sealed tube in vacuo, but still, only compound **3** has been detected in the reaction solution. Possibly the steric bulk of the $C(O)OCH_3$ group prevents the situation III in Scheme II. This is suggested by the structure of $[((\mu\text{-}SCH_3)Fe(COe)(P(CH_3)_3)_2)_2CH_3OC(O)C{=}CHC(O)OCH_3]^+$ in which the vinyl group is not π bonded but is bonded by a vinylic carbon for one iron atom and by an oxygen atom of the α-carbonyl ester group for the other. This strained situation could prevent further carbon–carbon coupling to lead to type **4** like products. Nevertheless, this difference of reaction pathways could be more subtle. To get a better insight of this problem, we are presently extending this study to other families of alkynes and binuclear iron systems bridged by other vinyl groups.

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Registry No. **2**, 89891-19-0; **3**, 89891-21-4; **4**, 89891-23-6; **5**, 89891-25-8; $[HFe_3(CO)_{11}][P(C_6H_5)_4]$, 40806-49-3; diphenylacetylene, 501-65-5; dimethyl acetylenedicarboxylate, 762-42-5; hexafluorobutyne, 692-50-2.

Supplementary Material Available: Tables of anisotropic thermal parameters and structure factors (16 pages). Ordering information is given on any current masthead page.

Phosphido-Bridged Mixed-Metal (Ru/Co) Compounds via the Reaction of (arene)$RuCl_2(PPh_2X)$ (X = H, Cl) with $Co_2(CO)_8$: X-ray Structure of $RuCo_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_7$

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A strategy for the synthesis of heterobi- and heterotrinuclear phosphido-bridged complexes via the reactions of the readily available η^6-arene compounds (*p*-cymene)$RuCl_2(PPh_2X)$ (X = H, Cl) with $Co_2(CO)_8$ is described. This route has afforded heterobinuclear $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**3**), (*p*-cymene)(CO)$Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**7**), small amounts of $Ru_2(\mu\text{-}PPh_2)_2(CO)_6$ (**4**), and the heterotrinuclear clusters $Ru_2Co(\mu\text{-}PPh_2)(CO)_{10}$ (**5**) and $RuCo_2(\mu\text{-}PPh_2)_2(CO)_8$ (**6**). These compounds have been characterized by microanalysis and mass, infrared, and NMR (^1H, ^{13}C, ^{31}P) spectroscopy. Single crystals of $RuCo_2(\mu\text{-}PPh_2)_2(CO)_8$ are monoclinic of space group $P2_1/n$ with a = 12.714 (2) Å, b = 15.600 (3) Å, c = 17.246 (3) Å, β = 108.33 (1)°, and Z = 4. The structure was solved and refined by using 3610 unique, observed reflections measured on a Syntex $P2_1$ diffractometer to R and R_w values of 0.034 and 0.039. In the triangular cluster the trans axial PPh_2 groups bridge the Ru–Co(1) and Co(1)–Co(2) edges with a semibridging CO group across the remaining Ru–Co bond.

Introduction

The chemistry of transition-metal cluster compounds has seen an explosive growth over the past decade, stimulated in part by the belief that such compounds may have potential applications as homogeneous catalysts or catalyst precursors. A specific class of cluster compounds, those which contain two or more different catalytic metals, is now receiving special attention because of the possibility of using these mixed-metal compounds for the preparation of supported polymetallic, heterogeneous catalysts or to promote unique patterns of substrate activation via cooperative interactions. Mixed ruthenium–cobalt systems are especially attractive for the following substantial reasons: (i) Cobalt carbonyls have found wide application as carbonylation catalysts, particularly for hydroformylation. (ii) Ruthenium compounds are among the most effective catalysts for hydrogenation. Moreover as one of the cheaper catalytically active platinum metals, efforts are being made to develop ruthenium catalysts to replace the more expensive rhodium systems. (iii) There is accumulating evidence that selectivity for ethanol synthesis via methanol homologation using cobalt catalysts is substantially improved by additions of ruthenium derivatives.[1,2] Recent work by Hidai and co-workers also suggests that mixed ruthenium–cobalt systems are very effective in homologation.[3]

In developing a strategy for the synthesis of robust Ru/Co complexes, we were faced with two problems. The first of these was to find an appropriate source of mononuclear ruthenium containing a phosphorus group to combine with the cobalt reagent of choice $Co_2(CO)_8$. Previous syntheses have generally employed metathetical reactions of $RuCl_3{\cdot}XH_2O$,[3,4] $[Ru(CO)_3Cl_2]_2$,[5] and Ru(H)-

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$(Cl)CO(Ph_3P)_3$[6] with $Co(CO)_4^-$ or the addition of $Co(CO)_4^-$ to $Ru_3(CO)_{12}$.[7] A second major difficulty, a perennial problem in cluster chemistry, is that even under mild carbonylating conditions, known Ru/Co clusters suffer irreversible fragmentation to $Ru_3(CO)_{12}$, thus presumably limiting their application to catalysis as discrete species.[8] A possible solution to the latter problem is to incorporate strongly bound bridging ligands into the cluster to help maintain the polynuclear integrity of the molecule if M–M′ bond cleavage occurs. An appropriate choice is the phosphido bridge that has been shown to function as a strong supporting ligand in cluster chemistry under conditions where CO addition cleaves one or more M–M bonds.[9] Our efforts therefore focussed on the design of a synthetic procedure for the simultaneous introduction of Ru, Co and μ-PPh_2 groups into complexes. This has been accomplished by using, as ruthenium precursors, mononuclear η^6-arene complexes of the type (arene)$RuCl_2(PPh_2X)$ readily accessible via the reaction of [(arene)$RuCl_2]_2$ with diphenylphosphine or diphenylchlorophosphine. Dehalogenation with $Co_2(CO)_8$ affords heterobi- and heterotrimetallic compounds containing μ-PPh_2 units. That such a route might provide a ready entry into phosphido-bridged Ru/Co clusters was indicated by our synthesis of $RuCo_3(\mu\text{-}PPh_2)(HC{\equiv}C\mathit{t}Bu)(CO)_9$ via the reaction of $Co_2(CO)_8$ with the phosphinoacetylene complex (p-cymene)$RuCl_2(Ph_2PC{\equiv}C\mathit{t}Bu)$.[10] In this paper we describe the synthesis and characterization of heterobi- and heterotrinuclear products derived from (arene)$RuCl_2$-(PPh_2X) (X = H, Cl) and a full single-crystal X-ray structure determination of the bis(phosphido)-bridged mixed-cluster $RuCo_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_7$. A preliminary account of part of this work has appeared.[11]

Experimental Section

General Procedures. Standard techniques, using Schlenk type equipment for the manipulation of air-sensitive compounds under a blanket of nitrogen, were employed. All solvents were dried (sodium benzophenone ketyl for THF, CaH_2 for hexane and benzene, and P_2O_5 for CH_2Cl_2) and nitrogen saturated prior to use. Chromatographic separations on thick layer plates used Merck Silica Gel.

Instrumentation. Infrared spectra were recorded on Perkin-Elmer 457 and 180 instruments using either Nujol mulls or cyclohexane solutions in matched 0.5-mm NaCl cells. Mass spectra at 70 eV were recorded at the Centre de Mêsures de l'Quest, Universitê de Rennes, using a Varian MAT 311 double-focussing spectrometer. ^1H and ^{31}P NMR spectra were generally measured on Bruker WP-80 spectrometers operating at 80 MHz for ^1H and 32.38 MHz for ^{31}P. Selected ^{31}P spectra were recorded at 101.2 MHz on a Bruker AM-250 system (Bruker Spectrospin (Canada), Milton, Ontario). ^{31}P spectra were proton noise decoupled, and shifts are reported relative to external 85% H_3PO_4. ^1H shifts are relative to Me_4Si. Microanalyses were obtained from the CNRS, Villeurbanne laboratory.

Synthesis of $RuCl_2(PPh_2X)$(p-cymene) (1, X = Cl, and 2, X = H). These compounds were synthesized according to the general procedure described by Zelonka and Baird[12] but starting with $[RuCl_2(p\text{-cymene})]_2$.[13] To a suspension of $[RuCl_2(p\text{-cymene})]_2$ (2.02 g, 3.3 mmol) in dry CH_2Cl_2 (50 mL) was added 6.6 mmol of the phosphorus ligand and the mixture stirred at room temperature for 3–4 h. The CH_2Cl_2 was then evaporated and the residue extracted with diethyl ether. The red, extracted product 1 or 2 was recrystallized from hexane/CH_2Cl_2 or ether/CH_2Cl_2.

1 (X = Cl): 3.12 g (90%); mp 178–179 °C; ^1H NMR ($CDCl_3$) δ 8.10 (m, C_6H_5), 7.60 (m, C_6H_5), 5.53 (s, C_6H_4), 2.80 (spt, $CH(CH_3)_2$), 2.08 (s, CH_3), 1.22 (d, $CH(CH_3)_2$, $^3J_{H-H}$ = 7.0 Hz); ^{31}P NMR ($CDCl_3$) δ +30.0. Anal. Calcd for $C_{22}H_{24}Cl_3PRu$: C, 50.14; H, 4.56; Cl, 20.23. Found: C, 50.07; H, 4.57; Cl, 20.40.

2 (X = H): 3.05 g (94%); mp 196–198 °C; ^1H NMR ($CDCl_3$) δ 7.50 (m, C_6H_5), 6.46 (d, Ph_2PH, ^1J = 411.9 Hz), 5.41 (s, C_6H_4), 2.57 (spt, $CH(CH_3)_2$, $^3J_{H-H}$ = 7.0 Hz), 1.97 (s, CH_3), 0.99 (d, $CH(CH_3)_2$, $^3J_{H-H}$ = 7.0 Hz); ^{31}P NMR ($CDCl_3$) δ +22.5. Anal. Calcd for $C_{22}H_{25}Cl_2PRu$: C, 53.66; H, 5.08; Cl, 14.48; Found: C, 53.02; H, 5.12; Cl, 14.67.

Dehalogenation of 1 with $Co_2(CO)_8$. The complexes 1 (1.053 g, 2 mmol) and $Co_2(CO)_8$ (1.368 g, 4 mmol) were introduced into a Schlenk tube, and 40 mL of THF was added. The red-black reaction mixture was stirred for 12 h at room temperature. Solvent was then evaporated and the crude mixture dissolved in CH_2Cl_2 and chromatographed on thick-layer, silica gel plates by using 6:1 hexane/CH_2Cl_2 mixtures for the separation. In order of decreasing R_f values the following compounds were successively isolated and recrystallized from the solvents indicated: **3** (red, 40%, hexane), **4** (yellow, 3%, hexane), **5** (yellow, 4%, dichloromethane/hexane), **7** (red-black, 30%, dichloromethane/hexane).

Reaction of 2 with $Co_2(CO)_8$. The diphenylphosphine complex **2** (0.984 g, 2 mmol) and $Co_2(CO)_8$ (1.368 g, 4 mmol) in THF (40 mL) were stirred for 1 h at room temperature and then refluxed for 10 h. Silica gel, thick-layer chromatography (developer 6:1 hexane/CH_2Cl_2) allowed the separation of the following components in order of decreasing R_f: **3** (40%), **4** (2%), **6** (black, 10%, dichloromethanehexane), **7** (30%). Subsequent experiments demonstrated that the same product mixture was obtained from 1 and $Co_2(CO)_8$ on heating and that **5**, produced in the room temperature reaction, converted to **3** and an unidentified ruthenium complex on heating.

Characterization of Compounds. $RuCo(\mu\text{-}PPh_2)(CO)_7$ (3): mp 79–80 °C; mass spectrum, m/e 541.855 (calcd for **3**, $C_{19}H_{10}O_7PCo^{102}Ru$ 541.854), 513.860 (calcd for $(M - CO)^+$ $C_{18}H_{10}O_6PCo^{102}Ru$ 513.859), and 507.858 (calcd for $(M - CO)^+$ $C_{18}H_{10}O_6PCo^{96}Ru$ 507.862); IR (C_6H_{12}, cm^{-1}) 2107 (m), 2046 (sh), 2039 (s), 2022 (vs), 2015 (w), 1967 (w); ^{31}P NMR (CD_2Cl_2) δ +187.3 (223 K), +187.7 (193 K); ^1H NMR (CD_2Cl_2, 300 K) δ 7.50 (m, C_6H_5); ^{13}C NMR (20.115 MHz, CD_2Cl_2, 193 K) δ 208.8 (d, $^2J_{PC}$ = 6.86 Hz, $Co(CO)_3$), 197.8 (d, $^2J_{PC}$ = 39.8 Hz, RuCO (equatorial, trans to PPh_2)), 193.6 (d, $^2J_{PC}$ = 13.7 Hz, $Ru(CO)_2$ (axial)), 191.4 (s, RuCO (equatorial, trans to Ru–Co)), 139.5 (d), 133.1 (d), 130.7 (s), 129.1 (d), (C_6H_5). Anal. Calcd for $C_{19}H_{10}O_7PCoRu$: C, 42.16; H, 1.86; P, 5.73; Co, 10.90, Ru, 18.67. Found: C, 42.15; H, 1.70; P, 5.77; Co, 9.92; Ru, 18.12.

$Ru(\mu\text{-}PPh_2)_2(CO)_6$ (4): mp 175–180 °C; IR (cm^{-1}, Nujol) 2075 (s), 2040 (s), 2005 (s br), 1980 (s), 1965 (s br), 1935 (w); mass spectrum, m/e 742 (M^+), 713.884 (calcd for $(M - CO)^+$ $C_{29}H_{20}O_5P_2Ru_2$ 713.887); ^{31}P NMR ($CDCl_3$, 223 K) °C) δ +110.0. Anal. Calcd for $C_{30}H_{20}O_6P_2Ru_2$: C, 48.65; H, 2.70, P, 8.40. Found: C, 48.42; H, 2.67; P, 8.80.

$Ru_2Co(\mu\text{-}PPh_2)(CO)_{10}$ (5): mp 138–140 °C; IR (C_6H_{12}, cm^{-1}) 2114 (w), 2072 (m), 2054 (m), 2045 (s), 2022 (m), 2009 (w), 1994 (m), 1983 (w), 1953 (w); mass spectrum, m/e 671.756 (calcd for $(M - 2CO)^+$ $C_{22}H_{20}O_8PCo^{102}Ru_2$ 671.753) and peaks corresponding to the successive loss of eight carbonyl groups; ^{31}P NMR (223 K, CD_2Cl_2) δ +166.8.

$RuCo(\mu\text{-}PPh_2)(CO)_4$($p$-cymene) (7): mp 138–140 °C; IR (Nujol, cm^{-1}) 2000 (s), 1958 (m), 1925 (s), 1915 (s); mass spectrum, m/e 592 (M^+), 563.982 (calcd for $(M - CO)^+$ $C_{25}H_{24}O_3PCo^{102}Ru$ 563.984), 536 ($(M - 2CO)^+$), 508 $(M - 3CO)^+$, 480 ($(M - 4CO)^+$);

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Table I. Crystal Data, Intensity Collection, and Refinement for $RuCo_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_7$

formula	$RuCo_2P_2O_8C_{32}H_{20}$
mol wt	813.40
cryst class	monoclinic
space group	$P2_1/n$
a, Å	12.714 (2)
b, Å	15.600 (3)
c, Å	17.246 (3)
β, deg	108.33 (1)
V, Å^3	3247.0 (9)
Z	4
ρ_{measd}, g cm^{-1}	1.66
ρ_{calcd}, g cm^{-3}	1.664
$F(000)$	1.616
μ(Mo Kα), cm^{-1}	16.46
cryst size, mm	0.12 × 0.24 × 0.29
monochromator	single crystal, graphite
max 2θ, deg	48
scan speed, deg min^{-1}	variable (2.55–29.3)
scan width, deg	0.8 below Kα_1 to 0.8 above Kα_2
standards	026, 244 (every 100 measurements)
variance of standards	2%
background	stationary crystal/counter; beginning and end of each scan for half of total count time
unique data	5130
obsd data ($I \geqslant 3\sigma(I)$)	3610
R	0.034
R_w	0.039

Table II. Atomic Positions (Fractional ×10^4) for $RuCo_2(CO)_8(\mu\text{-}PPh_2)_2$

A. Heavy Atoms

atom	x	y	z
Ru	1904.4 (3)	2354.1 (3)	2408.1 (2)
Co(1)	1241.0 (5)	3506.9 (4)	1176.7 (4)
Co(2)	1782.0 (6)	2013.3 (4)	836.4 (4)
P(1)	166.9 (11)	2951.2 (9)	1813.5 (8)
P(2)	2717.9 (11)	3216.3 (9)	872.7 (8)
O(1)	4347 (3)	1796 (3)	2790 (3)
O(2)	2439 (4)	3829 (3)	3620 (3)
O(3)	1344 (4)	1116 (3)	3576 (3)
O(4)	−313 (5)	4045 (3)	−377 (3)
O(5)	1853 (4)	5143 (3)	1981 (3)
O(6)	−226 (5)	1878 (4)	−551 (3)
O(7)	3351 (6)	948 (4)	376 (4)
O(8)	1077 (4)	550 (2)	1552 (3)
C(1)	3472 (5)	2029 (3)	2627 (4)
C(2)	2243 (4)	3282 (3)	3170 (3)
C(3)	1589 (5)	1562 (4)	3139 (3)
C(4)	296 (5)	3842 (4)	219 (4)
C(5)	1625 (4)	4504 (3)	1678 (3)
C(6)	546 (5)	1947 (4)	5 (4)
C(7)	2732 (6)	1358 (4)	565 (4)
C(8)	1388 (5)	1233 (3)	1477 (3)
C(9)	−1081 (4)	2341 (3)	1277 (3)
C(10)	−1219 (5)	1510 (4)	1495 (4)
C(11)	−2176 (6)	1075 (5)	1083 (5)
C(12)	−2977 (6)	1450 (5)	463 (4)
C(13)	−2850 (5)	2277 (5)	251 (4)
C(14)	−1901 (5)	2734 (4)	659 (4)
C(15)	−304 (4)	3578 (3)	2543 (3)
C(16)	−369 (5)	4459 (4)	2510 (4)
C(17)	−581 (7)	4898 (5)	3158 (5)
C(18)	−744 (6)	4467 (5)	3801 (4)
C(19)	−705 (5)	3607 (5)	3809 (4)
C(20)	−503 (5)	3150 (4)	3187 (4)
C(21)	4120 (4)	3395 (3)	1555 (3)
C(22)	4350 (5)	3891 (4)	2247 (4)
C(23)	5417 (5)	4004 (4)	2750 (4)
C(24)	6274 (5)	3628 (5)	2572 (5)
C(25)	6072 (5)	3146 (5)	1897 (5)
C(26)	5002 (5)	3022 (4)	1371 (4)
C(27)	2844 (4)	3646 (3)	−84 (3)
C(28)	2341 (6)	3267 (4)	−824 (4)
C(29)	2428 (7)	3617 (5)	−1529 (4)
C(30)	3017 (7)	4338 (5)	−1510 (4)
C(31)	3483 (7)	4745 (5)	−784 (5)
C(32)	3432 (7)	4390 (5)	−70 (4)

B. Hydrogen Atoms and Isotropic Thermal Parameters

atom	x	y	z	U_{iso}, Å^2
H(10)	−80 (5)	127 (4)	196 (4)	81 (22)
H(11)	−226 (5)	58 (5)	128 (4)	90 (24)
H(12)	−366 (6)	121 (4)	13 (4)	92 (23)
H(13)	−340 (6)	249 (5)	−14 (4)	70 (24)
H(14)	−177 (5)	330 (4)	51 (4)	78 (19)
H(16)	−32 (4)	472 (3)	205 (3)	61 (18)
H(17)	−56 (6)	541 (5)	306 (4)	80 (25)
H(18)	−85 (5)	475 (4)	424 (4)	82 (22)
H(19)	−85 (6)	334 (5)	421 (4)	84 (27)
H(20)	−42 (5)	255 (4)	325 (4)	65 (23)
H(22)	385 (4)	406 (3)	238 (3)	33 (14)
H(23)	557 (4)	433 (3)	323 (3)	53 (15)
H(24)	698 (5)	364 (4)	287 (4)	87 (22)
H(25)	656 (5)	289 (4)	175 (3)	58 (19)
H(26)	488 (5)	270 (4)	87 (3)	57 (18)
H(28)	184 (4)	277 (3)	−81 (3)	67 (16)
H(29)	201 (5)	332 (4)	−205 (4)	76 (19)
H(30)	303 (6)	458 (5)	−196 (4)	91 (25)
H(31)	389 (6)	505 (5)	−80 (4)	74 (25)
H(32)	369 (5)	467 (4)	41 (4)	67 (19)

^{1}H NMR ($CDCl_3$) δ 7.77, 7.37 (m, C_6H_5), 5.61 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 38 Hz, $p\text{-}CH_3C_6\mathit{H}_4CH(CH_3)_2$) 5.22 (dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 50 Hz, $p\text{-}CH_3C_6\mathit{H}_4CH(CH_3)_2$), 2.67 (spt, $C\mathit{H}(CH_3)_2$, $^2J_{HH}$ = 7.0 Hz), 1.96 (s, CH_3), 1.29 (d, $CH(C\mathit{H}_3)_2$, $^3J_{HH}$ = 7.0 Hz); ^{31}P NMR (32.38 MHz, (CH_2Cl_2, 193 K) δ +201.0. Anal. Calcd for $C_{29}H_{24}O_7PCoRu$: C, 52.80; H, 4.09; P, 5.23; Co, 9.96; Ru, 17.08. Found: C, 51.75; H, 4.09; P, 5.28; Co, 9.49; Ru, 16.53.

$RuCo_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_7$ (6): mp 165–170 °C dec; IR (C_6H_{12}, cm^{-1}) 2069 (m), 2030 (s), 2015 (vs), 1985 (m), 1863 (w); mass spectrum, m/e 730 ((M − 3CO)$^+$, 702 ((M − 4CO)$^+$), 674 (M − 5CO)$^+$ $C_{26}H_{20}O_2P_2Co_2Ru$ 645.865)), 646 ((M − 6CO)$^+$), 618 ((M − 7CO)$^+$), 590 ((M − 8CO)$^+$); ^{31}P NMR (193 K, CD_2Cl_2) δ 225.4, 180.4 (AB pattern, $^2J_{PP'}$ = 96.4 Hz). Anal. Calcd for $C_{32}H_{20}O_8P_2Co_2Ru$: C, 47.25; H, 2.44; P, 7.60; Co, 14.49; Ru, 12.43. Found, C, 47.21; H, 2.51; P, 7.09; Co, 13.87; Ru, 12.31.

X-ray Structural Analysis of $RuCo_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_7$. Collection and Reduction of X-ray Data. A black fragment cut from a clump of crystals was attached to a glass fiber, placed on a eucentric goniometer head, and mounted on a Syntex P2$_1$ automatic diffractometer. Fifteen reflections well dispersed in reciprocal space were precisely centered, and using the standard Syntex autoindexing and cell refinement procedures afforded the monoclinic cell constants listed in Table I. Confirmation of the space group $P2_1/n$ was obtained by a systematic check of the absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$.

Intensities were measured at 297 ± 2° by using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) as described in Table I. Data were corrected for Lorentz and polarization effects but not for absorption.

Solution and Refinement of the Structure. The ruthenium, cobalt, and phosphorus atoms were located via a Patterson map. A Fourier synthesis phased with these atoms readily revealed the remainder of the molecular skeleton. Refinement of positions and isotropic thermal parameters for all 45 non-hydrogen atoms gave an R value ($R = \sum|F_o| - |F_c|/\sum|F_o|$) of 0.066. Conversion to anisotropic parameters followed by several cycles of full-matrix least-squares refinement yielded R = 0.042 at which stage a difference Fourier synthesis revealed reasonable positions for all hydrogen atoms. In subsequent cycles of least-squares refinement, these were included and isotropic temperature coefficients refined. The final R value was 0.032 with the weighted R_w ($R_w = [\sum_w(|F_o| - |F_c|)^2/\sum_w(|F_o|)^2]^{1/2}$) = 0.039 where the weights allotted to each reflection were assigned according to the scheme $w^{-1} = 1.69 - 0.0182|F_o| + 0.0002|F_o|^2$. The function minimized in refinement was $\sum_w(\Delta|F|)^2$. In a final difference map the maximum residual electron density was at the level of 0.68 e Å^{-3}. Scattering factors used including corrections for anomalous dispersion for the heavy-metal atoms were taken from ref 14. Computations using

Table III. A Selection of Important Bond Lengths (Å) and Angles (deg) for $RuCo_2(CO)_8(\mu\text{-}PPh_2)_2$

A. Bond Lengths

Ru-Co(1)	2.7073 (7)	Ru-Co(2)	2.7182 (7)
Ru-P(1)	2.318 (1)	Ru-C(1)	1.975 (6)
Ru-C(2)	1.911 (5)	Ru-C(3)	1.896 (6)
Ru-C(8)	2.325 (5)	Co(1)-Co(2)	2.5497 (9)
Co(1)-P(1)	2.183 (2)	Co(1)-P(2)	2.151 (2)
Co(1)-C(4)	1.788 (6)	Co(1)-C(5)	1.771 (5)
Co(2)-P(2)	2.213 (2)	Co(2)-C(6)	1.766 (7)
Co(2)-C(7)	1.754 (7)	Co(2)-C(8)	1.818 (6)
P(1)-C(9)	1.832 (6)	P(1)-C(15)	1.836 (6)
P(2)-C(21)	1.823 (6)	P(2)-C(27)	1.835 (5)
C(1)-O(1)	1.119 (7)	C(2)-O(2)	1.127 (7)
C(3)-O(3)	1.138 (8)	C(4)-O(4)	1.121 (8)
C(5)-O(5)	1.121 (7)	C(6)-O(6)	1.141 (9)
C(7)-O(7)	1.141 (10)	C(8)-O(8)	1.157 (7)

B. Bond Angles

Co(1)-Ru-Co(2)	56.1 (0)	Co(1)-Ru-P(1)	50.8 (0)
Co(1)-Ru-C(1)	111.6 (1)	Co(1)-Ru-C(2)	89.0 (1)
Co(1)-Ru-C(3)	151.1 (1)	Co(1)-Ru-C(8)	90.4 (1)
Co(2)-Ru-P(1)	83.7 (0)	Co(2)-Ru-C(1)	83.0 (1)
Co(2)-Ru-C(2)	139.8 (1)	Co(2)-Ru-C(3)	125.3 (1)
Co(2)-Ru-C(8)	41.3 (1)	P(1)-Ru-C(1)	162.2 (1)
P(1)-Ru-C(2)	88.7 (1)	P(1)-Ru-C(3)	100.6 (1)
P(1)-Ru-C(8)	88.5 (1)	C(1)-Ru-C(2)	93.9 (2)
C(1)-Ru-C(3)	96.7 (2)	C(1)-Ru-C(8)	89.3 (2)
C(2)-Ru-C(3)	94.9 (2)	C(2)-Ru-C(8)	176.7 (2)
C(3)-Ru-C(8)	84.0 (2)	Ru-Co(1)-Co(2)	62.2 (0)
Ru-Co(1)-P(1)	55.4 (0)	Ru-C(1)-P(2)	88.3 (0)
Ru-Co(1)-C(4)	150.7 (2)	Ru-Co(1)-C(5)	103.3 (1)
Co(2)-Co(1)-P(1)	90.5 (0)	Co(2)-Co(1)-P(2)	55.4 (0)
Co(2)-Co(1)-C(4)	101.9 (2)	Co(2)-Co(1)-C(5)	149.5 (1)
P(1)-Co(1)-P(2)	140.5 (0)	P(1)-Co(1)-C(4)	103.7 (2)
P(1)-Co(1)-C(5)	102.9 (1)	P(2)-Co(1)-C(4)	102.7 (2)
P(2)-Co(1)-C(5)	100.2 (1)	C(4)-Co(1)-C(5)	101.3 (2)
Ru-Co(2)-Co(1)	61.8 (0)	Ru-Co(2)-P(2)	86.8 (0)
Ru-Co(2)-C(6)	125.3 (2)	Ru-Co(2)-C(7)	123.5 (2)
Ru-Co(2)-C(8)	57.6 (1)	Co(1)-Co(2)-P(2)	53.1 (0)
Co(1)-Co(2)-C(6)	90.3 (2)	Co(1)-Co(2)-C(7)	148.4 (2)
Co(1)-Co(2)-C(8)	109.0 (1)	P(2)-Co(2)-C(6)	113.9 (2)
P(2)-Co(2)-C(7)	95.3 (2)	P(2)-Co(2)-C(8)	143.1 (1)
C(6)-Co(2)-C(7)	105.1 (3)	C(6)-Co(2)-C(8)	96.3 (2)
C(7)-Co(2)-C(8)	96.7 (2)	Ru-P(1)-Co(1)	73.9 (0)
Ru-P(1)-C(9)	124.6 (1)	Ru-P(1)-C(15)	112.4 (1)
Co(1)-P(1)-C(9)	122.1 (1)	Co(1)-P(1)-C(15)	121.6 (1)
C(9)-P(1)-C(15)	101.8 (2)	Co(1)-P(2)-Co(2)	71.5 (0)
Co(1)-P(2)-C(21)	124.2 (1)	Co(1)-P(2)-C(27)	118.2 (1)
Co(2)-P(2)-C(21)	123.8 (1)	Co(2)-P(2)-C(27)	118.9 (1)
C(21)-P(2)-C(27)	100.4 (2)	Ru-C(1)-O(1)	174.6 (2)
Ru-C(2)-O(2)	179.7 (2)	Ru-C(3)-O(3)	175.9 (2)
Co(1)-C(4)-O(4)	178.6 (2)	Co(1)-C(5)-O(5)	178.5 (2)
Co(2)-C(6)-O(6)	176.6 (2)	Co(2)-C(7)-O(7)	178.3 (3)
Ru-C(8)-Co(2)	81.0 (1)	Ru-C(8)-O(8)	130.4 (2)
Co(2)-C(8)-O(8)	148.6 (2)		

an IBM 4341 system were processed in the University of Waterloo Computing Centre. Programs have been described elsewhere.[15] Table II shows atomic coordinates and Table III an appropriate selection of bond lengths and angles. Table V, thermal parameters, and Table VI, remaining bond lengths and angles, have been deposited. Structure factors are available on request from the authors.

Results and Discussion

A convenient route to mononuclear arene complexes of ruthenium of the type (arene)$RuCl_2L$ (L = phosphine) is that of Zelonka and Baird[12] involving halogen bridge cleavage of the dimer $[(C_6H_6)RuCl_2]_2$ by phosphines. This method was adapted to the synthesis of (*p*-cymene)$RuCl_2(Ph_2PX)$ (**1**, X = Cl, and **2**, and X = H) by the addition of 2 equiv of diphenylchlorophosphine or diphenylphosphine to the dimer [(*p*-cymene)$RuCl_2]_2$.[13] Excellent yields of **1** (90%) and **2** (94%) were obtained.

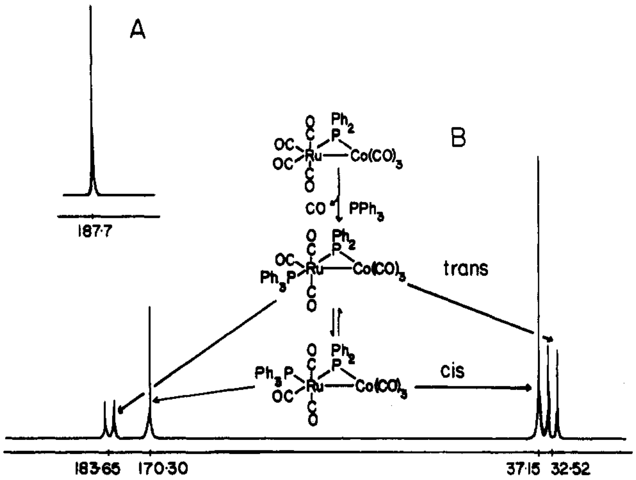

Figure 1. The $^{31}P\{^1H\}$ NMR spectrum (32.380 MHz) of $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (A) and $(PPh_3)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ (B)in CD_2Cl_2 at 193 K.

Under mild conditions it is known that $Co_2(CO)_8$ in THF functions as an effective dehalogenating agent.[4,16] Treatment of **1** and **2** with 2 equiv of $Co_2(CO)_8$ at ambient temperature for 12 h followed by chromatographic separation afforded the known homonuclear dimer $[Ru(CO)_3(\mu\text{-}PPh_2)]_2$[17] (**4**, 3%), the heterobimetallics $RuCo(\mu\text{-}PPh_2)(CO)_7$ (**3**, 40%) and (*p*-cymene)(CO)$RuCo(\mu\text{-}PPh_2)(CO)_3$ (**7**, 30%), and the heterotrimetallic $Ru_2Co(\mu\text{-}PPh_2)(CO)_{10}$ (**5**, 4%). On heating in THF a further heterotrimetallic, $RuCo_2(\mu\text{-}PPh_2)_2(CO)_8$ (**6**), is formed and the mixed cluster **5** is converted into **3** and an unidentified ruthenium complex.

The major product of the reaction is **3** for which analytical and spectroscopic data are consistent with a structure having an Ru–Co bond bridged by a single phosphido group. The infrared spectrum exhibits only terminal CO bands, and the mass spectrum shows a molecular ion at *m/e* 542 followed by ions due to successive loss of seven CO groups. The proton-decoupled ^{31}P NMR spectrum at room temperature shows a single broad resonance at low field (+185.0 ppm) that sharpens notably at 223 K indicative of an acute angle at phosphorus and a metal–metal interaction.[18] Broadening of this resonance can be attributed to the effects of the quadrupolar ^{59}Co ($I = {}^7/_2$) nucleus. Confirmation of the validity of the ^{31}P shift as an indicator of the $\mu\text{-}PPh_2$ (Ru–Co) structure can be seen from a comparison with other ^{31}P shift–structure correlations shown in Table IV. The cis (to PPh_2) PPh_3 substitution product of **3**, namely, $(PPh_3)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ has recently been characterized by X-ray diffraction;[19] the $\mu\text{-}PPh_2$ group bridges a strong Ru–Co bond (Ru–Co = 2.7681 (4) Å). At 193 K (CH_2Cl_2), the ^{31}P spectrum of $(PPh_3)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ exhibits two

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Table IV. ^{31}P NMR and Structural Parameters for RuCo(μ-PPh$_2$) Systems

compound	$\delta(^{31}P)$ ($^2J_{P-P}$, Hz)	Ru–Co, Å	Ru–P–Co, deg	Ru–P, Å	Co–P, Å
$(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (3)	187.3				
$(Ph_3P)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$[19]	trans 187.3 (104.2) cis 170.3 (5)	2.768 (1)	75.5 (0)	2.355 (1)	2.161 (1)
$(Ph_3P)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_2PPh_3$[6]	trans 139.8 (91.9)	2.750 (1)	74.6 (1)	2.359 (2)	2.173 (13)
(p-cymene)$(CO)Ru(\mu\text{-}PPh_2)Co(CO)_3$ (7)	201.0				
$RuCo_2(\mu\text{-}PPh_2)_2(CO)_8$ (6)	180.4 P (Ru–Co) 225.4 P (Co–Co) (96.4)	2.7073 (7)	73.9 (0)	2.318 (1)	2.183 (2)
$RuCo_3(\mu\text{-}PPh_2)(CO)_9(t\text{-}BuC{\equiv}CH)$[10]	222.05	2.558 (1)	69.84 (3)	2.328 (1)	2.131 (1)
$Ru_2Co(\mu\text{-}PPh_2)(CO)_{10}$ (5)	166.8				

low field doublets, one at 183.7 ppm due to the phosphorus atom of the phosphido bridge trans to PPh$_3$ in the trans isomer ($^2J_{PP'}$ = 104.2 Hz) and the other at 170.3 ppm with a very small coupling, resolvable only under high-resolution conditions, attributable to the cis isomer (PPh$_2$ cis to PPh$_3$) (Figure 1). The disubstituted derivative of 3, (PPh$_3$)(CO)$_3$Ru(μ-PPh$_2$)Co(CO)$_2$(PPh$_3$), synthesized via the reaction of NaCo(CO)$_4$ with Ru(H)Cl(CO)(PPh$_3$)$_3$ and fully characterized by X-ray diffraction,[6] has been reported to react with CO affording in solution both the monosubstituted complex (PPh$_3$)(CO)$_3$Ru(μ-PPh$_2$)Co(CO)$_3$ [δ 184.1 (d)] and the parent 3 for which δ (^{31}P) was given as 170.4 (s) ppm. Our results confirm that the former assignment is correct for the trans isomer of (PPh$_3$)(CO)$_3$Ru(μ-PPh$_2$)Co(CO)$_3$. The resonance at ~170.4 ppm is however due to the cis (PPh$_3$ cis to PPh$_2$) isomer of the monosubstituted compound rather than the parent 3 for which (vide supra) δ equals 187.3 ppm (223 K).

The homobinuclear complex 4 has previously been prepared via the pyrolysis of Ru$_3$(CO)$_9$(PPh$_3$)$_3$[17a] and irradiation of Ru$_3$(CO)$_9$(PPh$_2$H)$_3$.[17b] The measured ^{31}P shift (+110 ppm) is close to that reported for the μ-PPh$_2$ group in *cis*-(Ph$_2$PC≡C-*i*-Pr)(CO)$_2$Ru(μ-PPh$_2$)(μ-η^2-C≡C-*i*-Pr)-Ru(CO)$_3$ (δ +108),[18a] and it is likely that the Ru–P–Ru bond angle and Ru–Ru bond length in 4 are similar to those in the acetylide derivative (Ru–Ru = 2.7951 (4) Å; Ru–P–Ru = 73.4 (0)°).[18a,20]

Compound 5 is trinuclear and has a single phosphido group, two ruthenium atoms, and a cobalt atom. Accurate mass analysis of a fragment ion at *m/e* 671.756 corresponds to the formula [Ru$_2$Co(PPh$_2$)(CO)$_8$]$^+$. A closed-shell 48-electron structure requires 10 carbonyl groups. The ^{31}P NMR spectrum at 300 K shows a broad downfield singlet resonance that sharpens markedly at low temperature (δ +166.8 (223 K), appropriate for a μ-PPh$_2$ group across a Ru–Co bond. Only terminal ν(CO) bands are present in the infrared. An appropriate structure is that shown in Scheme I.

Also produced in 30% yield is 7, a red-black derivative of molecular formula RuCo(PPh$_2$)(CO)$_4$(p-cymene). The mass spectrum of 7 exhibits a parent ion at *m/e* 592 and ions resulting from the successive loss of four CO groups. Both accurate mass analysis of the ion at *m/e* 563.982 ((M – CO)$^+$) and ^{1}H NMR indicate retention of the original arene ligand. ^{31}P NMR (δ 201 (193 K)) confirms the presence of a μ-PPh$_2$ group. The structure of 7 is formally related to that of 3 by replacement of three CO groups of the latter by an η^6-arene ligand and may be a precursor of 3.

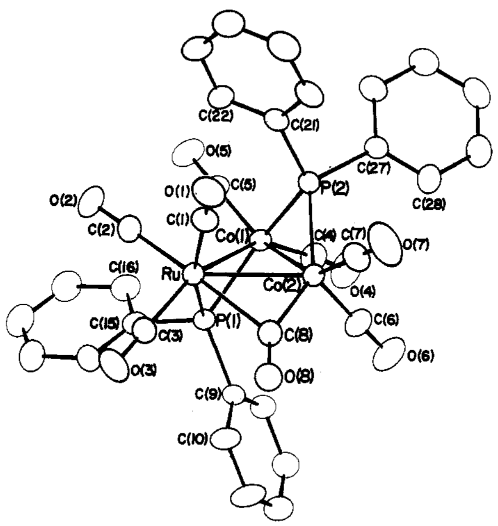
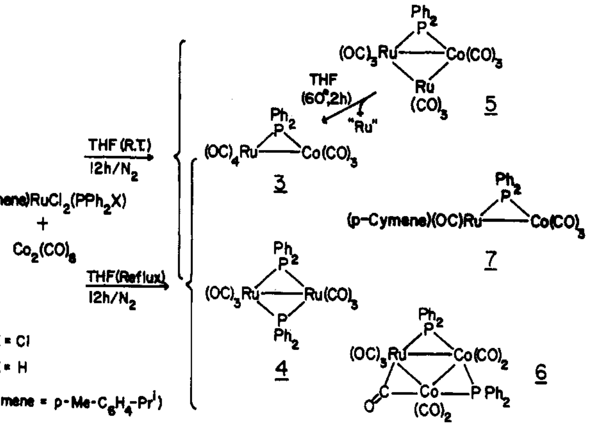


Figure 2. A perspective view of the molecular structure of RuCo$_2$(CO)$_8$(μ-PPh$_2$)$_2$ showing the atomic numbering.

Scheme I



Workable yields of a black trinuclear cluster for which microanalysis, high resolution mass spectroscopy and 18-electron rule considerations suggest the formula RuCo$_2$(PPh$_2$)$_2$(CO)$_8$ were also obtained from the reaction of 1 or 2 with Co$_2$(CO)$_8$. The ^{31}P NMR spectrum consists of an AB pattern of resonances at low field (225.4, 180.4 ppm) with $^2J_{PP}$ of 96.4 Hz indicative of two bridging PPh$_2$ groups. A bridging CO band appears in the solution IR at 1863 cm^{-1}. Confirmation of the proposed structure (Scheme I) with a RuCo$_2$ trinuclear framework, bridged on two sides by μ-PPh$_2$ groups and along the third edge by a carbonyl ligand, comes from a single-crystal X-ray structural study.

Description and Discussion of the Structure of RuCo$_2$(μ-PPh$_2$)$_2$(μ-CO)(CO)$_7$. The gross structural features of the molecule, notably a triangle of two cobalt atoms and one ruthenium atom with two phosphido

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bridges and a μ-carbonyl group (Figure 2), are those that could readily be predicted from the available spectroscopic data. Significant details are however revealed by a closer examination of the stereochemistry and molecular parameters. The two phosphido bridges lie above and below the $RuCo_2$ plane such that the atoms P(1) and P(2) bear an approximate trans axial relationship to one another with respect to Co(1) [P(1)–Co(1)–P(2) = 140.5 (0)°]. Thus one phenyl ring of each phosphido bridge lies either above (C(21)–C(26)), or below (C(9)–C(14)), the $RuCo_2$ ring. It is clear that a mutual cis axial arrangement of PPh_2 groups around the triangle would lead to unfavorable steric interactions between phenyl substituents. Furthermore Figure 2 suggests that a cis axial, equatorial configuration would also be disfavored with respect to phenyl group contact. As expected from the low field ^{31}P shifts of the phosphorus atoms,[18] the angles Ru–P(1)–Co(1) (73.9 (0)°) and Co(1)–P(2)–Co(2) (71.5 (0)°) are acute. The smaller value of the latter reflects the shorter M–M distance (Co(1)–Co(2) = 2.5497 (9) Å vs. Ru–Co(1) = 2.7073 (7) Å) bridged by P(2). The $MM'_2(\mu\text{-}PPh_2)_2$ skeleton of **6** bear a close structural similarity to that of the iron analogue $FeCo_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_7$[1e] and homotrinuclear clusters such as $(\mu\text{-}H)_2Fe_3(CO)_8(\mu\text{-}PPh_2)_2$.[1f]

Within the metal triangle the two Ru–Co bond lengths are comparable despite the presence of different edge-bridging ligands. The average Ru–Co distance of 2.7127 Å is somewhat shorter than the corresponding values in the heterobinuclear compounds $(Ph_3P)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_2(PPh_3)$ (2.750 (1) Å)[6] and $(Ph_3P)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ (2.7681 (4) Å)[19] but longer than Ru–Co bond lengths in the tetranuclear compounds $RuCo_3(\mu_4\text{-}\eta^2\text{-}t\text{-}BuC{\equiv}CH)(\mu\text{-}PPh_2)(CO)_9$[10] (average 2.634 Å), PPN $[RuCo_3(CO)_{12}]$[3] (average 2.633 Å), PPN$[Ru_3Co(CO)_{13}]$[7] (average 2.618 Å), $(Ph_3P)AuRuCo_3(CO)_{12}$[21] (average 2.677 Å), $Ru_2Co_2(CO)_{13}$[5] (average 2.694 Å), and $Et_4N[RuCo_3(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)(CO)_{10}]$[23] (average 2.581 Å). Thus the Ru–Co bond lengths show a general decrease with increasing nuclearity. The lowest ν(CO) frequency for **6** (1863 cm^{-1}) suggests the presence of a bridging CO group in the molecule. The bond angles Co(2)–C(8)–O(8) (148.6 (2)°) and Ru–C(8)–O(8) (130.4 (2)°) confirm that the C(8)–O(8) group is an asymmetrically bridging carbonyl rather than a semibridging group.

Correlation of ^{31}P Shifts and Structural Parameters for Phosphide-Bridged Ru/Co Compounds. There is now abundant evidence to suggest that *when sensibly used* the ^{31}P NMR chemical shift of a μ-PPh_2 group can be a useful diagnostic probe of the presence or absence of metal–metal bonding.[18] Indeed, within series of closely related compounds, for example, $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}X)$ where X is a three-electron donor ligand, $\delta(^{31}P)$ correlates well with M–P–M bond angle and M–M bond length.[22] These correlations when carefully applied have recently been used with considerable success in structure elucidation.[18] Sufficient data have now been accumulated for mixed Ru–Co systems to allow an assessment of the utility of $\delta(^{31}P)$ for structural assignments. In Table IV are gathered ^{31}P shifts and structural parameters for μ-PPh_2 (Ru/Co) systems.

Table IV shows that the range of $\delta(^{31}P)$ is 139.8–225.1. These shifts are therefore far downfield of H_3PO_4. In contrast, for those Ru/Co compounds with terminal phosphines, $\delta(PPh_3)$ lies close to +30 ppm for ruthenium-bonded ligands and +70 ppm for cobalt-bound phosphine. The Ru–Co bond lengths range from 2.558 (1) Å for tetranuclear $RuCo_3(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}HC{\equiv}C\text{-}t\text{-}Bu)(CO)_9$[10] to 2.7681 (4) Å for $(Ph_3P)(CO)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$.[19] Angles are all acute, and Ru–P–Co varies from 75.5 (0)° to 69.84 (3)°. The largest downfield shifts are, perhaps fortuitously, associated with the shortest M–M bond lengths and smallest M–P–M angles: $\delta(^{31}P)$ 222.05 vs. Ru–Co = 2.558 (1) Å and Ru–P–Co = 69.84 (3)° in $RuCo_3(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}HC{\equiv}C\text{-}t\text{-}Bu)(CO)_9$[10] and $\delta(^{31}P)$ 225.4 vs. Co–Co = 2.5497 (9) Å and Co–P–Co = 71.5 (0)° in $RuCo_2(\mu\text{-}PPh_2)_2(CO)_9$, but the latter compound is strictly not comparable since the bridge is across a Co–Co bond. Phosphine substitution on ruthenium or cobalt, particularly cis substitution, appears to effect an upfield shift of $\delta(^{31}P)$ (PPh_2) presumably due to shielding effects of the bulky ligand. Table IV also illustrates the important point that the M–P–M angle is a function not only of M–M′ bond length but also of M′–P and M–P bond lengths. Thus any further speculation on the detailed interrelationship of $\delta(^{31}P)$, Ru–Co bond length, and Ru–P–Co angle must await the accumulation of substantially more ^{31}P NMR and structural data. However for clusters of differing nuclearity, bearing different ligands it is not unlikely that *systematic* variations in $\delta(^{31}P)$ with the M–M bond length and the M–P–M bond angle will be observed.

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada (A.J.C.) and from the Centre National de la Recherche Scientifique of France (P.H.D.). R.R. is grateful to the University of Waterloo for facilities provided during a 4-month visit.

Registry No. **1**, 84779-39-5; **2**, 84779-40-8; **3**, 82544-75-0; **4**, 38685-25-5; **5**, 89746-54-3; **6**, 89746-55-4; **7**, 84779-41-9; $[RuCl_2(p\text{-}MeC_6H_4Pr\text{-}i)]_2$, 52462-29-0; PPh_2Cl, 1079-66-9; PPh_2H, 829-85-6; $Co_2(CO)_8$, 10210-68-1; Co, 7440-48-4; Ru, 7440-18-8.

Supplementary Material Available: Table V, anisotropic thermal parameters (×10^3), Table VI, remaining bond lengths (Å) and Angles (deg), and Table VII, structure factor tables for $RuCo_2(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_7$ (20 pages). Ordering information is given on any masthead page.

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