κ^1 modes of bonding for the two ligands **2** by opening of one of the rhodium-pyrazolyle bonds. The same type of dynamic process was previously observed for the $[Ir(PN)_2(CO)][PF_6]$ complex (PN = 1-(2-pyridyl)-2-(diphenylphosphino)ethane) [23] and this is frequently observed in complexes containing two hemilabile didentate ligands.[2,3] The scheme 4 summarises our observations.

The catalytic activity of complexes **4** and **7** has been evaluated for the hydroformylation of styrene. In our experimental conditions (dichloromethane as solvent, 20 bar of a 1:1 mixture of CO and H_2, 50°C) a low conversion was observed (1% for **4** and 10% for **7**) and only the branched aldehyde was detected.

Conclusions

In this work we have described the synthesis of the new potentially hemilabile N, P didentate ligand, the 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**2**). The reaction of **2** and the related N,N' didentate ligand 1-[(N-ethyl)-2-aminoethyl]-3,5-dimethylpyrazole (**1**) with the rhodium(I) complex $[Rh(COD)(THF)_2]BF_4$ has led to the complexes $[Rh(COD)(\mathbf{1})]BF_4$ (**3**) and $[Rh(COD)(\mathbf{2})]BF_4$ (**4**) which have been fully characterised. Both these compounds exhibit a fluxional process in solution that can be interpreted in terms of an hemilabile behaviour of the ligand **1** in complex **3**, and a boat-boat ring inversion of the 6-membered ring formed upon coordination of the ligand **2** in complex **4**. The 1,5-COD ligand in complex **3** and **4** can easily be displaced by carbon monoxide leading to the complexes $[Rh(CO)_2(\mathbf{1})]BF_4$ (**5**) and $[Rh(CO)_2(\mathbf{2})]BF_4$ (**6**) respectively. The reaction of two equivalents of **2** with $[Rh(COD)(THF)_2]BF_4$ leads to $[Rh(\mathbf{2})_2][BF_4]$ (**7**) in which the phosphorus atoms are in a *cis* position. The later complex absorbs reversibly one molecule of CO to afford complex $[Rh(\mathbf{2})_2(CO)][BF_4]$ (**8**) for which NMR studies have evidenced a dynamic exchange between κ^2 and κ^1 modes of bonding for

the two ligands **2** by opening of one of the rhodium-pyrazolyle bonds. In spite of this hemilabile property of ligand **2**, complex **7** shows a low activity for the catalytic hydroformylation of styrene.

Experimental Section

General Procedures. All chemicals were used as received from commercial suppliers, unless otherwise indicated. Reactions were carried out under dinitrogen atmosphere using vacuum line and Schlenk techniques. Solvents were dried and distilled according to standard procedures and stored under nitrogen. NMR spectra were acquired on a Bruker AC200, AC250, Avance DPX250 or Avance DRX500 spectrometer in $CDCl_3$ solutions unless otherwise indicated. All the chemical shift are given in ppm and are referenced with respect to residual protons in the solvent for ^{1}H spectra, to solvent signals for ^{13}C spectra and to external H_3PO_4 for ^{31}P spectra. IR spectra were recorded on a Perkin Elmer 2000 spectrophotometer with KBr pellets or in dichloromethane solutions with CaF_2 cells. Elemental analysis were performed at the Laboratoire de Chimie de Coordination on a Perkin-Elmer 2400 CHN analyser or at the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 apparatus. Electronic impact mass spectra were measured by the staff of the Mass Spectrometry Service at the Université Paul Sabatier (Toulouse). $[Rh(COD)Cl_2]$ was prepared according to literature procedure.[25]

Synthesis of 1-(chloroethyl)-3,5-dimethylpyrazole.[18] 3,5-dimethylpyrazole (1.00 g, 10.4 mmol), 40% aq. NaOH 12 mL, tetrabutylammonium bromide (TBAB, 0.483 g, 1.5 mmol), toluene (20 mL) and 1-bromo-2-chloroethane (10 mL, 17.23 g, 120 mmol) were mixed and heated to reflux for 48 h. The mixture was allowed to cool to room temperature, the phases were separated and the aqueous phase was extracted with 3x20 mL of dichloromethane. The extracts were combined with the organic phase and the solvents were then removed under vacuum. The addition of diethyl ether (15 mL), filtration and evaporation of the solvent yielded the 1-(chloroethyl)-3,5-dimethylpyrazole as colourless oil. Yield: 88%. M. p.: 20-22 ºC. Anal. Calcd for $C_7H_{11}ClN_2$ (%): C, 53.00; H, 6.99; N, 17.66. Found: C, 52.69; H, 6.63; N, 17.83. IR (neat between KBr cells) $\nu(cm^{-1})$: 3046 ($\nu C\text{-}H_{ar}$), 2967-2871 ($\nu C\text{-}H_{al}$), 1555 ($\nu C{=}C_{ar}$, $\nu C{=}N_{ar}$), 1463 (δCH_{3as}), 1426 ($\delta C{=}C_{ar}$, $\delta C{=}N_{ar}$), 1388-1188 ($\nu C\text{-}N$), 860 ($\nu C\text{-}Cl$). NMR ^{1}H (250 MHz, $CDCl_3$, 20°C): δ = 5.74 [s, 1H, C*H* pyrazole], 4.19 [t, $^{3}J_{H,H}$ = 6.3 Hz, 2H, C$H_2$$CH_2Cl$], 3.79 [t, $^{3}J_{H,H}$ = 6.3 Hz, 2H, CH_2CH_2Cl], 2.21 [s, 3H, CCH_3], 2.15 [s, 3H, CCH_3]. NMR $^{13}C\{^{1}H\}$ (63 MHz, $CDCl_3$, 20°C): δ = 148.2 [*C*CH_3],

139.7 [*C*CH_3], 105.1 [*C*H pyrazole], 49.6 [*C*H_2CH_2Cl], 43.0 [CH_2*C*H_2Cl], 13.4 [C*C*H_3], 11.0 [C*C*H_3]. Mass spectral data (EI, m/e): [$M^{+\cdot}$] = 158, [M^+- Cl] = 122, [M^+- CH_2Cl] = 109, [$M^{+\cdot}$- C_2H_3Cl] = 96.

Synthesis of 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (2). 100 µl (1.6 mmol) of n-BuLi (solution 1.6 M in hexane) were added dropwise to a stirred solution of 300 µl (1.724 mmol) of PPh_2H in 10 mL of tetrahydrofuran at 0ºC. After 30 min, the solution of PPh_2Li was added dropwise to a stirred solution of 0.325 g (2.0 mmol) of 1-(chloroethyl)-3,5-dimethylpyrazole in 20 mL of tetrahydrofuran at 0ºC. The mixture was maintained at 0ºC for 1 h. The temperature was then raised to room temperature and after 15 h of stirring the solvent was evaporated under vacuum. 40 mL of dichloromethane were added to the residue and the salts were extracted with 2x10 mL of distilled water. The evaporation of the solvent from the organic phase gives the 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**2**) as a colourless oil. Yield: 83%. M. p.: 20-22 ºC. Anal. Calcd for $C_{19}H_{21}N_2P$ (%): C, 74.01; H, 6.86; N, 9.08. Found: C, 73.72; H, 6.68; N, 9.28. IR (neat between KBr cells) ν(cm^{-1}): 3074-3046 (νC-H_{ar}), 2923 (νC-H_{al}), 1553 (νC=C_{ar}, νC=N_{ar}), 1482 (δCH_{3as}), 1435 (δC=C_{ar}, δC=N_{ar}), 1387-1184 (νC-N), 764-704 (νP-C, δC-H_{oop}). NMR ^{1}H (200 MHz, $CDCl_3$, 20°C): δ = 7.48-7.29 [m, 10H, PPh_2], 5.71 [s, 1H, C*H* pyrazole], 4.10-3.99 [m, 2H, C*H*$_2CH_2PPh_2$], 2.61-2.53 [m, 2H, CH_2C*H*$_2PPh_2$], 2.19 [s, 3H, CC*H*$_3$], 2.06 [s, 3H, CC*H*$_3$]. NMR ^{13}C{^{1}H} (63 MHz, $CDCl_3$, 20°C): δ = 147.3 [*C*CH_3], 138.2 [*C*CH_3], 132.7-128.3 [PPh_2], 104.8 [*C*H pyrazole], 45.4 [d, $^2J_{C-P}$ = 25.0 Hz, *C*$H_2CH_2PPh_2$], 29.4 [d, $^1J_{C-P}$ = 14.4 Hz, CH_2*C*H_2PPh_2], 13.4 [C*C*H_3], 10.8 [C*C*H_3]. NMR ^{31}P{^{1}H} (81 MHz, $CDCl_3$, 20°C): δ= -20.9 [PPh_2]. Mass spectral data (EI, m/e): [$M^{+\cdot}$] = 308, [M^+- Ph] = 231, [M^+- PPh_2] = 123, [M^+- CH_2PPh_2] = 109, [$M^{+\cdot}$- $C_2H_3PPh_2$] = 96.

Synthesis of [Rh(COD)(1)][BF_4] (3). 0.062 g (0.320 mmol) of $AgBF_4$ were added to a solution of [Rh(COD)Cl_2] (0.079 g, 0.160 mmol) in tetrahydrofuran (20 mL). A white solid precipitated (AgCl). After 30 min. under stirring the solid was filtered off and 0.054 g (0.320 mmol) of 1-[(N-ethyl)-2-aminoethyl]-3,5-dimethylpyrazole ligand (**1**) were added to the filtrate, leading to the precipitation of the complex **3** as a yellow solid. The complex was crystallized in a dichloromethane/ether mixture. Yield: 89%. M. p.: 135-137 ºC (dec.). Anal. Calcd for $C_{17}H_{29}BF_4N_3Rh$ (%): C, 43.90; H, 6.28; N, 9.03. Found: C, 43.82; H, 6.16; N, 8.90. IR (KBr) ν(cm^{-1}): 3275 (νN-H), 2960-2835 (νC-H_{al} ligand+COD), 1553 (νC=C_{ar}, νC=N_{ar}), 1469 (δCH_{3as} ligand / δCH_2 COD), 1432 (δC=C_{ar} ligand+COD, δC=N_{ar}), 1386-1188 (νC-N), 1069-964 (νB-F), 801 (δ=CH_{oop} COD), 771 (δC-H_{oop} ligand+COD). NMR

^{1}H (500 MHz, $CDCl_3$, 20°C): δ = 5.87 [s, 1H,C*H* pyrazole]; 5.51, 4.56 [AB, 2H, C*H*$_2$CH$_2$NHEt]; 4.49, 4.40, 4.30, 4.21 [m, 4H, =C*H* COD]; 4.15 [b, 1H, N*H*]; 3.54, 2.41 [AB, 2H, CH$_2$C*H*$_2$NHEt]; 2.64 [m, 2H, CH$_2$ COD], 2.41 [m, 1H, C*H*$_2$CH$_3$]; 2.31 [s, 3H, CC*H*$_3$]; 2.28 [s, 3H, CC*H*$_3$]; 2.19-2.11, 1.67 [m, 6H, CH$_2$ COD]; 1.71-1.65 [m, 4H, CH*H*$_{endo}$ COD]; 1.44 [t, $^{3}J_{H,H}$ = 7.0 Hz, 3H, CH$_2$C*H*$_3$], 1.30 [m, 1H, C*H*$_2$CH$_3$];. NMR ^{13}C{^{1}H} (63 MHz, $CDCl_3$, 20°C): δ = 149.4 [*C*CH$_3$]; 142.4 [*C*CH$_3$]; 108.0 [*C*H pyrazole]; 83.6-81.4 [m, =*C*H COD]; 49.8, 49.3 [*C*H$_2$*C*H$_2$NHCH$_2$CH$_3$]; 32.2 [*C*H$_2$CH$_3$]; 29.0,28.6 [*C*H$_2$ COD]; 15.6 [CH$_2$*C*H$_3$]; 14.0 [C*C*H$_3$]; 11.3 [C*C*H$_3$].

Synthesis of [Rh(COD)(2)][BF$_4$] (4). 0.062 g (0.320 mmol) of $AgBF_4$ were added to a solution of [Rh(COD)Cl_2] (0.079 g, 0.160 mmol) in tetrahydrofuran (20mL). A white solid precipitated (AgCl). The solid was then filtered of and 0.099 g (0.320 mmol) of 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**2**) were added to the filtrate solution. After 1 h of stirring, the solvent was evaporated under vacuum and the residue was crystallised in a dichloromethane/ether mixture to give yellow crystals of complex **4**. Yield: 94%. M. p.: 208-210 ºC (dec.). Anal. Calcd for $C_{27}H_{33}BF_4N_2PRh$ (%): C, 53.48; H, 5.50; N, 4.62. Found: C, 53.06; H, 5.17; N, 4.41. IR (KBr) ν(cm^{-1}): 3074 (νC-H$_{ar}$), 2994-2828 (νC-H$_{al}$ ligand+COD), 1555 (νC=C$_{ar}$, νC=N$_{ar}$), 1483-1467 (δCH$_{3as}$ ligand / δCH$_2$ COD), 1436-1428 (δC=C$_{ar}$ ligand+COD, δC=N$_{ar}$), 1389-1162 (νC-N), 1102-948 (νB-F), 862 (δ=CH$_{oop}$ COD), 777-700 (νP-C, δC-H$_{oop}$ ligand+COD). NMR ^{1}H (250 MHz, $CDCl_3$, 20°C): δ = 7.37 [b, 10H, PPh$_2$]; 5.59 [s, 1H, C*H* pyrazole]; 5.29 [b, 2H, =C*H* COD *trans* P]; 5.33, 5.15 [AB, 2H, C*H*$_2$CH$_2$PPh$_2$]; 3.71 [b, 2H, =C*H* COD *trans* N]; 2.67 [b, 2H, CH$_2$C*H*$_2$PPh$_2$]; 2.48 [b, 4H, CH*H*$_{exo}$ COD]; 2.34 [s, 3H, CC*H*$_3$]; 2.22 [s, 3H, CC*H*$_3$]; 2.16 [b, 4H, CH*H*$_{endo}$ COD]. NMR ^{13}C{^{1}H} (50 MHz, $CDCl_3$, 20°C): δ = 149.4 [*C*CH$_3$], 143.1 [*C*CH$_3$], 132.7-128.6 [PPh$_2$], 108.0 [*C*H pyrazole], 104.8-103.4 [m, =*C*H COD *trans* P], 78.6-77.5 [m, =*C*H COD *trans* N], 48.5 [d, $^{2}J_{C\text{-}P}$ = 5.8 Hz, *C*H$_2$CH$_2$PPh$_2$], 27.9-27.4 [*C*H$_2$ COD], 27.6 [d, $^{1}J_{C,P}$ = 27.7 Hz, CH$_2$*C*H$_2$PPh$_2$], 15.2 [C*C*H$_3$], 11.3 [C*C*H$_3$]. NMR ^{31}P{^{1}H} (81 MHz, $CDCl_3$, 20°C): δ = 28.4 [d, $^{1}J_{P,Rh}$ = 146.3 Hz, PPh$_2$].

Synthesis of [Rh(CO)$_2$(1)][BF$_4$] (5). Carbon monoxide was bubbled for 1 h into a solution of [Rh(COD)(**1**)][BF_4] (0.098 g, 0.211 mmol)in dichloromethane (20 mL) and **5** was obtained in 98% yield after evaporation of the solvent and liberated 1,5-COD under vacuum. Anal. Calcd for $C_{11}H_{17}BF_4N_3O_2Rh$ (%): C, 31.99; H, 4.15; N, 10.17. Found: C, 32.34 ; H, 4.12 ; N, 9.87. IR (CH_2Cl_2 solution, CaF_2 cells) ν(cm^{-1}): 2099 and 2033 (νCO). NMR ^{1}H (250 MHz, $CDCl_3$, 20°C): δ = 6.08 [s, 1H,C*H* pyrazole]; 5.60, 4.45 [AB, 2H,

C*H*$_2$CH$_2$NHEt]; 4.48 [b, 1H, NH], 3.61, 2.65 [AB, 2H, CH$_2$C*H*$_2$NHEt]; 2.88 [m, 2H, C*H*$_2$CH$_3$]; 2.43 [s, 3H, CC*H*$_3$]; 2.38 [s, 3H, CC*H*$_3$]; 1.34 [t, $^3J_{H,H}$ = 7.2 Hz, 3H, CH$_2$C*H*$_3$]. NMR $^{13}C\{^1H\}$ (63 MHz, $CDCl_3$, 20°C): δ = 182.5 [d, $J_{Rh,C}$ = 69.8 Hz, *C*O]; 181.1 [d, $J_{Rh,C}$ = 67.3 Hz, *C*O] ; 151.3 [*C*CH$_3$]; 144.1 [*C*CH$_3$]; 107.6 [*C*H pyrazole]; 50.4, 49.6, 47.8 [*C*H$_2$*C*H$_2$NHCH$_2$CH$_3$, *C*H$_2$CH$_3$]; 14.5 [C*C*H$_3$]; 14.6 [CH$_2$*C*H$_3$]; 11.1 [C*C*H$_3$].

Synthesis of [Rh(CO)$_2$(2)][BF$_4$] (6). Carbon monoxide was bubbled for 1 h into a solution of [Rh(COD)(**2**)][BF_4] (0.170 g, 0.280 mmol) in dichloromethane (20 mL) and **6** was obtained. The complex partially reverted to reactants when the solvent was evaporated under vacuum, and six cycles of bubbling carbon monoxide and evaporation under vacuum were done before isolating **6** in pure form. Anal. Calcd for $C_{21}H_{21}BF_4N_2O_2PRh$ (%): C, 45.52; H, 3.82; N, 5.06. Found: C, 45.02 ; H, 3.49 ; N, 5.21. IR (CH_2Cl_2 solution, CaF_2 cells) ν(cm^{-1}): 2103 and 2042 (νCO). NMR ^1H (200 MHz, CD_3COCD_3, 20°C): δ = 7.82-7.56 [m, 10H, PPh$_2$], 6.01 [s, 1H, C*H* pyrazole], 5.08-4.91 [m, 2H, C*H*$_2$CH$_2$PPh$_2$], 3.30-3.19 [m, 2H, CH$_2$C*H*$_2$PPh$_2$], 2.38 [s, 3H, CC*H*$_3$], 2.32 [s, 3H, CC*H*$_3$]. NMR $^{13}C\{^1H\}$ (63 MHz, CD_2Cl_2, 20°C): δ = 184.8 [dd, $J_{Rh,C}$ = 67 Hz, $J_{P,C}$ = 15.8 Hz *C*O], 179.9 [dd, $J_{Rh,C}$ = 60 Hz, $J_{P,C}$ = 103.5 Hz *C*O], 151.3 [*C*CH$_3$], 145.0 [*C*CH$_3$], 133.7-128.6 [PPh$_2$], 108.3 [*C*H pyrazole], 47.2 [*C*H$_2$CH$_2$PPh$_2$], 27.2 [d, $^1J_{C-P}$ = 30.3 Hz, CH$_2$*C*H$_2$PPh$_2$], 15.3 [C*C*H$_3$], 11.5 [C*C*H$_3$]. NMR $^{31}P\{^1H\}$ (81 MHz, CD_3COCD_3, 20°C): δ = 30.2 [d, $^1J_{P,Rh}$ = 120.9 Hz, PPh$_2$].

Synthesis of [Rh(2)$_2$][BF$_4$] (7). 0.062 g (0.32 mmol) of $AgBF_4$ were added to a solution of [Rh(COD)Cl_2] (0.079 g, 0.160 mmol) in tetrahydrofuran (20 mL). After filtration of AgCl, 0.221 g (0.717 mmol) of 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**2**) were added to the filtrate solution. The solvent was then removed under vacuum and the yellow-orange residue of complex **7** was washed with pentane and crystallized in a dichloromethane/ether mixture. Yield: 92%. M. p.: 147-150 ºC (dec.). Anal. Calcd for $C_{39}H_{44}BCl_2F_4N_4P_2Rh$ (%): C, 52.55; H, 4.98; N, 6.29. Found: C, 52.57; H, 4.93; N, 6.19. IR (KBr) ν(cm^{-1}): 3054 (νC-H$_{ar}$), 2960-2919 (νC-H$_{al}$), 1551 (νC=C$_{ar}$, νC=N$_{ar}$), 1480-1466 (δCH$_{3as}$), 1435-1429 (δC=C$_{ar}$, δC=N$_{ar}$), 1392-1177 (νC-N), 1098-999 (νB-F), 744-696 (νP-C, δC-H$_{oop}$). NMR ^1H (, 250 MHz, $CDCl_3$, 20°C): δ = 7.65 [b, 20H, PPh$_2$], 5.57 [s, 2H, C*H* pyrazole], 4.75 [m, 4H, C*H*$_2$CH$_2$PPh$_2$], 2.70 [m, 4H, CH$_2$C*H*$_2$PPh$_2$], 2.29 [s, 6H, CC*H*$_3$], 1.79 [s, 6H, CC*H*$_3$]. NMR $^{13}C\{^1H\}$ (63 MHz, $CDCl_3$, 20°C): δ = 150.6 [*C*CH$_3$], 140.6 [*C*CH$_3$], 135.2-127.8 [PPh$_2$], 106.7 [*C*H pyrazole], 47.2 [*C*H$_2$CH$_2$PPh$_2$], 33.5 [d, $^1J_{C,P}$

= 28.0 Hz, $CH_2CH_2PPh_2$], 13.4 [CCH_3], 11.3 [CCH_3]. NMR $^{31}P\{^1H\}$ (101 MHz, $CDCl_3$, 20°C): δ = 44.9 [d, $^1J_{P,Rh}$ = 171.1 Hz, PPh_2].

Synthesis of [Rh(CO)(2)$_2$][BF$_4$] (8). 0.070 g (0.087 mmol) of [Rh(**2**)$_2$][BF_4] in dichloromethane (20 mL) were bubbled with carbon monoxide for 1 h and [Rh(CO)(**2**)$_2$][BF_4] was obtained. The complex was characterized in solution after bubbling nitrogen to eliminate dissolved carbon monoxide, as it reverted to **8** when the solvent was evaporated in vacuum. IR (CH_2Cl_2 solution, CaF_2 cells) ν(cm^{-1}): 2088 and 2014 (νCO). NMR ^1H (250 MHz, $CDCl_3$, 20°C): δ = 7.96-6.70 [m, 20H, PPh_2], 5.50 [s, 2H, C*H* pyrazole], 4.53 [m, 4H, $CH_2CH_2PPh_2$], 2.94 [broad, 4H, $CH_2CH_2PPh_2$], 2.09 [s, 6H, CCH_3], 1.85 [s, 6H, CCH_3]. NMR $^{13}C\{^1H\}$ (63 MHz, $CDCl_3$, 20°C): δ = 190.1 [broad d, *C*O, $J_{Rh,C}$ = 72 Hz], 148.8 [CCH_3], 141.5 [CCH_3], 135.4-127.9 [PPh_2], 106.5 [*C*H pyrazole], 45.9 [$CH_2CH_2PPh_2$], 29.7 [t, $J_{C,P}$ = 12.5 Hz, $CH_2CH_2PPh_2$], 14.0 [CCH_3], 10.97 [CCH_3]. NMR $^{31}P\{^1H\}$ (101 MHz, $CDCl_3$, 20°C): δ = 25.8 [d, $^1J_{P,Rh}$ = 122.5 Hz, PPh_2].

X-ray Crystallographic Study.

Crystals of **3**, **4** and **7** suitable for X-ray diffraction were obtained through recrystallisation from dichloromethane/diethylether mixtures. Data were collected at 293K for **3** and 160K for **4** and **7** on a STOE IPDS diffractometer. Full crystallographic data for the three complexes are gathered in Table 2. All calculations were performed on a PC-compatible computer using the WinGX system.[26] The structures were solved by using the SIR92 program,[27] which revealed in each instance the position of most of the non-hydrogen atoms. All remaining non-hydrogen atoms were located by the usual combination of full matrix least-squares refinement and difference electron density syntheses by using the SHELXS97 program.[28] Atomic scattering factors were taken from the usual tabulations.[29] Anomalous dispersion terms for Rh, and P (for complexes **4** and **7**) were included in F_c.[30] All non-hydrogen atoms were allowed to vibrate anisotropically. All the hydrogen atoms were set in idealized position (R_3CH, C-H = 0.96 Å; R_2CH_2 = 0.97 Å; C(sp^2)-H = 0.93 Å; U_{iso} 1.2 time greater than the U_{eq} of the carbon atom to which the hydrogen atom is attached) and held fixed during refinements. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication n°CCDC 184360 for **3**, 184358 for **4**, and 184359 for **7**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk.

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Table 1: Selected bond length (Å) and angles (º) for compounds [Rh(COD)(**1**)][BF_4] (**3**), [Rh(COD)(**2**)][BF_4] (**4**), and [Rh(**2**)$_2$][BF_4] (**7**).

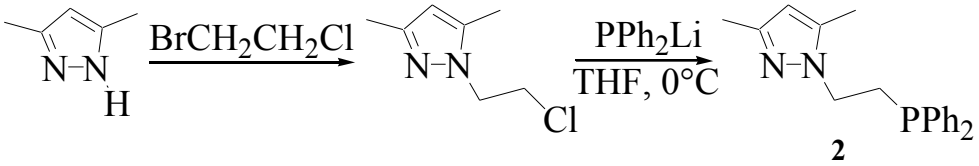
	3		**4**		**7**
C10-C11	1.385(7)	C34-C35	1.372(4)	N1-Rh1	2.119(2)
C10-Rh1	2.158(4)	C34-Rh1	2.236(2)	N3-Rh1	2.113(2)
C11-Rh1	2.133(4)	C35-Rh1	2.216(2)	P1-Rh1	2.207(1)
C14-C15	1.365(7)	C31-C38	1.392(3)	P2-Rh1	2.223(1)
C14-Rh1	2.135(4)	C31-Rh1	2.132(2)	C3-N1-N2	105.2(2)
C15-Rh1	2.125(5)	C38-Rh1	2.129(2)	C3-N1-Rh1	130.54(18)
N1-Rh1	2.116(3)	N1-Rh1	2.141(2)	N2-N1-Rh1	123.31(17)
N3-Rh1	2.148(3)	P1-Rh1	2.2743(6)	C8-N3-N4	106.1(2)
C8-N3-C7	111.2(4)	C21-P1-C11	103.88(10)	C8-N3-Rh1	132.0(2)
C8-N3-Rh1	112.5(3)	C21-P1-C7	105.48(10)	N4-N3-Rh1	121.83(17)
C7-N3-Rh1	111.2(3)	C11-P1-C7	106.01(10)	N3-Rh1-N1	88.37(9)
N1-Rh1-C15	165.68(17)	C21-P1-Rh1	110.32(7)	N3-Rh1-P1	176.60(6)
N1-Rh1-C11	93.48(16)	C11-P1-Rh1	122.77(7)	N1-Rh1-P1	89.13(7)
C15-Rh1-C11	96.06(18)	C7-P1-Rh1	107.13(7)	N3-Rh1-P2	83.43(6)
N1-Rh1-C14	155.60(18)	C38-Rh1-C31	38.13(9)	N1-Rh1-P2	171.77(6)
C15-Rh1-C14	37.37(19)	C38-Rh1-N1	152.51(8)	P1-Rh1-P2	99.03(3)
C11-Rh1-C14	82.32(18)	C31-Rh1-N1	168.78(8)	C21-P1-C31	103.58(12)
N1-Rh1-N3	82.90(14)	C38-Rh1-C35	81.90(9)	C21-P1-C12	102.49(13)
C15-Rh1-N3	92.02(17)	C31-Rh1-C35	97.09(9)	C31-P1-C12	100.43(12)
C11-Rh1-N3	158.13(17)	N1-Rh1-C35	90.01(8)	C21-P1-Rh1	118.66(9)
C14-Rh1-N3	92.08(16)	C38-Rh1-C34	88.02(9)	C31-P1-Rh1	119.34(9)
N1-Rh1-C10	100.18(16)	C31-Rh1-C34	80.46(9)	C12-P1-Rh1	109.66(9)
C15-Rh1-C10	81.23(18)	N1-Rh1-C34	100.71(8)	C51-P2-C41	102.25(13)
C11-Rh1-C10	37.66(18)	C35-Rh1-C34	35.89(9)	C51-P2-C14	102.07(13)
C14-Rh1-C10	91.14(17)	C38-Rh1-P1	97.17(6)	C41-P2-C14	103.47(13)
N3-Rh1-C10	164.19(17)	C31-Rh1-P1	92.81(6)	C51-P2-Rh1	126.40(9)
		N1-Rh1-P1	82.68(5)	C41-P2-Rh1	111.87(10)
		C35-Rh1-P1	162.20(7)	C14-P2-Rh1	108.31(10)
		C34-Rh1-P1	161.72(7)		

Table 2: Crystal data for compounds [Rh(COD)(**1**)][BF_4] (**3**), [Rh(COD)(**2**)][BF_4] (**4**), and [Rh(**2**)$_2$][BF_4] (**7**).

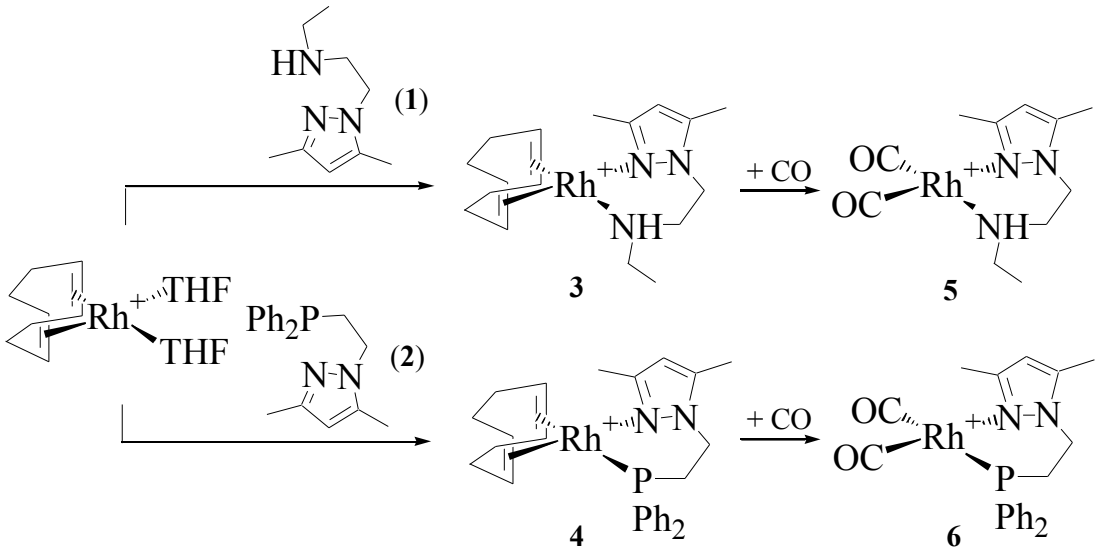
	3	**4**	**7**
empirical formula	C_{17} H_{29} B F_4 N_3 Rh	C_{27} H_{33} B F_4 N_2 P Rh	C_{39} H_{44} B Cl_2 F_4 N_4 P_2 Rh
formula weight, g	465.15	606.24	891.34
temperature, K	293(2)	160(2)	160(2)
wavelength, Å	0.71073	0.71073	0.71069
crystal system	triclinic	monoclinic	monoclinic
space group	P1 bar	$P2_1/n$	$P2_1/n$
a, Å	7.2584(1)	14.168(1)	10.997(5)
b, Å	10.872(2)	14.742(1)	18.247(5)
c, Å	13.297(2)	12.550(11)	20.073(5)
α, deg	95.55(2)	90	90
β, deg	104.51(2)	90.55(1)	102.518(5)
γ, deg	98.66(2)	90	90
volume, Å^3	994.3(2)	2621.1(4)	3932(2)
Z	2	4	4
$D_{calcd.}$, g·cm^{-3}	1.554	1.536	1.506
μ, mm^{-1}	0.900	0.760	0.705
F(000)	476	1240	1824
θ range, deg	3.95 - 25.97	2.13 - 26.03	2.20 – 26.05
index ranges	-8<=h<=8	-17<=h<=17	-13<=h<=13
	-13<=k<=13	-18<=k<=18	-22<=k<=22
	-16<=l<=16	-15<=l<=15	-24<=l<=24
reflections collected	9568	20361	30207
independent reflections	3530 [R(int) = 0.0528]	5134 [R(int) = 0.0337]	7643 [R(int) = 0.0380]
completeness to θ_{max}, %	90.5	99.1	98.1
refinement method	full-matrix least-squares on F^2		
data / restraints / parameters	3530 / 0 / 233	5134 / 0 / 327	7643 / 0 / 482
goodness of fit on F^2	1.084	1.028	1.021
Final *R* indices [I>2σ(I)]	R1 = 0.0436	R1 = 0.0266	R1 = 0.0395
	wR2 = 0.1220	wR2 = 0.0623	wR2 = 0.1016
R indices (all data)	R1 = 0.0456	R1 = 0.0369	R1 = 0.0421
	wR2 = 0.1281	wR2 = 0.0655	wR2 = 0.1041
resid. elec. density e.Å^{-3}	0.970 and -0.725	0.556 and -0.320	1.536 and –1.151

Captions of figures

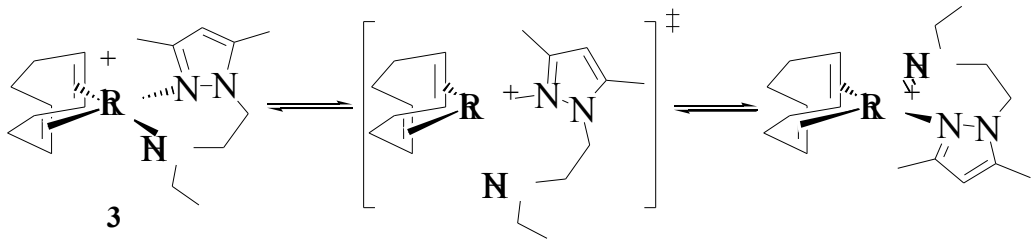
Figure 1:-A perspective view of the cation [Rh(COD)(**1**)]$^{+}$ showing the numbering scheme
Figure 2:- A perspective view of the cation [Rh(COD)(**2**)]$^{+}$ showing the numbering scheme
Figure 3:- A perspective view of the cation [Rh(**2**)$_2$]$^{+}$ showing the numbering scheme



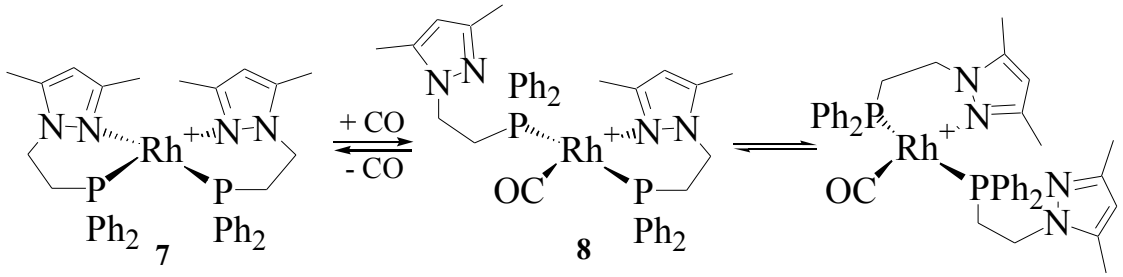
Scheme1



Scheme 2



Scheme 3



7 **8**

Scheme 4

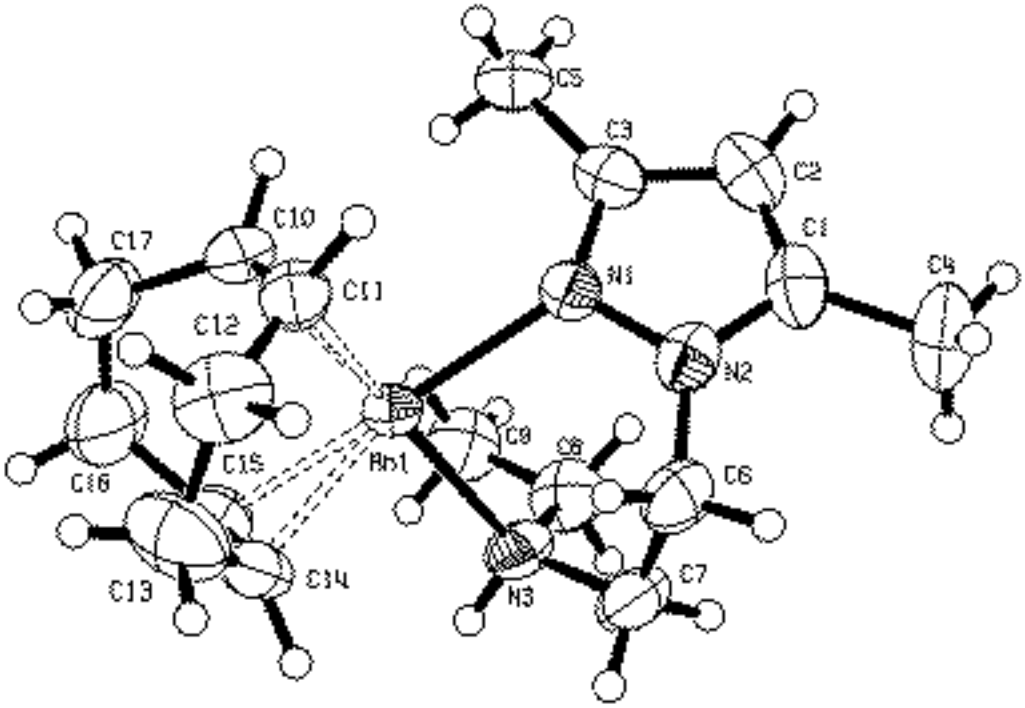

C5
C3
C2
C1
C4
N1
N2
C10
C17
C11
C12
C16
C15
Rh1
C9
C8
C6
C13
C14
N3
C7

Figure 1

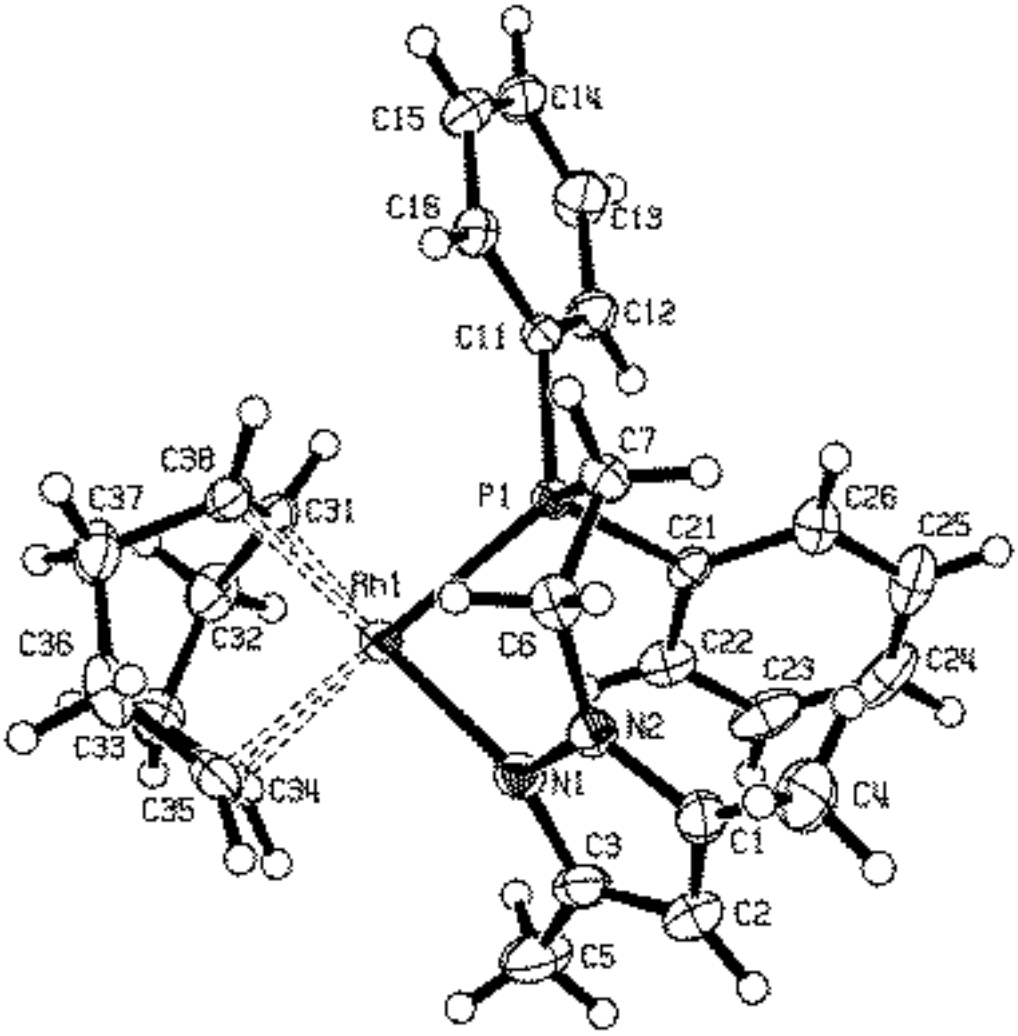

C14
C15
C16
C19
C12
C11
C7
C38
C37
C31
P1
C26
C21
C25
Rh1
C32
C6
C22
C23
C24
C36
C33
N2
C34
N1
C4
C35
C1
C3
C2
C5

Figure 2

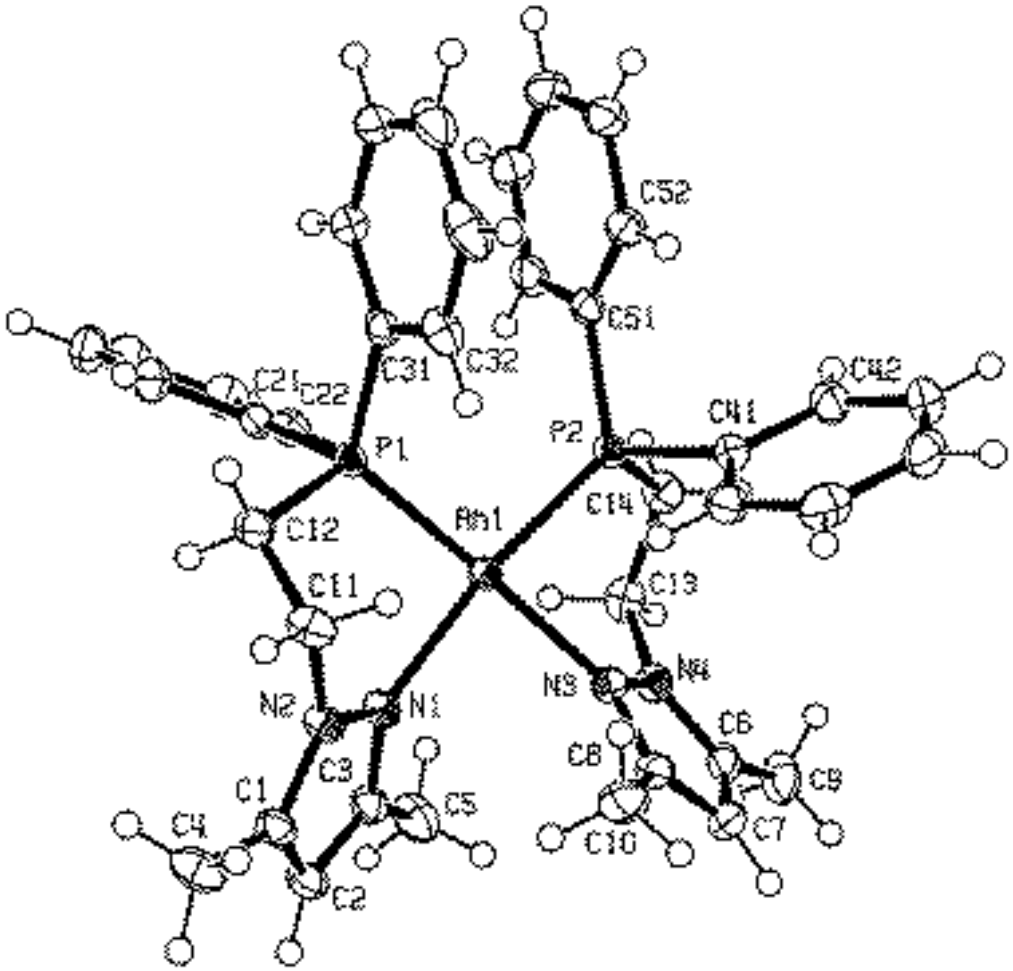

C52
C51
C31
C32
C21
C22
P1
P2
C41
C42
C12
Rh1
C14
C11
C13
N2
N1
N3
N4
C1
C3
C5
C8
C6
C9
C4
C2
C10
C7

Figure 3

Synthesis of Ru(II) complexes with the 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole ligand and study of their reactivity toward terminal alkynes.

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The reaction between $[RuCl_2(PPh_3)_3]$ and one or two equivalent amounts of 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**1**) in dichloromethane gave $[RuCl_2(PPh_3)(\mathbf{1})]$ or $[RuCl_2(\mathbf{1})_2]$ respectively, in good yields. Activation of propynylic alcohol derivatives with $[RuCl_2(\mathbf{1})_2]$ in refluxing dichloromethane and in the presence of $NaBPh_4$ led to the novel dark red allenylideneruthenium complexes, $[RuCl(\mathbf{1})_2(C{=}C{=}CPhCH_3)][BPh_4]$ and $[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BPh_4]$. The reaction between $[RuCl_2(\mathbf{1})_2]$ and phenylacetylene in dichloromethane and in the presence of KPF_6 afforded the vinylidene complex $[RuCl(\mathbf{1})_2(C{=}CHPh)][PF_6]$. The X-ray diffraction studies of $[RuCl_2(PPh_3)(\mathbf{1})]$, $[RuCl_2(\mathbf{1})_2]$, and $[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BPh_4]$ are reported.

Introduction

Transition-metal complexes with polydentate ligands containing both hard and soft donor groups have been extensively used in coordination and organometallic chemistry. The majority of such ligands are functionalised phosphines, where the phosphorus is the soft donor and either oxygen or nitrogen is the hard donor.[1,2] Furthermore, complexes with P-O and P-N ligands have been found to facilitate several stoichiometric transformations of organic molecules such as acetylene to vinylidene tautomerizations.[3]

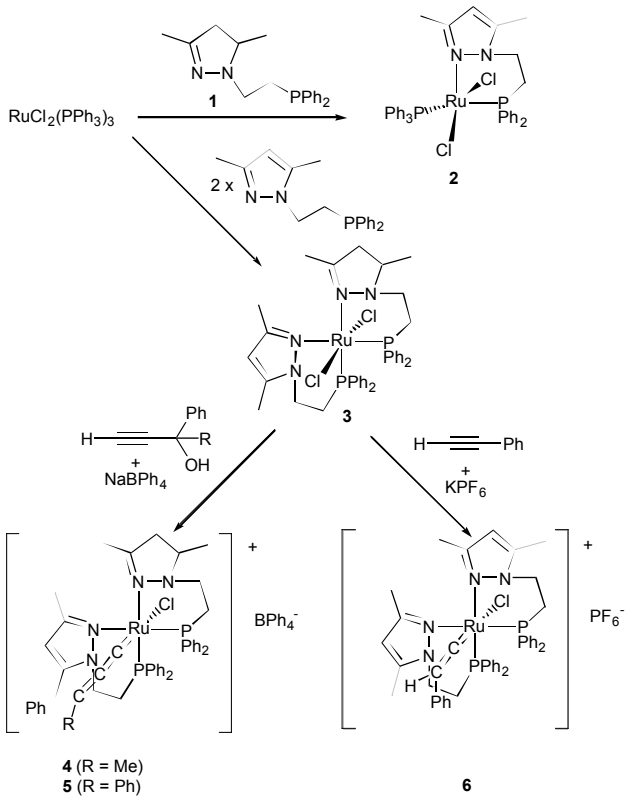
The increasing attention brought to the chemistry of ruthenium(II) complexes containing unsaturated carbene ligands $Ru{=}(C{=})_nCRR'$ (n = 0, 1)[4-7] is due to their potential ability to promote selective carbon-carbon coupling reactions and to their activity in catalytic transformations involving terminal alkynes,[8] ring opening metathesis polymerization (ROMP) or ring closing metathesis (RCM) of cyclic or acyclic olefins.[9]

We have recently shown that the new P-N bidentate ligand 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**1**) associated to rhodium(I) shows hemilabile properties.[10] So it was tempting to extend our studies of the complexing properties of **1** toward ruthenium(II). In this paper we report the synthesis and full characterisation (including the X-ray crystal structure) of two new ruthenium(II) complexes containing this ligand and the study of their reactivity toward phenylacetylene and propargyl alcohols leading to vinylidene and allenylidene complexes. The X-ray crystal structure of a new allenylideneruthenium is presented.

Results and discussion

1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole was synthesised as we described earlier[10] by reaction of 1-(chloroethyl)-3,5-dimethylpyrazole[11] and PPh_2Li in tetrahydrofurane.

The reaction of one equivalent amount of 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**1**) with one equivalent amount of $[RuCl_2(PPh_3)_3]$ in dichloromethane at room temperature gave $[RuCl_2(PPh_3)(\mathbf{1})]$ (**2**) in 96% yield (Scheme 1). The complex was analytically and spectroscopically (IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$NMR) characterised (see Experimental Section). ^1H and $^{13}C\{^1H\}$NMR spectra were consistent with the proposed formulation and showed the coordination of the ligand **1** to the Ru(II) atom. The $^{31}P\{^1H\}$NMR spectrum exhibited the expected AX pattern: two doublets at 84.6 and 48.0 ppm ($^2J_{P\text{-}P}$=44.0 Hz) due to the phosphorus atom of the (**1**) ligand and the one of the triphenylphosphine ligand, respectively were observed. The coupling constant is in agreement with two phosphine ligands in *cis* position.[12, 13]



Scheme 1.

The structure of **2** was established by an X-ray diffraction study. The details of data collection and crystal data are summarised in Table 1, selected interatomic distances and angles are provided in Table 2, and the molecular structure of $[RuCl_2(PPh_3)(\mathbf{1})]$ is

shown in Figure 1. The ruthenium atom is coordinated to the nitrogen and phosphorus atoms of ligand **1**, the triphenylphosphine phosphorus atom, and two chlorine atoms. The geometry around this pentacoordinated ruthenium atom is intermediate between a square pyramid and a trigonal bipyramid. Reedijk et al. index of trigonality was used to describe the complex geometry as a square pyramid with a 19% distortion

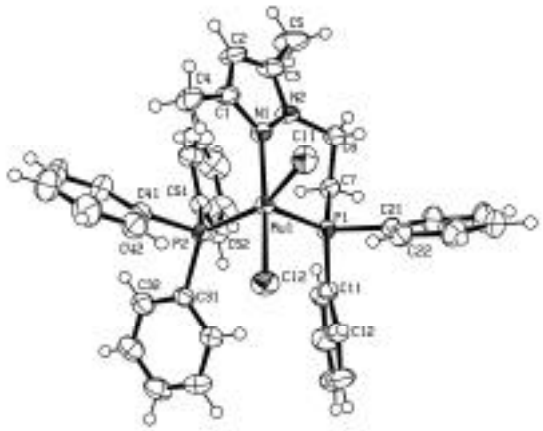


Fig. 1: View of the molecular structure of 2.

toward a trigonal bipyramid.[14] In this distorted rectangular pyramid the phosphorus atom of **1** lies in the apical position and the triphenylphosphine phosphorus atom, the nitrogen atom, and the chlorine atoms describe the base of the pyramid. The ruthenium atom is 0.327 Å above the mean plane defined by these last four atoms. This allows the N(1)-Ru(1)-P(1) angle to be larger than observed for the same ligand in square-planar rhodium complexes(94.24(6)º compared to 89.13(7) for rhodium complex).[10] Due to the steric bulk of the triphenylphosphine ligand, the P(2)-Ru(1)-Cl(2) and the N(1)-Ru(1)-P(2) angles are greater than 90º (94.09(3) and 92.32(6)º, respectively) to minimize the interaction with the methyl group of the pyrazolyl cycle and accordingly the N(1)-Ru(1)-Cl(1) and the Cl(2)-Ru(1)-Cl(1) angles are lower than 90º (82.99(6) and 86.92(3)º, respectively). The bond lengths Ru(1)-N(1) (2.105(2) Å), Ru(1)-Cl(1) (2.3979(7) Å) and Ru(1)-Cl(2) (2.3767(7) Å) are similar with reported values for similar complexes.[12, 15]

The reaction of $[RuCl_2(PPh_3)_3]$ with two equivalent amounts of **1** in dichloromethane solution at room temperature led to $[RuCl_2(\mathbf{1})_2]$ (**3**) in 90% yield (Scheme 1). The analytical and spectroscopic data for this complex were fully consistent with this formulation. The $^{31}P\{^1H\}$NMR spectrum in $CDCl_3$ showed only one signal at 36.2 ppm for the PPh_2 groups of ligand **1** indicating that the two phosphino groups were equivalent and suggesting a C_2 symmetry axis in the molecule.[16,17] The structure of complex **3** was established by X-ray diffraction. The details of data collection and crystal data are given in Table 1 and selected bond lengths and angles are provided in Table 2. The complex crystallises with two independent molecules per unit cell, which present the same geometry with the respective distances and angles being equal within experimental errors. A view of one of the two independent molecules (molecule **A**) is shown in Figure 2. The molecular structure of $[RuCl_2(\mathbf{1})_2]$ presents a distorted octahedral geometry around the ruthenium atom, with the two phosphorus and nitrogen atoms in *cis* position and the chlorine atoms in *trans* position respectively. The distortion from an idealised octahedral geometry can be attributed to the steric crowding of the two close PPh_2 groups and the two close 3,5-dimethylpyrazole groups. To minimise the steric bulk of these groups the P(2)-Ru(1)-Cl(2) and N(1)-Ru(1)-Cl(2) angles are larger than 90º (90.45(6) and 97.89(15)º, respectively) and the N(3)-Ru(1)-Cl(2) and P(1)-Ru(1)-Cl(2) angles are smaller than 90º (87.67(15) and 86.03(6)º, respectively). The more sterically demanding group is PPh_2 and as a consequence the P(2)-Ru(1)-P(1) angle is the largest (103.73(6)º). The Ru-N distances of 2.216(5) and 2.214(5) Å and the Ru-P bond lengths of 2.2986(16) and 2.3023(16) Å are larger than those found in complex **2** but fall between the experimental values reported for

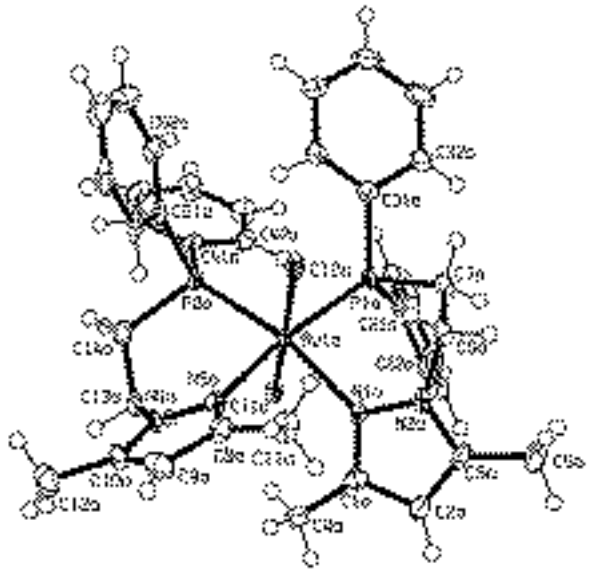


Fig. 2: View of the molecular structure of 3.

similar complexes.[16,17]

The reactivity of the complexes **2** and **3** toward terminal alkynes has been undertaken to check if the properties of ligand **1** could induce special features.

We tried to obtain allenylidene or vinylidene complexes by reaction of the $16e^-$ complex **1** with propargylic alcohols or terminal acetylene derivatives, but only decomposition to metallic ruthenium and free ligands was apparent. This is a quite unexpected result as there are precedent for the formation of neutral vinylidene complexes starting from the 16e $RuCl_2(PPh_3)_3$ complex and a terminal alkyne[18] or from 16 e $RuCl_2(PPh_3)$(P-N) compounds and terminal alkynes or propargylic alcohols.[19]

These negative results led us to envisage a most classical route to cationic vinylidene or allenylidene complexes starting from the 18 e complex **2** and an halogen abstractor in the presence of the alkyne.[20,21]

The reaction of the $18e^-$ complex **3** with 2-phenyl-3-butyn-2-ol or 1,1-diphenyl-2-propyn-1-ol in refluxing dichloromethane and in the presence of $NaBPh_4$ gave the dark red allenylideneruthenium complexes, $[RuCl(\mathbf{1})_2(C{=}C{=}CPhCH_3)][BPh_4]$ (**4**) and $[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BPh_4]$ (**5**) in 82 and 80% yield, respectively (Scheme 1). Both allenylidene complexes were characterized by microanalysis and infrared and NMR spectroscopies. The presence of the allenylidene ligand was established especially in the IR spectra by the observation of a strong $\nu(C{=}C{=}C_{as})$ absorption in the range 1936-1923 cm^{-1}.[20]

The introduction of the allenylidene moiety in these species induces the lost of the C_2 axis present in **3** and as a result the two molecules of the ligand **1** are non equivalent, and this is supported by the split of the NMR signals. ^1H NMR spectra exhibits split resonances due to the two molecules of **1**, in particular the four couples of diastereotopic protons of the ethylenic chains appear as eight multiplets. The $^{31}P\{^1H\}$ NMR spectra of these allenylideneruthenium complexes showed also two doublets corresponding to the slightly non equivalent phosphorus atoms of the **1** with a coupling constants of $^2J_{P\text{-}P}$=31.4 Hz consistent with two phosphorus atoms in *cis* position.

The $^{13}C\{^1H\}$ NMR spectra of **4** and **5** shows the typical low-

field resonance expected for C_q of the metal carbene moiety as a double doublet at 305.4 ppm ($^2J_{C-P}$=16 Hz and $^2J_{C-P}$=19 Hz) and 303.5 ($^2J_{C-P}$=17.Hz and $^2J_{C-P}$=19 Hz), respectively. Resonances due of C_β and C_γ appeared as triplets at 210.8 ppm ($^3J_{C-P}$=3.7 Hz) and 157.1 ppm ($^4J_{C-P}$=1.8 Hz) respectively for **4**, and at 217.9 ppm ($^3J_{C-P}$=3.4 Hz) and 156.6 ppm ($^4J_{C-P}$=1.8 Hz) respectively for **5**. These data are similar to the data reported in the bibliography for other allenylideneruthenium complexes.[21-25]

The crystal structure of complex **5** has been determined. The crystal data and details of structure refinement are summarized in Table 1 and selected interatomic distances and angles provided in Table 2. The structure consists of two independent ion pairs per unit cell, the two allenylideneruthenium cations (**A** and **B**) and the two tetraphenylborate anions. A view of the two cations is shown in Figure 3. For each independent cation the ethylenic chain of one ligand **1** is located above the P-Ru-N plane towards the allenylidene moiety while the ethylenic chain of the other ligand **1** is situated below this plane towards the chlorine atom. Due to this ligand **1** conformation the two independent cations correspond to the two enantiomers of δδ and λλ forms. The cationic part of both enantiomers consists of a

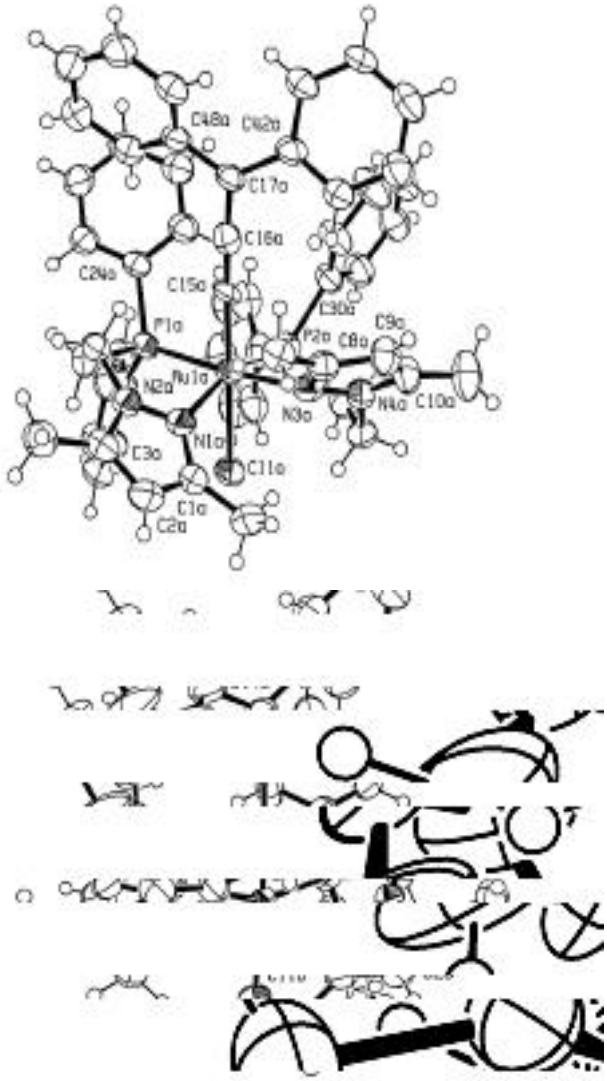


Fig. 3: .View of the molecular structure of **5 A and 5 B.**

distorted octahedral geometry with angles at Ru in the range 81.2-98.9º and 164.6-179.0º for cation **A**, and 83.1-97.5º and 165.3-173.4º for cation **B**. The geometry around the ruthenium atom for both complexes is similar to the **3** complex and the allenylidene moiety replaces one of the two chlorine atom. The C(15)-Ru-Cl(1) angle is larger for **A** (178.97(18)º) than for **B** (173.40(19)º). Due to steric crowding, the P-Ru-P angle (96.20(6)º and 103.30(6)º, respectively for cations **A** and **B**) is larger than 90º and as a consequence the N-Ru-N angle (86.43(18)º and 83.04(19)º, respectively for cations **A** and **B**) are lower than 90º. In both cases the angles for the two isomers are significantly different. For instance the N-P-N angles are significantly larger for cation **A** (91.27(13) and 87.86(14)º, than for cation **B** (89.29(14) and 85.42(14)º). The diphenylallenylidene ligand is bonded to ruthenium in a nearly linear fashion: Ru-C(15)-C(16) = 178.0(5)º and 178.1(5)º, C(15)-C(16)-C(17) = 176.9(6)º and 176.5(7)º, respectively for cations **A** and **B**. The bond lengths compare well to those reported for other ruthenium allenylidene complexes (Ru-C(15) 1.878(5) Å and 1.877(6) Å, C(15)-C(16) 1.250(8) Å and 1.252(9) Å, and C(16)-C(17) 1.384(8) Å and 1.364(9) Å, respectively for cations **A** and **B**).[23,24,26, 27] In both isomers the Ru-P and Ru-N bond lengths for one (**1**) ligand are shorter than for the other but the distances fall into the expected values for this type of complexes (Ru(1)-N(1) 2.171(5) Å and 2.173(5) Å, Ru(1)-N(3) 2.207(5) Å and 2.216(5) Å, Ru(1)-P(1) 2.3129(16) Å and 2.3334(16) Å, and Ru(1)-P(2) 2.3628(16) Å and 2.3560(16) Å, respectively for cations **A** and **B**).[25,26]

In order to check a possible fluxional behavior between both enantiomers in solution, the phase-sensitive NOESY spectrum was recorded for complex **4**. It was possible to observe the chemical exchange of some methylene protons of ligand **1** proving that both isomers were in equilibrium. To confirm this point, we carried out a high-temperature ^{1}H-NMR spectroscopic study but no significant changes were observed in the range 293-320 K confirming a high-energy barrier for this equilibrium (the solvent and the thermal stability of the complex did not allow acquisition of spectra above this temperature).

The reaction of phenylacetylene with complex **3** in dichloromethane at room temperature and in the presence of KPF_6 leads to the vinylidene complex [RuCl(**1**)$_2$(C=CHPh)][PF_6] **(6)** as a green solid in 86% yield.[16, 28] This novel vinylidene complex was characterised by microanalysis and infrared and NMR spectroscopies. Strong infrared absorptions were found at 1623 and 841 cm^{-1} corresponding to the ν(C=C) band of a vinylidene ligand and to the [PF_6]$^-$ anion, respectively.[16, 23, 28, 29] The NMR data of the vinylidene complex like for the allenylidene complexes shows the splitting of the signals for the two unequivalent molecules of ligand **1** due to the introduction of the vinylidene ligand. The most remarkable feature of the ^{1}H-NMR spectrum is the presence of a triplet signal at 2.97 ppm ($^4J_{P-H}$=4.3 Hz) assigned to the C=C*H*Ph proton.[23,28] The ^{13}C{^{1}H}-NMR data of the complex **6** were in accord with the presence of the cumulene moiety, and could be compared to those reported for other octahedral ruthenium(II) vinylidene derivatives. [16,23,28,29] Significantly, the typical low-field resonance of the carbenic carbon (Ru=C_α) appeared as a double doublet at 356.8 ppm ($^2J_{C-P}$=16.4 Hz, $^2J_{C-P}$=19.2 Hz) and the C_β of the vinylidene moiety appeared as a singlet at 111.3 ppm. The ^{31}P{^{1}H}-NMR spectrum exhibited two doublets at 24.4 ppm ($^2J_{P-P}$=31.4 Hz) and 22.0 ppm ($^2J_{P-P}$=31.4 Hz) due to the two non equivalent phosphorus atoms and the small shift difference is consistent with a structure similar to the structure of **5** (Scheme 1).

Conclusion

In conclusion, we have shown that the bidentate ligand 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole (**1**) forms, depending the stoechiometry of reactants, the 16-electrons [$RuCl_2(PPh_3)$(**1**)] and the 18-electrons [$RuCl_2$(**1**)$_2$] complexes by reaction with [$RuCl_2(PPh_3)_3$]. The [$RuCl_2$(**1**)$_2$] complex in the

presence of chloride abstractors activates terminal alkynes leading to the formation of new cationic metallacumulenes: the vinylidene complex $[RuCl(\mathbf{1})_2(C{=}CHPh)][PF_6]$ and the two allenylidene complexes $[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BPh_4]$ and $[RuCl(\mathbf{1})_2(C{=}C{=}CPhCH_3)][BPh_4]$.

Experimental

General

All chemicals were used as received from commercial suppliers, unless otherwise indicated. Reactions were carried out under dinitrogen atmosphere using vacuum line and Schlenk techniques. Solvents were dried and distilled according to standard procedures before to use and stored under dinitrogen. NMR spectra were run on a Bruker AC200, AC250, Avance DPX250 or Avance DRX500 spectrometers in $CDCl_3$ solutions at room temperature. All the chemical shift values are given in ppm and are referenced with respect to residual protons in the solvent for ^1H spectra, to solvent signals for ^{13}C spectra, to external H_3PO_4 for ^{31}P spectra, and to external $C_6H_5CF_3$ for ^{19}F spectra. IR spectra were recorded on a Perkin Elmer 2000 spectrophotometer with KBr pellets or in CH_2Cl_2 solutions with CaF2 cells. Elemental analysis were performed at the Laboratoire de Chimie de Coordination on a Perkin-Elmer 2400 CHN analyser or at the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 apparatus. $[RuCl_2(PPh_3)_3]$ was prepared according to literature methods[30] and 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole ligand was synthesised as we previously reported.[10]

Synthesis of $[RuCl_2(PPh_3)(1)]$ (2). 0.049 g (0.160 mmol) of the ligand 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole were added to a solution of 0.153 g (0.160 mmol) of $[RuCl_2(PPh_3)_3]$ in 20 ml de dichloromethane. The green solution was stirred for 5 h. After evaporation under vacuum, the addition of 5 ml of acetone gave the compound as a red precipitate which was filtrated and washed with pentane. The complex was then crystallised in a dichloromethane/acetone mixture. Yield: 96%. Anal. Calcd for $C_{37}H_{36}N_2P_2Cl_2Ru{\cdot}1/2CH_2Cl_2$ (%): C, 57.37; H, 4.75; N, 3.57. Found: C, 57.81; H, 4.78; N, 3.43. IR (KBr) ν(cm^{-1}): 3050 (νC-H_{ar}), 2980-2918 (νC-H_{al}), 1554 (νC=C_{ar}, νC=N_{ar}), 1482-1464 (δCH_{3as}), 1434 (δC=C_{ar}, δC=N_{ar}), 1394-1157 (νC-N), 1090-998 (δC-H_{ip}), 872 (δ=CH_{oop}), 719 (νP-C, δC-H_{oop}). NMR ^1H (Solution $CDCl_3$, 200 MHz) δ(ppm): 7.56-7.07 [m, 25H, PPh_2, PPh_3], 5.93 [s, 1H, C*H* pyrazole], 4.17 [m, 2H, C$H_2$$CH_2PPh_2$], 2.57 [m, 2H, $CH_2CH_2PPh_2$], 2.24 [s, 3H, CCH_3], 2.19 [s, 3H, CCH_3]. NMR $^{13}C\{^1H\}$ (Solution $CDCl_3$, 50 MHz) δ(ppm): 148.1 [*C*CH_3], 140.8 [*C*CH_3], 140.2-127.3 [PPh_2, PPh_3], 106.9 [*C*H pyrazole], 41.9 [*C*$H_2CH_2PPh_2$], 31.6 [d, $^1J_{C\text{-}P}$=33.6 Hz, $CH_2CH_2PPh_2$], 15.1 [C*C*H_3], 11.5 [C*C*H_3]. NMR $^{31}P\{^1H\}$ (Solution $CDCl_3$, 81 MHz) δ(ppm): 84.6 [d, $^2J_{P\text{-}P}$=44.0 Hz, PPh_2], 48.0 [d, $^2J_{P\text{-}P}$=44.0 Hz, PPh_3].

Synthesis of $[RuCl_2(1)_2]$ (3). 0.211 g (0.684 mmol) of the ligand 1-[(P-diphenyl)-2-phosphinoethyl]-3,5-dimethylpyrazole were added to a solution of 0.306 g (0.320 mmol) of $[RuCl_2(PPh_3)_3]$ in 20 ml of dichloromethane. The brown solution was stirred for 5 h. After evaporation under vacuum, the addition of 5 ml of acetone gave the compound as a red precipitate which was filtrated and washed with pentane. The complex was crystallised in a dichloromethane/acetone mixture. Yield: 90%. Anal. Calcd for $C_{38}H_{42}Cl_2N_4P_2Ru$ (%): C, 57.87; H, 5.37; N, 7.10. Found: C, 57.14; H, 4.65; N, 6.73. IR (KBr) ν(cm^{-1}): 3054 (νC-H_{ar}), 2964-2919 (νC-H_{al}), 1554 (νC=C_{ar}, νC=N_{ar}), 1480 (δCH_{3as}), 1435 (δC=C_{ar}, δC=N_{ar}), 1371-1154 (νC-N), 1096-1030 (δC-H_{ip}), 717 (νP-C, δC-H_{oop}). NMR ^1H (Solution $CDCl_3$, 250 MHz) δ(ppm): 7.26-7.02 [m, 20H, PPh_2], 5.84 [s, 2H, C*H* pyrazole], 5.17 [m, 4H, C$H_2$$CH_2PPh_2$], 2.72 [m, 4H, $CH_2CH_2PPh_2$], 2.27 [s, 6H, CCH_3], 1.99 [s, 6H, CCH_3]. NMR $^{13}C\{^1H\}$ (Solution $CDCl_3$, 63 MHz) δ(ppm): 155.0 [*C*CH_3], 140.3 [*C*CH_3], 134.3-126.9 [PPh_2], 108.4 [*C*H pyrazole], 43.8 [*C*$H_2CH_2PPh_2$], 33.5 [d, $^1J_{C\text{-}P}$=25.7 Hz, $CH_2CH_2PPh_2$], 15.5 [C*C*H_3], 12.0 [C*C*H_3]. NMR $^{31}P\{^1H\}$ (Solution $CDCl_3$, 101 MHz) δ(ppm): 36.2 [b, PPh_2].

Synthesis of $[RuCl(1)_2(C{=}C{=}CPhCH_3)][BPh_4]$ (4). 0.034 g (0.231 mmol) of 2-phenyl-3-butyn-2-ol in dichloromethane and 0.032 g (0.093 mmol) of $NaBPh_4$ in the minimum methanol were added to a solution of 0.073 g (0.093 mmol) of $[RuCl_2(\mathbf{1})_2]$ in 10 ml of dichloromethane. The mixture was heated to reflux for 1 hour. The solvents were then evaporated under reduced pressure. The residue was dissolved in 10 ml of dichloromethane and the salts were separated by filtration. After evaporation, the red solid was washed with diethyl ether and dried under vacuum. The complex was cristallizated in dichloromethane/diethyl ether double phase. Yield: 82%. Anal. Calcd for $C_{72}H_{70}BClN_4P_2Ru$ (%): C, 72.03; H, 5.88; N, 4.67. Found: C, 71.94; H, 6.13; N, 4.70. IR (KBr) ν(cm^{-1}): 3050-3034 (νC-H_{ar}), 2994-2922 (νC-H_{al}), 1936 (νC=C=C_{as}), 1557 (νC=C_{ar}, νC=N_{ar}), 1479 (δCH_{3as}), 1434 (δC=C_{ar}, δC=N_{ar}), 1370-1161 (νC-N), 1095-1030 (δC-H_{ip}), 721 (νB-C, νP-C, δC-H_{oop}). NMR ^1H (Solution $CDCl_3$, 250 MHz) δ(ppm): 7.38-6.79 [m, 45H, PPh_2, C*Ph*CH_3, BPh_4], 6.39 [m, 1H, C*H*HCH_2PPh_2], 5.90 [s, 1H, C*H* pyrazole], 5.87 [s, 1H, C*H* pyrazole], 4.53 [m, 1H, C*H*HCH_2PPh_2], 4.43 [m, 1H, CH*H*CH_2PPh_2], 4.02 [m, 1H, CH*H*CH_2PPh_2], 2.90 [m, 1H, $CH_2CHHPPh_2$], 2.74 [m, 1H, $CH_2CHHPPh_2$], 2.70 [m, 1H, $CH_2CHHPPh_2$], 2.31 [s, 3H, CCH_3], 2.12 [m, 1H, $CH_2CHHPPh_2$], 2.07 [s, 3H, CCH_3], 2.01 [s, 3H, CCH_3], 1.31 [s, 3H, CCH_3], 1.26 [s, 3H, CPhCH_3]. NMR $^{13}C\{^1H\}$ (Solution $CDCl_3$, 63 MHz) δ(ppm): 305.4 [dd, $^2J_{C\text{-}P}$=16.5 Hz, $^2J_{C\text{-}P}$=19.6 Hz, Ru=*C*], 210.8 [t, $^3J_{C\text{-}P}$=3.7 Hz, Ru=C=*C*], 164.3 [q, $^1J_{C\text{-}11B}$=49.4 Hz, BPh_4], 164.3 [sept, $^1J_{C\text{-}10B}$=16.6 Hz, BPh_4], 157.1 [t, $^4J_{C\text{-}P}$=1.8 Hz, Ru=C=C=*C*], 155.7 [d, $^3J_{C\text{-}P}$=2.5 Hz, *C*CH_3], 154.2 [*C*CH_3], 142.9 [*C*CH_3], 142.5 [d, $^4J_{C\text{-}P}$=1.8 Hz, *C*CH_3], 136.4-121.7 [PPh_2, C*Ph*CH_3, BPh_4], 109.5 [d, $^4J_{C\text{-}P}$=2.5 Hz, *C*H pyrazole], 108.8 [d, $^4J_{C\text{-}P}$=1.8 Hz, *C*H pyrazole], 43.8 [*C*$H_2CH_2PPh_2$], 32.5 [d, $^1J_{C\text{-}P}$=33.1 Hz, $CH_2CH_2PPh_2$], 31.5 [d, $^1J_{C\text{-}P}$=33.1 Hz, $CH_2CH_2PPh_2$], 15.7 [C*C*H_3], 15.4 [CPh*C*H_3], 14.0 [C*C*H_3], 12.2 [2xC*C*H_3]. NMR $^{31}P\{^1H\}$ (Solution $CDCl_3$, 101 MHz) δ(ppm): 30.2 [d, $^2J_{P\text{-}P}$=31.4 Hz, PPh_2], 28.1 [d, $^2J_{P\text{-}P}$=31.4 Hz, PPh_2].

Synthesis of $[RuCl(1)_2(C{=}C{=}CPh_2)][BPh_4]$ (5). 0.046 g (0.222 mmol) of 1,1-diphenyl-2-propyn-1-ol in dichloromethane and 0.030 g (0.089 mmol) of $NaBPh_4$ dissolved in the minimum methanol were added to a solution of 0.070 g (0.089 mmol) of $[RuCl_2(\mathbf{1})_2]$ in 10 ml of dichloromethane. The mixture was heated to reflux for 1 hour. After cooling to room temperature, the solvents were removed under vacuum. The residue was extracted with dichloromethane and the salts were separated by filtration. The red solution was then removed under vacuum and the complex was cristallizated in dichloromethane/diethyl ether double phase. Yield: 80%. Anal. Calcd for $C_{77}H_{72}BClN_4P_2Ru$ (%): C, 73.24; H, 5.75; N, 4.44. Found: C, 73.07; H, 5.87; N, 4.42. IR (KBr) ν(cm^{-1}): 3051 (νC-H_{ar}), 2996-2931 (νC-H_{al}), 1923 (νC=C=C_{as}), 1558 (νC=C_{ar}, νC=N_{ar}), 1480 (δCH_{3as}), 1433 (δC=C_{ar}, δC=N_{ar}), 1374-1129 (νC-N), 1093-1030 (δC-H_{ip}), 720 (νB-C, νP-C, δC-H_{oop}). NMR ^1H (Solution $CDCl_3$, 250 MHz) δ(ppm): 7.41-6.82 [m, 50H, PPh_2, CPh_2, BPh_4], 6.36 [m, 1H, C*H*HCH_2PPh_2], 5.89 [s, 2H, C*H* pyrazole], 4.79 [m, 1H, C*H*HCH_2PPh_2], 4.34 [m, 1H, CH*H*CH_2PPh_2], 4.07 [m, 1H, CH*H*CH_2PPh_2], 2.90 [m, 1H, $CH_2CHHPPh_2$], 2.66 [m, 1H, $CH_2CHHPPh_2$], 2.61 [m, 1H, $CH_2CHHPPh_2$], 2.27 [s, 3H, CCH_3], 2.14 [m, 1H, $CH_2CHHPPh_2$], 2.06 [s, 3H, CCH_3], 2.02 [s, 3H, CCH_3], 1.37 [s, 3H, CCH_3]. NMR $^{13}C\{^1H\}$ (Solution $CDCl_3$, 63 MHz) δ(ppm): 303.5 [dd, $^2J_{C\text{-}P}$=17.5 Hz, $^2J_{C\text{-}P}$=19.3 Hz, Ru=*C*], 217.9 [t, $^3J_{C\text{-}P}$=3.4 Hz, Ru=C=*C*], 164.3 [q, $^1J_{C\text{-}11B}$=49.4 Hz, BPh_4], 164.3 [sept, $^1J_{C\text{-}10B}$=16.6 Hz, BPh_4], 156.6 [t, $^4J_{C\text{-}P}$=1.8 Hz, Ru=C=C=*C*], 155.6 [d, $^3J_{C\text{-}P}$=2.5 Hz, *C*CH_3], 154.1 [*C*CH_3], 144.8 [*C*CH_3], 142.8 [d, $^4J_{C\text{-}P}$=1.8 Hz, *C*CH_3], 136.3-121.6 [PPh_2, CPh_2, BPh_4], 109.6 [d, $^4J_{C\text{-}P}$=2.5 Hz, *C*H

pyrazole], 108.8 [d, $^4J_{C-P}$=1.8 Hz, *C*H pyrazole], 43.9 [d, $^2J_{C-P}$=28.8 Hz, 2x*C*$H_2CH_2PPh_2$], 33.0 [d, $^1J_{C-P}$=31.9 Hz, CH_2*C*H_2PPh_2], 32.2 [d, $^1J_{C-P}$=31.9 Hz, CH_2*C*H_2PPh_2], 15.7 [*C*CH_3], 14.3 [*C*CH_3], 12.1 [2x*C*CH_3]. NMR $^{31}P\{^1H\}$ (Solution $CDCl_3$, 101 MHz) δ(ppm): 31.2 [d, $^2J_{P-P}$=31.4 Hz, PPh_2], 26.6 [d, $^2J_{P-P}$=31.4 Hz, PPh_2].

Synthesis of [RuCl(1)$_2$(C=CHPh)][PF$_6$] (6). 19.5 μl (0.178 mmol) of phenylacetylene and 0.033 g (0.178 mmol) of potassium hexafluorophosphate were added to a solution of 0.070 g (0.089 mmol) of [$RuCl_2$(**1**)$_2$] in 25 ml of dichloromethane. After 4 hours of agitation the salts were separated by filtration and the solution was removed under vacuum. The green residue was washed with diethyl ether and dried in vacuo. Yield: 86%. Anal. Calcd for $C_{46}H_{48}ClF_6N_4P_3Ru{\cdot}O(CH_2CH_3)$ (%): C, 55.89; H, 5.44; N, 5.21. Found: C, 55.94; H, 5.84; N, 4.94. IR (KBr) ν(cm^{-1}): 3054 (νC-H_{ar}), 2978-2924 (νC-H_{al}), 1623 (νC=C), 1559 (νC=C_{ar}, νC=N_{ar}), 1487 (δCH_{3as}), 1434 (δC=C_{ar}, δC=N_{ar}), 1378-1159 (νC-N), 1096-1039 (δC-H_{ip}), 841 (νP-F), 720 (νP-C, δC-H_{oop}). NMR ^1H (Solution $CDCl_3$, 250 MHz) δ(ppm): 7.43-6.78 [m, 25H, PPh_2, CH*Ph*], 6.35 [m, 1H, C*H*HCH_2PPh_2], 5.96 [s, 1H, C*H* pyrazole], 5.92 [s, 1H, C*H* pyrazole], 5.74 [m, 1H, C*H*HCH_2PPh_2], 4.76 [m, 1H, CH*H*CH_2PPh_2], 4.57 [m, 1H, CH*H*CH_2PPh_2], 3.06 [m, 1H, CH_2C*H*$HPPh_2$], 2.97 [t, $^4J_{H-H}$=4.3 Hz, 1H, Ru=C=C*H*Ph], 2.84 [m, 1H, CH_2C*H*$HPPh_2$], 2.80 [m, 1H, CH_2CH*H*PPh_2], 2.44 [s, 3H, CC*H*$_3$], 2.36 [s, 3H, CC*H*$_3$], 2.25 [m, 1H, CH_2CH*H*PPh_2], 2.00 [s, 3H, CC*H*$_3$], 1.45 [s, 3H, CC*H*$_3$]. NMR $^{13}C\{^1H\}$ (Solution $CDCl_3$, 63 MHz) δ(ppm): 356.8 [dd, $^2J_{C-P}$=16.4 Hz, $^2J_{C-P}$=19.2 Hz, Ru=*C*], 156.9 [d, $^3J_{C-P}$=2.1 Hz, *C*CH_3], 154.6 [*C*CH_3], 144.6 [*C*CH_3], 144.1 [*C*CH_3], 134.7-126.2 [PPh_2, CH*Ph*], 111.3 [Ru=C=*C*HPh], 110.0 [*C*H pyrazole], 108.9 [*C*H pyrazole], 43.8 [d, $^2J_{C-P}$=34.1 Hz 2x*C*$H_2CH_2PPh_2$], 32.2 [d, $^1J_{C-P}$=32.7 Hz, CH_2*C*H_2PPh_2], 29.9 [d, $^1J_{C-P}$=33.4 Hz, CH_2*C*H_2PPh_2], 15.4 [*C*CH_3], 15.3 [*C*CH_3], 12.1 [2x*C*CH_3]. NMR $^{31}P\{^1H\}$ (Solution $CDCl_3$, 101 MHz) δ(ppm): 24.4 [d, $^2J_{P-P}$=31.4 Hz, PPh_2], 22.0 [d, $^2J_{P-P}$=31.4 Hz, PPh_2], -143.4 [sept, $^1J_{P-F}$=711.7 Hz, PF_6]. NMR $^{19}F\{^1H\}$ (Solution $CDCl_3$, 235 MHz) δ(ppm): -73.6 [d, $^1J_{F-P}$=711.7 Hz, PF_6].

X-ray Crystallography

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Table 1: Crystal data for compounds $[RuCl_2(PPh_3)(\mathbf{1})]$ (**2**), $[RuCl_2(\mathbf{1})_2]$ (**3**), and $[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BPh_4]$ (**5**).

	$[RuCl_2(PPh_3)(\mathbf{1})]$ (**2**)	$[RuCl_2(\mathbf{1})_2]$ (**3**)	$[[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BPh_4]$ (**5**)
empirical formula	C37 H36 Cl2 N2 P2 Ru	C76 H84 Cl4 N8 P4 Ru2	C154 H144 B2 Cl2 N8 P4 Ru2
formula weight, g	742.59	1577.33	2525.31
temperature, K	293(2)	163(2)	180(2)
wavelength, Å	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group		*P*21/n	*P*21/c
a, Å	10.5566(11)	10.9168(9)	23.526(3)
b, Å	22.1294(18)	43.867(5)	18.6030(14)
c, Å	14.849(2)	15.5946(12)	30.224(3)
α, deg	90	90	90
β, deg	105.010(14)	106.289(9)	105.869(11)
γ, deg	90	90	90
volume, $Å^3$	3350.6(7)	7168.2(11)	12724(2)
Z	4	4	4
$D_{calcd.}$, $g{\cdot}cm^{-3}$	1.472	1.462	1.318
μ, mm^{-1}	0.752	0.710	0.387
F(000)	1520	3248	5264
θ range, deg	2.20 - 25.91	1.95 - 24.25	1.80 – 22.60
index ranges	-12<=h<=12	-12<=h<=12	-25<=h<=25
	-27<=k<=27	-50<=k<=50	-20<=k<=19
	-18<=l<=18	-17<=l<=16	-32<=l<=32
reflections collected	24644	41978	65382
independent reflections	6414 [R(int) = 0.0520]	10785 [R(int) = 0.1136]	16562 [R(int) = 0.1205]
completeness to θ_{max}, %	98.4	93.0	98.2
refinement method	full-matrix least-squares on F^2		
data / restraints / parameters	6414 / 0 / 399	10785 / 0 / 852	16562 / 0 / 1309
goodness of fit on F^2	0.868	0.989	1.031
Final *R* indices [I>2σ(I)]	R1 = 0.0300	R1 = 0.0809	R1 = 0.0670
	wR2 = 0.0589	wR2 = 0.1831	wR2 = 0.1729
R indices (all data)	R1 = 0.0534	R1 = 0.1071	R1 = 0.0924
	wR2 = 0.0646	wR2 = 0.2065	wR2 = 0.1949
resid. elec. density $e.Å^{-3}$	0.409 and -0.603	4.678 and -2.321	0.966 and –0.992

Table 2: Selected bond length (Å) and angles (º) for compounds $[RuCl_2(PPh_3)(\mathbf{1})]$ (**2**), $[RuCl_2(\mathbf{1})_2]$ (**3**) (molecule **A**), and $[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BPh_4]$ (**5)** (cations **A** and **B**).

	$[RuCl_2(PPh_3)(\mathbf{1})]$		$[RuCl_2(\mathbf{1})_2]$		$[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BPh_4]$ (**A)**	$[RuCl(\mathbf{1})_2(C{=}C{=}CPh_2)][BPh_4]$ (**B)**
N1-Ru1	2.105(2)	N1-Ru1	2.216(5)	N1-Ru1	2.171(5)	2.173(5)
P1-Ru1	2.189(1)	N3-Ru1	2.214(5)	N3-Ru1	2.207(5)	2.216(5)
P2-Ru1	2.270(1)	P1-Ru1	2.299(2)	P1-Ru1	2.313(2)	2.333(2)
Cl1-Ru1	2.398(1)	P2-Ru1	2.302(2)	P2-Ru1	2.363(2)	2.356(2)
Cl2-Ru1	2.377(1)	Cl1-Ru1	2.431(2)	Cl1-Ru1	2.448(2)	2.469(2)
N1-Ru1-P1	94.24(6)	Cl2-Ru1	2.431(2)	C15-Ru1	1.878(5)	1.877(6)
N1-Ru1-P2	92.32(6)	N1-Ru1-P1	86.32(13)	C15-C16	1.250(8)	1.252(9)
P1-Ru1-P2	95.11(3)	N3-Ru1-P2	87.60(14)	C16-C17	1.384(8)	1.364(9)
N1-Ru1-Cl1	82.99(6)	N1-Ru1-P2	167.41(14)	C17-C48	1.464(6)	1.462(7)
P1-Ru1-Cl1	108.39(3)	N3-Ru1-P1	167.05(14)	C17-C42	1.494(6)	1.502(6)
P2-Ru1-Cl1	156.28(3)	N3-Ru1-N1	83.35(18)	N1-Ru1-P1	91.27(13)	89.29(14)
Cl2-Ru1-Cl1	86.92(3)	P1-Ru1-P2	103.73(6)	N3-Ru1-P2	87.86(14)	85.42(14)
N1-Ru1-Cl2	167.66(6)	N1-Ru1-Cl1	87.21(15)	N1-Ru1-P2	164.56(13)	165.31(14)
P1-Ru1-Cl2	95.67(3)	N3-Ru1-Cl1	97.40(15)	N3-Ru1-P1	172.09(13)	169.10(14)
P2-Ru1-Cl2	94.09(3)	P1-Ru1-Cl1	89.85(6)	N1-Ru1-N3	86.43(18)	83.04(19)
C11-P1-C21	99.73(12)	P2-Ru1-Cl1	85.29(5)	P1-Ru1-P2	96.20(6)	103.30(6)
C7-P1-C11	104.60(12)	Cl2-Ru1-Cl1	173.22(5)	N1-Ru1-Cl1	85.19(13)	88.45(13)
C7-P1-C21	103.58(12)	N1-Ru1-Cl2	97.89(15)	N3-Ru1-Cl1	96.29(13)	97.48(13)
C7-P1-Ru1	110.45(9)	N3-Ru1-Cl2	87.67(15)	P1-Ru1-Cl1	91.04(5)	90.02(5)
C11-P1-Ru1	123.03(9)	P1-Ru1-Cl2	86.03(6)	P2-Ru1-Cl1	81.19(6)	84.06(5)
C21-P1-Ru1	113.33(8)	P2-Ru1-Cl2	90.45(6)	C15-Ru1-Cl1	178.97(18)	173.40(19)
C51-P2-C41	106.46(13)	C31-P1-Ru1	123.4(2)	C15-Ru1-N1	94.9(2)	97.5(2)
C51-P2-C31	100.21(12)	C21-P1-Ru1	116.7(2)	C15-Ru1-N3	84.7(2)	86.1(2)
C41-P2-C31	99.50(12)	C7-P1-Ru1	111.1(2)	C15-Ru1-P1	87.93(17)	87.19(18)
C51-P2-Ru1	116.04(9)	C41-P2-Ru1	123.0(2)	C15-Ru1-P2	98.87(17)	90.76(18)
C41-P2-Ru1	103.74(9)	C51-P2-Ru1	119.7(2)	C16-C15-Ru1	178.0(5)	178.1(5)
C31-P2-Ru1	128.23(9)	C14-P2-Ru1	111.2(2)	C15-C16-C17	176.9(6)	176.5(7)

V. Referències Bibliogràfiques

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