distances in higher nuclearity cluster complexes. It becomes particularly important to obtain other measures of bond strength for these compounds besides structural information if we are to unravel the various interlocking factors of the M-M and M-L bonds. Combined infrared and resonance Raman spectroscopy provide one such additional measure, and we are now actively pursuing this avenue.

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Registry No. $Rh_2(OAc)_4(P(OPh)_3)_2$, 69970-91-8; $Rh_2(OAc)_4(PPh_3)_2$, 39773-08-5.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes for $Rh_2(OAc)_4(P(OPh)_3)_2{\cdot}C_7H_8$ and $Rh_2(OAc)_4(PPh_3)_2$ (34 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of the Bis(triphenylphosphine) and Bis(triphenyl phosphite) Adducts of Tetrakis(trifluoroacetato)dirhodium(II)

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The title compounds, $Rh_2(O_2CCF_3)_4(PPh_3)_2$ (**1**) and $Rh_2(O_2CCF_3)_4[P(OPh)_3]_2$ (**2**), have been prepared in crystalline form and their structures determined. They each form crystals in space group $P\bar{1}$ with the following dimensions: for **1** a = 9.974 (1) Å, b = 13.365 (2) Å, c = 9.154 (2) Å, α = 105.24 (1)°, β = 91.06 (1)°, γ = 107.42 (1)°, V = 1117.1 (7) Å^3; for **2** a = 9.772 (1) Å, b = 14.194 (2) Å, c = 9.565 (2) Å, α = 103.76 (1)°, β = 93.38 (2)°, γ = 74.90 (1)°, V = 1244.1 (6) Å^3. In each case, there is one formula unit in the unit cell and the molecules are very similar in structure, each consisting of the central $Rh_2(O_2CCF_3)_4$ unit, of which the $Rh_2(O_2CC)_4$ core has essentially D_{4h} symmetry, with PY_3 ligands in the axial positions. The only significant differences between the two molecular structures are in the Rh-Rh distances, 2.486 (1) Å for **1** and 2.470 (1) Å for **2**, and in the Rh-P distances, 2.494 (2) Å in **1** and 2.422 (2) Å in **2**. It is suggested that the former is only a necessary consequence of the latter and that the latter may be of mainly steric origin.

Introduction

The path to an understanding of the Rh-Rh bond in the $Rh_2(O_2CR)_4L_2$ compounds has not been a straight or smooth one, and despite the time which has passed since the earliest efforts, the goal has not yet been fully reached. Difficulties have arisen because the bond is a complicated one and also because the strengths of its components, σ, π, δ, δ^*, π^*, σ^*, are subject to considerable influence by changes in the nature of both R and L. The following paper will address some of the theoretical problems and give a survey of pertinent literature. It will suffice here to state briefly the reasons why the structures we are now reporting were determined.

Kawamura and co-workers have recently studied the ESR spectra of a number of $Rh_2(O_2CR)_4(PY_3)_2^+$ radical cations, some with R = alkyl[1,2] and some with R = CF_3.[2] The results of their studies appeared to indicate an electronic structure different from that which might most easily have been inferred by use of Norman and Kolari's theoretical results[3] for $Rh_2(O_2CH)_4$ and $Rh_2(O_2CH)_4(H_2O)_2$. It was decided to investigate this question by performing an SCF-Xα-SW calculation on the model compound $Rh_2(O_2CH)_4(PH_3)_2$. However, before doing that, it was considered desirable to have accurate structural results for some $Rh_2(O_2CR)_4(PY_3)_2$ molecules of the same type as Kawamura et al. used to generate their radical cations. It was learned that G. G. Christoph and co-workers were already working on the structures of $Rh_2(O_2CCH_3)_4(PY_3)_2$ with Y = C_6H_5; we, therefore, proceeded with the corresponding trifluoroacetate compounds. The results obtained by Christoph et al. are presented in the preceding paper,[4] our structural results are given here, and the SCF-Xα-SW calculation is reported in the following paper.[5]

Experimental Section

Compound Preparation. Rhodium(II) acetate was prepared by a literature method.[6] The trifluoroacetate complex was obtained from $Rh_2(O_2CCH_3)_4$ with the use of a carboxylate exchange procedure.[7] Typically, $Rh_2(O_2CCH_3)_4$ (1 g) was dissolved with heating in excess trifluoroacetic acid (10 mL). After 2 h, the solvent was removed under reduced pressure and water added to the residue to dissolve any unreacted $Rh_2(O_2CCH_3)_4$. The product was obtained by extracting the aqueous mixture with methylene chloride. Anhydrous $Rh_2(O_2CCF_3)_4$ was isolated by heating the product at 150 °C for 30 min.

$Rh_2(O_2CCF_3)_4(PPh_3)_2$ (1) precipitates immediately, as a microcrystalline yellow-brown solid having a purple sheen, upon mixing stoichiometric amounts of $Rh_2(O_2CCF_3)_4$ and PPh_3 in methanol. Crystals suitable for X-ray diffraction were obtained by the following procedure. $Rh_2(O_2CCF_3)_4$ was dissolved in a minimum volume of methanol, the solution placed in a 1 dram vial, and the vial sealed with a sheet of parafilm having a pinhole in it. The vial was inverted and placed in a beaker containing a stoichiometric amount of PPh_3 dissolved in methanol. The beaker was covered, and the two solutions were allowed to mix over a 1-week period by slow diffusion. Examination under a microscope of the portion of the parafilm sheet which had been inside the vial revealed several yellow-brown prismatic crystals of adequate size for X-ray data collection. Other attempts (slow cooling or evaporation) to obtain crystals produced only microcrystalline material.

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(1) Kawamura, T.; Fukamachi, K.; Hayashida, S. *J. Chem. Soc., Chem. Commun.* **1979**, 945.

(2) Kawamura, T.; Fukamachi, K.; Sowa, T.; Hayashida, S.; Yonezawa, T. *J. Am. Chem. Soc.* **1981**, *103*, 364.

(3) Norman, J. G.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791.

(4) Christoph, G. G.; Halpern, J.; Khare, G. P.; Koh, Y.-B.; Romanowski, C. *Inorg. Chem.*, preceding paper in this issue.

(5) Cotton, F. A.; Bursten, B. E. *Inorg. Chem.*, following paper in this issue.

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

(7) Johnson, S. A.; Hunt, H. R.; Neumann, H. M. *Inorg. Chem.* **1963**, *2*, 960.

0020-1669/81/1320-3037$01.25/0

Table I. Summary of Crystallographic Data and Data Collection Procedures

	1	2
formula	$Rh_2P_2F_{12}O_8C_{44}H_{30}$	$Rh_2P_2F_{12}O_{14}C_{44}H_{30}$
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.974 (1)	9.772 (1)
b, Å	13.365 (2)	14.194 (2)
c, Å	9.154 (2)	9.565 (2)
α, deg	105.24 (1)	103.76 (1)
β, deg	91.06 (1)	93.38 (2)
γ, deg	107.42 (1)	74.90 (1)
V, Å^3	1117.1 (7)	1244.1 (6)
d_{calcd}, g/cm^3	1.76	1.71
Z	1	1
formula wt	1182.46	1278.46
cryst size, mm	0.10 × 0.15 × 0.20	0.04 × 0.17 × 0.35
μ(Mo Kα); cm^{-1}	9.008	8.256
radiation	graphite-monochromated Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.710 73 Å)	
scan type	$\omega-2\theta$	$\omega-2\theta$
scan width ($\Delta\omega$), deg	0.90 + 0.35 tan θ	0.80 + 0.35 tan θ
aperture width, mm	1.5 + tan θ	1.5 + tan θ
max scan speed, deg/min	20.12	20.12
max counting time, s	30	30
data collectn range	$+h,\pm k,\pm l$; 3° ⩽ 2θ ⩽ 50°	$+h,\pm k,\pm l$; 3° ⩽ 2θ ⩽ 50°
no. of unique data	3898	4352
no. of data, $F_o^2 > 2\sigma(F_o^2)$	2476	2317
p	0.05	0.05
X-ray exposure time, h	32.4	32.7
no. of intens stds	3	3
time between measmts, s	3600	3600
cryst dec	negligible	negligible
no. of variables	307	334
R_1	0.055	0.054
R_2	0.062	0.056
esd	1.466	1.302
largest peak, e/Å^3 [a]	0.83	0.37
Δ/σ [b]	0.05	0.11

[a] Largest peak in the final difference Fourier map. [b] Largest shift (Δ) to error (σ) ratio in final least-squares cycle.

$Rh_2(O_2CCF_3)_4[P(OPh)_3]_2$ (2) was prepared as an orange-brown microcrystalline solid upon mixing stoichiometric quantities of $Rh_2(O_2CCF_3)_4$ and $P(OPh)_3$ in methanol. The solid was redissolved in methanol and the solution allowed to evaporate overnight in air, giving small yellow crystals, most of which were badly twinned when examined under a polarizing microscope. A few thin, clear yellow plates were selected and carefully mounted with the edges of the plates on glass fibers for X-ray diffraction analysis.

X-ray Crystallography. Collection of Data. The X-ray diffraction data for both compounds were collected on an Enraf-Nonius CAD-4F diffractometer at 26 ± 1 °C using the data collection procedures summarized in Table I. Further details concerning data collection and reduction have appeared previously for this diffractometer.[8] The final cell constants for the two compounds were obtained from a least-squares fit to 25 reflections in the range 25° < 2θ < 32°. Corrections for Lorentz and polarization effects were made for both compounds but absorption corrections were deemed unnecessary due to the low μ values (Table I).

Because of the platelike form of the crystals obtained for **2**, data were collected by using the FLAT scanning mode[9] as described before.[10] The vector parallel to the incident X-ray beam and normal to the plane of the platelike crystal was identified as (100) in the (hkl) crystal coordinate system. Consequently, with this vector as a reference point between the crystal morphology and the incident beam, the FLAT scanning mode proceeds in such a way as to calculate, during data collection, the azimuth position of minimum absorption, with the assumption of a crystal of small finite thickness but infinitely large surface area, and keeping the sum of the incident and diffracted beam path lengths at a minimum.

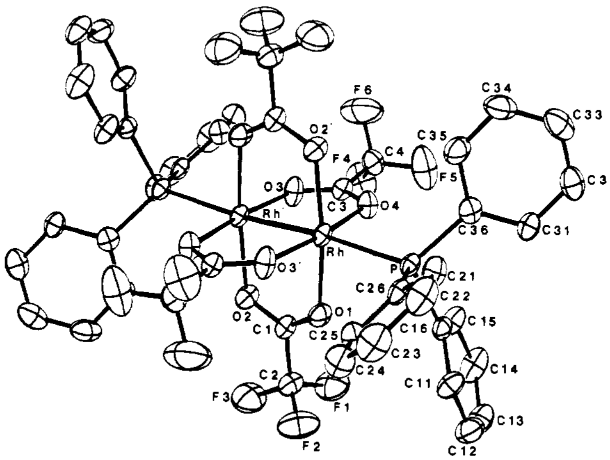

Figure 1. ORTEP view of $Rh_2(O_2CCF_3)_4(PPh_3)_2$ (**1**) showing the atom labeling scheme with thermal ellipsoids drawn at the 35% probability level. A crystallographic center of inversion is located at the midpoint of the Rh–Rh bond.

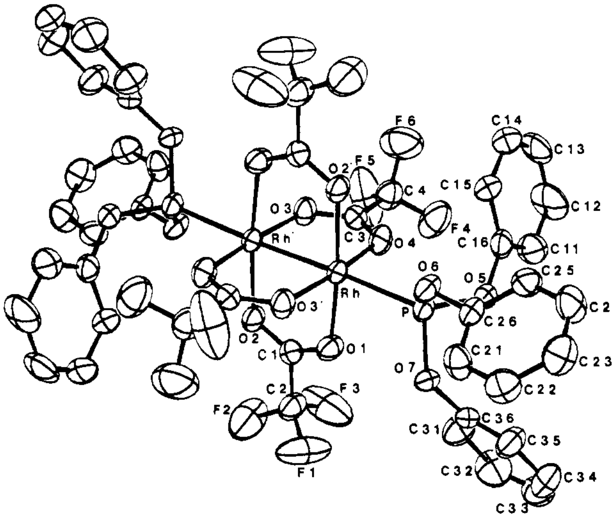

Figure 2. ORTEP drawing of $Rh_2(O_2CCF_3)_4[P(OPh)_3]_2$ (**2**) showing the atom labeling scheme. Vibrational ellipsoids have been scaled so as to enclose 35% of their electron density. An inversion center is located at the midpoint of the Rh–Rh bond.

Solution and Refinement of the Structures.[11] Crystals of compounds **1** and **2** were each found to be triclinic with cell volumes consistent with $Z = 1$. Structure solution and refinement were undertaken in the centrosymmetric space group $P\bar{1}$ for each compound. In each structure a three-dimensional Patterson map revealed the position of the Rh atom from the highest peak. The details of the refinement for each structure are given below.

$Rh_2(O_2CCF_3)_4(PPh_3)_2$ (1). Four cycles of least-squares refinement of positional and isotropic thermal parameters for the Rh atom produced residuals of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.32$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.39$. Successive difference Fourier maps followed by least-squares refinement of the atomic positional and thermal parameters revealed the positions of the remaining 33 nonhydrogen atoms. Anisotropic thermal parameters were assigned to all 34 nonhydrogen atoms. The 15 phenyl hydrogen atoms of the PPh_3 ligand were included in the refinement in calculated positions (C–H distances of 0.95 Å and C–C–H angles of 120°) with isotropic thermal parameters assigned on the basis of the attached carbon atoms: $B(H_i) = B(C_i) + 1.0$ (Å^2). None of the hydrogen atom parameters

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(8) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.
(9) CAD-4 Operation Manual, Enraf-Nonius: Delft, Holland, 1977.
(10) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 600.
(11) All crystallographic computing was done on PDP 11/45 or PDP 11/60 computers at the Molecular Structure Corp., College Station, Texas, with the Enraf-Nonius structure determination package with local modifications.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CCF_3)_4(PPh_3)_2$ (1)[a,b]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Rh	0.57893 (7)	0.59466 (5)	0.51577 (8)	2.29 (2)	2.03 (2)	2.53 (2)	−0.29 (2)	−0.14 (2)	0.59 (2)
P	0.7476 (2)	0.7773 (2)	0.5254 (2)	2.69 (8)	2.19 (8)	2.56 (8)	−0.06 (7)	0.12 (7)	0.66 (6)
F(1)	0.6188 (7)	0.4330 (5)	−0.0016 (6)	8.0 (3)	10.1 (3)	4.5 (3)	3.7 (3)	1.2 (3)	2.4 (2)
F(2)	0.8032 (6)	0.4364 (6)	0.1189 (7)	4.0 (3)	10.7 (4)	6.4 (3)	1.2 (3)	1.0 (2)	0.7 (3)
F(3)	0.6305 (7)	0.2903 (5)	0.0491 (7)	9.8 (4)	6.0 (3)	6.9 (3)	2.1 (3)	3.0 (3)	−0.2 (3)
F(4)	0.1214 (7)	0.4869 (5)	0.1624 (7)	6.7 (3)	6.7 (3)	8.0 (3)	1.5 (2)	−3.0 (3)	1.0 (3)
F(5)	0.2171 (7)	0.6549 (5)	0.2551 (9)	7.7 (3)	5.5 (3)	12.8 (5)	1.4 (2)	−3.2 (3)	3.0 (3)
F(6)	0.0861 (7)	0.5603 (7)	0.3823 (9)	8.0 (3)	17.1 (5)	9.1 (4)	7.6 (3)	3.6 (3)	4.7 (3)
O(1)	0.6533 (6)	0.5304 (4)	0.3200 (6)	3.5 (2)	2.7 (2)	4.2 (2)	−0.2 (2)	1.1 (2)	0.6 (2)
O(2)	0.5103 (6)	0.3598 (4)	0.2870 (6)	4.0 (3)	2.8 (2)	2.6 (2)	−0.1 (2)	0.3 (2)	0.2 (2)
O(3)	0.2801 (6)	0.4459 (4)	0.3654 (6)	3.7 (3)	3.2 (2)	4.4 (2)	−0.1 (2)	−1.2 (2)	1.7 (2)
O(4)	0.4192 (5)	0.6177 (4)	0.3977 (6)	3.3 (2)	2.7 (2)	3.8 (2)	0.2 (2)	−0.9 (2)	0.9 (2)
C(1)	0.6046 (8)	0.4332 (6)	0.2509 (8)	2.7 (3)	3.3 (3)	2.8 (3)	0.2 (3)	−0.1 (3)	1.1 (2)
C(2)	0.6662 (9)	0.3975 (7)	0.1058 (10)	3.8 (4)	4.0 (4)	3.6 (4)	0.5 (3)	0.8 (3)	0.8 (3)
C(3)	0.3068 (8)	0.5405 (6)	0.3554 (8)	2.6 (3)	3.2 (3)	3.0 (3)	0.4 (3)	−0.1 (3)	1.0 (2)
C(4)	0.1824 (10)	0.5614 (7)	0.2883 (10)	4.2 (4)	3.0 (3)	4.4 (4)	0.7 (3)	−0.1 (3)	0.4 (3)
C(11)	0.9361 (9)	0.7927 (7)	0.2991 (9)	3.1 (4)	5.0 (4)	3.4 (3)	0.4 (3)	0.1 (3)	1.7 (3)
C(12)	0.9655 (10)	0.7819 (8)	0.1499 (10)	4.6 (4)	6.3 (4)	4.5 (4)	1.8 (4)	1.7 (3)	2.5 (3)
C(13)	0.8618 (11)	0.7558 (8)	0.0360 (9)	6.2 (5)	5.0 (4)	2.5 (3)	0.5 (4)	0.3 (4)	1.3 (3)
C(14)	0.7245 (11)	0.7416 (8)	0.0708 (10)	5.5 (5)	5.2 (5)	3.0 (3)	−0.9 (4)	−1.4 (4)	1.2 (3)
C(15)	0.6932 (9)	0.7484 (7)	0.2177 (9)	3.1 (4)	4.8 (4)	3.1 (3)	−0.1 (3)	−0.6 (3)	2.0 (3)
C(16)	0.7983 (8)	0.7764 (6)	0.3346 (9)	3.3 (3)	2.1 (3)	3.0 (3)	0.2 (3)	0.6 (3)	0.7 (2)
C(21)	0.9726 (9)	0.9166 (7)	0.7487 (10)	3.5 (4)	2.9 (3)	4.1 (4)	−0.4 (3)	−0.6 (3)	0.9 (3)
C(22)	1.1012 (10)	0.9398 (8)	0.8366 (11)	4.5 (5)	4.2 (4)	4.2 (4)	−1.2 (4)	−1.2 (4)	0.6 (3)
C(23)	1.1690 (10)	0.8620 (9)	0.8158 (11)	3.5 (4)	6.6 (5)	5.6 (5)	−0.1 (4)	−1.2 (4)	2.2 (4)
C(24)	1.1130 (9)	0.7639 (8)	0.7135 (11)	3.3 (4)	6.0 (4)	5.9 (5)	1.2 (3)	−0.3 (4)	2.6 (3)
C(25)	0.9868 (9)	0.7398 (7)	0.6250 (9)	2.9 (3)	3.3 (3)	4.1 (4)	0.4 (3)	−0.5 (3)	0.8 (3)
C(26)	0.9145 (8)	0.8156 (6)	0.6440 (8)	2.9 (3)	2.3 (3)	2.8 (3)	−0.3 (3)	0.2 (3)	0.8 (2)
C(31)	0.7240 (9)	0.9830 (7)	0.5221 (9)	3.5 (4)	3.1 (3)	3.7 (3)	0.2 (3)	0.1 (3)	1.3 (3)
C(32)	0.6822 (10)	1.0740 (7)	0.5808 (11)	4.7 (4)	3.0 (4)	5.7 (5)	0.6 (3)	−0.9 (4)	0.7 (3)
C(33)	0.6066 (10)	1.0808 (7)	0.7023 (13)	3.8 (4)	3.6 (4)	7.0 (6)	1.0 (3)	−0.1 (4)	−0.3 (4)
C(34)	0.5718 (10)	0.9972 (8)	0.7710 (12)	5.1 (4)	4.9 (5)	5.8 (5)	1.5 (4)	2.0 (4)	−0.1 (4)
C(35)	0.6094 (10)	0.9055 (7)	0.7112 (11)	4.9 (4)	3.5 (4)	4.7 (4)	0.2 (4)	1.4 (4)	0.9 (3)
C(36)	0.6887 (8)	0.8976 (6)	0.5877 (9)	2.3 (3)	2.9 (3)	4.0 (4)	0.1 (3)	−0.4 (3)	0.7 (3)

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
H(11)	1.0106	0.8114	0.3773	4.83	H(24)	1.1602	0.7106	0.7016	5.85
H(12)	1.0604	0.7930	0.1267	5.74	H(25)	0.9497	0.6710	0.5509	4.63
H(13)	0.8832	0.7474	−0.0664	5.88	H(31)	0.7770	0.9791	0.4367	4.74
H(14)	0.6514	0.7270	−0.0073	5.54	H(32)	0.7069	1.1325	0.5355	5.51
H(15)	0.5975	0.7336	0.2391	4.80	H(33)	0.5773	1.1433	0.7405	6.04
H(21)	0.9260	0.9703	0.7613	4.46	H(34)	0.5223	1.0034	0.8590	6.10
H(22)	1.1410	1.0087	0.9099	5.59	H(35)	0.5808	0.8463	0.7547	6.08
H(23)	1.2563	0.8779	0.8743	6.01					

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$, where *a*, *b*, and *c* are reciprocal lattice constants. [b] Isotropic thermal parameters are given for hydrogen atoms. These are based on the isotropic thermal parameters of the attached carbon atoms: $B(H_i) = B(C_i) + 1.0$ (Å²).

was allowed to vary. The refinement proceeded one cycle at a time with each cycle followed by recalculation of the hydrogen atom positions until the shift-to-error ratio (Δ/σ) reached the value given in Table I. The final data-to-parameter ratio was 2476:307 or ~8.1:1, and the final residuals and goodness-of-fit (esd) are given in Table I.

$Rh_2(O_2CCF_3)_4[P(OPh)_3]_2$ (2). Four cycles of least-squares refinement of the Rh atom positional and thermal parameters gave $R_1 = 0.32$ and $R_2 = 0.39$. Subsequent difference Fourier maps followed by least-squares refinement gave the positions of the remaining 36 nonhydrogen atoms. With anisotropic thermal parameters for all 37 nonhydrogen atoms, the refinement continued with the 15 phenyl hydrogen atoms included in the same manner as in structure **1**. The refinement was concluded when the Δ/σ value reached that shown in Table I. The final data-to-parameter ratio was 2317:334 or ~6.9:1, and the values of the final discrepancy indices and esd are recorded in Table I.

Final difference Fourier maps revealed no peaks of structural significance in either structure; the sizes of the highest peaks recorded in Table I. In neither structure could effects due to extinction be found in an inspection of observed and calculated structure factors. Tables of observed and calculated structure factor amplitudes are available for data with $I > 2\sigma(I)$[12] for both structures.

Results

The two structures were solved and refined straightforwardly to give the positional and thermal parameters listed in Table II and III. ORTEP views of the molecules are shown in Figures 1 and 2. The numbering schemes have been chosen to correspond to closely as possible (only the addition of three oxygen atoms in **2** being required), and thus the bond lengths and bond angles are conveniently reported in Table IV for both molecules. The equations for a number of planes and the dihedral angles between them have been tabulated in Table V which is available as supplementary material. The molecules are packed with no unusual intermolecular contacts.

In each case the molecules reside on a crystallographic inversion center, and the central $Rh_2(O_2CC)_4$ portion of the molecule comes very close to having D_{4h} symmetry. In **1** the Rh–Rh–P angles (174.51 (7)°) differ a little more than those in **2** (177.45 (9)°) from linearity probably because of intramolecular repulsions that are not axially symmetric, due to the incompatibility of the 4-fold and 3-fold symmetries of the $Rh_2(O_2CCF_3)_4$ and PY_3 moieties, respectively. As is always the case in our experience, several fluorine atoms of the CF_3 groups refined with rather high thermal vibration amplitudes, but there was no indication of actual disordering of these

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(12) Supplementary material.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Rh_2(O_2CCF_3)_4[P(OPh)_3]_2$ (2)[a,b]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Rh	0.47500 (8)	0.08976 (5)	0.06124 (8)	3.77 (2)	2.52 (2)	3.53 (2)	−0.77 (2)	0.51 (2)	−0.11 (2)
P	0.4186 (2)	0.2645 (2)	0.1882 (2)	4.1 (1)	3.23 (9)	3.6 (1)	−0.86 (8)	0.16 (9)	−0.14 (8)
F(1)	0.2024 (8)	0.0132 (6)	0.3800 (8)	11.2 (4)	12.2 (5)	13.0 (4)	0.9 (4)	7.3 (3)	5.5 (3)
F(2)	0.2738 (9)	−0.1334 (5)	0.3075 (8)	27.0 (5)	9.8 (3)	10.5 (4)	−11.5 (3)	8.8 (3)	−1.0 (3)
F(3)	0.3923 (7)	−0.0553 (7)	0.4389 (7)	11.2 (4)	32.2 (6)	8.1 (3)	−11.7 (3)	−3.6 (3)	11.7 (3)
F(4)	0.8796 (6)	0.0115 (5)	0.3339 (7)	6.7 (3)	10.8 (4)	6.7 (3)	−0.1 (3)	−1.3 (3)	−1.0 (3)
F(5)	0.9186 (7)	−0.1395 (5)	0.2334 (9)	11.1 (4)	7.8 (3)	21.6 (6)	−3.1 (3)	−10.0 (4)	6.4 (4)
F(6)	0.9765 (7)	−0.0424 (7)	0.1354 (8)	6.2 (3)	20.1 (7)	9.4 (4)	−3.6 (4)	0.2 (3)	2.3 (5)
O(1)	0.3815 (6)	0.0536 (4)	0.2202 (6)	6.0 (3)	3.5 (2)	4.4 (3)	−1.2 (2)	1.5 (2)	0.6 (2)
O(2)	0.4263 (6)	−0.1105 (4)	0.1086 (6)	5.7 (3)	3.1 (2)	4.2 (3)	−1.4 (2)	0.9 (2)	−0.0 (2)
O(3)	0.7105 (6)	−0.1084 (4)	0.0509 (6)	4.1 (3)	3.5 (2)	4.9 (3)	−0.5 (2)	−0.2 (2)	0.1 (2)
O(4)	0.6632 (6)	0.0547 (4)	0.1623 (6)	5.6 (3)	2.9 (2)	5.1 (3)	−0.8 (2)	0.1 (3)	0.3 (2)
O(5)	0.5261 (5)	0.3110 (4)	0.2970 (6)	3.8 (2)	4.8 (3)	4.1 (3)	−1.3 (2)	0.5 (2)	−0.6 (2)
O(6)	0.3719 (6)	0.3368 (4)	0.0803 (6)	6.1 (3)	3.6 (2)	3.5 (3)	−0.8 (2)	1.0 (2)	0.1 (2)
O(7)	0.2839 (5)	0.2975 (4)	0.2923 (6)	3.6 (2)	5.7 (3)	3.7 (3)	−1.2 (2)	1.2 (2)	−0.6 (2)
C(1)	0.3802 (8)	−0.0350 (6)	0.2075 (9)	4.1 (4)	3.7 (3)	4.2 (4)	−1.2 (3)	0.3 (3)	0.7 (3)
C(2)	0.3145 (10)	−0.0558 (6)	0.3341 (10)	7.0 (5)	3.9 (4)	5.2 (5)	−1.0 (4)	1.6 (4)	0.5 (4)
C(3)	0.7375 (8)	−0.0332 (6)	0.1363 (9)	3.5 (3)	4.9 (4)	4.1 (4)	−1.5 (3)	0.1 (3)	0.4 (3)
C(4)	0.8768 (10)	−0.0520 (7)	0.2112 (11)	4.9 (4)	5.0 (4)	5.9 (5)	−0.3 (4)	−0.1 (4)	0.4 (4)
C(11)	0.7561 (10)	0.2768 (8)	0.3945 (11)	5.2 (5)	8.8 (6)	5.6 (5)	−2.3 (4)	−0.4 (4)	1.1 (5)
C(12)	0.9002 (10)	0.2543 (10)	0.3839 (14)	4.0 (4)	13.9 (8)	9.5 (7)	−3.3 (5)	−2.5 (5)	3.3 (6)
C(13)	0.9598 (10)	0.2404 (9)	0.2528 (15)	3.5 (4)	8.4 (6)	12.9 (9)	−2.5 (4)	1.7 (5)	−0.5 (6)
C(14)	0.8795 (11)	0.2504 (8)	0.1356 (12)	5.9 (5)	6.6 (5)	7.7 (6)	−1.8 (4)	2.7 (5)	−1.2 (5)
C(15)	0.7330 (10)	0.2737 (7)	0.1441 (10)	5.2 (4)	5.4 (4)	5.0 (5)	−1.5 (3)	1.6 (4)	−0.5 (4)
C(16)	0.6749 (9)	0.2850 (6)	0.2780 (10)	4.4 (4)	3.7 (4)	5.3 (5)	−1.2 (3)	−0.0 (4)	−0.2 (4)
C(21)	0.1731 (9)	0.4786 (7)	0.1318 (10)	4.3 (4)	4.8 (4)	6.3 (5)	−1.2 (3)	−1.3 (4)	1.2 (4)
C(22)	0.1171 (10)	0.5812 (7)	0.1710 (11)	4.9 (5)	6.4 (5)	6.2 (5)	−0.2 (4)	−0.1 (4)	1.8 (4)
C(23)	0.2059 (11)	0.6444 (7)	0.2016 (12)	7.1 (6)	3.9 (4)	8.2 (6)	0.4 (4)	0.1 (5)	1.4 (4)
C(24)	0.3475 (11)	0.6056 (7)	0.1961 (12)	6.5 (5)	3.9 (4)	9.0 (6)	−1.4 (4)	0.2 (5)	1.4 (4)
C(25)	0.4040 (9)	0.5042 (7)	0.1580 (10)	4.6 (4)	4.3 (4)	6.4 (5)	−0.5 (3)	1.3 (4)	0.6 (4)
C(26)	0.3144 (9)	0.4422 (6)	0.1258 (8)	4.8 (4)	3.0 (3)	3.1 (4)	−0.6 (3)	0.1 (3)	0.3 (3)
C(31)	0.3163 (11)	0.2657 (7)	0.5239 (10)	7.3 (6)	5.9 (5)	4.8 (5)	−0.8 (4)	0.5 (4)	1.6 (4)
C(32)	0.3023 (13)	0.3001 (9)	0.6733 (11)	11.1 (7)	12.3 (7)	4.8 (5)	−5.2 (5)	−0.5 (5)	3.8 (5)
C(33)	0.2609 (12)	0.3989 (10)	0.7318 (11)	9.8 (6)	15.2 (8)	3.6 (5)	−7.2 (5)	1.7 (5)	−1.0 (5)
C(34)	0.2218 (13)	0.4622 (9)	0.6472 (13)	11.5 (7)	8.9 (6)	6.7 (6)	−4.5 (5)	3.2 (6)	−3.0 (6)
C(35)	0.2314 (11)	0.4299 (7)	0.4985 (11)	7.9 (6)	5.0 (5)	5.1 (5)	−1.3 (4)	1.5 (5)	−0.1 (4)
C(36)	0.2807 (8)	0.3315 (6)	0.4426 (9)	3.6 (3)	4.9 (4)	3.6 (4)	−1.7 (3)	1.1 (3)	0.1 (3)

atom	*x*	*y*	*z*	*B*, Å²	atom	*x*	*y*	*z*	*B*, Å²
H(11)	0.7131	0.2868	0.4852	7.23	H(24)	0.4088	0.6492	0.2190	7.28
H(12)	0.9580	0.2484	0.4664	9.33	H(25)	0.5038	0.4771	0.1540	6.04
H(13)	1.0601	0.2234	0.2442	8.05	H(31)	0.3507	0.1962	0.4816	6.86
H(14)	0.9237	0.2413	0.0459	7.43	H(32)	0.3223	0.2536	0.7334	9.43
H(15)	0.6751	0.2816	0.0622	6.38	H(33)	0.2597	0.4230	0.8334	8.82
H(21)	0.1125	0.4345	0.1094	6.05	H(34)	0.1861	0.5316	0.6891	8.78
H(22)	0.0173	0.6081	0.1767	6.91	H(35)	0.2039	0.4761	0.4382	7.27
H(23)	0.1676	0.7150	0.2266	7.35					

[a] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3))]$, where *a*, *b* and *c* are reciprocal lattice constants. [b] Isotropic thermal parameters are given for hydrogen atoms. These are based on the isotropic thermal parameters of the attached carbon atoms: $B(H_i) = B(C_i) + 1.0$ (Å²).

groups. All other aspects of the refinement proceeded without difficulty to give the very satisfactory figures of merit recorded in Table I.

Discussion

The structures reported here, together with those in the preceding paper, afford the first opportunity to compare exactly analogous $Rh_2(O_2CR)_4L_2$ compounds that differ only in having R = CH_3 or R = CF_3. It will be recalled that previous studies of $Rh_2(O_2CR)_4[(CH_3)_2SO]_2$ compounds did not allow such a comparison because the mode of attachment of $(CH_3)_2SO$ changed from S bonded with R = CH_3 or C_2H_5 to O bonded for R = CF_3.

This and other comparisons we shall wish to make will draw on the data collected in Table VI. It can be seen that for L = PPh_3 and $P(OPh)_3$, the change from R = CH_3 to R = CF_3 causes increases in the Rh–Rh bond length of 0.036 (5) and 0.027 (4) Å, respectively. A less exactly matched pair of compounds, with R = CH_3 and L = H_2O for one and R = CF_3 and L = EtOH for the other, have a negligible difference of 0.007 (6) Å. It appears that the large change in electronic character on going from CH_3 to CF_3 as the R group in the acid has only a small effect (0.000–0.040 Å) on the Rh–Rh bond length.

A somewhat larger effect shown by the data in Table VI is that changing from an axial ligand having O or N as the donor atom to one with P as the donor atom increases the Rh–Rh bond length, both for R = CH_3 and for R = CF_3. Thus, in compounds **1**–**3** the Rh–Rh distances are in the range from 2.371 to 2.396 Å while in **8** and **9** the distances are 2.450 and 2.443 Å, a shift of roughly 0.064 Å. Again, in **12** and **13** the distances are about 0.067 Å shorter than in **10** and **11**. With the sulfur-donor axial ligands, $(CH_3)_2SO$ and C_4H_8S, and with CO, intermediate values of the Rh–Rh distance are found for R = CH_3 or C_2H_5. The explanation of this Rh–Rh bond lengthening effect by P-donor ligands will be one of the objectives of the following theoretical paper.[5]

The final point requiring comment here is the trend, consistent for both R = CH_3 and CF_3, for the Rh–$P(OPh)_3$ bond to be slightly shorter than the Rh–PPh_3 bond, by 0.065 (8) Å for R = CH_3 and by a highly significant 0.072 (3) Å for R = CF_3. At the same time, the Rh–Rh bonds are also shorter

Table IV. Bond Distances (Å) and Angles (Deg) for $Rh_2(O_2CCF_3)_4(PPh_3)_2$ (1) and $Rh_2(O_2CCF_3)_4[P(OPh)_3]_2$ (2)

Distances

	1	2		1	2
Rh-Rh′	2.486 (1)	2.470 (1)	O(6)-C(26)		1.423 (8)
Rh-P	2.494 (2)	2.422 (2)	O(7)-C(36)		1.403 (9)
Rh-O(1)	2.031 (5)	2.047 (5)	C(1)-C(2)	1.50 (1)	1.53 (1)
Rh-O(2′)	2.057 (5)	2.053 (5)	C(3)-C(4)	1.50 (1)	1.49 (1)
Rh-O(3′)	2.041 (5)	2.040 (5)	C(11)-C(12)	1.38 (1)	1.36 (1)
Rh-O(4)	2.051 (5)	2.026 (6)	C(11)-C(16)	1.38 (1)	1.34 (1)
P-O(5)		1.590 (5)	C(12)-C(13)	1.35 (1)	1.36 (2)
P-O(6)		1.590 (6)	C(13)-C(14)	1.38 (1)	1.34 (1)
P-O(7)		1.599 (5)	C(14)-C(15)	1.37 (1)	1.38 (1)
P-C(16)	1.825 (7)		C(15)-C(16)	1.38 (1)	1.39 (1)
P-C(26)	1.828 (7)		C(21)-C(22)	1.41 (1)	1.38 (1)
P-C(36)	1.830 (8)		C(21)-C(26)	1.381 (9)	1.34 (1)
F(1)-C(2)	1.333 (9)	1.28 (1)	C(22)-C(23)	1.38 (1)	1.38 (1)
F(2)-C(2)	1.298 (9)	1.23 (1)	C(23)-C(24)	1.34 (1)	1.35 (1)
F(3)-C(2)	1.321 (9)	1.22 (1)	C(24)-C(25)	1.39 (1)	1.37 (1)
F(4)-C(4)	1.303 (9)	1.30 (1)	C(25)-C(26)	1.39 (1)	1.37 (1)
F(5)-C(4)	1.311 (9)	1.27 (1)	C(31)-C(32)	1.38 (1)	1.40 (1)
F(6)-C(4)	1.301 (10)	1.30 (1)	C(31)-C(36)	1.38 (1)	1.32 (1)
O(1)-C(1)	1.226 (8)	1.237 (9)	C(32)-C(33)	1.35 (1)	1.34 (2)
O(2)-C(1)	1.259 (8)	1.250 (9)	C(33)-C(34)	1.38 (1)	1.32 (2)
O(3)-C(3)	1.240 (8)	1.257 (9)	C(34)-C(35)	1.37 (1)	1.39 (2)
O(4)-C(3)	1.246 (8)	1.245 (9)	C(35)-C(36)	1.39 (1)	1.34 (1)
O(5)-C(16)		1.415 (9)			

Angles

	1	2		1	2
Rh′-Rh-P	174.51 (7)	177.45 (9)	F(2)-C(2)-C(1)	113.0 (7)	115.4 (9)
Rh′-Rh-O(1)	85.7 (1)	86.7 (2)	F(3)-C(2)-C(1)	113.8 (7)	112.6 (9)
Rh′-Rh-O(2′)	87.2 (1)	87.4 (1)	O(3)-C(3)-O(4)	128.2 (7)	127.4 (8)
Rh′-Rh-O(3′)	85.8 (1)	87.0 (1)	O(3)-C(3)-C(4)	113.3 (6)	115.7 (8)
Rh′-Rh-O(4)	87.2 (1)	86.6 (2)	O(4)-C(3)-C(4)	118.4 (7)	116.8 (8)
P-Rh-O(1)	88.8 (1)	90.8 (2)	F(4)-C(4)-F(5)	106.0 (7)	108 (1)
P-Rh-O(2′)	98.2 (1)	95.1 (2)	F(4)-C(4)-F(6)	106.2 (8)	104.4 (9)
P-Rh-O(3′)	93.8 (1)	92.4 (2)	F(4)-C(4)-C(3)	112.7 (7)	113.7 (8)
P-Rh-O(4)	93.3 (1)	94.0 (2)	F(5)-C(4)-F(6)	108.7 (8)	105.5 (9)
O(1)-Rh-O(2′)	72.9 (2)	174.0 (2)	F(5)-C(4)-C(3)	112.7 (7)	113.7 (9)
O(1)-Rh-O(3′)	89.1 (2)	90.7 (2)	F(6)-C(4)-C(3)	110.2 (7)	111.1 (9)
O(1)-Rh-O(4)	91.7 (2)	88.6 (2)	C(12)-C(11)-C(16)	120.1 (7)	120 (1)
O(2′)-Rh-O(3′)	89.5 (2)	89.1 (2)	C(11)-C(12)-C(13)	121.4 (8)	119 (9)
O(2′)-Rh-O(4)	88.8 (2)	90.9 (2)	C(12)-C(13)-C(14)	119.0 (7)	121 (1)
O(3′)-Rh-O(4)	172.9 (2)	173.6 (2)	C(13)-C(14)-C(15)	120.3 (7)	121 (1)
Rh-P-O(5)		122.3 (2)	C(14)-C(15)-C(16)	121.0 (7)	117 (1)
Rh-P-O(6)		111.5 (2)	P-C(16)-C(11)	123.1 (6)	
Rh-P-O(7)		114.1 (2)	P-C(16)-C(15)	118.4 (5)	
Rh-P-C(16)	108.9 (2)		O(5)-C(16)-C(11)		117.7 (8)
Rh-P-C(26)	115.0 (2)		O(5)-C(16)-C(15)		120.6 (8)
Rh-P-C(36)	118.6 (2)		C(11)-C(16)-C(15)	118.2 (7)	121.7 (9)
O(5)-P-O(6)		105.5 (3)	C(22)-C(21)-C(26)	119.8 (8)	119.0 (8)
O(5)-P-O(7)		98.8 (3)	C(21)-C(22)-C(23)	119.6 (8)	120.0 (9)
O(6)-P-O(7)		102.2 (3)	C(22)-C(23)-C(24)	120.7 (8)	119.7 (9)
C(16)-P-C(26)	104.8 (3)		C(23)-C(24)-C(25)	120.5 (8)	120.8 (9)
C(16)-P-C(36)	104.6 (3)		C(25)-C(25)-C(26)	120.5 (7)	119.0 (8)
C(26)-P-C(36)	103.6 (3)		P-C(26)-C(21)	123.1 (6)	
Rh-O(1)-C(1)	121.2 (5)	118.5 (5)	P-C(26)-C(25)	118.0 (5)	
Rh-O(2′)-C(1′)	117.5 (4)	117.1 (5)	O(6)-C(26)-C(21)		118.9 (7)
Rh-O(3′)-C(3′)	120.3 (4)	118.8 (5)	O(6)-C(26)-C(25)		119.4 (7)
Rh-O(4)-C(3)	118.1 (5)	120.2 (5)	C(21)-C(26)-C(25)	118.9 (7)	121.6 (7)
P-O(5)-C(16)		124.8 (5)	C(32)-C(31)-C(36)	119.9 (7)	119 (1)
P-O(6)-C(26)		123.6 (5)	C(31)-C(32)-C(33)	120.7 (8)	120 (1)
P-O(7)-C(36)		127.6 (5)	C(32)-C(33)-C(34)	120.4 (8)	119 (1)
O(1)-C(1)-O(2)	128.2 (7)	130.3 (8)	C(33)-C(34)-C(35)	119.3 (8)	122 (1)
O(1)-C(1)-C(2)	116.6 (6)	114.9 (7)	C(34)-C(35)-C(36)	121.2 (8)	118 (1)
O(2)-C(1)-C(2)	116.1 (6)	114.8 (7)	P-C(36)-C(31)	123.3 (6)	
F(1)-C(2)-F(2)	106.5 (7)	104 (1)	P-C(36)-C(35)	118.3 (6)	
F(1)-C(2)-F(3)	105.4 (7)	104 (1)	O(7)-C(36)-C(31)		119.4 (8)
F(1)-C(2)-C(1)	109.8 (7)		O(7)-C(36)-C(35)		118.2 (9)
F(2)-C(2)-F(3)	107.7 (8)	109 (1)	C(31)-C(36)-C(35)	118.4 (7)	122.2 (9)

in the same order by a statistically insignificant amount for R = CH_3, namely, 0.007 (6)Å, but by 0.016 (1) Å for R = CF_3. As with so many questions in chemistry, especially structural ones, we need to consider both steric and electronic effects in seeking an answer. It should first be pointed out that the small changes in the Rh–Rh bond lengths can be considered (at least qualitatively) to be the natural electronic consequence of the changes in the Rh–P bond lengths, regardless of whether Rh–P σ bonding, π bonding, or both come into play. This point will be made clear in the following paper.

Table VI. Rh-Rh and Rh-L Distances (Å) in $Rh_2(O_2CR)_4L_2$ Molecules[a]

compd no.	R	L	Rh-Rh	Rh-L	ref
1	CMe_3	H_2O	2.371 (1)	2.295 (2)	14
2	CH_3	H_2O	2.3855 (5)	2.310 (3)	15
3	CH_3	py	2.3963 (2)	2.227 (3)	16
4	CH_3	Me_2SO	2.406 (1)	2.451 (1)	14
5	C_2H_5	Me_2SO	2.407 (1)	2.445 (1)	17
6	CH_3	THT	2.413 (1)	2.517 (1)	14
7	CH_3	CO	2.4191 (3)	2.091 (3)	18
8	CH_3	PPh_3	2.4505 (2)	2.477 (1)	4
9	CH_3	$P(OPh)_3$	2.4434 (6)	2.412 (1)	4
10	CF_3	PPh_3	2.486 (1)	2.494 (2)	this work
11	CF_3	$P(OPh)_3$	2.470 (1)	2.422 (2)	this work
12	CF_3	Me_2SO	2.420 (1)	2.240 (3)	17
13	CF_3	EtOH	2.403 (6)	2.27 (1)	19

[a] Equivalent distances and angles have been averaged where appropriate.

We thus focus attention on the decreases in the Rh-P bond lengths, by ca. 0.07 Å, upon replacing PPh_3 by $P(OPh)_3$.

We believe that steric factors alone may account for this. The steric repulsions between the atoms of the central $Rh_2(O_2CCF_3)_4$ unit and the PY_3 ligands are expected to be considerably greater at a given Rh-P distance for Y = C_6H_5 than for Y = OC_6H_5. This is apparent qualitatively by comparing Figures 1 and 2; the phenyl groups in **2** are directed outward by the orientations around the P-OC_6H_5 bonds, whereas the phenyl groups in **1** are required to approach the $Rh_2(O_2CCF_3)_4$ unit rather closely. This great steric difference between PPh_3 and $P(OPh_3)_3$ was described semiquantitatively some time ago by Tolman[13] in terms of his cone-angle criterion. On a scale ranging from about 100° to 200° for the commonly used PY_3 ligands, PPh_3 and $P(OPh_3)_3$ have cone angles of 145 and 121°, respectively. Thus, the ~0.07 Å greater Rh-PPh_3 distance could well be caused by the greater steric demand of PPh_3 compared to that of $P(OPh)_3$. It is also possible that, as suggested by Christoph et al.,[4] the bond radius of phosphorus is smaller in $P(OPh)_3$ than in PPh_3.

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Registry No. **1**, 77966-16-6; **2**, 77966-17-7; $Rh_2(O_2CCF_3)_4$, 31126-95-1.

Supplementary Material Available: Table V (least-squares planes and dihedral angles) and tables of observed and calculated structure factors for the two compounds (25 pages). Ordering information is given on any masthead page.

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(13) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.
(14) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 323.
(15) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr., Sect. B.* **1971**, *B27*, 1664.
(16) Koh, Y.-B.; Christoph, G. G. *Inorg. Chem.* **1978**, *17*, 2590.
(17) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 2347. Further refinement of the structure reported in ref 14 with the inclusion of all hydrogen atoms in the Me_2SO ligand led to the bond distances and angles given here. These results will be reported fully in a later paper.
(18) Koh, Y.-B.; Christoph, G. G. *Inorg. Chem.* **1979**, *18*, 1122.
(19) Porai-Koshits, M. A.; Dikareva, L. M.; Sadikov, G. G.; Baranovskii, I. B. *Russ. J. Inorg. Chem.* (*Engl. Trans.*) **1979**, *24*, 716.

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Electronic Structure of Phosphine Adducts of Tetrakis(carboxylato)dirhodium(II). Pronounced Influence of Axial Ligands

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The electronic structure of phosphine adducts of $Rh_2(O_2CR)_4$ has been investigated by means of an $X\alpha$-SW molecular orbital calculation on the model compound $Rh_2(O_2CH)_4(PH_3)_2$. The method used to perform a calculation on this low-symmetry (C_{2h}) molecule containing a fragment of high symmetry (D_{4h}) is described in detail. The qualitative nature of the interactions between the phosphine ligands and the $Rh_2(O_2CH)_4$ moiety are very similar to those reported for $Rh_2(O_2CH)_4(H_2O)_2$; the magnitudes of these interactions are far different, however, resulting in a very different electronic structure. Strong σ donation by the phosphine ligands results in a highest occupied molecular orbital of Rh-Rh σ and Rh-P σ^* symmetry, consistent with the ESR spectra of the radical cations of phosphine adducts. Contrary to previous assertions, no Rh→P back-bonding is evident. The radical cations of the phosphine adducts are predicted to have longer Rh-Rh bonds than those found in the neutral adducts, in contrast to the decrease in Rh-Rh bond length found for $[Rh_2(O_2CCH_3)_4(H_2O)_2]^+$.

Introduction

The rapid growth in the synthetic and structural chemistry of dinuclear transition-metal complexes containing strong metal-metal bonds has provided a wealth of information about the nature of metal-ligand and metal-metal interactions.[1] These systems provide interesting challenges to quantum chemical methods in that they afford compounds having a great variety of metals and ligands within a common structural genre. Discussions of the electronic structural aspects of dinuclear transition-metal complexes have not been without controversy, as in the case of the $Cr_2(O_2CR)_4L_2$ systems in which SCF-HF calculations without CI[2] have been found to give conclusions inconsistent with structural and more complete theoretical results.[3-5] Discussions of the electronic structures

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(1) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.
(2) Garner, C. D.; Hillier, I. H.; Guest, M. F.; Green, J. C.; Coleman, A. W. *Chem. Phys. Lett.* **1976**, *41*, 91.
(3) Cotton, F. A.; Stanley, G. G. *Inorg. Chem.* **1977**, *16*, 2668.
(4) Bénard, M. *J. Chem. Phys.* **1979**, *71*, 2546.