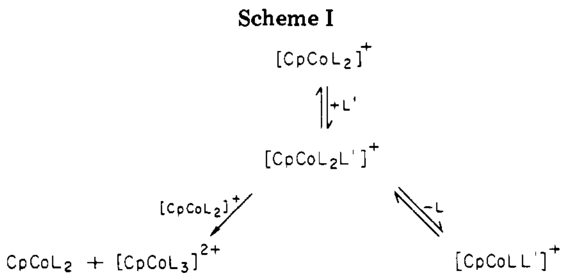
Scheme I



of reorganizing the ligands is not offset by the lowering energy of the two phosphorus donor electrons. In the $x = 2$ (A unoccupied) case, a clear net bonding interaction is achieved leading to a gain in energy. It is not surprising then that the $x = 1$ (singly occupied) case is between these two extremes, i.e., the energy loss of raising one electron plus the reorganization energy is just about offset by the lowered energy of the two phosphorus electrons; this leads to a much lower barrier (or maybe none) for the associative substitution pathway in the paramagnetic complex. Similar calculations have been carried out for other simple paramagnetic complexes such as the 17-electron complex $Mn(CO)_5$, and we obtain the same result and explanation; i.e., dissociative substitution may not be significantly different for the 17- and 18-electron complexes, but associative substitution can be expected to be significantly easier in 17-electron complexes.

Very similar arguments can explain the rapid disproportionation we observe in the presence of a small donor ligand such as $P(OMe)_3$. If the intermediate F is generated, then the singly occupied HOMO of F may be of sufficiently high energy (see Figure 3) to transfer the electron to the lower singly occupied HOMO of the starting complex E, resulting in disproportionation as indicated in Scheme I.

Registry No. 1, 79639-49-9; 2, 80719-10-4; $[CpCo(PEt_3)_2]I$, 80719-08-0.

Supplementary Material Available: Tables of positional and thermal parameters, general temperature factor expressions, and structure factor amplitudes for 1 and 2 and a stereoscopic crystal packing digram for 2 (29 pages). Ordering information is given on any current masthead page.

Metal–Metal Double Bond Formation via Steric Design. Synthesis and X-ray Crystal Structure of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)(PMe_3)]_2(Rh{=}Rh)$

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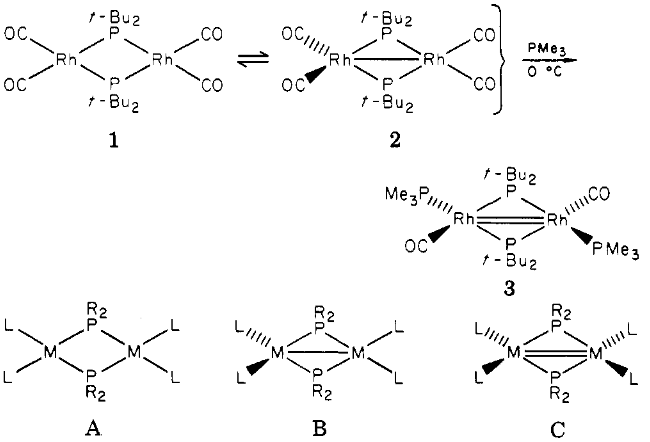
$[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ reacts with neat PMe_3 at room temperature to give $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)(PMe_3)]_2$ (3) quantitatively. 3 contains two Rh(I) atoms bridged by two $t\text{-}Bu_2P$ ligands. Each Rh carries one terminal CO and one PMe_3 ligand and has a distorted tetrahedral geometry. The Rh–Rh distance (2.550 (1) Å) and diamagnetism are consistent with a metal–metal bond of order 2. The structure has been determined by a single-crystal X-ray diffraction study. Crystal data for 1: $C_{24}H_{54}O_2P_4Rh_2$, $M = 704.40$, monoclinic, $P2_1/n$, $a = 10.791$ (7) Å, $b = 11.206$ (7) Å, $c = 14.398$ (8) Å, $\beta = 105.915$ (5)°, $U = 1674.3$ (5) Å^3, $D_{calcd} = 1.397$ g cm^{-1}, $Z = 2$ (dimers), λ(Mo K_α) = 0.71069 Å (graphite monochromator), μ(Mo K_α) = 11.8 cm^{-1}. Refinement of 2078 observed ($I > 2\sigma(I)$) reflections (2801 measured) gave a final $R = 0.0366$ and $R_w = 0.0434$.

Introduction

There are many examples where the addition of a Lewis base such as a phosphine (PR_3) or isocyanide (CNR) to a dinuclear or polynuclear complex results in the formation of species of lower nuclearity. This is often accompanied by the cleavage of a metal–metal bond if one is present in the original complex.[1]

We report here an example of a reaction in which the bond order between two metals in a dimer apparently increases upon addition of a Lewis base. The transformation occurs by simply changing the steric bulk of the terminal ligands.

Scheme I[a]



[a] M = Co, Rh, Ir; L = two-electron donor, CO, PR_3, etc.

As part of a study of the steric effects of phosphido (R_2P^-) ligands in organometallic chemistry, we recently described an unusual dinuclear Rh(I) system that exhibits the interesting feature of a facile reversible metal–metal

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[1] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; see chapters 3, 4 and 26 and references therein. For recent developments in complexes with metal–metal bonds see also: Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982. Chisholm, M. H., Ed. "Reactivity of Metal-Metal Bonds"; American Chemical Society: Washington DC 1981; *ACS Symp. Ser. No. 155.*

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bond cleavage accompanied only by a geometrical isomerism (see Scheme I).[2] We have also noted that for dinuclear phosphido-bridged complexes of the Co group, with roughly planar M_2P_2 central cores, three geometrical isomers have been observed: A, B, and C (see Scheme I).[3] On the basis of bond length considerations the approximate geometry about each metal (either tetrahedral or planar) may be correlated with metal–metal bonds of order 0, 1, and 2 in A, B, and C, respectively.[3] Theoretical calculations have also been performed for compounds of geometry A and C by Hoffmann and co-workers.[4]

The two isomers **1** and **2** are representative of types A and B, respectively, in having Rh–Rh bond distances consistent with metal–metal bonds of order 0 and 1, respectively. The precise reasons for the closeness of energy of these two isomers will probably be best answered by theoretical calculations.[5] It seems reasonable to assume that steric effects of the bulky μ-*t*-Bu$_2$P groups are at least partially responsible for the unusual behavior observed in this system. The square-planar tetrahedral interconversion of one end of the rhodium dimer is reminiscent of the equilibrium observed with mononuclear Ni(II) systems of the type NiX$_2$(PR$_3$)$_2$.[6] In these cases careful control of the steric bulk of the phosphine ligands permits the observation of square planar–tetrahedral equilibria.

If one considers our dinuclear Rh system, a tetrahedral, four-coordinate Rh atom (excluding any metal–metal interactions) should experience less steric strain than one having a square-planar geometry. We considered the possibility of forcing both Rh atoms to adopt tetrahedral geometries by increasing the size of the terminal ligands. Such a complex should then have a Rh–Rh double bond and be representative of complexes of type C. In order to test this hypothesis we reacted **1** and/or **2** with excess PMe$_3$ expecting one or both terminal CO ligands on each Rh atom to be replaced by the larger phosphine ligands. In fact the resulting complex [Rh(μ-*t*-Bu$_2$P)(CO)(PMe$_3$)]$_2$ (**3**) has only one PMe$_3$ per Rh. However, this is sufficient to force both Rh atoms into nearly tetrahedral geometries, and **3** has a Rh–Rh distance of 2.550 (1) Å consistent with a Rh–Rh double bond, thus confirming our initial ideas. We report here details of the synthesis, characterization, and X-ray crystal structure of **3**.

Experimental Section

All operations were performed under oxygen-free nitrogen. Microanalytical data were obtained from the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Hexane was dried over sodium and distilled from sodium/benzophenone under nitrogen before use. *Instruments*: IR, Perkin-Elmer 1330; NMR, Varian EM-390 (^{1}H, 90 MHz) and FT Varian EM-80 (^{31}P, 32.384 MHz). A mixture of the isomers of [Rh(μ-*t*-Bu$_2$P)(CO)$_2$]$_2$ (**1** and **2**) was prepared as previously described.[2]

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for [Rh(μ-*t*-Bu$_2$P)(CO)(PMe$_3$)]$_2$ (3)

formula	$C_{24}H_{54}O_2P_4Rh_2$
mol wt	704.40
space group	$P2_1/n$
cell constants	
a, Å	10.791 (7)
b, Å	11.206 (7)
c, Å	14.398 (8)
β, deg	105.915 (5)
cell vol, Å^3	1674.3 (5)
molecules/unit cell	2 (dimers)
D(calcd), g cm^{-3}	1.397
μ(calcd), cm^{-1}	11.80
radiation, Å	Mo Kα 0.710 69
temp, °C	23 ± 2
max crystal dimens, mm	0.25 × 0.22 × 0.17
std reflctns	$2,\bar{1},13$, $0,4,\overline{11}$
decay of stds	6.9% (linear), correction applied
reflctns measd	2801
2θ range, deg	2–48
reflctns obsd ($I > 2\sigma(I)$)	2078
no. of parameters varied	217
data/parameter ratio	9.41
R	0.0366
R_w	0.0434

[Rh(μ-*t*-Bu$_2$P)(CO)(PMe$_3$)]$_2$ (3). A mixture of the two known isomers of [Rh(μ-*t*-Bu$_2$P)(CO)$_2$]$_2$[2] (0.25 g, 0.41 mmol) was cooled to 0 °C, and PMe$_3$ (5.0 mL, 50 mmol) was added via syringe. The resulting deep red solution was stirred for 2 h and allowed to warm to room temperature in that time. Volatile materials were removed under vacuum, and the residue was extracted with hexane (25 mL). The solution was filtered, evaporated to ca. 10 mL, and cooled (−20 °C). After 12 h the dark red crystals of **3** were isolated and dried under vacuum: yield, quantitative; mp 123–124 °C dec; IR (Nujol mull, KBr plates) 1924 (s), 1292 (w), 1151 (m), 1010 (w), 936 (s), 883 (vw), 841 (vw), 796 (w), 715 (vs) cm^{-1}; ^{1}H NMR (in C$_6$D$_6$, at 25 °C, in ppm relative to Me$_4$Si, δ 0.0) δ 1.38 (m) (overlapping PMe$_3$ and *t*-Bu$_2$P resonances); ^{31}P{^{1}H} NMR (in C$_6$D$_6$, at 35 °C, in ppm relative to 85% H$_3$PO$_4$, δ 0.0, peaks to low field are positive) δ 317.49 (t, $^1J_{Rh-P}$ = 143.8 Hz, *t*-Bu$_2$P), −17.46 (d, $^1J_{Rh-P}$ = 114.99 Hz, PMe$_3$). Anal. Calcd for C$_{24}$H$_{54}$O$_2$P$_4$Rh$_2$: C, 40.89, H, 7.67; P, 17.60. Found: C, 40.15, H, 7.61; P, 16.53.

X-ray Analysis. Crystals of **3** suitable for crystallographic studies were grown from hexane at −20 °C and mounted under nitrogen in thin-walled glass capillaries. Data were collected on an Enraf-Nonius CAD-4 diffractometer controlled by a PDP 11/44 computer on which all subsequent structure solution and refinements were performed. Relevant crystal data and a summary of intensity data collection parameters are given in Table I.

With use of the program SEARCH, a program on the CAD-4 which automatically searches for and centers on strong reflections, the initial lattice parameters were determined with 16.0° < 2θ < 22.0° and subsequently refined by using higher angle data (26.0° < 2θ < 30.0°). Data were collected by using Mo Kα (graphite-monochromated) radiation. The diffracted intensities were collected by using the $\omega/2\theta$ scan method with 2.0° < 2θ < 48.0°. The scan rate was varied according to a prescan at 6.6° min^{-1} and calculated speeds, based on the net intensity gathered, ranged from 6.6 to 1.54° min^{-1}. Moving crystal–moving counter backgrounds were collected for 25% of the total scan width at each end of the scan range. In each intensity the scan width was determined by the equation: scan range = $A + B \tan\theta$ with A = 0.8° and B = 0.35°. Aperature settings were determined in a like manner with A = 4.0 mm and B = 1.0 mm. As a check on the stability of the crystal two reflections were monitored after every 0.5 h of exposure for intensity decay and also monitored after every 100 reflections for crystal orientation. Data were collected in reciprocal space for $+h,+k,\pm l$. A total of 2801 unique measured reflections were collected for which 2078 were considered observed with $I > 2\sigma(I)$.

The space group was uniquely determined by systematic absences to be $P2_1/n$. The intensities were corrected for Lorentz, polarization, and decay effects but not for absorption (μ = 11.8

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[2] Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 470.

[3] Referring to the approximate geometry about each metal as tetrahedral or planar. Type A: "planar/planar", examples, one isomer of [Rh(μ-*t*-Bu$_2$P)(CO)$_2$]$_2$ (**1**) (ref 2) and [Rh(μ-PPh$_2$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)]$_2$ (Fultz, W. C.; Rheingold, A. L.; Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 860). Type B: "planar/tetrahedral"; examples, another isomer of [Rh(μ-*t*-Bu$_2$P)(CO)$_2$]$_2$ (**2**) (ref 2) and Rh$_2$(μ-PPh$_2$)$_2$(PEt$_3$)$_2$(COD) (ref 8). Type C: "tetrahedral/tetrahedral", examples, [Co(μ-Ph$_2$)(CO)(PEt$_2$Ph)]$_2$ (ref 9), [Ir(μ-PPh$_2$)(CO)(PPh$_3$)]$_2$ (ref 11), and [Rh(μ-*t*-Bu(H)P)(PMe$_3$)$_2$]$_2$ (Jones, R. A.; Norman, N. C.; Seeberger, M. H.; Atwood, J. L.; Hunter, W. E. *Organometallics*, accepted for publication).

[4] Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

[5] Hoffmann, R., personal communication.

[6] See: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 793.

Table II. Table of Positional Parameters and Their Estimated Standard Deviations for 3[a]

atom	x	y	z	B, Å^2
Rh(1)	0.08322 (5)	0.07900 (5)	0.03866 (4)	2.390 (9)
P(1)	−0.1234 (2)	0.0734 (2)	0.0594 (1)	2.62 (3)
P(2)	0.1570 (2)	0.2662 (2)	0.0134 (2)	3.68 (4)
O(01)	0.2899 (7)	0.0312 (8)	0.2269 (4)	7.6 (2)
C(1)	−0.1369 (8)	0.0450 (7)	0.1875 (5)	3.9 (2)
C(01)	0.2109 (8)	0.0825 (8)	0.1552 (5)	4.6 (2)
C(2)	−0.2576 (7)	0.1813 (7)	−0.0024 (6)	3.8 (2)
C(3)	0.128 (1)	0.3796 (9)	0.0937 (8)	7.9 (3)
C(4)	0.105 (1)	0.3423 (9)	−0.1039 (8)	7.0 (3)
C(5)	0.3340 (9)	0.276 (1)	0.030 (1)	9.0 (4)
C(11)	−0.042 (1)	−0.0525 (9)	0.2306 (6)	6.4 (3)
C(12)	−0.092 (1)	0.1566 (9)	0.2508 (6)	6.4 (3)
C(13)	−0.271 (1)	0.007 (1)	0.1896 (7)	6.5 (3)
C(21)	−0.2270 (9)	0.2275 (9)	−0.0920 (7)	5.9 (2)
C(22)	−0.3857 (8)	0.1138 (9)	−0.0382 (8)	6.3 (3)
C(23)	−0.274 (1)	0.2869 (9)	0.0593 (3)	7.0 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

cm^{-1}) since a psi scan revealed no problem. The structure was solved and refined by using the Enraf-Nonius "SDP-PLUS" crystallographic package (B. A. Frenz and Associates, Inc., College Station, TX 77840, 4th edition, 1981). Equivalent reflections were averaged, and extinct reflections were rejected. Standard heavy-atom methods and difference Fourier maps revealed the positions of all the non-hydrogen atoms. Unit weights were used throughout. The structure was refined (full matrix, least squares) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were either located or placed in calculated positions by using idealized sp^3 geometry and a C–H bond length of 0.95 Å and refined with fixed isotropic thermal parameters (5.0 Å^2). In the final least-squares cycles refinement converged smoothly to give final residuals of $R = 0.0366$ and $R_w = 0.0434$, where $R = \sum|F_o| - |F_c|/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. A final difference Fourier showed no chemically significant peaks with no features greater than 0.4 e/Å^3.

Table III. Bond Distances (Å) for 3

atom 1	atom 2	dist	atom 1	atom 2	dist
Rh(1)	Rh(1′)	2.550 (1)	O(01)	C(01)	1.144 (6)
Rh(1)	P(1)	2.330 (1)	C(1)	C(11)	1.508 (10)
Rh(1′)	P(1)	2.332 (1)	C(1)	C(12)	1.545 (9)
Rh(1)	P(2)	2.308 (1)	C(1)	C(13)	1.511 (10)
Rh(1)	C(01)	1.857 (5)	C(2)	C(21)	1.508 (10)
P(1)	C(1)	1.917 (5)	C(2)	C(22)	1.535 (9)
P(1)	C(2)	1.909 (5)	C(2)	C(23)	1.525 (9)
P(2)	C(3)	1.800 (10)			
P(2)	C(4)	1.837 (8)			
P(2)	C(5)	1.862 (8)			

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

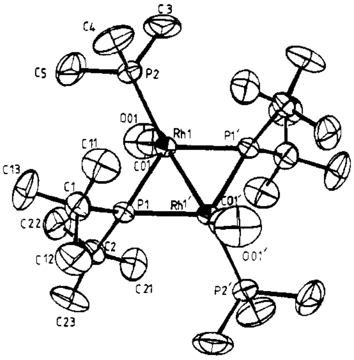

Figure 1. View of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)(PMe_3)]_2$ (3) showing atom numbering scheme. Hydrogen atoms have been omitted for clarity.

Results and Discussion

The addition of neat PMe_3 to either isomer of $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$ in the solid state results in the formation of a deep red homogeneous solution from which the bis PMe_3 complex $[Rh(\mu\text{-}t\text{-}Bu_2P)(CO)(PMe_3)]_2$ (3) can be isolated in quantitative yield (see Scheme I). This dark red complex can be handled in the air in the solid state when it appears almost black. In solution it decomposes immediately on exposure to the atmosphere.

The IR spectrum shows one strong band at 1923 cm^{-1} (ν_{CO}), indicating the presence of terminal carbonyls, while the $^{31}P\{^1H\}$ NMR spectrum shows a simple triplet and a doublet, which remain unchanged at −80 °C (PhMe-d_8). The former appears at low field and is assigned to the two t-Bu_2P units bridging two equivalent rhodium nuclei (δ 317.49 ($^1J_{Rh-P} = 143.8$ Hz)). The downfield shifts of this resonance is consistent with the phosphido units bridging a short metal–metal distance. Downfield shift in the ^{31}P NMR of diphenylphosphido groups bridging metal–metal bonds have already been noted by several groups of workers.[7,8] At present the only other bis(phosphido)-bridged dimer of rhodium containing a Rh=Rh double bond known is $[Rh(\mu\text{-}PH\text{-}t\text{-}Bu)(PMe_3)_2]_2$.[3] The ^{31}P NMR parameters for the bridging phosphorus nuclei in this complex are similar to those observed in 3; δ 207.25 (relative to H_3PO_4) (t, $^1J_{Rh-P} = 150.9$ Hz).

These ^{31}P NMR parameters can also be compared to those recently reported by Meek and co-workers for a number of diphenylphosphido-bridged rhodium dimers.[8] Thus, for example, in $(PPh_3)_2Rh(\mu\text{-}PPh_2)_2Rh(COD)$ which is a representative of complex type B, with a single Rh–Rh bond, $\delta(^{31}P)$ equals 216 (relative to H_3PO_4) with $^1J_{Rh-P} = 94$ and 166 Hz.

The ^{31}P spectrum of 3 also show little or no J_{P-P} coupling between the PMe_3 and μ-t-Bu_2P groups. Several other phosphido-bridged dimers of the cobalt triad containing terminal phosphine ligands and with pseudotetrahedral

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[7] Downfield shifts in the δ 50–200 range in the ^{31}P NMR of Ph_2P^- groups bridging metal–metal bonds have been noted by several groups of workers. See for example: Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53 and references therein. Similar downfield shifts have been noted for μ-t-Bu_2P complexes, see ref 2 and 10.

[8] Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319.

Table IV. Bond Angles (deg) for 3

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Rh(1)	Rh(1')	P(1)	56.86 (3)	C(12)	C(1)	C(13)	111.3 (6)
Rh(1')	Rh(1)	P(1)	56.81 (3)	Rh(1)	C(01)	O(01)	178.1 (6)
Rh(1)	Rh(1')	P(2)	142.62 (4)	P(1)	C(2)	C(21)	107.5 (4)
Rh(1)	Rh(1')	C(01')	131.9 (2)	P(1)	C(2)	C(22)	110.0 (4)
P(1)	Rh(1)	P(1')	113.67 (4)	P(1)	C(2)	C(23)	114.4 (5)
P(1)	Rh(1)	P(2)	115.35 (5)	C(21)	C(2)	C(22)	105.7 (6)
P(1)	Rh(1)	C(01)	112.6 (2)	C(21)	C(2)	C(23)	109.0 (6)
P(1)	Rh(1')	P(2')	116.13 (5)	C(22)	C(2)	C(23)	109.9 (6)
P(1)	Rh(1')	C(01')	110.3 (2)	C(3)	P(2)	C(1)	101.5 (5)
P(2)	Rh(1)	C(01)	85.4 (2)	C(3)	P(2)	C(5)	103.2 (6)
Rh(1)	P(1)	Rh(1')	66.33 (4)	C(1)	P(2)	C(5)	97.6 (5)
Rh(1)	P(1)	C(1)	117.1 (2)	P(1)	C(1)	C(11)	107.1 (4)
Rh(1)	P(1)	C(2)	123.6 (2)	P(1)	C(1)	C(12)	109.8 (4)
Rh(1')	P(1)	C(1)	122.5 (2)	P(1)	C(1)	C(13)	113.0 (5)
Rh(1')	P(1)	C(2)	115.1 (2)	C(11)	C(1)	C(12)	106.0 (6)
C(1)	P(1)	C(2)	107.8 (3)	C(11)	C(1)	C(13)	109.4 (6)
Rh(1)	P(2)	C(3)	114.4 (4)				
Rh(1)	P(2)	C(1)	122.3 (3)				
Rh(1)	P(2)	C(5)	115.0 (4)				

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

metals are known in which virtually no phosphorus–phosphorus coupling is observed.[8-10] The lack of P–P coupling is presumably due to different sets of metal orbitals used to bond to the bridging and terminal phosphorus nuclei.

X-ray Crystal Structure. The structure of **3** in the solid state has been determined by a single-crystal X-ray diffraction study. Details of intensity data collection and structure refinement are given in Table I and the Experimental Section. Atomic positional parameters, bond lengths, and bond angles are given in Tables II, III, and IV, respectively. A view of the molecule is shown in Figure 1.

Molecules of **3** possess a crystallographic inversion center at the midpoint of the Rh–Rh vector. Thus the central Rh_2P_2 core is vigorously planar; also, the rhodium-bridging phosphorus distances are equal to within experimental error (Rh(1)–P(1) = 2.330 (1) Å, Rh(1')–P(1) = 2.331 (1) Å) and can be compared with Rh–P distances of 2.418 (1) Å in **1** and 2.458 (2) and 2.244 (2) Å in **2**. The Rh–Rh distance (2.550 (1) Å) is consistent with a Rh–Rh double bond and is very similar to that observed in $[Rh(\mu\text{-}PH\text{-}t\text{-}Bu)(PMe_3)_2]_2$[3] (Rh–Rh = 2.552 (2) Å). Thus the Rh–Rh bond distances go from 3.717 (7) to 2.7609 (9) to 2.552 (2) Å in **1**, **2**, and **3**, respectively and reflect the apparent increase in bond order from 0 → 2. These changes are also accompanied by a progressive decrease in the Rh–P–Rh angles, which are 100.49 (6), 72.02 (7), and 66.33 (4)° in **1**, **2**, and **3**, respectively. In the cobalt triad there are few other complexes that have structures similar to that of **3** for comparison. These include $Co_2(\mu\text{-}Ph_2P)_2(CO)_2(PEt_2Ph)_2$,[9] $[Co(\mu\text{-}t\text{-}Bu_2P)CO(PMe_3)]_2$,[10] and $[Ir(\mu\text{-}Ph_2P)CO(PPh_3)]_2$.[11] Since the terminal PMe_3 and CO ligands on each Rh atom are considerably different in size the coordination geometry is distorted from that of a perfect tetrahedron. Thus the Rh(1')–Rh(1)–P(2) angle is 142.62 (4)° while that of Rh(1')–Rh(1)–C(01) is 131.9 (2)°. Also, the dihedral angle between the plane containing the C(01), P(2), and Rh(1) atoms and the plane of the central Rh_2P_2 core is 88.7 (2)°. This very slight distortion from 90° is also attributable to steric factors. A similar distortion was noted in $Co_2(\mu\text{-}Ph_2P)_2(CO)_2(PEt_2Ph)_2$.[9]

Acknowledgment. We thank the Dow Chemical Co., Midland, MI, the National Science Foundation (Grant CHE82-11883), and the Robert A. Welch Foundation (Grant F-816) for support. The X-ray diffractometer was purchased with funds from the National Science Foundation (Grant CHE82-05871) and The University of Texas at Austin. We also thank Johnson Matthey for a generous loan of $RhCl_3{\cdot}xH_2O$ and Perkin-Elmer Ltd for the donation of a thermocouple (P.E. 1330).

Registry No. **1**, 84623-35-8; **2**, 84454-21-7; **3**, 87451-47-6.

Supplementary Material Available: Listings of positional parameters including hydrogen atoms, atomic thermal parameters, and structure factors (24 pages). Ordering information is given on any current masthead page.

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