other systems in which mixed-metal species are formed under high-pressure conditions, and for which structural assignment may be feasible, should prove a valuable means of assessing gas-phase thermochemical data.

Conclusions

The utilization of an array of mass spectrometric techniques, including high-pressure mass spectrometery, high-resolution mass spectrometry, deuterium labeling, and tandem mass spectrometry, has provided abundant new information concerning the behavior of cobalt and zinc acetates in the gas phase. Previously misidentified ions in the spectra were correctly established.

High-pressure-source conditions have led to the formation of novel cluster ions with molecular weights in excess of 1000 daltons for both cobalt acetate and zinc acetate. These are formed through ion/molecule reactions that occur between abundant fragment ions and abundant neutral species. Those cluster ions that are dimers and trimers of the monomer $M_4O(OAc)_6$ probably involve one or more bridging carboxylate ligands between monomeric units. Identification of many cluster ions is, in the case of zinc, facilitated by comparison of the calculated and the measured isotope patterns. In the case of cobalt, the results of deuterium labeling aid in the identification of cluster ion formulas and provide a means of confirming hydrogen incorporation.

High-resolution mass spectrometry reveals a number of novel species of mass less than the molecular ion. Though only a few novel lower mass species were found for zinc acetate, a far greater number of ions were discovered for cobalt acetate. Novel mixed-metal cluster ions incorporating both zinc and cobalt were easily produced when a mixture of the two acetates was introduced. MS/MS experiments, which select by mass parent ions of a given metal content, indicate differing reactivity of metal-oxygen bonds toward collision-induced dissociation.

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Supplementary Material Available: Tabularized mass spectral data (13 pages). Ordering information is available on any current masthead page.

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Synthesis and Structure of Three (Tricyclohexylphosphine)rhodium Complexes and Their Interconversion with Carbon Monoxide and Hydrogen

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The reaction of $Rh(CO)_2acac$ with CO and H_2 in the presence of excess tricyclohexylphosphine (PCy_3) gave an easily separated mixture of $HRh(CO)(PCy_3)_2$ (**3**) and $(PCy_3)_2Rh(\mu\text{-}CO)_2Rh(CO)PCy_3$ (**7**). The structures of **3** and **7** were determined by X-ray crystallography and related to appropriate structures previously reported. Crystal data for **3**: monoclinic, $P2_1/c$ (C_{2h}^5, No. 14), $a = 10.066$ (2) Å, $b = 15.910$ (4) Å, $c = 23.438$ (6) Å, $\alpha = 90.00°$, $\beta = 94.13$ (2)°, $\gamma = 90.00°$, $Z = 4$. Crystal data for **7**: triclinic, $P\bar{1}$ (C_i^1), $a = 13.681$ (3) Å, $b = 14.261$ (4) Å, $c = 19.235$ (5) Å, $\alpha = 104.15$ (2)°, $\beta = 99.70$ (2)°, $\gamma = 84.98$ (2)°, $Z = 2$. **3** has a trans square-planar configuration. **7** contains a square-planar $Rh(CO)PCy_3$ and a distorted-tetrahedral $Rh(PCy_3)_2$. The ^{31}P NMR spectra of **7** indicated an intramolecular geminal phosphine site exchange process on $Rh(PCy_3)_2$. **3** and **7** both react with CO, forming $PCy_3(CO)_2Rh(\mu\text{-}CO)_2Rh(CO)_2PCy_3$ (**8**), which was stable only in the presence of CO, reverting back to **7** in the absence of CO. **7** reacted with H_2, re-forming **3**.

The structure and reactivity of rhodium(I) phosphine complexes are important to several areas of catalysis including α-olefin hydroformylation.[2] The mechanism of low-pressure hydroformylation, initially reported by Wilkinson and co-workers in the late 1960s, is still an area of active interest and controversy.[3-5] Wilkinson found that $HRh(CO)L_3$ (**1**), ($L = PPh_3$) reacted with carbon monoxide forming $HRh(CO)_2L_2$ (**2**), ($L = PPh_3$) via the intermediate $HRh(CO)L_2$ (**3**), ($L = PPh_3$).[3b] While neither complex could be isolated, **2** has recently been observed by NMR spectroscopy.[5b,c] According to Wilkinson this complex loses hydrogen in the presence of carbon monoxide, forming a yellow dimer, recently characterized by Chan and co-workers as $L_2(CO)Rh(\mu\text{-}CO)_2Rh(CO)_2L$ (**4**) ($L = PPh_3$).[6] Wilkinson found that **4** reacts with hydrogen, re-forming **3**, and that removal of

Scheme I

$$\mathrm{Rh(CO)_2(acac)} + \mathrm{L} \xrightarrow[a]{} \mathrm{Rh(CO)L(acac)} + \mathrm{CO} \xrightarrow[b]{}$$

$$\underset{\mathbf{3}}{\mathrm{HRh(CO)L_2}} + \underset{\mathbf{7}}{\mathrm{L_2Rh(\mu\text{-}CO)_2Rh(CO)L}} + \underset{\mathbf{8}}{\mathrm{L(CO)_2Rh(\mu\text{-}CO)_2Rh(CO)_2L}}$$

$$2(\mathbf{3}) + 4\mathrm{CO} \xrightarrow[c]{} \mathbf{8} + 2\mathrm{L} + \mathrm{H_2}$$

$$\mathbf{7} + 3\mathrm{CO} \underset{d}{\overset{c}{\rightleftharpoons}} \mathbf{8} + \mathrm{L}$$

$$\mathbf{7} + \mathrm{H_2} + \mathrm{L} \xrightarrow[e]{} 2(\mathbf{3}) + \mathrm{CO}$$

$$\mathrm{L} = \mathrm{PCy_3}$$

[a] 25 °C. [b] 80 °C, 8.3×10^3 kPa of CO + H_2, 15 min, excess PCy_3. [c] 25 °C, 1.0×10^2 kPa of CO, 5 min. [d] 25 °C, removal of CO. [e] 50 °C, 1.0×10^2 kPa H_2, 15 min.

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carbon monoxide from a methylene chloride solution of **4** reversibly produced the red dimer $L_2(S)Rh(\mu\text{-}CO)_2Rh(S)L_2$ (**5**) (L = PPh_3, S = CH_2Cl_2).[3b,7]

The recent use of sterically bulky phosphine ligands has produced stabilized and isolable coordinatively unsaturated, electron-deficient rhodium(I) monomers and rhodium(0) dimers of importance to catalysis. A number of three-coordinate $RhX(PCy_3)_2$ complexes and dinitrogen-bridged dimers were reported by Van Gaal et al.[8] Otsuka and co-workers reported the isolation of **3** (L = PCy_3), $Rh(OH)(CO)(P\text{-}i\text{-}Pr_3)_2$, and $L(CO)Rh(\mu\text{-}CO)_2Rh(CO)L$ (**6**) (L = $P\text{-}t\text{-}Bu_3$) from water gas shift catalysis experiments.[9] Both Otsuka and Shumann and Heisler[10] reported that the latter red dimer was produced from a yellow dimer precursor, which was stable only under a carbon monoxide atmosphere. Both groups proposed that the yellow dimer was $L(CO)_2Rh(\mu\text{-}CO)_2Rh(CO)_2L$ (**8**) (L = $P\text{-}t\text{-}Bu_3$). Otsuka reported that the series of bulky phosphine ligands $P\text{-}t\text{-}Bu_3$, $PPh\text{-}t\text{-}Bu_2$, and PCy_3 all formed yellow and red dimers with the structures of **6** and **8**. However, he claimed to have isolated a different red dimer for L = $P\text{-}i\text{-}Pr_3$: $L_2Rh(\mu\text{-}CO)_2Rh(CO)L$ (**7**).

Because of the potential catalytic importance of rhodium complexes with bulky phosphine ligands, we decided to investigate the chemistry of **3** (L = PCy_3) with carbon monoxide and hydrogen.[8c,11]

Results

The transformations achieved in this work are summarized in Scheme I. A mixture of **3**, **7**, and **8** (L = PCy_3) is easily obtained in reacting dicarbonyl(2,4-pentanedionato)rhodium(I) with carbon monoxide and hydrogen in the presence of a slight excess of tricyclohexylphosphine. Dimer **8** is stable only under a carbon monoxide atmosphere. Removal of the carbon monoxide results in the conversion of the mixture of **3**, **7**, and **8** to a mixture of **3** and **7** only. The different solubilities of **3** and **7** in *n*-hexane afford an easy method of separation.

Experimental Section

Syntheses. Addition of dicarbonyl(2,4-pentanedionato)rhodium(I) (Strem Chemical Co.; 1.03 g, 4.0 mmol) to an oxygen-free solution of tricyclohexylphosphine (2.48 g, 8.8 mmol) in cyclohexane (100 g) under argon produced $Rh(CO)(PCy_3)acac$ with evolution of carbon monoxide. The resulting solution was transferred to an Autoclave Engineers Inc. pressure vessel (300 cm^3 capacity) under argon and heated to 80 °C with stirring. The vessel was then pressurized with an equimolar mixture of carbon monoxide and hydrogen (8.3×10^3 kPa) and stirred for 15 min at 80 °C. After the vessel was cooled and the gas vented, the reaction mixture was transferred to a Schlenk flask. An infrared spectrum of the crude reaction mixture, while still saturated with carbon monoxide and hydrogen, indicated the carbonyl bands of 2,4-pentanedione and compounds **3**, **7**, and **8**. The latter was converted to **7** upon removal of carbon monoxide; see below. The solvent and 2,4-pentanedione were removed under reduced pressure at 40 °C. The semicrystalline residue was recrystallized from *n*-hexane (2 days at 5 °C), initially giving yellow needles of **3** (1.1 g, 1.59 mmol) and, after concentration of the mother liquor, red crystals of **7** (0.82 g, 0.75 mmol). Each compound was then purified by recrystallization.

Table I. Crystal Data for Compounds **3** and **7**[a]

	3	**7**
formula	$HRh(CO)(P(C_6H_{11})_3)_2$	$Rh_2(CO)_3(P(C_6H_{11})_3)_3\cdot C_6H_5CH_3\cdot C_5H_{10}$
fw	692.9	1293.6
cryst syst	monoclinic	triclinic
space group	$P2_1/c$ (C_{2h}^5, No. 14)	$P\bar{1}$ (C_i^1)
a, Å	10.066 (2)	13.681 (3)
b, Å	15.910 (4)	14.261 (4)
c, Å	23.438 (6)	19.235 (5)
α, deg	90.00	104.15 (2)
β, deg	94.13 (2)	99.70 (2)
γ, deg	90.00	84.98 (2)
V, $Å^3$	3,744 (2)	3,583 (2)
Z	4	2
d_{calcd}, g/cm^3	1.23	1.20
cryst shape	irregular	rectangular parallelepiped
cryst size, mm	0.60 min × 0.92 max	0.48 × 0.52 × 0.42
μ, cm^{-1}	5.6	5.6
γ(Mo Kα), Å	0.71073	0.71073
monochromator	graphite	graphite
scan method	ω	ω
scan range, deg	0.90	0.90
θ limits, deg	$3 \leqslant 2\theta \leqslant 55$	$3 \leqslant \theta \leqslant 45.8$
scan speed, deg/min	6 (2θ, 3–43°) 4 (2θ, 43–55°)	6 (2θ, 3–43°) 4 (2θ, 43–45.8°)
temp, °C	20 ± 1	20 [illegible] 1
total no. of reflcns measd[b]	8595	9869
no. of unique reflcns	8595	9869
no. of data used	5976	5515
no. of params refined	375	695
solution[c]	heavy-atom Patterson	direct[d]
abs cor	none	none
R_1[e]	0.032	0.046
R_2[e]	0.029	0.039

[a] The numbers in parentheses are the standard deviations in the last significant digit. [b] Background counts were measured at ω settings 0.90° above and below the calculated value for each reflection. [c] All hydrogen atom positions were located after refinement cycle no. 3. Cyclohexyl ring hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^3 hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms. The five ring hydrogen atoms of the toluene molecule of crystallization in **7** were also included in the structure factor calculations as idealized (assuming sp^2 hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms. The isotropic thermal parameters for these hydrogen atoms were fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon atoms to which they were covalently bonded. [d] Non-hydrogen atoms were located by using the SHELXTL direct methods programs. [e] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Reactions. Carbon monoxide was bubbled through a solution of **3** and a solution of **7** at 25 °C (1% by weight in cyclohexane, initially under argon). The yellow dimer **8** was formed within minutes in each case. Removal of carbon monoxide by bubbling argon or hydrogen regenerated **7** within minutes at 25 °C. Continued treatment of **7** with hydrogen at 50 °C in the presence of tricyclohexylphosphine completely converted it to **3** in 15 min.

Spectroscopy. The infrared spectra were obtained with a Beckman Model 4250 spectrophotometer. The NMR spectra were obtained with a JEOL Model GX-270 FTNMR spectrometer operating at 6.39 T; the ^1H frequency was 270 MHz, and the ^{31}P frequency was 109 MHz. ^1H chemical shifts are with respect to internal Me_4Si. ^{31}P chemical shifts are with respect to external 1.0 M H_3PO_4. To convert to an external 85% H_3PO_4 standard add 0.5 ppm to the reported δ value.

Crystallography. The X-ray crystal structures were determined by Crystalytics Co., Lincoln, NE, on single crystals of **3** grown from *n*-hexane solution and on single crystals of **7** grown from a solution of toluene and mixed hexane isomers containing cyclopentane. A computer-controlled four-circle Nicolet autodiffractometer was used.

Discussion

Structure of 3. The structure of **3**, a square-planar, 16-electron Rh(I) complex, is illustrated in Figure 1.[12a] This structure has

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Table II. Atomic Coordinates for $HRh(CO)(P(C_6H_{11})_3)_2$ (**3**)[a]

atom	10^4x	10^4y	10^4z
Rh	932.6 (2)	2339.7 (1)	2089.4 (1)
P_1	103.8 (6)	2518.4 (4)	1161.7 (3)
P_2	2054.2 (6)	2504.9 (4)	2970.7 (3)
O	-754 (3)	859 (2)	2352 (1)
C	-115 (3)	1424 (2)	2259 (1)
C_{11}	1467 (2)	2694 (2)	679 (1)
C_{12}	1118 (3)	2771 (2)	36 (1)
C_{13}	2338 (3)	3024 (2)	-270 (1)
C_{14}	3478 (3)	2414 (2)	-147 (2)
C_{15}	3833 (3)	2338 (2)	491 (1)
C_{16}	2621 (3)	2080 (2)	803 (1)
C_{21}	-980 (2)	3458 (1)	1054 (1)
C_{22}	-234 (3)	4286 (2)	1166 (1)
C_{23}	-1176 (3)	5037 (2)	1086 (2)
C_{24}	-2324 (3)	4970 (2)	1468 (2)
C_{25}	-3078 (3)	4153 (2)	1361 (2)
C_{26}	-2155 (3)	3393 (2)	1431 (1)
C_{31}	-999 (2)	1654 (1)	876 (1)
C_{32}	-257 (3)	832 (2)	810 (1)
C_{33}	-1211 (3)	95 (2)	703 (1)
C_{34}	-2170 (3)	249 (2)	188 (1)
C_{35}	-2897 (3)	1071 (2)	237 (1)
C_{36}	-1943 (3)	1808 (2)	342 (1)
C_{41}	3873 (2)	2616 (2)	2920 (1)
C_{42}	4747 (2)	2785 (2)	3471 (1)
C_{43}	6147 (3)	3048 (2)	3320 (1)
C_{44}	6767 (3)	2397 (2)	2954 (1)
C_{45}	5877 (3)	2189 (2)	2419 (1)
C_{46}	4487 (3)	1933 (2)	2568 (1)
C_{51}	1602 (2)	3483 (1)	3339 (1)
C_{52}	2118 (3)	4283 (2)	3061 (1)
C_{53}	1697 (3)	5067 (2)	3375 (1)
C_{54}	194 (3)	5115 (2)	3384 (1)
C_{55}	-346 (3)	4333 (2)	3661 (1)
C_{56}	81 (3)	3534 (2)	3364 (1)
C_{61}	1690 (3)	1668 (2)	3491 (1)
C_{62}	2223 (3)	806 (2)	3324 (1)
C_{63}	1618 (3)	109 (2)	3664 (1)
C_{64}	1841 (3)	247 (2)	4303 (1)
C_{65}	1373 (3)	1108 (2)	4473 (1)
C_{66}	1986 (3)	1811 (2)	4131 (1)
H	1863 (24)	3203 (15)	1933 (10)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for **3**[a]

$Rh-P_1$	2.290 (1)	Rh-H	1.72 (2)
$Rh-P_2$	2.297 (1)	C-O	1.136 (4)
Rh-C	1.858 (3)		
P_1-Rh-P_2	164.1 (1)	H-Rh-C	178.5 (8)
Rh-C-O	178.6 (3)		

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

some features similar to those reported by Ibers and co-workers for $[HRh(P\text{-}i\text{-}Pr_3)_2]_2(\mu\text{-}N_2)$ (Table III).[12b] The latter was reported to have a P-Rh-P angle of 163.3 (1)°, an average Rh-P bond length of 2.273 (3) Å and Rh-H bond lengths of 1.62 (5) and 1.60 (5) Å. Several other examples of the tendency of trans phosphine groups to bend toward a mutually cis hydrido ligand were cited by Ibers.

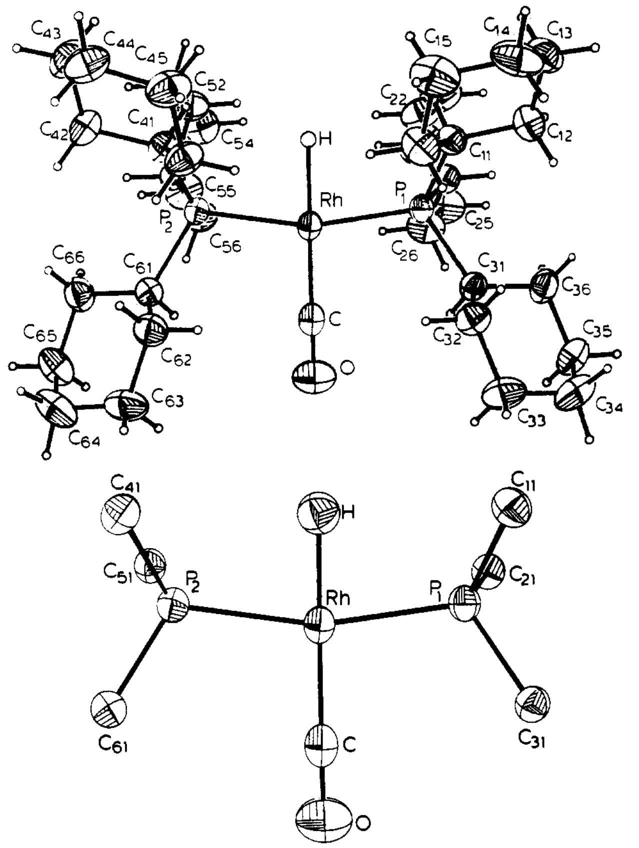

Figure 1. Structure and labeling scheme (top) and rhodium coordination group (bottom) for $HRh(CO)(P(C_6H_{11})_3)_2$ (**3**). Hydrogen atoms are drawn arbitrarily small, and thermal ellipsoids are 50% probability.

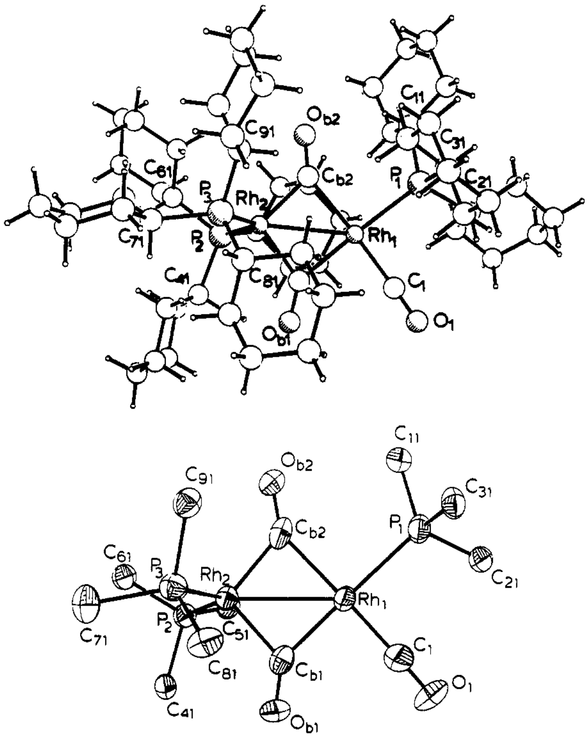

Figure 2. Structure and labeling scheme (top) and rhodium coordination groups (bottom) for $Rh_2(CO)_3(P(C_6H_{11})_3)_3$ (**7**). All atoms are drawn arbitrarily small for purposes of clarity (top), and thermal ellipsoids are 50% probability (bottom).

Structure of 7. The red complex **7** is a 30-electron dimer containing a square-planar Rh(0) and a distorted-tetrahedral Rh(0) (Figure 2). The two rhodium atoms, bridging carbonyls, P_1, and C_1 all lie in the same plane.[12c] The tetrahedral rhodium Rh_2 has a $P_2-Rh_2-P_3$ bond angle expanded from the theoretical 109.5° to 125.5 (1)°, and the $P_2Rh_2P_3$ plane is rotated 80.3° with respect to the $Rh_2C_{b1}C_{b2}Rh_1$ plane, rather than the expected 90°

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(12) (a) The deviations in Å from the plane of selected atoms of **3** were as follows: Rh, +0.0252; P_1, -0.0143; P_2, -0.0143; C, -0.0001; O -0.0007; H, +0.0040. (b) Yoshida, T.; Okano, T.; Thorn, D. L.; Tulip, T. H.; Otsuka, S.; Ibers, J. A. *J. Organomet. Chem.* **1979**, *181*, 183. (c) The deviations in Å from the plane of selected atoms of **7** were as follows: Rh_1, -0.0340; Rh_2 +0.0603; P_1 -0.0311; C_{b1}, -0.0958; C_{b2}, +0.0175; C_1, +0.0832.

Table IV. Atomic Coordinates for $Rh_2(CO)_3(P(C_6H_{11})_3)_3$ (7)[a]

atom	10^4x	10^4y	10^4z	atom	10^4x	10^4y	10^4z
Rh_1	1041 (1)	243 (1)	2140 (1)	C_{45}	1424 (7)	−5124 (6)	701 (5)
Rh_2	1466 (1)	−1285 (1)	2771 (1)	C_{46}	804 (7)	−4558 (5)	1266 (5)
P_1	191 (2)	1750 (1)	2389 (1)	C_{51}	−644 (6)	−2545 (5)	1707 (4)
P_2	552 (2)	−2707 (1)	2291 (1)	C_{52}	−1337 (6)	−1770 (6)	2108 (5)
P_3	2882 (2)	−1117 (1)	3705 (1)	C_{53}	−2306 (7)	−1598 (7)	1633 (6)
O_{b1}	2226 (4)	−1576 (4)	1432 (3)	C_{54}	−2137 (7)	−1334 (7)	953 (6)
O_{b2}	286 (4)	165 (4)	3567 (3)	C_{55}	−1488 (7)	−2107 (7)	533 (5)
O_1	1779 (7)	699 (5)	885 (4)	C_{56}	−508 (6)	−2277 (6)	1010 (4)
C_{b1}	1763 (6)	−1083 (5)	1874 (4)	C_{61}	239 (6)	−3346 (5)	2954 (4)
C_{b2}	695 (7)	−100 (6)	3068 (5)	C_{62}	101 (7)	−2654 (5)	3678 (4)
C1	1484 (8)	535 (6)	1355 (6)	C_{63}	−4 (7)	−3190 (6)	4250 (5)
C_{11}	−817 (6)	1837 (5)	2928 (4)	C_{64}	−848 (7)	−3871 (7)	4006 (6)
C_{12}	−1625 (6)	1130 (6)	2550 (5)	C_{65}	−742 (7)	−4560 (6)	3279 (5)
C_{13}	−2294 (7)	1042 (7)	3099 (5)	C_{66}	−656 (6)	−4025 (5)	2701 (5)
C_{14}	−2771 (7)	2000 (8)	3427 (6)	C_{71}	3466 (6)	−2173 (6)	4050 (5)
C_{15}	−1971 (8)	2747 (7)	3778 (5)	C_{72}	2752 (7)	−2843 (6)	4151 (5)
C_{16}	−1280 (7)	2836 (6)	3254 (5)	C_{73}	3247 (8)	−3790 (6)	4278 (6)
C_{21}	−286 (6)	2171 (5)	1550 (4)	C_{74}	4150 (9)	−3653 (8)	4869 (6)
C_{22}	−942 (7)	1451 (5)	995 (4)	C_{75}	4837 (8)	−2962 (8)	4790 (7)
C_{23}	−1159 (7)	1740 (6)	266 (4)	C_{76}	4338 (7)	−2023 (6)	4663 (5)
C_{24}	−1608 (7)	2769 (6)	343 (5)	C_{81}	3970 (6)	−683 (5)	3426 (4)
C_{25}	−944 (7)	3473 (6)	902 (5)	C_{82}	3730 (6)	319 (6)	3250 (5)
C_{26}	−756 (7)	3201 (5)	1636 (4)	C_{83}	4611 (7)	651 (7)	2991 (5)
C_{31}	1011 (6)	2716 (5)	2926 (4)	C_{84}	4914 (8)	−93 (8)	2343 (6)
C_{32}	1841 (7)	2835 (6)	2542 (5)	C_{85}	5194 (7)	−1051 (8)	2523 (5)
C_{33}	2531 (7)	3631 (7)	2989 (5)	C_{86}	4321 (6)	−1416 (6)	2789 (4)
C_{34}	2960 (8)	3430 (7)	3731 (6)	C_{91}	2620 (6)	−128 (5)	4492 (4)
C_{35}	2128 (8)	3290 (7)	4118 (5)	C_{92}	1825 (6)	−371 (5)	4897 (4)
C_{36}	1437 (7)	2506 (6)	3669 (4)	C_{93}	1459 (6)	528 (6)	5410 (5)
C_{41}	1280 (6)	−3596 (5)	1675 (4)	C_{94}	2311 (6)	1047 (6)	5929 (5)
C_{42}	2315 (6)	−3809 (6)	2046 (5)	C_{95}	3111 (6)	1264 (6)	5536 (4)
C_{43}	2962 (7)	−4399 (7)	1498 (6)	C_{96}	3489 (6)	339 (5)	5048 (4)
C_{44}	2463 (8)	−5316 (7)	1065 (6)				
Toluene Solvent Molecule							
C_{t1}	4707 (11)	1868 (11)	625 (8)	C_{t5}	5268 (21)	2352 (27)	−315 (16)
C_{t2}	5478 (16)	1157 (18)	707 (15)	C_{t6}	4636 (16)	2441 (14)	182 (11)
C_{t3}	6048 (27)	1062 (25)	207 (16)	C_{t7}	4014 (16)	2005 (17)	1205 (13)
C_{t4}	6003 (19)	1593 (25)	−324 (17)				
Cyclopentane Solvent Molecule							
C_{s1}	6399 (15)	5963 (23)	2134 (33)	C_{s4}	5949 (19)	4660 (34)	2734 (32)
C_{s2}	6358 (19)	5106 (33)	1513 (24)	C_{s5}	6208 (17)	5694 (36)	2905 (18)
C_{s3}	6127 (21)	4274 (19)	1846 (29)				

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for 7[a]

Rh_1–Rh_2	2.718 (1)	Rh_2–P_3	2.396 (2)
Rh_1–P_1	2.334 (2)	Rh_2–C_{b1}	1.929 (9)
Rh_1–C_1	1.867 (12)	Rh_2–C_{b2}	1.927 (8)
Rh_1–C_{b1}	2.046 (7)	C_1–O_1	1.13 (2)
Rh_1–C_{b2}	2.098 (10)	C_{b1}–O_{b1}	1.19 (1)
Rh_2–P_2	2.381 (2)	C_{b2}–O_{b2}	1.16 (1)
C_1–Rh_1–P_1	90.8 (3)	C_{b1}–Rh_1–C_{b2}	89.9 (3)
P_2–Rh_2–P_3	125.5 (1)	C_{b1}–Rh_2–C_{b2}	98.8 (4)
Rh_1–C_1–O_1	177.9 (9)		

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

for a tetrahedron. These distortions are probably due to a large steric interaction between the P_2 and P_3 phosphine ligands. The bond distances in **7** (Table V) are similar to those in a number of previously published rhodium structures,[6a,7b,c] the Rh–Rh bond length being typical for a single bond.[13a,c] The bridging carbonyl carbons are closer to Rh_2 than Rh_1 by 0.117 and 0.171 Å. While these differences are too small to consider the carbonyls as semibridging, the direction of asymmetry would imply that Rh_1 is more negatively charged than Rh_2.[13b] However, the difference in Lewis base strength and π acidity between a terminal carbonyl and trialkylphosphine ligand mandates the opposite. Recently Albright and co-workers attributed this type of asymmetry in phosphido-bridged square-planar–tetrahedral 32-electron rhodium(I) dimers to electronic differences between the rhodium atoms.[13c] They proposed that the square-planar rhodium used two Rh 5p atomic orbitals for bridge bonding while one 5p orbital remained nonbonding; the tetrahedral rhodium used all three 5p atomic orbitals in forming the shorter bridge bonds. This hypothesis should remain valid for a Rh(0) dimer such as **7**.[13d]

The structure of complex **7** fits the formula proposed by Otsuka for the P-*i*-Pr_3 analogue and not the formula he postulated for the P-*t*-Bu_3, PPh-*t*-Bu_2 and PCy_3 complexes.[9a]

Spectra. Otsuka reported three infrared carbonyl bands for **3** in Nujol at 1910, 1928, and 1945 cm^{-1}, one carbonyl band at 1949 cm^{-1} in benzene-d_6, and a Rh–H band at 1980 cm^{-1}.[9a] We observed one carbonyl band at 1953 cm^{-1} in cyclohexane solution (1949 cm^{-1} in Nujol) and no Rh–H bands. Exposure of the Nujol sample to air, however, produced a new band due to oxidation at 1994 cm^{-1}. Our ^1H NMR data agree with those previously reported: δ −5.9 (J(H–Rh) = 15.2 Hz, J(H–P) = 20.4 Hz.[9a] We obtained a ^{31}P signal at δ 59.3 with J(P–Rh) = 146.5 Hz.

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(13) (a) Cowie, M.; Dwight, S. K. *Inorg. Chem.* **1980**, *19*, 209. (b) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1 and references cited therein. (c) The structure of **7** is similar to several reported square planar-tetrahedral Rh_2 structures in which the bridging diorganophosphido groups are closer to the tetrahedral rhodium than they are to the square-planar rhodium. See: Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 470. Jones, R. A.; Wright, T. C. *Ibid.* **1983**, *2*, 1842, Meek, D. W.; Kreter, P. E.; Christoph, G. G. *J. Organomet. Chem.* **1982**, *231*, C53. Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319. Kang, S.; Albright, T. A.; Wright, T. A.; Jones, R. A. *Organometallics* **1985**, *4*, 666. (d) Private communication from T. A. Albright.

Compound **7** gave a terminal carbonyl infrared band at 1987 cm^{-1} and two bridge carbonyl bands at 1773 and 1728 cm^{-1} in cyclohexane solution. The ^{31}P spectra of **7** at 25 °C consisted of a doublet of doublets, relative intensity 2, at δ 50.5 (J(P–Rh) = 223 Hz, ^2J(P–Rh) = 9 Hz) and a doublet, relative intensity 1, at δ 42.8 (J(P–Rh) = 156 Hz). No J(P–P) couplings were observed. When the sample was cooled to −90 °C the δ 50.5 signal reversibly collapsed to a pair of broad doublets, δ 49 (J(P–Rh) = 240 Hz) and δ 52 (J(P–Rh) = 240 Hz), which we assigned to the pair of phosphines P_2 and P_3 on Rh_2, the δ 42.8 signal being assigned to P_1. The coalescence temperature was −83 °C, with calculated $\Delta F^{\ddagger} = 8.5 \pm 0.5$ kcal mol^{-1}. Since the crystal structure shows that the $P_2Rh_2P_3$ plane is rotated 80.3° with respect to the $Rh_2C_{b1}C_{b2}Rh_2$ plane, P_2 and P_3 occupy nonequivalent sites with respect to P_1 and C_1. A sufficiently rapid oscillation of P_2 and P_3 through the 90° tetrahedral position to the opposite and equivalent 80.3° position would render P_2 and P_3 magnetically equivalent on the NMR time scale and produce the observed spectra. This process should be lower in energy than either a site exchange of the P_1 phosphine and terminal CO on Rh_1, via rotation through a tetrahedral transition state, or exchange of phosphines P_2 and P_3 via complete rotation on Rh_2 through a sterically crowded square-planar transition state.

Reactions. The reaction of **3** or **7** with carbon monoxide at ambient conditions quantitatively produced a yellow complex, **8**, which exhibited complex terminal carbonyl bands and two bridging carbonyl bands in the infrared.[14] ^{31}P NMR spectra of these solutions exhibited a doublet at δ 49.5 with J(P–Rh) = 150 Hz and a singlet due to free tricyclohexylphosphine (intensity ratio 1/1 when **3** was reacted, 2/1 when **7** was reacted). When the sample was cooled, the doublet signal reversibly coalesced into the base line but the exchange rate was still too fast at −95 °C to resolve separate phosphorus signals. Sweeping the carbon monoxide from these solutions of **8** with argon or hydrogen produced **7** quantitatively at ambient conditions.

Treatment of **7** or **8** with hydrogen at atmospheric pressure (in the presence of at least two PCy_3 ligands per rhodium) generated **3** quantitatively at 50 °C over 15 min.

We believe **8** is bis(μ-carbonyl)tetracarbonylbis(tricyclohexylphosphine)dirhodium(0), the structure proposed by Otsuka[9] and Heisler.[10] Possible intermediates, in these reactions are **2** (L = PCy_3), $HRh(CO)_2PCy_3$ (**9**), and $HRh(CO)_3PCy_3$ (**10**). Infrared spectra of solutions of **3** at elevated pressures of equimolar carbon monoxide and hydrogen were obtained at ambient and elevated temperatures.[15] While the carbonyl bands of **8** were observed, we were unable to assign other bands observed in the terminal carbonyl region with certainty.

The dimerization of rhodium monohydrides via reductive elimination of H_2 has been proposed to proceed through a four-center transition state.[6b] Recently, however, the reductive elimination of H_2 from (μ-H)$_2$-bridged rhodium dimers[16–18] and the formation of monomeric rhodium hydrides from (μ-H)$_2$(μ-CO)-bridged rhodium dimers[7c] have been reported. Thus the interconversion of **3** and **7** probably proceeds through a (μ-H)$_2$-bridged transition state.

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Registry No. **3**, 77645-97-7; **7**, 101348-82-7; **8**, 101629-41-8; $Rh(CO)_2(acac)$, 14874-82-9; $Rh(CO)(PCy_3)acac$, 101348-81-6.

Supplementary Material Available: Listings of complete structure determination data, anisotropic thermal parameters, calculated atomic coordinates for hydrogen atoms, complete bond distances and bond angles, structure factor amplitudes, nonbonded distances, and least-squares planes and perspective ORTEP drawings of both the complete structures and Rh coordination groups of complexes **3** and **7** (122 pages). Ordering information is given on any current masthead page.

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(14) Terminal ν(CO): 2048 w, 2037 m, 2019 w, 2008 s, 1997 m, 1967 s, 1938 w cm^{-1}. Bridging ν(CO): 1800 w, 1781 m cm^{-1} in cyclohexane solution.

(15) High-pressure infrared spectra in cyclohexane solution were obtained with a cell purchased from Temco, Inc., Tulsa, OK 74151.

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(17) Private communication to R. Eisenberg; See: Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1984**, *23*, 4207.

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