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Tetra- and Octanuclear μ_4-Phosphinidene Complexes of Rhodium: Synthesis and X-ray Structures of $Rh_4(CO)_4(\mu\text{-}P(C_6H_{11})_2)_4(\mu_4\text{-}P(C_6H_{11}))$ and $Rh_8(CO)_9(\mu_4\text{-}P(C_5H_9))_6$ (C_6H_{11} = Cyclohexyl, C_5H_9 = Cyclopentyl)

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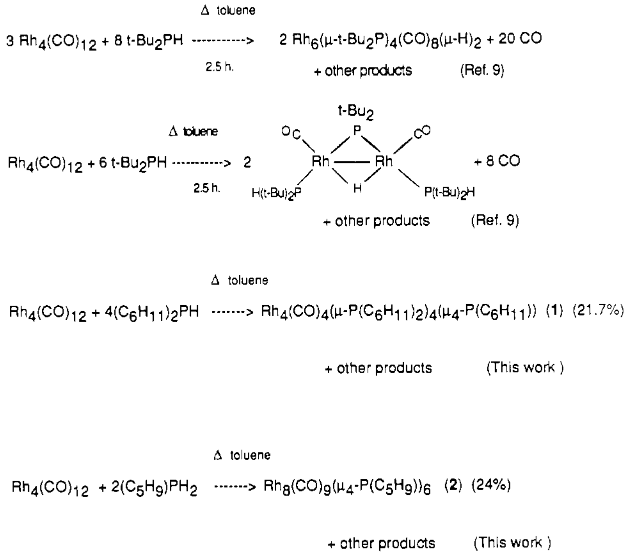
Reaction of $Rh_4(CO)_{12}$ with $(C_6H_{11})_2PH$ in toluene under reflux yields dark red crystalline $Rh_4(CO)_4(\mu\text{-}P(C_6H_{11})_2)_4(\mu_4\text{-}P(C_6H_{11}))$ (**1**) (22%) (C_6H_{11} = cyclohexyl). Reaction of $Rh_4(CO)_{12}$ with $(C_5H_9)PH_2$ in a sealed reaction vessel in toluene (110 °C) yields black $Rh_8(CO)_9(\mu_4\text{-}P(C_5H_9))_6$ (**2**) (24%) (C_5H_9 = cyclopentyl). The structures of **1** and **2** have been determined by X-ray crystallography. The molecular structure of **1** consists of four Rh atoms in a distorted plane. The Rh–Rh distances are all typical for single bonds, and each Rh atom bears a terminal CO unit. There are four edge-bridging $(C_6H_{11})_2P^-$ units and a μ_4 (capping), phosphinidene unit $(C_6H_{11})P$ bound to all four Rh atoms. The molecular structure of **2** consists of a central Rh_8 cube capped on each face by $\mu_4\text{-}C_5H_9P$ units. Each Rh atoms bears one terminal CO group except for one Rh atom which has two. Crystal data for **1**: $C_{72}H_{115}O_4P_5Rh_4$, $M_r = 1611.2$, triclinic, $P\bar{1}$, $a = 15.757$ (2) Å, $b = 18.311$ (3) Å, $c = 13.452$ (2) Å, $\alpha = 100.91$ (1)°, $\beta = 104.21$ (1)°, $\gamma = 83.26$ (1)°, $V = 3684.2$ (5) Å^3, $D_{calcd} = 1.452$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 10.17 cm^{-1}. Refinement of 4768 reflections ($I > 3\sigma(I)$) out of 10 504 unique observed reflections (3° < 2θ < 46°) gave R and R_w values of 0.058 and 0.066, respectively. Crystal data for **2**: $C_{39}H_{54}O_9P_6Rh_8$, $M_r = 1675.9$, monoclinic, $P2_1/n$, $a = 18.616$ (4) Å, $b = 21.864$ (3) Å, $c = 12.896$ (3) Å, $\beta = 90.16$ (2)°, $V = 5248.8$ (5) Å^3, $D_{calcd} = 2.121$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 26.41 cm^{-1}. Refinement of 3218 reflections ($I > 3\sigma(I)$) out of 6843 unique observed reflections (3° < 2θ < 45°) gave R and R_w values of 0.058 and 0.059, respectively.

Introduction

As part of a broad study of the chemistry of transition-metal phosphido (R_2P^-) and arsenido (R_2As^-) complexes we have investigated the chemistry of the bulky di-*tert*-butylphosphide (t-Bu_2P^-)[1] and di-*tert*-butylarsenide (t-Bu_2As^-) ligands.[2] In a number of cases we have observed the cleavage of P–C[3] or As–C[4] bonds, which results in the formation of a phosphinidene (t-BuP^{2-}) or arsinidene (t-$BuAs^{2-}$) unit. Pioneering work by Dahl,[5] Huttner,[6] Carty,[7] Vahrenkamp,[8] and others has clearly established that complexes containing this type of ligand are of interest since many undergo unusual organometallic transformations in addition to possessing novel structural features. The focus of this paper is the synthesis and structural determination of two unusual new phosphinidene complexes of rhodium.

Scheme I[a]



[a] C_6H_{11} = cyclohexyl; C_5H_9 = cyclopentyl.

In our previous studies we investigated the reaction of t-Bu_2PH with $Rh_4(CO)_{12}$. The novel Rh_6 cluster $Rh_6(\mu\text{-}t\text{-}Bu_2P)_4(CO)_8(H)_2$ is formed in this reaction in addition to the dinuclear complex $[Rh(CO)(t\text{-}Bu_2PH)]_2(\mu\text{-}H)(\mu\text{-}P\text{-}t\text{-}Bu_2)$ (Scheme I).[9] In contrast a variety of diphenylphosphido- (Ph_2P^-) bridged rhodium complexes are known and these are all tri- or tetranuclear.[10] Since the cyclohexyl group (Cy) is intermediate in size between t-Bu and Ph, we investigated the reaction of dicyclohexylphosphine (Cy_2PH) with $Rh_4(CO)_{12}$, expecting to form either a Rh_3 or a Rh_6 species. Suprisingly, this reaction produces the novel mixed tetraphosphido–phosphinidene complex $Rh_4(CO)_4(\mu\text{-}P(C_6H_{11})_2)_4(\mu_4\text{-}P(C_6H_{11}))$ (**1**) in moderate yield. Although the precise mechanism of formation of **1** is not clear, it must involve the cleavage of a P–C bond. Such processes are thought to be important in the deactivation of some transition-metal catalysts.[11] Since spectroscopic data for **1** is not structurally diagnostic, we determined the structure by a single-crystal X-ray diffraction study, the results of which are described below.

Having synthesized **1**, which contains a μ_4 phosphinidene unit capping four Rh atoms, our attention was drawn to other complexes involving μ_4-PR groups. One such complex is $Rh_4(COD)_4(\mu_4\text{-}P(C_6H_5))_2$ recently reported by Geoffroy and coworkers;[12] however, there are few other phosphinidene complexes of rhodium known. Of the well-studied phosphinidene complexes

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(1) Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888. Kang, S.-K.; Albright, T. A.; Jones, R. A.; Wright, T. C. *Organometallics* **1985**, *4*, 666. Arif, A. M.; Chandler, D. J.; Jones, R. A. *Organometallics* **1987**, *6*, 506. Arif, A. M.; Chandler, D. J.; Jones, R. J. *Inorg. Chem.* **1987**, *26*, 1780.

(2) Arif, A. M.; Jones, R. A.; Schwab, S. T.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1986**, *108*, 1703.

(3) Bright, T. A.; Jones, R. A.; Nunn, C. M., to be submitted for publication.

(4) Jones, R. A.; Whittlesey, B. R. *Organometallics* **1984**, *3*, 469. Jones, R. A.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1985**, *107*, 1078.

(5) See, for example: Rieck, D. F.; Montag, R. A.; McKechnie, T. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 1330.

(6) See, for example: Huttner, G.; Evertz, K. *Acc. Chem. Res.* **1986**, *19*, 406. Schneider, J.; Minelli, M.; Huttner, G. *J. Organomet. Chem.* **1985**, *294*, 75. Field, J. S.; Haines, R. J.; Smit, D. N.; Natarajan, K.; Scheidsteger, O.; Huttner, G. *J. Organomet. Chem.* **1982**, *240*, C23.

(7) See, for example: Lunniss, J.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* **1985**, *4*, 2066.

(8) See, for example: Vahrenkamp, H.; Wolters, D. *Organometallics* **1982**, *1*, 874. Vahrenkamp, H.; Wucherer, E. J.; Wolters, D. *Chem. Ber.* **1983**, *116*, 1219.

(9) Arif, A. M.; Jones, R. A.; Seeburger, M. H.; Whittlesey, B. R.; Wright, T. C. *Inorg. Chem.* **1986**, *25*, 3943. Arif, A. M.; Heaton, D. E.; Jones, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 1506.

(10) See, for example: Billig, E.; Jamerson, J. D.; Pruett, R. L. *J. Organomet. Chem.* **1980**, *192*, C49. Jamerson, J. D.; Pruett, R. L.; Billig, E.; Fiato, F. A. *J. Organomet. Chem.* **1980**, *193*, C43. Kreter, P. E.; Meek, D. W.; Christoph, G. G. *J. Organomet. Chem.* **1980**, *188*, C27. Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Organomet. Chem.* **1981**, *209*, C34. Haines, R. J.; Steen, N. D. C. T.; English, R. B. *J. Chem. Soc., Dalton Trans.* **1984**, 515.

(11) See, for example: Dubois, R. A.; Garrou, P. E.; Lavin, K. D.; Allcock, H. R. *Organometallics* **1984**, *3*, 649. Gastel, F. V.; Maclaughlin, S. A.; Lynch, M.; Carty, A. J.; Sappa, E.; Tiripicchio, A.; Camellini, M. T. *J. Organomet. Chem.* **1987**, *326*, C65, and references therein.

(12) Burkhardt, E. W.; Mercer, W. C.; Geoffroy, G.; Rheingold, A. L.; Fultz, W. C. *J. Chem. Soc., Chem. Commun.* **1983**, 1251.

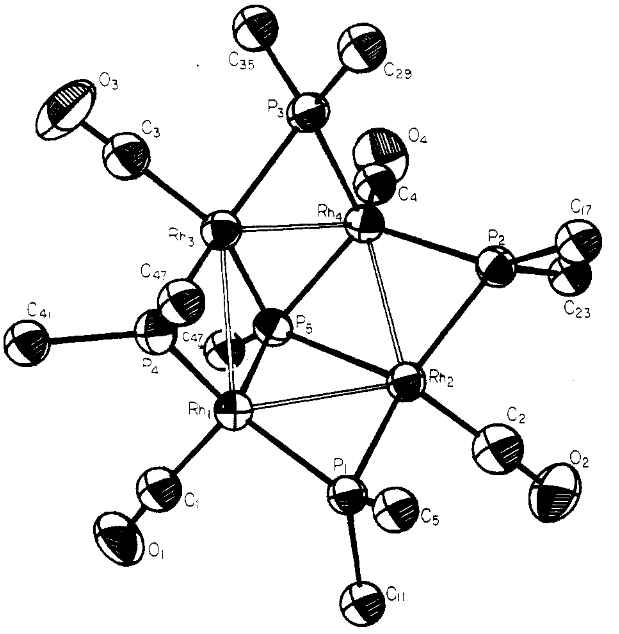

Figure 1. ORTEP view of **1** showing the atom-labeling scheme. Cyclohexyl groups have been omitted for clarity. Atoms are shown at the 50% probability level.

Table I. Crystal Structure Parameters for Complexes **1** and **2**

	1	**2**
	Description of Crystal	
color	dark red	black
habit	plate	prism
max cryst dimens, mm	0.30 × 0.29 × 0.10	0.40 × 0.32 × 0.14
	Unit Cell	
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
unit cell params		
a, Å	15.757 (2)	18.616 (4)
b, Å	18.311 (3)	21.864 (3)
c, Å	13.452 (2)	12.896 (3)
α, deg	100.91 (1)	90
β, deg	104.21 (1)	90.16 (2)
γ, deg	83.26 (1)	90
V, Å^3	3684.2 (5)	5248.8 (5)
molecules per unit cell	2	4
formula	$C_{72}H_{115}O_4P_5Rh_4$	$C_{39}H_{54}O_9P_6Rh_8$
mol wt	1611.2	1675.9
D_{calcd}, g cm^{-3}	1.452	2.121
μ(Mo Kα)$_{calcd}$, cm^{-1}	10.17	26.41
	Data Collection	
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
scan techniques	$\theta/2\theta$	$\theta/2\theta$
scan width, deg	0.8 + 0.35(tan θ)	0.8 + 0.35(tan θ)
range of indices: h,k,l	+16,±18,±13	+20,+23,±13
2θ range, deg	3.0–46.0	3.0–45.0
no. of reflcns measd	10504	7320
std reflcns		
intens	$2,\bar{5},6$, $5,9,\bar{1}$	$\bar{4},8,6$, $\bar{9},\bar{1},5$
orientation	$1,4,6$, $7,\bar{6},1$	$\overline{10},\bar{3},3$, $\overline{10},\bar{5},2$
decay of stds, %	6	14.6
min transmissn, %	78.54	84.35
max transmissn, %	99.94	99.99
av transmissn, %	93.99	92.84
agreement factor for avgd reflcns		
F_o	0.022	0.019
intens	0.026	0.019
	Structure Determination	
no. of reflcns used ($I > 3\sigma(I)$)	4768	3218
no. params varied	406	384
data/param ratio	11.74	8.38
shift/error ratio	0.135	0.594
esd. of an observn of unit wt	2.641	4.058
R	0.0575	0.0577
R_w	0.0664	0.0594

the classic compounds $Co_4(\mu_4\text{-}P(C_6H_5))_2(CO)_{10}$ and $Ni_8(CO)_8(\mu_4\text{-}P(C_6H_5))_6$ prepared by Dahl and co-workers stand out as landmark contributions to the field.[13,14] A particularly interesting feature is the stabilization of the unusual M_8 cubane-like geometry in $Ni_8(CO)_8(\mu_4\text{-}P(C_6H_5))_6$. More recently related Ni_8 cubane type clusters were reported by Fenske and co-workers.[15] Until the work described in this paper such compounds, which feature a central $M_8(\mu_4\text{-}PR)_6$ core, have not been reported for rhodium. We reasoned that the reaction of a small primary phosphine (RPH_2) with $Rh_4(CO)_{12}$ in the correct molar ratio might well produce the desired $M_8(\mu_4\text{-}PR)_6$ system. A systematic study of the reactions of primary phosphines (RPH_2) with $Rh_4(CO)_{12}$ was therefore undertaken, and full details of this study will be presented elsewhere. In the case where R = cyclopentyl (C_5H_9), the complex $Rh_8(CO)_9(\mu_4\text{-}P(C_5H_9))_6$ (**2**) is indeed formed, and this compound contains the $Rh_8(\mu_4\text{-}PR)_6$ core. The mechanism of formation of **2** is doubtless quite complex, and as for **1**, spectroscopic data is quite uninformative so we again turned to X-ray crystallography to provide unequivocal structural characterization. The X-ray structure of **2** revealed a further unusual feature in the presence of nine CO ligands per $Rh_8(\mu_4\text{-}(C_5H_9)P)_6$ unit. One Rh atom of the cluster bears two CO ligands while the rest have only one. The presence of the extra CO ligand is all that prevents **2** from being isostructural with $Ni_8(CO)_8(\mu_4\text{-}P(C_6H_5))_6$. This paper describes the synthesis and X-ray structures of **1** and **2**.

Results and Discussion

Syntheses of $Rh_4(CO)_4(\mu\text{-}P(C_6H_{11})_2)_4(\mu_4\text{-}P(C_6H_{11}))$ (1) and $Rh_8(CO)_9(\mu_4\text{-}P(C_5H_9))_6$ (2). Reaction of $Rh_4(CO)_{12}$[16] with $(C_6H_{11})_2PH$ in boiling toluene produces a deep red solution from which the tetranuclear complex $Rh_4(CO)_4(\mu\text{-}P(C_6H_{11})_2)_4(\mu_4\text{-}P(C_6H_{11}))$ (**1**) (C_6H_{11} = cyclohexyl) can be isolated following chromatography as dark red crystals in ca. 22% yield. Reaction of $Rh_4(CO)_{12}$ with $H_2P(C_5H_9)$[17] in a sealed reaction vessel in toluene (110 °C) produces a black solution from which the octanuclear complex $Rh_8(CO)_9(\mu_4\text{-}P(C_5H_9))_6$ (**2**) can be isolated as black crystals in ca. 24% yield (Scheme I). It is clear that there are other compounds produced in both cases. However despite many attempts at separation via chromatography, we have so far failed to isolate or characterize any of them.

Spectroscopic data for **1** and **2** are in accord with the structures as determined by X-ray crystallography. Thus, for both compounds, IR spectra have several strong bands in the region expected for terminal carbonyl groups. The $^{31}P\{^1H\}$ NMR of **1** in C_6D_6 (ambient temperature) shows two multiplets shifted well downfield, one more so than the other (δ 704.4 and 312.1) indicative of phosphinidene and phosphido groups bridging metal–metal bonds. The spectrum is essentially unchanged at −80 °C (toluene-d_8). The $^{31}P\{^1H\}$ NMR spectrum of **2** in toluene-d_8 shows a single broad resonance shifted downfield (δ 532.6, $\Delta w_{1/2}$ = 210 Hz; at −90 °C, $\Delta w_{1/2}$ = 260 Hz), which is consistent with the presence of only phosphinidene groups capping metal faces.

X-ray Structure of 1. Molecules of **1** crystallize in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. In addition, two molecules of toluene are present in each asymmetric unit. Figure 1 shows the molecular geometry and atom-numbering scheme of complex **1**. Selected bond lengths and angles and positional parameters are given in Tables II–IV. The molecular geometry of **1** consists of a butterfly arrangement of four Rh atoms with $\mu\text{-}P(C_6H_{11})_2$ units bridging metal–metal bonds on each of

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(13) Ryan, R. C.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6904.
(14) Lower, L. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1976**, *98*, 5046.
(15) For $Ni_8(CO)_4(PPh_3)_4(\mu_4\text{-}PPh)_6$ and $Ni_8Cl_4(PPh_3)_4(\mu_4\text{-}PPh)_6$, see: Fenske, D.; Hachgenei, J.; Rogel, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 982.
(16) Martinengo, S.; Giordano, G.; Chini, P. *Inorg. Synth.* **1980**, *20*, 209.
(17) Kosolapoff, G. M.; Maier, L. *Organic Phosphorus Compounds*; Wiley: New York, 1972; Vol. 1, p 4.

Table II. Selected Bond Lengths (Å) for **1**[a]

Rh(1)–Rh(2)	2.768 (2)	Rh(2)–C(2)	1.80 (2)
Rh(1)–Rh(3)	2.779 (2)	Rh(3)–Rh(4)	2.770 (2)
Rh(1)–P(1)	2.237 (4)	Rh(3)–P(3)	2.326 (4)
Rh(1)–P(4)	2.241 (5)	Rh(3)–P(4)	2.320 (4)
Rh(1)–P(5)	2.244 (4)	Rh(3)–P(5)	2.486 (5)
Rh(1)–C(1)	1.90 (2)	Rh(3)–C(3)	1.84 (2)
Rh(2)–Rh(4)	2.768 (2)	Rh(4)–P(2)	2.256 (4)
Rh(2)–P(1)	2.324 (4)	Rh(4)–P(3)	2.237 (5)
Rh(2)–P(2)	2.313 (4)	Rh(4)–P(5)	2.246 (4)
Rh(2)–P(5)	2.536 (4)	Rh(4)–C(4)	1.880 (15)

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

Table III. Selected Bond Angles (deg) for **1**[a]

Rh(2)–Rh(1)–Rh(3)	85.20 (5)	Rh(2)–Rh(4)–C(4)	130.9 (6)
Rh(2)–Rh(1)–P(1)	54.1 (1)	Rh(3)–Rh(4)–P(2)	122.4 (1)
Rh(2)–Rh(1)–P(4)	121.8 (1)	Rh(3)–Rh(4)–P(3)	54.1 (1)
Rh(2)–Rh(1)–P(5)	59.7 (1)	Rh(3)–Rh(4)–P(5)	58.3 (1)
Rh(2)–Rh(1)–C(1)	129.5 (5)	Rh(3)–Rh(4)–C(4)	131.0 (5)
Rh(3)–Rh(1)–P(1)	126.2 (1)	Rh(1)–P(1)–C(11)	120.2 (5)
Rh(3)–Rh(1)–P(4)	53.8 (1)	Rh(2)–P(1)–C(5)	114.6 (5)
Rh(3)–Rh(1)–P(5)	58.2 (1)	Rh(2)–P(1)–C(11)	114.5 (5)
Rh(3)–Rh(1)–C(1)	130.0 (5)	C(5)–P(1)–C(11)	104.7 (7)
P(1)–Rh(1)–P(4)	116.2 (2)	Rh(2)–P(2)–Rh(4)	74.6 (1)
P(1)–Rh(1)–P(5)	111.6 (1)	Rh(2)–P(2)–C(17)	111.6 (5)
P(1)–Rh(1)–C(1)	103.7 (5)	Rh(2)–P(2)–C(23)	118.7 (6)
P(4)–Rh(1)–P(5)	110.9 (2)	Rh(4)–P(2)–C(17)	133.1 (6)
P(4)–Rh(1)–C(1)	108.6 (5)	Rh(4)–P(2)–C(23)	116.7 (5)
P(5)–Rh(1)–C(1)	104.9 (5)	C(17)–P(2)–C(23)	101.1 (7)
Rh(1)–Rh(2)–Rh(4)	90.01 (5)	Rh(3)–P(3)–Rh(4)	74.7 (2)
Rh(1)–Rh(2)–P(1)	51.2 (1)	Rh(3)–P(3)–C(29)	114.4 (5)
Rh(1)–Rh(2)–P(2)	137.6 (1)	Rh(3)–P(3)–C(35)	115.8 (5)
Rh(1)–Rh(2)–P(5)	49.83 (9)	Rh(4)–P(3)–C(29)	124.8 (5)
Rh(1)–Rh(2)–C(2)	134.7 (6)	Rh(4)–P(3)–C(35)	120.4 (6)
Rh(4)–Rh(2)–P(1)	139.1 (1)	C(29)–P(3)–C(35)	104.4 (8)
Rh(4)–Rh(2)–P(2)	51.8 (1)	Rh(1)–P(4)–Rh(3)	75.0 (1)
Rh(4)–Rh(2)–P(5)	49.9 (1)	Rh(1)–P(4)–C(41)	118.9 (6)
Rh(4)–Rh(2)–C(2)	132.9 (5)	Rh(1)–P(4)–C(47)	130.3 (5)
P(1)–Rh(2)–P(2)	151.4 (2)	Rh(3)–P(4)–C(41)	119.0 (5)
P(1)–Rh(2)–P(5)	99.3 (1)	Rh(3)–P(4)–C(47)	110.9 (5)
P(1)–Rh(2)–C(2)	88.0 (6)	C(41)–P(4)–C(47)	101.5 (7)
P(2)–Rh(2)–P(5)	100.8 (1)	Rh(1)–P(5)–Rh(2)	70.5 (1)
P(2)–Rh(2)–C(2)	87.5 (6)	Rh(1)–P(5)–Rh(3)	71.7 (1)
P(5)–Rh(2)–C(2)	144.1 (6)	Rh(1)–P(5)–Rh(4)	121.4 (2)
Rh(1)–Rh(3)–Rh(4)	89.76 (5)	Rh(1)–P(5)–C(53)	115.7 (5)
Rh(1)–Rh(3)–P(3)	138.6 (1)	Rh(2)–P(5)–Rh(3)	96.8 (2)
Rh(1)–Rh(3)–P(4)	51.2 (1)	Rh(2)–P(5)–Rh(4)	70.5 (1)
Rh(1)–Rh(3)–P(5)	50.1 (1)	Rh(2)–P(5)–C(53)	134.7 (6)
Rh(1)–Rh(3)–C(3)	131.5 (5)	Rh(3)–P(5)–Rh(4)	71.5 (1)
Rh(4)–Rh(3)–P(3)	51.2 (1)	Rh(3)–P(5)–C(53)	128.3 (6)
Rh(4)–Rh(3)–P(4)	136.5 (1)	Rh(4)–P(5)–C(53)	122.9 (5)
Rh(4)–Rh(3)–P(5)	50.24 (9)	Rh(1)–C(1)–O(1)	174 (1)
Rh(4)–Rh(3)–C(3)	135.1 (5)	Rh(2)–C(2)–O(2)	176 (2)
P(3)–Rh(3)–P(4)	150.7 (2)	Rh(3)–C(3)–O(3)	176 (2)
P(3)–Rh(3)–P(5)	99.6 (2)	Rh(4)–C(4)–O(4)	176 (2)
P(3)–Rh(3)–C(3)	89.9 (5)	P(2)–Rh(4)–P(3)	116.3 (2)
P(4)–Rh(3)–P(5)	100.4 (2)	P(2)–Rh(4)–P(5)	112.3 (2)
P(4)–Rh(3)–C(3)	88.3 (5)	P(2)–Rh(4)–C(4)	106.4 (5)
P(5)–Rh(3)–C(3)	140.2 (5)	P(3)–Rh(4)–P(5)	110.2 (2)
Rh(2)–Rh(4)–Rh(3)	85.36 (5)	P(3)–Rh(4)–C(4)	103.2 (6)
Rh(2)–Rh(4)–P(2)	53.6 (1)	P(5)–Rh(4)–C(4)	107.6 (5)
Rh(2)–Rh(4)–P(3)	125.9 (1)	Rh(1)–P(1)–Rh(2)	74.7 (1)
Rh(2)–Rh(4)–P(5)	59.7 (1)	Rh(1)–P(1)–C(5)	125.4 (5)

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

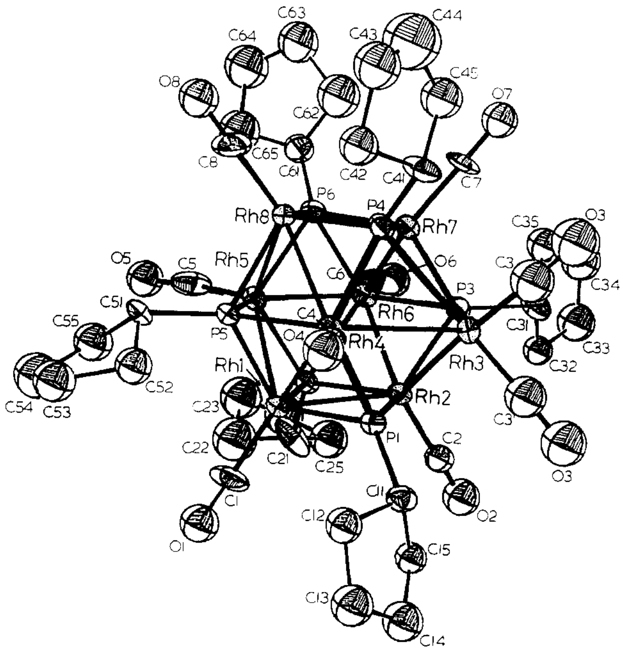

Figure 2. ORTEP view of **2** showing the atom-labeling scheme. Atoms are shown at the 30% probability level.

the four edges. In addition, there is a μ_4-P(C_6H_{11}) unit capping all four Rh atoms. Each Rh atom is also coordinated to a terminal carbonyl ligand. The butterfly arrangement of Rh atoms is much closer to that of a plane than to a tetrahedron with a dihedral angle between the planes [Rh(1), Rh(2), Rh(3)] and [Rh(2), Rh(3), Rh(4)] of 32.4°. Thus, the metal–metal vectors Rh(1)–Rh(4) and Rh(2)–Rh(3) are too long to be considered bonding interactions with distances of 3.91 and 3.75 Å, respectively. The four Rh–Rh bonds are within normal limits for single bonds with values ranging from 2.768 (2) to 2.779 (2) Å. The metal core geometry also results in considerable distortion of the bridging phosphido and capping phosphinidene units. The four phosphido groups are all bent back on the same side of the molecule away from the phosphinidene group. This results in roughly tetrahedral geometry for Rh(1) and Rh(4) and square-planar geometry for Rh(2) and Rh(3). In addition, the phosphinidene unit is capping in an asymmetric manner with the distances of P(5) from Rh(1) and Rh(4) of 2.244 (4) and 2.246 (4) Å while those of P(5) to Rh(2) and Rh(3) are 2.536 (4) and 2.486 (5) Å, respectively. The last two distances are considerably longer than those of a typical Rh–P bond.[9,18,19] The reason for this distortion of the metal core and the phosphido and phosphinidene groups may well be due to the steric bulk of the ligands. It has been previously noted that the use of sterically demanding phosphides or arsenides can dramatically alter the molecular geometries of larger metal clusters.[2,9] All other structural parameters for the molecule fall within reasonable limits. Thus, the Rh–P (phosphido) distances range from 2.237 (5) to 2.326 (4) Å, which may be compared with those in other Rh phosphido-bridged systems (ca. 2.3 Å).[9,18,20] Like $Rh_4(\mu_4\text{-}PPh)_2(COD)_4$,[12] compound **1** has an electron count of 60 and is four electrons deficient from the 64 electrons required for a saturated square-planar tetranuclear cluster.[21]

X-ray Structure of 2. Molecules of **2** crystallize in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. Figure 2 shows the molecular geometry and atom numbering scheme, and Figure 3 is a view of the central Rh_8P_6 core of the molecule. Selected bond lengths and angles are given in Tables V and VI, respectively. Positional parameters are given in Table VII. The molecular geometry of **2** consists of a distorted cube of eight Rh atoms with each of the six faces capped by μ_4-(C_5H_9)P units. Seven of the Rh atoms have a terminal CO group while Rh(3) is bonded to *two* carbonyls. To our knowledge, this is the first example of a cubic arrangement for a Rh_8 cluster and only the second octarhodium complex structurally characterized, the first being the carbido cluster $Rh_8(CO)_{19}C$.[22] The metal core in $Rh_8(CO)_{19}C$ is a monocapped prism with an edge-bridging Rh

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(18) Jones, R. A.; Wright, T. C. *Organometallics* **1983**, *2*, 470.

(19) Atwood, J. L.; Hunter, W. E.; Jones, R. A.; Wright, T. C. *Inorg. Chem.* **1983**, *22*, 993.

(20) Bullock, L. M.; Field, J. S.; Haines, R. J.; Minshall, E.; Smit, D. N.; Sheldrick, G. N. *J. Organomet. Chem.* **1986**, *310*, C47–C50.

(21) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.

(22) Albano, V. G.; Sensoni, M.; Chini, P.; Martinengo, S.; Strumolo, D. *J. Chem. Soc. Dalton Trans.*, **1975**, 305.

Table IV. Positional Parameters for 1

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Rh(1)	0.81060 (8)	−0.30607 (7)	0.90628 (9)	2.69 (3)	C(31)	0.911 (2)	−0.150 (1)	0.457 (2)	7.6 (6)*
Rh(2)	0.68196 (8)	−0.35488 (7)	0.73291 (9)	2.89 (3)	C(32)	0.847 (1)	−0.164 (1)	0.349 (2)	6.7 (5)*
Rh(3)	0.81449 (8)	−0.18731 (7)	0.80629 (9)	2.85 (3)	C(33)	0.778 (1)	−0.215 (1)	0.354 (1)	5.7 (5)*
Rh(4)	0.64519 (8)	−0.21056 (7)	0.69176 (9)	2.93 (3)	C(34)	0.727 (1)	−0.179 (1)	0.438 (1)	4.6 (4)*
P(1)	0.7928 (3)	−0.4248 (2)	0.8306 (3)	2.75 (9)	C(35)	0.717 (1)	−0.0381 (9)	0.671 (1)	4.0 (4)*
P(2)	0.6112 (3)	−0.3160 (2)	0.5776 (3)	3.1 (1)	C(36)	0.686 (1)	−0.006 (1)	0.773 (1)	4.5 (4)*
P(3)	0.7387 (3)	−0.1413 (2)	0.6568 (3)	3.2 (1)	C(37)	0.669 (1)	0.079 (1)	0.787 (1)	5.5 (4)*
P(4)	0.9311 (3)	−0.2581 (2)	0.8931 (3)	3.1 (1)	C(38)	0.599 (1)	0.099 (1)	0.693 (2)	7.1 (6)*
P(5)	0.6901 (3)	−0.2314 (2)	0.8565 (3)	2.86 (9)	C(39)	0.632 (2)	0.072 (1)	0.595 (2)	7.5 (6)*
O(1)	0.8249 (9)	−0.3143 (7)	1.1314 (9)	6.0 (4)	C(40)	0.647 (1)	−0.016 (1)	0.578 (1)	5.4 (4)*
O(2)	0.5817 (8)	−0.4894 (7)	0.662 (1)	6.7 (4)	C(41)	1.005 (1)	−0.2119 (9)	1.015 (1)	3.5 (3)*
O(3)	0.9235 (9)	−0.0576 (7)	0.866 (1)	7.2 (4)	C(42)	1.065 (1)	−0.275 (1)	1.068 (1)	4.3 (4)*
O(4)	0.4797 (8)	−0.1075 (8)	0.673 (1)	6.4 (4)	C(43)	1.132 (1)	−0.238 (1)	1.166 (1)	5.7 (5)*
C(1)	0.818 (1)	−0.3076 (9)	1.049 (1)	3.9 (4)*	C(44)	1.083 (1)	−0.187 (1)	1.240 (1)	5.3 (4)*
C(2)	0.623 (1)	−0.438 (1)	0.688 (1)	4.8 (4)*	C(45)	1.023 (1)	−0.128 (1)	1.190 (1)	5.7 (5)*
C(3)	0.884 (1)	−0.1086 (9)	0.842 (1)	4.0 (4)*	C(46)	0.956 (1)	−0.1623 (9)	1.091 (1)	4.2 (4)*
C(4)	0.541 (1)	−0.1478 (9)	0.683 (1)	3.9 (4)*	C(47)	1.012 (1)	−0.2954 (8)	0.808 (1)	3.2 (3)*
C(5)	0.868 (1)	−0.4847 (8)	0.755 (1)	3.1 (3)*	C(48)	1.081 (1)	−0.240 (1)	0.816 (1)	4.6 (4)*
C(6)	0.962 (1)	−0.4964 (9)	0.822 (1)	4.0 (4)*	C(49)	1.143 (1)	−0.275 (1)	0.743 (1)	5.2 (4)*
C(7)	1.024 (1)	−0.534 (1)	0.747 (1)	4.7 (4)*	C(50)	1.091 (1)	−0.292 (1)	0.631 (1)	5.6 (5)*
C(8)	0.992 (1)	−0.612 (1)	0.697 (1)	5.6 (5)*	C(51)	1.021 (1)	−0.349 (1)	0.622 (1)	5.1 (4)*
C(9)	0.896 (1)	−0.602 (1)	0.630 (1)	5.2 (4)*	C(52)	0.958 (1)	−0.3153 (9)	0.695 (1)	4.1 (4)*
C(10)	0.834 (1)	−0.560 (1)	0.700 (1)	4.6 (4)*	C(53)	0.633 (1)	−0.1865 (9)	0.960 (1)	3.7 (3)*
C(11)	0.753 (1)	−0.4900 (9)	0.898 (1)	3.6 (3)*	C(54)	0.695 (1)	−0.132 (1)	1.043 (2)	6.4 (5)*
C(12)	0.673 (1)	−0.452 (1)	0.940 (1)	4.5 (4)*	C(55)	0.653 (2)	−0.104 (1)	1.139 (2)	8.1 (6)*
C(13)	0.636 (1)	−0.509 (1)	0.988 (1)	5.7 (5)*	C(56)	0.569 (2)	−0.062 (1)	1.102 (2)	8.1 (6)*
C(14)	0.709 (1)	−0.533 (1)	1.080 (2)	5.9 (5)*	C(57)	0.504 (2)	−0.114 (1)	1.020 (2)	8.9 (7)*
C(15)	0.788 (1)	−0.572 (1)	1.037 (1)	5.4 (4)*	C(58)	0.548 (2)	−0.143 (1)	0.925 (2)	7.6 (6)*
C(16)	0.826 (1)	−0.5179 (9)	0.983 (1)	4.3 (4)*	C(59)	0.498 (2)	0.674 (2)	−0.005 (2)	10.2 (8)*
C(17)	0.658 (1)	−0.3681 (9)	0.467 (1)	3.4 (3)*	C(60)	0.450 (2)	0.688 (2)	−0.097 (3)	14 (1)*
C(18)	0.619 (1)	−0.444 (1)	0.419 (1)	4.5 (4)*	C(61)	0.368 (3)	0.720 (2)	−0.117 (3)	16 (1)*
C(19)	0.665 (1)	−0.486 (1)	0.331 (1)	5.6 (5)*	C(62)	0.329 (2)	0.741 (2)	−0.027 (3)	13 (1)*
C(20)	0.763 (1)	−0.497 (1)	0.374 (1)	5.4 (4)*	C(63)	0.370 (2)	0.731 (2)	0.075 (2)	11.8 (9)*
C(21)	0.802 (1)	−0.422 (1)	0.418 (1)	5.5 (4)*	C(64)	0.462 (2)	0.693 (2)	0.086 (3)	13 (1)*
C(22)	0.759 (1)	−0.3807 (9)	0.506 (1)	4.3 (4)*	C(65)	0.528 (3)	0.675 (3)	0.178 (4)	19 (2)*
C(23)	0.492 (1)	−0.3303 (9)	0.526 (1)	3.6 (3)*	C(66)	0.883 (2)	0.049 (1)	0.244 (2)	8.7 (7)*
C(24)	0.439 (1)	−0.313 (1)	0.611 (1)	5.1 (4)*	C(67)	0.885 (3)	0.056 (2)	0.346 (3)	16 (1)*
C(25)	0.340 (1)	−0.323 (1)	0.563 (1)	5.7 (5)*	C(68)	0.816 (2)	0.078 (2)	0.398 (3)	14 (1)*
C(26)	0.307 (1)	−0.273 (1)	0.477 (2)	7.0 (5)*	C(69)	0.743 (2)	0.088 (2)	0.310 (2)	11.4 (9)*
C(27)	0.356 (1)	−0.292 (1)	0.393 (1)	5.6 (5)*	C(70)	0.726 (2)	0.089 (2)	0.207 (3)	14 (1)*
C(28)	0.456 (1)	−0.281 (1)	0.440 (1)	4.5 (4)*	C(71)	0.816 (2)	0.063 (2)	0.173 (3)	15 (1)*
C(29)	0.793 (1)	−0.1669 (9)	0.545 (1)	3.8 (3)*	C(72)	0.796 (3)	0.063 (2)	0.078 (3)	18 (1)*
C(30)	0.863 (1)	−0.115 (1)	0.547 (1)	5.2 (4)*					

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

atom. The Rh–Rh distances in **2** are indicative of single metal–metal bonds, and all fall within normal limits ranging from 2.712 (3) to 2.881 (3) Å with an average of 2.772 Å. There is a distortion of the cube at opposite vertices—the Rh-Rh(3) distances are longer than average (Rh(2)–Rh(3) = 2.763 (3), Rh(4)–Rh(3) = 2.881 (3), Rh(7)–Rh(3) = 2.809 (3) Å) while the Rh–Rh(5) distances are shorter than average (Rh(1)–Rh(5) = 2.715 (3), Rh(6)–Rh(5) = 2.717 (3), Rh(8)–Rh(5) = 2.712 (3) Å). In addition, the three phosphinidene groups bound to Rh(3) cap asymmetrically, resulting in three very long Rh–P distances (Rh(3)–P(1) = 2.673 (7), Rh(3)–P(3) = 2.530 (7), Rh(3)–P(4) = 2.761 (7) Å). The remaining Rh–P distances are all typical of such bonds ranging from 2.246 (6) to 2.361 (7) Å.[9,18,19] These disortions may be attributed to the greater steric demands of the two CO units bound to Rh(3) as well as electronic factors since Rh(3) is relatively more electron rich than the other Rh atoms. The presence of the extra carbonyl ligand on Rh(3) should also result in a spectroscopic inequivalence of P(1), P(3), and P(4) from P(2), P(5), and P(6). However the $^{31}P\{^1H\}$ NMR, which remains essentially unchanged at −90 °C, is relatively uninformative. The broad signal that is observed probably consists of a number of overlapping multiplets that are not resolved.

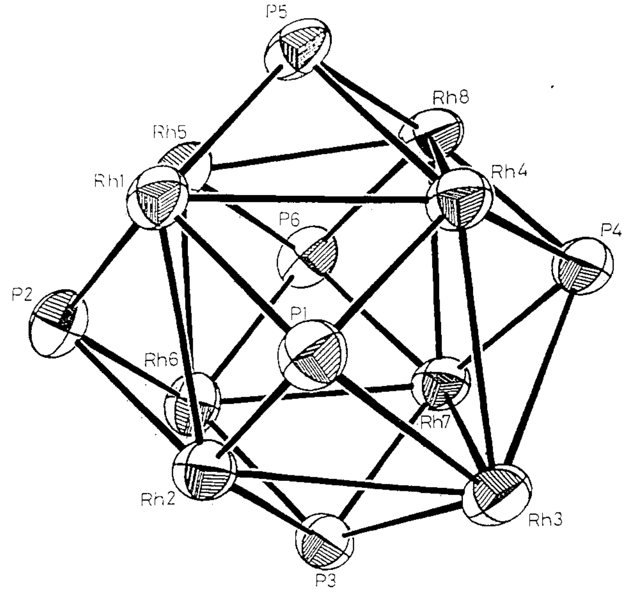

Figure 3. View of the central Rh_8P_6 core of **2**. Atoms are shown at the 50% probability level.

Experimental Section

All reactions were performed under oxygen-free nitrogen or under vacuum. Microanalyses were conducted by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Hexane, pentane, and toluene were dried over sodium and distilled from sodium/benzophenone under nitrogen before use. Instruments: IR, Perkin-Elmer 1330, Digilab FTS-40; NMR, Varian EM-390 (^{1}H 90 MHz), Nicolet NT 360 (^{1}H), GE QE-

Table V. Selected Bond Lengths (Å) for **2**[a]

Rh(1)–Rh(2)	2.776 (3)	Rh(4)–P(5)	2.354 (7)
Rh(1)–Rh(4)	2.787 (3)	Rh(4)–C(4)	1.70 (3)
Rh(1)–Rh(5)	2.715 (3)	Rh(5)–P(5)	2.327 (7)
Rh(1)–P(1)	2.267 (7)	Rh(5)–P(6)	2.302 (7)
Rh(1)–P(2)	2.342 (7)	Rh(5)–C(5)	1.63 (3)
Rh(1)–P(5)	2.315 (7)	Rh(6)–Rh(7)	2.776 (3)
Rh(1)–C(1)	1.82 (3)	Rh(6)–P(2)	2.361 (7)
Rh(2)–Rh(3)	2.763 (3)	Rh(6)–P(3)	2.278 (7)
Rh(2)–Rh(6)	2.776 (3)	Rh(6)–P(6)	2.341 (8)
Rh(2)–P(1)	2.285 (7)	Rh(6)–C(6)	1.74 (3)
Rh(2)–P(2)	2.310 (7)	Rh(7)–Rh(8)	2.774 (3)
Rh(2)–P(3)	2.271 (7)	Rh(7)–P(3)	2.268 (7)
Rh(2)–C(2)	1.82 (3)	Rh(7)–P(4)	2.257 (7)
Rh(3)–Rh(4)	2.881 (3)	Rh(7)–P(6)	2.318 (7)
Rh(3)–Rh(7)	2.809 (3)	Rh(7)–C(7)	1.77 (2)
Rh(3)–P(1)	2.673 (7)	Rh(8)–P(4)	2.263 (7)
Rh(3)–P(3)	2.530 (7)	Rh(8)–P(5)	2.336 (6)
Rh(3)–P(4)	2.761 (7)	Rh(8)–P(6)	2.354 (8)
Rh(3)–C(3)	1.76 (4)	Rh(8)–C(8)	1.83 (3)
Rh(3)–C(3′)	1.74 (4)	Rh(5)–Rh(6)	2.717 (3)
Rh(4)–Rh(8)	2.777 (3)	Rh(5)–Rh(8)	2.712 (3)
Rh(4)–P(1)	2.259 (7)	Rh(5)–P(2)	2.301 (7)
Rh(4)–P(4)	2.246 (6)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. A complete listing is provided in the supplementary material.

Table VI. Selected Bond Angles (deg) for **2**[a]

Rh(2)–Rh(1)–Rh(4)	80.39 (7)	Rh(3)–Rh(2)–P(1)	63.1 (2)
Rh(2)–Rh(1)–Rh(5)	84.99 (8)	Rh(3)–Rh(2)–P(2)	136.7 (2)
Rh(2)–Rh(1)–P(1)	52.7 (2)	Rh(3)–Rh(2)–P(3)	59.4 (2)
Rh(2)–Rh(1)–P(2)	52.8 (2)	Rh(3)–Rh(2)–C(2)	118 (1)
Rh(2)–Rh(1)–P(5)	116.9 (2)	Rh(6)–Rh(2)–P(1)	131.1 (2)
Rh(2)–Rh(1)–C(1)	128 (1)	Rh(6)–Rh(2)–P(2)	54.4 (2)
Rh(4)–Rh(1)–Rh(5)	85.88 (8)	Rh(6)–Rh(2)–P(3)	52.5 (2)
Rh(4)–Rh(1)–P(1)	51.9 (2)	Rh(6)–Rh(2)–C(2)	119 (1)
Rh(4)–Rh(1)–P(2)	116.2 (2)	P(1)–Rh(2)–P(2)	106.0 (3)
Rh(4)–Rh(1)–P(5)	54.0 (2)	P(1)–Rh(2)–P(3)	121.2 (2)
Rh(4)–Rh(1)–C(1)	131 (1)	P(1)–Rh(2)–C(2)	109 (1)
Rh(5)–Rh(1)–P(1)	120.8 (2)	P(2)–Rh(2)–P(3)	106.9 (3)
Rh(5)–Rh(1)–P(2)	53.5 (2)	P(2)–Rh(2)–C(2)	105 (1)
Rh(5)–Rh(1)–P(5)	54.4 (2)	P(3)–Rh(2)–C(2)	107.9 (9)
Rh(5)–Rh(1)–C(1)	129 (1)	Rh(2)–Rh(3)–Rh(4)	78.97 (7)
P(1)–Rh(1)–P(2)	105.5 (3)	Rh(2)–Rh(3)–Rh(7)	80.18 (8)
P(1)–Rh(1)–P(5)	105.8 (2)	Rh(2)–Rh(3)–P(1)	49.7 (2)
P(1)–Rh(1)–C(1)	110 (1)	Rh(2)–Rh(3)–P(3)	50.6 (2)
P(2)–Rh(1)–P(5)	107.8 (2)	Rh(2)–Rh(3)–P(4)	106.4 (2)
P(2)–Rh(1)–C(1)	113 (1)	Rh(2)–Rh(3)–C(3)	163 (1)
P(5)–Rh(1)–C(1)	115 (1)	Rh(2)–Rh(3)–C(3′)	87 (1)
Rh(1)–Rh(2)–Rh(3)	101.51 (8)	Rh(4)–Rh(3)–Rh(7)	77.32 (7)
Rh(1)–Rh(2)–Rh(6)	93.25 (8)	Rh(4)–Rh(3)–P(1)	47.8 (2)
Rh(1)–Rh(2)–P(1)	52.1 (2)	Rh(4)–Rh(3)–P(3)	107.7 (2)
Rh(1)–Rh(2)–P(2)	53.9 (2)	Rh(4)–Rh(3)–P(4)	46.8 (1)
Rh(1)–Rh(2)–P(3)	130.7 (2)	Rh(4)–Rh(3)–C(3)	117 (1)
Rh(1)–Rh(2)–C(2)	120.5 (9)	Rh(4)–Rh(3)–C(3′)	126 (1)
Rh(3)–Rh(2)–Rh(6)	99.34 (8)	Rh(7)–Rh(3)–P(1)	106.6 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. A complete listing is provided in the supplementary material.

Table VII. Positional Parameters for **2**

atom	*x*	*y*	*z*	*B*,[a] Å^2
Rh(1)	0.1475 (1)	0.14557 (8)	0.8755 (2)	4.94 (4)
Rh(2)	0.1025 (1)	0.19585 (8)	1.0620 (2)	5.02 (4)
Rh(3)	0.0207 (1)	0.29353 (9)	0.9942 (2)	5.53 (5)
Rh(4)	0.0807 (1)	0.25108 (8)	0.8016 (2)	4.82 (4)
Rh(5)	0.2657 (1)	0.21676 (9)	0.9014 (2)	5.76 (5)
Rh(6)	0.2320 (1)	0.25571 (9)	1.0954 (2)	5.73 (5)
Rh(7)	0.1573 (1)	0.34792 (8)	0.9937 (2)	5.21 (5)
Rh(8)	0.2098 (1)	0.31474 (8)	0.8006 (2)	5.43 (5)
P(1)	0.0365 (3)	0.1816 (3)	0.9142 (5)	5.2 (2)
P(2)	0.2151 (4)	0.1564 (3)	1.0278 (6)	5.8 (2)
P(3)	0.1192 (4)	0.2907 (3)	1.1296 (5)	5.3 (2)
P(4)	0.0990 (4)	0.3500 (3)	0.8401 (5)	5.4 (2)
P(5)	0.1939 (4)	0.2125 (3)	0.7536 (5)	5.5 (2)
P(6)	0.2736 (4)	0.3163 (3)	0.9585 (6)	6.2 (2)
O(1)	0.137 (1)	0.018 (1)	0.807 (2)	11.7 (7)*
O(2)	0.046 (1)	0.116 (1)	1.228 (2)	12.2 (7)*
O(3)	−0.051 (2)	0.412 (2)	0.997 (2)	17 (1)*
O(3′)	−0.096 (2)	0.236 (1)	1.117 (2)	16 (1)*
O(4)	−0.026 (1)	0.256 (1)	0.631 (2)	10.8 (6)*
O(5)	0.410 (1)	0.176 (1)	0.856 (2)	12.1 (7)*
O(6)	0.316 (1)	0.263 (1)	1.289 (2)	11.7 (7)*
O(7)	0.153 (1)	0.475 (1)	1.076 (2)	10.5 (6)*
O(8)	0.276 (1)	0.384 (1)	0.628 (2)	11.0 (6)*
C(1)	0.141 (2)	0.067 (1)	0.833 (2)	12 (1)
C(2)	0.066 (2)	0.147 (1)	1.164 (2)	8.6 (8)
C(3)	−0.027 (2)	0.363 (2)	0.990 (3)	14 (1)*
C(3′)	−0.051 (2)	0.261 (2)	1.061 (3)	13 (1)*
C(4)	0.018 (2)	0.255 (1)	0.705 (2)	8.6 (8)
C(5)	0.348 (2)	0.197 (1)	0.872 (3)	10 (1)
C(6)	0.283 (2)	0.261 (1)	1.208 (3)	10 (1)
C(7)	0.155 (2)	0.423 (1)	1.044 (2)	8.7 (9)
C(8)	0.251 (2)	0.356 (1)	0.694 (2)	10 (1)
C(11)	−0.048 (1)	0.141 (1)	0.900 (2)	6.0 (6)
C(12)	−0.055 (2)	0.110 (1)	0.790 (2)	8.9 (8)*
C(13)	−0.100 (2)	0.052 (2)	0.807 (3)	12 (1)*
C(14)	−0.106 (2)	0.043 (2)	0.924 (3)	12 (1)*
C(15)	−0.054 (1)	0.085 (1)	0.977 (2)	7.5 (7)*
C(21)	0.244 (2)	0.085 (1)	1.104 (3)	12 (1)
C(22)	0.295 (3)	0.055 (3)	1.048 (4)	19 (2)*
C(23)	0.352 (3)	0.084 (2)	1.107 (4)	17 (2)*
C(24)	0.342 (3)	0.077 (2)	1.218 (4)	17 (2)*
C(25)	0.258 (2)	0.085 (2)	1.222 (3)	15 (1)*
C(31)	0.089 (2)	0.321 (1)	1.258 (2)	7.1 (7)
C(32)	0.098 (2)	0.274 (1)	1.343 (2)	7.9 (7)*
C(33)	0.112 (2)	0.311 (2)	1.439 (3)	14 (1)*
C(34)	0.134 (2)	0.373 (2)	1.412 (3)	15 (1)*
C(35)	0.134 (2)	0.376 (2)	1.293 (3)	10 (1)*
C(11)	0.051 (2)	0.416 (1)	0.785 (2)	7.3 (7)
C(42)	0.063 (2)	0.416 (2)	0.662 (3)	9.5 (9)*
C(43)	0.067 (2)	0.484 (2)	0.635 (3)	14 (1)*
C(44)	0.092 (3)	0.512 (3)	0.716 (5)	21 (2)*
C(45)	0.085 (2)	0.477 (2)	0.814 (3)	12 (1)*
C(51)	0.219 (1)	0.189 (1)	0.617 (2)	7.0 (7)
C(52)	0.154 (2)	0.157 (1)	0.562 (2)	9.2 (8)*
C(53)	0.191 (2)	0.117 (2)	0.482 (3)	12 (1)*
C(54)	0.255 (2)	0.099 (2)	0.527 (4)	16 (1)*
C(55)	0.274 (2)	0.136 (2)	0.629 (3)	11 (1)*
C(61)	0.356 (2)	0.360 (1)	0.987 (3)	12 (1)
C(62)	0.346 (3)	0.426 (2)	1.008 (4)	17 (2)*
C(63)	0.418 (2)	0.456 (2)	0.970 (4)	15 (1)*
C(64)	0.463 (3)	0.410 (2)	0.944 (4)	18 (2)*
C(65)	0.410 (2)	0.351 (2)	0.917 (3)	15 (1)*

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

300 (^{1}H, ^{31}P). IR spectra were run as Nujol mulls by using NaCl disks or in solution (matched KBr cells). NMR spectra were recorded in C_6D_6 at ambient temperature unless otherwise stated and are in ppm referenced to Me_4Si (δ 0.0, ^{1}H) and 85% H_3PO_4(aq.) (δ 0.0, ^{31}P). Melting points were obtained in sealed capillaries under nitrogen (1 atm) and are uncorrected. $(C_6H_{11})_2PH$ was purchased from the Strem Chemical Co., Newburyport, MA, and was used as received. $Rh_4(CO)_{12}$[16] and $(C_5H_9)PH_2$[17] were prepared as previously described.

Synthesis of $Rh_4(CO)_4(\mu\text{-}P(C_6H_{11})_2)_4(\mu_4\text{-}P(C_6H_{11}))$ (1). To a solution of $Rh_4(CO)_{12}$ (0.24 g, 0.32 mmol) in toluene (50 mL) was added $(C_6H_{11})_2PH$ (0.28 mL, 1.28 mmol), with the immediate evolution of CO and darkening. The solution was heated under reflux (2.5 h) during which time it formed a deep red solution. Volatile materials were removed under vacuum, and the residue was extracted into hexane (3 × 30 mL). The filtered, combined extracts were reduced in volume under vacuum (ca. 40 mL) and chromatographed on an alumina column (3 cm × 5 cm). With hexane as the eluent, a red fraction was obtained which is presently under study. The use of toluene then produced a deep red fraction from which volatile materials were removed under vacuum. The residue was redissolved in hexane (30 mL) and cooled (−35 °C), producing dark red, air-stable crystals of **1**. They were collected and dried under vacuum. The mother liquors from this fraction contain other Rh-containing species, which are still under investigation. Yield: 0.10 g, 21.7% based on Rh. Mp: 191–197 °C dec. IR (Nujol mull, NaCl plates): 1979 w, 1962 m, 1935 s, 1898 w, 1881 w, 1446 s, 1374 m, 1332 m, 1288 w, 1259 s, 1189 w, 1174 m, 1165 m, 1109 m, sh, 1095 s, 1065 m, sh, 1040 m, sh, 1021 s, 997 m, 913 w, 882 m, 846 s, 813 s cm^{-1}. ^{1}H NMR (361.084 MHz): δ 1.74 (br mult). ^{31}P{^{1}H} NMR (121.556 MHz): δ 704.4 (mult, μ_4-$(C_6H_{11})P$), 312.1 (mult, μ-$(C_6H_{11})_2P$). Anal. Calcd for $C_{58}H_{99}O_4P_5Rh_4$: C, 48.82; H, 6.99; P, 10.85. Found: C, 49.28; H, 7.11; P, 10.59.

Synthesis of $Rh_8(CO)_9(\mu_4\text{-}P(C_5H_9))_6$ (2). To a solution of $Rh_4(CO)_{12}$ (0.22 g, 0.29 mmol) in toluene (20 mL) in a glass pressure vessel was added $(C_5H_9)PH_2$ (0.068 mL, 0.59 mmol), with immediate evolution of CO and darkening. The vessel was closed and the solution was heated (100 °C, 1 h) during which time it turned black. Volatile materials were removed under vacuum, and the residue extracted into hexane (2 × 30 mL). The filtered combined extracts were reduced in volume under vacuum (ca. 30 mL) and cooled (−35 °C), producing black air stable crystals of **2**. They were collected and dried under vacuum. Chromatography on alumina results in decomposition of **2** on the column. Other products of the reaction have yet to be fully characterized. Yield: 0.06 g, 24% based on Rh. IR: (hexane solution, KBr cells) 2056 w, 2035 m, 2008 w, sh, 1993 s, 1986 s, 1966 s, 1946 w, sh (cm^{-1}; (Nujol mull, NaCl plates), 2078 m, 2031 m, 1989 s, 1978 s, 1967 s, sh, 1936 m, sh, 1260 s, 1087 s, br, 1017 s, br, 901 m, br, 797 s cm^{-1}. ^{1}H NMR (300.152 MHz): δ 1.67 (br mult). ^{31}P{^{1}H} NMR: (121.555 MHz): δ 532.6 (br mult, μ_4-$(C_5H_9)P$). Anal. Calcd for $C_{39}H_{54}O_9P_6Rh_8$: C, 27.95; H, 3.25; P, 11.09. Found: C, 28.11; H, 3.34; P, 11.01.

X-ray Experimental Data. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 2 °C using graphite-monochromated Mo Kα radiation. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package "SDP-PLUS".[23] For each structure, the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (MULTAN)[24] and successive cycles of difference Fourier maps followed by least-squares refinement.

1. Crystals were grown from toluene solutions (−40 °C) and mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by centering 25 reflections having 2θ values between 22 and 26°. They indicated a choice of the triclinic space groups $P1$ and $P\bar{1}$. The space group $P\bar{1}$ was chosen to be the correct one on the basis of successful refinement of the structure. Data were collected in the $+h,\pm k,\pm l$ hemisphere between 2θ values of 3 and 46°. The check reflections indicated a 6% decrease in intensity over the course of data collection; hence, a decay correction was applied. A ψ scan of four reflections having χ values between 80 and 90° showed a minimum transmission of 78.5% and a maximum transmission of 99.9%. An empirical absorption correction was applied. The observed structure factors of equivalent reflections were averaged, with agreement factors of 0.026 for intensity and 0.022 on F_o. All non-hydrogen and non-carbon atoms were refined anisotropically. Atoms C(59)–C(72) are those of the two toluene molecules of solvation. Hydrogen atoms were not located, but their contributions were included in the final refinements. Data with intensities less than $3.0\sigma(I)$ and $(\sin\theta)/\lambda$ less than 0.10 were excluded, and a non-Poisson contribution weighting scheme with an experimental instability factor of $P = 0.06$ was used in the final stages of refinement.[25] The atoms were refined to final values of 0.0575 and 0.0664 for R and R_w respectively. The maximum peak in the final difference Fourier map had a height of 0.742 e/Å^3 and was located 1.075 Å from C(10).

2. Crystals were grown from pentane (−40 °C) and mounted in thin-walled glass capillaries under nitrogen. Unit cell parameters were obtained by centering 25 reflections having 2θ values between 24 and 26°. The monoclinic space group $P2_1/n$ (No. 14) was uniquely determined by the systematic absences $h0l$, $h + l$ odd, and $0k0$, k odd. Data were collected in the $+h,+k,\pm l$ quadrant between 2θ values of 3 and 45°. The check reflections indicated a 14.6% decrease in intensity over the course of data collection; hence, a decay correction was applied. A ψ scan of four reflections having χ values between 80 and 90° showed a minimum transmission of 84.4% and a maximum transmission of 99.99%. An empirical absorption correction was applied. The observed structure factors of equivalent reflections were averaged with agreement factors of 0.019 for intensity and 0.019 on F_o. Hydrogen atoms were not located, but their contributions were included in the final refinements. Data with intensities less than $3.0\sigma(I)$ were excluded, and a non-Poisson contribution weighting scheme with an experimental instability factor of $P = 0.06$ was used in the final stages of refinement.[25] All rhodium and phosphorus atoms were refined anisotropically as were the carbonyl carbon atoms and the carbon atoms of the cyclopentyl rings bound directly to phosphorus. The remaining carbon atoms were refined isotropically. The atoms were refined to final values of 0.0577 and 0.0594 for R and R_w respectively. The maximum peak in the final difference Fourier map had a height of 0.928 e/Å^3 and was located 1.221 Å and Rh(2). Scattering factors were taken from ref 26. Supplementary material is available.[27]

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Registry No. **1**, 111847-31-5; **2**, 111868-76-9; $Rh_4(CO)_{12}$, 19584-30-6; $(C_6H_{11})_2PH$, 829-84-5.

Supplementary Material Available: Complete tables of bond lengths, angles, and anisotropic thermal parameters for **1** and **2** and a complete ORTEP view of **1** (18 pages); tables of observed and calculated structure factors for **1** and **2** (40 pages). Ordering information is given on any current masthead page.

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(23) "SDP Plus", 4th ed.; B. A. Frenz and Associates, College Station, TX, 1981.

(24) Germain, G.; Main, P.; Wolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368.

(25) P is used in the calculation of $\sigma(I)$ to downweight intense reflections in the least-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 4(F_o)^2/[\sum(F_o)^2]^2$, where $[\sum(F_o)^2]^2 = [S^2(C + R^2B) + \{P(F_o)^2\}^2]/(Lp)^2$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count and Lp is the Lorentz-polarization factor.

(26) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4.

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