moieties have been compiled by other workers.[20]

Finally, it is worthy of mention that the Fe to CO bond lengths decrease with the carbonyl content of the molecules within the series $Fe_2(CO)_9$,[5] $Fe_2(CO)_8(\mu\text{-}CH_2)$ (**1**), $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)_2$,[22] $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (**2**). This, of course, is indicative of increasing $d\pi_{Fe} \rightarrow p\pi^*_{CO}$ back-bonding and is in agreement with the established electronic structure of these complexes, in which the $\eta^5\text{-}C_5H_5$ ligands, principally, and the μ-CRR′ ligands lack the electron-acceptor characteristics of CO.[18,23]

Acknowledgment. This work was supported by the Robert A. Welch Foundation (Grant F-233). We are also indebted to the National Science Foundation for purchase of the Syntex $P2_1$ diffractometer (Grant GP-37028) and to Professor Rowland Pettit, Charles Sumner, and Paul Lu for supplying excellent single crystals of the subject complexes.

Registry No. **1**, 73448-08-5; **2**, 75811-60-8.

Supplementary Material Available: Listings of observed and calculated structure factors for $Fe_2(CO)_8(\mu\text{-}CH_2)$ at −35 and 22 °C and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CHCH_3)$ (18 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, The University of Chicago, Chicago, Illinois 60637, and The Ohio State University, Columbus, Ohio 43210

Interpretation of σ and π Components in M–P Bonds. Comparison of the Bis(triphenylphosphine) and Bis(triphenyl phosphite) Adducts of Dirhodium Tetraacetate

G. G. CHRISTOPH,* J. HALPERN,* G. P. KHARE, Y. B. KOH, and CYNTHIA ROMANOWSKI

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The structures of the red bis(triphenyl phosphite) and bis(triphenylphosphine) adducts of dirhodium tetraacetate have been characterized by single-crystal X-ray diffraction studies. The $P(OPh)_3$ adduct crystallizes with monoclinic cell constants $a = 26.134$ (9) Å, $b = 9.951$ (2) Å, $c = 22.512$ (7) Å, and $\beta = 118.55$ (2)°, with four molecules of the complex and four molecules of toluene solvent per unit cell. The structure was solved with the assumption of space group $C2/c$ and refined to conventional R factors: $R(F) = 0.068$ and $R_w(F^2) = 0.075$ for 7073 unique intensities. The PPh_3 adducts forms triclinic crystals with cell constants $a = 9.56$ (1) Å, $b = 9.19$ (1) Å, $c = 12.85$ (1) Å, $\alpha = 110.09$ (5)°, $\beta = 102.56$ (5)°, and $\gamma = 88.85$ (5)°, with one molecule per unit cell, and space group $P\bar{1}$. The structure was solved and refined by full-matrix least-squares to disagreement indices $R(F) = 0.022$ and $R_w(F^2) = 0.075$ for 3557 unique reflections. The dirhodium tetraacetate nucleus in both complexes is essentially identical in structure with that found for the bis(aquo) and bis(pyridine) adducts, except that the Rh–Rh bond is somewhat longer, being 2.4434 (6) Å in the bis($P(OPh)_3$) adduct and 2.4505 (2) Å in the bis(PPh_3) adduct. The Rh–P distances are both extraordinarily long, 2.412 (1) and 2.477 (1) Å, respectively, some 0.1–0.3 Å longer than in normal mononuclear Rh(I) or Rh(III) complexes. As such, any Rh→P π back-bonding is expected to be very much weaker than normal. The results are strongly contrasted against those from a reported comparative study of the $P(OPh)_3$ and PPh_3 complexes of $Cr(CO)_5$, in which π back-bonding effects dominated the M–P bonding. The conclusion is drawn that arguments on the existence of π back-bonding are only valid in limited series of very similar compounds. The structures of the bridged, semibridged, and nonbridged dirhodium complexes $Rh_2(OAc)_4(PPh_3)_2$, $Rh_2(OAc)_2(dmg)_2(PPh_3)_2$, and $Rh_2(dmg)_4(PPh_3)_2$ are briefly compared.

Introduction

The intimate interactions between the metal atoms in cluster complexes permit the electronic influence of various ligands to be both dramatic and pervasive, in the sense that "these can be transmitted through the cluster from one metal atom to another."[1] Thus the mutual interactions of metal–metal and metal–ligand bonds portend to be an extremely important aspect of the versatile and growing chemistry of cluster-based systems. We have consequently undertaken a systematic, high-precision structural study of an extended homologous series of dinuclear rhodium complexes in the expectation that an understanding of substituent effects on the metal–metal interactions in clusters will be best achieved by first understanding the cumulative bonding effects in the smallest of metal cluster compounds.

We have chosen the dirhodium tetraacetate nucleus for these studies for four primary reasons. First, the metal–metal bond is unusually short[2] and, by implication, quite strong, thus assuring the ready transmission of electronic substituent effects. Second, it has proven possible to prepare a wide variety of axial ligand adducts of this nucleus,[3] thereby availing us the opportunity to probe the Rh–Rh bond with a broad range of ligand strengths. Third, the essentially octahedral coordination of the rhodium atoms yields a very stable configuration of the bridging acetate groups. This leaves the axial sites extraordinarily unrestricted and presumably would even permit axial ligands with cone angles[4] as great as 180° to be accommodated without steric difficulty. Fourth, the Rh–Rh bond in the tetracarboxylate complexes has been described as both triple[2,5] and as single[6,7] by different research groups, and we hoped by our studies to contribute to a resolution of the question of the character of the metal–metal bond in this system. This

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* To whom correspondence should be addressed: G.G.C., The Ohio State University; J.H., The University of Chicago.

(1) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959.
(2) Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr., Sect. A* **1971**, *A27*, 1664.
(3) Johnson, S. A.; Hunt, H. R.; Neumann, H. M. *Inorg. Chem.* **1963**, *2*, 960. Das, K.; Kadish, K. M.; Bear, J. L. *Ibid.* **1978**, *17*, 930. Shafranskii, V. N.; Mal'kova, T. A. *Zh. Obsch. Khim.* **1976**, *46*, 1197. Winkhaus, G; Ziegler, P. *Z. Anorg. Allg. Chem.* **1967**, *350*, 51. Richman, R. M.; Kuechler, T. C.; Tanner, S. P.; Drago, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 1055.
(4) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956; *Chem. Rev.* **1970**, *77*, 313.
(5) Cotton, F. A.; Norman, J. G. *J. Am. Chem. Soc.* **1971**, *93*, 80. Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1.
(6) Dubicki, L.; Martin, R. L. *Inorg. Chem.* **1970**, *9*, 673.
(7) Norman, J. G.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791.

particular interest is further heightened by the recent report by Kawamura et al. on the ESR spectra of frozen solutions of the cation radicals[8] of Rh$_2$(OAc)$_4$(PPh$_3$)$_2$ and Rh$_2$(OAc)$_4$(P(OPh)$_3$)$_2$ and by Bursten and Cotton's report of Xα–SW–SCF calculations on Rh$_2$(O$_2$CH)$_4$(PH$_3$)$_2$.[9]

The existence of metal-to-phosphorus π back-bonding has been both inferred and criticized on the basis of much accumulated spectroscopic and structural data,[10] and the problem of the magnitudes of the σ and π components in M–L bonds remains a current topic of active interest and controversey.[11] The situation is complicated in that the σ and π interactions, if they *are* both present, are inextricably intertwined; a strengthening of M$\rightarrow$P back-bonding generally leads to a shorter metal–phosphorus bond and thus to a stronger σ component through the synergic interaction, even when the σ component by itself is expected to weaken. for example, changing the R substituent in the ligand PR$_3$ from R = phenyl to R = phenoxy should augment π back-bonding while making the phosphorus a poorer σ donor by rendering it more electronegative. In a comparative structural study of Cr(CO)$_5$PPh$_3$ and Cr(CO)$_5$P(OPh)$_3$ by Grim and co-workers,[12] such π-back-bonding effects were found to be dominating. However, Carty and co-workers found such π-back-bonding arguments unnecessary in comparing the structures of Pd(NCS)$_2$(PPh$_3$)$_2$ and Pd(SCN)$_2$(P(OPh)$_3$)$_2$.[13] As the availability of metal d electrons in π symmetry orbitals will in general differ from metal to metal, and, even in different oxidation states of the same metal, one should expect to find a whole range of trans-influence effects as the proportions and magnitudes of the σ and π components are altered.[14] We report here the structure determinations of Rh$_2$(OAc)$_4$(PPh$_3$)$_2$ and Rh$_2$(OAc)$_4$(P(OPh$_3$)$_2$ in which the phosphine and phosphite ligands show considerably different behavior toward the metal atoms than in the chromium pentacarbonyl analogues and remark on the contribution of steric effects to the Rh–Rh and Rh–P bond lengths in the molecules Rh$_2$(OAc)$_4$(PPh$_3$)$_2$, Rh$_2$(dmg)$_2$(OAc)$_2$(PPh$_3$)$_2$,[15] and Rh$_2$(dmg)$_4$(PPh$_3$)$_2$.[16]

Experimental Section

Preparation and Crystallization. Rh$_2$(OAc)$_4$(P(OPh)$_3$)$_2$. Rh$_2$(OAc)$_4$(CH$_3$OH)$_2$ was prepared by a known procedure[17] from RhCl$_3$·3H$_2$O (Alfa Inorganics). Rh$_2$(OAc)$_4$ was prepared immediately before use by boiling the finely powdered bis(methanol) adduct in benzene until IR spectra showed no peaks attributable to the axial ligand (ca. 10 min). A few drops of liq. P(OPh)$_3$ (aldrich Chemical Co.) were added to 10 mL of toluene (J. T. Baker) containing approximately 20 mg of fresh Rh$_2$(OAc)$_4$. The resulting orange-red solution was evaporated to dryness under nitrogen at room temperature to obtain red needlelike crystals.

Rh$_2$(OAc)$_4$(PPh$_3$)$_2$ was prepared by the method previously described.[18] Single crystals suitable for X-ray studies were grown from acetone.

Solvents and reagents were used as received without further purification.

X-ray Data Collection. Rh$_2$(OAc)$_4$(P(OPh)$_3$)$_2$. A fragment of a needle-shaped crystal with dimensions of 0.33 × 0.38 × 0.25 mm was mounted on a goniometer with the needle axis (010) collinear with the ϕ axis. The systematic absences determined from precession photographs were consistent with either space group $C2/c$ or Cc: $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$. Accurate cell dimensions were determined from a least-squares analysis of the centering angles of 15 reflections in the region $14.0° < 2\theta < 27.0°$ (Mo Kα); a = 26.134 (9) Å, b = 9.951 (2) Å, c = 22.512 (7) Å, β = 118.55 (2)°, V = 5143 (2) Å^3, d_{measd} = 1.42 (1) g/cm^3, and d_{calcd} = 1.489 g/cm^3 for Z = 4. The density could not be accurately measured because the compound proved to be somewhat soluble in the density standards employed.

A total of 9796 intensities were measured on a Syntex P$\bar{1}$ automated four-circle diffractometer using graphite-monochromatized Mo K$\bar{\alpha}$ radiation (λ = 0.71069 Å). The data were collected for 2θ values in the range 4.0° to 60.0° at 20 ± 1 °C by the ω–2θ scan technique. The scan rate was varied from 2°/min for reflections giving less than 200 counts during a 2-s preliminary scan to 24°/min for those giving more than 2000 counts. The background was measured at the extremes of each scan for a period of half the total scan time at 1.0° in 2θ below the Kα_1 and above the Kα_2 line. Seven standard reflections were remeasured after every 93 reflections in order to monitor the crystal and electronic stability. Reflections (002) and (00$\bar{2}$) were not measured due to overflowed counting rates. The scan counts were converted into integrated intensities by use of the formula

$$I = R(C - T(B_1 + B_2))$$

where R is the scan rate, C is the scan counts, B_1 and B_2 are the background counts, and T is the ratio of the scan time to the total background counting time. Decay and Lorentz and polarization corrections were applied and the data were scaled by means of a Wilson plot.[19] A total of 7073 independent reflections remained after the multiply measured reflections were averaged and the systematically absent intensities deleted. Of these, 4028 reflections had intensities greater than 3$\sigma(I)$. Absorption corrections were deemed unnecessary because ϕ scans for a number of reflections showed no more than a 4% variation from their average values, and the linear absorption coefficient (for Mo K$\bar{\alpha}$ radiation) was only 7.5 cm^{-1}. All reflections were assigned estimated standard errors according to

$$\sigma^2(I) = R(C + T^2(B_1 + B_2) + (pI)^2)$$

where p = 0.02 was chosen to account for the errors expected to be proportional to the diffracted intensity.[20]

Rh$_2$(OAc)$_4$(PPh$_3$)$_2$. A tabular crystal of approximate dimensions 0.30 × 0.20 × 0.15 mm was mounted along what was later found to be the {100} direction. Precession photographs ($h0l$, $h1l$, $hk0$, and hkl zones) using Cu Kα radiation indicated the crystal system was triclinic, with probable space group $P1$ or $P\bar{1}$. Unit cell dimensions resulting from least-squares fitting of the diffractometer setting angles for 25 carefully centered reflections (Mo K$\bar{\alpha}$ radiation) are: a = 9.557 (10) Å, b = 9.190 (14) Å, c = 12.853 (14) Å, α = 110.09 (5)°, β = 102.56 (5)°, and γ = 88.85 (5)°. The calculated and observed densities (flotation method, carbon tetrachloride/hexane) are in good agreement, 1.55 g/cm^3 and 1.56 (2) g/cm^3, respectively, for one molecule per unit cell.

Intensity data were collected by the ω–2θ scan technique on a Picker FACS-I automated diffractometer using Zr-filtered, graphite-monochromatized Mo Kα radiation. The takeoff angle was 1.5° and the scan rate and scan width were respectively 1.0°/min and 1.6° in 2θ. Stationary counter backgrounds were counted for 20 s at the ends of the each scan. Attenuators were automatically inserted whenever the counting rate exceeded 10000 Hz. The intensities of three strong reflections were measured periodically to monitor the

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

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

(10) Venanzi, L. M. *Chem. Br.* **1968**, *4*, 162. Tolman, C. A. *J. Am. Chem. Soc.*, **1970**, *92*, 2953. Strohmeier, W.; Müller, F. J. *Chem. Ber.* **1967**, *100*, 2812. Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1. Kruck, T. *Angew, Chem., Int. Ed. Engl.* **1967**, *6*, 53. Nixon, J. F. *Endeavor* 1973, *32*, 19; Clark, R. J.; Busch, M. A. *Acc. Chem. Res.* **1973**, *6*, 246. Angelici, R. J.; Malone, M. D. *Inorg. Chem.* **1967**, *6*, 1731.

(11) Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1980**, *19*, 1805. Bursten, B. E.; Freier, D. G.; Fenske, R. F. *Ibid.* 1810. Chen, H. W.; Jolly, W. L. *Ibid.* **1979**, *18*, 2548. Zeigler, T.; Rauk, A. *Ibid.*, **1755**. Johnson, B. V.; Ouseph, P. J.; Hsieh, J. S.; Steinmetz, A. L.; Shade, J. E. *Ibid.* **1796**.

(12) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *J. Am. Chem. Soc.* **1969**, *91*, 4326; *Inorg. Chem.* **1973**, *12*, 265.

(13) Carty, A. J.; Chieh, P. C.; Taylor, N. J.; Wong, Y. S. *J. Chem. Soc., Dalton Trans.* **1976**, 572.

(14) Chistoph, G. G.; Koh, Y. B. *J. Am. Chem. Soc.* **1979**, *101*, 1422. Koh, Y. B.; Christoph, G. G. *Inorg. Chem.* **1979**, *18*, 1122.

(15) Halpern, J.; Kimura, E.; Molin-Case, J.; Wong, C. S. *J. Chem. Soc. D* **1971**, 1207.

(16) Caulton, K. G.; Cotton, F. A. *J. Am. Chem. Soc.* **1969**, *91*, 6518; *Ibid.* **1971**, *93*, 1914.

(17) Rempel, G. A.; Legzdins, P.; Smith, H.; Wilkinson, G. *Inorg. Synth.* **1971**, *13*, 90.

(18) Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Hefter, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

(19) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151.

crystal and instrumental stability. None of these standards deviated more than 2% from their mean values.

The intensities of 3854 reflections with 2θ values in the range 5.0–50.0° were measured and 3104 of these had intensities greater than or equal to $3\sigma(I)$; however, all 3559 unique reflections were used in the solution and refinement of the structure. As $\mu(\text{Mo K}\alpha)$ was only 9.14 cm^{-1}, no absorption corrections were deemed necessary. The intensities were corrected in the normal way for Lorentz–polarization effects and standard deviations in the net intensities were calculated by using the above formula with $p = 0.04$. The centric space group was verified by the intensity statistics.

Solution and Refinement of the Structures

$Rh_2(OAc)_4(P(OPh)_3)_2$. The position of Rh and P were determined from a three-dimensional Patterson map. A Fourier map based on the heavy-atom positions revealed the structure of the acetate groups and fragments of the phenoxy groups (*C*2/*c* was assumed in calculating the Fourier map and the successful refinement of the structure confirmed that this was the correct space group). Remaining atoms were found from additional Fourier and difference Fourier calculations. Least-squares refinement of the positions and isotropic temperature factors gave, in four cycles, the conventional agreement factors $R = 0.18$ and $R_w = 0.34$. The temperature factors for atoms having no hydrogen atoms were allowed to refine anisotropically in the next few cycles. A difference synthesis calculated at this stage showed the presence of disordered solvent molecules (toluene) at the crystallographic centers of symmetry, the electron densities of individual atoms being no more than 3.5 e/Å^3. An unsuccessful attempt was made to separately refine two half-weight toluene molecules, after which the solvent carbon atoms were allowed to refine independently, with population factors of 0.5. Examination of general planes of a difference synthesis perpendicular to the acetate C–CH$_3$ axes revealed the positions of hydrogen atoms. The phenyl hydrogen atoms were placed at calculated positions 0.95 Å from the carbon atoms to which they were bonded. No attempts were made to locate the hydrogen atoms of the solvent molecules. In the final cycles the toluene carbon atoms C(41), C(44), and C(45) were given a population factor of 0.5 and the hydrogen atom coordinates and temperature factors were allowed to refine. The refinement was terminated when all shifts were less than one-tenth of the standard deviations for nonhydrogen atoms and less than one-fifth for hydrogen atoms. The final agreement factors were $R = 0.068$, $R_w(F^2) = 0.075$, and GOF $= [\sum w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{1/2} = 1.25$ where $n_o = 7073$ data and $n_p = 409$ parameters. The maximum and minimum peaks in the final difference map were 0.96 and -0.80 e/Å^3, respectively, the former in the proximity of C(4) and the latter not associated with any particular atom. Elimination of reflections with intensities less than $3\sigma(I)$ significantly improved the agreement factors to $R = 0.036$ and $R_w = 0.063$, although the goodness of fit increased slightly to 1.43 for 4028 data and 409 parameters. The results given in Table I, however, are from the final least-squares cycle based on 7073 independent reflections.

The functions minimized in the full-matrix least-squares refinement was of the form $w(k^2F_o^2 - F_c^2)^2$, where k is a scale factor and w the weight given by $1/[\sigma^2(F_o^2)]$. The scattering factors for O, C, and P were taken from ref 21a and that for Rh from ref 21b. The form factor of H was that of Stewart, Davidson, and Simpson.[21c] The scattering factor for Rh was corrected for the real component of anomalous dispersion by using the values given in ref 21b. All computations were carried out with the use of the locally modified CRYM crystallographic computing system.[22] Tables of observed and calculated structure factor amplitudes are included in the supplementary material.[23]

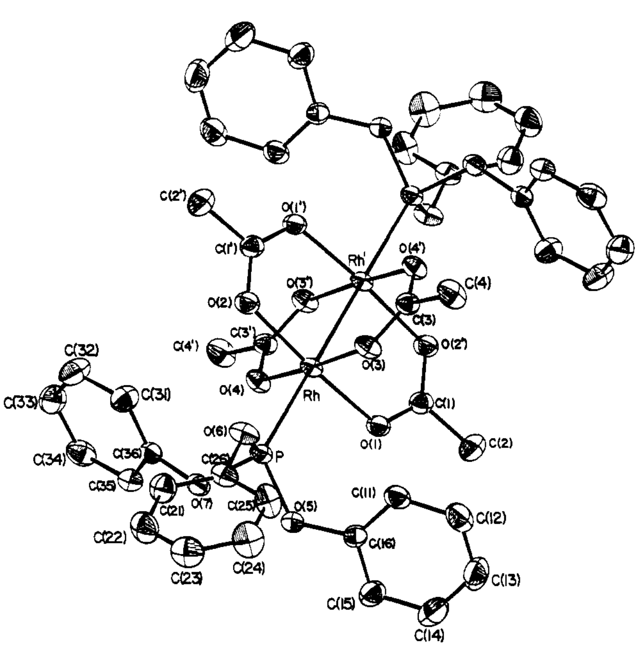

Figure 1. ORTEP diagram showing the conformation, thermal motion (ellipsoids are shown at 25% level), and atom numbering for $Rh_2(OAc)_4(P(OPh)_3)_2$.

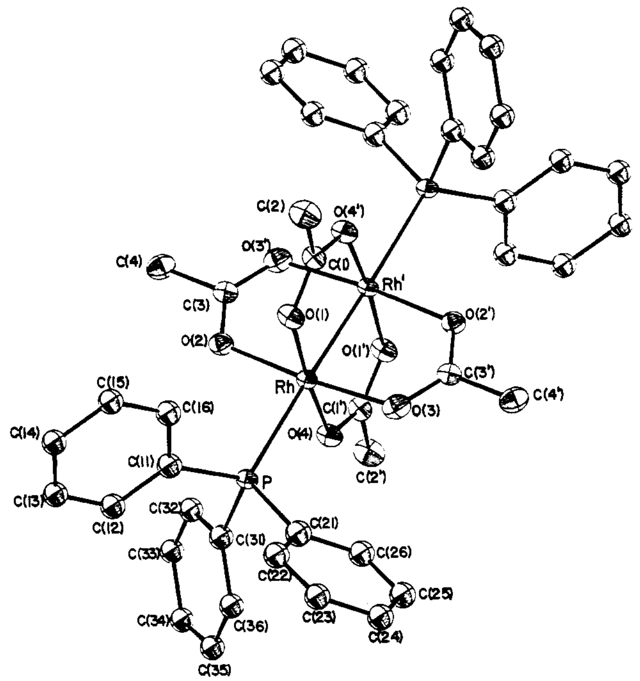

Figure 2. ORTEP diagram for $Rh_2(OAc)_4(PPh_3)_2$. The thermal vibrational ellipsoids are shown at the 25% level.

$Rh_2(OAc)_4(PPh_3)_2$. The structure was solved by the heavy-atom Patterson method. The positions of the rhodium and phosphorus atoms were obtained from the Patterson map, while those of the remaining nonhydrogen atoms were determined from difference Fourier maps phased by using the Rh and P coordinates. Methyl hydrogen atoms were located on difference Fourier maps after several cycles of least-squares refinement of the heavy-atom parameters while the phenyl hydrogen atoms were placed at idealized positions. In the final cycles of full-matrix least-squares refinement, the coordinates of all atoms (including hydrogen atoms), anisotropic thermal parameters of the nonhydrogen atoms, isotropic temperature factors for the hydrogen atoms, and the scale and secondary extinction parameters were all varied. Convergence was assumed when no atomic parameter shift exceeded 5% of its standard deviation. The final conventional R factor was 0.022, the weighted $R_w(F^2)$ was 0.057, and the GOF $= [\sum w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{1/2} = 0.987$ for 3557 reflections (the 201 and 501 were given zero weight due to probable data errors). The final difference Fourier map showed no peak greater than ±0.26 e/A^3 nor less than 0.29 e/Å^3; the average noise level of the map was ±0.15 e/Å^3. Atomic scattering factors were taken from the same sources as above, and all computations were carried out with use of the CRYM

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(20) Busing, W. R.; Levy, H. A. *J. Chem. Phys.* **1957**, *26*, 563.

(21) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England: (a) **1962**; Vol. III. (b) **1974**, Vol. IV. (c) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3157.

(22) DuChamp, D. J. "Program and Abstracts", Paper B-14, Meeting of the American Crystallographic Association, Bozeman, MT, 1965.

(23) See paragraph at end of paper regarding availability of supplementary material.

Table I. Fractional Coordinates (× 10^5) and Anisotropic Thermal Parameters (× 10^4) of $Rh_2(OAc)_4(P(OPh)_3)_2$[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	equiv iso B, Å^2
Rh	22918 (1)	−16822 (2)	2290 (1)	485 (1)	301 (1)	430 (1)	−6 (1)	285 (1)	−43 (1)	2.98
P	18822 (3)	−677 (8)	6832 (4)	507 (5)	341 (4)	427 (4)	20 (4)	259 (4)	−48 (4)	3.24
O(1)	31188 (8)	−13133 (20)	9667 (10)	507 (12)	422 (12)	510 (13)	−10 (10)	248 (11)	−94 (10)	3.77
O(2)	14924 (9)	−21789 (21)	−5335 (10)	501 (13)	488 (13)	579 (14)	3 (11)	274 (12)	−100 (11)	4.07
O(3)	22412 (9)	−32130 (20)	8032 (10)	706 (14)	397 (12)	575 (13)	1 (12)	462 (12)	−7 (11)	3.90
O(4)	23739 (9)	−2892 (20)	−3805 (10)	658 (14)	355 (11)	558 (13)	32 (11)	397 (12)	35 (10)	3.78
O(5)	22479 (9)	6076 (20)	14138 (10)	622 (13)	458 (12)	428 (12)	94 (12)	176 (11)	−92 (10)	4.21
O(6)	13290 (9)	−6775 (21)	7157 (11)	650 (14)	443 (13)	808 (16)	−93 (12)	485 (14)	−169 (12)	4.55
O(7)	16659 (10)	13785 (20)	3322 (10)	812 (16)	377 (12)	464 (12)	98 (12)	267 (12)	0 (10)	4.45
C(1)	35367 (14)	−19710 (29)	9847 (15)	559 (20)	425 (19)	462 (18)	−44 (15)	240 (16)	−17 (14)	3.82
C(2)	41241 (17)	−17268 (53)	15796 (24)	584 (21)	861 (28)	681 (25)	19 (28)	109 (21)	−153 (25)	6.22
C(3)	24302 (13)	−43617 (30)	7702 (15)	549 (19)	394 (17)	466 (18)	−41 (15)	263 (16)	−8 (14)	3.64
C(4)	24231 (22)	−54219 (39)	12464 (22)	1144 (33)	515 (21)	686 (24)	74 (25)	608 (24)	156 (20)	5.61
C(11)	27469 (16)	−12842 (35)	21378 (17)	744 (25)	488 (19)	562 (20)	55 (19)	365 (20)	−52 (17)	4.56
C(12)	32311 (21)	−17191 (43)	27313 (20)	1184 (34)	611 (24)	632 (24)	253 (26)	523 (25)	104 (21)	6.10
C(13)	36446 (21)	−8371 (55)	31347 (21)	889 (32)	1127 (38)	528 (24)	330 (31)	206 (25)	64 (26)	6.93
C(14)	35973 (20)	4996 (51)	29686 (20)	807 (30)	965 (38)	624 (26)	−108 (30)	151 (25)	−117 (25)	6.93
C(15)	31271 (17)	9476 (39)	23941 (17)	722 (24)	633 (23)	482 (20)	−57 (21)	213 (20)	−9 (19)	5.07
C(16)	27115 (13)	478 (32)	19830 (14)	549 (20)	538 (19)	383 (16)	59 (17)	254 (15)	−43 (15)	3.77
C(21)	6109 (17)	8130 (41)	7301 (20)	588 (23)	734 (26)	704 (26)	23 (21)	317 (21)	15 (22)	5.30
C(22)	3309 (16)	13352 (45)	10698 (24)	594 (23)	806 (29)	1012 (32)	146 (23)	436 (25)	−33 (25)	6.18
C(23)	4902 (17)	9431 (47)	17090 (23)	701 (25)	927 (31)	988 (32)	−24 (24)	610 (26)	−135 (27)	6.21
C(24)	9286 (20)	673 (50)	20305 (22)	921 (30)	1004 (34)	872 (31)	−92 (28)	660 (26)	173 (27)	6.60
C(25)	12156 (17)	−4691 (40)	17072 (21)	730 (25)	718 (25)	852 (27)	163 (22)	525 (23)	239 (22)	5.57
C(26)	10522 (14)	−925 (33)	10568 (17)	525 (19)	444 (18)	712 (22)	−51 (17)	385 (18)	−83 (17)	4.13
C(31)	9485 (16)	9257 (38)	−8193 (18)	702 (23)	594 (22)	570 (21)	−162 (20)	287 (20)	1 (18)	4.96
C(32)	6976 (18)	13196 (44)	−15001 (20)	792 (26)	857 (30)	582 (23)	−249 (25)	199 (22)	−89 (22)	6.29
C(33)	9086 (20)	24011 (43)	−16905 (19)	1058 (32)	702 (26)	515 (23)	23 (27)	308 (24)	100 (20)	6.21
C(34)	13828 (18)	30841 (34)	−12131 (19)	941 (28)	469 (22)	765 (25)	−62 (20)	530 (24)	15 (18)	5.32
C(35)	16379 (15)	27156 (34)	−5432 (17)	594 (21)	439 (18)	574 (21)	−29 (17)	267 (19)	−59 (16)	4.27
C(36)	14114 (13)	16492 (32)	−3576 (14)	545 (18)	392 (15)	462 (17)	53 (17)	242 (15)	−22 (15)	3.67
Solvent Molecule										
C(41)	3085 (41)	−48112 (164)	+246 (57)	627 (58)	1972 (144)	929 (76)	597 (76)	418 (59)	896 (92)	9.13
C(42)	6989 (38)	−49651 (133)	−1448 (45)	1755 (74)	2994 (112)	1698 (74)	873 (84)	1027 (68)	1330 (77)	16.31
C(43)	1372 (39)	−39498 (78)	+3202 (29)	1598 (63)	1842 (77)	900 (44)	1020 (60)	479 (47)	611 (45)	11.80
C(44)	−2456 (72)	−39224 (141)	+4141 (61)	1501 (127)	1317 (115)	1202 (103)	754 (101)	371 (97)	638 (88)	11.48
C(45)	6795 (56)	−38447 (114)	+2167 (49)	1264 (95)	1025 (82)	769 (65)	153 (75)	208 (70)	329 (59)	8.95

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(1)	432 (2)	−229 (5)	170 (2)	11 (1)	H(22)	50 (1)	116 (3)	31 (2)	5 (1)
H(2)	437 (2)	−121 (6)	153 (3)	13 (2)	H(23)	6 (1)	190 (3)	83 (2)	5 (1)
H(3)	421 (2)	−118 (6)	201 (2)	13 (2)	H(24)	28 (1)	132 (4)	192 (2)	7 (1)
H(4)	247 (2)	−512 (4)	168 (2)	8 (1)	H(25)	106 (2)	−18 (4)	246 (2)	8 (1)
H(5)	272 (2)	−605 (5)	140 (2)	11 (1)	H(26)	157 (1)	−108 (3)	195 (2)	6 (1)
H(6)	217 (2)	−589 (6)	105 (3)	14 (2)	H(32)	81 (1)	22 (3)	68 (1)	5 (1)
H(12)	250 (1)	−186 (3)	188 (1)	4 (1)	H(33)	38 (2)	64 (4)	182 (2)	10 (1)
H(13)	317 (1)	−260 (3)	279 (1)	5 (1)	H(34)	74 (1)	263 (3)	219 (2)	7 (1)
H(14)	393 (2)	−106 (4)	356 (2)	7 (1)	H(35)	157 (1)	384 (3)	140 (1)	6 (1)
H(15)	389 (2)	106 (4)	321 (2)	9 (1)	H(36)	196 (1)	320 (3)	19 (2)	6 (1)
H(16)	307 (1)	183 (3)	224 (2)	6 (1)					

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2klb^*c^*U_{23})]$. Hydrogen atom coordinates have been multiplied by 10^3.

programs. The final values for the atomic parameters are given in Table II. The listings of the observed and calculated structure factor amplitudes are included with the supplementary material.[23]

Results and Description of the Structures

The bond distances and angles for $Rh_2(OAc)_4(P(OPh)_3)_2$ are presented in Tables III and IV and those for $Rh_2(OAc)_4(PPh_3)_2$ in Tables V and VI.. Perspective ORTEP views showing the numbering schemes are drawn in Figure 1 for the bis(phosphite) and in Figure 2 for the bis(phosphine) complex.

Both molecules possess a crystallographic center of symmetry at the midpoint of the Rh–Rh axis. The disordered toluene solvent in the bis(phosphite) structure is situated at a crystallographic center of symmetry between the phosphite moieties, as shown in Figure 3. The molecular packing is dominated by normal van der Waals interactions. In both structures the rhodium atom is displaced approximately 0.1 Å from its four equatorial oxygen atoms toward the phosphorus atom. The acetate groups are strictly planar; the dihedral angles between the two crystallographically independent acetate groups are 93 (2)° in the bis(phosphite) adduct and 92 (2)° in the bis(phosphine) adduct; neither are significantly different from 90°, and the dirhodium tetraacetate nucleus in both compounds thus possesses essentially D_{4h} symmetry.

The average chemically equivalent distances and angles, respectively for the bis(phosphite) and bis(phosphine) complexes, are as follows: Rh–O, 2.039 (3) and 2.045 (4) Å; C–O, 1.258 (6) and 1.260 (3) Å; C–CH_3, 1.505 (7) and 1.502 (2) Å; ∠Rh–Rh–O, 87.3 (1) and 87.1 (1)°; ∠O–C–O, 126.4 (4) and 125.7 (4)°; ∠Rh–O–C, 119.5 (3) and 120.0 (4)°. All are within two standard deviations of each other. While the acetate frameworks in the two adducts are essentially identical in these respects, the Rh–Rh distance in the bis(phosphite)

Table II. Fractional Coordinates ($\times 10^5$) and Anisotropic Thermal Parameters ($\times 10^4$) of $Rh_2(OAc)_4(PPh_3)_2$[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	equiv iso B, Å^2
Rh	7946 (1)	1218 (1)	9168 (1)	304 (1)	254 (1)	238 (1)	28 (1)	27 (1)	88 (1)	2.14
P	24841 (5)	1788 (5)	26925 (4)	297 (3)	271 (3)	259 (3)	22 (2)	22 (2)	95 (2)	2.22
O(1)	−1255 (16)	21716 (16)	15922 (12)	532 (9)	318 (7)	307 (8)	100 (6)	26 (7)	62 (6)	3.24
O(2)	−7958 (15)	−10804 (16)	11919 (12)	379 (8)	434 (8)	348 (8)	−8 (6)	49 (6)	189 (7)	2.98
O(3)	22294 (15)	13092 (17)	4953 (13)	375 (8)	491 (9)	400 (9)	−64 (6)	−8 (7)	226 (7)	8.30
O(4)	15969 (16)	−19049 (16)	902 (12)	472 (8)	368 (7)	329 (8)	149 (6)	61 (7)	107 (6)	8.16
C(1)	−10770 (22)	26293 (21)	9496 (17)	431 (11)	296 (10)	368 (11)	51 (8)	124 (9)	110 (9)	2.85
C(2)	−16529 (35)	41871 (28)	14453 (25)	772 (19)	370 (12)	559 (17)	195 (12)	185 (4)	112 (11)	4.56
C(3)	−19515 (21)	−15288 (21)	4396 (18)	380 (11)	294 (9)	393 (11)	58 (8)	101 (9)	123 (8)	2.78
C(4)	−30892 (28)	−23977 (31)	6757 (25)	467 (13)	500 (14)	547 (15)	−12 (10)	144 (11)	23 (12)	3.84
C(11)	18899 (20)	9055 (22)	40277 (16)	303 (10)	370 (10)	289 (10)	2 (8)	24 (8)	87 (8)	2.64
C(12)	21804 (24)	2032 (25)	48434 (19)	423 (12)	434 (12)	362 (11)	0 (9)	44 (9)	138 (9)	3.27
C(13)	17128 (27)	7979 (29)	58730 (20)	565 (14)	583 (14)	311 (11)	−105 (11)	38 (10)	157 (11)	3.90
C(14)	9537 (27)	21131 (30)	60419 (21)	541 (14)	648 (15)	353 (13)	−67 (12)	138 (11)	19 (11)	4.32
C(15)	6588 (29)	28306 (30)	52449 (22)	615 (15)	557 (14)	488 (14)	163 (12)	178 (12)	56 (12)	4.58
C(16)	11065 (27)	22240 (27)	42373 (21)	565 (14)	482 (12)	408 (13)	133 (11)	96 (11)	156 (11)	3.86
C(21)	42026 (21)	12765 (21)	30203 (18)	348 (10)	309 (10)	394 (11)	19 (8)	20 (9)	164 (9)	2.76
C(22)	47893 (26)	23835 (26)	40733 (21)	495 (13)	455 (12)	423 (13)	−69 (10)	2 (11)	160 (10)	3.72
C(23)	61088 (29)	31452 (31)	42547 (25)	573 (15)	583 (15)	601 (17)	−183 (12)	−113 (13)	211 (13)	4.90
C(24)	68453 (28)	28046 (33)	34072 (28)	411 (14)	686 (16)	896 (22)	−137 (12)	−14 (14)	423 (16)	5.12
C(25)	62731 (26)	17266 (31)	23583 (27)	432 (13)	645 (15)	798 (19)	50 (11)	213 (13)	358 (14)	4.61
C(26)	49432 (24)	9687 (26)	21569 (22)	402 (11)	420 (11)	514 (14)	54 (9)	107 (10)	180 (10)	3.48
C(31)	30494 (21)	−17730 (21)	26075 (16)	388 (11)	300 (9)	286 (10)	32 (8)	49 (8)	110 (8)	2.58
C(32)	19953 (24)	−29919 (24)	21697 (20)	404 (12)	381 (11)	479 (13)	4 (9)	60 (10)	172 (10)	3.33
C(33)	23658 (29)	−44763 (25)	20950 (23)	602 (15)	333 (11)	614 (15)	−58 (10)	54 (12)	147 (11)	4.21
C(34)	37805 (29)	−47862 (26)	24147 (22)	730 (16)	331 (11)	544 (14)	136 (11)	102 (13)	181 (10)	4.23
C(35)	48269 (27)	−35978 (27)	28349 (22)	493 (13)	473 (13)	577 (15)	161 (11)	70 (12)	221 (11)	4.06
C(36)	44653 (24)	−20931 (26)	29333 (20)	404 (12)	404 (11)	484 (13)	42 (9)	17 (10)	187 (10)	3.44

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(1)	−2610 (38)	4094 (37)	1262 (30)	7.89 (0.86)	H(22)	4265 (24)	2603 (26)	4681 (21)	4.14 (0.53)
H(2)	−1200 (41)	4892 (43)	1295 (35)	9.65 (1.04)	H(23)	6450 (28)	3826 (29)	4972 (24)	5.28 (0.62)
H(3)	−1429 (40)	4520 (40)	2159 (35)	8.89 (0.98)	H(24)	7692 (30)	3279 (30)	3517 (24)	5.61 (0.65)
H(4)	−3085 (28)	−3339 (34)	210 (25)	5.79 (0.69)	H(25)	6769 (25)	1441 (26)	1753 (22)	4.65 (0.57)
H(5)	−3949 (32)	−2057 (34)	461 (27)	6.85 (0.76)	H(26)	4636 (23)	216 (27)	1437 (21)	3.97 (0.52)
H(6)	−2967 (30)	−2226 (31)	1435 (28)	6.14 (0.71)	H(32)	1053 (23)	−2709 (19)	1962 (19)	3.52 (0.48)
H(12)	2688 (24)	−669 (26)	4707 (20)	3.91 (0.51)	H(33)	1622 (27)	−5231 (30)	1777 (23)	5.79 (0.67)
H(13)	1915 (25)	355 (26)	6357 (22)	4.46 (0.56)	H(34)	4041 (23)	−5752 (26)	2358 (20)	3.88 (0.51)
H(14)	581 (27)	2396 (28)	6716 (24)	5.18 (0.60)	H(35)	5796 (28)	−3808 (29)	3071 (24)	5.58 (0.64)
H(15)	130 (28)	3752 (31)	5390 (24)	5.95 (0.67)	H(36)	5177 (25)	−1294 (25)	3221 (20)	4.10 (0.53)
H(16)	914 (25)	2712 (26)	3767 (21)	4.17 (0.55)					

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + ... + 2klb^*c^*U_{23})]$. Hydrogen atom coordinates have been multiplied by 10^4.

Table III. Bond Distances (Å) of $Rh_2(OAc)_4(P(OPh)_3)_2$ with Estimated Standard Deviations

Rh-Rh′	2.4434 (6)	O(6)-C(26)	1.408 (6)
Rh-P	2.412 (1)	C(26)-C(21)	1.368 (7)
Rh-O(1)	2.033 (3)	C(21)-C(23)	1.388 (8)
Rh-O(2)	2.048 (3)	C(22)-C(23)	1.350 (7)
Rh-O(3)	2.043 (2)	C(23)-C(24)	1.343 (8)
Rh-O(4)	2.033 (2)	C(24)-C(25)	1.378 (9)
P-O(5)	1.603 (2)	C(25)-C(26)	1.367 (6)
P-O(6)	1.602 (4)		
P-O(7)	1.609 (2)	O(7)-C(36)	1.393 (3)
		C(36)-C(31)	1.364 (6)
O(1)-C(1)	1.257 (6)	C(31)-C(32)	1.404 (5)
O(2′)-C(1)	1.264 (4)	C(32)-C(33)	1.368 (8)
O(3)-C(3)	1.262 (4)	C(33)-C(34)	1.371 (7)
O(4′)-C(3)	1.258 (5)	C(34)-C(35)	1.376 (5)
C(1)-C(2)	1.498 (7)	C(35)-C(36)	1.374 (6)
C(3)-C(4)	1.511 (6)		
O(5)-C(16)	1.391 (4)	O(1)···O(2′)	2.248 (4)
C(16)-C(11)	1.363 (5)	O(3)···O(4′)	2.248 (4)
C(11)-C(12)	1.399 (6)	Solvent Molecule	
C(12)-C(13)	1.351 (8)	C(41)-C(42)	1.25 (2)
C(13)-C(14)	1.371 (7)	C(41)-C(43)	1.29 (2)
C(14)-C(15)	1.365 (7)	C(43)-C(45)	1.40 (20)
C(15)-C(16)	1.370 (6)	C(43)-C(44)	1.12 (3)

adduct (2.4434 (6) Å) is slightly but significantly shorter than the 2.4505 (2)-Å Rh-Rh distance found in the bis(phosphine) compound.

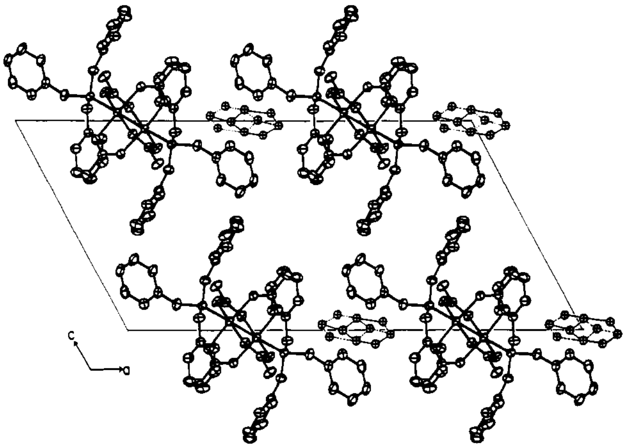

Figure 3. Packing diagram for $Rh_2(OAc)_4(P(OPh)_3)_2$ showing the location of the disordered toluene solvent molecules (the solvent is arbitrarily represented by isotropic spheres of B = 3.0 Å^2, 25% probability level).

The Rh-P bond lengths, 2.412 (1) Å for $P(OPh)_3$ and 2.477 (1) Å for PPh_3, are both longer by more than 0.1 Å than the values found for most mononuclear rhodium-phosphite or -phosphine species, which are rarely greater than 2.30 Å for

Table IV. Bond Angles (Deg) of $Rh_2(OAc)_4(P(OPh)_3)_2$ with Estimated Standard Deviations

Rh'-Rh-P	179.91 (3)	C(12)-C(13)-C(14)	120.5 (5)
Rh'-Rh-O(1)	87.20 (7)	C(13)-C(14)-C(15)	119.9 (5)
Rh'-Rh-O(2)	87.31 (8)	C(14)-C(15)-C(16)	119.4 (4)
Rh'-Rh-O(3)	86.96 (8)	C(15)-C(16)-C(11)	121.9 (3)
Rh'-Rh-O(4)	87.55 (8)	C(16)-C(11)-C(12)	117.7 (4)
O(1)-Rh-P	92.71 (7)	P-O(6)-C(26)	125.4 (2)
O(2)-Rh-P	92.78 (8)	O(6)-C(26)-C(21)	120.0 (3)
O(3)-Rh-P	93.00 (8)	O(6)-C(26)-C(25)	119.5 (4)
O(4)-Rh-P	92.48 (8)	C(21)-C(22)-C(23)	120.2 (5)
Rh-P-O(5)	123.14 (12)	C(22)-C(23)-C(24)	120.7 (6)
Rh-P-O(6)	111.11 (9)	C(23)-C(24)-C(25)	120.4 (4)
Rh-P-O(7)	120.71 (11)	C(24)-C(25)-C(26)	119.3 (5)
O(1)-Rh-O(3)	89.02 (10)	C(25)-C(26)-C(21)	120.5 (5)
O(1)-Rh-O(4)	90.83 (10)	C(26)-C(21)-C(22)	118.8 (4)
O(2)-Rh-O(3)	90.94 (10)	P-O(7)-C(36)	126.1 (2)
O(2)-Rh-O(4)	88.69 (10)	O(7)-C(36)-C(31)	121.6 (4)
Rh-O(1)-C(1)	120.12 (19)	O(7)-C(36)-C(35)	116.3 (3)
Rh-O(2)-C(1')	119.01 (25)	C(31)-C(32)-C(33)	120.9 (4)
Rh-O(3)-C(3)	119.51 (26)	C(32)-C(33)-C(34)	119.5 (4)
Rh-O(4)-C(3')	119.48 (19)	C(33)-C(34)-C(35)	120.7 (4)
O(1)-C(1)-O(2')	126.3 (5)	C(34)-C(35)-C(36)	119.1 (4)
O(1)-C(1)-C(2)	116.6 (3)	C(35)-C(36)-C(31)	122.0 (3)
O(3)-C(3)-O(4')	126.4 (3)	C(36)-C(31)-C(32)	117.8 (4)
O(3)-C(3)-C(4)	116.9 (4)	O(5)-P-O(6)	102.8 (2)
O(4')-C(3)-C(4)	116.7 (3)	O(6)-P-O(7)	104.4 (2)
P-O(5)-C(16)	127.4 (2)	O(5)-P-O(7)	91.5 (1)
O(5)-C(16)-C(11)	123.2 (3)		
O(5)-C(16)-C(15)	114.9 (3)		
C(11)-C(12)-C(13)	120.6 (4)		

Table V

Bond Distances (Å) of $Rh_2(OAc)_4(PPh_3)_2$ with Estimated Standard Deviations

Rh-Rh'	2.4505 (2)	C(14)-C(15)	1.376 (3)
Rh-O(1)	2.054 (1)	C(15)-C(16)	1.381 (3)
Rh-O(2)	2.056 (1)	C(16)-C(11)	1.389 (2)
Rh-O(3)	2.038 (1)	C(21)-C(22)	1.388 (3)
Rh-O(4)	2.031 (1)	C(22)-C(23)	1.390 (3)
Rh-P	2.4771 (5)	C(23)-C(24)	1.368 (4)
O(1)-C(1)	1.258 (2)	C(24)-C(25)	1.372 (4)
O(2)-C(3)	1.267 (2)	C(25)-C(26)	1.392 (2)
O(3)-C(3)	1.257 (2)	C(26)-C(21)	1.389 (3)
O(4)-C(1')	1.260 (2)	C(31)-C(32)	1.397 (2)
C(1)-C(2)	1.501 (2)	C(32)-C(33)	1.379 (2)
C(3)-C(4)	1.502 (2)	C(33)-C(34)	1.379 (3)
P-C(11)	1.826 (2)	C(34)-C(35)	1.374 (3)
P-C(21)	1.835 (2)	C(35)-C(36)	1.388 (2)
P-C(31)	1.837 (1)	C(36)-C(31)	1.384 (2)
C(11)-C(12)	1.387 (2)	∠C-H(methyl)	0.88
C(12)-C(13)	1.374 (3)	∠C-H(phenyl)	0.92
C(13)-C(14)	1.373 (3)		
Nonbonded Intermolecular Distances (Å)			
O(1)···C(16)	3.330 (3)	O(3)···C(21)	3.390 (2)
O(1)···H(16)	2.63 (2)	O(4)···C(32)	3.108 (2)
O(2)···C(32)	3.414 (2)	O(4)···H(32)	2.90 (2)
O(2)···H(32)	2.55 (2)	O(4)···C(31)	3.192 (2)
O(3)···C(26)	3.067 (2)	O(1)···H(33)	2.85 (2)
O(3)···H(26)	2.70 (2)		

Table VI. Bond Angles (Deg) of $Rh_2(OAc)_4(PPh_3)_2$ with Estimated Standard Deviations

Rh'-Rh-P	175.52 (1)	P-C(11)-C(12)	123.2 (1)
Rh'-Rh'-O(1)	87.22 (4)	P-C(11)-C(16)	118.5 (1)
Rh'-Rh-O(2)	87.32 (4)	P-C(21)-C(22)	123.6 (1)
Rh'-Rh-O(3)	86.85 (4)	P-C(21)-C(26)	117.4 (1)
Rh'-Rh-O(4)	87.00 (4)	P-C(31)-C(32)	118.0 (1)
O(1)-Rh-P	97.25 (5)	P-C(31)-C(36)	123.2 (1)
O(2)-Rh-P	92.87 (4)	C(11)-C(12)-C(13)	121.0 (2)
O(3)-Rh-P	92.98 (4)	C(12)-C(13)-C(14)	120.2 (2)
O(4)-Rh-P	88.53 (4)	C(13)-C(14)-C(15)	119.7 (2)
O(1)-Rh-O(2)	90.27 (4)	C(14)-C(15)-C(16)	120.3 (2)
O(1)-Rh-O(3)	88.99 (4)	C(15)-C(16)-C(11)	120.4 (2)
O(3)-Rh-O(4)	89.73 (5)	C(16)-C(11)-C(12)	118.3 (2)
O(4)-Rh-O(2)	90.42 (4)	C(21)-C(22)-C(23)	119.9 (2)
Rh-O(1)-C(1)	119.1 (1)	C(22)-C(23)-C(24)	120.6 (2)
Rh-O(2)-C(3)	119.4 (1)	C(23)-C(24)-C(25)	120.2 (2)
Rh-O(3)-C(3')	121.0 (1)	C(24)-C(25)-C(26)	120.0 (2)
Rh-O(4)-C(1')	120.4 (1)	C(25)-C(26)-C(21)	120.3 (2)
Rh-P-C(11)	118.79 (5)	C(26)-C(21)-C(22)	119.0 (2)
Rh-P-C(21)	115.27 (6)	C(31)-C(32)-C(33)	120.1 (2)
Rh-P-C(31)	111.26 (6)	C(32)-C(33)-C(34)	120.6 (2)
O(1)-C(1)-O(4')	126.1 (1)	C(33)-C(34)-C(35)	119.7 (2)
O(2)-C(3)-O(3')	125.4 (1)	C(34)-C(35)-C(36)	120.3 (2)
O(1)-C(1)-C(2)	118.0 (2)	C(35)-C(36)-C(31)	120.4 (2)
O(4')-C(1)-C(2)	115.9 (2)	C(36)-C(31)-C(32)	118.8 (1)
O(2)-C(3)-C(4)	117.7 (2)		
O(3')-C(3)-C(4)	116.9 (2)		

phosphite[24] and 2.40 Å for phosphine.[25] The Rh–P distance in the phosphine adduct is surprisingly close to the distance of 2.485 (9) Å observed for $Rh_2(OAc)_2(dmg)_2(PPh_3)_2$,[15] but it is significantly longer than the 2.438 (4) Å reported for $Rh_2(dmg)_4(PPh_3)_2$.[16] The Rh–Rh–P linkage is essentially linear (179.91 (3)°) in the bis(phosphite) adduct, while it deviates slightly from linearity (175.52 (1)°) in the bis(phosphine) complex.

The phosphite ligand shows no appreciable structural differences, other than in gross conformation, from that determined in the complexes RhI(*trans*-RhI(*trans*-H)NC)C=C-(CN)H)$(P(OPh)_3(p\text{-}CH_3OC_6H_4NC)_2$,[26] $Pd(SCN)_2(P(OPh)_3)_2$,[13] $Cr(CO)_5(P(OPh)_3)$,[12] and *trans*-$Cr(CO)_4(P(OPh)_3)_2$.[27] The average P–O distance (1.605 (3) Å) agrees well with the average values in the Pd(II), Cr(0), and Rh(I) complexes, while the O–C(phenyl) distance (1.397 (4) Å) observed in our complex is intermediate between the 1.377 (5) Å found in the Rh(I) complex and the 1.420 (7) Å in the Pd(II) complex. The C_β–C_α–$C_{\beta'}$ angles in the phenyl rings are about 1° larger on the average than the neighboring C–C–C angles, suggesting that the oxygen nonbonding electrons are partially delocalizing through the aromatic ring as suggested by Guss and Mason.[28] The effect of this electronic interaction may also be seen in the angles involving the ortho carbon atoms. Angular distortions around phosphorus are severe, the O–P–O angles ranging from 91.5 (1) to 104.4 (2)°, with an average of 99.6°. The average Rh–P–O angle is 118.3 (1)°. Such a spread of the angles around phosphorus is not unusual in phosphite coordination complexes.

The structure of the phosphine ligand agrees within the error of measurement with that of free triphenylphosphine,[29] an indication that the bond angles and distances are little affected on coordination. In contrast to the O–P–O linkages, the C–P–C angles show far less angular irregularity, but their average is 103.2 (2)°, significantly greater than that for the O–P–O bond angles. It is not clear whether the smaller Rh–P–C angles (average 115.1) in comparison with those of the Rh–P–O angles are due to intramolecular steric interactions of the R groups or due to the increase in the s character in the bonding orbital of phosphorus as the phenyl groups are replaced with the more electronegative phenoxy groups.[30]

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(24) Coetzer, J.; Gafner, G. *Acta Crystallogr., Sect. B* **1970**, *B26*, 985. $P(OPh)_3$ trans to Cl, 2.142 (5) Å.

(25) Doyle, M. J.; Lappert, M. F.; McLaughlin, G. M.; McMeeking, J. *J. Chem. Soc., Dalton Trans.* **1974**, 1494. PPh_3 trans to PPh_3, 2.290 (4) Å. Muir, K. W.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 440. PPh_3 trans to PPh_3, 2.338 (4) Å. Cowie, M.; Ibers, J. A. *Ibid.* **1976**, *15*, 552. PPh_3 trans to PPh_3, 2.378 (2) Å.

(26) Gaughan, A. P.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 3073.

(27) Preston, H. S.; Stewart, J. M.; Plastas, H. J.; Grim, S. O. *Inorg. Chem.* **1972**, *11*, 161.

(28) Guss, J. M.; Mason, R. *J. Chem. Soc., Dalton Trans.* **1972**, 2193.

(29) Daly, J. J. *J. Chem. Soc.* **1964**, 3799.

Table VII. Bond Parameters in Cr(0) Carbonyl Complexes

compd	obsd Cr–X, Å	normal Cr–X, Å	Cr–C (trans to X), Å	Cr–C (cis to X), Å
$Cr(CO)_6$[a]	1.909 (3)	1.909 (3)	1.909 (3)	1.909 (3)
$(CO)_5CrP(OPh)_3$[b]	2.309 (1)	2.252 (1)[c]	1.861 (4)	1.896 (4)
$(CO)_5CrPPh_3$[b]	2.422 (1)	2.381 (5)[d]	1.844 (4)	1.880 (4)
$(CO)_3Cr(dien)$[e]			1.816 (5)	
$(CO)_5CrSP(CH_3)_3$[f]	2.510 (2)	2.52	1.815 (8)	1.900 (4)

[a] Whitaker, A.; Jeffery, J. W. *Acta Crystallogr.* **1967**, *23*, 977. [b] Reference 12. [c] Preston, H. S.; Stewart, J. M.; Plastas, H. J.; Grim, S. O. *Inorg. Chem.* **1972**, *11*, 161. [d] Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 7000. [e] dien = diethylenetriamine: Cotton, F. A.; Richardson, D. C. *Inorg. Chem.* **1966**, *5*, 1851. [f] Baker, E. N.; Reay, B. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2205.

Discussion

The features of particular interest in the title compounds are the Rh–Rh and Rh–P distances. Whereas the predictions of π-back-bonding theory appear to be well fulfilled in the substituted mononuclear chromium carbonyls, $Cr(CO)_5X$, the structural results for the dirhodium complexes are definitely not in accord with expectations derived from the theory.

Structural data for $Cr(CO)_5L$ for L = CO, PPh_3, and $P(OPh)_3$ (Table VII) support the conclusion that as the Cr–L bond decreases in multiple-bond character, despite increasing L σ-donor ability, the Cr–C bond trans to it shortens and strengthens. The cis Cr–C bonds are affected by other ligands L to a much smaller degree, although the observed general shortening is indicative of the somewhat greater availability of d-electron density on the metal, a consequence of the greater relative σ donation by ligands L than from CO. CO is from this data the strongest π acceptor, though it is generally accepted to be a relatively quite weak σ donor. For L = $P(OPh)_3$ and PPh_3, the Cr–P distances are both about 0.05 Å longer than normal (as estimated from compounds in which L is trans to L), as is expected if the CO trans to L is more effective at competing for the Cr bonding orbitals. This is confirmed by the substantial shortening of Cr–C(trans) from 1.909 (3) to 1.861 (4) Å for L = $P(OPh)_3$ and 1.844 (4) Å for L = PPh_3. Comparison with the Cr–C(trans) distances for L = dien and $SP(CH_3)_3$ suggest that the Cr–P bonds do possess some multiple character, though less than that of the Cr–CO bonds. The surprisingly large differences in the Cr–P distances for L = $P(OPh)_3$ and L = PPh_3 are more difficult to interpret than the Cr–C distances because of the synergic effects; additionally, Cr–P distances reflect (vide infra) the different covalent radii of phosphorus in the two ligands. The differences in the Cr–P and Cr–C(trans) distances for the two ligands are, however qualitatively consistent with the expectation that for PR_3 increasingly electronegative R groups will make P a better π acceptor and a poorer σ donor (the latter is reflected in the Cr–C(cis) distances).

In our dirhodium system, the strong Rh–Rh bond trans to the phosphorus ligands exerts an intense trans-influence effect upon them,[14] and the Rh–P(phosphite) distance of 2.412 (1) Å is perhaps 0.25 Å longer than normal[24] while the Rh–P(phosphine) distance of 2.477 (1) Å is ca. 0.10–0.18 Å longer than expected.[25] On the basis of the chromium(0) carbonyl results, we should expect that the Rh–Rh bond should be longer for L = $P(OPh)_3$ than for L = PPh_3. The observed Rh–Rh distances differ by over ten standard deviations from each other, but the difference is in the opposite direction than expected. We rationalize the lack of effect of the differing putative π-acceptor strengths of $P(OPh)_3$ and PPh_3 on the Rh–Rh length as being due to the extraordinarily long Rh–P distances, which preferentially reduce the magnitude of the metal–phosphorus π overlaps.[14] unlike the Cr(0) complexes, then, we should expect the σ component of the Rh–P bond to be dominating, and this is confirmed by the observed difference in Rh–Rh distances. The import of this result for the Rh–Rh bonding is that it relaxes our earlier concern with the symmetry of the metal orbitals involved in back-bonding. A new explanation, which relies only upon σ effects, of the origins of the differing Rh–Rh distances for hard and soft donor ligands now must be sought.

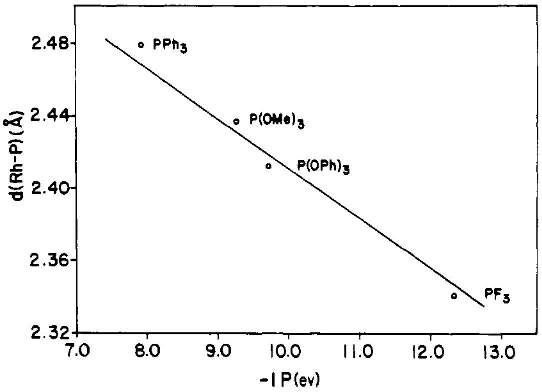

Figure 4. Graph of Rh–P distances in $Rh_2(OAc)_4(PR_3)_2$ complexes vs. phosphorous ligand lone-pair ionization potentials for various phosphine and phosphite ligands. Data from ref 14.

Since PPh_3 should be the better donor, and thus possess the stronger Rh–P bond, it is natural to question why the Rh–$P(OPh)_3$ distance is shorter than the Rh–PPh_3 distance. The difference between them is 0.067 Å whereas the corresponding difference between Cr–P(phosphite) and Cr–P(phosphine) is 0.113 Å. For the simple borane–phosphine adducts, H_3B-PR_3, in which the σ interactions are predominant, one also predicts on the basis of phosphorus σ-donor strength that the B–P distance for R = Me would be shorter than for R = F. Yet the B–P bond is, on the contrary, observed to be much shorter for R = F (1.836 Å) than for R = Me (1.901 Å),[31] a difference of 0.065 Å. Photoelectron spectra in conjunction with ab inito calculations for H_3BPF_3 recommend only a small B–P π–bond population (0.08).[32] A body of other data (e.g., dipole moments, infrared spectra, force field calculations, thermodynamic measurements) is admittedly consistent with this interpretation of a very small π component in the phosphine boranes (and to a greater extent in some metal–phosphorus compounds).[10,33] However, it should be apparent that very nearly all of the shortening of $B-PR_3$ bonds as R increase in electron-withdrawing power results from a decreasing covalent radius of the phosphorus and an increasing ionic component of the B–P bond. (A steric origin for these bond length changes is ruled out by an examination of the molecules $t\text{-}Bu_nPF_{3-n}$ for n = 1–3: the P–F *and* the P–C bond lengths *increase almost linearly* with n, but the C–P–F *and* the C–P–C bond angles *both decrease* with increasing n. Steric effects, which should yield the *opposite* angle changes, are not the cause of the bond lengthening.[34]) One must conclude that increasing the availability of electrons to the phosphorus does yield a larger covalent radius, and that this can amply account for the observed difference in or Rh–P distances, without any

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(30) Wayland, B. B.; Abd-Elmageed, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 4809.

(31) Bryan, P. S.; Kuczkowski, R. L. *Inorg. Chem.* **1972**, *11*, 855. Kuczkowski, R. L.; Lide, D. R. *J. Chem. Phys.* **1967**, *46*, 357. Rudolph, R. W.; C. W. Schultz, *J. Am. Chem. Soc.* **1971**, *93*, 6814.

(32) Hillier, I. H.; Marriott, J. C.; Saunders, V. R.; Ware, M. J.; Lloyd, D. R.; Lynaugh, N. *J. Chem. Soc. D.* **1970**, 1586.

(33) Cowley, A. H.; Damasco, M. C. *J. Am. Chem. Soc.* **1971**, *93*, 6815.

(34) Oberhammer, H.; Schmutzler, R.; Stelzer, O. *Inorg. Chem.* **1978**, *17*, 1254.

Table VIII. Bond Parameters in Dirhodium Complexes

	dist, Å			dist of Rh from equatorial plane,[e] Å	dmg-dmg dihedral angle,[f] deg	Rh-Rh-P, deg	comments
	Rh-Rh	Rh-P					
$Rh_2(OAc)_4(PPh_3)_2$ (I)	2.449 (2)	2.479 (3)		0.1		174.44 (4)	
$Rh_2(OAc)_2(dmg)_2(PPh_3)_2$ (II)	2.618 (5)[a]	2.476 (9) 2.494 (9)	2.485 (9)	*d*		172-173	away from dmg
$Rh_2(dmg)_4(PPh_3)_2$ (III)	2.936 (2)[b]	2.430 (5) 2.447 (5)	2.438 (5)	0.025	176.4	176.2 (1)	
$Rh(dmg)_2PPh_3Cl$[c] (IV)		2.327 (1)		0.126	162.9	178.25 (5)	(Cl-Rh-P)

[a] Reference 15. [b] Reference 16. [c] Reference 5. [d] Unavailable. [e] Plus means toward P. [f] Angle is across Rh.

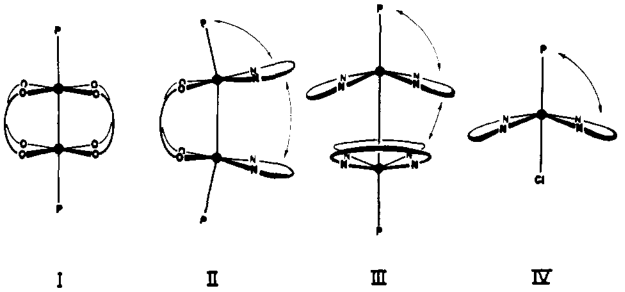

Figure 5. Configurations and conformations of various dmg (dimethylglyoximato) and phosphine complexes of rhodium: I, $Rh_2(OAc)_4(PPh_3)_2$; II, $Rh_2(OAc)_2(dmg)_2(PPh_3)_2$; III, $Rh_2(dmg)_4(PPh)_2$; IV, $Rh(dmg_2)Cl(PPh_3)$.

recourse to M-P π-back-bonding arguments.

In Figure 4 we have plotted the available Rh-P distances for the $Rh_2(OAc)_4$ complexes of several phosphine and phosphite ligands against the vertical ionization potentials for the lone-pair electrons of the free ligands. The straight-line fit is surprisingly good. Bearing in mind that the gas-phase proton affinity (PA) is excellently correlated with ligand lone-pair vertical ionization potentials,[35] one is tempted to conclude that the Rh-P bond *in these complexes* behaves just like an H-P bond and thus *possesses* no *π component*. For Pt(II), Muir and co-workers have found an excellent correlation of Pt and Pt-C distances with the quantity $S^2/\Delta E$,[36] a "σ only" estimate of the Pt-L bond strength.[37] However, it must be remembered that all of the measurable quantities mentioned above are strongly intercorrelated, and the σ and π component cannot, in general, be simply separated. For example, the plot in Figure 4, which suggests that changes in the σ-only covalent radii are responsible for the variations in the Rh-P distances, is equally consistent with any bonding model in which the π strength also varies *linearly* with IP. Thus, although we cannot categorically deny the existence of π components in the Rh-P linkages, we reiterate, that in contrast to the Cr-P systems, in this series of compounds we should expect the π interactions to be very much weaker than usual because of the much longer than normal Rh-P distances.

Comparison of Structural Features of $Rh_2(dmg)_4(PPh_3)_2$, $Rh_2(OAc)_2(dmg)_2(PPh_3)_2$, and $Rh_2(OAc)_4(PPh_3)_2$. The configuration of the bridging acetate groups leaves the axial sites in these dirhodium complexes relatively underhindered. Triphenylphosphine has the largest cone angle (145°) of any of the ligands we have used in our structural studies[14] (PF_3 = 104°, $P(OMe)_3$ = 107°, $P(OPh)_3$ = 118°),[4] and we have, therefore, carefully examined the derived structure for short intramolecular contacts. We find several contacts between phenyl β-carbons and acetate oxygens of ca. 3.1-3.2 Å. Although the hydrogen atoms are somewhat closer (2.5-2.9 Å), all contacts nevertheless appear to be normal van der Waals interactions. Severe steric crowding in phosphine complexes usually makes itself apparent in two ways: first, by distortions of the coordination geometry at the metal and, second, by adjustments in the internal geometry of the phosphine ligand itself. Both these effects are operational in the highly crowded $Rh(PPh_3)_3Cl$[38] and $Rh(PPh_3)_3H$,[39] where the trans P-Rh-P angles deviate nearly 30° from linearity. Thus, in the following comparison, the effects of steric interactions must be borne in mind: the structures of the series $Rh_2(OAc)_4(PPh_3)_2$, $Rh_2(OAc)_2(dmg)_2(PPh_3)_2$, and $Rh_2(dmg)_4(PPh_3)_2$ are now all known and invite interpretation of the Rh-Rh and Rh-P distances as functions of the degree of bridging of the Rh-Rh nucleus. Bond parameters of interest are given in Table VIII. The Rh-Rh distance increases dramatically as the acetate groups are replaced by the nonbridging dimethylglyoximato (dmg) ligands. Steric interactions between the dmg groups in II and III are quite severe, causing substantial distortions from normal geometry. In II the dmg planes make an angle of ca. 15° with each other, which is reflected in Rh-Rh-P angles of 172-173°, the direction of the bending being *away* from the dmg groups; the Rh-Rh bond consequently appears to be somewhat bent. In III, the bis(dmg) groups are staggered almost 90° from each other to minimize repulsion between the methyl groups; however, in contrast to II, the dmg groups in III are bent *toward* each other, away from the PPh_3 groups, just as in the structure of IV. These distortions are all exaggerated in Figure 5 to emphasize the senses of the deviations. In view of the severity of these interactions, the interpretation of the Rh-Rh and Rh-P distances is not straightforward. One would like to show an inverse correlation between Rh-Rh and Rh-P distances as is expected from trans-influence arguments: as the M-M bond becomes stronger the M-P bond should become weaker. Yet a 0.15-Å increase in Rh-Rh distance (from I to II) leaves the Rh-P distance essentially unchanged. The reason, we feel, lies in the PPh_3-dmg steric interactions. In IV the dmg groups are bent back more strongly than in III; the dihedral angles between the dmg groups on *each* Rh atom are only 3.6° in III, but 17.1° in IV. It is apparent from this that the tension on the Rh-Rh bond in III must be quite severe, and the greater length of the Rh-P bond in III (relative to that in IV) must be in large part due to strong steric repulsions between the dmg groups and the PPh_3 groups. The same forces are seen to be operating in II, wherein the phosphine groups are bent away from the dmg groups.

The substantial repulsive steric effects in II and III make interpretation of the Rh-Rh bond distances in these compounds difficult and mitigate their usefulness in comparisons for M-M bond-order arguments. Further, if such difficulties are present in these very well-defined small cluster complexes, it behooves us to be particularly cautious in interpeting M-M

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(35) DeKock, R. L.; Barbachyn, M. R. *J. Am. Chem. Soc.* **1979**, *101*, 6516.
(36) Manojlovic-Muir, L.; Muir, K. W.; Solomun, T. *J. Organomet. Chem.* **1977**, *142*, 265.
(37) McWeeney, R.; Mason, R.; Towl, A. D. C. *Discuss. Faraday Soc.* **1969**, *47*, 20. Mason, R.; Towl, A. D. C. *J. Chem. Soc. A* **1970**, 1601.
(38) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, *16*, 655.
(39) Strauss, S. H.; Diamond, S. E.; Mares, F.; Shriver, D. F. *Inorg. Chem.* **1978**, *17*, 3064.

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.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

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

F. ALBERT COTTON,* TIMOTHY R. FELTHOUSE, and SIMONETTA KLEIN

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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