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Rhodium(I) complexes with the polydentate ligand 3,5-bis(4-methylpyrazol-1-yl)-4-methylpyrazole

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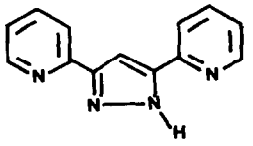
Abstract

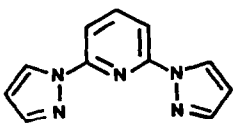
The behaviour towards Rh^I of a new ligand containing three linked pyrazoles (HLL) has been studied. Depending on which diolefin, COD or TFB, is used, mono or dinuclear complexes are obtained. The structures of the four complexes, [RhCl(COD)(HLL)], [{RhCl(TFB)}$_2$(μ-HLL)], [Rh(LL)(COD)] and [{Rh(TFB)}$_2$(μ-LL)]BF_4, have been established by ^1H and ^{13}C NMR spectroscopy. In most cases, the NMR spectra reveal fluxional processes involving not only the Rh^I metal but also the N-H proton and the diolefin.

Introduction

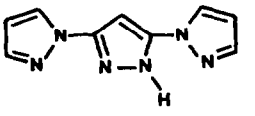
The chemistry of polydentate ligands has attracted increasing interest in recent years [1]. Among these ligands there are very few of the terpyridine type in which one (**1**), two (**2**), or the three (**3**) pyridine rings are replaced by pyrazole rings.



(1)



(2)



(3)

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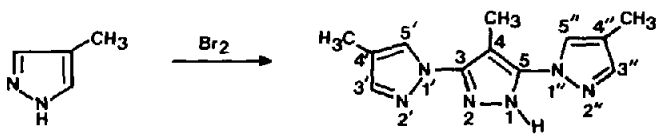
3,5-Bis(2-pyridyl)pyrazole (**1**) was first described by Ball and Blake [2] and subsequently studied by Casabó et al. [3], who prepared the bis[μ-3,5-bis(2-pyridyl)pyrazolato-$N^1, N' : N^2, N''$]-bis[dimethanolnickel(II)] dichloride. Use of 3,5-bis(pyrazol-l-yl)pyridine (**2**) [4] as a possible substitute for terpyridine was reported recently. The chemistry of bispyrazolylpyrazole (**3**) goes back to Hüttel [5], who obtained two such compounds during the halogenation of pyrazoles, but did not study their ligating properties. We consider in this paper one such ligand especially, its ^{1}H and ^{13}C NMR behaviour that of its Rh$^{\text{I}}$ complexes.

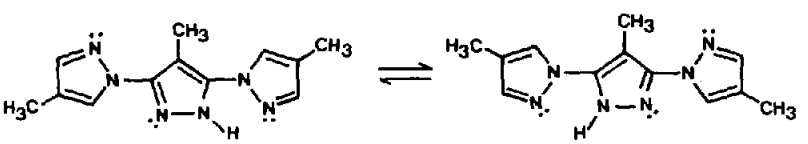
Results and discussion

3,5-Bis(4-methylpyrazol-1-yl)-4-methylpyrazole (**5**) was obtained in 20% yield when 4-methylpyrazole (**4**) was brominated [5].



(4) (5)

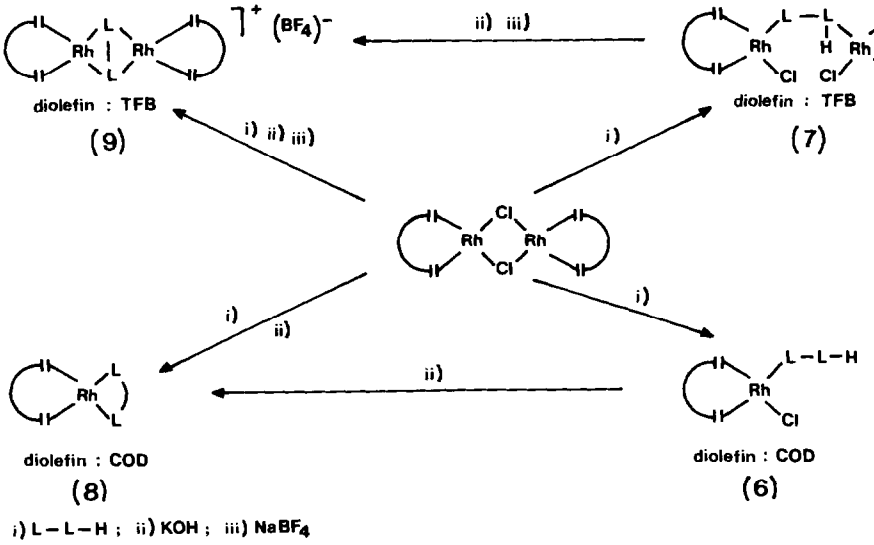
The structures originally proposed by Hüttel [5] proved to be incorrect and the actual structure of the trimer was established by ^{1}H NMR spectroscopy at 60 MHz in several solvents [6]. When we recorded the spectrum of **5** at 500 MHz, nothing unusual was observed in deuterochloroform, but in DMSO-d_6 at the same frequency, the $H_{3'}$ ($H_{3''}$) signal is very broad. In the latter solvent, due to a H-bridge to DMSO, even at room temperature the prototropic exchange N_1–H $\rightleftharpoons$ N_2–H is quite slow. This is seldom the case for pyrazoles and so we suggest that in compound **5** the prototropy involves the rotation of the two lateral pyrazoles about the C_3–N_1, and C_5–$N_{1''}$ bonds:



(5a) (5b)

Rhodium(I) complexes: syntheses

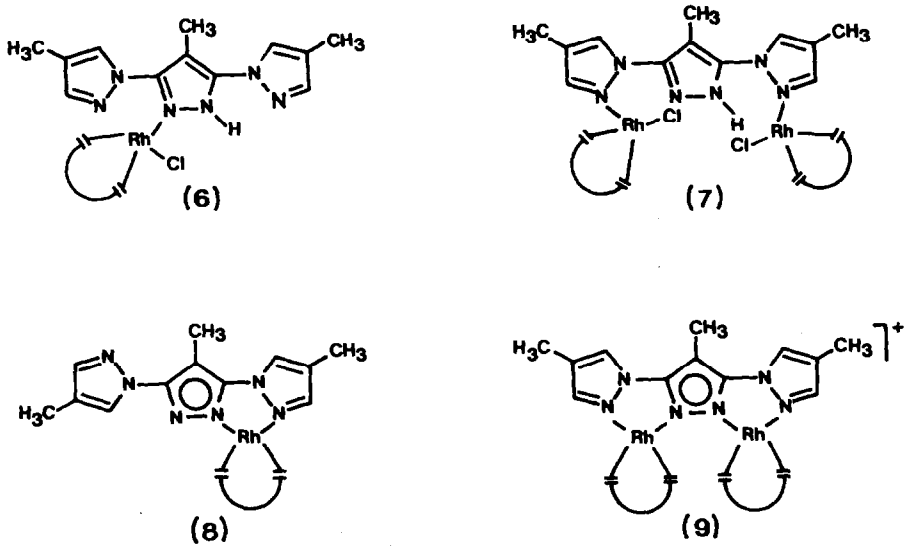
The reaction of the chloride-bridged diolefinic complex [RhCl(COD)]$_2$ (COD = 1,5-cylooctadiene) with 3,5-bis(4-methylpyrazol-1-yl)-4-methylpyrazole (**5**) (subsequently denoted by $\widehat{HLL}$) gave the mononuclear neutral compound [RhCl(COD)($\widehat{HLL}$)] (**6**) (Scheme 1), by cleavage of the halogen bridge. Nevertheless, when the tetrafluorobenzobarrelene (TFB = tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene; see Scheme 4) derivative [RhCl(TFB)]$_2$ was treated with the same ligand, the dinuclear complex [[RhCl(TFB)}$_2$(μ-$\widehat{HLL}$)] (**7**) was obtained. The low molar conductivities of the samples in acetone (16 and $17.3 \cdot 10^{-4}$ ohm^{-1} m^2 mol^{-1}, respectively) support the formulations as neutral species. The acidic N–H proton of the central pyrazole ring in complexes **6** and **7** can be removed by treatment with KOH,



Scheme 1

giving the mononuclear complex [Rh(LL)(COD)] (**8**) and the dinuclear [{Rh(TFB)}$_2$(μ-LL)]BF_4 (**9**). In the latter case, one equivalent of $NaBF_4$ must be added to remove the chloride anions completely.

Complex **8** can also be prepared by treating the acetylacetonate complex [Rh(acac)(COD)] with HLL in dichloromethane. Interestingly, the nuclearity of the resulting complexes depends on the nature of the diolefin used. This behaviour, previously found for other nitrogen donor rhodium(I) complexes [7–9], has been attributed to the differing electronic properties of these ancillary ligands.



Scheme 2

Table 1

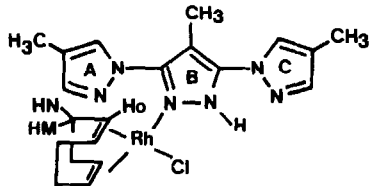
Analyses, molecular weights, yields, and IR data [a] for the rhodium complexes

Complex	Analysis [found (calcd.)] (%)			Mol. wt. ($CHCl_3$) [found(calcd.)]	Yield (%)	IR bands (cm^{-1})
	C	H	N			
[RhCl(COD)(HLL)] (**6**)	49.0 (49.1)	5.6 (5.4)	17.2 (17.2)	421 (488)	62	2300–2350 [ν(NH)], 1600w, 1590sh, 1580s, 1550s [ν(CN)], 375m [ν(RhCl)].
[{RhCl(TFB)}$_2$(μ-HLL)] (**7**)	44.9 (44.5)	2.9 (2.7)	8.2 (8.6)	–	81	3100br [ν(NH)], 1610m, 1590sh, 1580m, 1555m [ν(CN)], 300m [ν(RhCl)]
[Rh(LL)(COD)] (**8**)	52.2 (53.1)	5.4 (5.6)	18.5 (18.6)	577 (452)	65	1600w, 1575 [ν(CN)]
[{Rh(TFB)}$_2$(μ-LL)]BF_4 (**9**)	44.1 (43.8)	2.6 (2.5)	8.5 (8.5)	–	78	1050vs (BF_4^-)

[a] Nujol mulls. br, broad; vs, very strong; s, strong; m, medium; w, weak.

Table 2

^1H and ^{13}C NMR chemical shifts and coupling constants for [RhCl(COD)(HLL)] (**6**) (solvent: $CDCl_3$)



	T (K)	Ring A				Ring B				Ring C				COD		
		H_3	4-Me	H_5		H_3	4-Me	H_5		H_3	4-Me	H_5		H_O	H_M	H_N
^1H NMR	293	7.30	2.17	8.40		–	2.53	–		7.30	2.17	8.40		4.92	2.02	2.47 [b]
(250 MHz)	248.5	7.57	2.21	8.79		–	2.55	–		7.10	2.16	7.87		4.70 [a]	2.06	2.48
		$\Delta G_c^{\ddagger} = 11.9$ kcal·mol^{-1}												5.22 [a]		
	T (K)	C_3	C_4	C_5	4-Me	C_3	C_4	C_5	4-Me	C_3	C_4	C_5	4-Me	$C(sp^2)$	$C(sp^3)$	
^{13}C NMR	293	142.2	119.6	129.4	8.84	143.5	93.2	143.5	8.65	142.2	119.6	129.4	8.84	82.4	30.4	
(62.9 MHz)														$^1J = 157.3$	$^1J = 128.8$	
	245	143.3	120.1	130.4	8.89	146.0	92.9	141.0	8.50	139.7	118.2	127.0	8.89	79.4 [a]	30.1 [a]	
														85.3 [a]	30.3 [a]	

[a] On cooling, 248.5 and 245 K for ^1H and ^{13}C NMR respectively, the COD became less symmetrical. [b] $J(MN) = 8.0$ Hz.

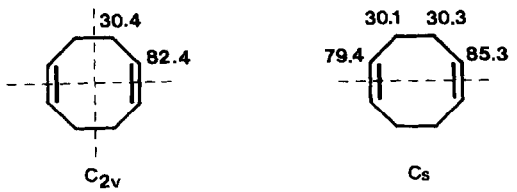
Table 1 lists analytical data, molecular weights, yields, and IR data for complexes **6–9**.

Structure of the complexes

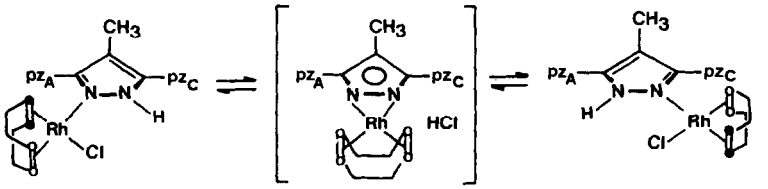
Since no suitable crystal could be obtained, the structures of the complexes (Scheme 1) were established by NMR spectroscopy taking account of the molecular formulae (see Table 1). Scheme 2 presents the four structures.

The ^{1}H and ^{13}C NMR data for [RhCl(COD)(HLL)] are listed in Table 2. At room temperature the spectra correspond to a C_{2v} structure, with identical signals for rings **A** and **C** and for the olefinic part of COD. However, when the ^{1}H NMR spectrum was recorded at 500 MHz the signal corresponding to H_3 (δ: 7.30) is broad and that corresponding to H_5 (δ: 8.40) is lost in the base line. A variable-temperature study affords not only all the signals corresponding to a C_s structure (at low temperatures) but also the activation energy ($\Delta G^{\ddagger} = 49.8$ kJ mol^{-1}) for the process involved.

The chemical shifts of the ^{13}C signals from the COD at room and low temperature were as follows:

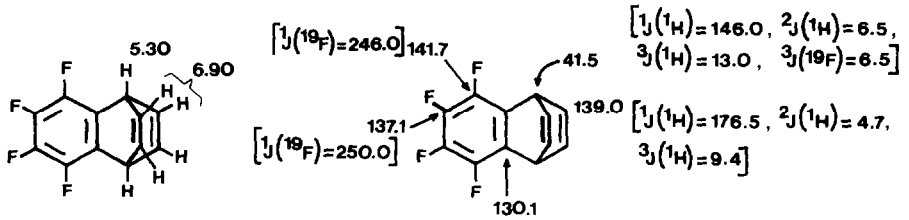


In order to explain the C_{2v} nature of the COD we suggest a mechanism involving concomitant prototropy and metallotropy of the pyrazole ring **B**:



Scheme 3

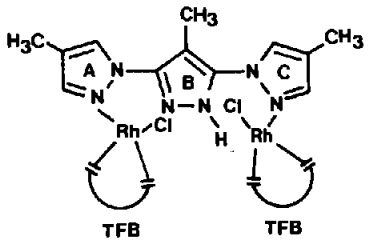
The NMR spectra of the [{RhCl(TFB)}$_2$(μ-HLL)] (**7**) complex are very complicated and temperature dependent. In order to understand them we decided to study tetrafluorobenzobarrelene itself, since no reliable information on its ^{1}H and ^{13}C spectra was available. The spectra of TFB are very complex (the system formed by the protons and the fluorine atoms is an AA'BB'B''B''' XX'YY' with only two anisochronous protons). We show in Scheme 4 the most notable features (solvent: $CDCl_3$):

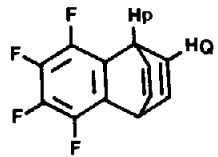


Scheme 4

Table 3

^{1}H and ^{13}C NMR chemical shifts and coupling constants for [{RhCl(TFB)}$_2$(μ-HLL)] (7) [a]

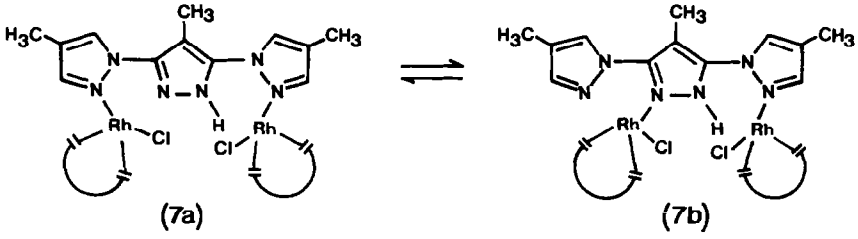




		T = 293 K	Ring A			Ring B			Ring C			TFB	
			H_3	4-Me	H_5	H_3	4-Me	H_5	H_3	4-Me	H_5	H_P	H_Q
^{1}H NMR (200 MHz)	$CDCl_3$		7.84(b)	2.15	8.61(b)	–	2.48	–	7.84(b)	2.15	8.61(b)	4.09(vb)	5.50(b)
	CD_3COCD_3		7.74	2.42	8.70	–	2.51	–	7.74	2.42	8.70	4.20(vb)	5.78(b)
	CD_3OD		7.49	2.38	8.45	–	2.63	–	7.49	2.38	8.45	4.10(vb)	5.82(b)
		T = 183 K											
	CD_3COCD_3		7.65(b)	2.3(vb)	8.60(b) 8.42(b)	–	2.4(b)	–	7.18	2.3(vb)	8.21(b) 8.04(b)	4.45 3.80	5.55; 5.70 5.98; 6.22
			Ring A			Ring B			Ring C			TFB	
^{13}C NMR (125 MHz)	$CDCl_3$		C_3: 141.2 C_4: n.o C_5: 127.0 4-Me: 9.0			C_3: n.o. C_4: n.o. C_5: n.o. 4-Me: 9.0			C_3: 141.2 C_4: n.o. C_5: 127.0 4-Me: 9.0			$C(sp^3)$: 41.5 $C(sp^2)$: 139.9	
(100 MHz)	Solid state		C_3: 147.6 C_4: 120.6 C_5: 127.0 4-Me: 7.8			C_3: m C_4: 87.7 C_5: m 4-Me: 7.8			C_3: 141.5 C_4: 120.6 C_5: 127.0 4-Me: 7.8			$C(sp^3)$: 40.2(b) $C(sp^2)$: 139.7	

[a] n.o.: not observed; m: masked; b: broad; vb: very broad.

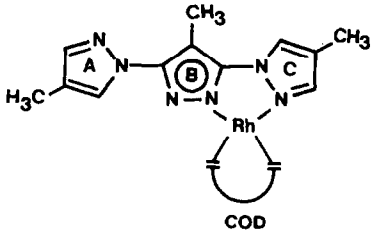
To account for the spectral properties (Table 3) of compound 7 we suggest the formula represented in Scheme 2. In solution at room temperature there is a classical prototropic exchange in the central pyrazole, and this exchange is slowed down at low temperature in acetone and in the solid state (CP-MAS technique). However, the splitting of some signals at low temperature, such as those of H_5 and H_Q, is too complex to be accounted for by prototropic tautomerism. Some fluxionality or slow rotation about the N–Rh bond must also be involved. One possibility is depicted in Scheme 5.



Scheme 5

Table 4

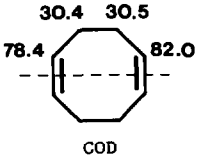
^1H and ^{13}C NMR chemical shifts and coupling constants for [Rh(LL)(COD)] (8) (solvent: $CDCl_3$)



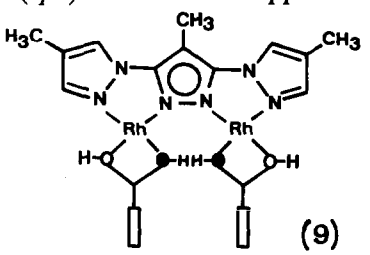
$T = 293$ K	Ring A				Ring B			
	H_3	4-Me	H_5		H_3	4-Me	H_5	
^1H NMR (200 MHz)	7.47	2.14	7.67 J(Me) = 0.9		–	2.29	–	
	C_3	C_4	C_5	4-Me	C_3	C_4	C_5	4-Me
^{13}C NMR (50 MHz)	140.7 $^1J = 182.0$ $^3J(H) = 8.0$ $^3J(Me) = 4.0$	118.2 $^2J = 7.4$ $^2J = 7.4$ $^2J(Me) = 7.4$	128.0 $^1J = 186.8$ $^3J(H) = 5.0$ $^3J(Me) = 5.0$	8.84 $^1J = 128.7$	149.0 $^2J(Rh) = 2.1$	91.3 $^2J(Me) = 6.8$	145.1 $^3J = 4.0$ $^3J = 4.0$	8.0 $^1J = 127.9$

$T = 293$ K	Ring C				COD		
	H_3	4-Me	H_5		H_O	H_M	H_N
^1H NMR (200 MHz)	7.00(b)	2.11	7.62		4.32 4.92	2.00	2.47 $J_{MN} = 8.4$
	C_3	C_4	C_5	4-Me	$C(sp^2)$	$C(sp^3)$	
^{13}C NMR (50 MHz)	137.7 $^1J = 186.9$ $^3J(H) = 8.0$ $^3J(Me) = 4.0$ $^2J(Rh) = 2.2$	115.8 $^2J = 7.4$ $^2J = 7.4$ $^2J(Me) = 6.1$	124.5 $^1J = 190.1$ $^3J(H) = 5.0$ $^3J(Me) = 5.0$	8.80 $^1J = 125.9$	78.4 $^1J(Rh) = 12.9$ 82.0 $^1J(Rh) = 11.8$	30.4	

The spectra of [Rh(LL)(COD)] (**8**) are very simple; owing to the absence of fluxionality, tautomerism, and slow motions, all the signals are well resolved, allowing the measurement of small coupling constants. A heteronuclear ($^1H-^{13}C$) 2D-correlation experiment related protons to C–H carbons of Table 4. Small $^2J(^{13}C-N-^{103}Rh)$ coupling constants identify C_3 carbons of rings **B** and **C**. The $^1J(^1H-^{13}C)$ coupling constant of carbon C_5 in ring **C** (190.1 Hz) is larger than in ring **A** (186.8 Hz) due to the N–Rh bond [10]. As in compound **6**, the COD shows C_s symmetry.



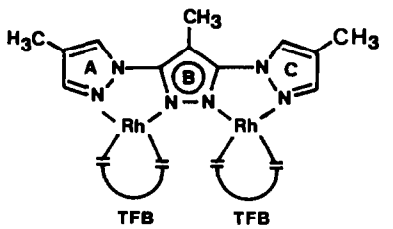
The dinuclear complex **9** is a salt, $[\{Rh(TFB)\}_2(\mu\text{-}LL)]BF_4$, and for this reason is much less soluble in NMR solvents than the preceding compounds. The ^1H NMR signals from the TFB ligand are broad, but the broadening does not decrease when the temperature is lowered to 183 K (in acetone-d_6). The proposed structure (see below) accounts for the NMR results (Table 5), except for the fact that H_Q and $C(sp^2)$ nuclei in TFB appear to be isochronous.



(9)

Table 5

^1H and ^{13}C NMR chemical shifts and coupling constants for $[(Rh(TFB)]_2(\mu\text{-LL})]BF_4$ (**9**)

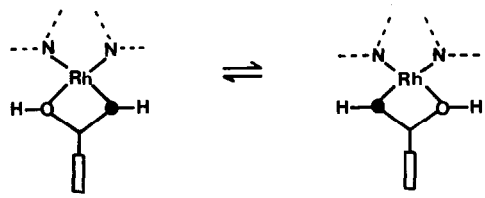


$T = 293$ K	Solvent	Ring B [a]	Rings A and C [b]			TFB	
		4-Me	3	5	4-Me	$C(sp^2)-H_Q$	$C(sp^3)-H_P$
^1H	$CDCl_3$	2.36	7.11	8.12	2.23	5.55(b)	4.02(b)
(200 MHz)	CD_3COCD_3	2.66	7.63	8.65	2.34	5.88(b)	4.42(b)
	CD_3OD	2.65	7.47	8.45	2.37	5.86(b)	4.30(b)
^{13}C	$CDCl_3$	9.65	140.1	128.0	9.65	40.4	139.7
(50 MHz)	CD_3OD	9.0	142.4	128.1	9.0	41.6	140.0

[a] Quaternary carbons C_3, C_4, C_5 of ring B are not observed, [b] Quaternary carbon C_4 of rings A and C is not observed; b: broad.

The origin of the broadening is unknown. (Even the pyrazole signals are slightly broadened.) Possibly compound **9** is not planar and the three pyrazole rings adopt a helical conformation by small twists about the $C_{3(5)}$–$N_{1'(1'')}$ bonds in order to avoid interactions between the inner H_Q's. If the conformational motions were restricted, this could result in a signal broadening.

The isochrony of some TFB nuclei, *vide supra*, can be explained in terms of rotation of the diolefins:



This behaviour has been demonstrated for square-planar rhodium(I) complexes (diolefin = COD or cyclooctatetraene) [11] and postulated for another rhodium(I) complex (diolefin = TFB) [12,13].

The great potential of the 3,5-bis(4-methylpyrazol-1-yl)-4-methylpyrazole ligand is shown in its rhodium(I) complexes. Depending on the diolefin used, COD or TFB, and on the experimental conditions, it behaves like $\widehat{HLL}$ (**6**), $-\widehat{HLL}$ (**7**), $\widehat{LL}$ (**8**) or $-\widehat{LL}$ (**9**). In three cases, **6**, **7** and **9**, fluxionality was observed; such behaviour will be more frequently detected as NMR instruments are improved.

Experimental

All reactions were carried out under nitrogen by standard Schlenk techniques. The starting materials 3,5-bis(4-methylpyrazol-1-yl)-4-methylpyrazole ($\widehat{HLL}$) (**5**) [5] (NMR data in Table 6), $[RhCl(diolefin)]_2$ (diolefin = COD [14], TFB [15]) and [Rh(acac)(COD)] [14] were prepared by published methods.

C, H, N analyses were carried out with a Perkin–Elmer 240B microanalyzer. IR spectra were recorded on a Perkin–Elmer 1330 spectrophotometer (Nujol mulls). Conductivities were measured in 10^{-4} *N* acetone solutions with a Crison 525 conductimeter. Molecular weights were determined in $CHCl_3$ solutions with a Knauer vapour-pressure osmometer. The NMR spectra were taken with a Bruker AC200, working at 200.13 MHz for ^1H and 50.32 MHz for ^{13}C, and a Bruker AM500, operating at 500.13 MHz for ^1H and 125.76 MHz for ^{13}C, spectrometers. Both spectrometers were equipped with variable temperature units. The temperature of the probe was calibrated by use of the standard methanol technique (± 0.5 K). ^1H and ^{13}C chemical shifts (δ) are given relative to internal TMS with an accuracy of ± 0.01 and ± 0.1 ppm, respectively. Coupling constants (J) were determined with a digital resolution of 0.2 and 0.6 Hz, respectively.

The spectrum of compound **7** in the solid state was recorded on a Bruker CXP400, at 100.63 MHz. The Toss technique was used to suppress the side bands.

*Preparation of complexes [RhCl(COD)($\widehat{HLL}$)] (**6**) and [{RhCl(TFB)}$_2$(μ-$\widehat{HLL}$)] (**7**). Reaction between [RhCl(diolefin)]$_2$ and ($\widehat{HLL}$)*

To a suspension of the dinuclear complexes $[RhCl(diolefin)]_2$ (0.2 mmol) in

Table 6

^{1}H and ^{13}C NMR chemical shifts and coupling constants for (HLL) (5) [a]

Nucleus (frequency)	Solvent	Central ring				Lateral rings			
		3	4	5	4-Me	3'(3'')	4'(4'')	5'(5'')	4'(4'')-Me
^{1}H (500 MHz)	$CDCl_3$	–	–	–	2.35	7.56	–	7.70(q) $J_{5'(Me)} = 0.85$	2.14(d)
	DMSO-d_6	–	–	–	2.17	7.61(b)	–	7.94	2.11(b)
^{13}C (125 MHz)	$CDCl_3$	142.9	96.5 $^{2}J(Me) = 6.5$	142.9	8.3 $^{1}J = 129.1$	142.0 $^{1}J = 183.8$ $^{3}J(H) = 8.0$ $^{3}J(Me) = 4.0$	117.7 $^{2}J(H_{3'}) = 9.4$ $^{2}J(H_{5'}) = 7.2$ $^{2}J(Me) = 6.6$	127.5 $^{1}J = 187.8$ $^{3}J(H) = 4.6$ $^{3}J(Me) = 4.6$	8.7 $^{1}J = 127.6$

[a] d: doublet; q: quartet; b: broad signal.

acetone (20 ml) was added the ligand ($\widehat{HLL}$) (diolefin = COD, L = 0.2 mmol; diolefin = TFB, L = 0.1 mmol). The starting materials dissolved and a pale-yellow solid separated immediately. After 1 h stirring the suspension was vacuum-concentrated to half its volume and the product was filtered off, washed with hexane, and air-dried.

Preparation of [Rh($\widehat{LL}$)(COD)] (8)

Method A. A mixture of $[RhCl(COD)]_2$ (0.1 mmol), ligand ($\widehat{HLL}$) (0.2 mmol) with a mixture of a methanolic solution of KOH (2.3 ml, 0.088 *N*, 0.2 mmol) and acetone (15 ml) was stirred for 2 h. The solution was then evaporated to dryness and the residue extracted with dichloromethane (15 ml), and the extract filtered to remove KCl and concentrated to ca. 2 ml. Addition of hexane gave a yellow solid, which was filtered off, washed with hexane, and air-dried.

Method B. Addition of ($\widehat{HLL}$) (0.3 mmol) to a dichloromethane solution (15 ml) of [Rh(acac)(COD)] (0.3 mmol) gave a bright yellow solution. After 1 h stirring the solution was vacuum-concentrated to ca 2 ml and hexane was added. The solid formed was filtered off, washed with hexane and air-dried.

Preparation of [{Rh(TFB)}$_2$(μ-$\widehat{LL}$)]BF_4 (9)

To a suspension of $[RhCl(TFB)]_2$ (0.1 mmol) in acetone (15 ml), ligand ($\widehat{HLL}$) (0.1 mmol) were added an excess of $NaBF_4$ (0.2 mmol) and a methanolic solution of KOH (1.5 ml, 0.088 *N*, 0.1 mmol). The starting complex dissolved and a pale-yellow solid precipitated out. The suspension was stirred for 4 h, evaporated to dryness, and the residue extracted with dichloromethane (15 ml). Removal of KCl by filtration gave a yellow solution, which was concentrated under reduced pressure. Addition of hexane gave a yellow solid, which was filtered off and air-dried.

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