to the ^{130}Te mass peaks and correspond to the parent ion peak in each case: CH$_2$(TeMe)$_2$, retention time (minutes) 2.38, m/e 302; CH$_2$(TeEt)$_2$, retention time 3.68, m/e 330; CH$_2$(Te-i-Pr)$_2$, retention time 6.12, m/e 386; CH$_2$(Te-s-Bu)$_2$, retention time 6.05, m/e 386; CH$_2$(Te-t-Bu)$_2$, retention time 4.95, m/e 386. Bis-(phenyltelluro)methane was prepared in the same way from diphenyl ditelluride and diazomethane and characterized by C and H analysis. Anal. Calcd for C$_{13}$H$_{12}$Te$_2$: C, 36.79; H, 2.83. Found: C, 36.88; H, 2.88.

The halide derivatives were prepared in essentially quantitative yield by reaction of the bis(methyltelluro)methanes with elemental halogen in CCl$_4$ at room temperature and were characterized by chemical analysis. Anal. Calcd for C$_3$H$_8$Cl$_4$Te$_2$: C, 8.18; H, 1.80. Found: C, 8.24; H, 1.77. Calcd for C$_3$H$_8$Br$_4$Te$_2$: C, 5.80; H, 1.29. Found: C, 5.89; H, 1.10. Calcd for C$_3$H$_8$I$_4$Te$_2$: C, 4.47; H, 0.99. Found: C, 4.46; H, 0.98. The halides of the bis(phenyltelluro)-methanes were similarly prepared and characterized. Anal. Calcd for C$_{13}$H$_{12}$Cl$_4$Te$_2$: C, 27.56; H, 212. Found: C, 27.23; H, 2.06. Calcd for C$_{13}$H$_{12}$Br$_4$Te$_2$: C, 20.97; H, 1.61. Found: C, 20.07; H, 1.55. Calcd for C$_{13}$H$_{12}$I$_4$Te$_2$: C, 16.79; H, 1.29. Found: C, 16.68; H, 1.20. The trichloride CH$_2$(TeCl$_3$)$_2$ was prepared as previously described. Anal. Calcd for CH$_2$Cl$_6$Te$_2$: C, 2.49; H, 0.41. Found: C, 2.53; H, 0.33.

Spectroscopic Characterization. The ^{125}Te NMR spectra were obtained on a Brüker WM 400 spectrometer at 126.24 MHz, operating at ambient temperature.[3,4] The resonances were found by utilizing 166-kHz sweep widths, 10-μs pulse widths, and a 0.01-s delay between acquisitions. Final spectra were obtained at the appropriate frequency, generally using a 5-kHz sweep width and 90° pulse widths with no delay. No broad-band decoupling was employed. Data acquisition consisted of 16K data points, which were zero filled to 32K data points for the Fourier transform. The line widths were 6–12 Hz. The ^{125}Te chemical shifts were reported with reference to neat Me$_2$Te.

Mössbauer spectra were recorded by using a Harwell Instruments constant acceleration drive, based on a Harwell 200 series wave form generator and amplifier. A 2-mCi ^{125}Sb/Cu source (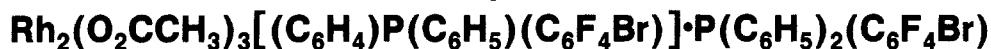New England Nuclear) was used. The source and absorbers were immersed in liquid helium in a Harwell Instruments Dewar. The 35.5-keV Mössbauer γ-ray was monitored through the 6-keV escape peak in a Xe/CO$_2$ proportional counter. The spectra were accumulated in a Nuclear Data 66 analyzer as 256-channel spectra and were subsequently computer-fitted to Lorentzians using the N.D. 66 as a computer terminal for transmitting data to, and for computation on, the University IBM 4341 main-frame computer. The spectrometer was routinely calibrated by using a ^{57}Co/Rh source and an iron foil absorber at room temperature. The ^{125}Te isomer shifts were reported with respect to ^{125}I/Cu as a reference standard, and this entailed adding 0.15 mm s^{-1} to the shifts measured against ^{125}Sb/Cu as the source.

In recording the spectra of the liquid bis(alkyltelluro)methanes, 150 mg of liquid was absorbed onto a glass fiber filter paper mounted in a Teflon holder prior to freezing. This method of sample mounting ensured a more even distribution of the frozen liquid than that obtained simply on freezing the neat liquid in the Teflon absorber holder. Mössbauer parameters obtained on the frozen neat liquid and on the liquid absorbed into the filter paper were identical.

Synthesis and Structure of the Ortho-Metalated Dirhodium(II) Compound
Rh$_2$(O$_2$CCH$_3$)$_3$[(C$_6$H$_4$)P(C$_6$H$_5$)(C$_6$F$_4$Br)]·P(C$_6$H$_5$)$_2$(C$_6$F$_4$Br)

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Reaction of Rh$_2$(O$_2$CCH$_3$)$_4$·2MeOH with the phosphine P(C$_6$H$_5$)$_2$(C$_6$F$_4$Br) in CH$_2$Cl$_2$ leads to the bis-(phosphine) adduct Rh$_2$(O$_2$CCH$_3$)$_4$[P(C$_6$H$_5$)$_2$(C$_6$F$_4$Br)]$_2$ (1) which was characterized by spectroscopic and chemical analysis. In refluxing toluene 1 is converted to the ortho-metalated dirhodium complex Rh$_2$-(O$_2$CCH$_3$)$_3$[P(C$_6$H$_5$)$_2$(C$_6$F$_4$Br)][(C$_6$H$_4$)P(C$_6$H$_5$)(C$_6$F$_4$Br)] (2) in ca. 50% yield. Molecules of 2 consist of a metal–metal bonded dirhodium unit which is bridged by two cisoid acetate groups as well as by a phosphine ortho metalated at one of the unsubstituted phenyl rings. The fourth equatorial coordination site on one rhodium atom is occupied by a phosphine which also provides the axial ligand by means of the bromine atom. On the other rhodium atom there is a chelating acetate ion that provides both equatorial and axial ligation. The compound crystallizes in the monoclinic space group $P2_1/n$ with cell parameters: $a = 16.656$ (10) Å, $b = 10.522$ (6) Å, $c = 24.978$ (11) Å; $\beta = 103.77$ (2); $V = 4251.6$ Å^3; $Z = 4$.

Introduction

Dinuclear rhodium(II) complexes with a set of homo-leptic bridging ligands are known in large numbers, and they have been extensively studied.[1] In contrast, only a limited number of dirhodium(II) complexes with a mixed set of bridging ligands is on record.[2]

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(1) (a) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982; pp 192–198. (b) Felthouse, T. R. *Prog. Inorg. Chem.* 1982, 29, 73. (c) Boyer, E. B.; Robinson, S. D. *Coord. Chem. Rev.* 1983, 50, 109.
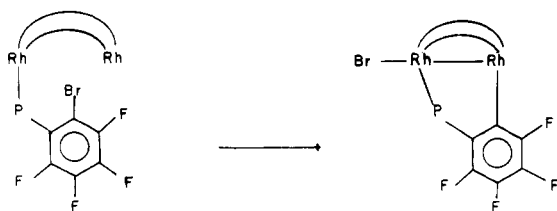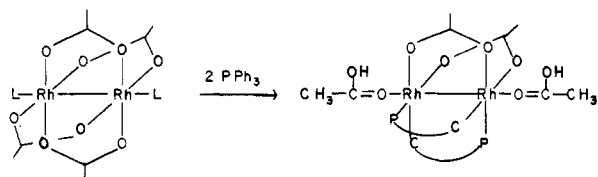
Scheme I

Scheme II

One of the chemically attractive routes to such complexes proceeds through ortho metalation involving a phenyl-substituted phosphine. The "classical" ortho metalation is an oxidative addition and was as a two-center reaction successfully performed on a binuclear Rh(I) complex (Scheme I).[3]

A different mechanism has to be invoked for the ortho-metalation reaction observed on dirhodium tetracarboxylates[4] (Scheme II). No net redox process occurs during the reaction, and formally the displacement of two acetate ligands by two ortho-metalated phosphines entails merely the transfer of protons from the ortho positions of phenyl rings to the acetate anions.

In this paper we report reactions of dirhodium tetraacetate with a phosphine which is potentially capable of either or both of these reaction routes. We have obtained a product in which one acetate is replaced by an orthometalated phosphine, via a formal proton-transfer process. A second acetate which is partly displaced by a phosphine ligand then occupies both an axial and an equatorial position. We have not been able to identify products resulting from oxidative addition, which would probably lead to rupture of the dinuclear unit.

Experimental Section

The complex $Rh_2(O_2CCH_3)_4\cdot 2MeOH$[5] and the ligand $P(C_6H_5)_2(C_6F_4Br)$[6] were synthesized according to published procedures. Solvents were of analytical grade and distilled under argon prior to use.

Preparation of $Rh_2(O_2CCH_3)_4\cdot 2L$ (1). A mixture of $Rh_2(O_2CCH_3)_4\cdot 2MeOH$ (0.11 g, 0.22 mmol) and $P(C_6H_5)_2(C_6F_4Br)$ (0.19 g, 0.46 mmol) in dichloromethane (15 mL) was stirred for 15 min at room temperature. The dark red solution was concentrated under vacuum. A brown-red solid precipitated upon slow addition of hexane. It was filtered off, washed with hexane, and dried under vacuum; yield 0.24 g, 87%. Anal. Calcd for $C_{44}H_{32}O_8F_8P_2Br_2Rh_2$: C, 41.6; H, 2.5. Found: C, 41.9; H, 2.6. ^{1}H NMR: 7.86 (8 H), 7.38 (12 H), 1.67 ppm (12 H). ^{31}P NMR: 13 ppm (br s). Molecular weight (osmometry in C_6H_6): calcd 1268, found 1180.

Preparation of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_4Br)]$-$[P(C_6H_5)_2(C_6F_4Br)]$ (2). A weighed amount (0.5 g) of 1 was boiled

(2) (a) Cotton, F. A.; Thompson, J. L. *Inorg. Chim. Acta* 1984, *81*, 193. (b) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* 1981, *20*, 584.

(3) Barcelo, F.; Lahuerta, P.; Ubeda, M. A.; Foces-Foces, C.; Cano, F. H.; Martinez-Ripoll, M. *J. Chem. Soc., Chem. Commun.* 1985, 43.

(4) 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.

(5) Rempel, G. A.; Legzdins, P.; Smith, H.; Wilkinson, G. *Inorg. Synth.* 1972, *13*, 90.

(6) Kemmit, R. D. W.; Rimmer, D. *J. Inorg. Nucl. Chem.* 1973, *35*, 3155.

Table I. Crystal Data

formula	$C_{42}H_{28}O_6F_8P_2Br_2Rh_2$
fw	1208.25
space group	$P2_1/n$
systematic absences	$h0l, h + l = 2n; 0k0, k = 2n$
a, Å	16.656 (10)
b, Å	10.522 (6)
c, Å	24.978 (11)
α, deg	90.00
β, deg	103.77 (2)
γ, deg	90.00
V, Å^3	4251.6
Z	4
d_{calcd} g/cm^3	1.88
cryst size, mm	0.09 × 0.2 × 0.3
μ(Mo Kα), cm^{-1}	27.805
data collectn instrument	Nicolet P3/F
radiatn (monochromated in incident beam)	Mo Kα (λ_α = 0.710 73 Å)
orientatn reflns, no., range (2θ)	25
temp, °C	25
scan method	ω–2θ
data collectn range, 2θ, deg	4–45
no. of unique data, total with $F_o^2 > 3\sigma(R_o^2)$	1869
no. of parameters refined	301
R^a	0.0547
R_w ^{b}	0.0534
quality-of-fit indicator^c	1.56
largest shift/esd, final cycle	0.164
largest peak, e/Å^3	0.91

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|) + 0.000\,845F^2$. ^{c} Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.
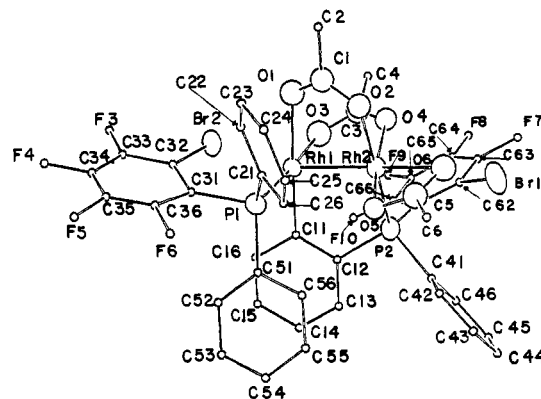
Figure 1. ORTEP drawing of $Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_4Br)]\cdot P(C_6H_5)_2(C_6F_4Br)$ (2).

under reflux in toluene for 3 h during which time a color change from red to green was observed. The resulting reaction mixture was evaporated to dryness and the residue recrystallized from dichloromethane–isooctane: yield 0.25 g, 50%. 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. ^{1}H NMR (CDCl$_3$): 7.6–6.4 (19 H), 1.72 (6 H), 1.42 ppm (3 H). ^{31}P NMR (CDCl$_3$): δ 56.4 ($^1J_{Rh-P}$ = 177.7 Hz), 20.3 ($^1J_{Rh-P}$ = 152.2 Hz).

X-ray Crystallography. Crystals of 2 suitable for diffraction work were obtained by slow evaporation of a solution in CH_2Cl_2/EtOH. The specimen selected for data collection was a rectangular plate of dimensions 0.09 × 0.2 × 0.3 mm^3. Unit-cell parameters were obtained by applying the autoindexing routine to 25 centered reflections; they were confirmed, together with the Laue class, by axial photographs. Data of a unique quadrant ($+h,+k,\pm l$) were collected between 4° and 45° (in 2θ). The monoclinic space group $P2_1/n$ was uniquely determined by the systematic absences.

A trial structure including the positions of the two independent Rh atoms and the axial Br atom was derived from a combination of direct methods (MULTAN) and Patterson techniques. A difference Fourier map based on this model, interpreted with the

Table II. Positional Parameters and Their Estimated Standard Deviations for
$Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_4Br)]\cdot P(C_6H_5)_2(C_6F_4Br)^a$

atom	x	y	z	B, Å^2
Rh1	0.4616 (1)	0.4778 (2)	0.13347 (7)	2.05 (5)
Rh2	0.3296 (1)	0.5116 (2)	0.16417 (7)	2.34 (5)
Br1	0.1050 (2)	0.5158 (3)	0.1120 (1)	4.30 (8)
Br2	0.5929 (2)	0.3800 (3)	0.1087 (1)	3.19 (8)
P1	0.5440 (4)	0.6158 (7)	0.1892 (3)	2.4 (2)
P2	0.2808 (4)	0.6225 (7)	0.0881 (3)	2.5 (2)
F(33)	0.7748 (9)	0.348 (2)	0.1280 (6)	5.4 (5)
F(34)	0.8970 (8)	0.487 (2)	0.1947 (7)	6.1 (5)
F(35)	0.8585 (9)	0.679 (2)	0.2570 (6)	5.8 (5)
F(36)	0.7038 (9)	0.732 (1)	0.2543 (6)	4.5 (4)
F(63)	0.0218 (9)	0.336 (2)	0.0268 (7)	6.7 (6)
F(64)	0.068 (1)	0.247 (2)	-0.0630 (7)	7.9 (6)
F(65)	0.209 (1)	0.335 (2)	-0.0875 (6)	7.0 (6)
F(66)	0.3015 (8)	0.504 (2)	-0.0249 (5)	4.9 (4)
O(1)	0.478 (1)	0.324 (2)	0.1950 (7)	3.7 (5)
O(2)	0.380 (1)	0.401 (2)	0.2330 (7)	3.3 (5)
O(3)	0.395 (1)	0.342 (2)	0.0790 (6)	3.5 (5)
O(4)	0.2929 (9)	0.347 (2)	0.1237 (6)	2.7 (5)
O(5)	0.3564 (9)	0.662 (2)	0.2171 (6)	2.7 (5)
O(6)	0.243 (1)	0.571 (2)	0.2258 (6)	3.5 (5)
C(1)	0.439 (1)	0.322 (3)	0.231 (1)	2.7 (5)*
C(2)	0.458 (2)	0.222 (3)	0.276 (1)	4.3 (7)*
C(3)	0.331 (2)	0.295 (3)	0.092 (1)	3.6 (6)*
C(4)	0.298 (1)	0.167 (3)	0.063 (1)	3.5 (6)*
C(5)	0.297 (2)	0.649 (3)	0.240 (1)	3.0 (6)*
C(6)	0.300 (2)	0.745 (3)	0.288 (1)	4.5 (7)*
C(12)	0.3649 (8)	0.680 (2)	0.0605 (6)	2.0 (5)*
C(13)	0.3533 (8)	0.784 (2)	0.0248 (6)	3.2 (6)*
C(14)	0.4175 (8)	0.825 (2)	0.0019 (6)	4.2 (6)*
C(15)	0.4933 (8)	0.762 (2)	0.0147 (6)	3.6 (6)*
C(16)	0.5049 (8)	0.658 (2)	0.0504 (6)	2.8 (5)*
C(11)	0.4407 (8)	0.617 (2)	0.0733 (6)	2.4 (5)*
C(21)	0.555 (1)	0.601 (2)	0.2635 (5)	2.9 (5)*
C(22)	0.594 (1)	0.492 (2)	0.2892 (5)	4.6 (6)*
C(23)	0.610 (1)	0.480 (2)	0.3464 (5)	4.8 (6)*
C(24)	0.586 (1)	0.576 (2)	0.3778 (5)	5.7 (8)*
C(25)	0.547 (1)	0.685 (2)	0.3520 (5)	6.4 (8)*
C(26)	0.532 (1)	0.698 (2)	0.2948 (5)	3.0 (5)*
C(31)	0.652 (1)	0.573 (2)	0.188 (1)	3.1 (6)*
C(32)	0.671 (1)	0.475 (2)	0.1570 (8)	2.3 (5)*
C(33)	0.756 (2)	0.443 (3)	0.159 (1)	3.4 (6)*
C(34)	0.817 (1)	0.516 (3)	0.193 (1)	3.5 (5)*
C(35)	0.801 (1)	0.609 (3)	0.227 (1)	3.8 (6)*
C(36)	0.720 (2)	0.634 (3)	0.224 (1)	3.1 (6)*
C(41)	0.2127 (9)	0.761 (1)	0.0858 (7)	2.2 (5)*
C(42)	0.2214 (9)	0.834 (1)	0.1334 (7)	4.0 (6)*
C(43)	0.1702 (9)	0.939 (1)	0.1337 (7)	4.7 (7)*
C(44)	0.1101 (9)	0.971 (1)	0.0863 (7)	3.2 (5)*
C(45)	0.1013 (9)	0.897 (1)	0.0387 (7)	5.0 (7)*
C(46)	0.1526 (9)	0.793 (1)	0.0384 (7)	3.6 (6)*
C(51)	0.538 (1)	0.784 (1)	0.1713 (7)	3.9 (6)*
C(52)	0.601 (1)	0.846 (1)	0.1531 (7)	3.8 (6)*
C(53)	0.593 (1)	0.975 (1)	0.1392 (7)	4.7 (6)*
C(54)	0.523 (1)	1.041 (1)	0.1434 (7)	3.9 (6)*
C(55)	0.460 (1)	0.979 (1)	0.1616 (7)	5.6 (7)*
C(56)	0.468 (1)	0.851 (1)	0.1756 (7)	3.7 (6)*
C(61)	0.215 (1)	0.521 (2)	0.0377 (9)	2.5 (5)*
C(62)	0.139 (1)	0.471 (2)	0.0475 (8)	2.2 (5)*
C(63)	0.090 (2)	0.382 (3)	0.015 (1)	3.7 (6)*
C(64)	0.114 (2)	0.336 (3)	-0.031 (1)	3.9 (6)*
C(65)	0.185 (2)	0.384 (3)	-0.044 (1)	4.1 (6)*
C(66)	0.234 (2)	0.469 (3)	-0.010 (1)	3.9 (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 $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

help of the initial E-map and the Patterson map, led to the position of the second Br atom and the P atoms. From here on the structure developed smoothly. Because of the limited amount of data the two unsubstituted phenyl rings were refined as rigid groups, and anisotropic displacement parameters were assigned only to atoms other than carbon. The refinement converged at residuals of $R = 0.055$, $R_w = 0.053$, for the fit of 301 parameters

Table III. Selected Bond Distances (Å) and Bond Angles (deg) in
$Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)(C_6F_4Br)]\cdot P(C_6H_5)_2(C_6F_4Br)$

(a) Bond Distances			
Rh(1)-Rh(2)	2.519 (3)	Rh(2)-P(2)	2.213 (7)
Rh(1)-P(1)	2.241 (7)	-O(2)	2.08 (2)
-O(1)	2.20 (2)	-O(4)	2.02 (2)
-O(3)	2.10 (2)	-O(5)	2.04 (2)
-C(11)	2.07 (2)	-O(6)	2.43 (2)
-Br	2.62 (2)		

(b) Bond Angles			
Rh(1)-Rh(2)-P(2)	89.0 (2)	Rh(2)-Rh(1)-P(1)	99.7 (2)
-O(2)	87.7 (5)	-C(11)	96.5 (4)
-O(4)	84.8 (5)	-O(1)	82.0 (5)
-O(5)	103.5 (4)	-O(3)	85.9 (5)
		-Br	164.7 (1)
O(1)-Rh(1)-O(3)	84.8 (6)	O(2)-Rh(2)-O(4)	87.1 (6)
-C(11)	176.9 (5)	-O(5)	85.2 (6)
O(3)-Rh(1)-C(11)	92.4 (6)	O(4)-Rh(2)-O(5)	168.4 (7)
P(1)-Rh(1)-O(1)	94.9 (4)	P(2)-Rh(2)-O(2)	176.3 (5)
P(1)-Rh(1)-O(3)	174.3 (5)	-O(4)	90.9 (5)
-C(11)	87.9 (4)	-O(5)	97.2 (5)

Table IV. Some Important Bond Distances (Å) and Bond Angles (deg) in
$Rh_2(O_2CCH_3)_3[(C_6H_4)P(C_6H_5)(C_6H_4Br)]\cdot P(C_6H_5)_2(C_6F_4Br)$ (2), $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot 2CH_3CO_2H$ (3), and $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)_2]_2\cdot 2C_5H_5N$ (4)

	2	3	4
Rh-Rh	2.519 (3)	2.508 (1)	2.556 (2)
Rh-P	2.241 (7)	2.210 (2)	2.216 (3)
Rh-O(trans to P)	2.10 (2)	2.136 (4)	2.118 (8)
Rh-O(trans to C)	2.20 (2)	2.190 (4)	2.182 (7)
Rh-C	2.07 (2)	1.996 (6)	2.011 (11)
Rh-Rh-P	99.7 (2)	88.31 (5)	89.95 (8)
Rh-Rh-C	96.5 (4)	97.5 (2)	96.1 (3)
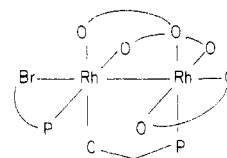
Figure 2. The bonding scheme around the Rh$_2$ unit.

to 1869 variables. Data pertaining to data collection and refinement are summarized in Table I. Table II lists the atomic coordinates, and important bond distances and angles are listed in Table III.

Results and Discussion

Molecular Structure of 2. Figure 1 shows a perspective view of 2 and also defines the atom numbering scheme. Figure 2 shows a schematic drawing of the bonding scheme around the Rh$_2$ unit. The molecule is a dinuclear Rh(II) compound with a single bond linking the metal centers. It is similar to the ortho-metalated dimers reported earlier[4] in that two cisoid bridging acetate ligands are retained during the reaction. One acetate group has been completely displaced by an ortho-metalated phosphine which is a three-atom-bridging bidentate ligand in its own right. In the fourth bridging site the acetate displacement is incomplete. The previously bridging acetate is shifted to a mode of ligation that is intermediate between chelating and monodentate. One of its oxygen atoms forms a short bond, 2.04 (2) Å, at an equatorial site, while the other is loosely bonded, 2.43 (3) Å, in an approximately axial position. The equatorial site on the other Rh atom is now taken by a phosphine which is of appropriate dimensions and properly oriented to introduce the o-Br atom

of the C_6F_4Br ring into the second axial site.

For comparison the bond lengths within the core are given in Table IV together with those of previously published ortho-metalated dimers. Clearly the Rh–Rh bond length is well within the range spanned by differences in axial substituents.

An especially noteworthy feature of this molecule is the unprecedented way in which double-axial ligation is achieved. On one end of the dimer we find an acetate group in a chelating mode so that in addition to filling one equatorial position it also fills the adjacent axial position. Although it is not a common one, there are precedents for this arrangement.[7,8] The axial site on the other metal atom is occupied by a Br atom attached to one of the phosphine phenyl rings. This Br atom, despite its being an integral part of the perfluorophenyl ring, has a contact distance with the Rh which is, by all standards, a strong axial ligation.

Chemical Reaction. The reaction of dirhodium tetraacetate with $P(C_6H_5)_2(C_6F_4Br)$ is fundamentally similar to its reaction with triphenylphosphine, but there are a number of differences in detail. Two phosphine ligands are added to the dirhodium unit, but only one becomes ortho metalated, and in neither one is the bromine–carbon bond broken.

One $P(C_6H_5)_2(C_6F_4Br)$ molecule becomes ortho metalated on one of its phenyl rings by formal proton transfer to an acetate anion, which is entirely eliminated from the product. As we noted earlier,[4] this formal acid–base reaction is not favorable and the overall transformation must be thermodynamically driven by other factors, such as the (presumably favorable) replacement of the two Rh–O bonds to a bridging acetate group by the Rh–P and Rh–C bonds in the product.

In the present case, the first ortho metalation is not followed by a second one. Instead, the second molecule of $P(C_6H_5)_2(C_6F_4Br)$ only partially displaces an acetate group whereby an equatorial Rh–P bond is formed. However, this phosphine molecule then orients itself so that its bromine atom can form a rather good donor bond to the same rhodium atom at the axial position. The partially displaced acetate ion then occupies the neighboring equatorial position and also fills the other axial site.

A question that naturally arises is: Why has not the second molecule of phosphine undergone ortho metalation in this case, as in the earlier one?[4] We suggest, as a tentative answer, that molecule 2 does not react further in refluxing toluene because it is stabilized by the internal formation of axial bonds which would be partly or entirely sacrificed if the second phosphine became ortho metalated in the same way as the first one. In pure toluene there are no exogenous axial ligands and thus compound 2 is stable. In the reaction of $Rh_2(O_2CCH_3)_4$ with PPh_3 in refluxing acetic acid, the acetic acid molecules were able to occupy the axial positions. We are currently doing further work to see how important this medium effect is and specifically to see if we can find a way to drive compound 2 to undergo the second ortho metalation and thus produce a product of the type $Rh_2(O_2CCH_3)_2[(C_6H_4)P(C_6H_5)(C_6F_4Br]_2 \cdot L_2$ where L is some suitable axial ligand. Work done so far shows that both 1 and 2 can undergo a variety of reactions and that conditions will have to be carefully controlled to achieve a specific predetermined result.

Supplementary Material Available: Complete tables of bond distances and angles, anisotropic displacement parameters, and structure factors (16 pages). Ordering information is given on any current masthead page.

(7) Cotton, F. A.; Lay, D. G. *Inorg. Chem.* 1981, 20, 935.

(8) Chisholm, M. H.; Extine, M. W.; Cotton, F. A.; Stults, B. R. *J. Am. Chem. Soc.* 1976, 98, 4683.

Communications

The Easy Interconversion of Diplatinum(I) and Platinum(0)–Platinum(II) Complexes by Reversible Carbonyl Addition

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Summary: The complexes $[HPt(\mu$-$PP)_2PtCO]^+$, PP = $Et_2PCH_2PEt_2$ or $Ph_2PCH_2PPh_2$, add reversibly and very rapidly at room temperature one or two carbonyl groups to give $[HPt(\mu$-$PP)_2Pt(CO)_2]^+$ and $[H(CO)Pt(\mu$-$PP)_2Pt$-$(CO)_2]^+$. Evidence is presented that the reactions essentially involve disproportionation of diplatinum(I) to give the first reported platinum(0)–platinum(II) species and the results give new insights into the mechanism of ligand substitution at platinum(I).

Mixed-valence compounds of platinum are of considerable importance, but there are very few mixed-valence *molecular* compounds and no platinum(0)–platinum(II) derivatives.[1-3] This article describes how very easy disproportionation of diplatinum(I) complexes to give platinum(0)–platinum(II) complexes can be induced by addition of carbon monoxide, as shown in Scheme I.

The reversible addition of CO to complexes 2, prepared as shown in Scheme I,[4] is rapid on the NMR time scale at room temperature, and so the new complexes 3 and 4 could not be isolated but were identified by multinuclear (^1H, ^{13}C, ^{31}P, and ^{195}Pt) NMR in acetone-d_6 at -90 °C.[4,5]

(1) Clark, R. J. H. *Chem. Soc. Rev.* 1985, 219.

(2) Balch, A. L. *Comments Inorg. Chem.* 1984, 3, 51.

(3) Parsons, E. J.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* 1985, 107, 1793.

(4) Fisher, J. R.; Mills, A. J.; Sumner, S.; Brown, M. P.; Thomson, M. A.; Puddephatt, R. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W. *Organometallics* 1982, 1, 1421. Manojlović-Muir, Lj.; Muir, K. W. *J. Organomet. Chem.* 1981, 219, 129.