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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. © 2001 Elsevier Science B.V. All rights reserved.

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

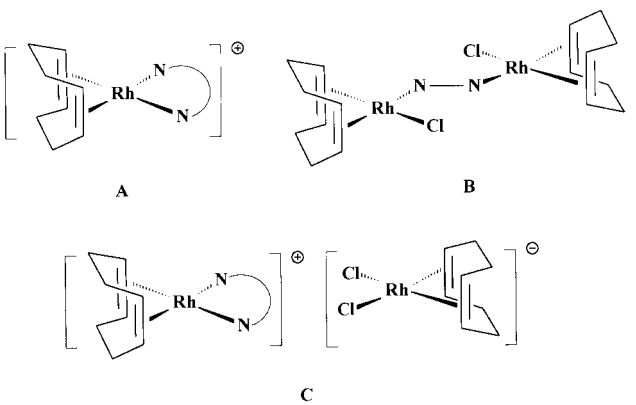

Fig. 1.

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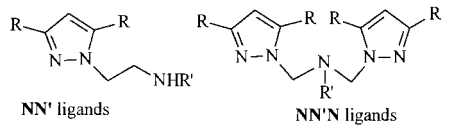


R = R = Me; R' = Et **(deae)**
R = R = Me; R' = i-Pr **(deai)**
R = R = H; R' = Et **(eae)**
R = R = H; R' = i-Pr **(eai)**

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.

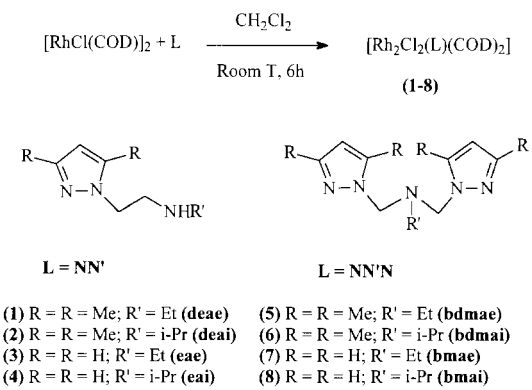
Table 5
IR [a], ^{1}H- and ^{13}C-NMR data of ligands of the type *NN′N*

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**)

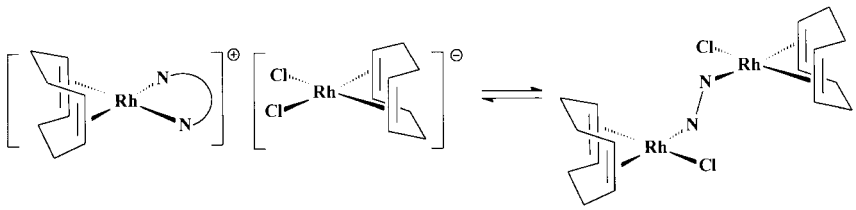
Complex	IR (KBr) ν (cm^{-1})	^{1}H-NMR 250 MHz $CDCl_3$ δ (ppm)	$^{13}C\{^1H\}$-NMR 62 MHz $CDCl_3$ δ (ppm)
Rh_2Cl_2(deae)(cod)$_2$ (**1**)	3161 (νN–H), 2928–2834 (νC–H_{al} ligand+cod), 1677 (δ N–H), 1595–1556 (νC=C_{ar}, νC=N_{ar}), 1452 (δ CH_{3as} ligand/δ CH_2 cod), 1423 (δ C=C_{ar} ligand+cod, 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.

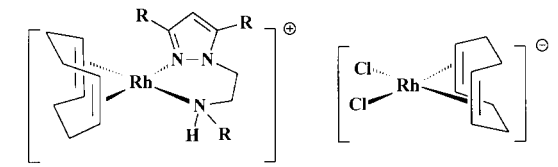
Table 7
IR [a], ^{1}H- and ^{13}C-NMR data of ligands of complexes with ligands of the type *NN′N* (**5**–**8**)

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)$_2$]

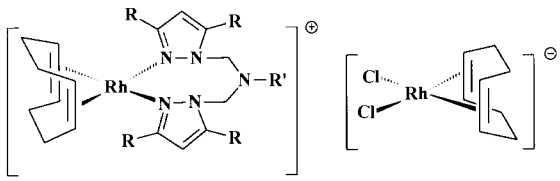
[a] al = aliphatic, ar = aromatic, as = asymmetric, oop = out of plane, ip = in plane, s = singlet, d = doublet, t = triplet, q = quadruplet, septd = septuplet, b = broad signal, m = multiplet.



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.

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