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CARBONYLRHODIUM(I) DERIVATIVES OF 3,5-DIMETHYL- AND 3,5-BIS(TRIFLUOROMETHYL)PYRAZOLE

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Summary

Binuclear pyrazolato-bridged complexes such as $[(OC)_2Rh(\mu\text{-pyrazolato-}N,N')]_2$, I or II, were obtained in alkaline solution from $(OC)_4Rh_2Cl_2$ and 3,5-dimethylpyrazole (pz'H) or 3,5-bis(trifluoromethyl)pyrazole (pz"H), while in the absence of alkali $(OC)_2RhCl(pz'H\text{-}N)$ was formed. With the appropriate ligand, I and II gave binuclear or ionic species: $[(OC)(Ph_3P)Rh(\mu\text{-pyrazolato-}NN')]_2$ or $[\{Ph_2P(CH_2)_nPPh_2\}_2Rh(OC)_m][pz'']$, respectively, where $m = 0$ and $n = 2, 3$ or $m = 1$ and $n = 3$. On the other hand, *trans*-$(Ph_3P)_2(OC)RhCl$ in the presence of alkali reacted with pz"H to give the mononuclear $(Ph_3P)_2(OC)Rh(pz''\text{-}N)$ and with pz'H to give binuclear complex $[(OC)(Ph_3P)Rh(\mu\text{-}pz')]_2$. The pz' ligand was always found to be exobidentate, while pz" could also be monodentate or anionic.

In transition metal chemistry the pyrazolato anion * and its analogues have generally been considered exobidentate (i.e. bidentate and bridging, or μ-pz-*N,N'* or 1,2-dihaptopyrazolide) ligands [1], only a few exceptions being known, e.g. in the case of platinum(II) and palladium(II) these ligands may be monodentate in complexes like $(Ph_2PCH_2)_2M(pz\text{-}N)_2$ [2,3], which, in turn, may act as bidentate nitrogen donors towards Lewis acids [4].

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* A generic pyrazole is indicated by pzH, unsubstituted pyrazole ($C_3H_4N_2$) by PzH, 3,5-dimethylpyrazole by pz'H and 3,5-bis(trifluoromethyl)pyrazole by pz"H.

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The possibility of monodentate or exobidentate behaviour appears to be connected with the nature of the substituents on the pyrazolato ring and of the ligands on the metal center. Thus, during our investigations on the pyrazolato derivatives of gold(I) it was observed that the 3,5-dimethyl-4-nitropyrazolato ligand could be mono- or exobidentate as in the following reactions [5]:

$$3\ \mathrm{Me_2SAuCl} + 3\ \mathrm{pz^-} \rightarrow 3\ \mathrm{Me_2S} + 3\ \mathrm{Cl^-} + [(\mu\text{-pz-}N,N')\mathrm{Au}]_3$$

$$\mathrm{Ph_3PAuCl} + \mathrm{pz^-} \rightarrow \mathrm{Cl^-} + \mathrm{Ph_3PAu(pz\text{-}}N)$$

To develop our interest in rhodium(I) chemistry [6,7] we decided to investigate the coordinating ability of 3,5-bis(trifluoromethyl)pyrazole, pz″H, and of 3,5-dimethylpyrazole, pz′H, the anions of which are symmetric and so cannot give isomers upon coordination. These two pyrazoles were chosen because (a) comparisons are possible between the derivatives of the two analogous ligands, especially through NMR spectra (^{1}H, ^{19}F and ^{13}C), (b) the presence of two strongly electron-withdrawing groups should facilitate monodentate coordination with the derivatives of pz″H; and (c) the fluorine-containing ligands should produce volatile compounds, even with a heavy metal.

Results and discussion

The reactions carried out and the products obtained are indicated in Scheme 1. All the compounds, I—IX, (Table 1) were characterized by analyses, molecular weight determinations, the electrical conductivity of their solutions, and spectroscopy (mass, IR, and ^{1}H, ^{19}F, ^{31}P and ^{13}C NMR).

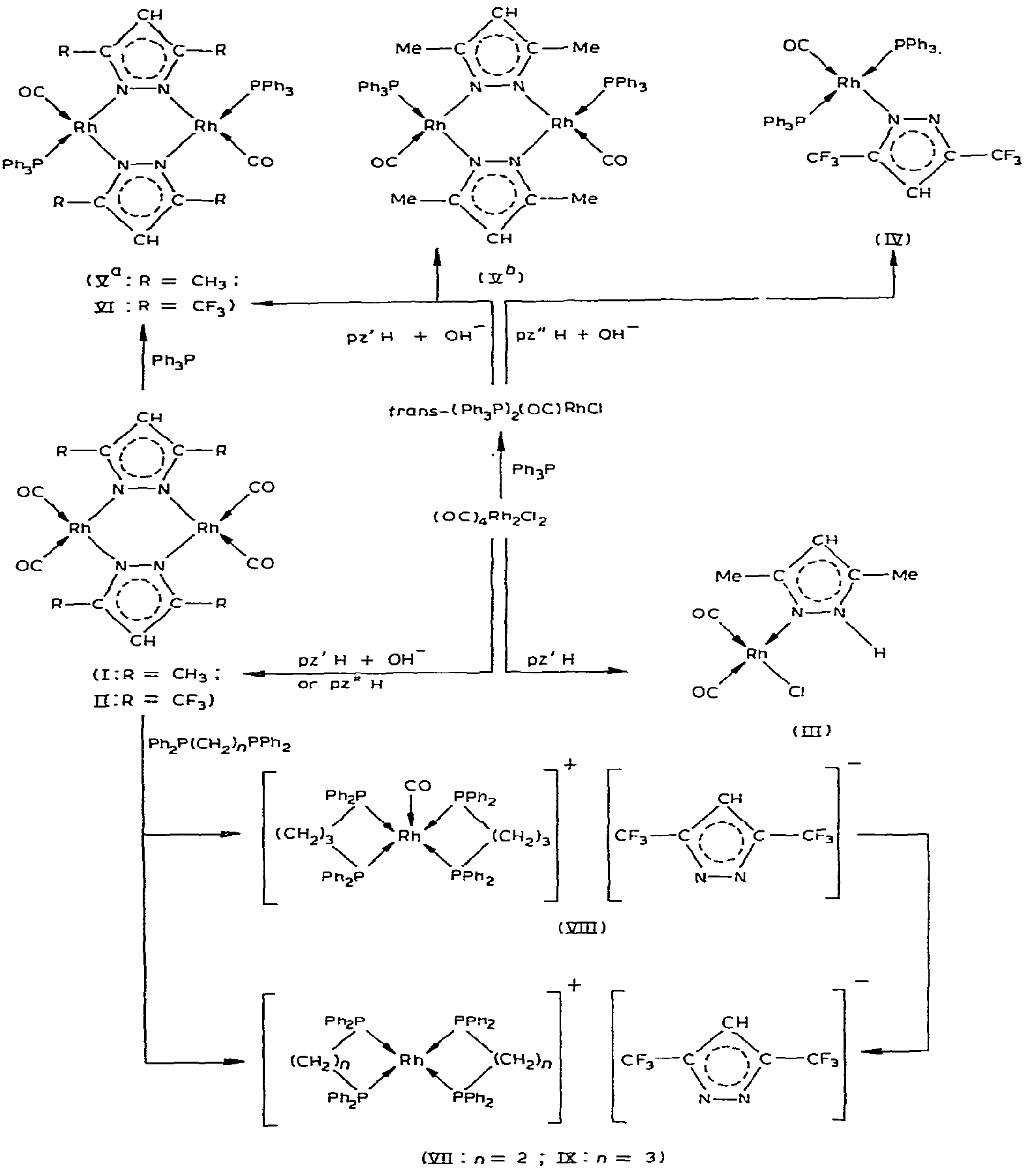
With dimeric rhodium dicarbonyl chloride both pz′H and pz″H in an alkaline medium readily gave the corresponding $[(\mathrm{OC})_2\mathrm{Rh}(\mu\text{-pz-}N,N')]_2$, I and II. Structures containing a boat-shaped, six-membered ring are likely for I and II in view of the geometric requirements of the pyrazolato ligand and of the usual square planar coordination of the rhodium(I) atoms. The thermal stability of these rings is remarkable, since both I and II can be sublimed under vacuum, the latter more easily. The stability towards further reaction is moderate. Reaction with a monodentate ligand, such as Ph$_3$P, does not destroy the six-membered ring and only carbon monoxide replacement takes place, affording the $[(\mathrm{Ph_3P})(\mathrm{OC})\mathrm{Rh}(\mu\text{-pz-}N,N')]_2$ complexes V and VI. On the other hand, reaction of II with a diphosphine such as $\mathrm{Ph_2P(CH_2)}_n\mathrm{PPh_2}$ (L-L) gives the compounds $[(\mathrm{L\text{-}L})_2\mathrm{Rh}][\mathrm{pz''}]$, VII, when $n = 2$, or VIII, $[(\mathrm{L\text{-}L})_2\mathrm{Rh(CO)}][\mathrm{pz''}]$, and then IX, $[(\mathrm{L\text{-}L})_2\mathrm{Rh}][\mathrm{pz''}]$, when $n = 3$. In these complexes the inorganic ring has disappeared and the $[\mathrm{pz''}]^-$ ligand has now been forced out of the first coordination sphere of the rhodium atom, as evidenced inter alia by the conductivity of their solutions.

The stability of the cation $[\{(\mathrm{Ph_2P(CH_2)}_n\mathrm{PPh_2}\}_2\mathrm{Rh(CO)}]^+$ with $n = 3$ was discussed recently by Pignolet et al. [8], who for different experimental conditions found that such cations, formed as in the following equation,

$$[\mathrm{Rh}\{\mathrm{Ph_2P(CH_2)}_n\mathrm{PPh_2}\}_2]^+ + \mathrm{CO} \rightarrow [(\mathrm{OC})\mathrm{Rh}\{\mathrm{Ph_2P(CH_2)}_n\mathrm{PPh_2}\}_2]^+$$

could be isolated as tetrafluoroborate for $n = 1$, 3, or 4 but not for $n = 2$.

The differing nucleophilicities of the pz′ and the pz″ anions is revealed by



SCHEME 1

a Only the *trans* isomer was isolated. *b* The *cis* isomer was detected, along with the *trans* isomer.

their reaction with *trans*-$(Ph_3P)_2(OC)RhCl$. While the methylated compound gives a binuclear species, $[(Ph_3P)(OC)Rh(\mu\text{-pz}'\text{-}N,N')]_2$ (V) bridged by two pz′ ligands, the less nucleophilic fluorinated analogue gives $(Ph_3P)_2(OC)Rh(\text{pz}''\text{-}N)$ (IV) in which the pz″ ligand is monodentate, although the fluorinated analogue, VI, of the binuclear species V, is stable and can be obtained from II.

TABLE 1

MELTING POINTS, AND ANALYTICAL AND MOLECULAR WEIGHT DATA

Compound [a]	M.p. (°C)	Analyses: Found (calcd.) (%)				Notes
		C	H	N	M.W.	
I, $(OC)_2Rh(pz')_2Rh(CO)_2$	161	33.43 (33.07)	2.91 (2.76)	10.91 (11.02)	512 [b] (508)	c, d [20]
II, $(OC)_2Rh(pz'')_2Rh(CO)_2$	102	23.82 (23.20)	0.18 (0.28)	7.91 (7.73)	732 [e] (724)	c, d
III, $(OC)_2RhCl(pz'H)$	77	29.72 (28.96)	2.75 (2.76)	9.86 (9.66)	 (290)	c
IV, *trans*-$(Ph_3P)_2(OC)Rh(pz'')$	185—190	58.50 (58.75)	3.84 (3.61)	3.08 (3.26)	837 [e] (858)	f, g
V { *trans*-$[(Ph_3P)(OC)Rh(pz')]_2$ [j]	246	59.41	4.82	5.38	940 [e]	c, j, g
{ $[(Ph_3P)(OC)Rh(pz')]_2$ [h]	243	59.42 (59.02)	4.96 (4.51)	5.77 (5.74)	920 [e] (976)	c, i, h
VI, $[(Ph_3P)(OC)Rh(pz'')]_2 + 0.5\ C_5H_{12}$ [k]	255	49.36 (49.35)	2.94 (3.09)	4.59 (4.56)	1180 [e] (1192)	d
VII, $[\{Ph_2PCH_2)_2\}_2Rh]^+[pz'']^-$	193—195	61.65 (62.07)	4.52 (4.46)	2.28 (2.54)	1117 [b] (1102)	l
VIII, $[Ph_2P(CH_2)_3PPh_2]_2Rh(CO)(pz'') \cdot H_2O$	119 dec.	60.20 (61.22)	4.69 (4.68)	2.12 (2.38)	— (1176)	—
IX, $[\{Ph_2P(CH_2)_3PPh_2\}_2Rh][pz''] \cdot H_2O$	114 dec.	61.12 (61.67)	4.80 (4.79)	2.13 (2.44)	— (1148)	m

[a] pz'H is 3,5-dimethylpyrazole, pz"H is 3,5-bis(trifluoromethyl)pyrazole. All the compounds are yellow except IX which is beige. [b] Osmometry in chloroform solution. [c] The parent ion was found in the mass spectrum. [d] Not conducting in dichloromethane. [e] Osmometry in benzene solution. [f] The molecular weight determination was carried out at 1.48 and 0.95% (w/w). [g] Not conducting in acetone. [h] *cis* and *trans* isomers. [i] Prepared from $(Ph_3P)_2(OC)RhCl$ (see text). [j] Prepared from I (see text). [k] C_5H_{12} is n-pentane. [l] $\Lambda = 121.0$ (acetone, 3.6×10^{-4} *M*) or 55.2 (CH_2Cl_2, 7.6×10^{-4} *M*) $ohm^{-1}\ cm^2\ mol^{-1}$ at 22°C. [m] $\Lambda =$ 45 (CH_2Cl_2, 3.8×10^{-4} *M*) $ohm^{-1}\ cm^2\ mol^{-1}$ at 20°C.

The mononuclear complex *trans*-$(Ph_3P)_2(OC)Rh(pz''$-*N*), IV, has to be compared with two other mononuclear rhodium(I) pyrazolates obtained recently, namely *trans*-$(R_3P)_2(SC)Rh(Pz$-*N*) [9], with R = Ph or cyclohexyl. One of these compounds (R = Ph) is not stable and above —50°C dimerizes with phosphine loss to [*trans*-$(Ph_3P)(SC)Rh(\mu$-Pz-*N,N'*)$]_2$, while the other (R = cyclohexyl) is stable at room temperature and is not reported to give the binuclear compound. We suggest that in the case of $(Cy_3P)_2(SC)Rh(Pz$-*N*) the monodentate behaviour is likely to be controlled by the nature of the other ligands on the metal, and that dimerization is prevented by the steric requirements of the tris(cyclohexyl)phosphine, while in our case dimerization does not occur owing to the lower nucleophilicity of the fluorinated pyrazolato group.

The binuclear species $[(Ph_3P)(OC)Rh(\mu$-pyrazolato-*N,N'*)$]_2$ like V (or VI) may exist as geometrical isomers, *cis* and *trans*, and indeed both isomers were detected by proton NMR in the product obtained from *trans*-$(Ph_3P)_2(OC)RhCl$ and $[pz']^-$. On the other hand, only the *trans* isomer was detected and isolated by direct replacement of CO by phosphine in the binuclear complexes I or II. The *trans* isomers thus seem to be the more easily obtained.

The fluorinated compound $[(OC)_2Rh(\mu$-pz"-*N,N'*)$]_2$, II, can be obtained even in the absence of alkali, thus providing another example of the formation of a pyrazolato derivative rather than the neutral pyrazole adduct expected under such conditions. Several other examples of such proton loss exist, e.g.:

$$2\ \mathrm{Pd(OAc)_2} + 4\ \mathrm{pz'H} \rightarrow [(\mathrm{pz'H})(\mathrm{AcO})\mathrm{Pd}(\mu\text{-}\mathrm{pz'}\text{-}N,N')]_2 + 2\ \mathrm{AcOH} \qquad [10a]$$

$$\mathrm{Cu(PzH)_4}^{2+} + \mathrm{Cu} \rightarrow 2/n[\mathrm{Cu}(\mu\text{-}\mathrm{Pz}\text{-}N,N')]_n + 2\ \mathrm{PzH_2}^{+} \qquad [10b]$$

Although such proton loss is fairly common, and an explanation for it has been suggested [11], it is by no means general. With the same $(OC)_4Rh_2Cl_2$, pz′H behaves differently from the more acidic pz″H, giving, instead of I, a volatile, four-coordinate 1 : 1 adduct, *cis*-$(OC)_2RhCl$(pz′-H-*N*), III. This adduct was mentioned in a preliminary note [12] and reported to be fluxional but no indication of the solvent or of temperature was given. In our hands the ^1H and ^{13}C NMR spectra gave no evidence of fluxional behaviour at room temperature; equivalence of the two methyl protons was reached above 50°C in $CDCl_3$.

Infrared spectral data (Table 2) support the structure proposed for the compounds I—IX. In addition to the carbonyl stretching frequencies, the intense C—H stretching vibration(s) due to the single proton of the pseudoaromatic ring is present above 3100 cm^{-1} both in I and II. The compound III shows the expected N—H and Rh—Cl stretching vibrations, which are obviously missing in all the remaining compounds. A band at 1520—1530 cm^{-1} is present in the compounds containing a coordinated pyrazolato ligand, and is assigned to the ring breathing vibration of the heterocyclic molecule; the absorption is displaced to 1575 cm^{-1} in the adduct of neutral pyrazole, $(OC)_2RhCl$(pz′-H-*N*), III.

TABLE 2

INFRARED DATA

Compound	1500—1600 cm^{-1} region [a]	CO stretching region	Others
I	1520m	Nujol: 2080s, 2050s, 2020s, 2000s, 1970(sh) $CHCl_3$: 2080s, 2060s, 2005s	3120w [b], 3100vw
II	1530s	Nujol: 2095s, 2080s, 2040s, 2023s, 1990(sh) $CHCl_3$: 2110s, 2090s, 2050s	3140m [b]
III	1575	Nujol: 2080s, 2070s, 2010s, 1970(sh) $CHCl_3$: 2090s, 2010s	3180s [c], 3140s, 3040m [b], 290m [d]
IV	1520w	Nujol: 1990vs, 1940w(sh) C_6H_6 or $CHCl_3$: 1990s	—
V [e]	1520m	Nujol: 1980vs, 1960vs, 1930w(sh), 1910w(sh) C_6H_6: 1975s, broad	—
V [f]	1520m	Nujol: 1980s, 1960s, 1950s, 1910w(sh) C_6H_6: 1975s(br)	—
V [g]	1520m	Nujol: 1980vs, 1960vs, 1910(sh) C_6H_6 or CH_2Cl_2: 1975s(br)	—
VI	1530w(br)	Nujol: 1990vs, 1980vs, 1940w(sh) $CHCl_3$: 1995s	—
VII	not detected	Nujol: no absorption	—
VIII	not detected	Nujol: 1930s(br)	—
IX	not detected	Nujol: no absorption	3380w(br)

[a] Pyrazole ring vibration. [b] C—H stretching vibration of the pyrazole. [c] N—H stretching. [d] Rh—Cl stretching, broad. [e] Sample prepared from $(Ph_3P)_2(OC)RhCl$; the carbonyl stretching vibrations are well separated, the compound is *trans*. [f] Mixture of *cis*- and *trans*-isomers, prepared from $(Ph_3P)_2(OC)RhCl$; the ν(CO) vibrations are overlapping. [g] Prepared from the compound I; the product is the *trans* isomer.

The solution spectra in the carbonyl stretching region show three strong absorptions for both the pz′- and the pz″-bridged dicarbonyl derivatives, $[(OC)_2Rh(pz)]_2$, I or II, the higher set of values being observed for the bis(trifluoromethyl)pyrazolate owing to the lower basicity and/or better π-acceptor ability of the fluorinated ligand. A smaller shift in the same direction (<20 cm^{-1}) was observed in the two couples dicarbonyl(pentan-2,4-dionato)metal(I) and dicarbonyl(1,1′,1″,5,5′,5″-hexafluoropentan-2,4-dionato)metal(I) where the metal is either rhodium [6] or iridium [13]. The difference (up to 30 cm^{-1}) between any of the carbonyl stretching vibrations of I and the corresponding vibration of II is notably higher than that (<10 cm^{-1}) observed for any pair of the series of μ-diarylformimidato-bridged carbonylrhodium compounds, $\{(OC)_2Rh[N(Ar){=}CH{-}N(Ar)]_2Rh(CO)_2\}$ [14]. Therefore, transmission of electronic effects through the molecules I and II must be easy, since the influence of replacing hydrogens by fluorines is felt on $\nu(CO)$, a vibration which takes place five bonds away from the atoms concerned.

Substitution of one CO group by PPh_3 in either I or II lowers the carbonyl stretching frequencies by ca. 100 cm^{-1}, as expected, so that the values are found in the same range as those for *trans*-$(Ph_3P)_2(OC)RhCl$ (1983 cm^{-1} in $CHCl_3$). This shift takes place both in the mononuclear *trans*-$(Ph_3P)_2(OC)Rh(pz''\text{-}N)$ (IV) and in the binuclear $[(OC)(Ph_3P)Rh(\mu\text{-pz-}N,N')]_2$ (V or VI); as with the dicarbonyl derivatives I and II, the fluorine-containing species, VI, has a higher $\nu(CO)$ than the fluorine-free complex, V.

When both *cis*- and *trans*-isomers are formed, as in the case of V, differences in the carbonyl stretching region are to be expected, and the isolated *trans* isomer indeed shows fewer bands than the mixture. The *cis* compound was not isolated pure, and since in the mixture there is some broadening and overlapping of $\nu(CO)$ bands, only the vibration at 1950 cm^{-1} may be assigned with certainty to this isomer.

The ^1H, ^{19}F, ^{31}P, and ^{13}C NMR data were recorded for some of the compounds and the data are listed in Tables 3 and 4. They all support the formulae suggested. The difference between the chemical shifts of the 4-H resonance of the compounds I and II is the same (ca. 1 ppm) as in the parent pyrazoles pz′H and pz″H. In addition the location of 4-H makes it very sensitive both to the molecular environment (e.g.: *cis* and *trans* V and IV, VI or VII) and to the solvent employed (e.g.: IV). The resonances from the 3- and 5-methyl groups of the azole ring are shifted from the value observed for the free ligand by amounts depending upon the molecular environment, as observed previously [2,5,11].

The signals due to ^{19}F nuclei fall within rather restricted range (59.5—60.9 ppm). They are generally sharp when they belong to an ionic (IV) or exobidentate (II or VI) ligand, but they are broad (20 cm^{-1} at half height) in the case of the monodentate ligand pz″ in the compound IV, suggesting a fluxional Rh—N bond.

From the ^{31}P NMR spectra of IV and VII at room temperature the $^1J(^{103}Rh{-}^{31}P)$ are identical (134 Hz) and also very close to the value reported (133 Hz) for other rhodium(I) complexes having two mutually *trans* phosphorus atoms, such as $[(cis\text{-}Ph_2PCH{=}CHPPh_2)_2Rh]^+$ or $[(Ph_2PCH_2)_2Rh]Cl$ [15].

The ^{13}C NMR spectra were recorded only for the compounds I—III; the sig-

TABLE 3

PROTON, FLUORINE AND PHOSPHORUS NMR SPECTRA

Compound ^{a}	Solvent	Proton NMR ^{b}			^{19}F ^{c}	^{31}P ^{d}
		4-CH	3- and 5-CH_3	Aryl (others)		
I, $[(OC)_2Rh(pz')]_2$	$CDCl_3$	4.20s	7.75s	—	—	—
— pz'H	$CDCl_3$	4.25s	7.79s	—	—	—
II, $[(OC)_2Rh(pz'')]_2$	$CDCl_3$	3.15s	—	—	60.9s	—
— pz''H	$CDCl_3$	3.0s	—	—		—
III, $(OC)_2RhCl(pz'H)$	$CDCl_3$	4.02s	7.59s, 7.73s	−1.31br(NH)	—	—
IV, *trans*-$(OC)(Ph_3P)_2Rh(pz'')$	$CDCl_3$	4.0s	—	2.4—2.8m	59.6s broad	30.2s $J = 134.3$
IV, *trans*-$(OC)(Ph_3P)_2Rh(pz'')$	C_6D_6	3.69	—	2.2—2.5m, 2.7—3.1m	—	—
V ^{e}, [*trans*-$(OC)(Ph_3P)Rh(pz')]_2$	C_6D_6	4.44s	7.38s, 8.14s	2.0—2.4m, 2.8—3.0m	—	—
V ^{e,f}, [*trans*-$(OC)(Ph_3P)Rh(pz')]_2$ + [*cis*-$(OC)(Ph_3P)Rh(pz')]_2$	C_6D_6	4.46s 4.04s 4.59s	7.38s, 8.14s 7.30s, 8.10s	2.2—2.5m, 2.8—3.0m	—	—
V ^{g}, [*trans*-$(OC)(Ph_3P)(pz')]_2$	C_6D_6	4.45s	7.38s, 8.14s	2.2—2.4m, 2.8—3.0m	—	42.7s $J = 151.4$
VI, [*trans*-$(OC)(Ph_3P)Rh(pz'')]_2$	$CDCl_3$	3.74	—	2.3—2.8m ^{i}	59.9s ^{h} 60.2s	44.2s $J = 158.7$
VII, $[\{(Ph_2PCH_2)_2\}_2Rh][pz'']$	$CDCl_3$	3.40s	—	2.5—3.3m 7.88m, br(CH_2)	59.5s	57.5s $J = 134.3$

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[a] pz'H is 3,5-dimethylpyrazole, pz''H is 3,5-bis(trifluoromethyl)pyrazole. [b] Varian XL-100; τ units; s = singlet; m = multiplet. [c] Bruker instrument operating at 24 MHz; ppm upfield from internal $CFCl_3$. [d] Bruker instrument operating at 56 MHz; ppm downfield from external 85% H_3PO_4; all doublets. [e] Sample prepared from $(Ph_3P)_2$-(OC)RhCl (see text). [f] ca. 1/2 *cis/trans* ratio according to integration. [g] Sample prepared from the compound I (see text). [h] 1 : 1 ratio. [i] Pentane gives absorptions at 8.50s, 8.70 complex and 9.12 complex.

TABLE 4

^{13}C NMR DATA IN DEUTEROCHLOROFORM SOLUTION [a]

Compound [b]	Signals			
	C-3 and C-5	C-4	3- and 5-CX_3	Carbonyls (doublets)
— pz″H	139.4q, $^2J = 40.7$	104.3s	X = F: 119.4q, $^1J = 269.2$	—
II, $[(OC)_2Rh(pz'')]_2$	144.3q, $^2J = 39.6$	106.1s	X = F: 119.5q, $^1J = 269.6$	182.2, ^1J(Rh—C) = 69.2
— pz′H	144.0 broad	103.8s	X = H: 12.1s	—
I, $[OC)_2Rh(pz')]_2$	149.3s	104.3s	X = H: 14.5s	185.3, ^1J(Rh—C) = 65.8
III, $(OC)_2RhCl(pz'H)$	142.1s, 151.9s	106.6s	X = H: 10.9s, 15.1s	not detected

[a] ppm from internal tetramethylsilane; s = singlet, q = quartet, *J* in Hz. Temperature was 28°C. [b] pz′H is 3,5-dimethylpyrazole, pz″H is 3,5-bis(trifluoromethyl)pyrazole.

nals were assigned by comparison with the spectra of the corresponding ligands (Table 4). The chemical shifts and the ^{103}Rh—^{13}C coupling constants of the carbonyl carbons are found to be within the range established for a series of other rhodium(I) carbonyl complexes [14,16], i.e. 177—187 ppm and 64—75 Hz. Moreover, according to Varshavskii's rule [16], the compound having the higher ν(CO), i.e. II, shows the lower ^{13}C chemical shift for the carbonyl groups. The presence of two methyl signals in the spectrum of III again shows that it is not fluxional at room temperature in $CDCl_3$.

The molecular mass could be determined precisely from the mass spectra in several cases, and agree with molecular weight determinations in solution. They also show that the six-membered inorganic ring present in the compounds I or II is very stable; even after stepwise loss of the four carbonyl groups the $Rh(pz)_2Rh$ fragment was present.

Conclusions

The results reported in this paper show that the 3,5-bis(trifluoromethyl)-pyrazole and the corresponding anion behave differently than the dimethyl analogues, probably because of their lower nucleophilic character. The 3,5-bis-(trifluoromethyl)pyrazolato ligand may behave in three ways towards a given metal centre, e.g. Rh^I:

(a) monodentate as in VI; such ligation to transition metals was known previously only for a few platinum, palladium [2,3] or gold [5] compounds, and, very recently, two rhodium derivatives [9].

(b) exobidentate, as in II or VI; this is the commonest mode of ligation, and that usually assumed for pyrazolates [1].

(c) ionic, as in VII—IX; although such anions are likely to be present in sodium or potassium pyrazolate [17], such behaviour had not previously been observed in transition metal chemistry.

It is evident that pyrazoles are versatile ligands which show a variety of behaviour.

Experimental

Evaporation was always carried out under reduced pressure (water aspirator). The analytical samples were always pumped to constant weight at room temperature under vacuum (ca. 1 Torr). The analyses were carried out in the Microanalytical Laboratory of the University of Milan. Infrared spectra (Table 2) were recorded on Beckman 4210 or Perkin-Elmer 457 instrument. Bis(trifluoromethyl)pyrazole was prepared according to the literature [18].

Tetracarbonyldi(μ-3,5-dimethylpyrazolato-N,N′)dirhodium(I), $[(OC)_2Rh(pz')]_2$, *I.* 3,5-Dimethylpyrazole (340 mg; 3.54 mmol) and then potassium hydroxide in methanol (17 ml, 0.216 *M*; 3.67 mmol) were added to a stirred ethereal solution (50 ml) of $(OC)_4Rh_2Cl_2$ (650 mg; 1.67 mmol). The residue left after evaporation was extracted with benzene; concentration of the extract in the presence of methanol gave the yellow compound I (702 mg, 83%), which was further purified by vacuum sublimation (70° C, ca. 0.8 Torr). The compound is soluble in ether and hydrocarbons.

Tetracarbonyldi[μ-3,5-bis(trifluoromethyl)pyrazolato-N,N′]dirhodium (I), $[(OC)_2Rh(pz'')]_2$, *II.* The compound was prepared and purified similarly (71% yield); it is soluble in ether and hydrocarbons and can be sublimed (35° C, ca. 0.8 Torr). It was also obtained by use of a suspension of excess barium carbonate in the place of potassium hydroxide, or even in the absence of alkali, though in lower yield (28%).

cis-Dicarbonyl(3,5-dimethylpyrazole-N)chlororhodium(I), $(OC)_2(pz'H)RhCl$, *III.* To an ethereal solution (30 ml) of $(OC)_4Rh_2Cl_2$ (169.7 mg; 0.436 mmol) and pz′H (93 mg; 0.97 mmol) hexane (50 ml) was added. Upon concentration the yellow product (152 mg) separated out and was purified by sublimation (45° C, ca. 0.5 Torr) to give an analytical sample. It is sparingly soluble in aliphatic hydrocarbons.

trans-Bis(triphenylphosphine)carbonyl[3,5-bis(trifluoromethyl)pyrazolato-N]rhodium(I), $(Ph_3P)_2(OC)Rh(pz'')$, *IV.* A mixture of *trans*-$(Ph_3P)_2(OC)$-RhCl [19] (486.5 mg; 0.705 mmol), benzene (60 ml), pz″H (194.2 mg; 0.732 mmol) and potassium hydroxide in methanol (7.0 ml, 0.216 *M*; 1.51 mmol) was stirred for 24 hours. After concentration to small volume, the yellow solution was filtered, ethanol was added, and the solution further concentrated to give a precipitate (403 mg; 67%), which was recrystallized from benzene/ethanol to afford an analytical sample. The yellow complex is soluble in acetone and dichloromethane.

Dicarbonylbis(triphenylphosphine)di(μ-3,5-dimethylpyrazolato-N,N′)dirhodium(I), $[(OC)(Ph_3P)Rh(pz')]_2$, *V.* (i) Triphenylphosphine (406 mg; 1.55 mmol) was added to an ethereal solution (30 ml) of I (95.5 mg; 0.385 mmol). Gas was evolved. After 1.5 h the yellow precipitate was filtered off and recrystallized by vacuum concentration of a benzene/methanol solution (305 mg; ca. 80%). Since C, H, N analyses indicated the presence of clathrated benzene, the sample was either pumped at 76° C and ca. 0.1 Torr or recrystallized from toluene/methanol, to give an analytical sample of V, the *trans*-isomer. (ii) 3,5-Dimethylpyrazole (57 mg; 0.59 mmol) and then a solution of potassium hydroxide in methanol (2.0 ml, 0.30 *M*; 0.6 mmol) were added to a benzene solution (40 ml) of *trans*-$(Ph_3P)_2(OC)RhCl$ [19] (375 mg; 0.54 mmol). After

2.5 hours' stirring, the solution was evaporated to dryness, the oily residue was extracted with benzene, and the yellow solid (188 mg) obtained upon addition of hexane to the extract was recrystallized from toluene/ethanol to give V as the *trans* isomer (75 mg). This was sparingly soluble in acetone, hexane or methanol. Concentration of the mother liquor (benzene/hexane) gave another yellow product (123 mg), which was purified by washing with hexane and by crystallization from toluene/ethanol affording an analytical sample of V as a mixture of the *cis* and *trans*-isomers (according to ^{1}H NMR, Table 3). This mixture was sparingly soluble in acetone, hexane and methanol, and soluble in $CHCl_3$ or CH_2Cl_2.

trans-Dicarbonylbis(triphenylphosphine)di-μ-[3,5-bis(trifluoromethyl)-pyrazolato-N,N']dirhodium(I), $[(OC)(Ph_3P)Rh(pz'')]_2$, *VI.* Triphenylphosphine (435 mg; 1.66 mmol) was added to a pentane solution of the compound II (297.4 mg; 0.41 mmol). After six hours' stirring the yellow product (235 mg) was filtered off and recrystallized from pentane to give an analytical sample (171 mg). The complex is soluble in benzene and dichloromethane and sparingly soluble in methanol.

Di[1,2-bis(diphenylphosphino)ethane]rhodium(I) 3,5-bis(trifluoromethyl)-pyrazolate, $[(Ph_2PCH_2CH_2PPh_2)_2Rh]^+[pz'']^-$, *VII.* An ethereal solution of 1,2-bis(diphenylphosphino)ethane (324 mg; 0.814 mmol) was added to a solution of II (164 mg; 0.2 mmol) in the same solvent (30 ml). The yellow precipitate was filtered off, washed with ether and recrystallized from methanol/ether to give an analytical sample (258 mg; 58%). The complex is soluble in acetone or chloroform, sparingly soluble in benzene, and insoluble in ether or petroleum ether.

Di[1,3-bis(diphenylphosphino)propane](carbonyl)rhodium(I) or di[1,3-bis(diphenylphosphino)propane]rhodium(I) 3,5-bis(trifluoromethyl)-pyrazolate, monohydrate, $[\{Ph_2P(CH_2)_3PPh_2\}_2Rh(CO)][pz''] \cdot H_2O$, *VIII, or* $[\{Ph_2P(CH_2)_3PPh_2\}_2Rh][pz''] \cdot H_2O$, *IX.* 1,3-Bis(diphenylphosphino)propane (184 mg; 0.447 mmol) in ether (20 ml) was added to a solution of II (80.6 mg; 0.111 mmol) in the same solvent (30 ml). After 15 min the orange solution was concentrated in the presence of pentane to give the compound VIII (148 mg), which was washed with pentane and recrystallized from ether (or benzene)/pentane, to give a (beige) analytical sample of IX. Compound VIII decomposes slowly even in the solid state to give IX. The latter is soluble in ether, benzene and dichloromethane, but insoluble in pentane.

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