

Steric Effects on the Ortho-Metalation Reactions at Binuclear Pyrazolyl-Bridged Rhodium Compounds. Molecular Structure of $\text{Rh}_2(3,5\text{-dmpz})_2[\mu\text{-P}(o\text{-C}_6\text{F}_4)\text{Ph}_2]\text{Br}(\text{CO})(\eta^2\text{-PCBr})(\text{H}_2\text{O})$ [3,5-dmpz = 3,5-Dimethylpyrazolyl; PCBr = P(*o*-BrC₆F₄)Ph₂]

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Complexes of the type $[\text{Rh}(\text{Pz})(\text{CO})(\text{PCBr})]_2$ (Pz = pyrazolyl (pz), 1; 3-methylpyrazolyl (3-mpz), 2; 4-methylpyrazolyl (4-mpz), 3; PCBr = P(*o*-BrC₆F₄)Ph₂) are obtained by reacting $[\text{Rh}(\text{Pz})(\text{CO})_2]_2$ with PCBr or $\text{Rh}(\text{acac})(\text{CO})(\text{PCBr})$ with HPz. The reaction between $[\text{Rh}(3,5\text{-dmpz})(\text{CO})_2]_2$ (3,5-dmpz = 3,5-dimethylpyrazolyl) with PCBr leads only to the isolation of $\text{Rh}_2(3,5\text{-dmpz})_2(\text{CO})_3(\text{PCBr})$ (4); however, $[\text{Rh}(3,5\text{-dmpz})(\text{CO})(\text{PCBr})]_2$ (5) is obtained by reacting $\text{Rh}(\text{acac})(\text{CO})(\text{PCBr})$ with an excess of Na(3,5-dmpz). Complexes 1 and 2 undergo ortho-metalation by thermal reaction in refluxing xylene, leading to dirhodium(II) complexes $\text{Rh}_2(\text{Pz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})$ (6 (Pz = pz) and 7 (Pz = 3-mpz); PC = P(*o*-C₆F₄)Ph₂). 5 does not react under the same conditions, but the homologous ortho-metalated compound with 3,5-dmpz, $\text{Rh}_2(3,5\text{-dmpz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})(\text{H}_2\text{O})$ (8), is obtained by reacting 4 and PCBr (1:1 molar ratio). The thermal reaction of 4 in refluxing xylene gives $\text{Rh}_2(3,5\text{-dmpz})_2(\mu\text{-PC})\text{Br}(\text{CO})_3$ (9) as a major product. Compound 8 has been analyzed by X-ray diffraction. It crystallizes in the monoclinic $P2_1/n$ space group, with cell parameters $a = 13.8667$ (4) Å, $b = 26.0451$ (14) Å, $c = 14.4031$ (4) Å, and $\beta = 97.242$ (2)°. The structure consists of a dinuclear unit, with a Rh-Rh bond distance of 2.583 (1) Å. Two 3,5-dmpz ligands are bridging the rhodium atoms (Rh1-N1 = 2.069 (5), Rh1-N11 = 2.045 (4), Rh2-N2 = 2.143 (5), Rh2-N12 = 2.054 (5) Å), and one ortho-metalated phosphine acts also as bridging ligand (Rh1-P1 = 2.278 (1), Rh2-C26 = 2.056 (5) Å). One bromine atom and one carbonyl ligand complete the coordination sphere around one metal (Rh1-Br1 = 2.697 (1), Rh1-C1 = 1.881 (5) Å). The coordination on the other rhodium atom is completed by a PCBr ligand that is bonded via its P and Br atoms in a η^2 -mode (Rh2-P2 = 2.291 (1), Rh2-Br2 = 2.644 (1) Å). The two Rh-Br distances are very similar, reflecting the strong ligation of the neutral bidentate phosphine.

Introduction

Ortho-metalation reactions of P donor ligands at a single metallic center are well-known both for mono- and binuclear complexes.¹ However, very few examples of ortho metalation at bimetallic centers containing metal-metal bonds have been described to date. The compound $[\text{Pt}\{\mu\text{-}(o\text{-C}_6\text{H}_4)\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2\}]_2$ provided the first fully characterized example of such behavior.^{2,3} Recently, this type of reaction has also been observed in one compound containing a metal-metal multiple bond,⁴ $\text{Re}_2\text{Cl}_3[\mu\text{-}(P(o\text{-C}_6\text{H}_4)\text{Phpy})](\text{PPh}_2\text{py})_2$.

The occurrence of ortho-metalation in dichlorotetrakis(acetate)diosmium^{5,6} and tetrakis(acetate)dirhodium^{5,7} phosphine complexes has also been reported recently. Of special interest to us were complexes containing a mixed-ligand bridging system, $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2$

(P(*o*-C₆H₄)Ph₂)₂·2L, since a similar system was under study in our laboratory at that time. By using the (*o*-haloaryl)phosphine PCBr, we obtained the intermediate of the double metalation reaction $\text{Rh}_2(\text{O}_2\text{CCH}_3)_3[\text{P}(o\text{-C}_6\text{H}_4)(o\text{-BrC}_6\text{F}_4)\text{Ph}](\text{PCBr})^8$ that gave some insight into the mechanism of the formation of these doubly metalated species. The metalation reaction apparently occurs by partial displacement of an acetate group and formal proton transfer from the ortho hydrogen of a phenyl ring.

In a previous communication¹⁰ we have reported that the complex $[\text{Rh}(\text{pz})(\text{CO})(\text{PCBr})]_2$ (1) (Figure 1a) undergoes ortho-metalation by a 2c-2e oxidative addition reaction yielding $\text{Rh}_2(\text{pz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})$ (6) (Figure 1b) in low yield. The ³¹P NMR data obtained for this reaction indicate that most of the reaction products are the result of 1c-2e oxidative addition of the C-Br bond of the phosphine, as evidenced by the appearance of a set of high-field signals.⁹

In this paper we present further results on this subject showing that when substituted pyrazolyl ligands are used,

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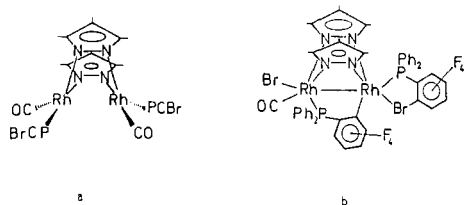


Figure 1. General schematic structures for the complexes of the type $[\text{Rh}(\text{Pz})(\text{CO})(\text{PCBr})]_2$ (a) and $\text{Rh}_2(\text{Pz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})$ (b).

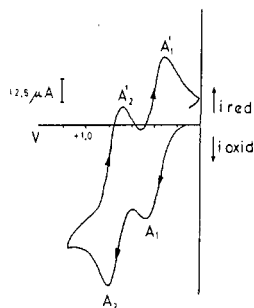


Figure 2. Cyclic voltammogram of compound **5** in THF/TBAPF₆, $\nu = 200 \text{ mV s}^{-1}$, at a stationary platinum electrode (E in V vs SCE).

the ortho-metalation reaction becomes more selective. We also report the crystal structure of $\text{Rh}_2(3,5\text{-dmpz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})(\text{H}_2\text{O})$ (**8**).

Experimental Section

General Comments. Complexes of the type $[\text{Rh}(\text{Pz})(\text{CO})(\text{PCBr})]_2$ were prepared according to literature methods.¹¹ Pyrazole and derivatives were purchased from Aldrich Chemical Co. Inc. and were used without further purification. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Johnson Matthey. PCBr was prepared by a published method,¹² as was $\text{Rh}(\text{acac})(\text{CO})_2$.¹³ Solvents were of reagent grade and were distilled and dried prior to use. All the reactions were carried out under an atmosphere of dry argon. Crystals of compound **8** were grown by slow diffusion of hexane into a dichloromethane solution of the complex. Table I shows the details of the analysis. The NMR spectra were recorded with a Bruker AC 200 spectrometer operating at 200.132 (¹H), 50.323 (¹³C), and 81.015 MHz (³¹P) in CDCl_3 solutions. TMS was the internal reference for both ¹H and ¹³C NMR studies. H_3PO_4 (85%) was the external standard for the ³¹P NMR studies. The infrared spectra were recorded with a Philips SP2000 spectrophotometer in CHCl_3 solutions. Elemental analyses were carried out at the Institut de Química Bio-Orgánica, Barcelona, Spain.

Synthesis of $[\text{Rh}(\text{Pz})(\text{CO})(\text{PCBr})]_2$ ($\text{Pz} = \text{pz}$, **1; $\text{Pz} = 3\text{-mpz}$, **2**; $\text{Pz} = 4\text{-mpz}$, **3**).** $\text{Rh}(\text{acac})(\text{CO})(\text{PCBr})$ (200 mg, 0.309 mmol) was dissolved in a mixture of dichloromethane–methanol (5 mL + 5 mL), and an excess (ca. 10%) of the corresponding pyrazole was added. The resulting solution was stirred until TLC showed no starting product. Evaporation of the dichloromethane and slow addition of water precipitated the corresponding $[\text{Rh}(\text{Pz})(\text{CO})(\text{PCBr})]_2$ (**1–3**) complexes as yellow solids.

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Table I. Crystal Analysis Parameters at Room Temperature

Crystal Data	
formula	$\text{C}_{45}\text{H}_{30}\text{N}_4\text{O}_2\text{F}_8\text{P}_2\text{Br}_2\text{Rh}_2 \cdot \text{H}_2\text{O}$
cryst habit	prismatic, dark orange
cryst size (mm)	$0.56 \times 0.37 \times 0.20$
symmetry	monoclinic, $P2_1/n$
unit-cell	least-squares fit from 98 reflectns ($\theta < 45^\circ$)
determinatn	
unit cell dimens	13.8667 (4), 26.0451 (14), 14.4031 (4) Å
packing	90, 97.242 (2), 90°
V (Å ³), Z	5160.3 (4), 4
D_{calcd} (g·cm ⁻³), M	1.597, 1240.33,
$F(000)$	2432
μ (cm ⁻¹)	83.20
Experimental Data	
technique	four-circle diffractometer: Philips Pw1100
	bisecting geometry
	graphite-oriented monochromator Cu K α
	$\omega/2\theta$ scans, scan width: 1.5°
	detector apertures $1 \times 1^\circ$, up $\theta_{\text{max}} = 57^\circ$
	1 min/reflectn
no. of reflectns	
independent	6924
obsd	6482 ($3\sigma(I)$ criterion)
std reflectns	2 reflectns every 90 min
	no variation
max–min transmissn	1.602–0.786 ¹⁵
factors	
Solution and Refinement	
soln	Patterson
refinement	LS on F_o with 2 blocks
parameters	
no. of variables	603
degrees of freedom	5879
ratio of freedom	10.7
H atoms	difference synthesis
final shift/error	0.11
ω scheme	empirical as to give no trends in $(\omega\Delta^2 F)$ versus (F_o) and $(\sin \theta)/\lambda$
max thermal value	$U(33)(C7) = 0.147$ (9) Å ²
final ΔF peaks	$1.3 \text{ e} \text{ \AA}^{-3}$ around the Br atoms
final R and R_w	0.048, 0.057
computer and programs	Vax 11/750, XRAY76 ¹⁴
scattering factors	ref 16

Compound 1: yield 73%; IR $\nu(\text{CO})$ 1985 cm^{-1} ; ¹H NMR δ 5.8, 6.4 (2 H, 2 H, pyrazolyl), 7.2–7.9 (22 H, aromatic and two pyrazolyl protons); ³¹P NMR δ +46.9 (¹J(Rh–P) = 161 Hz). Anal. Calcd for $\text{C}_{44}\text{H}_{26}\text{N}_4\text{O}_2\text{F}_8\text{P}_2\text{Br}_2\text{Rh}_2$: C, 43.2; H, 2.1; N, 4.4. Found: C, 43.1; H, 2.0; N, 4.3.

Compound 2: yield 75%; IR $\nu(\text{CO})$ 1980 cm^{-1} ; ¹H NMR δ 2.4 (6 H, methyl), 5.6, 6.1 (2 H, 2 H, pyrazolyl), 7.2–7.9 (20 H, aromatic); ³¹P NMR δ +46.1 (¹J(Rh–P) = 162 Hz). Anal. Calcd for $\text{C}_{46}\text{H}_{30}\text{N}_4\text{O}_2\text{F}_8\text{P}_2\text{Br}_2\text{Rh}_2$: C, 44.2; H, 2.4; N, 4.5. Found: C, 44.0; H, 2.3; N, 4.4.

Compound 3: yield 74%; IR $\nu(\text{CO})$ 1985 cm^{-1} ; ¹H NMR δ 1.7 (6 H, methyl), 6.2 (2 H, pyrazolyl), 7.2–7.9 (22 H, aromatic and two pyrazolyl protons); ³¹P NMR δ +48.0 (¹J(Rh–P) = 161 Hz). Anal. Calcd for $\text{C}_{46}\text{H}_{30}\text{N}_4\text{O}_2\text{F}_8\text{P}_2\text{Br}_2\text{Rh}_2$: C, 44.2; H, 2.4; N, 4.5. Found: C, 44.1; H, 2.4; N, 4.5.

Synthesis of $\text{Rh}_2(3,5\text{-dmpz})_2(\text{CO})_3(\text{PCBr})$ (4**).** $[\text{Rh}(3,5\text{-dmpz})(\text{CO})_2]_2$ (200 mg, 0.422 mmol) and 92 mg (0.422 mmol) of PCBr were dissolved in a mixture of dichloromethane–methanol (5 mL + 5 mL). After 15 min of stirring the solution was concentrated and addition of water yielded 250 mg of **4**: yield 89%; IR $\nu(\text{CO})$ 1990 (s), 2010 (s), 2085 (s) cm^{-1} ; ¹H NMR δ 1.45, 2.24, 2.26, 2.35 (3 H, 3 H, 3 H, 3 H, methyl), 5.52, 5.76 (1 H, 1 H, pyrazolyl), 7.1–7.9 (10 H, aromatic); ¹³C NMR δ 13.38, 14.13, 14.25, 14.73 (methyl), 103.50, 104.61 (CH, pyrazolyl), 127–137 (aromatic carbons), 186.74 (¹J(Rh–C) = 65 Hz (carbonyl)), 189.25 (¹J(Rh–C) = 65 Hz (carbonyl)), 192.14 (¹J(Rh–C) = 68 Hz, ²J(P–C) = 18 Hz (carbonyl)); ³¹P NMR δ +43.2 (¹J(Rh–P) = 161 Hz). Anal. Calcd for $\text{C}_{31}\text{H}_{24}\text{N}_4\text{O}_3\text{F}_4\text{PBrRh}_2$: C, 41.7; H, 2.7; N, 6.3. Found: C, 41.7; H, 2.3; N, 5.9.

Synthesis of $[\text{Rh}(3,5\text{-dmpz})(\text{CO})(\text{PCBr})]_2$ (5**).** $\text{Rh}(\text{acac})(\text{CO})(\text{PCBr})$ (500 mg, 0.773 mmol) and 200 mg (2×0.773 mmol, ca. 100% excess) of Na(3,5-dmpz) were dissolved in a mixture

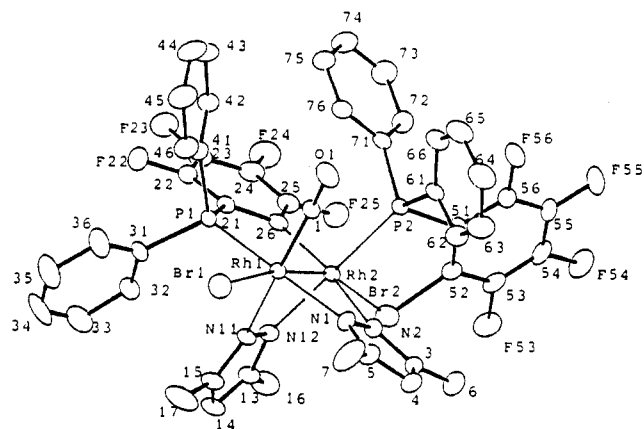


Figure 3. Molecular structure of compound 8, with the same atomic numbering as for the previously described 6.¹⁰

of dichloromethane-methanol (5 mL + 15 mL) and were stirred for 24 h. Dichloromethane was then evaporated, and slow addition of water gave 440 mg of compound 5: yield 90%; IR $\nu(\text{CO})$ 1975 cm^{-1} ; ^{13}C NMR δ 13.63, 14.74 (methyl), 103.16 (CH, pyrazolyl), 128–137 (aromatic), 191.11 ($^1J(\text{Rh}-\text{C}) = 69$ Hz, $^2J(\text{P}-\text{C}) = 19$ Hz (carbonyl)); ^{31}P NMR δ +43.0 ($^1J(\text{Rh}-\text{P}) = 162$ Hz). Anal. Calcd for $\text{C}_{46}\text{H}_{34}\text{N}_4\text{O}_2\text{F}_8\text{P}_2\text{Br}_2\text{Rh}_2$: C, 43.9; H, 3.1; N, 4.1. Found: C, 43.9; H, 3.1; N, 4.1.

Synthesis of $\text{Rh}_2(\text{Pz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})$ ($\text{Pz} = \text{pz}$, 6; $\text{Pz} = 3\text{-mpz}$, 7; $\text{Pz} = 3,5\text{-dmpz}$, 8). The corresponding $[\text{Rh}(\text{Pz})(\text{CO})_2]_2$ (0.363 mmol) ($\text{Pz} = \text{pz}$, 3-mpz, and 3,5-dmpz) and 0.762 mmol (300 mg) of PCBr were dissolved in xylene (10 mL). The resulting orange solution was refluxed for 20 min, the color becoming dark red. The solution was then evaporated to dryness, the resulting red oil was redissolved in a mixture of dichloromethane-hexane (2 mL + 4 mL), and the solution was chromatographed on a column (30 \times 1.5 cm) packed with silica gel in hexane. The chromatographic separations were as follows. (a) For pz: elution with dichloromethane-hexane (2:1) separated a red band that contained compound 6. (b) For 3-mpz: after the column was washed with chloroform-hexane (1:1) and further with chloroform-hexane-diethyl ether (10:10:1), elution with diethyl ether-hexane (1:1) separated a red band that contained compound 7. (c) For 3,5-dmpz: elution with chloroform-hexane-diethyl ether (10:10:1) yielded a red band that contained compound 8. Compounds 6, 7, and 8 were isolated as red solids after the separated bands were recrystallized from dichloromethane/hexane.

Compound 6: yield 5%; IR $\nu(\text{CO})$ 2060 cm^{-1} ; ^{31}P NMR δ +55.8 ($^1J(\text{Rh}-\text{P}) = 140$ Hz), +31.9 ($^1J(\text{Rh}-\text{P}) = 105$ Hz). Anal. Calcd for $\text{C}_{45}\text{H}_{26}\text{N}_4\text{O}_4\text{F}_8\text{P}_2\text{Br}_2\text{Rh}_2\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$: C, 42.3; H, 2.4; N, 4.3. Found: C, 42.8; H, 2.2; N, 4.4.

Compound 7: yield 15%; IR $\nu(\text{CO})$ 2055 cm^{-1} ; ^1H NMR δ 2.1, 2.4 (3 H, 3 H, methyl), 5.75 (2 H, pyrazolyl), 6.8–7.4 (22 H, aromatic and includes two pyrazolyl protons); ^{31}P NMR δ +54.3 ($^1J(\text{Rh}-\text{P}) = 138$ Hz), +28.2 ($^1J(\text{Rh}-\text{P}) = 108$ Hz). Anal. Calcd for $\text{C}_{45}\text{H}_{30}\text{N}_4\text{O}_4\text{F}_8\text{P}_2\text{Br}_2\text{Rh}_2\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$: C, 42.2; H, 2.6; N, 3.7. Found: C, 42.1; H, 2.5; N, 3.7.

Compound 8: yield 45%; IR $\nu(\text{CO})$ 2075 cm^{-1} ; ^1H NMR δ 1.43, 1.96, 2.07, 2.34 (3 H, 3 H, 3 H, methyl), 5.49, 5.59 (1 H, 1 H, pyrazolyl), 6.2–8.2 (20 H, aromatic); ^{31}P NMR δ +57.2 ($^1J(\text{Rh}-\text{P}) = 136$ Hz), +26.3 ($^1J(\text{Rh}-\text{P}) = 104$ Hz). Anal. Calcd for $\text{C}_{47}\text{H}_{34}\text{N}_4\text{O}_4\text{F}_8\text{P}_2\text{Br}_2\text{Rh}_2$: C, 43.1; H, 2.7; N, 3.5. Found: C, 43.2; H, 2.9; N, 3.2.

Synthesis of $\text{Rh}_2(3,5\text{-dmpz})_2(\mu\text{-PC})\text{Br}(\text{CO})_3$ (9). $\text{Rh}_2(3,5\text{-dmpz})_2(\text{CO})_3(\text{PCBr})$ (100 mg, 0.112 mmol) was dissolved in xylene (7 mL) and refluxed for 20 min. The obtained red solution was evaporated to dryness, and the resulting oil was redissolved in a mixture of chloroform/hexane (1 mL + 2 mL). This solution was transferred to a column (30 \times 1.5 cm) packed with silica gel in hexane. First washing with chloroform-hexane (1:1) and further elution with diethyl ether-hexane (3:1) gave an orange band. Evaporation to dryness and recrystallization from methanol/water yielded 20 mg of compound 9: yield 20%; IR $\nu(\text{CO})$ 2040 (s), 2070 (s), 2090 (s) cm^{-1} ; ^1H NMR δ 1.58, 1.62, 2.14, 2.37 (3 H, 3 H, 3 H, 3 H, methyl), 5.44, 5.60 (1 H, 1 H, pyrazolyl), 6.8–8.1 (10 H, aromatic); ^{31}P NMR δ +27.0 ($^1J(\text{Rh}-\text{P}) = 107$ Hz). Anal. Calcd

Table II. Final Atomic Coordinates

atom	x/a	y/b	z/c
C31	0.1895 (5)	0.1157 (3)	0.0014 (4)
C32	0.1151 (6)	0.0833 (3)	-0.0385 (5)
C33	0.1090 (9)	0.0695 (4)	-0.1328 (8)
C34	0.1812 (13)	0.0873 (6)	-0.1830 (7)
C35	0.2565 (11)	0.1184 (6)	-0.1437 (7)
C36	0.2603 (7)	0.1332 (4)	-0.0510 (6)
C41	0.3113 (4)	0.1470 (2)	0.1746 (4)
C42	0.3556 (5)	0.1170 (3)	0.2479 (5)
C43	0.4490 (5)	0.1285 (4)	0.2914 (6)
C44	0.4983 (5)	0.1690 (4)	0.2604 (7)
C45	0.4579 (5)	0.1987 (3)	0.1892 (7)
C46	0.3642 (5)	0.1885 (3)	0.1455 (6)
F22	0.2703 (3)	0.0314 (2)	0.1251 (3)
F23	0.2304 (4)	-0.0505 (2)	0.2259 (4)
F24	0.0793 (4)	-0.0462 (2)	0.3302 (4)
F25	-0.0266 (3)	-0.0361 (2)	0.3344 (3)
C21	0.1425 (4)	0.0801 (2)	0.1797 (4)
C22	0.1952 (5)	0.0348 (2)	0.1761 (4)
C23	0.1755 (5)	-0.0079 (2)	0.2264 (5)
C24	0.0992 (5)	-0.0055 (2)	0.2801 (5)
C25	0.0455 (5)	0.0388 (2)	0.2808 (4)
C26	0.0618 (4)	0.0834 (2)	0.2314 (4)
P1	0.18545 (10)	0.13659 (5)	0.12178 (9)
Br1	0.16589 (5)	0.26045 (3)	0.02281 (5)
Rh1	0.08291 (3)	0.20345 (1)	0.13765 (3)
C1	0.1685 (4)	0.2335 (2)	0.2341 (4)
O1	0.2225 (4)	0.2537 (2)	0.2852 (4)
N1	-0.0332 (3)	0.2491 (2)	0.1626 (4)
N2	-0.0971 (3)	0.2195 (2)	0.2035 (3)
C3	-0.1774 (4)	0.2480 (3)	0.2104 (4)
C4	-0.1633 (5)	0.2965 (3)	0.1719 (5)
C5	-0.0724 (5)	0.2959 (2)	0.1426 (5)
C6	-0.2636 (5)	0.2306 (3)	0.2537 (6)
C7	-0.0189 (7)	0.3373 (3)	0.0992 (9)
N11	-0.0166 (3)	0.1693 (2)	0.0401 (3)
N12	-0.0632 (3)	0.1339 (2)	0.0878 (3)
C13	-0.1286 (5)	0.1095 (2)	0.0266 (5)
C14	-0.1238 (6)	0.1304 (3)	-0.0622 (5)
C15	-0.0522 (5)	0.1673 (3)	-0.0505 (5)
C16	-0.1921 (6)	0.0676 (3)	0.0549 (6)
C17	-0.0185 (8)	0.2018 (4)	-0.1226 (6)
Rh2	-0.02615 (3)	0.14683 (1)	0.22852 (3)
Br2	-0.18624 (5)	0.10507 (3)	0.27699 (5)
P2	0.01894 (10)	0.16146 (5)	0.33479 (9)
F53	-0.3239 (3)	0.0855 (2)	0.4128 (3)
F54	-0.3112 (3)	0.1067 (2)	0.5961 (4)
F55	-0.1538 (4)	0.1575 (2)	0.6826 (3)
F56	-0.0066 (3)	0.1813 (2)	0.5896 (3)
C51	-0.0859 (4)	0.1481 (2)	0.4476 (4)
C52	-0.1695 (4)	0.1232 (2)	0.4050 (4)
C53	-0.2449 (4)	0.1098 (3)	0.4556 (5)
C54	-0.2393 (5)	0.1207 (3)	0.5475 (5)
C55	-0.1594 (5)	0.1460 (3)	0.5920 (5)
C56	-0.0837 (5)	0.1592 (2)	0.5423 (5)
C61	0.0570 (4)	0.2259 (2)	0.4248 (4)
C62	-0.0028 (5)	0.2668 (3)	0.3954 (5)
C63	0.0250 (7)	0.3165 (3)	0.4191 (7)
C64	0.1132 (7)	0.3256 (3)	0.4698 (6)
C65	0.1753 (6)	0.2854 (3)	0.4994 (6)
C66	0.1453 (5)	0.2351 (3)	0.4785 (5)
C71	0.1092 (4)	0.1176 (2)	0.4447 (4)
C72	0.0859 (5)	0.0801 (3)	0.5059 (5)
C73	0.1572 (6)	0.0451 (3)	0.5447 (6)
C74	0.2509 (6)	0.0481 (4)	0.5211 (6)
C75	0.2734 (5)	0.0846 (3)	0.4602 (5)
C76	0.2038 (5)	0.1197 (3)	0.4209 (4)
O2	0.5293 (12)	0.0096 (6)	0.6177 (11)
O3	0.4279 (21)	0.0361 (12)	0.7456 (21)

for $\text{C}_{31}\text{H}_{24}\text{N}_4\text{O}_3\text{F}_4\text{PBrRh}_2\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$: C, 41.7; H, 2.7; N, 6.3. Found: C, 41.9; H, 2.4; N, 5.8.

X-ray Crystallography. Table I shows the crystal data and the main characteristics of the analysis. Two disordered water molecules, each with population of one half and an oxygen...oxygen contact of 2.55 (4) Å are present in the asymmetric unit. Water hydrogen atoms could not be located. The final difference synthesis shows an isolated peak of 1.3 e Å^{-3} that can be assigned

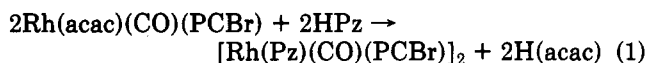
Table III. Selected Bond Distances (Å) and Angles (deg)

(A) Bond Distances			
Rh1-Rh2	2.583 (1)		
Rh1-Br1	2.597 (1)	Rh2-Br2	2.644 (1)
Rh1-P1	2.278 (1)	Rh2-P2	2.291 (1)
Rh1-C1	1.881 (5)	Rh2-C26	2.052 (5)
Rh1-N1	2.069 (5)	Rh2-N2	2.143 (5)
Rh1-N11	2.045 (4)	Rh2-N12	2.054 (5)
C1-O1	1.113 (8)	Br2-C52	1.890 (6)
P1-C21	1.828 (6)	P2-C51	1.840 (6)
P1-C31	1.825 (6)	P2-C61	1.831 (6)
P1-C41	1.834 (6)	P2-C71	1.828 (6)
N1-N2	1.363 (7)	N11-N12	1.360 (7)
N1-C5	1.350 (8)	N11-C15	1.336 (8)
N2-C3	1.352 (8)	N12-C13	1.343 (8)
C3-C4	1.402 (9)	C13-C14	1.400 (10)
C4-C5	1.379 (10)	C14-C15	1.378 (10)
(B) Bond Angles			
Rh2-Rh1-C1	102.6 (2)	Rh1-Rh2-P2	107.4 (1)
Rh2-Rh1-P1	91.6 (1)	Rh1-Rh2-C26	94.9 (2)
Rh2-Rh1-Br1	169.7 (1)	Rh1-Rh2-Br2	159.0 (1)
Rh2-Rh1-N11	73.3 (1)	Rh1-Rh2-N12	71.5 (1)
Rh2-Rh1-N1	73.9 (1)	Rh1-Rh2-N2	72.3 (1)
C1-Rh1-P1	92.8 (2)	P2-Rh2-C26	91.5 (2)
C1-Rh1-Br1	86.8 (2)	P2-Rh2-Br2	86.8 (1)
C1-Rh1-N11	175.8 (2)	P2-Rh2-N12	178.6 (1)
C1-Rh1-N1	93.7 (2)	P2-Rh2-N2	94.7 (1)
Br1-Rh1-P1	92.3 (1)	Br2-Rh2-C26	100.4 (2)
Br1-Rh1-N11	97.2 (1)	Br2-Rh2-N12	94.6 (1)
Br1-Rh1-N1	101.5 (1)	Br2-Rh2-N2	91.4 (1)
P1-Rh1-N11	88.5 (1)	C26-Rh2-N12	87.9 (2)
P1-Rh1-N1	165.0 (1)	C26-Rh2-N2	167.0 (2)
N1-Rh1-N11	84.1 (2)	N2-Rh2-N12	85.7 (2)
Rh1-C1-O1	173.8 (6)	Rh2-C26-C21	122.8 (4)
Rh1-N11-N12	105.6 (3)	Rh2-N12-N11	105.6 (3)
Rh1-N1-N2	108.2 (3)	Rh2-N2-N1	105.2 (3)
Rh1-P1-C21	109.0 (2)	Rh2-P2-C51	108.5 (2)
Rh1-P1-C31	114.7 (2)	Rh2-P2-C61	119.6 (2)
Rh1-P1-C41	114.8 (2)	Rh2-P2-C71	116.5 (2)
		Rh2-Br2-C52	98.7 (2)

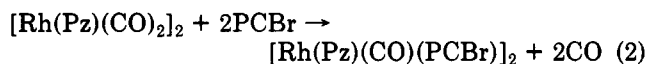
to another water molecule much less populated than those already given. Final fractional coordinates appear in Table II, with the corresponding numbering given in Figure 3. The principal characteristics of the molecular geometry are given in Tables III and IV. List of structure factors, thermal factors, and hydrogen parameters can be obtained from the authors on request and are deposited as supplementary material.

Results

Starting products of the type $[\text{Rh}(\text{Pz})(\text{CO})(\text{PCBr})_2]$ (1-3) have been prepared by reaction of $\text{Rh}(\text{acac})(\text{CO})(\text{PCBr})^{9a}$ and the corresponding pyrazole in a mixture of dichloromethane-methanol at room temperature (eq 1).¹¹



No reaction is observed when $\text{H}(3,5\text{-dmpz})$ is used. Compounds 1-3 can also be prepared by reacting stoichiometric amounts of $[\text{Rh}(\text{Pz})(\text{CO})_2]^{11}$ and the phosphine PCBr under the same reaction conditions (eq 2). Again the

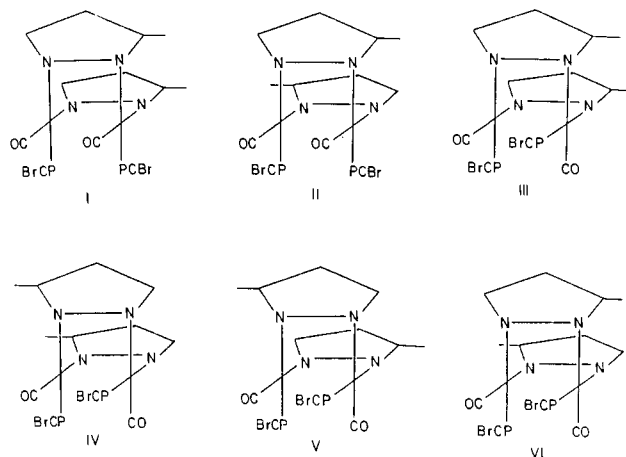


$3,5\text{-dmpz}$ derivative behaves in a different way, and only the partially substituted compound $\text{Rh}_2(3,5\text{-dmpz})_2(\text{CO})_3(\text{PCBr})$ (4) is obtained, even in the presence of a large excess of the phosphine. However, the disubstituted compound $[\text{Rh}(3,5\text{-dmpz})(\text{CO})(\text{PCBr})_2]$ (5) is prepared in high yield by reacting $\text{Rh}(\text{acac})(\text{CO})(\text{PCBr})$ and $\text{Na}(3,5\text{-dmpz})$.

All these complexes, 1-5, have been characterized by elemental microanalysis and infrared and ^1H , ^{31}P , and, in

Table IV. Selected Conformational Parameters (deg)

(A) Torsion Angles				
Rh1-P1-C21-C26	-4.0 (9)	Rh2-P2-C51-C52	11.7 (5)	
P1-C21-C26-Rh2	10.1 (6)	P2-C51-C52-Br2	-4.2 (7)	
C21-C26-Rh2-Rh1	-8.9 (4)	C51-C52-Br2-Rh2	-4.3 (5)	
C26-Rh2-Rh1-P1	4.2 (1)	C52-Br2-Rh2-P2	8.2 (2)	
Rh2-Rh1-P1-C21	-0.9 (2)	Br2-Rh2-P2-C51	-10.3 (2)	
Rh1-P1-C21-C26	-4.9 (5)	Rh2-P2-C51-C52	11.7 (5)	
Rh1-P1-C31-C36	95.7 (6)	Rh2-P2-C61-C62	50.7 (6)	
Rh1-P1-C41-C46	-58.5 (6)	Rh2-P2-C71-C72	-106.3 (5)	
Br1-Rh1-P1-C21	-171.3 (2)			
Br1-Rh1-P1-C31	-55.0 (2)	Br2-Rh2-P2-C61	-128.5 (2)	
Br1-Rh1-P1-C41	69.9 (2)	Br2-Rh2-P2-C71	102.4 (2)	
Br1-Rh1-Rh2-Br2	-20.4 (2)	C1-Rh1-Rh2-N12	-175.1 (2)	
C1-Rh1-Rh2-P2	4.1 (2)	C1-Rh1-Rh2-C26	-89.0 (2)	
N1-Rh1-Rh2-N2	3.2 (2)	P1-Rh1-Rh2-P2	97.3 (1)	
N11-Rh1-Rh2-N12	6.1 (2)	Br1-Rh1-Rh2-P2	-150.6 (1)	
C1-Rh1-Rh2-Br2	134.3 (2)	N11-Rh1-Rh2-P2	-174.7 (1)	
C1-Rh1-Rh2-N2	93.5 (2)	N1-Rh1-Rh2-P2	-86.2 (1)	
(B) Dihedral Angles between Least-Squares Planes through Some Relevant Atomic Sets				
set	planarity	atoms		
i	no	Rh2, P2, C51, C52, Br2		
ii	yes	N1, N2, C3, C4, C5		
iii	yes	N11, N12, C13, C14, C15		
iv	no	C1, Rh1, N11, N12, Rh2, P2		
v	no	P1, Rh1, N1, N2, Rh2, C26		
vi	no	P2, C26, N12, N2, Rh2		
vii	no	C1, P1, N11, N1, Rh1		
sets: i-iv	ii-iv	iii-iv	iv-v	iv-vi
angle: 1.90 (1)	7.7 (2)	10.7 (2)	88.2 (1)	79.7 (1)
sets: iv-vii	v-vi	v-vii	vi-vii	
angle: 80.4 (1)	70.4 (1)	76.5 (1)	38.4 (1)	

Chart I. Possible Isomers for $[\text{Rh}(\text{Pz})(\text{CO})(\text{PCBr})_2]^a$ 

^a Each one of them has its corresponding enantiomer.

some cases, ^{13}C NMR spectroscopy. Compounds 1-5 exhibit one $\nu(\text{CO})$ stretching band in the 1980-1985 cm^{-1} region, typical of monocarbonylrhodium(I) complexes.¹⁷ Compound 4 shows two additional bands above 2000 cm^{-1} , corresponding to the dicarbonylrhodium(I) moiety. There is a number of possible isomers for a compound of general stoichiometry $[\text{Rh}(\text{Pz})(\text{CO})(\text{PCBr})_2]$, as shown in Chart I.

The ^1H and ^{31}P NMR for complexes 1-3 and 5 show the presence of only one isomer in solution. By analogy with the closely related $[\text{Rh}(\text{pz})(\text{CO})(\text{P}(\text{OPh})_3)_2]^{11c}$ in which the phosphite ligands are trans to each other, we believe that this isomer should have the same arrangement of phosphine ligands. Since isomers I and II have cis geometry

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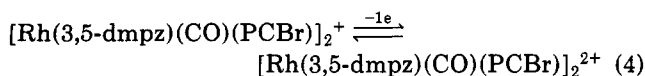
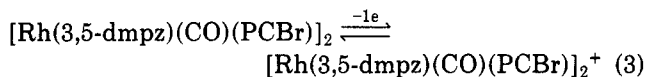
and III through VI are equivalent in the case of symmetric pyrazolyl ligands, compounds 1–3 and 5 should have the structure shown in Figure 1a.

Isomers III–VI have to be considered for compound 2 containing the asymmetric pyrazolyl ligand 3-mpz. The ^1H NMR spectrum of this compound shows only one methyl resonance at δ 2.40. In view of that, isomers III and IV must be rejected since they have two inequivalent methyl groups. Of the two possible isomers left, V and VI, VI was chosen; the value of the methyl chemical shift in $[\text{Rh}(3\text{-mpz})(\text{CO})(\text{PCBr})]_2$, δ 2.40, compares better to those of the methyl groups trans to CO in $\text{Rh}_2(3,5\text{-dmpz})_2(\text{CO})_3(\text{PCBr})$, δ 2.24–2.35, than to that of the methyl group trans to PCBr, δ 1.45.

The thermal reaction of $[\text{Rh}(\text{pz})(\text{CO})(\text{PCBr})]_2$ in refluxing xylene (20 min) gives a very complicated mixture of compounds. The ^{31}P NMR spectrum of the crude reaction product shows two blocks of signals in the range of chemical shifts +30 through +60 ppm and –20 through –45 ppm. From this reaction mixture compound $\text{Rh}_2(\text{Pz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})$ (6) is isolated in low yield. It shows a $\nu(\text{CO})$ stretching band at 2060 cm^{-1} and two doublets in the ^{31}P NMR spectrum at δ +55.4 ($^1J(\text{Rh-P}) = 139\text{ Hz}$) and δ +31.2 ($^1J(\text{Rh-P}) = 106\text{ Hz}$). A similar behavior is observed for the compound $[\text{Rh}(4\text{-mpz})(\text{CO})(\text{PCBr})]_2$. The corresponding metalated compound is identified in solution by spectroscopic means as a minor product of the reaction mixture. This compound has not been isolated in analytically pure state.

The thermal reaction of compound $[\text{Rh}(3\text{-mpz})(\text{CO})(\text{PCBr})]_2$ (2) in refluxing xylene also allows the isolation of the ortho-metalated species $\text{Rh}_2(3\text{-mpz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})$ (7) in a moderate yield. Compound $\text{Rh}_2(3,5\text{-dmpz})_2(\text{CO})_3(\text{PCBr})$ (4) under the same reaction conditions yields $\text{Rh}_2(3,5\text{-dmpz})(\mu\text{-PC})\text{Br}(\text{CO})_3$ (9) as the only isolable product. The reaction of 9 with PCBr allows the isolation of $\text{Rh}_2(3,5\text{-mpz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})$ (8), which can be also prepared by reacting $[\text{Rh}(3,5\text{-dmpz})(\text{CO})_2]_2$ and PCBr in a refluxing xylene (1:2 molar ratio). This last method became a general procedure for the synthesis of compounds 6–8.

We have also explored the electrochemical properties of compounds 4, 5, 8, and 9. The only compound showing a clearly defined behavior was $[\text{Rh}(3,5\text{-dmpz})(\text{CO})(\text{PCBr})]_2$ (5). The cyclic voltammogram (Figure 2) of 5 in THF exhibits two reversible oxidation waves at 0.42 and 0.76 V. This behavior parallels that observed for $[\text{Ir}(\text{pz})(\text{COD})]_2^{18}$ and can be interpreted in a similar way. Thus, these waves may correspond to two successive 1e oxidations to the Rh(I)–Rh(II) and Rh(II)–Rh(II) cationic compounds (eq 3 and 4).



The different chemical behavior observed for the 3,5-dmpz derivatives that we assume to be due to steric effects prompted us to solve the molecular structure of 8, hoping to obtain some additional information about this point.

Crystal Structure of Compound. $\text{Rh}_2(3,5\text{-dmpz})_2[\mu\text{-P}(\text{o-C}_6\text{F}_4)\text{Ph}_2]\text{Br}(\text{CO})(\eta^2\text{-PCBr})(\text{H}_2\text{O})$ (8). The complex presents a dinuclear molecule quite analogous to

the unmethylated analogue already reported 6^{10} (Figure 1b). The overall molecular geometry in both complexes presents the ligands distributed with a pseudo binary symmetry around a line passing through the Rh–Rh axis and roughly bisecting the two 3,5-dmpz rings (see Figure 3). Two main atomic sets (those numbered as IV and V in Table IVb) define the above-mentioned distribution. These sets are not planar, within the achieved precision, and make an overall angle of $88.2(1)^\circ$ ($88.7(1)^\circ$ in complex 6). Atomic deviations from their best least-squares planes range in $\pm 0.115(5)$ and $\pm 0.091(5)$ Å for sets IV and V, respectively.

Each Rh atom is octahedrally coordinated. The relative position of their ligands is such that pairs of atoms P1 and C26, N12 and N11, N1 and N2, and C1 and P2 are almost eclipsing each other, as viewed along the Rh–Rh axis (see Table III). The Br1 and Br2 stay just $-20.4(2)^\circ$ apart from the eclipsing conformation (see torsion angles in Table IV). The coordination of the metal atoms to the bridging 3,5-dmpz rings (which present the usual geometrical features) and that of the Rh2 to a phenyl carbon atom of the $\text{P}(\text{o-C}_6\text{F}_4)\text{Ph}_2$ group seem to compel that pair grouping.

The Rh–Rh separation is indicative of the presence of an intermetallic bond. $^{5,19-22}$ The Rh–N–N angles present lower values than those in other pyrazolyl dirhodium complexes, with longer Rh–Rh separation. Moreover the coordination makes the angles Rh–P–C(phenyl) to be lower at C21 and C51, and it distinguishes the two Rh–Br bonds, shorter at Br2 (as this one is bonded to the fluorinated phenyl ring 23,36). The angles Rh–Rh–Br are also different, and the five-membered rings (defined by Rh1, P1, C21, C26, and Rh2 and Rh2, P2, C51, C52, and Br2) are not planar.

The differences between 6 and 8 are almost within the achieved precision, the main different points being that in 6 the two Rh–Br are more aligned and the distances more alike. Both pyrazolyl rings are also geometrically more similar in 6 than in 8. The two five-membered rings mentioned above interchange conformation in 8 with respect to those present in 6.

Ortho-Metalation Reactions. The thermal reaction of compounds of the type $[\text{Rh}(\text{Pz})(\text{CO})(\text{PCBr})]_2$ leads to the corresponding ortho-metalated complexes $\text{Rh}_2(\text{Pz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})$ (Pz = pz (6) and 3-mpz (7)). Compound $[\text{Rh}(3,5\text{-dmpz})(\text{CO})(\text{PCBr})]_2$ does not react in the same way. This is perhaps due to steric effects between the four methyl groups on the pyrazolyl ligands and the phosphines. However, the thermal reaction of $\text{Rh}_2(3,5\text{-dmpz})_2(\text{CO})_3(\text{PCBr})$ and PCBr (1:1 molar ratio) allows the isolation of the metalated complex $\text{Rh}_2(3,5\text{-dmpz})_2(\mu\text{-PC})\text{Br}(\text{CO})(\eta^2\text{-PCBr})$ (8), which is analogous to 6 and 7.

The ortho-metalation reaction in this series of compounds occurs via an apparent formal 2c–2e oxidative addition of the phosphine by labilization of the C–Br bond. The occurrence of 2c–2e oxidative addition to d^8 bimetallic centers has been reported for a number of Rh(I) and Ir(I) dimers $^{24-34}$ containing a variety of bridging ligands, with

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several oxidizing agents. In all these cases, the reaction is concomitant with the formation of a single metal-metal bond.

Although there are in the literature some examples of bridging ortho-metalated phosphines, they are generated via reductive processes²⁻⁴ or by proton-transfer reactions.⁵⁻⁸ As far as we know, the complexes 6-9 are the first examples of formal 2c-2e oxidative additions in which the substrate is a previously coordinated P donor ligand that finally acts as a bridging ortho-metalated ligand. It is possible that this reaction might take place through an Rh(I)-Rh(III) intermediate resulting from 1c-2e oxidative addition with concomitant Rh-C and Rh-Br bond formation on the same metal center. Further bromide migration from one rhodium center to another would result in the isolated Rh(II)-Rh(II) compound. However, we do not have any experimental evidence to support this mixed-valence intermediate.

We have found that ³¹P NMR spectroscopy is a powerful tool in discerning the coordination mode of the phosphine PCBr. According to our previously related ³¹P NMR results,^{8,23,35-37} we have assigned the lower field signal (ca. +55 ppm) in compounds 6-8 to the η²-PCBr phosphine and the higher field signal (ca. +30 ppm) to the μ-PC bridging phosphine.

The yields of the preparation of compounds 6-8 increase with the substitution at the 3- and 5-carbons of the pyrazolyl ligands. The influence of this substitution can be observed in the 3-mpz derivative, but it is especially important in the 3,5-dmpz compound. We believe this is mainly due to steric effects generated by the methyl groups, making the intranuclear ortho-metalation more difficult. This fact can be seen in the ³¹P NMR spectrum of the solution resulting from the thermal reaction of compounds 1 and 2 of stoichiometry [Rh(Pz)(CO)(PCBr)]₂. In the case of 1 (Pz = pz) the spectrum shows small resonances due to 6 (δ +55.8, +31.9), but the strongest signals are observed in the high-field region, as a complicated set between -20 and -40 ppm. These data clearly indicate that the major products of this reaction are the result of an intranuclear ortho-metalation reaction (1c-2e oxidative addition reaction). The compounds so formed containing four-membered metalated phosphines show the characteristic high-field resonances in the ³¹P NMR spectrum.⁹

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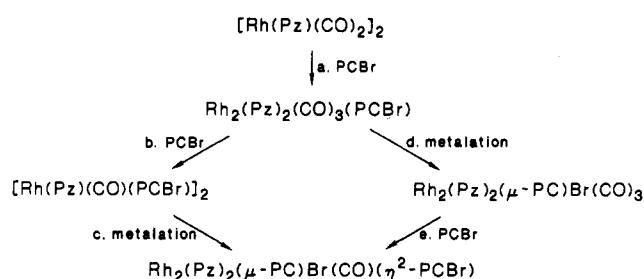
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Scheme I



In the case of 2 (Pz = 3-mpz) the spectrum exhibits, in addition to the resonances assigned to Rh₂(3-mpz)₂(μ-PC)Br(η²-PCBr) (7) (δ +54.3, +28.2), two well-defined doublets in the high-field region (δ -37.1 (¹J(Rh-P) = 82 Hz), -46.2 (¹J(Rh-P) = 67 Hz)). Both the chemical shift values and the small ¹J(Rh-P) indicate that a four-membered metalated Rh(III) compound is obtained in addition to compound 7. Even though this additional compound has not been fully characterized, we can conclude that in the reaction of [Rh(3-mpz)(CO)(PCBr)]₂ both inter- and intranuclear ortho-metalation occur to practically the same extent. In the thermal reaction of [Rh(3,5-dmpz)(CO)]₂ and PCBr (1:2 molar ratio) the ³¹P NMR spectrum of the crude reaction mixture shows no high-field signals and mainly resonances corresponding to compound 8 (δ +57.2, +26.3), indicating that the reaction goes selectively via the intranuclear ortho-metalation (2c-2e oxidative addition).

These spectroscopic data reveal that two reactions compete in these systems: internuclear 2c-2e oxidative addition and intranuclear 1c-2e oxidative addition. The intranuclear ortho-metalation reaction becomes progressively more difficult by increasing the methyl substitution in the 3- and 5-positions of the pyrazolyl ring, so making the 2c-2e oxidative addition more selective.

Similar steric effects must be responsible for the observed difficulty of preparing [Rh(3,5-dmpz)(CO)(PCBr)]₂ (5) by the carbonyl substitution in Rh₂(3,5-dmpz)₂(CO)₃(PCBr) (4). If the thermal reaction is used, the ortho metalation of the phosphine is promoted in 4 prior to the CO substitution. Moreover, compound 5 does not undergo ortho-metalation under the same experimental conditions as do 1-3. However, such reaction is possible for a less sterically hindered compound as 4.

The reactivity pattern for these systems is shown in Scheme I. For compounds 1-3 the reaction goes via (a), (b), and (c), whereas in the case of the 3,5-dmpz derivative it proceeds via (a), (d), and (e).

The crystallographic data available in the literature for other pyrazolyl rhodium and iridium dimers in oxidation states (I, I) and (II, II) show that a decrease of the M-N-N angles^{24,38} is concomitant with the metal-metal bond formation. The steric effects between the terminal ligands and the substituents in the bridging pyrazolyl groups must be less important in the M(II)-M(II) species due to these structural changes. Thus, we observe that 9 reacts with PCBr to give 8, but the reaction of 4 with PCBr to yield 5 does not occur. The greater steric hindrance in 4 compared to 9 must be responsible of this behavior.

It is noteworthy that the ortho-metalated complexes 6-9 are obtained via an intermediate species that has been detected by ³¹P NMR. Even compound 5, which does not yield any metalated species, shows after prolonged reflux

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in xylene new signals in the ^{31}P NMR spectrum in the same range of chemical shifts (ca. $\delta +38$) that compounds 1-3 do. All the efforts to isolate these intermediate species in analytically pure states have been unsuccessful to date. The ^{31}P NMR data do not give any conclusive structural information about them. Moreover, the presence of the four fluorine atoms in the phosphine also complicates the aromatic region in the ^{13}C NMR spectra.

Further investigation on these intermediates is required. It might be more informative to use the homologous compounds with $\text{P}(o\text{-BrC}_6\text{H}_4)_2$, assuming that they will show similar behavior as the PCBr complexes.

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Registry No. 1, 96411-10-8; 2, 112173-10-1; 3, 112173-11-2; 4, 112173-12-3; 5, 112195-84-3; 6, 96411-08-4; 7, 112173-13-4; 8, 112173-14-5; 9, 112173-15-6; PZ , 288-13-1; 3-MPZ, 1453-58-3; 4-MPZ, 7554-65-6; PCBr , 27384-33-4; $\text{Rh}(\text{acac})(\text{CO})(\text{PCBr})$, 112173-16-7; $[\text{Rh}(3,5\text{-dmpz})(\text{CO})_2]_2$, 33701-63-2; $[\text{Rh}(\text{PZ})(\text{CO})_2]_2$, 77244-11-2; $[\text{Rh}(3\text{-MPZ})(\text{CO})_2]_2$, 99324-32-0; $\text{Na}(3,5\text{-dmpz})$, 41253-18-3; Rh , 7440-16-6.

Supplementary Material Available: Tables of hydrogen coordinates and thermal parameters (3 pages); a listing of observed and calculated structure factors (47 pages). Ordering information is given on any current masthead page.

Novel Chelating (N,O) Bis(carbene) Complexes of Chromium and Tungsten: Synthesis and Structure

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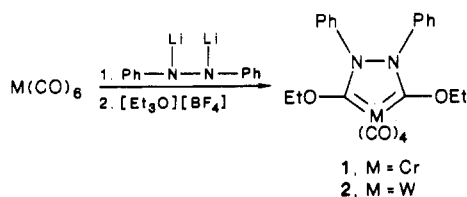
Addition of N,N' -dithiohydrazobenzene to hexacarbonylchromium and -tungsten followed by alkylation affords tetracarbonyl complexes containing chelating bis(carbene) ligands that are characterized by spectroscopic means. A symmetrical planar metallocycle with slightly staggered phenyl substituents (dihedral angle = 49.4°) and a distorted octahedral coordination at the metal center is established by X-ray analysis for the chromium compound.

Introduction

The sequential addition of a nucleophile and an electrophile across the C-O bond of metal carbonyls represents the most versatile synthetic route to transition metal carbene complexes.¹ Recently, this methodology has been successfully extended to the addition of *vic* dianionic systems to homoleptic metal carbonyls.^{2,3} This route provides a new entry to compounds containing chelating bis(carbene) ligands, a class of compounds of which only very few examples have been reported and characterized by reactivity and X-ray studies.²⁻¹³ Interestingly, the compound regarded as the first isolated carbene complex¹⁴ was of this type, but it was recognized as such only 55 years later.¹⁵ In an effort to probe the general applicability of a chelating addition of nucleophiles to metal carbonyl systems, we have studied the reactivity of dimetalated hydrazines toward hexacarbonyl chromium and tungsten.

Results and Discussion

$\text{Cr}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ reacts with N,N' -dithiohydrazobenzene to give the chelating bis(acylmetalate) complexes that can be alkylated by $[\text{Et}_3\text{O}][\text{BF}_4]$ to give the alkoxyaminobis(carbene) chelates 1 and 2. The new complexes



are diamagnetic and air-sensitive. According to the N,O-heterosubstitution of the metal-coordinated carbene car-

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