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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. © 2000 Elsevier Science S.A. All rights reserved.

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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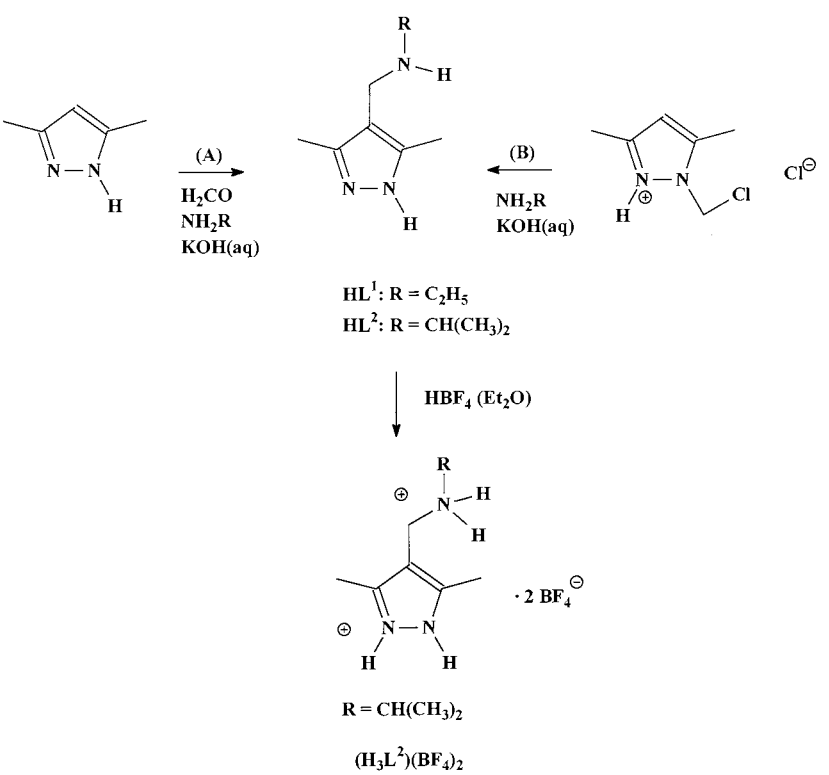
considerable interest thanks to their catalytic activity [9]. Here, we report the synthesis of new pyrazoles with an aminomethyl group at the position 4: 3,5-dimethyl-4-(ethylamino)methylpyrazole (HL^1) and 3,5-dimethyl-4-(isopropylamino)methylpyrazole (HL^2). These ligands have two main properties: 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.

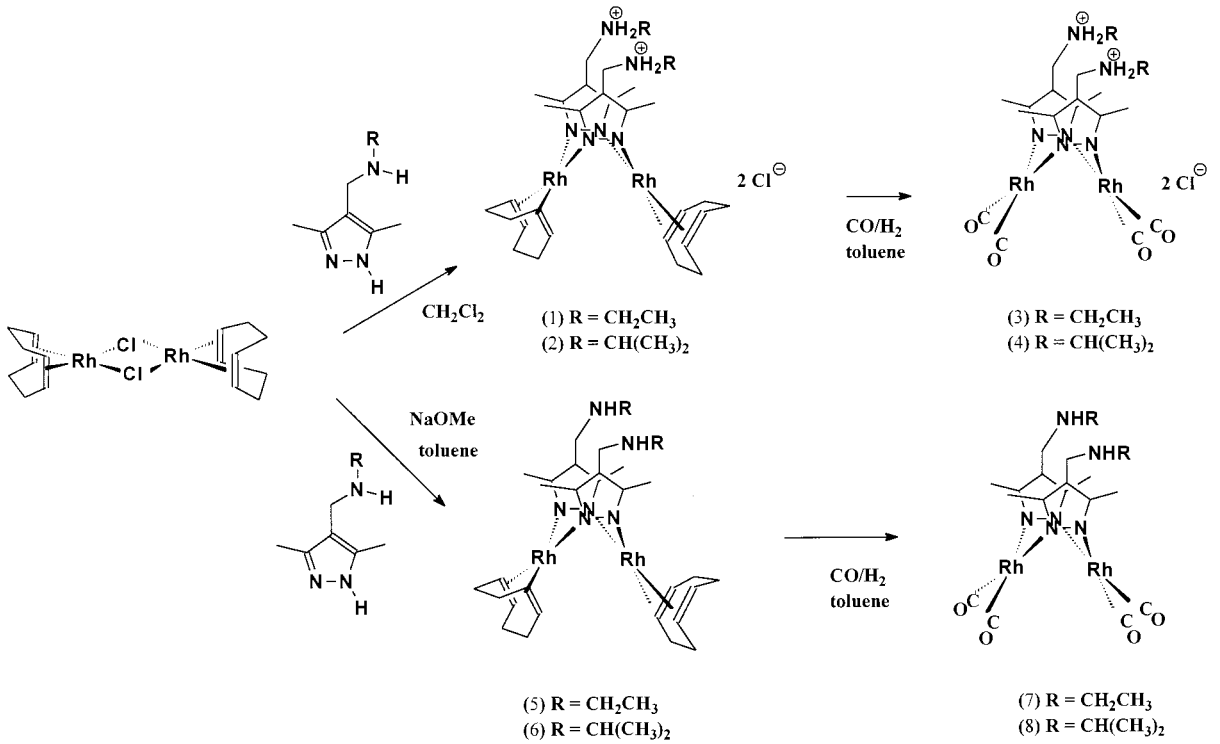
2. Results and discussion

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

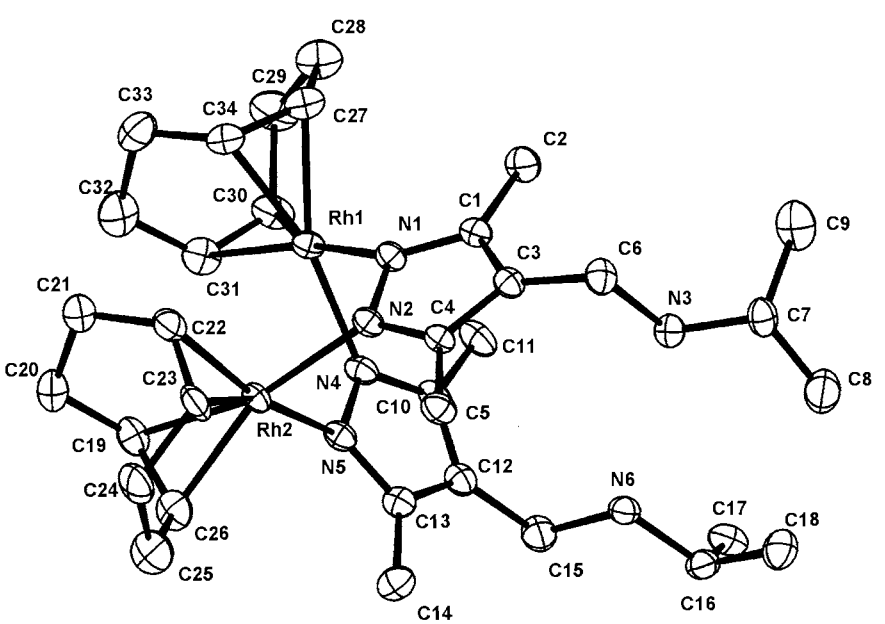


Fig. 1. Molecular structure of the cation complex in **2**.

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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