Binuclear Pentamethylcyclopentadienylrhodium(III) Phosphido–Pyrazolate Complexes. X-ray Structure of $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})_2(\mu\text{-PPh}_2)]BF_4$ (pz = pyrazolate)

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Phosphido-bridged transition-metal complexes represent an important class of binuclear compounds. Phosphido bridges have been found to maintain the integrity of the binuclear framework during chemical transformations [1,2] although some examples have recently become available of reactions that lead to cleavage of M_2–(μ-PR_2) bonds [3,4]. Additionally, the ability of bridging PR_2 units to tolerate a wide variety of metals and bond distances, permits the preparation of binuclear complexes that frequently exhibit unusual and interesting structures [5,6] and chemical reactivities [7,8].

On the other hand, we are interested in the bi- and polynuclear chemistry of nitrogen-donor ligands with platinum metals [9]. In particular, pyrazolate-type groups, acting as exobidentate ligands, are versatile anions which permit a wide range of intermetallic separations [10] and are reasonably strong in retaining the binuclear nature of the complexes during chemical [11] or catalytic [12] transformations.

This letter focuses on the important role that the pyrazolate ligand plays in the addition of $HPPh_2$ to $(C_5Me_5)Rh^{III}$-containing complexes, permitting the entry into the pentamethylcyclopentadienylrhodium(III) phosphido chemistry, until now very scarcely represented [13].

Experimental

All operations were performed under nitrogen or under vacuum. The C, H and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. ^1H and ^{31}P NMR spectra were recorded in $CDCl_3$, at room temperature, on a Varian XL 200 spectrometer using $SiMe_4$ and 85% H_3PO_4 as external standard, respectively, with downfield chemical shifts reported as positive. IR spectra were run on a Perkin-Elmer 1330 spectrophotometer.

Preparation of $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})_2(\mu\text{-PPh}_2)]BF_4$ *(2)*

A mixture of $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})_2(\mu\text{-OH})]BF_4$ [14] (500.0 mg, 0.79 mmol) and $HPPh_2$ (206 μl, 1.19 mmol) in 30 ml of acetone was stirred for 2 h. Red crystals of complex **2** were isolated by slow diffusion of diethyl ether into the acetone solution. Yield: 65%.

Preparation of $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-PPh}_2)_2]BF_4$ *(3)*

A mixture of $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-OMe})_2]BF_4$ [14] (200.0 mg, 0.29 mmol) and $HPPh_2$ (101 μl, 0.58 mmol) in 20 ml of acetone was stirred for 1 h. After successive crystallizations, by diffusion of diethyl ether into the acetone solutions, red crystals of complex **3** were obtained in 20% yield.

Preparation of $[\{(C_5Me_5)Rh\}_2(\mu\text{-Pz})(\mu\text{-OH})(\mu\text{-PPh}_2)]BF_4$ *[Pz = mpz (5), dmpz (6), bmpz (7)]*

A mixture of the tri-μ-hydroxo complex **1** (196.5 mg, 0.32 mmol), the corresponding pyrazole HPz (0.32 mmol) and $HPPh_2$ (56 μl, 0.32 mmol), in 50 ml of acetone, was stirred for 5 h. After partial vacuum-evaporation, the orange complexes **5**–**7** were precipitated by addition of diethyl ether. The products were recrystallized from acetone diethyl ether. Yield: 25% (**5**), 35% (**6**), 50% (**7**). ν(OH) = 3515m (**5**), 3520m (**6**), 3520w (**7**) cm^{-1}.

X-ray Crystallographic Analysis of Complex 2

A suitable crystal of **2** was formed by slow diffusion of diethyl ether into a solution of **2** in chloroform. Crystal data: $M = 882.4$; monoclinic, space group $P2_1/n$; $a = 31.1995(16)$, $b = 11.5270(2)$, $c = 10.4073(2)$ Å, $\beta = 91.635(4)°$; $Z = 4$; $F(000) = 1792$; $\rho = 1.57$ g cm^{-3}; $\mu(Cu\ K\alpha) = 81.53$ cm^{-1}. The structure was solved by Patterson functions completed through the DIRDIF system [15] and refined by least-squares procedure on F_{obs} to conventional R of 0.040 and R_w of 0.046. A total of 6348 reflections, with $I > 3\sigma(I)$, were measured on a Philips PW 1100 diffractometer and corrected for absorption [16] (Cu Kα radiation, $\lambda = 1.5418$ Å up to 65° in θ).

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Results and Discussion

The interaction of $[\{(C_5Me_5)Rh\}_2(\mu\text{-}OH)_3]BF_4$ (1) with $HPPh_2$ in the presence of pyrazole (1 equivalent) at room temperature yields a deep red homogeneous solution containing a mixture of compounds mainly formed by $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)_2(\mu\text{-}PPh_2)]BF_4$ (2), $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}PPh_2)_2]BF_4$ (3) and $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}OH)(\mu\text{-}PPh_2)]BF_4$ (4).

Complex 2 was prepared in a pure state by reacting the recently reported di-μ-pyrazolate complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)_2(\mu\text{-}OH)]BF_4$ [14] with $HPPh_2$. The molecular structure of complex 2 is displayed in Fig. 1 [17]. The Rh1 ... Rh2 distance of 3.6463(4) Å excludes any metal–metal interaction. The distances of the metal atoms to the centroids of the C_5Me_5 rings are 1.856(3) and 1.860(3) Å. The lengthening of these distances, compared with 1.775(3) and 1.781(3) Å for the related μ-hydroxo complex [14] is supported by steric reasons because of the size of the diphenylphosphide ligand. The methyl groups stay out of the plane defined by the five membered ring and are pointing away from the rhodium atoms. The C_5Me_5 groups are inclined to one another at an angle of 29.6(2)° and the two pyrazolate rings make an angle of 64.2(2)°. The values are smaller than those of the complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)_2(\mu\text{-}OH)][BF_4]^+$ previously reported [14] (43.3(3) and 74.8(3)°, respectively), reflecting the different sizes of the PPh_2 and the hydroxo groups.

The recently reported di-μ-methoxo complex $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}OMe)_2]BF_4$ [14] reacts with $HPPh_2$ in a 1:2 molar ratio giving a mixture of products with two major phosphorus containing components (3 and 4) according to spectroscopic measurements. Fractional crystallization of the mixture permits the separation and analytic* and spectroscopic characterization of the di-μ-phosphido compound $[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}PPh_2)_2]BF_4$ (3) (see Table 1).

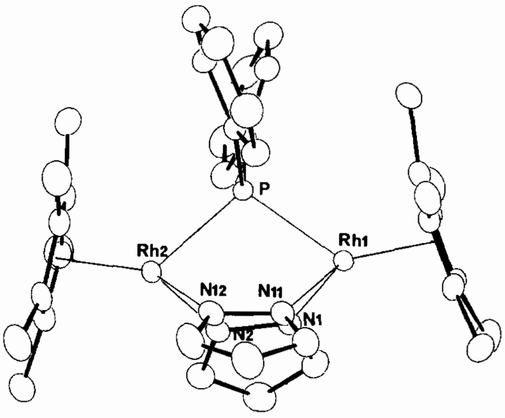

Fig. 1. An ORTEP [17] representation of complex 2. Selected bond distances and angles are: Rh(1)–P 2.335(1), Rh(2)–P 2.332(1), Rh(1)–N(1) 2.094(4), Rh(1)–N(11) 2.096(4), Rh(2)–N(2) 2.088(4), Rh(2)–N(12) 2.090(4) Å; N(1)–Rh(1)–P 82.5(1), N(2)–Rh(2)–P 83.7(1), N(1)–Rh(1)–N(11) 85.6(1), N(2)–Rh(2)–N(12) 85.7(2), N(11)–Rh(1)–P 83.1(1), N(12)–Rh(2)–P 82.1(1), Rh(1)–P–Rh(2) 102.76(4), N(1)–Rh(1)–CM1 130.1(1), N(2)–Rh(2)–CM2 129.1(1), N(11)–Rh(1)–CM1 129.0(1), N(12)–Rh(2)–CM2 129.9(1), P–Rh(1)–CM1 129.6(1), P–Rh(2)–CM2 129.6(1)°. CM1 and CM2 are the centroids of the C_5Me_5 rings.

The related di-μ-methoxo complexes $[\{(C_5Me_5)Rh\}_2(\mu\text{-}Pz)(\mu\text{-}OMe)_2]BF_4$ with substituted pyrazolate

TABLE 1. ^{31}P and ^1H NMR Spectral Data

Complex		^{31}P		^1H	
		$\delta(P)$ (ppm)	$^1J(Rh-P)$ (Hz)	$\delta(C_5Me_5)$ (ppm)	$^4J(P-H)$ (Hz)
$[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)_2(\mu\text{-}PPh_2)]BF_4$	(2)	73.6t	112	1.30d	3.3
$[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}PPh_2)_2]BF_4$	(3)	−12.3t	97	1.38t	2.9
$[\{(C_5Me_5)Rh\}_2(\mu\text{-}pz)(\mu\text{-}OH)(\mu\text{-}PPh_2)]BF_4$	(4)	44.1t	116	1.14d	2.7
$[\{(C_5Me_5)Rh\}_2(\mu\text{-}mpz)(\mu\text{-}OH)(\mu\text{-}PPh_2)]BF_4$	(5)	48.3t	116.5	1.50d 1.49d	2.9 2.9
$[\{(C_5Me_5)Rh\}_2(\mu\text{-}dmpz)(\mu\text{-}OH)(\mu\text{-}PPh_2)]BF_4$	(6)	50.8t	117	1.52d	2.5
$[\{(C_5Me_5)Rh\}_2(\mu\text{-}bmpz)(\mu\text{-}OH)(\mu\text{-}PPh_2)]BF_4$	(7)	50.6t	117	1.53bs 1.54bs	
$[\{(C_5Me_5)Rh\}_2(\mu\text{-}mpz)(\mu\text{-}PPh_2)_2]BF_4$	(8)	−14.9t	99		
$[\{(C_5Me_5)Rh\}_2(\mu\text{-}bmpz)(\mu\text{-}PPh_2)_2]BF_4$	(9)	−17.5t	99		

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*Satisfactory elemental analyses were obtained for all new isolated compounds.

bridging ligands [Pz* = 3-methylpyrazolate (mpz), 3,5-dimethylpyrazolate (dmpz), 3(5)-bromo,5(3)-methylpyrazolate (bmpz)] react with two equivalents of $HPPh_2$ giving the μ-hydroxo-μ-phosphido compounds $[\{(C_5Me_5)Rh\}_2(\mu\text{-Pz})(\mu\text{-OH})(\mu\text{-PPh}_2)]BF_4$ [Pz = mpz (5), dmpz (6), bmpz (7)] as principal products. Small amounts of $[\{(C_5Me_5)Rh\}_2(\mu\text{-Pz})(\mu\text{-PPh}_2)_2]BF_4$ [Pz = mpz (8), bmpz (9)] were also observed although the formation of the corresponding dmpz derivative was not detected. Complex 4 was characterized as the μ-hydroxo-μ-phosphido compound $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-OH})(\mu\text{-PPh}_2)]BF_4$ (ν(OH) = 3515w cm^{-1}) by comparison of its spectroscopic properties with those of complexes 5–7. The latter complexes are better prepared by reacting the tri-μ-hydroxo complex 1 with equimolecular amounts of the corresponding HPz and $HPPh_2$ in acetone.

Table 1 collects the more significant ^1H and $^{31}P\{^1H\}$ NMR data of the new reported complexes.

All the reactions reported in this communication imply the displacement of the methoxo or hydroxo bridging groups by the diphenylphosphine ligand, accompanied, in some cases, by the hydrolysis of the methoxo groups. No metal–hydrido resonances have been observed even working at −50 °C. Presumably, the operating mechanism implies the protonation of the corresponding oxygen atoms by the phosphine followed by displacement of the neutral molecules formed (H_2O or MeOH). It is interesting to point out the influence of the pyrazolate coordinated groups in the observed reactivity (complex 1 readily reacts with Hpz giving $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})(\mu\text{-OH})_2]BF_4$ and $[\{(C_5Me_5)Rh\}_2(\mu\text{-pz})_2(\mu\text{-OH})]BF_4$ [14]). Probably, this type of group acts, on the one hand, increasing the electronic density on the oxygen bridging atoms favoring their protonation and, on the other, retaining the binuclear nature of the complex cations in the course of the reactions allowing the formation of the final isolated products.

Further studies in this area are currently in progress.

Supplementary Material

Detailed reports for structure determinations including tables for fractional coordinates of non-hydrogen atoms, interatomic distances and intramolecular angles, anisotropic thermal parameters, hydrogen parameters and structure factors (26 pages) are available from the authors on request.

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References

1 A. J. Carty, *Pure Appl. Chem., 54* (1982) 113.

2 W. C. Fultz, A. L. Rheingold, P. E. Kreter and D. W. Meek, *Inorg. Chem., 22* (1983) 319.

3 L. Chen, D. J. Kountz and D. W. Meek, *Organometallics, 4* (1985) 598.

4 S.-G. Shyu, M. Calligaris, G. Nardin and W. Wojcicki, *J. Am. Chem. Soc., 109* (1987) 3617, and refs. therein.

5 R. A. Jones, T. C. Wright, J. L. Atwood and W. E. Hunter, *Organometallics, 2* (1983) 470.

6 A. H. Arif, R. A. Jones, M. H. Seeberger, B. R. Whittlesey and T. C. Wright, *Inorg. Chem., 25* (1986) 3943.

7 S. Rosenberg, G. L. Geoffroy and A. L. Rheingold, *Organometallics, 4* (1985) 1184, and refs. therein.

8 A. H. Arif, D. J. Chandler and R. A. Jones, *Organometallics, 6* (1987) 506.

9 L. A. Oro, M. A. Ciriano, B. E. Villarroya, A. Tiripicchio and F. J. Lahoz, *J. Chem. Soc., Dalton Trans.*, (1985) 1891; L. A. Oro, M. T. Pinillos, C. Tejel, C. Foces-Foces and F. H. Cano, *J. Chem. Soc., Dalton Trans.*, (1986) 1087; M. A. Ciriano, S. Sebastián, L. A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini and F. J. Lahoz, *Angew. Chem., Int. Edn. Engl., 27* (1988) 402.

10 L. A. Oro, D. Carmona, M. P. Lamata, C. Foces-Foces and F. H. Cano, *Inorg. Chim. Acta, 97* (1985) 19; L. A. Oro, D. Carmona, M. P. Puebla, M. P. Lamata, C. Foces-Foces and F. H. Cano, *Inorg. Chim. Acta, 112* (1986) L11.

11 L. A. Oro, D. Carmona, J. Reyes, C. Foces-Foces and F. H. Cano, *Inorg. Chim. Acta, 112* (1986) 35; L. A. Oro, D. Carmona and J. Reyes, *J. Organomet. Chem., 302* (1986) 417.

12 P. Kalck, A. Thorez, M. T. Pinillos and L. A. Oro, *J. Mol. Catal., 31* (1985) 311.

13 B. Klingert and H. Werner, *J. Organomet. Chem., 252* (1983) C47; *333* (1987) 119.

14 L. A. Oro, D. Carmona, M. P. Lamata, M. C. Apreda, C. Foces-Foces, F. H. Cano and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, (1984) 1823.

15 P. T. Beurskens, P. W. Bosman, H. M. Doesburg, R. O. Gould, Th. E. M. Van den Hark, P. A. J. Prick, J. H. Noordijk, G. Beurskens, V. Parthasarathi, H. J. Bruins Slot and R. C. Haltiwanger, *Dirdif System*, Crystallography Laboratory, Toernooivel, Nijmegen, The Netherlands, 1983.

16 N. Walker and D. Stuart, Difabs, *Acta Crystallogr., Sect. A, 39* (1983) 158.

17 C. K. Johnson, *ORTEP, Report ORNL-3794*, Oak Ridge National Laboratory, TN, 1965.

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*A generic pyrazole is indicated by HPz and unsubstituted pyrazole ($C_3H_4N_2$) itself by Hpz.