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Further Studies on the Ortho-Metalation Reaction of Dirhodium Tetraacetate: Syntheses and Structures of $Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2(H_2O)$ and $Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2$

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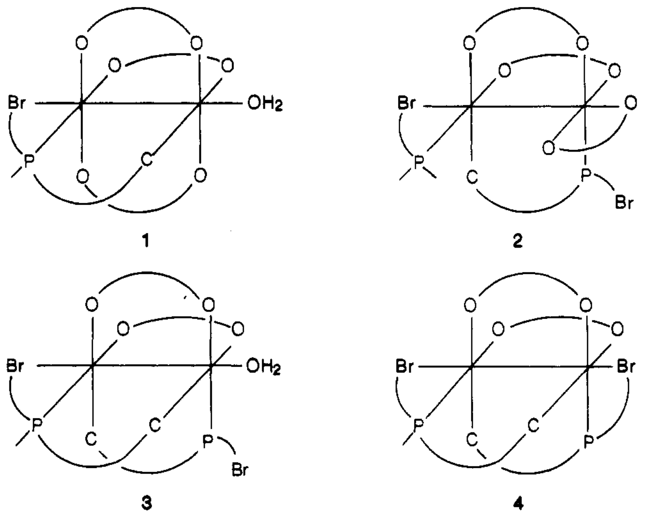
Reaction of $Rh_2(O_2CCH_3)_4{\cdot}2P(C_6F_4Br)(C_6H_5)_2$ in refluxing toluene–acetic acid mixtures or in refluxing acetic acid leads to four major products. $Rh_2(O_2CCH_3)_3[P(C_6H_4)(C_6H_5)(C_6F_4Br)]{\cdot}2H_2O$ (1) was characterized by spectroscopic and chemical analysis. $Rh_2(O_2CCH_3)_3[P(C_6H_4)(C_6H_5)(C_6F_4Br)]{\cdot}P(C_6H_5)_2(C_6F_4Br)$ (2) had been identified before as the sole product of the ortho-metalation reaction in pure toluene. $Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2{\cdot}H_2O$ (**3**) consists of a metal–metal-bonded dirhodium unit that is bridged by two cisoid acetate groups and two phosphines, each ortho-metalated at one of the unsubstituted phenyl rings. One axial coordination site is occupied by the bromine atom of the C_6F_4Br ring of one of the phosphines while a molecule of water occupies the second axial coordination site. The latter is easily displaced by exogenous donor molecules such as acetic acid, pyridine, or Me_2SO. $Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2$ (4) was characterized by spectroscopic and chemical analyses and by a single-crystal structure determination. It is a doubly ortho-metalated dirhodium complex without exogenous axial ligands; viz., both phosphines assume the η^3,μ-mode of ligation. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with cell parameters: $a = 13.488$ (4) Å, $b = 12.548$ (3) Å, $c = 14.385$ (4) Å, $\alpha = 98.83$ (2)°, $\beta = 108.63$ (2)°, $\gamma = 71.97$ (2)°, $V = 2190$ (2) Å^3, $Z = 2$. Compounds **4** crystallizes in the monoclinic space group $C2/c$ with cell parameters: $a = 25.591$ (9) Å, $b = 9.804$ (4) Å, $c = 22.335$ (8) Å, $\beta = 124.39$ (2)°, $Z = 4$, $V = 4625$ (6) Å^3.

Introduction

Ortho-metalation reactions involving two metal centers have been observed when the dirhodium(II) and diosmium(III) tetracarboxylates react with triphenylphosphine in refluxing acetic acid solvent.[1] In each case, however, only one product, $M_2(O_2CR)_2(P(o\text{-}C_6H_4)(C_6H_5)_2$, was isolated, even though its formation must certainly involve a sequence of reaction steps. No doubt the reaction medium, i.e., the pure acid RCO_2H, is also critical to the success of these ortho-metalation reactions. Kinetic studies of the conventional type are scarcely feasible under the reaction conditions, and the isolation of intermediates is likely to be the only fruitful avenue to understanding the mechanisms of these reactions.

We have recently discovered that by employing a modified arylphosphine such intermediates are stabilized and can be isolated.[2] For example, the reaction of $Rh_2(O_2CCH_3)_4{\cdot}2PCBr$ (PCBr = $P(C_6H_5)_2(C_6F_4Br)$) in toluene affords a product in which only one of the phosphines has undergone ortho-metalation while the second one functions as a chelating bidentate ligand (P, Br) at one of the rhodium centers (Chart I). One of its phenyl rings is thereby oriented toward the second rhodium atom in a fashion favorable for ortho metalation which suggests that 2 might be a precursor of the doubly metalated product. However, there is no evidence that this second metalation occurs in toluene solvent, even at prolonged reaction times. We reasoned that the axial interaction of the chelating PCBr was instrumental to the stability of 2 and that this axial coordination prevented the metalation of the second phosphine. The double metalation of PPh_3 in acetic acid[1] therefore appeared to be facilitated by the absence of such an interaction as well as by potential axial ligation by solvent molecules. Consequently we repeated the reaction of the PCBr adduct of $Rh_2(O_2CCH_3)_4$ in the presence of acetic acid and found that four products can be isolated, two of which are double metalated.

Chart I. Bonding Modes of PCBr in Ortho-Metalated Dirhodium(II) Dimers



Experimental Section

Synthesis of Compounds 1–4. $Rh_2(O_2CCH_3)_4{\cdot}2PCBr$ (500 mg, 0.394 mmol) was boiled under reflux in 15 mL of acetic acid in an atmosphere of argon for 1 h during which the color of the solution changed from red to green. The solvent was removed

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(1) (a) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *J. Chem. Soc., Chem. Commun.* **1984**, 501; Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A.; Tocher, J. H. *Organometallics* **1985**, *4*, 8. (b) Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4697.

(2) Barcelo, F.; Cotton, F. A.; Lahuerta, P.; Llusar, R.; Sanau, M.; Schwotzer, W.; Ubeda, M. A. *Organometallics* **1986**, *5*, 808.

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under reduced pressure and the residual oil dissolved in 5 mL of CH_2Cl_2. Hexane (5 mL) was added and the solution chromatographed on a column (1.5 × 30 cm; silica/hexane). Elution with acetone–hexane (1:7) allowed the separation of a green band containing compound **4** from a blue and a green band (compounds **3** and **2**) which were collected together. Increasing polarity (acetone–hexane, 1:2) finally eluted a purple band containing compound **1**. The fraction containing the mixture of **2** and **3** was evaporated to dryness and redissolved in $CHCl_3$. The two compounds were separated by chromatography on alumina and elution with 1:2 acetone–hexane mixture (compound **2**) followed by methanol (compound **3**).

Compound **1**·H_2O: pale violet; 45 mg, 14%. Anal. Calcd for $C_{24}H_{20}PO_7F_4BrRh_2$: C, 35.4; H, 2.5. Found: C, 35.1; H, 2.4. Compound **2**: green; 150 mg, 31%. Anal. Calcd for $C_{42}H_{28}O_6F_8P_2Br_2Rh_2$: C, 41.7; H, 2.3. Found: C, 42.0; H, 2.1. Compound **3**: green; 65 mg, 14%. Anal. Calcd for $C_{40}H_{26}O_5F_8P_2Br_2Rh_2$: C, 41.1; H, 2.2. Found: C, 41.5; H, 2.4. Compound **4**: green; 35 mg, 8%. Anal. Calcd for $C_{40}H_{24}O_4F_8P_2Br_2Rh_2$: C, 42.2; H, 2.3. Found: C, 42.3; H, 2.3.

Substitution Reactions. Solutions of **3** in CH_2Cl_2 react with excess of donor ligands such as CH_3COOH, pyridine, and Me_2SO with concomitant color change from blue to green (CH_3COOH) or purple (Me_2SO, pyridine). The substitution was monitored by ^{31}P NMR (Table VII).

Spectroscopy. ^1H and ^{31}P NMR spectra were recorded on a Bruker 200AC FT spectrometer. Chemical shifts are referred to internal Me_4Si (^1H) or external 85% H_3PO_4 in H_2O (^{31}P). A list of chemical shifts and coupling constants is given in Tables VII–IX. Because of unresolved long-range coupling with the F substituents on the aromatic ring only the splitting due to the direct Rh–P scalar coupling was extracted from the ^{31}P spectra.

Further Observations on 1. Compound **1** can be obtained in low yield from the thermal reaction of $Rh_2(O_2CCH_3)_4 \cdot 2PCBr$ in toluene or acetic acid. After chromatographic separation **1** is isolated as a water adduct $Rh_2(O_2CCH_3)_3(\mu\text{-}\eta^3\text{-PCBr})H_2O$ [**1**·H_2O]. The water molecule can be easily displaced by PCBr, HO_2CCH_3, or py, yielding the corresponding adducts [**1**·PCBr], [**1**·CH_3CO_2H], and [**1**·py]:

$$Rh(O_2CCH_3)_3(\mu\text{-}\eta^3\text{-PCBr})H_2O + L = RH_2(O_2CCH_3)_3(\mu\text{-}\eta^3\text{-PCBr})L + H_2O$$

The ^{31}P NMR data for these adducts, which were not isolated, are given in Tables VII and IX. The ^{31}P NMR spectrum indicates that in the reaction mixture compound **1** exists as PCBr adduct and during the workup exchange of PCBr by water occurs. The exchange of ligands is reversible. The four adducts are also characterized by their visible spectra, which consist in each case of a single band. The band positions, λ_{max} (in nm) and ϵ (in M^{-1} cm^{-1}), for each one are as follows. [**1**·H_2O], 552 (2650); [**1**·PCBr], 448 (1190); [**1**·CH_3CO_2H], 542 (3760); [**1**·py], 490 (7060).

X-ray Crystallography. The structure of $Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2 \cdot H_2O$ (**3**) was determined by applying the general procedures described elsewhere.[3] A crystal of approximate dimensions 0.3 × 0.3 × 0.2 mm was mounted on the tip of a glass fiber. The unit-cell dimensions were determined on an Enraf-Nonius CAD-4 four-circle automated diffractometer, on which the intensity data were also collected. Trial positions for the metal atoms and the bromine atoms were obtained by direct methods (MULTAN),[4] and the remainder of the structure was developed by consecutive cycles of least-squares refinement and difference Fourier maps. The final cycle included the fit of 558 parameters to 5178 unique data with $F_o^2 \geq 3\sigma(F_o^2)$. The refinement converged to the residuals, $R = 0.053$ and $R_w = 0.074$. Two atoms of solvent molecules, C(41) and O(6), yielded somewhat high thermal parameters ($B_{eq} = 12.1$ and 13.8, respectively) and were refined with isotropic thermal parameters.

Table I. Crystal Data for $\{Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2(H_2O)\} \bullet H_2O \bullet CH_2Cl_2$ (3) and $\{Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2\} \bullet 2CH_2Cl_2$ (4)

	3	**4**
formula	$Rh_2Br_2Cl_2P_2F_8O_6C_{41}H_{30}$	$Rh_2Br_2Cl_4P_2F_8O_4C_{42}$
fw	1269.2	1314.0
space group	$P\bar{1}$	$C2/c$
a, Å	13.488 (4)	25.591 (9)
b, Å	12.548 (3)	9.804 (4)
c, Å	14.385 (4)	22.335 (8)
α, deg	98.83 (2)	
β, deg	108.63 (2)	124.3 (2)
γ, deg	71.97 (2)	
V, Å^3	2190 (2)	4625 (6)
Z	2	4
d_{calcd}, g/cm^3	1.93	1.89
cryst size, mm	0.3 × 0.3 × 0.2	0.4 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	28.2	27.9
data collectn instrument	Enraf-Nonius CAD-4	
radiatn (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
orientatn reflctns, no., range (2θ)	25, 15–35	25, 20–32
temp, °C	22	22
scan method	ω–2θ	ω–2θ
data collectn range, 2θ, deg	4–50	4–50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6721, 5178	2500, 1842
no. of parameters refined	558	289
R^a	0.053	0.053
$R_w{}^b$	0.074	0.063
quality-of-fit indicator^c	1.9	1.5
largest shift/esd, final cycle	0.1	0.4
largest peak, e/Å^3	0.9	0.7

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

The structure of **4** was determined analogously. The systematic absences limited the choice of space groups to $C2/c$ or Cc. A model for the positions of the heavy atoms in $C2/c$ was found by direct methods. The remainder of the structure was developed and refined without difficulties. A cluster of electron density peaks in the difference Fourier map was unrelated to the main molecule and was interpreted as a CH_2Cl_2 molecule of crystallization. It was refined with full occupancy. The refinement of its atomic positions converged with satisfactory geometry albeit with somewhat high thermal parameters. Data pertaining to data collection and refinement are listed in Table I. Tables II and III contain the lists of fractional coordinates for **3** and **4**, respectively.

Results and Discussion

Structural Results. A perspective drawing of compound **3** is shown in Figure 1, and important bond distances and angles are listed in Table IV. The overall structure is based on that of a quadruply bridged M_2L_8 dimer in which the metal atoms are linked by a M–M bond. Thus no fundamental structural rearrangement occurs during the ortho-metalation reaction, which, consequently, can be viewed formally as a ligand substitution of two cisoid acetate groups by two ortho-metalated phosphines with concomitant proton transfer. The Rh–Rh bond distance, 2.486 (1) Å, falls well within the range spanned by many dirhodium(II) compounds of comparable structure.[5a] One of the ortho-metalated phosphines is so

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[3] Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

[4] Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with the Enraf-Nonius VAX-SDP software package.

Table II. Positional Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CCH_3)_2[P(C_6H_5)(C_6H_5)(C_6F_4Br)]_2 \bullet H_2O$ (3)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Rh(1)	–0.06569 (5)	–0.19360 (5)	–0.33143 (4)	2.21 (1)
Rh(2)	0.11721 (5)	0.07707 (5)	0.18904 (4)	2.20 (1)
Br(1)	–0.09465 (8)	0.32800 (9)	0.43723 (7)	4.01 (2)
Br(2)	0.36884 (8)	–0.07017 (8)	0.07153 (8)	4.21 (2)
Cl(1)	0.3629 (6)	0.5890 (5)	0.2956 (5)	16.8 (2)
Cl(2)	0.4808 (6)	0.6418 (6)	0.1896 (5)	18.5 (2)
P(1)	–0.0370 (2)	0.3305 (2)	0.2353 (2)	2.35 (5)
P(2)	0.2739 (2)	0.1252 (2)	0.2353 (2)	2.25 (4)
F(1)	–0.3245 (4)	0.3256 (6)	0.3976 (4)	6.4 (2)
F(2)	–0.4808 (4)	0.3215 (6)	0.2276 (6)	7.5 (2)
F(3)	–0.4419 (5)	0.3263 (6)	0.0542 (5)	6.8 (2)
F(4)	–0.2486 (4)	0.3348 (6)	0.0520 (4)	5.3 (2)
F(5)	0.2397 (4)	0.3641 (4)	0.1661 (4)	4.4 (1)
F(6)	0.2881 (5)	0.4140 (5)	0.0191 (5)	6.4 (2)
F(7)	0.3640 (5)	0.2543 (6)	–0.1083 (4)	6.7 (2)
F(8)	0.3997 (4)	0.0337 (6)	–0.0817 (4)	5.6 (2)
O(1)	0.1565 (5)	0.0534 (5)	0.4162 (4)	3.3 (1)
O(2)	–0.0577 (4)	0.1037 (5)	0.2974 (4)	2.9 (1)
O(3)	0.1644 (5)	–0.0604 (5)	0.2821 (4)	3.6 (1)
O(4)	–0.0408 (4)	0.0490 (5)	0.1463 (4)	3.0 (1)
O(5)	0.1326 (5)	–0.0668 (5)	0.0706 (5)	4.1 (2)
O(6)	0.087 (1)	0.051 (1)	0.580 (1)	13.8 (5)*
C(1)	–0.1796 (6)	0.3344 (8)	0.2245 (7)	3.4 (2)
C(2)	–0.2015 (7)	0.3308 (7)	0.3140 (6)	3.0 (2)
C(3)	–0.3022 (7)	0.3277 (8)	0.3151 (7)	4.0 (2)
C(4)	–0.3832 (7)	0.3272 (9)	0.2265 (9)	5.2 (3)
C(5)	–0.3641 (7)	0.3302 (9)	0.1409 (7)	4.2 (3)
C(6)	–0.2615 (7)	0.3333 (8)	0.1405 (7)	3.8 (2)
C(7)	–0.0148 (6)	0.3058 (7)	0.1159 (5)	2.4 (2)
C(8)	0.0547 (6)	0.2005 (6)	0.0958 (6)	2.4 (2)
C(9)	0.0707 (6)	0.1823 (7)	0.0015 (6)	2.9 (2)
C(10)	0.0238 (7)	0.2658 (8)	–0.0660 (6)	3.6 (2)
C(11)	–0.0415 (8)	0.3684 (8)	–0.0435 (6)	3.8 (2)
C(12)	–0.0602 (7)	0.3913 (7)	0.0487 (4)	3.5 (2)
C(13)	–0.0404 (7)	0.4776 (7)	0.2687 (6)	2.8 (2)
C(14)	–0.1337 (8)	0.5591 (8)	0.2826 (7)	4.3 (3)
C(15)	–0.130 (1)	0.6723 (9)	0.3071 (8)	5.2 (3)
C(16)	–0.0363 (9)	0.7024 (8)	0.3199 (7)	4.6 (3)
C(17)	0.0542 (9)	0.6214 (8)	0.3050 (7)	4.4 (3)
C(18)	0.0540 (7)	0.5069 (7)	0.2793 (6)	3.3 (2)
C(19)	0.3049 (6)	0.1666 (7)	0.1321 (6)	2.5 (2)
C(20)	0.3444 (6)	0.0839 (7)	0.0629 (6)	2.9 (2)
C(21)	0.3687 (7)	0.1135 (9)	–0.0148 (7)	3.8 (2)
C(22)	0.3449 (7)	0.2254 (9)	–0.0311 (7)	4.1 (2)
C(23)	0.3062 (7)	0.3064 (8)	0.0331 (7)	4.3 (2)
C(24)	0.2840 (6)	0.2784 (7)	0.1122 (7)	3.3 (2)
C(25)	0.2706 (6)	0.2420 (6)	0.3287 (6)	2.8 (2)
C(26)	0.1858 (6)	0.2651 (6)	0.3733 (5)	2.3 (2)
C(27)	0.1915 (7)	0.3438 (7)	0.4566 (7)	3.5 (2)
C(28)	0.2769 (8)	0.3917 (8)	0.4925 (7)	3.7 (2)
C(29)	0.3590 (8)	0.3672 (8)	0.4444 (7)	3.9 (2)
C(30)	0.3569 (7)	0.2909 (7)	0.3643 (7)	3.6 (2)
C(31)	0.4075 (7)	0.0311 (7)	0.2966 (7)	3.1 (2)
C(32)	0.5033 (8)	0.0433 (9)	0.2890 (8)	5.0 (3)
C(33)	0.6048 (8)	–0.019 (1)	0.3429 (8)	5.1 (3)
C(34)	0.6102 (9)	–0.101 (1)	0.4003 (9)	6.1 (4)
C(35)	0.516 (1)	–0.116 (1)	0.404 (1)	8.7 (4)
C(36)	0.4139 (9)	–0.049 (1)	0.3517 (9)	6.3 (3)
C(37)	0.1737 (7)	–0.0436 (7)	0.3712 (6)	3.3 (2)
C(38)	0.211 (1)	–0.1442 (8)	0.4355 (8)	5.7 (3)
C(39)	–0.0851 (6)	0.0581 (7)	0.2178 (6)	3.0 (2)
C(40)	–0.1827 (7)	0.0088 (8)	0.1896 (8)	4.9 (3)
C(41)	0.343 (2)	0.673 (2)	0.205 (1)	12.1 (6)*

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table III. Positional Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CCH_3)_2[P(C_6H_4)(C_6H_5)(C_6F_4Br)]_2$ (4)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Rh(1)	0.51681 (4)	0.4351 (1)	0.31395 (4)	2.64 (2)
Br(1)	0.51513 (5)	0.4021 (1)	0.43577 (6)	3.79 (3)
Cl(1)	0.1776 (3)	0.822 (1)	0.5657 (4)	15.9 (3)
Cl(2)	0.2295 (6)	0.589 (1)	0.5456 (5)	25.5 (6)
P(1)	0.4437 (1)	0.5866 (3)	0.2894 (1)	2.71 (7)
F(1)	0.4233 (3)	0.2689 (9)	0.4573 (33)	5.5 (2)
F(2)	0.2968 (3)	0.274 (1)	0.3789 (4)	8.1 (3)
F(3)	0.2332 (3)	0.427 (1)	0.2555 (4)	8.8 (3)
F(4)	0.2944 (3)	0.567 (1)	0.2139 (4)	6.8 (3)
O(1)	0.4486 (3)	0.2700 (8)	0.2782 (4)	3.7 (2)
O(2)	0.5841 (3)	0.2803 (8)	0.3370 (4)	4.1 (2)
C(1)	0.3950 (4)	0.492 (1)	0.3151 (5)	3.2 (3)
C(2)	0.4273 (5)	0.415 (1)	0.3790 (5)	3.1 (3)
C(3)	0.3929 (5)	0.345 (2)	0.3967 (6)	4.6 (4)
C(4)	0.3279 (5)	0.346 (2)	0.3566 (6)	4.9 (4)
C(5)	0.2963 (5)	0.423 (2)	0.2961 (7)	5.5 (4)
C(6)	0.3300 (5)	0.491 (1)	0.2746 (6)	4.3 (4)
C(7)	0.3991 (4)	0.637 (1)	0.1959 (5)	2.9 (3)
C(8)	0.4151 (4)	0.579 (1)	0.1508 (5)	2.6 (3)
C(9)	0.3813 (5)	0.625 (1)	0.0781 (5)	3.7 (3)
C(10)	0.3369 (5)	0.727 (1)	0.0541 (6)	4.0 (4)
C(11)	0.3217 (5)	0.788 (1)	0.0982 (6)	4.5 (4)
C(12)	0.3548 (5)	0.743 (1)	0.1726 (6)	4.0 (4)
C(13)	0.4593 (5)	0.747 (1)	0.3385 (5)	3.4 (3)
C(14)	0.4993 (5)	0.839 (1)	0.3352 (7)	4.0 (4)
C(15)	0.5099 (6)	0.971 (1)	0.3682 (6)	4.7 (4)
C(16)	0.4806 (6)	1.007 (2)	0.4025 (7)	5.6 (4)
C(17)	0.4405 (7)	0.914 (2)	0.4038 (7)	6.6 (4)
C(18)	0.4287 (5)	0.780 (2)	0.3719 ((6)	4.5 (4)
C(19)	0.5852 (5)	0.233 (1)	0.2861 (6)	3.7 (3)
C(20)	0.6324 (6)	0.118 (2)	0.3038 (7)	6.4 (5)
C(21)	0.171 (1)	0.707 (3)	0.501 (1)	17 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

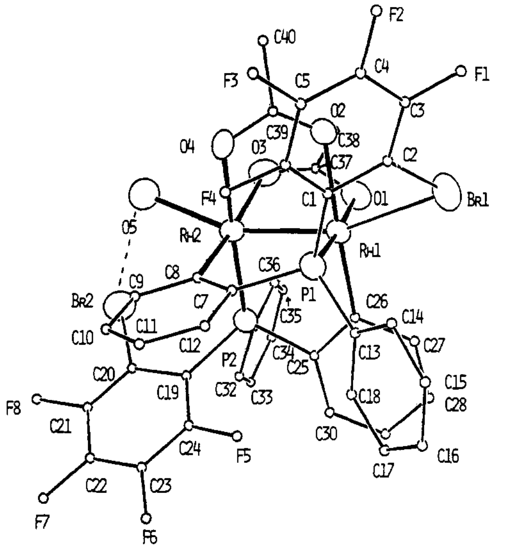

Figure 1. ORTEP drawing of compound 3. Carbon and fluorine atoms were drawn with arbitrary radii for clarity. Core atoms are drawn at 50% probability level.

oriented as to provide not only a three-atom bridge but also one axial ligand in the form of the ortho Br atom of the C_6F_4Br ring. This mode of axial ligation is unusual and will be discussed in conjunction with compound 4.

A drawing of compound 4 is shown in Figure 2. Important bond distances and angles are listed in Table V. The overall geometry once again is that of a M_2L_8 dimer with a M–M bond length of 2.475 (1) Å. The acetate ligands and the ortho-metalated phosphines are in a cisoid arrangement with crystallographically imposed C_2 symmetry.

Turning our attention to the axial coordination sites, we find that there are no exogenous ligands in 4 as both or-

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(5) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982; p 311. (b) *Ibid.*, p 373.

Table IV. Important Bond Distances (Å) and Angles (deg) for Compound 3[a]

(a) Bond Distances

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Rh(1)	Rh(2)	2.485 (1)	Rh(2)	O(4)	2.146 (6)	P(2)	C(19)	1.848 (10)
Rh(1)	Br(1)	2.983 (1)	Rh(2)	O(5)	2.292 (6)	P(2)	C(25)	1.830 (8)
Rh(1)	P(1)	2.194 (2)	Rh(2)	C(8)	2.004 (8)	P(2)	C(31)	1.846 (7)
Rh(1)	O(1)	2.110 (5)	Br(1)	C(2)	1.892 (7)	O(1)	C(37)	1.278 (10)
Rh(1)	O(2)	2.181 (6)	Br(2)	C(20)	1.874 (9)	O(2)	C(39)	1.198 (9)
Rh(1)	C(26)	1.976 (9)	P(1)	C(1)	1.866 (9)	O(3)	C(37)	1.238 (11)
Rh(2)	P(2)	2.246 (2)	P(1)	C(7)	1.800 (8)	O(4)	C(39)	1.320 (11)
Rh(2)	O(3)	2.159 (6)	P(1)	C(13)	1.825 (9)			

(b) Bond Angles

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Rh(2)	Rh(1)	Br(1)	153.36 (3)	Rh(1)	Rh(2)	O(3)	84.0 (2)	Rh(1)	P(1)	C(7)	112.0 (2)
Rh(2)	Rh(1)	P(1)	90.15 (6)	Rh(1)	Rh(2)	O(4)	86.5 (1)	Rh(1)	P(1)	C(13)	123.5 (2)
Rh(2)	Rh(1)	O(1)	87.3 (2)	Rh(1)	Rh(2)	O(5)	160.1 (2)	C(1)	P(1)	C(7)	110.4 (4)
Rh(2)	Rh(1)	O(2)	84.1 (2)	Rh(1)	Rh(2)	C(8)	96.3 (2)	C(1)	P(1)	C(13)	101.2 (4)
Rh(2)	Rh(1)	C(26)	97.2 (2)	P(2)	Rh(2)	O(3)	99.6 (2)	C(7)	P(1)	C(13)	104.1 (4)
Br(1)	Rh(1)	P(1)	75.96 (6)	P(2)	Rh(2)	O(4)	174.2 (2)	Rh(2)	P(2)	C(19)	113.1 (2)
Br(1)	Rh(1)	O(1)	104.7 (2)	P(2)	Rh(2)	O(5)	106.7 (2)	Rh(2)	P(2)	C(25)	110.8 (3)
Br(1)	Rh(1)	O(2)	74.8 (1)	P(2)	Rh(2)	C(8)	87.8 (3)	Rh(2)	P(2)	C(31)	123.8 (3)
Br(1)	Rh(1)	C(26)	105.4 (2)	O(3)	Rh(2)	O(4)	84.5 (2)	C(19)	P(2)	C(25)	108.0 (4)
P(1)	Rh(1)	O(1)	175.2 (2)	O(3)	Rh(2)	O(5)	82.1 (2)	C(19)	P(2)	C(31)	100.7 (4)
P(1)	Rh(1)	O(2)	95.0 (1)	O(3)	Rh(2)	C(8)	172.6 (3)	C(25)	P(2)	C(31)	98.7 (3)
P(1)	Rh(1)	C(26)	90.6 (2)	O(4)	Rh(2)	O(5)	77.9 (2)	Rh(1)	O(1)	C(37)	118.0 (5)
O(1)	Rh(1)	O(2)	80.7 (2)	O(4)	Rh(2)	C(8)	88.1 (3)	Rh(1)	O(2)	C(39)	120.8 (7)
O(1)	Rh(1)	C(26)	93.7 (3)	O(5)	Rh(2)	C(8)	95.6 (3)	Rh(2)	O(3)	C(37)	121.3 (5)
O(2)	Rh(1)	C(26)	174.2 (3)	Rh(1)	Br(1)	C(2)	86.2 (3)	Rh(2)	O(3)	C(37)	121.3 (5)
Rh(1)	Rh(2)	P(2)	89.71 (6)	Rh(1)	P(1)	C(1)	104.9 (3)	Rh(2)	O(4)	C(39)	116.0 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Important Bond Distances (Å) and Angles (deg) for Compound 4[a]

(a) Bond Distances

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Rh(1)	Rh(1)	2.475 (1)	Rh(1)	O(2)	2.129 (8)	P(1)	C(7)	1.794 (11)
Rh(1)	Br(1)	2.764 (2)	Rh(1)	C(8)	2.027 (10)	P(1)	C(13)	1.831 (12)
Rh(1)	P(1)	2.203 (3)	Br(1)	C(2)	1.859 (10)			
Rh(1)	O(1)	2.175 (8)	P(1)	C(1)	1.882 (14)			

(b) Bond Angles

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Rh(1)	Rh(1)	Br(1)	161.37 (5)	Br(1)	Rh(1)	C(8)	100.8 (3)	Rh(1)	P(1)	C(1)	102.1 (4)
Rh(1)	Rh(1)	P(1)	91.17 (9)	P(1)	Rh(1)	O(1)	91.0 (2)	Rh(1)	P(1)	C(7)	111.5 (5)
Rh(1)	Rh(1)	O(1)	83.8 (2)	P(1)	Rh(1)	O(2)	176.9 (3)	Rh(1)	P(1)	C(13)	124.3 (4)
Rh(1)	Rh(1)	O(2)	89.2 (2)	P(1)	Rh(1)	C(8)	92.8 (3)	C(1)	P(1)	C(7)	113.3 (5)
Rh(1)	Rh(1)	C(8)	96.4 (3)	O(1)	Rh(1)	O(2)	86.0 (3)	C(1)	P(1)	C(13)	101.5 (6)
Br(1)	Rh(1)	P(1)	80.8 (1)	O(1)	Rh(1)	C(8)	176.1 (4)	C(7)	P(1)	C(13)	104.0 (5)
Br(1)	Rh(1)	O(1)	79.6 (2)	O(2)	Rh(1)	C(8)	90.2 (4)				
Br(1)	Rh(1)	O(2)	98.0 (3)	Rh(1)	Br(1)	C(2)	90.3 (4)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

tho-metalated PCBr moieties assume the η^3,μ-mode of ligation. In compound 3 only one of the PCBr molecules exhibits η^3,μ-coordination while the second one is merely bridging (η^2,μ) so as to allow a molecule of water to occupy the second axial site. There is structural evidence for the presence of a hydrogen bond between the axial H_2O molecule and the ortho Br atom of the second PCBr ligand. The O···Br distance is 3.170 (7) Å, which is less than the sum of the van der Waals radii, and the Rh–O···Br bond angle is 95.2 (2)°, viz., close to tetrahedral.

The η^3,μ-coordination mode of the phosphine is an unprecedented one. We have observed in other complexes that the shape and dimensions of PCBr are favorable for a chelating bonding mode in an octahedral coordination geometry whereby this ligand provides several examples of halocarbon coordination to a transition element.[6-8] Clearly, the constraints imposed by the ortho-metalated μ-bonding mode do not exclude a simultaneous chelate formation via the Br and the P atoms. In both compounds 3 and 4, however, the Rh–Br distances are 0.36 and 0.14 Å, respectively, longer than that in compound 2. A plausible explanation for these differences may be found from a comparison of the geometrical data for the core dimensions of all known ortho-metalated dirhodium compounds (Table VI). It includes "normalized" axial interactions that were calculated by subtracting the covalent radii of the donor atom from the M–L distances. Corrections for angular overlap were omitted because the details of the axial bonding are not known. In a qualitative sense the data corroborate earlier theoretical work[5b] in that axial ligation and M–M bonding are competitive. For example, the Rh–Br distances correlate with the reciprocal of the second axial interaction; i.e., their substantial variation appears to stem from a trans influence of the second axial ligand, mediated by the M–M bond. Additionally, there

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(6) Cotton, F. A.; Lahuerta, P.; Sanau, M.; Schwotzer, W.; Solana, I. *Inorg. Chem.* **1986**, *25*, 3526.

Table VI. Core Geometries of Ortho-Metalated Dirhodium Compounds

compd[a]	2	3	4	5	6
axial ligands	η^2-PCBr η^2-O_2CCH_3	η^3-PCBr H_2O	η^3-PCBr	CH_3COOH	pyridine
Rh–Rh	2.519 (3)	2.486 (1)	2.475 (1)	2.508 (1)	2.556 (2)
Rh–L_{ax}	2.62 (2) [Br] 2.43 (2) [Ac]	2.981 (2) [Br] 2.289 (8) [H_2O]	2.764 (2) [Br]	2.342 (5) [HAc]	2.281 (9) [py]
normalized[b] Rh–L_{ax}	1.48 [Br] 1.70 [O]	1.84 [Br] 1.56 [O]	1.62 [Br]	1.61 [O]	1.53 [N]
Rh–Rh–L_{ax}	164.7 (1) [Br]	153.3 (4) [Br] 160.1 (3) [H_2O]	161.4 (1)	163.6 (1)	162.0 (2)

[a] **2**: $Rh_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-PCBr})(\eta^2\text{-PCBr})(\eta^2\text{-}O_2CCH_3)$. **5**: $Rh_2(\mu\text{-}O_2CC_3)_2(\mu\text{-}PPh_3)_2(HO_2CCH_3)_2$.[1a] **6**: $Rh_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}PPh_3)_2(\text{pyridine})_2$.[1a] [b] Normalized axial interaction was obtained by subtracting the covalent radius of the donor atom (Br, O, N) from Rh–L_{ax}.

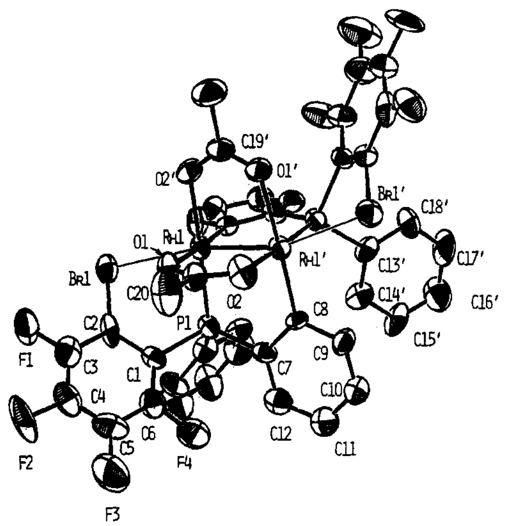

Figure 2. Perspective drawing of compound 4. Atoms are represented by thermal ellipsoids at 50% probability level.

is an inverse relation between the M–M bond lengths and the sum of the normalized axial distances.

Chemical Reactions. While the reaction of PPh_3 with $Rh_2(O_2CCH_3)_4$ affords only the doubly metalated product, a mixture of compounds is obtained with the functionalized arylphosphine PCBr. In nonprotic solvents such as toluene one main product, **2**, is isolated, accompanied by trace amounts of **1**. On the basis of spectroscopic data (see below) and chemical analysis, we propose that **1** contains only one ortho-metalated PCBr ligand (Chart I). In compound **2**, which was characterized by an X-ray structure analysis,[2] only one of the two PCBr ligands underwent ortho metalation.

We now find that addition of acetic acid to the reaction mixture or the use of acetic acid as a solvent promotes the second ortho-metalation step. In addition to the previously isolated compounds **1** and **2**, two new products are detected in the reaction mixture. Both title compounds, **3** and **4**, are doubly ortho-metalated dimers of Rh(II). In **3** one of the PCBr ligands exhibits a η^3,μ-coordination (Chart I), thereby occupying one axial ligand site. The second axial position was found to be occupied by a molecule of water. However, ^{31}P NMR spectroscopy of the reaction mixture shows that this site is initially occupied by a molecule of acetic acid which is displaced by water during the workup procedures, viz., chromatography. The water molecule can be quantitatively exchanged for a variety of other donor molecules such as pyridine or Me_2SO. The concomitant changes in the ^{31}P NMR spectrum are discussed below.

Compound **4** bears a close structural resemblance to **3** but does not contain any exogenous axial ligands. Instead both PCBr moieties assume the η^3,μ-mode of ligation. The interconversion between **3** and **4** is slow. Specifically, chromatography of either **3** or **4** under the workup conditions does not afford the other species. However, it was observed that with prolonged reaction times, there is an increase in the relative yield of **4** which makes it appear to be the thermodynamically favored product.

Table VII. NMR Data for Compounds 1–4

		^{31}P NMR	
compd	^1H NMR δ[a]	δ_P[b]	$^1J(\text{Rh–P})$[c]
1	1.36 (3 H) 1.43 (3 H) 2.41 (3 H) 6.9–7.5 (9 H)	+36.1	145
2	1.72 (6 H) 1.42 (3 H) 7.6–6.4 (19 H)	+56.4 +20.2	178 152
3	1.71 (2 H) 1.93 (6 H) 6.4–7.4 (18 H)	+38.6 +32.2	147 158
4	1.71 (6 H) 6.7–7.4 (18 H)	+34.9	172

[a] In ppm; in $CDCl_3$; $\delta > 0$ for resonances downfield from Me_4Si. [b] In ppm; in $CDCl_3$; $\delta > 0$ for resonances downfield from 85% H_3PO_4 in H_2O. [c] In Hz.

Table VIII. Additional NMR Data for $Rh_2(O_2CMe)_2(\mu\text{-}\eta^3\text{-PCBr})(\mu\text{-PCBr})L$ (3)

		^{31}P NMR	
L[d]	^1H NMR δ[a]	δ_P[b]	$^1J(\text{Rh–P})$[c]
$MeCO_2H$		+34.0 +16.3	168 180
py	1.43 (3 H) 2.19 (3 H) 6.3–8.2 (21 H) 8.76 (2 H)	+36.5 +13.8	172 170
Me_2SO		+35.2 +17.2 +30.7 +20.2	156 169 174 161

[a] In ppm; in $CDCl_3$; $\delta > 0$ for resonances downfield from Me_4Si. [b] In ppm; in $CDCl_3$; $\delta > 0$ for resonances downfield from 85% H_3PO_4 in H_2O. [c] In Hz. [d] For L = H_2O, see Table VII.

Spectroscopy. There is now a sufficient number of structurally characterized examples of PCBr complexes of rhodium available to allow the NMR spectroscopic parameters to assume diagnostic value. $^{31}P\{^1H\}$ spectroscopy is thereby especially convenient because the spectra can be recorded in undeuteriated solvents such as the reaction media. This permits monitoring the course of the reactions without prior workup. Because of long-range scalar coupling with the aromatic F substituents only, the ^1J coupling with ^{103}Rh is generally resolved with splittings in the range of 140–180 Hz.

Important spectroscopic data for compounds **1**–**4** are summarized in Table VII. Compound **2**, in agreement with the solid-state structure, shows two resonances at δ +56.4 (J_{Rh-P} = 178 Hz) and +20.3 (J_{Rh-P} = 152 Hz). By comparison with other η^2-PCBr complexes of rhodium,

Table IX. Additional NMR Data for $Rh_2(O_2CMe)_3(\mu\text{-}\eta^3\text{-PCBr})L$ (1)

		^{31}P NMR	
L^d	^1H NMR δ^a	$\delta_P{}^b$	$^1J(Rh\text{-}P)^c$
$MeCO_2H$	1.39 (3 H)	+36.1	146
	1.42 (3 H)		
	2.40 (3 H)		
py	1.37 (3 H)	+34.5	155
	1.67 (3 H)		
	2.23 (3 H)		
PCBr	1.19 (3 H)	+36.0	160
	1.32 (3 H)	+8.0	109
	1.91 (3 H)		

[a] In ppm; in $CDCl_3$; $\delta > 0$ for resonances downfield from Me_4Si. [b] In ppm; in $CDCl_3$; $\delta > 0$ for resonances downfield from 85% H_3PO_4 in H_2O. [c] In Hz. [d] For L = H_2O, see Table VII.

which span a range between +50 to +60 ppm,[7,8] we assign the signal at 56.4 ppm to the chelating PCBr ligand. The chemical shift of the ortho-metalated PCBr then agrees well with that of the doubly metalated PPh_3 derivative, viz., +19.4 ppm ($J_{Rh\text{-}P}$ = 165 Hz).

Compound 3 shows two separated resonances at δ +38.6 ($J_{Rh\text{-}P}$ = 147 Hz) and +32.2 ($J_{Rh\text{-}P}$ = 158 Hz). The chemical shifts fall between the ranges for purely chelating and purely ortho-metalated ligation. A tentative assignment of the high-frequency resonance to the η^3,μ-bonded PCBr is supported by the spectral changes induced by the substitution of the axial molecule of water, which is H-bonded to the second PCBr, by other donor solvents. It can easily be seen from the data in Table VIII that while the resonance at higher frequencies is only slightly affected by such substitutions, the other one is shifted into the range of 14–20 ppm which was found for η^2,μ-bonded phosphines with exogenous axial ligands. It is interesting that substitution by Me_2SO affords two sets of resonances. This can be rationalized by the two possible coordination modes of Me_2SO, via O or S, and there is precedence for both modes being present in an equilibrium mixture.[9]

For compound 4 both the ^1H and ^{31}P NMR spectra are fully in accord with the C_2 symmetry of the molecule. There is only one signal for the equivalent H_3CCO_2 protons and only one for the equivalent phosphorus atoms.

On the basis of what we learn from comparing the NMR spectra with the structures of compounds 2–4, we can say confidently that the structure shown in Chart I for compound 1 is strongly supported by NMR data. In Table IX are presented the spectra for compound 1 with four different axial ligands. It can be seen that, in keeping with the observations already discussed, a ^{31}P resonance at ca. 36 ppm is always present, with a $^1J(Rh\text{-}P)$ coupling constant of ca. 150 Hz regardless of the changes made in the axial ligand present at the other rhodium atom. In addition, there are always three H_3CCO_2 signals, as required by the proposed structure.

Acknowledgment. We thank the National Science Foundation and the C.A.I.C.Y.T. for support.

Supplementary Material Available: Complete tables of bond distances and angles and anisotropic thermal parameters for compounds 3 and 4 (10 pages); listings of observed and calculated structure factors for 3 and 4 (36 pages). Ordering information is given on any current masthead page.

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