

6) suggests that the condensation of the two latter species could be responsible for the formation of the former one. This proposal is probably validated by the predominance of  $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$  in the solid fractions above in which  $[\text{Rh}_{22}(\text{CO})_{35}\text{H}_{x+n}]^{(5-n)-}$  is present. We believe that the aggregation of  $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$  with  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  in the presence of protons, e.g., provided by a nonoxidizing protonic acid such as trifluoromethylsulfonic, could produce the 22 rhodium atom cluster.<sup>24</sup>

We are attempting to optimize the synthesis of  $[\text{Rh}_{22}(\text{CO})_{35}\text{H}_{x+n}]^{(5-n)-}$ , on the last hypothesis, and to obtain evidence for the processes involved in cluster growth, mainly by studying the redox reactions of high-nuclearity rhodium carbonyl clusters,<sup>25a</sup> e.g.,  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ ,  $[\text{Rh}_{13}(\text{CO})_{24}\text{H}_x]^{(5-x)-}$ ,  $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ ,  $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$ , and  $[\text{Rh}_{22}(\text{CO})_{35}\text{H}_{x+n}]^{(5-n)-}$ , and

(24) J. L. Vidal and R. C. Schoening, submitted for publication in *J. Organomet. Chem.*

(25) (a) J. L. Vidal and R. C. Schoening, to be submitted for publication in *J. Am. Chem. Soc.*; (b) J. L. Vidal and R. C. Schoening, submitted for publication in *J. Organomet. Chem.*; (c) J. L. Vidal and R. C. Schoening, submitted for publication in *Inorg. Chem.*

the Brønsted acid-base chemistry of  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$  and  $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$ .<sup>25b</sup>

Finally, it should be noted that the synthetic procedure followed for the preparation of  $[\text{Rh}_{22}(\text{CO})_{35}\text{H}_{x+n}]^{(5-n)-}$  has also provided an unexpected new synthesis for  $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$ . This cluster can now be prepared in 63% yield by the procedure described in this work from commercially available  $\text{Rh}(\text{CO})_2\text{acac}$ . Nevertheless, we will report soon another synthesis that results practically in quantitative yields of  $[\text{Rh}_{15}(\text{CO})_{27}]^{3-}$  with very short working time.<sup>25c</sup>

**Acknowledgment.** The authors appreciate the authorization for publication of this work by Union Carbide Corp. and the encouragement toward applied basic research from Dr. George L. O'Connor.

**Registry No.**  $\text{Rh}(\text{CO})_2\text{acac}$ , 14874-82-9;  $\text{CsPhCO}_2$ , 17265-04-2;  $[\text{Ph}_3\text{P}=\text{NPPH}_3]_3[\text{Rh}_{15}(\text{CO})_{27}]$ , 75506-17-1; Cs, 7440-46-2; 18-crown-6, 17455-13-9.

**Supplementary Material Available:** Complete tables of structural factors, atomic distances and angles, and positional and thermal parameters (42 pages). Ordering information is given on any current masthead page.

Contribution from Union Carbide Corporation,  
South Charleston, West Virginia 25303

## $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$ . A Transition-Metal Carbonyl Cluster with a Metal Polyhedron Based on the Biccapped Square Antiprism As Illustrated by the Structural Study of the Benzyltriethylammonium Salt

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Received November 12, 1979

The reaction of  $\text{Rh}(\text{CO})_2\text{acac}$  with triphenylphosphine in the presence of cesium benzoate and cesium borohydride in tetraethylene glycol dimethyl ether solution resulted in the selective formation of  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  (76% yield) after 4 h of contact time under 400 atm of carbon monoxide and hydrogen ( $\text{CO}:\text{H}_2 = 1$ ) at 140–160 °C. The cluster has been isolated as the cesium and benzyltriethylammonium salts, both of which are stable to moisture and oxygen. These salts are soluble in polar organic solvents, e.g., acetone, but insoluble in solvents of lower polarity. The  $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3][\text{Rh}_{10}\text{P}(\text{CO})_{22}]$  complex has been characterized via a complete three-dimensional X-ray diffraction study. The complex crystallizes in the space group *Cc* with  $a = 25.011$  (3) Å,  $b = 16.348$  (4) Å,  $c = 18.267$  (4) Å,  $\alpha = \gamma = 90.0$  (1)°,  $\beta = 101.47$  (1)°,  $V = 7319.7$  Å<sup>3</sup>, and  $\rho(\text{calcd}) = 2.045$  g cm<sup>-3</sup>, for a molecular weight of 2253.24 and  $Z = 4$ . Diffraction data were collected with an Enraf-Nonius CAD 4 automated spectrometer using graphite-monochromatized Mo  $K\alpha$  radiation. The structure was solved by direct methods and refined by difference-Fourier and least-squares techniques. The rhodium cluster was found to have a 50:50 disorder when rotated 45° about the noncrystallographic fourfold axis in the cluster. All nonhydrogen atoms have been located and refined: final discrepancy indices are  $R_F = 6.4\%$  and  $R_{wF} = 7.7\%$  for 2700 reflections in the range of  $0.5^\circ < 2\theta < 45^\circ$ . The anion's structure shows 10 rhodium atoms on the corners of a biccapped square antiprism with the phosphorus atom placed on the center of the cluster. This is the first instance in which this polyhedron has been reported for a transition-metal cluster. Average bonding distances for the anion are in the ranges  $\text{Rh}-\text{Rh} = 2.864\text{--}3.007$  Å and  $\text{Rh}-\text{P} = 2.446\text{--}3.012$  Å with  $\text{Rh}-\text{C}$  and  $\text{C}-\text{O}$  distances similar to those usually observed for these complexes. <sup>13</sup>C and <sup>31</sup>P NMR results are interpreted as indicative of the fluxionality of the carbon monoxide and rhodium atoms cores, respectively. The reversibility of the reaction  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-} + 3\text{CO} \rightleftharpoons [\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-} + [\text{Rh}(\text{CO})_4]^-$  has been established under ambient- and high-pressure conditions.

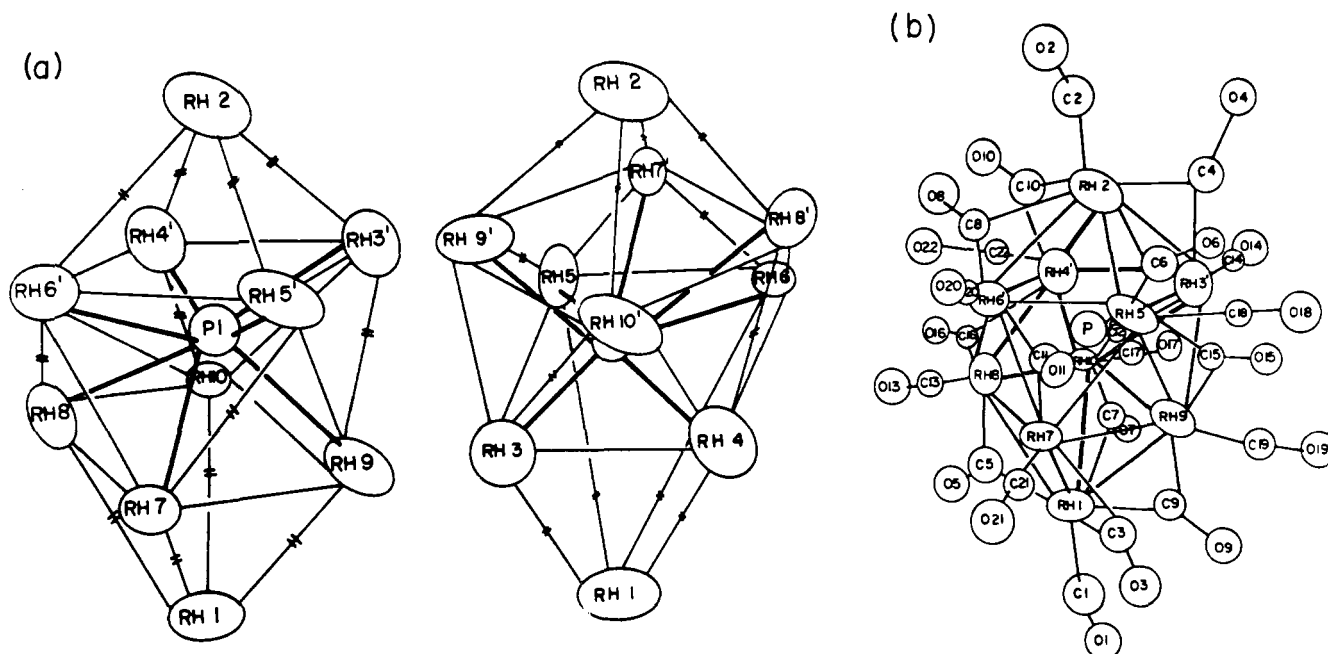
### Introduction

The ability of rhodium carbonyl clusters to accommodate atoms of the elements in the main groups of the periodic table was first illustrated in  $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$  and similar carbide species<sup>2</sup> and more recently for sulfur and phosphorus with  $[\text{Rh}_7(\text{S})_2(\text{CO})_{32}]^{3-}$  and  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ .<sup>3,4</sup> These anions were found to be more stable than rhodium carbonyl clusters in which the heteroatom was absent, e.g.  $\text{Rh}_6(\text{CO})_{16}$  or  $[\text{Rh}_7(\text{CO})_{16}]^{3-}$ , at least with respect to the transformation usually

observed for the latter type of species under high pressures of carbon monoxide and hydrogen into  $[\text{Rh}_5(\text{CO})_{15}]^-$  and  $[\text{Rh}(\text{CO})_4]^-$ .<sup>5</sup>

- (1) Dr. Jan Troup of Molecular Structure Corp. conducted the structural studies reported in this work.
- (2) V. Albano, P. Chini, G. Ciani, S. Martinengo, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 299 (1974); *J. Chem. Soc., Dalton Trans.*, 305 (1975).
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<sup>†</sup> Deceased.



**Figure 1.** ORTEP diagrams of  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  showing (a) the disorder present in the cluster as indicated by a  $45^\circ$  rotation around the fourfold symmetry axis defined by  $\text{Rh}(1)\text{--P}(1)\text{--Rh}(2)$  (a terminal carbonyl is bonded to each rhodium atom and the edge-bridging carbonyls are represented by ++ and (b) the complete cluster including the carbonyl ligands (the cluttered figure results from the disorder present in the structure).

Synthetic methods suitable for the preparation of large amounts of rhodium carbonyl clusters have been under investigation in this laboratory for some time. The importance and difficulties found in such tasks have been already mentioned by Chini,<sup>6</sup> whose group has developed preparative methods for a number of rhodium carbonyl clusters.<sup>7</sup> The experience obtained in this laboratory<sup>3,4,8</sup> indicated that high-pressure synthesis could provide us with high yields of species previously unknown, e.g.,  $[\text{Rh}_{17}(\text{S})_2(\text{CO})_{32}]^{3-}$  and  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ , and of others also prepared recently under atmospheric conditions, e.g.,  $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ .

A continuation of these efforts has resulted in the characterization of  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$ . This cluster is another example of the ability of atomic phosphorus to act as a ligand donating its five valence-shell electrons as previously found in  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ . The synthesis, structure, and the behavior of the new cluster under high pressure of carbon monoxide and hydrogen are now described.

### Experimental Part

The reagents, solvents, procedures, and equipment are the same as previously described.<sup>3-5</sup> Cesium borohydride was supplied by Ventron and used without purification.

**Synthesis of  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$ .** A solution of  $\text{Rh}(\text{CO})_2\text{acac}$  (12.06 g, 46.03 mmol), cesium benzoate (2.800 g, 11.03 mmol), and triphenylphosphine (2.071 g, 7.87 mmol) in 500 mL of the dimethyl ether of tetraethylene glycol,  $\text{CH}_3(\text{OCH}_2\text{CH}_2)_4\text{OCH}_3$ , was mixed with another solution of cesium borohydride (15.0 g, 101.0 mmol) in 300 mL of the same solvent. This mixture was charged to a high-pressure autoclave and stirred for 12 h at  $150\text{--}160^\circ\text{C}$  under 6000 psi of carbon monoxide and hydrogen. The final solution was worked up by Schlenk techniques at atmospheric pressure. Small amounts of solids present were removed by filtration, and the filtrate was treated with toluene, 3 L. The resulting oil was redissolved in acetone, and the filtered extract was precipitated with an equal volume of a 2-propanol solution of benzyltriethylammonium chloride (1 g in 15 mL). A dark brown

solid precipitated slowly; the material was collected by filtration, washed with fresh 2-propanol, and vacuum dried. The final product (7.29 g) corresponds to a yield of 76.2% based on rhodium compound. Anal. Calcd for  $\text{C}_{61}\text{H}_{66}\text{N}_3\text{O}_{22}\text{PRh}_{10}$ : C, 32.52; H, 2.95; N, 1.86; P, 1.37; Rh, 45.67. Found: C, 31.94; H, 2.80; N, 1.85; P, 1.35; Rh, 45.40.

Single crystals were obtained by vapor diffusion of isopentane into an acetone solution of the compound.

**Structural Determination.** The structural study was conducted at Molecular Structure Corp.<sup>1</sup> The description of the diffractometer, computer facilities, and experimental details are similar to those previously described,<sup>3,4</sup> as well as the manipulations of the crystal.<sup>10</sup> Data collection and reduction were conducted with similar procedures<sup>11</sup> as previously used with similar clusters.<sup>3,4</sup> The structure was solved by direct methods<sup>12</sup> following the procedure already reported.<sup>3,4</sup> The structure solution was performed by the use of the direct-methods program MULTAN 74 as part of the Enraf-Nonius Structure Determination Package (SDP). All rhodium atoms were located in the space group *Cc*. All rhodium atoms including the disordered ar-

(10) A black prismatic crystal of  $0.25 \times 0.30 \times 0.15$  mm was selected for this study. Crystal data for the  $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3]_3[\text{Rh}_{10}\text{P}(\text{CO})_{22}]$  crystal system: monoclinic; space group *Cc*; extinctions  $h0l$  for  $l \neq 2n$ ; cell constants  $a = 25.011$  (3) Å,  $b = 16.348$  (4) Å,  $c = 18.267$  (4) Å,  $\alpha = \gamma = 90.0$  (1)°,  $\beta = 101.47$  (1)°,  $V = 7319.7$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho$ (calcd) = 2.045 g cm<sup>-3</sup>.

(11) Intensity data have been collected with a graphite-crystal incident-beam monochromator using Mo  $K\alpha$  ( $\lambda$  0.71073 Å) radiation, with takeoff angle  $2.8^\circ$ , scan type  $\theta\text{--}2\theta$ , and scan speed  $4\text{--}20^\circ/\text{min}$ . The scan range was from  $[2\theta(\text{Mo } K\alpha_1) - 0.5]^\circ$  to  $[2\theta(\text{Mo } K\alpha_2) + 0.5]^\circ$ . Moving-crystal, moving-counter background counts were taken at each end of the scan range. The ratio  $R$  of scan time to background counting time was 2.0. Intensities and standard deviations were calculated as described in ref 3 and 4. Three standard reflections were periodically measured as a check of crystal and electronic stability without significant change. Because of this, no correction was necessary for changes in the intensities of these reflections; an extinction correction was not needed. Lorentz and polarization corrections were applied to the data; and an absorption correction was made using the  $\psi$ -scan technique, with the percent transmission found to vary from 80.5 to 100.0. A total of 5314 reflections were collected with 5196 of them independent.

(12) A total of 32 phase sets were produced by using 400 reflections with  $|E_{\text{min}}|$  of 1.80 and 2000 phase relationships. A total of 15 atoms were initially located in an  $E$  map prepared from the phase set showing the best probability statistics (absolute figure of merit 1.1135, residual 24.07; both understood as defined in MULTAN 74). These atoms included in least-squares refinement, resulting in agreement factors of  $R_F = 28.9\%$  and  $R_wR_F = 36.2\%$ . The remaining nonhydrogen atoms were located in succeeding difference Fourier syntheses.

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Table I. Positional Parameters and Their Esd's for  $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3]_3[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^a$ 

atom	x	y	z	atom	x	y	z
Rh(1)	0.13190 (0)	0.1980 (2)	0.5011 (0)	C(10)	0.3410 (9)	0.306 (1)	0.378 (1)
Rh(2)	0.36818 (9)	0.3008 (2)	0.4989 (2)	C(11)	0.2124 (9)	0.436 (1)	0.523 (1)
Rh(3)	0.17365 (16)	0.3411 (3)	0.4675 (3)	C(12)	0.2850 (18)	0.044 (3)	0.487 (2)
Rh(3')	0.32502 (16)	0.1561 (3)	0.5369 (2)	C(13)	0.1383 (16)	0.383 (2)	0.346 (2)
Rh(4)	0.21374 (17)	0.2606 (3)	0.6117 (3)	C(14)	0.3648 (13)	0.102 (2)	0.615 (2)
Rh(4')	0.28551 (17)	0.2389 (3)	0.3896 (2)	C(15)	0.2810 (13)	0.207 (2)	0.688 (2)
Rh(5)	0.19001 (20)	0.1918 (3)	0.3853 (2)	C(16)	0.2199 (9)	0.259 (1)	0.312 (1)
Rh(5')	0.30707 (16)	0.3131 (3)	0.6174 (3)	C(17)	0.1941 (14)	0.083 (2)	0.358 (2)
Rh(6)	0.22863 (17)	0.1025 (3)	0.5314 (3)	C(18)	0.3126 (15)	0.403 (2)	0.684 (2)
Rh(6')	0.26758 (17)	0.3951 (3)	0.4699 (3)	C(19)	0.2402 (16)	0.083 (2)	0.645 (2)
Rh(7)	0.19306 (16)	0.3467 (3)	0.5582 (2)	C(20)	0.2597 (14)	0.471 (2)	0.393 (2)
Rh(7')	0.30354 (18)	0.1558 (3)	0.4401 (3)	C(21)	0.1828 (14)	0.382 (2)	0.648 (2)
Rh(8)	0.18128 (16)	0.2922 (3)	0.3963 (2)	C(22)	0.3117 (12)	0.160 (2)	0.333 (2)
Rh(8')	0.32096 (17)	0.2065 (3)	0.6055 (3)	C(23)	0.8288 (11)	0.324 (2)	0.567 (2)
Rh(9)	0.23536 (16)	0.1761 (3)	0.6083 (2)	C(24)	0.8131 (14)	0.288 (2)	0.635 (2)
Rh(9')	0.26750 (18)	0.3212 (3)	0.3937 (2)	C(25)	0.8032 (13)	0.197 (2)	0.645 (2)
Rh(10)	0.22031 (21)	0.1235 (3)	0.4502 (3)	C(26)	0.8060 (23)	0.140 (4)	0.585 (3)
Rh(10')	0.28077 (15)	0.3760 (3)	0.5524 (2)	C(27)	0.8179 (12)	0.172 (2)	0.509 (2)
P(1)	0.2527 (5)	0.252 (1)	0.5044 (7)	C(28)	0.8321 (12)	0.276 (2)	0.499 (2)
O(1)	0.0247 (8)	0.128 (1)	0.515 (1)	C(29)	0.8417 (9)	0.315 (2)	0.444 (1)
O(2)	0.4706 (12)	0.400 (2)	0.505 (2)	C(30)	0.9407 (18)	0.354 (3)	0.506 (2)
O(3)	0.0749 (8)	0.368 (1)	0.516 (1)	C(31)	0.9287 (18)	0.433 (3)	0.529 (2)
O(4)	0.4277 (11)	0.155 (2)	0.475 (2)	C(32)	0.9137 (15)	0.196 (2)	0.420 (2)
O(5)	0.0789 (8)	0.190 (1)	0.330 (1)	C(33)	0.8740 (14)	0.153 (2)	0.361 (2)
O(6)	0.4246 (9)	0.276 (1)	0.666 (1)	C(34)	0.9046 (14)	0.331 (2)	0.353 (2)
O(7)	0.1351 (11)	0.008 (2)	0.463 (2)	C(35)	0.9614 (12)	0.335 (2)	0.341 (2)
O(8)	0.3570 (11)	0.491 (2)	0.487 (2)	C(36)	0.6681 (14)	0.200 (2)	0.417 (2)
O(9)	0.1373 (9)	0.192 (1)	0.673 (1)	C(37)	0.6854 (14)	0.248 (2)	0.359 (2)
O(10)	0.3615 (8)	0.359 (1)	0.330 (1)	C(38)	0.6949 (12)	0.314 (3)	0.383 (2)
O(11)	0.1971 (13)	0.506 (2)	0.543 (2)	C(39)	0.6983 (12)	0.350 (2)	0.431 (2)
O(12)	0.3003 (9)	-0.016 (1)	0.480 (1)	C(40)	0.6855 (13)	0.299 (2)	0.489 (2)
O(13)	0.1156 (11)	0.449 (2)	0.337 (1)	C(41)	0.6703 (10)	0.237 (2)	0.482 (1)
O(14)	0.3916 (9)	0.071 (1)	0.673 (1)	C(42)	0.6546 (12)	0.204 (2)	0.563 (2)
O(15)	0.2902 (8)	0.243 (1)	0.755 (1)	C(43)	0.5745 (12)	0.279 (2)	0.569 (2)
O(16)	0.2124 (8)	0.300 (1)	0.250 (1)	C(44)	0.6050 (14)	0.326 (2)	0.648 (2)
O(17)	0.1755 (14)	0.036 (2)	0.301 (2)	C(45)	0.5947 (13)	0.138 (2)	0.632 (2)
O(18)	0.3134 (11)	0.461 (2)	0.707 (1)	C(46)	0.5334 (19)	0.127 (3)	0.645 (3)
O(19)	0.2439 (16)	0.010 (2)	0.675 (2)	C(47)	0.5592 (11)	0.172 (2)	0.500 (2)
O(20)	0.2510 (12)	0.519 (2)	0.346 (2)	C(48)	0.5627 (14)	0.073 (2)	0.503 (2)
O(21)	0.1739 (13)	0.427 (2)	0.692 (2)	C(49)	0.4535 (16)	0.214 (2)	0.237 (2)
O(22)	0.3265 (9)	0.107 (1)	0.298 (1)	C(50)	0.4546 (18)	0.132 (3)	0.259 (3)
N(1)	0.9001 (8)	0.306 (1)	0.435 (1)	C(51)	0.5071 (20)	0.086 (2)	0.268 (2)
N(2)	0.5926 (11)	0.208 (2)	0.573 (2)	C(52)	0.5376 (23)	0.119 (4)	0.241 (3)
N(3)	0.5050 (18)	0.409 (1)	0.248 (3)	C(53)	0.5395 (16)	0.208 (2)	0.207 (2)
C(1)	0.0563 (20)	0.157 (3)	0.497 (3)	C(54)	0.4963 (12)	0.248 (2)	0.212 (2)
C(2)	0.4322 (8)	0.348 (1)	0.496 (1)	C(55)	0.4993 (18)	0.332 (3)	0.177 (2)
C(3)	0.1137 (10)	0.323 (1)	0.517 (1)	C(56)	0.5582 (17)	0.390 (3)	0.296 (2)
C(4)	0.3863 (22)	0.179 (3)	0.503 (3)	C(57)	0.5498 (20)	0.341 (3)	0.354 (3)
C(5)	0.1114 (9)	0.208 (1)	0.378 (1)	C(58)	0.4542 (18)	0.411 (3)	0.274 (2)
C(6)	0.3648 (12)	0.278 (2)	0.624 (2)	C(59)	0.4591 (22)	0.474 (3)	0.333 (3)
C(7)	0.1629 (10)	0.071 (2)	0.487 (1)	C(60)	0.5269 (23)	0.483 (3)	0.208 (3)
C(8)	0.3290 (19)	0.440 (3)	0.475 (3)	C(61)	0.4624 (26)	0.502 (4)	0.118 (3)
C(9)	0.1592 (18)	0.163 (3)	0.624 (2)				

<sup>a</sup> The weights for the rhodium atoms Rh(3) to Rh(10) are 0.5. In all other cases they are 1.

angement of rhodium atoms were located in the *E* map with the best figure of merit (figure of merit is defined in the documentation for MULTAN 74). The cluster was found to be disordered as a 50:50 arrangement about the fourfold axis of the cluster. Atoms on the fourfold axis at full occupancy are Rh(1), Rh(2), and R(1). All other rhodium atoms are related to their 50% occupancy counterpart through a noncrystallographic inversion center at *P*1. The inversion-related rhodium atoms do not comprise one unique cluster but rather the group through the inversion center that are rotated by 45° about the cluster fourfold axis. One unique cluster at half-occupancy could be defined by Rh(1), Rh(2), Rh(3'), Rh(4'), Rh(5'), Rh(6'), Rh(7), Rh(8), Rh(9), Rh(10), and P(1). The other unique cluster at half-occupancy is defined by Rh(1), Rh(2), Rh(3), Rh(4), Rh(5), Rh(6), Rh(7'), Rh(8'), Rh(9'), and P(1).

Although the cluster and two of the three cations would fit and refine in space group *C*2/*c*, the third cation would require an imposed crystallographic twofold axis and this symmetry does not exist in the cation. A disorder scheme for the third cation would allow it to fit in the higher centric space group *C*2/*c*. However, in space group *C*c

disorder was not necessary; therefore, *C*c was chosen as the correct space group.<sup>13</sup>

The rhodium cluster was found to have a 50:50 disorder when rotated 45° about the noncrystallographic fourfold axis in the cluster (Table I). Rhodium atoms off the fourfold axis were refined at half-occupancy, however. The carbonyl groups were found to closely overlap when the structure was rotated by 45° about the fourfold axis,

- (13) Least-squares refinement of the positional and anisotropic thermal parameters for all nonhydrogen atoms was carried out as described in ref 3 and 4. For the 105 atoms studied, the number of variable parameters considered was 514, with 2700 reflections showing  $|F_o|^2 > 3\sigma_{|F_o|^2}$  used in the refinement. The esd of an observation of unit weight was then 2.300, while the maximum parameter shift was 1.0 times its esd. The cycle of least-squares refinement led to values of  $R_F = 6.4\%$  and  $R_{wF} = 7.7\%$ . The final difference Fourier map showed no residual electron density as high as carbon atoms in the previous difference Fourier map with a residual electron density of  $0.37 \text{ e } \text{Å}^{-3}$ , and no unusual trends were detected for plots of the function  $\sum w(|F_o| - |F_c|)^2$  vs.  $|F_o|$ ,  $\lambda^{-1} \sin \theta$ , and reflection order in data collection.

and so they were refined at full occupancy.

## Results and Discussion

The structure of  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  (Figure 1) consists of a square antiprism capped by two rhodium atoms sitting on the square faces and with a bare phosphorus atom located inside the cluster's polyhedron, in a situation that resembles that previously found in  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ .<sup>4</sup> The cluster has an idealized  $C_4$  symmetry with the quaternary axis going through the  $\text{Rh}(2)\text{-P-Rh}(1)$  group. This cluster is the first example of a rhodium cluster consisting of a 10-vertex polyhedron with all its corners occupied by metal atoms.<sup>6,7</sup> In this respect, and because of the analogies between transition metal clusters and boron hydrides having been used as the basis for some theories of bonding in clusters,<sup>14</sup> it is probably interesting to note the similarity between the polyhedra of  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  and  $[\text{B}_{10}\text{H}_{10}]^{2-}$ .<sup>15</sup> Both  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$  and  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  follow Wade's rules,<sup>14</sup> as expected on the basis of the borane analogy. The latter cluster does not obey the noble gas rule as is usually the case with high-nuclearity clusters.<sup>16</sup>

The disorder present in the crystal is an obvious source of concern, although the final agreement factors are quite satisfactory.<sup>13</sup> The disorder in  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  resembles closely the one in  $\text{Fe}_3(\text{CO})_{12}$ .<sup>17</sup> The disorder in this case is about the threefold axis of the structure with the carbonyl groups overlapping. The former cluster showed a similar disorder except it is about a fourfold axis of symmetry. The carbonyl ligands are also overlapping in this instance. In any case, the average rhodium-rhodium contacts (Table II) vary with the shortest being inside normal values for this type of species<sup>6,7</sup> with lengths of 2.851 (8) Å between the apical rhodium atoms and those on the parallel layers and 2.864 (10) Å between the atoms on the corners of these layers. In contrast, a longer than usual contact of 3.007 (10) Å is found for the intralayer distances. Similar rhodium-rhodium distances have been previously reported for  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$  and  $[\text{Rh}_{14}(\text{CO})_{25}]^{4-}$ <sup>8,9</sup> and suggested to be bonding interactions. The steric demands of the central phosphorus atoms could be responsible for this enlargement as noted for  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ .<sup>4</sup> The phosphorus atom in  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  is located on the geometrical center of the cluster at average lengths of 2.435 (14) Å from eight rhodium atoms on the two layers and of 3.012 (14) Å from the two apical rhodium atoms. These distances could correspond to bonding and nonbonding interactions, respectively, and they are comparable to similar distances of 2.401–2.449 (4) and 3.057 (3) Å found in  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ .

The distribution of the carbonyl ligands is the one expected on the basis of the structure of the parent compound,  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ , with a terminal carbonyl bonded to each rhodium atom and four edge-bridging carbonyls located on the alternative rhodium-rhodium edges between the layers, with the eight remaining bridging carbonyls placed four around each apical rhodium atom (Figure 1). The effects of the disorder present in the structure are felt more drastically in the parameters concerned with the carbonyl ligands and it results in some undesirable scattering of the rhodium-carbon and carbon-oxygen distances. In spite of that, it has been possible to estimate mean distances for Rh-C and C-O bonds

Table II. Selected Interatomic Distances and Angles with Their Respective Esd's for  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$

(a) Rh-Rh and Rh-P Distances (Å)			
Rh(1)-Rh(3)	2.682 (7)	Rh(5)-Rh(6)	3.026 (10)
Rh(1)-Rh(4)	2.770 (8)	Rh(5)-Rh(7)	2.878 (10)
Rh(1)-Rh(5)	2.796 (7)	Rh(5)-Rh(9')	2.853 (10)
Rh(1)-Rh(6)	2.840 (7)	Rh(6')-Rh(7)	2.810 (8)
Rh(1)-Rh(7)	2.950 (8)	Rh(6')-Rh(8)	2.853 (9)
Rh(1)-Rh(8)	2.916 (7)	Rh(6)-Rh(7')	2.879 (9)
Rh(1)-Rh(9)	2.940 (7)	Rh(6)-Rh(8')	2.969 (10)
Rh(1)-Rh(10)	2.838 (8)	Rh(7)-Rh(8)	3.046 (9)
Rh(2)-Rh(3')	2.746 (8)	Rh(7)-Rh(9)	3.057 (9)
Rh(2)-Rh(4')	2.764 (7)	Rh(7')-Rh(8')	3.078 (10)
Rh(2)-Rh(5')	2.894 (7)	Rh(7')-Rh(9')	2.522 (10)
Rh(2)-Rh(6')	2.908 (7)	Rh(8)-Rh(10)	3.024 (10)
Rh(2)-Rh(7')	2.948 (8)	Rh(8')-Rh(10')	3.040 (9)
Rh(2)-Rh(8')	2.911 (7)	Rh(9)-Rh(10)	2.963 (10)
Rh(2)-Rh(9')	2.867 (7)	Rh(9)-Rh(10')	2.989 (9)
Rh(2)-Rh(10')	2.845 (6)	Rh(2)-P	3.015 (14)
Rh(3')-Rh(4')	2.998 (8)	Rh(3)-P	2.440 (15)
Rh(3')-Rh(5')	3.035 (10)	Rh(3')-P	2.379 (15)
Rh(3')-Rh(9)	2.828 (8)	Rh(4)-P	2.361 (15)
Rh(3')-Rh(10)	2.878 (8)	Rh(4')-P	2.408 (14)
Rh(3)-Rh(4)	2.937 (9)	Rh(5)-P	2.61 (2)
Rh(3)-Rh(5)	2.936 (10)	Rh(5')-P	2.446 (15)
Rh(3)-Rh(9')	2.948 (9)	Rh(6)-P	2.59 (2)
Rh(3)-Rh(10')	2.873 (8)	Rh(6')-P	2.47 (2)
Rh(4')-Rh(6')	3.021 (9)	Rh(7)-P	2.483 (15)
Rh(4')-Rh(8)	2.774 (8)	Rh(7')-P	2.483 (15)
Rh(4')-Rh(10)	2.857 (9)	Rh(8)-P	2.474 (15)
Rh(4)-Rh(6)	3.032 (10)	Rh(8')-P	2.372 (15)
Rh(4)-Rh(8')	2.848 (8)	Rh(9)-P	2.380 (15)
Rh(4)-Rh(10')	2.874 (8)	Rh(9')-P	2.408 (15)
Rh(5')-Rh(6')	2.996 (9)	Rh(10)-P	2.40 (2)
Rh(5')-Rh(7)	2.894 (8)	Rh(10')-P	2.26 (2)
Rh(5')-Rh(9)	2.853 (10)		

(b) Angles Involving the P Atom and Rh-Rh-Rh Moieties (Deg)			
Rh(3)-Rh(1)-Rh(4)	65.2 (2)	Rh(2)-Rh(7)-Rh(9')	58.5 (2)
Rh(3)-Rh(1)-Rh(5)	64.8 (1)	Rh(5)-Rh(7)-Rh(6)	63.4 (2)
Rh(3)-Rh(1)-Rh(6)	99.7 (2)	Rh(5)-Rh(7')-Rh(9')	58.9 (2)
Rh(4)-Rh(1)-Rh(5)	98.4 (2)	Rh(6)-Rh(7)-Rh(8')	59.7 (2)
Rh(4)-Rh(1)-Rh(6)	65.4 (2)	Rh(2)-Rh(8')-Rh(10')	57.1 (2)
Rh(5)-Rh(1)-Rh(6)	65.0 (2)	Rh(4)-Rh(8')-Rh(6)	62.8 (2)
Rh(7)-Rh(2)-Rh(8')	63.4 (2)	Rh(4)-Rh(8')-Rh(10')	58.3 (2)
Rh(7)-Rh(2)-Rh(9')	60.3 (2)	Rh(2)-Rh(9')-Rh(10')	58.1 (2)
Rh(7)-Rh(2)-Rh(10')	94.0 (2)	Rh(3)-Rh(9')-Rh(5)	60.8 (2)
Rh(8')-Rh(2)-Rh(10')	63.7 (2)	Rh(3)-Rh(9')-Rh(10')	57.9 (2)
Rh(8')-Rh(2)-Rh(9')	95.2 (2)	Rh(3)-Rh(10')-Rh(4)	61.5 (2)
Rh(9')-Rh(2)-Rh(10')	63.1 (2)	Rh(3)-P-Rh(4)	75.4 (4)
Rh(1)-Rh(3)-Rh(4)	58.9 (2)	Rh(3)-P-Rh(5)	71.0 (4)
Rh(4)-Rh(3)-Rh(10')	59.3 (2)	Rh(3)-P-Rh(10')	75.3 (5)
Rh(5)-Rh(3)-Rh(9')	58.0 (2)	Rh(3)-P-Rh(9')	74.9 (5)
Rh(9')-Rh(3)-Rh(10')	61.8 (2)	Rh(3)-P-Rh(6)	114.1 (6)
Rh(1)-Rh(4)-Rh(6)	58.4 (2)	Rh(4)-P-Rh(6)	75.4 (5)
Rh(6)-Rh(4)-Rh(8')	60.6 (2)	Rh(4)-P-Rh(5)	115.8 (6)
Rh(8')-Rh(4)-Rh(10')	64.2 (2)	Rh(7)-P-Rh(8')	79.1 (5)
Rh(1)-Rh(5)-Rh(6)	58.2 (2)	Rh(7')-P-Rh(9')	73.7 (5)
Rh(7')-Rh(5)-Rh(9')	61.3 (2)	Rh(7)-P-Rh(10')	127.4 (6)
Rh(7')-Rh(6)-Rh(8')	63.5 (2)	Rh(8')-P-Rh(9')	126.5 (6)
Rh(5)-Rh(6)-Rh(7')	58.3 (2)	Rh(8')-P-Rh(10')	82.0 (5)
Rh(2)-Rh(7)-Rh(8')	57.7 (2)		

present in the terminal carbonyls of 1.88 (5) and 1.19 (4) Å. The bridging ligands located around the apical rhodium atoms are asymmetric with average apical rhodium-carbon distances of 2.24 (3) Å and with average intralayer rhodium-carbon distances of 1.92 (4) Å, with a C-O length of 1.27 (3) Å. In contrast, the interlayer bridging carbonyls are symmetrical with Rh-C and C-O mean lengths of 2.05 (4) and 1.25 (4) Å, respectively. These values agree well with those previously reported for  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ .<sup>4</sup>

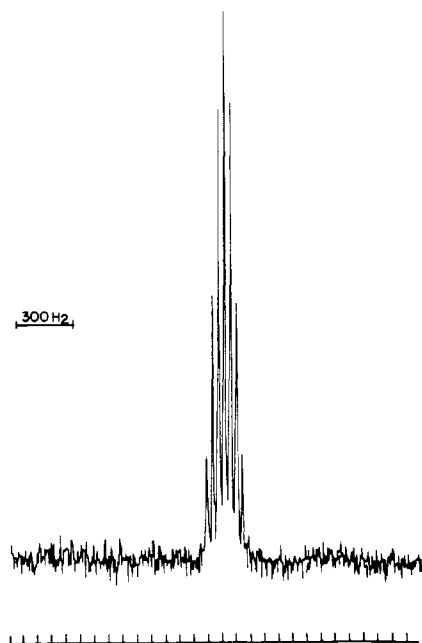
<sup>13</sup>C NMR results show the scrambling of the carbonyl ligands occurring at 40 °C, as concluded from a broad resonance at 210 ppm downfield from tetramethylsilane. The rhodium skeleton of  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  appears to be also fluxional (Figure 2) as concluded from <sup>31</sup>P NMR results. The

(14) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976), and references therein.

(15) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, 1963, p 58.

(16) The noble gas rule requires a number of electrons for  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$ ,  $N_3 = 18N_1 - 2N_2$ , or  $132 = (18 \times 10) - (2 \times 24)$ , but the anion has a total of 142 electrons =  $(9 \times 10) + (2 \times 22) + (1 \times 5) + 3$ . Application of Wade's rule<sup>14</sup> to the anion,  $N_3 = 14N_1 + x$ ,  $142 = (14 \times 10) + x$ , results in  $x = 2$ , as required on the basis of these rules for a closo cluster such as this. Equations were taken from ref 7, with the meanings for  $N_1$ ,  $N_2$ , and  $N_3$  given there.

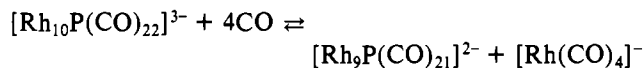
(17) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 1351 (1969).



**Figure 2.**  $^{31}\text{P}$  NMR spectrum of  $[\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3]_3[\text{Rh}_{10}\text{P}(\text{CO})_{22}]$  in perdeuterioacetone at  $40^\circ\text{C}$ . Chemical shift is reported with respect to phosphoric acid used as external standard:  $-369.3$  ppm;  $J(^{31}\text{P}\text{-Rh}) = 32.1$  Hz.

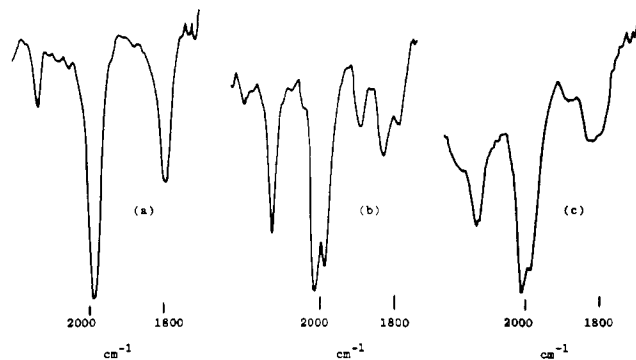
presence of an odd-line pattern consisting of 11 lines at  $-369.3$  ppm is consistent with this. The constancy of this pattern even at  $-45^\circ\text{C}$  probably indicates the persistence of skeletal scrambling at low temperatures. A precedent for this behavior is provided by  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ .<sup>4</sup> The fluxionality of the metal skeletons of these two clusters together with other results<sup>18</sup> may suggest that mobility of the transition-metal atoms in clusters may be more pervasive than previously considered.<sup>19</sup> The study of such mobility may shed some light on the steps involved in the reconstructions of some surfaces.<sup>9,19,20</sup>

The reactivity of  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  is the one expected in the presence of an encapsulated main-group element atom. Thus, the anion does not react under high pressures of carbon monoxide and hydrogen to form  $[\text{Rh}_5(\text{CO})_{15}]^-$  and  $[\text{Rh}(\text{C}-\text{O})_4]^-$  as is the case with rhodium carbonyl clusters.<sup>5</sup> It behaves, in this respect, as previously observed for  $[\text{Rh}_6(\text{CO})_{15}\text{C}]^{2-}$ ,  $[\text{Rh}_{17}(\text{S})_2(\text{CO})_{32}]^{3-}$ , and  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ .<sup>5</sup> Instead,  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  reacts at 12 500 psi and  $240^\circ\text{C}$ , yielding the former cluster and tetracarbonylrhodate (Figure 3):



The occurrence of the reverse reaction has been confirmed by

- (18) C. Brown, B. T. Heaton, P. Chini, A. Fumagalli, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 309 (1977); B. F. G. Johnson, *ibid.*, 309 (1976).  
 (19) O. Gansow, D. S. Gill, F. J. Bennis, J. R. Hutchison, J. L. Vidal, and R. C. Schoening, *J. Am. Chem. Soc.*, **102**, 2449 (1980).  
 (20) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); **85**, 451 (1976); *Science*, **196**, 389 (1977); *Angew. Chem., Int. Ed. Engl.*, **17**, 545 (1978); E. L. Muetterties, T. N. Rhodin, E. Bond, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, **79**, 91 (1979).



**Figure 3.** Infrared study under high pressures of  $\text{CO}-\text{H}_2$  of a sulfonate solution of  $[\text{Cs}(\text{C}_{12}\text{H}_{24}\text{O}_6)_{\sim 2.0}]_3[\text{Rh}_{10}\text{P}(\text{CO})_{22}]$ : (a) after 3 h at 8000 psi and  $200^\circ\text{C}$  with absorption bands assigned to the anion at 1995 and  $1790\text{ cm}^{-1}$ ; (b) after 3 h at 12 5000 psi and  $200^\circ\text{C}$  with suggested assignments of the bands at 1995 and  $1790\text{ cm}^{-1}$  to  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$ , 2015 and  $1830\text{ cm}^{-1}$  to  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ , and  $1890\text{ cm}^{-1}$  to  $[\text{Rh}(\text{CO})_4]^-$ ; (c) after 3 h at 12 500 psi and  $250^\circ\text{C}$  with assignments similar to those in (b).

monitoring, by  $^{31}\text{P}$  NMR and infrared spectroscopy, the reaction of  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$  and  $[\text{Rh}(\text{CO})_4]^-$  under 1 atm of argon at atmospheric pressure and by the isolation of  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  from that reaction mixture.<sup>21</sup>

Similar participation of the tetracarbonylrhodate anion in fragmentation-condensation redox reactions like the one above has been well established with more conventional rhodium carbonyl clusters such as the  $[\text{Rh}_7(\text{CO})_{16}]^{3-}/[\text{Rh}_6(\text{CO})_{15}]^{2-}$  couple.<sup>7</sup>

Although the structures of  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$  and  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$  are very similar, some minor, but perhaps important, differences exist between them. Thus, the interlayer bridge carbonyls are of asymmetrical and symmetrical character, respectively. Besides, the phosphorus atom is located on the geometrical center of the latter cluster, while it is shifted upward from it, ca.  $0.2\text{ \AA}$ , on the former anion. These differences could result from the restrictions introduced on the initial nine-vertex structure by the addition of the extra rhodium carbonyl moiety. Because of this, it is possible to ascribe the different chemical stability of these clusters to the relief of the larger steric crowding present in  $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$ .

**Acknowledgment.** We appreciate the authorization for publication of this work extended by Union Carbide Corp. and the continuous support and encouragement by Dr. G. L. O'Connor.

**Registry No.**  $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3]_3[\text{Rh}_{10}\text{P}(\text{CO})_{22}]$ , 75802-05-0;  $[\text{Cs}(\text{C}_{12}\text{H}_{24}\text{O}_6)_2]_3[\text{Rh}_{10}\text{P}(\text{CO})_{22}]$ , 75802-06-1;  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$ , 68417-41-4;  $[\text{Rh}(\text{CO})_4]^-$ , 44797-04-8;  $\text{Rh}(\text{CO})_2\text{acac}$ , 14874-82-9;  $\text{PPH}_3$ , 603-35-0.

**Supplementary Material Available:** Complete tables of structural factors, atomic distances and angles, and positional and thermal parameters (52 pages). Ordering information is given on any current masthead page.

- (21) The reaction was conducted by mixing a solution of  $[(\text{CH}_3)_4\text{N}]_2[\text{Rh}_9\text{P}(\text{CO})_{21}]$  in dry tetrahydrofuran with increasing amounts of a solution of  $[(\text{CH}_3)_4\text{N}]^+[\text{Rh}(\text{CO})_4]^-$  in this solvent. The occurrence of the back-reaction is detected at ratios of  $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}:[\text{Rh}(\text{CO})_4]^-$  of 1:1.7. Precipitation of  $[(\text{CH}_3)_4\text{N}]_3[\text{Rh}_{10}\text{P}(\text{CO})_{22}]$  occurred at even higher ratios. This product was isolated and characterized.