Synthesis and Ligand Exchange Reactions of Heterobimetallic Di-*tert*-butylphosphido-Bridged Complexes of Cr–Co, Cr–Rh, and Fe–Co. X-ray Crystal Structures of $(CO)_5Cr(\mu\text{-}t\text{-}Bu_2P)Rh(COD)(\mathit{Cr}\text{–}\mathit{Rh})$ (COD = 1,5-Cyclooctadiene), $(CO)_3(PMe_3)Cr(\mu\text{-}t\text{-}Bu_2P)(\mu\text{-}CO)Co(PMe_3)(CO)(\mathit{Cr}\text{–}\mathit{Co})$, and $(CO)_3(PMe_3)Fe(\mu\text{-}t\text{-}Bu_2P)Co(CO)_2(PMe_3)(\mathit{Fe}\text{–}\mathit{Co})$

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Reaction of $Cr(CO)_5(t\text{-}Bu_2PLi)$, generated in situ from $Cr(CO)_5(t\text{-}Bu_2PH)$ and *n*-BuLi, with $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) or $CoCl(PMe_3)_3$ yields the new heterobimetallic complexes $(CO)_5Cr(\mu\text{-}t\text{-}Bu_2P)Rh(COD)$ (**1**) (45%) and $(CO)_3(PMe_3)Cr(\mu\text{-}CO)(\mu\text{-}t\text{-}Bu_2P)Co(PMe_3)CO$ (**6**) (56%). Reaction of $Fe(CO)_4(t\text{-}Bu_2PLi)$ with $CoCl_2(PMe_3)_2$ in THF yields $(CO)_3(PMe_3)Fe(\mu\text{-}t\text{-}Bu_2P)Co(CO)_2(PMe_3)$ (**7**) (40%). All three complexes contain metal–metal bonds of order 1, which are bridged by single di-*tert*-butylphosphido ($\mu\text{-}t\text{-}Bu_2P$) units. In the formation of **6** and **7** exchange of PMe_3 and CO occurs between Co and Cr or Co and Fe. Complex **6** also has a bridging CO unit. The approximate coordination geometries of the metals in these complexes are as follows: **1** and **6**, Rh and Co, square planar, and Cr, capped octahedral; **7**, Fe and Co, trigonal bipyramid. In contrast, the reaction of $Mo(CO)_5(t\text{-}Bu_2PLi)$ with $CoCl(PMe_3)_3$ or $NiCl_2(PMe_3)_2$ yields $CoCl(PMe_3)_2(CO)_2$ and *cis*-$Mo(CO)_4(PMe_3)_2$, respectively, as the only isolable products. The reactions of the heterobimetallic complexes with H_2, C_2H_4, CO, and PMe_3 have been studied. **1** reacts with (CO) (3 atm) to give $(CO)_5Cr(\mu\text{-}t\text{-}Bu_2P)Rh(CO)_2(\mathit{Cr}\text{-}\mathit{Rh})$ (**3**) that reacts in turn with PMe_3 to give $(CO)_4(PMe_3)Cr(\mu\text{-}t\text{-}Bu_2P)Rh(CO)(PMe_3)$ (**2**), which was previously prepared from $(CO)_5Cr(\mu\text{-}t\text{-}Bu_2PLi)$ and $RhCl(PMe_3)_3$. $(CO)_4(PMe_3)Cr(\mu\text{-}t\text{-}Bu_2P)NiCl(PMe_3)$ (**4**) reacts with CO (3 atm) to give $(CO)_4(PMe_3)Cr(\mu\text{-}t\text{-}Bu_2P)NiCl(CO)$ (**5**). All of these ligand displacement reactions are quantitative. The new complexes have been characterized spectroscopically (IR, NMR), and the structures of **1**, **6**, and **7** in the solid state have been determined by single-crystal X-ray diffraction studies. Crystal data for **1**: $C_{21}H_{30}CrO_5PRh$, $M_2 = 548.35$, monoclinic $P2_1/c$ (no. 14), $a = 9.535\ (7)$ Å, $b = 28.146\ (8)$ Å, $c = 9.399\ (6)$ Å, $\beta = 113.506\ (3)°$, $U = 2313.1\ (1)$ Å^3, $D_{calcd} = 1.574$ g cm^{-3}, $Z = 4$, $\lambda(\text{Mo K}\alpha) = 0.710\,69$ Å, $\mu(\text{Mo K}\alpha) = 12.56$ cm^{-1}, final $R = 0.0491$, $R_w = 0.0702$ from 2786 observed reflections ($I > 3\sigma(I)$), 4174 measured. Crystal data for **6**: $C_{19}H_{36}CoCrO_5P_3$, $M_r = 548.35$, monoclinic, $P2_1/n$ (a nonstandard setting of $P2_1/c$ (no. 14), $a = 8.527\ (1)$ Å, $b = 18.772\ (4)$ Å, $c = 16.870\ (1)$ Å, $\beta = 101.59\ (2)°$, U = 2645.5 (5) Å^3, $D_{calcd} = 1.377$ g cm^{-1}, $Z = 4$, $\lambda(\text{Mo K}\alpha) = 0.710\,69$ Å, $\mu(\text{Mo K}\alpha) = 12.30$ cm^{-1}, final $R = 0.0445$, $R_w = 0.0564$ from 3037 observed reflections ($I > 3\sigma(I)$), 4809 measured. Crystal data for **7**: $C_{19}H_{36}CoFeO_5P_3$, $M_r = 551.78$, orthorhombic, *Pnma* (no. 62), $a = 11.468\ (1)$ Å, $b = 13.007\ (3)$ Å, $c = 17.509\ (3)$ Å, $U = 2611.8\ (5)$ Å^3, $D_{calcd} = 1.389$ g cm^{-3}, $Z = 4$, $\lambda(\text{Mo K}\alpha) = 0.710\,69$ Å, $\mu(\text{Mo K}\alpha) = 13.90$ cm^{-1}, final $R = 0.0668$, $R_w = 0.0786$, from 1060 observed reflections ($I > 3\sigma(I)$), 2629 measured.

Introduction

Heterobimetallic complexes of the d-block transition metals are currently of interest in organometallic chemistry. We recently reported the synthesis and X-ray structures of two mixed-metal complexes of Cr–Ni and Cr–Rh (**2** and **4**) that were synthesized via the interaction of the coordinated lithiated phosphine complex $(CO)_5Cr(P\text{-}t\text{-}Bu_2)Li$ with the appropriate metal halide complex.[1] There were several aspects of the synthesis and structures of **2** and **4** which we found interesting. One was that for both complexes a mutual exchange of PMe_3 and CO ligands between Cr and the other metal must have occurred during the course of the reaction. Secondly although the Cr moiety of each molecule has apparently virtually identical ligand sets ($(CO)_4(PMe_3)(\mu\text{-}t\text{-}Bu_2P)(M)$ (M = Ni, Rh)) in the solid state they crystallized with significantly different stereochemistries. One (**4**) had the Cr–PMe_3 virtually trans to the phosphorus atom of the $\mu\text{-}t\text{-}Bu_2P$ group while the other (**2**) had the ligand in a cis position. Lastly ^{31}P NMR data indicated that both complexes exist in solution as mixtures of isomers.

In order to extend the general scope of these types of reactions and to gain more information concerning the ligand exchange properties of these and related complexes containing the $\mu\text{-}t\text{-}Bu_2P$ ligand.[2,3] we have investigated the reactions outlined in Scheme I. New heterobinuclear complexes (**1** and **6**) are readily isolated from the reactions of $(CO)_5Cr(\mu\text{-}t\text{-}Bu_2P)Li$ with $[Rh(COD)Cl]_2$ and $CoCl(PMe_3)_3$. However, with $(CO)_5Mo(t\text{-}Bu_2P)Li$ the only isolable products were $Co(CO)_2(PMe_3)_2Cl$[4] and *cis*-$Mo(CO)_4(PMe_3)_2$.[5] The reasons for this difference in going from Cr to Mo are not immediately obvious. We have also synthesized the Fe–Co heterobimetallic complex **7** by a similar route (see Scheme I). General features of the mixed-metal $\mu\text{-}t\text{-}Bu_2P$ bridged systems are the presence of labile ligands as well as stereochemical nonrigidity in solution. Fluxional behavior is frequently observed for complexes containing five- or seven-coordinate metals[6] and many of the systems described do have metals with coordination numbers of seven or five. Thus reactions of **1** with excess PMe_3 in THF yields **2** directly, and **1** is also

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[1] Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stuart, A. L.; Wright, T. C.; Whittlesey, B. R. *Organometallics* **1984**, *3*, 114.

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

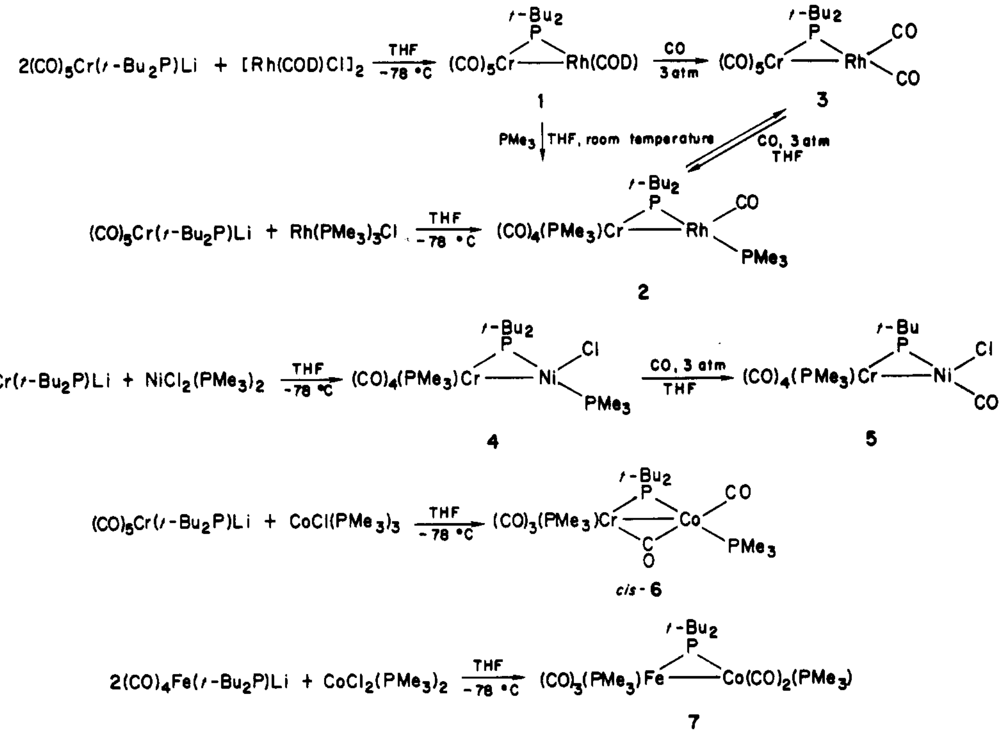
[3] Jones, R. A.; Wright, T. C. *Organometallics* **1983**, *2*, 1842.

[4] Klein, H. F.; Karsch, H. H. *Inorg. Chem.* **1975**, *14*, 473.

[5] Poilblanc, R.; Biorgne, M. *C. R. Hebd. Seances Acad. Sci.* **1961**, *252*, 3054.

[6] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 2, pp 50–53.

Scheme I



converted to **3** by reaction with CO (3 atm). For **4**(*Cr–Ni*) the Ni–PMe$_3$ group is labile and may be readily replaced by CO (3 atm) to give **5** while the Cr–PMe$_3$ unit appears to be unaffected under these conditions.

We describe here the synthesis and characterization of the new complexes **1**, **3**, **5**, **6**, and **7** and the X-ray crystal structures of **1**, **6**, and **7**.

Results and Discussion

Synthesis and Reactions of Cr–Rh Complexes. The interaction of (CO)$_5$Cr(*t*-Bu$_2$P)Li with [Rh(COD)Cl]$_2$ (COD = cycloocta-1,5-diene), in THF at low temperature yields red-brown crystalline (CO)$_5$Cr(μ-*t*-Bu$_2$P)Rh(COD) (**1**) in ca. 45% yield after workup. This hexane-soluble material is air stable in the solid state for short periods but decomposes rapidly in solution when exposed to the atmosphere. Spectroscopic data is in accord with the solid-state structure (Figure 1) as determined by X-ray crystallography. The ^{31}P{^{1}H} spectrum shows a single downfield doublet (δ 215.0 ($^1J_{Rh-P}$ = 123 Hz)) for the μ-*t*-Bu$_2$P group,[7] and the IR spectrum shows only terminal ν_{CO} absorptions.

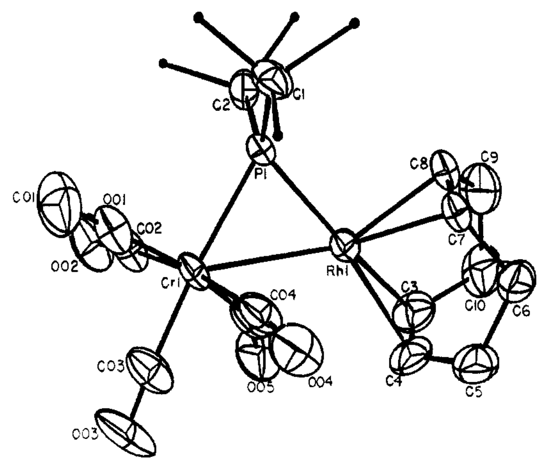


Figure 1. General view of **1**.

The related complex (CO)$_4$(PMe$_3$)Cr(μ-*t*-Bu$_2$P)Rh(CO)(PMe$_3$) (**2**), previously reported, is essentially isoelectronic with **1** and was found to exist in solution as a complex mixture of isomers. Since **2** exists in the solid state as a single isomer, ligand exchange processes of some kind must occur in solution in order for several isomers to be observed. Exchange reactions of **1** with CO and PMe$_3$ indicate that the ligands in the Cr–Rh system in general are quite labile. Thus the reaction of **1** with excess PMe$_3$ in THF yields **2** directly, indicating that both the COD and CO ligands are labile in the presence of phosphine donor ligands. The COD ligand of **1** is also readily displaced by CO (3 atm) to give (CO)$_5$Cr(μ-*t*-Bu$_2$P)Rh(CO)$_2$ (**3**), which in turn reacts with PMe$_3$ to give **2**. Analytical and spectroscopic data for **3** is in accord with the suggested structure (see Experimental Section and Scheme I) in which the central CrRhP core having a Cr–Rh bond is retained. The Rh atom most likely has a square-planar geometry typical of mononuclear Rh(I) systems. All of these ligand replacements are essentially quantitative. The displacement of the coordinated PMe$_3$ groups in **2** cannot be achieved by treatment with CO, H$_2$, or C$_2$H$_4$ (all at 3 atm), and **2** does not react further with excess PMe$_3$. However the related Cr–Ni complex **4** reacts readily with CO (3 atm) to give **5**. Spectroscopic data for **5** indicate that only one PMe$_3$ ligand has been replaced. Thus the ^{31}P{^{1}H} NMR spectrum consists of two doublets at δ 238.34 and δ 24.34 ($^2J_{P-P}$ = 21.9 Hz). The ^{31}P chemical shifts of PMe$_3$ phosphorus nucleii in other di-*tert*-butylphosphido Ni–PMe$_3$ systems are all upfield (ca. δ −20),[8] and most

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[7] Downfield shifts in the δ 50–200 range in the ^{31}P NMR of the Ph$_2$P groups bridging metal–metal bonds have been noted by several groups of workers. See, for example: Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. Kreter, P. E.; Meek, D. W. *Inorg. Chem.* **1983**, *22*, 319. Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53 and references therein. Similar downfield shifts have been noted for μ-*t*-Bu$_2$P complexes, see ref 1–3 and references therein.

[8] Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 874.

Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinements for 1, 6, and 7

	$C_{21}H_{30}CrO_5PRh$ (1)	$C_{19}H_{36}CoCrO_5P_3$ (6)	$C_{19}H_{36}CoFeO_5P_3$ (7)
mol wt	548.35	548.35	551.78
space group	$P2_1/c$	$P2_1/n$	*Pnma*
cell constants			
a, Å	9.535 (7)	8.527 (1)	11.469 (1)
b, Å	28.146 (8)	18.772 (4)	13.007 (3)
c, Å	9.399 (6)	16.870 (1)	17.509 (3)
β, deg	113.506 (3)	101.59 (2)	90
cell vol, $Å^3$	2313.1 (1)	2645.5 (5)	2611.8 (1)
molecules/unit cell	4	4	4
D_{calcd}, g cm^{-3}	1.574	1.377	1.389
μ(calcd), cm^{-1}	12.56	12.30	13.90
radiation, Å	Mo Kα 0.710 69	Mo Kα 0.710 69	Mo Kα, 0.710 69
max cryst dimens, mm	0.30 × 0.28 × 0.27	0.21 × 0.19 × 0.23	0.20 × 0.20 × 0.10
scan width, deg	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
std reflctns	$\bar{5},10,1, 5,\overline{10},\bar{2}$	$\bar{1},3,11, 4,\bar{9},0$	$7,\bar{2},1, 0,\bar{8},0$
decay of stds	<2%	<2%	<2%
reflctns measd	4174	4809	2629
2θ range, deg	2-50	2-50	2-50
reflctns obsd ($I > 3\sigma(I)$)	2786	3037	1060
no. of parameters varied	262	262	152
data/parameter ratio	10.634	11.592	6.97
R	0.0491	0.0445	0.0668
R_w	0.0702	0.0564	0.0786

Table II. Positional Parameters and Their Estimated Standard Deviations for 1[a]

atom	*x*	*y*	*z*	*B*, $Å^2$
Rh(1)	0.08380 (6)	0.13744 (2)	0.36295 (6)	2.71 (1)
Cr(1)	−0.0538 (1)	0.09815 (4)	0.0735 (1)	2.87 (2)
P(1)	−0.1728 (2)	0.12291 (7)	0.2418 (2)	2.42 (4)
O(01)	−0.3175 (8)	0.0324 (3)	−0.0990 (8)	6.9 (2)
O(02)	−0.2048 (8)	0.1650 (3)	−0.1943 (7)	6.5 (2)
O(03)	0.1222 (7)	0.0614 (3)	−0.1029 (6)	7.2 (2)
O(04)	0.1423 (7)	0.0226 (2)	0.2958 (7)	5.7 (2)
O(05)	0.1932 (7)	0.1710 (3)	0.1117 (6)	6.2 (2)
C(1)	−0.2742 (8)	0.0785 (3)	0.3209 (8)	3.3 (2)
C(01)	−0.219 (1)	0.0572 (3)	−0.0304 (8)	4.2 (2)
C(2)	−0.2836 (9)	0.1823 (3)	0.1940 (8)	3.3 (2)
C(02)	−0.155 (1)	0.1405 (3)	−0.0908 (8)	4.1 (2)
C(03)	0.053 (1)	0.0752 (3)	−0.0376 (8)	4.5 (2)
C(3)	0.3011 (9)	0.1798 (3)	0.456 (1)	4.6 (2)
C(4)	0.3408 (8)	0.1326 (4)	0.452 (1)	5.0 (2)
C(04)	0.0644 (9)	0.0524 (3)	0.2235 (8)	3.8 (2)
C(05)	0.1085 (9)	0.1441 (3)	0.1321 (8)	4.2 (2)
C(5)	0.3950 (9)	0.0986 (4)	0.590 (1)	4.7 (2)
C(6)	0.3027 (9)	0.1027 (3)	0.6943 (9)	4.5 (2)
C(7)	0.1345 (8)	0.1146 (3)	0.5994 (8)	3.8 (2)
C(8)	0.0756 (9)	0.1618 (3)	0.5800 (8)	4.1 (2)
C(9)	0.170 (1)	0.2073 (4)	0.636 (1)	6.0 (3)
C(10)	0.319 (1)	0.2074 (4)	0.608 (1)	5.9 (3)
C(11)	−0.192 (1)	0.0305 (3)	0.3406 (9)	4.7 (2)
C(12)	−0.2702 (8)	0.0924 (3)	0.4805 (8)	3.8 (2)
C(13)	−0.4453 (9)	0.0730 (4)	0.204 (1)	5.4 (2)
C(21)	−0.426 (1)	0.1788 (4)	0.0342 (9)	5.2 (2)
C(22)	−0.170 (1)	0.2188 (3)	0.182 (1)	4.3 (2)
C(23)	−0.3431 (9)	0.1978 (3)	0.3163 (9)	4.5 (2)

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

Cr–PMe_3 signals in μ-*t*-Bu_2P systems appear downfield of external H_3PO_4 (δ 0.0) at ca. δ +20 ppm.[1] On this basis we tentatively assign the structure of **5** as having the PMe_3 group attached to Cr with a new Ni–CO group.

X-ray Structure of 1(*Cr–Rh*). In order to unequivocally determine the structure of **1** and to compare it with **2**, a single-crystal X-ray diffraction study was undertaken. A general view of the molecule is shown in Figure 1. Atomic positional parameters and bond lengths and angles for **1** are given in Tables II, III, and IV, respectively. The structure consists of a central CrRhP core in which a single Cr–Rh bond is bridged by a *t*-Bu_2P unit. The Cr atom also bears five CO units. Its geometry is best described as a capped octahedron that is not uncommon for seven-coordinate Cr complexes.[9] The geometry of the central core is similar to that found in **2**.[1] Thus the Cr(1)–Rh(1), Cr(1)–P(1), and Rh(1)–P(1) distances are 2.738 (1), 2.389 (1), and 2.286 (1) Å, respectively, in **1** vs. 2.689 (1), 2.449 (2), and 2.296 (1) Å in **2**. Speculation on the reasons for these minor differences in bond lengths is probably unwarranted. The geometry about the Rh atom consisting of Cr, P, and the midpoints of the two double bonds of the COD ligand is virtually square planar. Deviations from the best least-squares plane through Cr(1)–P(1)–Rh(1) and the midpoints of C(3)–C(4) and C(7)–C(8) are relatively small,[10] and the sum of the angles about Rh(1) is 361.8°.[10] The (1,5-COD) ligand is bonded in the expected boat or tub comformation as found in literally scores of other transition-metal–COD complexes.[11] The carbon–carbon double-bond lengths are the same to within experimental error (3σ) (C(3)–C(4) = 1.385 (9) Å and C(7)–C(8) = 1.426 (8) Å) and fall within the values generally found in many other cases. They are slightly larger than that of a free double bond.

Synthesis and Characterization of $(CO)_3(PMe_3)Cr(\mu$-*t*-$Bu_2P)(\mu$-CO)Co(PMe_3)CO(*Cr–Co*) (6). The interaction of 1 equiv of $(CO)_5Cr(t$-$Bu_2P)Li$ (prepared in situ) with 1 equiv of $CoCl(PMe_3)_3$ yields the yellow-brown crystalline complex (**6**) in ca. 56% yield. Spectroscopic data for this moderately air-sensitive, hexane-soluble complex are consistent with the structure as determined by X-ray crystallography. Thus the IR spectrum has strong bands at 1918, 1865, and 1790 cm^{-1}. The former two are assigned to terminal CO stretches and the latter to the bridging CO unit. At first, NMR (^1H and ^{31}P) data appeared to be deceptively simple. At ambient temperature (C_6D_6) the ^1H NMR spectrum (90 MHz) is a single broad resonance that can best be described as a lopsided

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(9) See, for example: Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67.

(10) Deviations (Å) from the least-squares plane through Rh(1)–P(1)–Cr(1) and the midpoints of C(3)–C(4) (CNT(3)) and C(7)–C(8) (CNT(7)) are as follows: Rh(1), 0.116; P(1), 0.278; Cr(1), −0.262; CNT(3), 0.145; CNT(7), −0.278. The angles (deg) subtended by the four points around Rh are as follows: Cr(1)–Rh(1)–CNT(3) = 120.6; Cr(1)–Rh(1)–CNT(7) = 147.4; P(1)–Rh(1)–CNT(7) = 99.3; P(1)–Rh(1)–CNT(3) = 173.4; CNT(3)–Rh(1)–CNT(7) = 86.0; P(1)–Rh(1)–Cr(1) = 55.9.

(11) Omae, I. *Coord. Chem. Rev.* **1983**, *51*, 1 and references therein. Ibers, J. A.; Snyder, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 495.

Table III. Bond Distances (Å) for 1^a

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Rh(1)	Cr(1)	2.738 (1)	Cr(1)	C(05)	1.921 (6)	C(2)	C(22)	1.527 (8)
Rh(1)	P(1)	2.286 (1)	P(1)	C(1)	1.903 (5)	C(2)	C(23)	1.534 (7)
Rh(1)	C(3)	2.243 (5)	P(1)	C(2)	1.933 (5)	C(3)	C(4)	1.385 (9)
Rh(1)	C(4)	2.256 (5)	O(01)	C(01)	1.142 (7)	C(3)	C(10)	1.576 (9)
Rh(1)	C(05)	2.282 (5)	O(02)	C(02)	1.131 (6)	C(4)	C(5)	1.521 (8)
Rh(1)	C(7)	2.175 (5)	O(03)	C(03)	1.138 (6)	C(5)	C(6)	1.564 (8)
Rh(1)	C(8)	2.183 (5)	O(04)	C(04)	1.145 (6)	C(6)	C(7)	1.529 (8)
Cr(1)	P(1)	2.389 (1)	O(05)	C(05)	1.178 (7)	C(7)	C(8)	1.426 (8)
Cr(1)	C(01)	1.880 (6)	C(1)	C(11)	1.535 (7)	C(8)	C(9)	1.531 (9)
Cr(1)	C(02)	1.883 (6)	C(1)	C(12)	1.536 (7)	C(9)	C(10)	1.550 (10)
Cr(1)	C(03)	1.839 (6)	C(1)	C(13)	1.570 (8)			
Cr(1)	C(04)	1.910 (6)	C(2)	C(21)	1.577 (7)			

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

Table IV. Bond Angles (deg) for 1^a

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cr(1)	Rh(1)	P(1)	55.91 (3)	Rh(1)	P(1)	Cr(1)	71.66 (4)
Cr(1)	Rh(1)	C(3)	127.1 (2)	Rh(1)	P(1)	C(1)	122.2 (2)
Cr(1)	Rh(1)	C(4)	111.4 (2)	Rh(1)	P(1)	C(2)	109.8 (2)
Cr(1)	Rh(1)	C(05)	43.8 (2)	Cr(1)	P(1)	C(1)	121.1 (2)
Cr(1)	Rh(1)	C(7)	136.0 (2)	Cr(1)	P(1)	C(2)	117.3 (2)
Cr(1)	Rh(1)	C(8)	150.9 (2)	C(1)	P(1)	C(2)	110.1 (2)
P(1)	Rh(1)	C(3)	158.1 (2)	P(1)	C(1)	C(11)	108.2 (3)
P(1)	Rh(1)	C(4)	164.3 (2)	P(1)	C(1)	C(12)	113.3 (4)
P(1)	Rh(1)	C(05)	92.1 (2)	P(1)	C(1)	C(13)	109.9 (4)
P(1)	Rh(1)	C(7)	102.3 (2)	C(11)	C(1)	C(12)	107.0 (5)
P(1)	Rh(1)	C(8)	95.2 (2)	C(11)	C(1)	C(13)	109.4 (5)
C(3)	Rh(1)	C(4)	35.8 (2)	C(12)	C(1)	C(13)	108.9 (4)
C(3)	Rh(1)	C(05)	84.1 (2)	Cr(1)	C(01)	O(01)	177.0 (5)
C(3)	Rh(1)	C(7)	88.0 (2)	P(1)	C(2)	C(21)	110.6 (4)
C(3)	Rh(1)	C(8)	80.9 (2)	P(1)	C(2)	C(22)	105.1 (4)
C(4)	Rh(1)	C(05)	81.4 (2)	P(1)	C(2)	C(23)	113.8 (4)
C(1)	Rh(1)	C(7)	80.5 (2)	C(21)	C(2)	C(22)	110.0 (5)
C(4)	Rh(1)	C(8)	96.3 (2)	C(21)	C(2)	C(23)	107.1 (5)
C(05)	Rh(1)	C(7)	158.6 (2)	C(22)	C(2)	C(23)	110.3 (5)
C(05)	Rh(1)	C(8)	156.7 (2)	Cr(1)	C(02)	O(02)	173.6 (6)
C(7)	Rh(1)	C(8)	38.2 (2)	Cr(1)	C(03)	O(03)	178.0 (6)
Rh(1)	Cr(1)	P(1)	52.43 (3)	Rh(1)	C(3)	C(4)	72.6 (3)
Rh(1)	Cr(1)	C(01)	137.2 (2)	Rh(1)	C(3)	C(10)	111.3 (4)
Rh(1)	Cr(1)	C(02)	116.4 (2)	C(4)	C(3)	C(10)	124.3 (6)
Rh(1)	Cr(1)	C(03)	123.5 (2)	Rh(1)	C(4)	C(3)	71.6 (3)
Rh(1)	Cr(1)	C(04)	68.4 (2)	Rh(1)	C(4)	C(5)	107.8 (4)
Rh(1)	Cr(1)	C(05)	55.4 (2)	C(3)	C(4)	C(5)	125.8 (6)
P(1)	Cr(1)	C(01)	90.2 (2)	Cr(1)	C(04)	O(04)	169.3 (5)
P(1)	Cr(1)	C(02)	97.9 (2)	Rh(1)	C(05)	Cr(1)	80.8 (2)
P(1)	Cr(1)	C(03)	173.6 (2)	Rh(1)	C(05)	O(05)	123.0 (5)
P(1)	Cr(1)	C(04)	90.2 (2)	Cr(1)	C(05)	O(05)	155.9 (5)
P(1)	Cr(1)	C(05)	98.9 (2)	C(4)	C(5)	C(6)	113.6 (5)
C(01)	Cr(1)	C(02)	85.1 (3)	C(5)	C(6)	C(7)	111.8 (5)
C(01)	Cr(1)	C(03)	91.5 (3)	Rh(1)	C(7)	C(6)	114.5 (4)
C(01)	Cr(1)	C(04)	95.4 (3)	Rh(1)	C(7)	C(8)	71.2 (3)
C(01)	Cr(1)	C(05)	166.8 (2)	C(6)	C(7)	C(8)	123.2 (5)
C(02)	Cr(1)	C(03)	88.4 (2)	Rh(1)	C(8)	C(7)	70.6 (3)
C(02)	Cr(1)	C(04)	171.9 (2)	Rh(1)	C(8)	C(9)	110.6 (4)
C(02)	Cr(1)	C(05)	84.2 (3)	C(7)	C(8)	C(9)	126.0 (5)
C(03)	Cr(1)	C(04)	83.5 (2)	C(8)	C(9)	C(10)	113.2 (5)
C(03)	Cr(1)	C(05)	80.5 (3)	C(3)	C(10)	C(9)	112.4 (5)
C(04)	Cr(1)	C(05)	94.1 (3)				

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

triplet (see Experimental Section). At 200 MHz the pattern is better resolved and two doublets are observed: δ 1.37 ($^2J_{P-H}$ = 13.07 Hz), 1.22 ($^2J_{P-H}$ = 7.76 Hz). These resonances are assigned to the μ-*t*-Bu$_2$P and PMe$_3$ groups, respectively. At 25 °C in toluene-d_8 the $^{31}P\{^1H\}$ spectrum shows only a simple doublet (δ 11.64 ($^2J_{P-P}$ = 30.51 Hz) assigned to a PMe$_3$ group. There are no other resonances observed at this temperature. However, on cooling two broad humps appear at ca. −45 °C. These sharpen on further cooling and a well-resolved spectrum is observed at −85 °C. This consists of a low-field doublet of doublets (δ 164.69 ($^2J_{P-P_{Co}}$ = 79.35 Hz, $^2J_{P-P_{Cr}}$ = 30.52 Hz)) and two doublets (δ 17.01 $^2J_{P-P_{Co}}$ = 79.35 Hz), 12.15 ($^2J_{P-P_{Cr}}$ = 30.52 Hz)). The former resonance is assigned to the μ-*t*-Bu$_2$P group and the latter two signals to PMe$_3$ resonances. Low-field shifts for phosphido groups bridging metal–metal bonds have been observed in many other systems.[7] It is of interest to note that for the rhodium analogue which we have previously reported[1] ((CO)$_4$PMe$_3$Cr(μ-*t*-Bu$_2$P)-Rh(CO)(PMe$_3$) (**2**) the $^{31}P\{^1H\}$ NMR spectra indicated that a complex mixture of isomers was present in solution. Although we were unable to detect the presence of different isomers in the $^{31}P\{^1H\}$ spectra of **6**, the observed spectral changes indicate fluxional behavior at room temperature that is frozen out on cooling. The formation of **6** is accompanied by the transfer of a PMe$_3$ ligand from

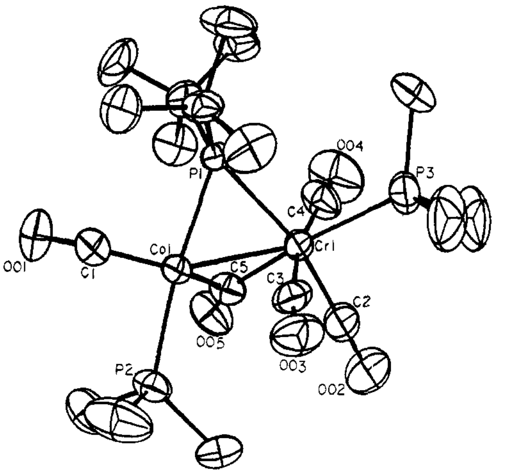

Figure 2. General view of **6**.

Co to Cr. The Co atom also now bears a terminal CO ligand which must have come from the Cr atom. The actual mechanism by which **6** is formed is at present unknown.

X-ray Structure of 6(*Cr–Co*). A general view of the molecule is shown in Figure 2. Atomic positional parameters and bond lengths and angles for **6** are given in Tables V, VI, and VII, respectively. The structure consists of discrete molecules with no short intermolecular contacts. The Cr and Co atoms are linked by a single metal–metal bond that is bridged by a single t-Bu_2P unit and by a bridging CO group. The Cr atom is seven-coordinate, and its geometry is best described as a distorted capped octahedron. The carbon atoms of three carbonyls (C(3), C(4) and C(5)) and P(3) are virtually planar; the sum of the angles around Cr(1) equals 358.7° while there are some angular distortions from the 90° angles expected in a symmetrical square plane (see Table VII). The bridging phosphido phosphorus atom P(1) is essentially trans to C(2); P(1)–Cr(1)–C(2) = 166.5 (2)° with Co acting as the capping atom (Co(1)–Cr(1)–C(2) = 113.3 (2)°). The coordination geometry about the Co atom, but excluding the bridging CO group, is nearly planar (the sum of the angles around it is 361.8°), and the deviations from the least squares plane through P(1)–Co(1)–C(1)–Cr(1) and P(2) are relatively small.[12] In **6** there is now a fully bridging CO (C(5)–O(5)) that has similar Co(1)–C(5) and Cr(1)–C(5) distances (1.946 (4) and 1.984 (5) Å, respectively). If a bridging carbonyl is preferred in the systems **2** and **6**, the change from semi to full bridging on changing from Rh to Co (**2** to **6**) may simply be a reflection of the better ability to span a shorter metal–metal bond in **6**. The Cr–Rh bond length in the Rh analogoue is 2.689 (1) Å vs. 2.505 (1) Å for Cr–Co in **6**.

Synthesis of $(PMe_3)(CO)_3Fe(\mu$-t-$Bu_2P)Co(CO)_2(PMe_3)$(*Fe–Co*) (7). We have used the general salt elimination reaction used to synthesize **1**, **2**, **4** and **6** to prepare a new heterobimetallic complex of Fe and Co. Thus the reaction of $(CO)_4Fe(t$-$Bu_2PLi)$, prepared in situ from $Fe(CO)_4(t$-$Bu_2PH)$ and n-BuLi, with $CoCl_2(PMe_3)_2$ in THF at −78 °C yields $(PMe_3)(CO)_3Fe(\mu$-t-$Bu_2P)Co(CO)_2(PMe_3)$ (**7**) in ca. 40% yield. This green-yellow, hexane-soluble, crystalline material is air stable for short periods in the solid state but decomposes rapidly in solution when exposed to the atmosphere. The IR spectrum contains only terminal ν_{CO} bonds while the ^1H NMR spectrum shows three doublets assigned to the protons of the μ-t-Bu_2P and two PMe_3 groups (δ 1.63 ($^3J_{P-H}$ = 12.0 Hz, 18 H), 1.35 ($^2J_{P-H}$ = 9.0 Hz, 9 H), 1.20 ($^2J_{P-H}$ = 9.0 Hz, 9 H). As found for **6** at ambient temperature in C_6D_6 or PhMe-d_8 the $^{31}P\{^1H\}$ NMR spectrum of **7** is deceptively simple. A single sharp doublet is observed at δ 41.04 (J_{P-P} = 12.21 Hz). No resonances attributable to a μ-t-Bu_2P group are observed. However, on cooling to −80 °C (PhMe-d_8), two more sets of resonances appear and the spectrum can be interpreted on a first-order basis. A low-field doublet of doublets at δ 274.51 (J_{P-P} = 91.60, 12.21 Hz) is assigned to the bridging phosphido group, and the two remaining doublets are due to PMe_3 groups attached to Fe and Co (δ 43.49 (J_{P-P} = 12.21 Hz), 13.31 (J_{P-P} = 91.53 Hz)). The low-temperature $^{31}P\{^1H\}$ NMR data is in accord with the solid-state structure that was determined by a single-crystal X-ray diffraction study (see below). The absence of signals at higher temperatures is consistent with a stereochemically nonrigid molecule on the NMR time scale.

Table V. Positional Parameters and Their Estimated Standard Deviations for **6**[a]

atom	x	y	z	B, Å^2
Co(1)	0.5543 (1)	0.41596 (5)	0.26294 (5)	2.94 (2)
Cr(1)	0.3791 (1)	0.31580 (6)	0.29106 (6)	3.00 (2)
P(1)	0.4205 (2)	0.35210 (9)	0.16067 (9)	2.71 (3)
P(2)	0.7108 (2)	0.4597 (1)	0.3737 (1)	3.94 (4)
P(3)	0.3249 (3)	0.1930 (1)	0.2736 (1)	5.09 (5)
O(01)	0.6322 (9)	0.5338 (3)	0.1697 (4)	8.5 (2)
O(02)	0.3577 (8)	0.3069 (4)	0.4661 (3)	8.3 (2)
O(03)	0.7244 (7)	0.2762 (3)	0.3586 (3)	6.1 (1)
O(04)	0.0192 (7)	0.3202 (4)	0.2491 (4)	8.8 (2)
O(05)	0.3180 (6)	0.4661 (3)	0.3484 (3)	5.5 (1)
C(1)	0.605 (1)	0.4839 (4)	0.2059 (4)	4.8 (2)
C(2)	0.366 (1)	0.3091 (4)	0.3976 (4)	5.1 (2)
C(3)	0.5960 (9)	0.2951 (4)	0.3285 (4)	4.0 (2)
C(4)	0.1567 (9)	0.3195 (4)	0.2631 (5)	5.0 (2)
C(5)	0.3755 (8)	0.4184 (4)	0.3187 (4)	3.7 (1)
C(11)	0.5598 (8)	0.3079 (4)	0.0996 (4)	3.7 (1)
C(12)	0.2522 (8)	0.4000 (4)	0.0883 (4)	4.3 (2)
C(21)	0.692 (1)	0.5559 (5)	0.3863 (6)	7.1 (3)
C(22)	0.690 (1)	0.4265 (5)	0.4738 (4)	6.1 (2)
C(23)	0.925 (1)	0.4458 (7)	0.3762 (6)	8.1 (3)
C(31)	0.495 (1)	0.1307 (5)	0.3017 (7)	7.9 (3)
C(32)	0.188 (1)	0.1594 (5)	0.3364 (6)	9.1 (3)
C(33)	0.228 (1)	0.1609 (5)	0.1724 (6)	8.6 (3)
C(111)	0.6650 (9)	0.2547 (5)	0.1558 (5)	5.3 (2)
C(112)	0.466 (1)	0.2665 (5)	0.0250 (4)	6.1 (2)
C(113)	0.6739 (9)	0.3623 (5)	0.0704 (5)	5.8 (2)
C(121)	0.1231 (9)	0.3453 (5)	0.0500 (5)	5.4 (2)
C(122)	0.314 (1)	0.4408 (5)	0.0195 (5)	6.9 (2)
C(123)	0.176 (1)	0.4545 (5)	0.1379 (6)	5.9 (2)

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

X-ray Crystal Structure of $(CO)_3(PMe_3)Fe(\mu$-t-$Bu_2P)Co(CO)_2(PMe_3)$ (7). Atomic positional parameters and bond lengths and angles for **7** are given in Tables VIII, IX, and X, respectively. Molecules of **6** crystallize from hexane in the orthorhombic space group *Pnma* (no. 62) with four molecules in the unit cell. A view of the molecule is shown in Figure 3. The structure consists of a central Co–P–Fe core in which one t-Bu_2P group bridges a single Co–Fe bond (Co–Fe v 2.752 (3) Å). The Fe atom bears a PMe_3 group roughly trans to the μ-t-Bu_2P unit (P(2)–Fe–P(1) = 176.0 (2)°) in addition to three terminal carbonyl groups. The coordination geometry about Fe, excluding the Co atom, can best be described as a trigonal bipyramid with the three CO units in the equatorial plane (C(1)–Fe–C(2) = 115.3 (4)°). The Co atom essentially caps one face of this geometry. The Co atom bears two CO ligands

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[12] Deviations (Å) from the least-squares plane through Co(1)–P(1)–C(1)–Cr(1)–P(2) are as follows: Co(1), 0.004; P(1), 0.217; C(1), −0.192; Cr(1), −0.166; P(2), 0.138.

Table VI. Bond Distances (Å) for 6[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Co(1)	Cr(1)	2.505 (1)	Cr(1)	C(5)	1.984 (5)	O(02)	C(2)	1.171 (6)
Co(1)	P(1)	2.219 (1)	P(1)	C(11)	1.911 (4)	O(03)	C(3)	1.166 (5)
Co(1)	P(2)	2.224 (1)	P(1)	C(12)	1.912 (5)	O(04)	C(4)	1.148 (6)
Co(1)	C(1)	1.706 (5)	P(2)	C(21)	1.829 (6)	O(05)	C(5)	1.180 (5)
Co(1)	C(5)	1.946 (4)	P(2)	C(22)	1.842 (5)	C(11)	C(111)	1.536 (7)
Cr(1)	P(1)	2.396 (1)	P(2)	C(23)	1.839 (6)	C(11)	C(112)	1.557 (6)
Cr(1)	P(3)	2.358 (1)	P(3)	C(31)	1.848 (7)	C(11)	C(113)	1.558 (7)
Cr(1)	C(2)	1.829 (5)	P(3)	C(32)	1.841 (6)	C(12)	C(121)	1.548 (7)
Cr(1)	C(3)	1.871 (5)	P(3)	C(33)	1.842 (6)	C(12)	C(122)	1.566 (7)
Cr(1)	C(4)	1.862 (5)	O(01)	C(1)	1.165 (6)	C(12)	C(123)	1.547 (7)

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

Table VII. Bond Angles (deg) for 6[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cr(1)	Co(1)	P(1)	60.58 (3)	Cr(1)	P(1)	C(11)	126.4 (2)
Cr(1)	Co(1)	P(2)	113.46 (4)	Cr(1)	P(1)	C(12)	119.3 (2)
Cr(1)	Co(1)	C(1)	153.8 (2)	C(11)	P(1)	C(12)	109.1 (2)
Cr(1)	Co(1)	C(5)	51.1 (2)	C(01)	P(2)	C(21)	114.2 (2)
P(1)	Co(1)	P(2)	168.77 (6)	Co(1)	P(2)	C(22)	119.6 (2)
P(1)	Co(1)	C(1)	96.6 (2)	Co(1)	P(2)	C(23)	113.1 (2)
P(1)	Co(1)	C(5)	93.3 (1)	C(21)	P(2)	C(22)	101.6 (3)
P(2)	Co(1)	C(1)	91.2 (2)	C(21)	P(2)	C(23)	104.3 (3)
P(2)	Co(1)	C(5)	88.9 (1)	C(22)	P(2)	C(23)	102.0 (3)
C(1)	Co(1)	C(5)	124.6 (2)	Cr(1)	P(3)	C(31)	117.5 (2)
Co(1)	Cr(1)	P(1)	53.79 (3)	Cr(1)	P(3)	C(32)	113.2 (2)
Co(1)	Cr(1)	P(3)	145.03 (5)	Cr(1)	P(3)	C(33)	118.4 (2)
Co(1)	Cr(1)	C(2)	113.3 (2)	C(31)	P(3)	C(32)	101.1 (4)
Co(1)	Cr(1)	C(3)	68.5 (2)	C(31)	P(3)	C(33)	102.3 (4)
Co(1)	Cr(1)	C(4)	122.7 (2)	C(32)	P(3)	C(33)	101.7 (4)
Co(1)	Cr(1)	C(5)	49.7 (1)	Co(1)	C(1)	O(01)	174.5 (5)
P(1)	Cr(1)	P(3)	102.99 (5)	Cr(1)	C(2)	O(02)	178.1 (5)
P(1)	Cr(1)	C(2)	166.5 (2)	Cr(1)	C(3)	O(03)	171.2 (4)
P(1)	Cr(1)	C(3)	92.9 (1)	Cr(1)	C(4)	O(04)	176.9 (6)
P(1)	Cr(1)	C(4)	95.0 (2)	Co(1)	C(5)	Cr(1)	79.2 (2)
P(1)	Cr(1)	C(5)	87.2 (1)	Co(1)	C(5)	O(05)	131.0 (4)
P(3)	Cr(1)	C(2)	90.3 (2)	Cr(1)	C(5)	O(05)	149.8 (4)
P(3)	Cr(1)	C(3)	89.7 (2)	P(1)	C(11)	C(111)	107.4 (3)
P(3)	Cr(1)	C(4)	80.8 (2)	P(1)	C(11)	C(112)	112.3 (3)
P(3)	Cr(1)	C(5)	165.2 (1)	P(1)	C(11)	C(113)	112.4 (4)
C(2)	Cr(1)	C(3)	84.7 (2)	C(111)	C(11)	C(112)	108.4 (5)
C(2)	Cr(1)	C(4)	89.4 (2)	C(111)	C(11)	C(113)	107.3 (4)
C(2)	Cr(1)	C(5)	80.2 (2)	C(112)	C(11)	C(113)	108.8 (4)
C(3)	Cr(1)	C(4)	168.8 (2)	P(1)	C(12)	C(121)	109.5 (4)
C(3)	Cr(1)	C(5)	100.5 (2)	P(1)	C(12)	C(122)	112.6 (4)
C(4)	Cr(1)	C(5)	87.7 (2)	P(1)	C(12)	C(123)	108.0 (3)
Co(1)	P(1)	Cr(1)	65.63 (3)	C(121)	C(12)	C(122)	109.3 (4)
Co(1)	P(1)	C(11)	112.0 (1)	C(121)	C(12)	C(123)	108.8 (4)
Co(1)	P(1)	C(12)	116.5 (2)	C(122)	C(12)	C(123)	108.5 (5)

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

and a PMe$_3$ group. Here, the geometry including the Fe atom can again be described as a trigonal bipyramid, although the P(3)–Co–P(2) angle, which should be 180° in this configuration, is considerably distorted at 159.8 (2)°. The Fe–P(2)–Co angle is 76.0 (1)°, which is typical of the angles subtended at the phosphorus atoms of phosphido groups bridging metal–metal bonds.[13]

There is a crystallographically imposed mirror plane that passes through the Co–P(2)–Fe–P(3)–C(301)–P(1)–C(101)–C(2) and O(2) atoms.

If one considers the Co–Fe bond as a 2c–2e interaction in which each metal contributes one electron and the bridging phosphido group to use one electron to bond to Fe and two to Co, then each metal can be considered to have an 18-electron count.

Reactions with (CO)$_5$Mo(*t*-Bu$_2$P)Li. Isolation of CoCl(CO)$_2$(PMe$_3$)$_2$ and *cis*-Mo(CO)$_4$(PMe$_3$)$_2$. Unlike the reactions of (CO)$_5$Cr(*t*-Bu$_2$P)Li with NiCl$_2$(PMe$_3$)$_2$ or CoCl(PMe$_3$)$_3$ which yield heterobimetallic complexes in fairly good yields,[1] we were unable to isolate any mixed-metal species from analogous reactions with (CO)$_5$Mo(*t*-Bu$_2$P)Li. The only complexes which we were able to isolate in reasonable yields were CoCl(CO)$_2$(PMe$_3$)$_2$[4] (34%) and *cis*-Mo(CO)$_4$(PMe$_3$)$_2$[5] (53%). At present we have no data that might suggest a reason for this difference in reactivity or why there is a preference for the formation of these complexes in each reaction.

Experimental Section

All reactions were performed under oxygen-free nitrogen or under vacuum. Microanalyses were by the Schwartzkopf Microanalytical Laboratory, Woodside, NY. Hexane and THF were dried over sodium and distilled from sodium/benzophenone under nitrogen before use.

Instruments: IR, Perkin Elmer 1330; NMR, Varian EM-390 (^{1}H, 90 MHz), FT-80 (^{31}P, 32.384 MHz), Bruker WM-90 (^{31}P, 36.43 MHz), Nicolet NT-200 (^{1}H and ^{31}P). IR spectra were recorded as Nujol mulls (KBr plates) or in solution using matched KBr cells unless otherwise stated. NMR spectra were recorded in C$_6$D$_6$ at ambient temperature and are referenced to Me$_4$Si (δ 0.0, ^{1}H) and 85% H$_3$PO$_4$(aq) (δ 0.0, ^{31}P). Melting points were in sealed

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[13] See references 1 through 3 and 6 and references therein.

Table VIII. Positional Parameters and Their Estimated Standard Deviations for 7[a]

atom	*x*	*y*	*z*	*B*, Å^2
Fe	0.3009 (2)	0.250	0.5486 (2)	2.98 (7)
Co	0.1386 (2)	0.250	0.4329 (2)	2.88 (6)
P(1)	0.2870 (5)	0.250	0.6741 (3)	4.2 (2)
P(2)	0.3290 (5)	0.250	0.4200 (3)	3.1 (1)
P(3)	−0.0345 (5)	0.250	0.4884 (3)	3.4 (1)
O(1)	0.1942 (9)	0.0496 (9)	0.5678 (6)	6.2 (3)
O(2)	0.553 (1)	0.250	0.5707 (9)	7.6 (5)
O(3)	0.0709 (9)	0.0704 (9)	0.3475 (6)	6.3 (3)
C1	0.234 (1)	0.128 (1)	0.5526 (8)	4.3 (4)
C2	0.452 (2)	0.250	0.560 (1)	4.8 (6)
C3	0.104 (1)	0.138 (1)	0.3858 (8)	4.0 (4)
C(101)	0.140 (2)	0.250	0.717 (1)	8.0 (9)
C(102)	0.355 (1)	0.138 (1)	0.7224 (8)	5.8 (5)
C(200)	0.399 (1)	0.371 (1)	0.3744 (8)	4.8 (4)*
C(201)	0.357 (1)	0.468 (1)	0.4151 (9)	5.7 (4)*
C(202)	0.371 (1)	0.379 (1)	0.2889 (9)	5.3 (4)*
C(203)	0.533 (2)	0.371 (2)	0.386 (1)	8.0 (5)*
C(301)	−0.157 (2)	0.250	0.419 (1)	5.8 (7)
C(302)	−0.075 (1)	0.359 (1)	0.5481 (8)	5.0 (4)

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

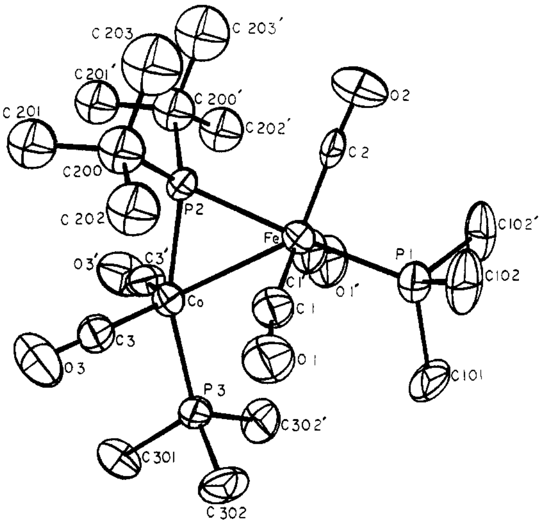

Figure 3. General view of 7.

capillaries under nitrogen (1 atm) and are uncorrected. Cr(CO)$_5$(*t*-Bu$_2$PLi),[1] [Rh(COD)Cl]$_2$,[14] and CoCl(PMe$_3$)$_3$[15] were prepared as previously described.

(CO)$_5$Cr(μ-*t*-Bu$_2$P)Rh(COD)(*Cr–Rh*) (1). A solution of Cr(CO)$_5$(*t*-Bu$_2$P)Li[1] (3.77 mmol) in THF (20 mL) was cooled to −90 °C and added to a solution of [Rh(COD)Cl]$_2$ (0.93 g, 1.88 mmol) in THF (40 mL) at −90 °C. An immediate color change from yellow to red-orange was observed. The mixture was allowed to warm slowly to −20 °C. The color darkened to brown at ca. −25 °C, and volatile materials were removed under vacuum as soon as the temperature reached −20 °C. The brown residue was extracted into hexane (2 × 10 mL) and the solution filtered. The volume was reduced to 10 mL under vacuum, and cooling (−20 °C) gave crystals of 1 after 48 h. They were collected and recrystallized from hexane (−20 °C). The red-brown crystals of 1 were finally isolated and dried under vacuum: yield 0.93 g (45%); mp (darkens at 95 °C) 125–130 °C dec; ^{1}H NMR δ 5.0 (br m, 4 H, COD), 1.89 (br m, 8 H, COD), 1.18 (d, 18 H, $^2J_{P-H}$ = 16.6 Hz, μ-*t*-*Bu*$_2$P); ^{31}P{^{1}H} NMR δ 215.0 (d, $^2J_{P-Rh}$ = 123 Hz, μ-*t*-Bu$_2$*P*); IR (hexane solution) 2025 (s), 1974 (m), 1950 (m), 1927 (m), 1855 (m) cm^{-1}; IR (NaCl plates, Nujol mull) 2019 (s), 1972 (s), 1870 (s br), 1335 (m), 1305 (w), 1168 (m), 1072 (w), 1018 (m), 990 (w), 955 (m), 930 (w), 868 (w), 845 (w), 820 (w), 805 (m), 768 (w), 720 (w) cm^{-1}. Anal. Calcd for C$_{21}$H$_{30}$CrO$_5$PRh: C, 46.0; H, 5.51. Found: C, 46.5; H, 5.27.

(CO)$_5$Cr(μ-*t*-Bu$_2$P)Rh(CO)$_2$ (3). 1 (0.2 g, 0.36 mmol) was placed in a Fischer-Porter vessel and was dissolved in hexane (30 mL). The vessel was charged to 3 atm with CO. An immediate color change from red to orange was observed. The solution was stirred under CO for 1.5 h. Volatile residues were removed under vacuum, and the residue was extracted into hexane (2 × 10 mL). The solution was filtered and evaporated to 10 mL under vacuum. Cooling (−20 °C) gave red-brown crystals of 3. The crystals were collected and dried under vacuum: yield quantitative; mp 120–123 °C; IR (KBr, hexane) 2026 (s), 1996 (m), 1968 (m), 1940 (s) cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 1.1 (d, J_{P-H} = 13.5 Hz); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 253.88 (d, $^1J_{Rh-P}$ = 100.76 Hz). Anal. Calcd for C$_{15}$H$_{18}$CrP$_1$RhO$_7$: C, 36.30; H, 3.62. Found: C, 36.72; H, 3.67.

(CO)$_4$(PMe$_3$)Cr(μ-*t*-Bu$_2$P)Rh(CO)(PMe$_3$) (2) from (CO)$_5$Cr(μ-*t*-Bu$_2$P)Rh(COD) (1) or (CO)$_5$Cr(μ-*t*-Bu$_2$P)Rh(CO)$_2$ (3). Upon addition of PMe$_3$ (0.10 g, 1.44 mmol) to a solution containing 1 or 3 (0.36 mmol) in THF (30 mL) at −78 °C an immediate color change to orange was observed. The solution was allowed to warm to room temperature over 2 h. Volatile residues were removed under vacuum, and the residue was extracted into hexane (2 × 10 mL). The solution was filtered and then cooled (−20 °C). After 4 h red crystals of (CO)$_4$(PMe$_3$)Cr(μ-*t*-Bu$_2$P)Rh(CO)(PMe$_3$) (2) were obtained in quantitative yield. The spectroscopic and physical properties of the product (mp, IR, ^{1}H and ^{31}P{^{1}H} NMR) matched those previously reported.[1]

(Cl)(CO)Ni(μ-*t*-Bu$_2$P)Cr(CO)$_4$(PMe$_3$) (5). Treatment of a THF solution of (Cl)(PMe$_3$)Ni(μ-*t*-Bu$_2$P)Cr(CO)$_4$PMe$_3$ (4) (0.2 g, 0.36 mmol in 30 mL of THF) with CO at 3 atm for 11 h gave a green-brown solution. This was evaporated to dryness under vacuum, and the residue was extracted into hexane (10 mL). The volume was reduced to 5 mL before cooling (−20 °C). Pale yellow-green prisms of 5 formed over 48 h: yield quantitative; mp 103–104 °C; IR (KBr, hexane) 2000 (m), 1945 (m), 1890 (s) cm^{-1}. ^{1}H NMR (C$_6$D$_6$) δ 1.37 (d, $^2J_{P-H}$ = 14.4 Hz, 18 H, μ-*t*-Bu$_2$P), 1.1 (d, $^2J_{P-H}$ = 9 Hz, 9 H, PMe$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 238.34 (d, J_{P-P} = 21.9 Hz, μ-*t*-Bu$_2$*P*), 24.34 (d, J_{P-P} = 21.9 Hz, PMe$_3$). Anal. Calcd for C$_{16}$H$_{27}$ClP$_2$NiCrO$_5$: C, 37.80; H, 5.31. Found: C, 38.45; H, 5.50.

(CO)$_3$PMe$_3$Cr(μ-CO)(μ-*t*-Bu$_2$P)Co(PMe$_3$)CO(*Cr–Co*) (6). A solution of Cr(CO)$_5$(*t*-Bu$_2$P)Li[1] (1.85 mmol) in THF (40 mL) was cooled to −100 °C and added to a solution of CoCl(PMe$_3$)$_3$ (0.60 g, 1.85 mmol) in THF (80 mL) at −100 °C over 5 min. At −95 °C no color change was noted. The mixture was allowed to warm slowly to room temperature. At −10 °C the initial green color darkened and turned brown at 0 °C. The solution was stirred at room temperature (3 h), and volatile materials were removed under vacuum (12 h). The residue was extracted into hexane (20 mL) and the solution filtered. Cooling (−20 °C) gave yellow-brown crystals of 6 (after 48 h) which were collected and dried under vacuum. The complex decomposes in air over several hours and immediately when in solution: yield 0.55 g (56%); mp 123–128 °C dec; ^{1} H NMR (200 MHz) δ 1.37 (d, 18 H, $^2J_{P-H}$ = 13.07 Hz, *t*-Bu$_2$P), 1.22 (d, 18 H, $^2J_{P-H}$ = 7.76 Hz, PMe$_3$); ^{31}P{^{1}H} NMR see text, at 20 °C (36.43 MHz, PhMe-*d*$_8$), δ 11.64 (d, $^2J_{P-P}$ = 30.51 Hz, PMe$_3$), at −85 °C, δ 164.69 (dd, $^2J_{P-P_{Co}}$ = 79.35 Hz, $^2J_{P-P_{Cr}}$ = 30.52 Hz, μ-*t*-Bu$_2$P), 17.01 (d, $^2J_{P-P_{Co}}$ = 79.35 Hz, CoPMe$_3$), 12.15 (d, $^2J_{P-P_{Cr}}$ = 30.52 Hz, CrPMe$_3$); IR (PhMe solution) 1918 (s), 1865 (sbr), 1790 (s); IR (hexane) 1962 (w, sh), 1949 (w, sh), 1920 (s), 1905 (s), 1878 (s), 1848 (s), 1790 (m, br) cm^{-1}. Anal. Calcd for C$_{19}$H$_{36}$CoCrO$_5$P$_3$: C, 41.62; H, 6.62. Found: C, 41.74; H, 6.84.

(CO)$_3$PMe$_3$Fe(μ-*t*-Bu$_2$P)Co(CO)$_2$PMe$_3$ (7). A solution of Fe(CO)$_5$ (1.50 g, 7.66 mmol) in hexane (50 mL) was cooled (−40 °C)8 and *t*-Bu$_2$PH (1.12 g, 7.66 mmol) was added via syringe. The yellow solution was allowed to warm to room temperature, stirred (18 h), and then cooled (−78 °C), and a THF solution of *n*-butyllithium (2.48 mg, 7.66 mmol) was added dropwise. After warming to room temperature, the resulting dark brown solution was again cooled (−78 °C) and a solution of CoCl$_2$(PMe$_3$)$_2$[16] (1.07 g, 3.80 mmol) in THF (50 mL) was added dropwise. The dark

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Table IX. Bond Distances (Å) for 7[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Fe	Co	2.752 (3)	Co	C(3)	1.721 (12)	O(1)	C(1)	1.156 (11)
Fe	P(1)	2.203 (5)	P(1)	C(101)	1.841 (15)	O(2)	C(2)	1.174 (15)
Fe	P(2)	2.274 (4)	P(1)	C(102)	1.853 (11)	O(3)	C(3)	1.168 (11)
Fe	C(1)	1.757 (12)	P(2)	C(200)	1.941 (11)	C(200)	C(201)	1.517 (14)
Fe	C(2)	1.740 (15)	P(3)	C(301)	1.850 (13)	C(200)	C(202)	1.533 (13)
Co	P(2)	2.196 (4)	P(3)	C(302)	1.823 (10)	C(200)	C(203)	1.559 (14)
Co	P(3)	2.211 (4)						

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

Table X. Bond Angles (deg) for 7[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Co	Fe	P(1)	133.2 (2)	Fe	P(2)	Co	76.0 (1)
Co	Fe	P(2)	50.7 (1)	Fe	P(2)	C(200)	117.7 (3)
Co	Fe	C(1)	74.6 (4)	Co	P(2)	C(200)	116.8 (3)
Co	Fe	C(2)	139.1 (5)	Co	P(3)	C(301)	113.1 (5)
P(1)	Fe	P(2)	176.0 (2)	Co	P(3)	C(302)	118.8 (4)
P(1)	Fe	C(1)	85.9 (4)	C(301)	P(3)	C(302)	100.5 (5)
P(1)	Fe	C(2)	87.6 (5)	Fe	C(1)	O(1)	169 (1)
P(2)	Fe	C(1)	95.8 (4)	Fe	C(2)	O(2)	177 (1)
P(2)	Fe	C(2)	88.4 (5)	Co	C(3)	O(3)	171 (1)
C(1)	Fe	C(2)	115.3 (4)	P(2)	C(200)	C(201)	110.5 (7)
Fe	Co	P(2)	53.3 (1)	P(2)	C(200)	C(202)	111.8 (8)
Fe	Co	P(3)	106.5 (1)	P(2)	C(300)	C(203)	110.6 (8)
Fe	Co	C(3)	120.6 (4)	C(201)	C(200)	C(202)	110 (1)
P(2)	Co	P(3)	159.8 (2)	C(201)	C(200)	C(203)	104 (1)
P(2)	Co	C(3)	100.4 (3)	C(202)	C(200)	C(203)	109.7 (9)
P(3)	Co	C(3)	90.2 (3)	C(1)	Fe	C(1)′	128.9 (4)
Fe	P(1)	C(101)	118.0 (6)	C(3)	Co	C(3)′	115.1 (4)
Fe	P(1)	C(102)	115.1 (4)	C(200)	P(2)	C(200)′	108.4 (5)
C(101)	P(1)	C(102)	101.5 (5)				

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

solution was allowed to warm to room temperature and filtered, and volatile materials were removed under vacuum. The residue was extracted with hexane (40 mL), filtered, evaporated (ca. 15 mL), and cooled (−20 °C). After 12 h the yellow-green crystals of 7 were isolated and dried under vacuum: yield 0.80 g (40%); mp 142–144 °C; IR (solution hexane) 2023 (s), 1980 (w), 1970 (w), 1940 (vs), 1908 (vs), 1880 (vs), 1873 (sh), 935 (s), 638 (s), 612 (s), 593 (sh), 580 (s) cm^{-1}; ^1H NMR (in C_6D_6 at 25 °C, in ppm relative to Me_4Si, δ 0.0) 1.63 (d, $^3J_{P-H}$ = 12.0 Hz, 18 H, *t*-Bu_2P), 1.35 (d, $^2J_{P-H}$ = 9.0 Hz, 9 H, PMe_3), 1.20 (d, $^2J_{P-H}$ = 9.0 Hz, 9 H, PMe_3); $^{31}P\{^1H\}$ (−80 °C, 36.43 MHz, in PhMe-d_8) δ 274.51 (dd, J_{P-P} = 91.60, 12.21 Hz), 43.39 (d, J_{P-P} = 12.21 Hz), 13.31 (d, J_{P-P} = 91.53 Hz), at 20 °C (C_6D_6), δ 41.04 (d, J_{P-P} = 12.21 Hz). Anal. Calcd for $C_{19}H_{36}CoFeO_5P_3$: C, 41.32; H, 6.52; P, 16.85. Found: C, 41.39; H, 6.46; P, 16.52.

Reaction of $(CO)_5Mo(t\text{-}Bu_2P)Li$ with $CoCl(PMe_3)_3$–$CoCl(PMe_3)_2(CO)_2$. A solution of $(CO)_5Mo(t\text{-}Bu_2P)Li$ (1.92 mmol, in THF 30 mL) was prepared in situ in a manner analogous to that used for $(CO)_5Cr(t\text{-}Bu_2P)Li$.[1] It was added over a 5-min period to a solution of $CoCl(PMe_3)_3$ (0.62 g, 1.92 mmol) in THF (40 mL) at −90 °C. No immediate color change was observed. However the color did change from green to brown at 0 °C. The mixture was allowed to warm to room temperature and was stirred for a further 1.5 h. Volatile materials were removed under vacuum, and the brown residue was washed with hexane (50 mL) and extracted into Et_2O (15 mL). The solution was filtered and cooled to −20 °C. Pale yellow crystals of $CoCl(PMe_3)_2(CO)_2$ were obtained after 24 h. They were collected and dried under vacuum. No other complexes could be isolated: yield 0.2 g (34%). Microanalytical and spectroscopic data (mp, IR, ^1H and ^{31}P NMR) agreed closely with that previously reported.[4]

Reaction of $(CO)_5Mo(t\text{-}Bu_2P)Li$ with $NiCl_2(PMe_3)_2$–*cis*-$Mo(CO)_4(PMe_3)_2$. A solution of $(CO)_5Mo(t\text{-}Bu_2P)Li$ (2.61 mmol) in THF (35 mL) was added over a 7 min period to a solution of $NiCl_2(PMe_3)_2$ (0.737 g, 2.61 mmol) in THF (40 mL) at −78 °C. An immediate color change from red to dark green was observed. The solution was allowed to warm to room temperature and stirred at this temperature a further 2 h. Volatile materials were removed under vacuum. The residue was extracted with hexane (2 × 10 mL) and toluene (10 mL). The filtered extracts were combined, and the volume of the solution was reduced to ca. 10 mL under vacuum. Cooling (−20 °C) gave light brown needles that were collected and recrystallized from hexane (5 mL) at −20 °C. The product *cis*-$Mo(CO)_4(PMe_3)_2$ was collected and dried under vacuum. No other complexes were isolated: yield 0.5 g (53%). Microanalytical and spectroscopic data were in accord with that previously reported.[5]

X-ray Experimental Data. Crystals of 1, 6, and 7 suitable for X-ray studies were mounted in thin-walled glass capillaries under nitrogen (1 atm). Final lattice parameters were determined from 25 high angle reflections (26 ° > 2θ > 30°) carefully centered on an Enraf-Nonius CAD-4 diffractometer. Data were collected by the $\omega/2\theta$ scan technique at 23 ± 2 °C. Details of crystal data and a summary of intensity data collection parameters for 1, 6, and 7 are given in Table I. For 1 and 6 the space groups were uniquely defined by systematic absences. For 7 systematic absences indicated either *Pnma* or $Pna2_1$ as the space group. *Pnma* was chosen on the basis of successful refinement. The data for 1, 6, and 7 were corrected for Lorentz and polarization effects. An absorption correction was applied for all three using an empirical psi scan method ((1) transmission maximum 99.93%, minimum 79.04%; (6) transmission maximum 99.88%, minimum 88.79%; (7) transmission maximum 99.81%, minimum 88.57%). All three structures were solved by using standard heavy-atom methods and successive difference Fourier maps using the Enraf-Nonius software package SDP-PLUS (B.A. Frenz and Associates, College Station, TX 77840, 4th ed., 1981) on a PDP 11/44 computer. Scattering factors were taken from ref 17, and unit weights were used throughout. Final refinements were by full-matrix least-squares methods ($R = \sum(|F_o| - |F_c|/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$). Hydrogen atoms were not located in any of the structures. No chemically significant peaks were present in the final difference Fourier map. The highest peaks in the final difference Fourier maps were as follows: 1, 0.9 e $Å^{-3}$; 6, 0.5 e $Å^{-3}$; 7, 0.8 e $Å^{-3}$. Atomic parameters and tables of observed and calculated structure factors are available.[18]

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Registry No. **1**, 91781-59-8; **2**, 87555-82-6; **3**, 91781-60-1; **4**, 87555-81-5; **5**, 91781-61-2; **6**, 91781-62-3; **7**, 91781-63-4; $CoCl(PMe_3)_2(CO)_2$, 91840-41-4; *cis*-$Mo(CO)_4(PMe_3)_2$, 16027-45-5; $Cr(CO)_5$(*t*-Bu_2P)Li, 91781-64-5; $[Rh(COD)Cl]_2$, 12092-47-6; $CoCl(PMe_3)_3$, 55516-89-7; $Fe(CO)_5$, 13463-40-6; $CoCl_2(PMe_3)_2$, 53432-22-7; $(CO)_5Mo$(*t*-Bu_2P)Li, 91781-65-6; $NiCl_2(PMe_3)_2$, 19232-05-4; *t*-Bu_2PH, 819-19-2.

Supplementary Material Available: Tables of atomic thermal parameters and structure factors for **1**, **6**, and **7** (74 pages). Ordering information is given on any current masthead page.

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(18) See paragraph at end of text regarding supplementary material.

Lewis Acid Bonding to Triruthenium and Triosmium Clusters. The Crystal and Molecular Structure of $Ru_3(\mu\text{-}Ph_2PCH_2PPh_2)_2(CO)_8(\mu\text{-}AgO_2CCF_3)\cdot{}^1/_2CH_2Cl_2$ and Spectroscopic Studies of Related Adducts

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$Ru_3(\mu\text{-dpm})_2(CO)_8$ (dpm is bis(diphenylphosphino)methane) forms weakly bound adducts $Ru_3(\mu\text{-dpm})_2(CO)_8\cdot(\mu\text{-A})$ (A = AgO_2CCF_3, $Hg(O_2CCF_3)_2$, $Cu(NCCH_3)BF_4$, HO_2CCF_3) that have been characterized by electronic, infrared, and ^{31}P NMR spectroscopy. Equilibrium constants for adduct formation increase in the order $H^+ < Ag^+ < Hg^{2+} < Cu^+$. $Ru_3(\mu\text{-dpm})_2(CO)_8(\mu\text{-}AgO_2CCF_3)\cdot{}^1/_2CH_2Cl_2$ crystallizes in the orthorhombic space group $Pca2_1$ (No. 29) with four molecules per unit cell of dimensions a = 20.706 (9) Å, b = 15.693 (11) Å, and c = 18.447 (5) Å at 140 K. The structural study shows that the AgO_2CCF_3 unit binds through silver across the exposed edge of the triruthenium cluster. The adduct contains two adjacent, nearly coplanar triangles of the four metal atoms. The addition of Ag^+ to the Ru–Ru bond results in an 0.167 Å lengthening of the Ru–Ru separation and some bending of the in-plane carbonyl groups away from the silver binding site. Similar adducts of silver trifluoroacetate with $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and some substituted derivations of $Ru_3(CO)_{12}$ have been detected in solution.

Introduction

The structural similarity and isolobal relationship between the proton and the group 1B cations, particularly Au(I), has recently received wide recognition. As a consequence, there have been many reports on the ability of an Au(I) center, generally in the form $AuPPh_3^+$, to bind to anionic metal complexes and polynuclear clusters in a fashion that produces analogues of neutral metal hydrides.[1-15] The R_3PAu^+ group is a versatile ligand. It can act as a terminal ligand,[15] span a metal–metal bond,[2,4,7-13] coordinate to the triangular face of a metal cluster,[1,111,14] and add to a square face of a metal cluster.[5] However, extensions to the binding of group 1B metals to neutral clusters are rare.[16] Moreover, the use of related metal ions (Ag(I),[16-18] Cu(I),[18] and Hg(II),[19,20] which are all isoelectronic and isolobal with Au(I), for this type of mixed-metal cluster formation has been limited to a few isolated examples.

Here we report on the observation of binding of metal ions including Au(I), Cu(I), and Hg(II) to neural triruthenium and triosmium clusters and describe the detailed structure of one of these. It has been known for some time that $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ undergo reversible protonation in strongly acidic media.[21] Although

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