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Synthesis, Structural Characterization, and Reactivity Studies of $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$

Henry C. Foley,[1a] William C. Finch,[1a] Cortlandt G. Pierpont,[1b] and Gregory L. Geoffroy*[1a]

Departments of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and University of Colorado, Boulder, Colorado 80309

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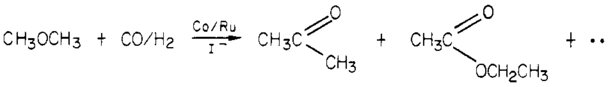
The new heterobimetallic phosphido-bridged complex $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ has been prepared via the reaction of $Na[Co(CO)_4]$ with $RuH(Cl)(CO)(PPh_3)_3$. This reaction proceeds via coupling of the hydride ligand with a phenyl substituent of a PPh_3 ligand to give benzene and the phosphido-bridged product. Also formed in the reaction are $RuH(Cl)(CO)_2(PPh_3)_2$ and $Ru(CO)_3(PPh_3)_2$. The new complex has been characterized spectroscopically and by a complete single-crystal X-ray structure determination. It crystallizes in the space group $P\bar{1}$ with $a = 10.861$ (3) Å, $b = 19.447$ (4) Å, $c = 12.109$ (3) Å, $\alpha = 93.23$ (4)°, $\beta = 115.69$ (3)°, $\gamma = 93.26$ (3)°, $V = 2291$ (1) Å^3, and $Z = 2$. The Ru is coordinated by three CO's, one PPh_3, the μ-PPh_2 bridge, and Co. The Co is coordinated by two CO's, one PPh_3, the μ-PPh_2 bridge, and Ru. The Ru–Co bond length of 2.750 (1) Å implies a direct single bond between these atoms. $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ has been observed to react with CO to replace the PPh_3 ligands, successively forming $RuCo(\mu\text{-}PPh_2)(CO)_6(PPh_3)$ and $RuCo(\mu\text{-}PPh_2)(CO)_7$. Reaction with HCl gives two isomers of $RuCoH(Cl)(\mu\text{-}PPh_2)(CO)_4$.

Introduction

Heteronuclear metal–metal bonded compounds are currently of high interest because of the unique reactivity features which should result as a consequence of adjacent metals with differing sets of chemical properties.[2] Compounds containing ruthenium and cobalt are particularly interesting because of the promoting effect which ruthenium compounds have been shown to display in cobalt catalyzed homologation reactions.[3] For example, addition of Ru enhances the selectivity for ethanol in the Co-catalyzed homologation of methanol with synthesis gas (eq 1)[3c–e,4] and also greatly increases the selectivity for ethyl

$$CH_3OH + CO/H_2 \xrightarrow[I^-]{Co/Ru} CH_3CH_2OH + CH_3CHO + CH_3COOH + \ldots \quad (1)$$

acetate in the Co-catalyzed homologation of dimethyl ether (eq 2).[3b] Prior to this work, the only RuCo complexes



$$CH_3OCH_3 + CO/H_2 \xrightarrow[I^-]{Co/Ru} CH_3C(=O)CH_3 + CH_3C(=O)OCH_2CH_3 + \cdots \quad (2)$$

reported were $H_3Ru_3Co(CO)_{12}$,[5] $HRu_3Co(CO)_{13}$,[6] $[Ru_3Co(CO)_{13}]^-$,[6] $Ru_2Co_2(CO)_{13}$,[7] $RuCo_2(CO)_{11}$,[7] $HRuCo_3(CO)_{12}$,[8] $[RuCo_3(CO)_{12}]^-$,[4] and $RuCo(\eta\text{-}C_5H_5)(CO)_6$.[9] Several of these have been used as catalyst precursors in homologation reactions.[4,10]

One of the persistent problems with clusters such as those listed above is the relative ease with which they can be cleaved by CO. For example, both $HRu_3Co(CO)_{13}$ and $[Ru_3Co(CO)_{13}]^-$ were found to completely fragment when placed under 1 atm of CO to give the products shown in eq 3 and 4.[11] Such fragmentation renders mechanistic

$$HRu_3Co(CO)_{13} + CO \xrightarrow{25\ ^\circ C,\ 1\ h} Ru_3(CO)_{12} + Ru(CO)_5 + H_2 + \text{“Co products”} \quad (3)$$

$$[Ru_3Co(CO)_{13}]^- + CO \xrightarrow{25\ ^\circ C,\ 96\ h} Ru_3(CO)_{12} + [Co(CO)_4]^- \quad (4)$$

interpretation of catalysis experiments difficult and may also remove any multimetallic effects by destroying the polynuclear character of the complexes. One way to retard such fragmentation is to use bridging ligands to assist in holding adjacent metals together. Bridging phosphido and arsenido ligands are particularly attractive in that they resemble the ubiquitous PR_3 ligands found in many mononuclear catalysts and they are not easily displaced from their polynuclear complexes.[12,13] We thus set out to prepare a series of phosphido-bridged di- and polynuclear Ru–Co complexes for evaluation as possible homologation

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catalysts. Herein we report the preparation and characterization of the first member of this series, RuCo(μ-PPh_2)$(CO)_5(PPh_3)_2$, a complex which derives by benzene elimination from a triphenylphosphine hydride complex.

Experimental Section

The complexes RuHCl(CO)$(PPh_3)_3$,[14] Ru$(CO)_3(PPh_3)_2$,[14] RuHCl$(CO)_2(PPh_3)_2$,[15] and Na[Co$(CO)_4$][16] were prepared via published procedures. All manipulations were carried out in standard Schlenk glassware under N_2 that had been purified by passage over BASF catalysator and Linde 4-Å molecular sieves. Solvents were dried by stirring over Na/benzophenone (THF, Et_2O, hexane, petroleum ether, benzene) or BaO (CH_2Cl_2) followed by distillation under N_2.

Preparation of RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$. A suspension of Na[Co$(CO)_4$] (0.100 g, 0.52 mmol) and RuHCl(CO)$(PPh_3)_3$ (0.500 g, 0.54 mmol) in THF (150 mL) was stirred at ~40 °C for 12 h under N_2 in a 250-mL three-necked round-bottomed flask during which time the color changed from yellow to dark red. The THF was removed under vacuum, and the resultant oily dark-red solid was redissolved in ~40 mL of benzene. This solution was filtered through Celite 545, and the solvent was evaporated under vacuum to give an oily red solid. This material completely dissolves in Et_2O at 25 °C, and, when it was left standing, RuCo(μ-PPh_2)$(CO)_5(PPh_3)_2$ precipitates as a red powder (0.53 g, 0.151 mmol, 28%) over the course of ~1 h. Alternatively, the reaction mixture can be chromatographed on deactivated neutral alumina by using 1/1 hexane–CH_2Cl_2 as eluting solvent to give a yellow band which is ~90% RuCo(μ-PPh_2)$(CO)_5(PPh_3)_2$/~10% Ru$(CO)_3(PPh_3)_2$ followed by a colorless band of HRuCl$(CO)_2(PPh_3)_2$: UV-vis (CCl_4) λ_{max} 495 nm (sh, ϵ 782 L mol^{-1} cm^{-1}), 384 (8720), 261 (38840); IR (CH_2Cl_2) ν_{CO} 2058 (w), 1993 (vs), 1981 (s, sh), 1924 (m), 1877 (m) cm^{-1}. Anal. Calcd for $C_{53}H_{46}O_5P_3CoRu$: C, 63.00; H, 3.97. Found: C, 62.02; H, 4.22.

Spectral Measurements. NMR spectra were recorded on JEOL PS100, Bruker WP200, or Bruker WM360 Fourier transform NMR spectrometers. ^{31}P spectra are referenced to external H_3PO_4 with downfield chemical shifts reported as positive. IR spectra were recorded on a Perkin-Elmer 580 grating IR spectrophotometer using 0.5-mm path length NaCl solution IR cells. UV–visible spectra were recorded on a Cary 17 UV–visible spectrophotometer in degassable 1-cm quartz cells. Gas chromatographic measurements were carried out by using a Varian aerograph series 1440 chromatograph equipped with a 5-ft 10% Carbowax on Chromosorb W column.

Molecular Structure Determination of RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$. Crystals suitable for X-ray diffraction were grown by slow diffusion of petroleum ether into a THF/Et_2O solution of RuCo(μ-PPh_2)$(CO)_5(PPh_3)_2$. Preliminary photographs taken on these crystals indicated triclinic symmetry. A crystal suitable for data collection was mounted and aligned on a Syntex P$\bar{1}$ automated diffractometer equipped with a graphite crystal monochromator. The centered settings of 35 reflections (Mo Kα radiation) were refined by least-squares procedures to give the cell constants listed in Table I. Intensity data were collected to a 2θ value of 50°, although much of the high angle data was of low intensity. The data was processed as described earlier.[17] The locations of atoms within the inner coordination sphere were determined by direct methods using a locally modified version of MULTAN. Phenyl rings of the structure were refined as rigid groups with an assumed C–C length of 1.392 Å and C–H length of 0.98 Å. Complete anisotropic refinement of nongroup atoms and refinement of group atoms with isotropic thermal parameters converged with $R_F = 0.057$ and $R_{wF} = 0.063$. Pertinent crystal and intensity data are listed in Table I. Final positional and thermal parameters of nongroup atoms and positional parameters of rigid groups are given in Tables II and III. Tables IV and V list the more important bond lengths and bond angles, respectively. Tables of structure factor amplitudes and the derived positions of group atoms are available as supplementary material.

Table I. Crystallographic Data for RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$

fw 1009.44
triclinic
space group P$\bar{1}$
$a = 10.861$ (3) Å
$b = 19.447$ (4) Å
$c = 12.109$ (3) Å
$\alpha = 93.23$ (4)°
$\beta = 115.69$ (3)°
$\gamma = 93.26$ (3)°
$V = 2291$ (1) Å^3
$Z = 2$
$\mu = 9.41$ cm^{-1} (not corrected)

d(calcd) = 1.464 g cm^{-3}
d(exptl) = 1.44 (2) g cm^{-3}
Mo Kα radiation: $\lambda = 0.71069$ Å
scan rate: 4°/min
scan range: ±0.7°
2θ limits: $3° \leq 2\theta \leq 50°$
data collected: 8293
data $F_o^2 > 3\sigma(F_o)^2$: 3002
$p = 0.04$
$R = 0.057$
$R_w = 0.063$

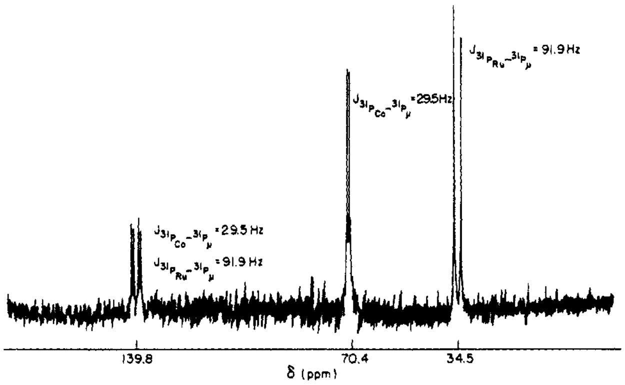

Figure 1. $^{31}P\{^1H\}$ NMR spectrum of RuCo(μ-PPh_2)$(CO)_5(PPh_3)_2$ in toluene-d_8 solution at −55 °C.

Results

Synthesis and Spectroscopic Characterization of RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$. Our approach to the preparation of a phosphido-bridged Ru–Co complex was to initially prepare an unbridged metal–metal bonded Ru–Co complex followed by addition of PPh_2H across the metal–metal bond. Following the strategy we had earlier demonstrated for the preparation of (CO)$(PEt_3)_2$Rh–Co$(CO)_4$ via the addition of Na[Co$(CO)_4$] to *trans*-RhCl(CO)$(PEt_3)_2$,[18] it was anticipated that reaction of Na[Co$(CO)_4$] with RuHCl(CO)$(PPh_3)_3$ would yield the binuclear complex H(CO)$(PPh_3)_3$Ru–Co$(CO)_4$. Quite unexpectedly, the mixture of products shown in eq 5 was obtained when

$$\mathrm{RuHCl(CO)(PPh_3)_3 + Na[Co(CO)_4] \xrightarrow[\text{THF}]{25\ °C} RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2 + RuHCl(CO)_2(PPh_3)_2 + Ru(CO)_3(PPh_3)_2 + NaCl} \quad (5)$$

these reagents were stirred in THF solution at 40 °C for 12 h. Integration of the ^{31}P NMR spectrum of the crude reaction mixture indicated that the three Ru-containing products were formed in the following relative yields: RuCo(μ-PPh_2)$(CO)_5(PPh_3)_2$, 37%, RuHCl$(CO)_2(PPh_3)_2$, 44%, and Ru$(CO)_3(PPh_3)_2$, 19%. The RuHCl$(CO)_2(PPh_3)_2$ and Ru$(CO)_3(PPh_3)_2$ products were identified by comparison of their IR and ^{31}P NMR spectral data to reported data or to data obtained from independently prepared samples.[19,20]

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(19) RuHCl$(CO)_2(PPh_3)_2$: IR ν_{CO} (CH_2Cl_2), 2042 (s), 1983 (s) cm^{-1};[21] $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6) δ 39.9 (s); ^1H NMR (25 °C, benzene-d_6) δ −3.9 (t, $J_{^1H-^{31}P} = 19$ Hz).[21]
(20) Ru$(CO)_3(PPh_3)_2$: IR ν_{CO} (CH_2Cl_2) 1900 (s) cm^{-1};[22] $^{31}P\{^1H\}$ NMR (25 °C, benzene-d_6) δ 55.0 (s).[15,23]

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $CoRu(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ru	0.2240 (1)	0.31187 (7)	0.3076 (1)	2.10 (6)	2.76 (7)	2.10 (6)	0.10 (5)	0.33 (5)	−0.13 (5)
Co	0.0181 (2)	0.2105 (1)	0.2666 (2)	2.3 (1)	3.1 (1)	2.6 (1)	0.20 (9)	0.75 (9)	0.30 (9)
P1	0.0217 (4)	0.2757 (2)	0.1279 (4)	2.6 (2)	3.0 (2)	2.5 (2)	0.0 (2)	0.8 (2)	0.1 (2)
P2	0.3956 (4)	0.3206 (2)	0.5184 (4)	3.1 (2)	3.2 (2)	2.2 (2)	0.1 (2)	0.7 (2)	0.1 (2)
P3	−0.1850 (4)	0.1573 (2)	0.2013 (2)	2.5 (2)	3.2 (2)	3.4 (2)	0.2 (2)	1.1 (2)	0.2 (2)
C1	0.114 (2)	0.3702 (9)	0.353 (1)	4.3 (10)	4 (1)	3.6 (9)	1.0 (8)	2.4 (8)	−0.4 (7)
O1	0.047 (1)	0.4058 (7)	0.378 (1)	4.4 (7)	5.8 (8)	4.9 (7)	0.9 (6)	1.3 (6)	−1.1 (6)
C2	0.306 (2)	0.3774 (9)	0.256 (1)	4.1 (9)	3.9 (10)	1.4 (7)	1.6 (8)	0.3 (6)	0.6 (7)
O2	0.355 (1)	0.4205 (7)	0.219 (1)	5.2 (7)	5.1 (8)	7.0 (8)	0.9 (6)	2.6 (6)	1.8 (6)
C3	0.309 (2)	0.2380 (10)	0.269 (1)	3.7 (9)	4 (1)	3.3 (8)	−0.7 (8)	2.2 (7)	−0.7 (7)
O3	0.363 (1)	0.1946 (7)	0.250 (1)	4.2 (7)	5.0 (8)	7.1 (8)	0.3 (6)	2.6 (6)	−0.9 (6)
C4	0.017 (2)	0.2440 (9)	0.397 (2)	2.5 (8)	5 (1)	4.1 (10)	0.2 (7)	1.6 (7)	0.9 (8)
O4	0.017 (1)	0.2622 (7)	0.493 (1)	5.8 (7)	6.9 (8)	4.6 (7)	−0.3 (6)	2.8 (6)	−0.5 (6)
C5	0.105 (2)	0.1359 (10)	0.275 (2)	3.2 (9)	4 (1)	4.6 (10)	−0.5 (8)	2.0 (8)	−0.4 (8)
O5	0.152 (1)	0.0840 (7)	0.287 (1)	6.0 (8)	4.7 (8)	6.8 (8)	2.2 (6)	2.5 (6)	1.2 (6)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. The quantities given in the table are in units of $Å^2$.

Table III. Rigid-Group Parameters

group	x_c[a]	y_c	z_c	δ[b]	ϵ	η
P1R1	−0.1836 (7)	0.3949 (4)	0.0125 (6)	−0.851 (6)	−3.029 (6)	−3.023 (7)
P1R2	0.0490 (7)	0.2201 (4)	−0.1159 (7)	−2.802 (7)	−2.824 (7)	−1.516 (7)
P2R1	0.7003 (8)	0.3817 (4)	0.5705 (7)	−0.11 (1)	−2.176 (7)	−0.44 (1)
P2R2	0.3042 (7)	0.4208 (4)	0.6828 (7)	−0.200 (9)	2.508 (7)	2.013 (9)
P2R3	0.4726 (8)	0.1788 (4)	0.6490 (7)	−1.309 (7)	3.184 (8)	0.365 (7)
P3R1	−0.4424 (8)	0.2484 (4)	0.0852 (7)	−0.642 (9)	−2.444 (7)	−3.115 (9)
P3R2	−0.2376 (8)	0.0916 (4)	0.4177 (7)	−1.965 (8)	3.097 (7)	1.084 (7)
P3R3	−0.2535 (7)	0.0287 (4)	−0.0001 (7)	2.314 (9)	−2.391 (7)	−1.965 (10)

[a] x_c, y_c, and z_c are the fractional coordinates of the origin of the rigid group. [b] The rigid-group orientation angles δ, ϵ, and and η (radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511.

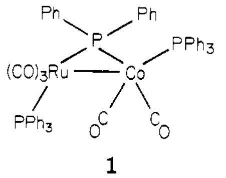
Table IV. Selected Bond Lengths (Å) for $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$

Ruthenium-Ligand Bond Lengths			
Ru-Co	2.750 (1)	Ru-C1	1.917 (11)
Ru-P1	2.359 (2)	Ru-C2	1.802 (12)
Ru-P2	2.410 (3)	Ru-C3	1.892 (12)
Cobalt-Ligand Bond Lengths			
Co-P1	2.173 (13)	Co-C4	1.676 (14)
Co-P3	2.167 (3)	Co-C5	1.159 (15)
Carbonyl Bond Lengths			
C1-O1	1.147 (12)	C4 -O4	1.195 (12)
C2-O2	1.179 (13)	C5-O5	1.146 (13)
C3-O3	1.129 (13)		

Table V. Selected Bond Angles (Deg) for $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$

Co-Ru-P1	49.61 (7)	Ru-Co-P1	55.81 (7)
Co-Ru-P2	111.01 (8)	Ru-Co-P3	160.81 (7)
Co-Ru-C1	84.1 (2)	Ru-Co-C4	86.9 (2)
Co-Ru-C2	151.9 (3)	Ru-Co-C5	100.6 (3)
Co-Ru-C3	83.6 (3)	P1-Co-P3	109.1 (1)
P1-Ru-P2	160.6 (1)	P1-Co-C4	121.5 (3)
P1 -Ru-C1	86.5 (2)	P1-Co-C5	113.1 (3)
P1-Ru-C2	102.4 (2)	P3-Co-C4	93.0 (3)
P1-Ru-C3	88.8 (2)	P3-Co-C5	96.4 (2)
P2-Ru-C1	90.3 (2)	C4-Co-C5	117.2 (3)
P2-Ru-C2	97.0 (2)	Ru-P1-Co	74.6 (1)
P2-Ru-C3	90.2 (2)	Ru-C1-O1	178.3 (11)
C1-Ru-C2	97.8 (3)	Ru-C2-O2	177.8 (12)
C1-Ru-C3	166.9 (3)	Ru-C3-O3	177.3 (12)
C2-Ru-C3	95.1 (3)	Co-C4-O4	174.2 (13)
		Co-C5-O5	171.7 (13)

The new complex $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ was characterized by spectroscopic methods and by a complete single-crystal X-ray diffraction study (see below) which showed structure 1. The $^{31}P\{^1H\}$ NMR spectrum of



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$RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ is shown in Figure 1. It shows a doublet of doublets at δ 139.8 ($J_{^{31}P_\mu-^{31}P_{Ru}}$ = 92 Hz, $J_{^{31}P_\mu-^{31}P_{Co}}$ = 30 Hz) attributable to the bridging μ-PPh_2 ligand, a doublet at δ 70.4 ($J_{^{31}P_{Co}-^{31}P_\mu}$ = 30 Hz) which is assigned to the PPh_3 ligand on Co and another doublet at δ 34.5 ($J_{^{31}P_{Ru}-^{31}P_\mu}$ = 92 Hz) due to the PPh_3 bound to Ru. The PPh_3 ligands were distinguished on the basis of the magnitude of their coupling to the μ-PPh_2 ligand. The PPh_3 attached to Ru is trans to the PPh_2 bridge and should thus show larger ^{31}P–^{31}P coupling than PPh_3 on Co which is cis to the μ-PPh_2 ligand.[24] This analysis assumes that the structure determined by X-ray diffraction is maintained in solution. The latter is evidenced by the similar IR spectra obtained in THF solution and in a pressed KBr pellet. As in many other $(PR_3)M(\mu\text{-}PPh_2)M'(PR_3)$ complexes prepared in this laboratory,[25] $RuCo(\mu\text{-}PPh_2)$-

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$(CO)_5(PPh_3)_2$ does not show ^{31}P–^{31}P coupling between PPh_3 ligands on the adjacent metals. The downfield position of the μ-PPh_2 resonance is consistent with that ligand bridging two metals that are joined by a metal–metal bond (Co–Ru = 2.759 (1) Å; see below). The μ-PR_2 ligands in compounds with metal–metal bonds generally show downfield (δ 50 → δ 300) ^{31}P NMR resonances whereas upfield (δ 50 → δ – 200) resonances are observed for compounds in which the μ-PR_2 ligand bridges two metals not joined by a metal–metal bond.[26] The 25 °C $^{31}P\{^1H\}$ NMR spectrum is similar to the –55 °C spectrum except for considerable broadening of the resonances of the ^{31}P nuclei attached to the quadrapolar ^{59}Co nucleus.

The electronic absorption spectrum of $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ shows a shoulder at 495 nm (ϵ 782 L mol^{-1} cm^{-1}) and an intense band at 384 nm (ϵ 8720 L mol^{-1} cm^{-1}). These are assigned respectively to $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions on the basis of similar assignments for other metal–metal bonded compounds.[27] Thus $Co_2(CO)_6(PPh_3)_2$ shows a $\sigma \rightarrow \sigma^*$ transition at 445 nm (ϵ 23 800 L mol^{-1} cm^{-1})[27b] and $Ru_2(\eta\text{-}C_5H_5)_2(CO)_4$ shows a corresponding band at 330 nm (ϵ 6300 L mol^{-1} cm^{-1}).[27e] It is interesting to note that the 384-nm (2.60 μm^{-1}) $\sigma \rightarrow \sigma^*$ transition of $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ is close to the energy average (2.64 μm^{-1}) of the $\sigma \rightarrow \sigma^*$ transitions for the Co_2 and Ru_2 complexes. Such correspondences have been previously noted for other metal–metal bonded compounds.[27b,c] Also for comparison $FeCo(\mu\text{-}AsMe_2)(CO)_7$ shows a $\sigma \rightarrow \sigma^*$ transition at 437 nm (ϵ 2700 L mol^{-1} cm^{-1})[27d] and $FeCo(n\text{-}C_5H_5)(CO)_6$ apparently shows two bands at 358 and 384 nm (ϵ ~10 000 L mol^{-1} cm^{-1}).[27f]

A few experiments were conducted to determine the manner by which the products of eq 5 are formed. Benzene was detected by gas chromatographic analysis in the THF solvent after reaction, implying that the phosphido bridge of $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ forms through coupling of a PPh_3 phenyl group with the hydride initially on Ru. $HRuCl(CO)(PPh_3)_3$ is known to rapidly react with CO to produce $RuHCl(CO)_2(PPh_3)_2$ (eq 6),[15] and thus this

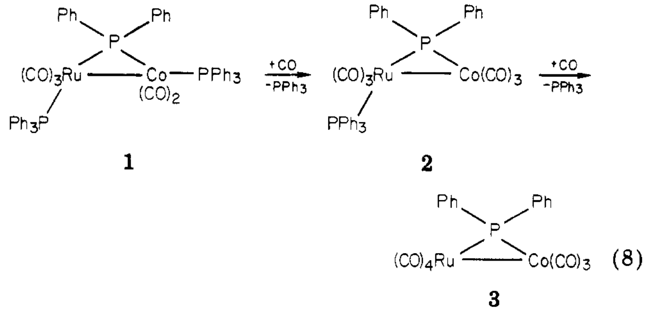
$$RuHCl(CO)(PPh_3)_3 + CO \rightarrow RuHCl(CO)_2(PPh_3)_2 + PPh_3 \quad (6)$$

latter product must derive from scavenging of released CO. In a separate experiment it was found that $RuHCl(CO)_2(PPh_3)_2$ reacts with $Na[Co(CO)_4]$ to produce $Ru(CO)_3(PPh_3)_2$ and apparently $HCo(CO)_4$ (eq 7). This latter product was not directly detected although Co metal was

$$RuHCl(CO)_2(PPh_3)_2 + Na[Co(CO)_4] \xrightarrow{40\ °C,\ 4\ h} Ru(CO)_3(PPh_3)_2 + \text{“}HCo(CO)_4\text{”} + NaCl \quad (7)$$

deposited. No $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ was produced in this latter reaction.

Reaction of $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ with CO. $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ reacts with CO at 1-atm pressure to give stepwise substitution of CO for PPh_3 (eq 8). When being stirred at 25 °C for 12 h under 1 atm of CO, the initially dark red solution of $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ changes color to orange. The –80 °C $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture in toluene-d_8 is shown in Figure A of the supplementary material. The resonances due to $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ have completely disappeared and have been replaced by resonances at δ 184.1 (d, $J_{^{31}P_{Ru}-^{31}P_{\mu}}$ = 104 Hz), 170.4 (s), 33.7 (d, $J_{^{31}P_{Ru}-^{31}P_{\mu}}$ = 104 Hz), and –5 (s, not shown in Figure A). The singlet which appears at δ –5 is due to free PPh_3.[28] The doublets at δ 184.1 and 33.7 are assigned to a binuclear product in which CO has replaced PPh_3 on Co, **2**. Substitution at Co is suggested because the δ 70.4 (d) for the PPh_3 ligand attached to Co in the initial compound has disappeared, and no new resonances appear in this chemical shift region. The δ 33.7 resonance of this product is in the same spectral region as the δ 34.5 resonance of PPh_3 on Ru in the parent complex, implying that a PPh_3 ligand is still attached to Ru in **2**. The singlet at δ 170.4 is assigned to a product in which both PPh_3 ligands have been replaced with CO, **3**. These spectral changes cleanly reverse upon heating the solution under reduced pressure, indicating that the substitution reactions of eq 8 are completely reversible.



Attempts to separate the substitution products from the parent compound and from each other did not meet with success due to extensive decomposition during chromatography. Thus IR spectra of the pure products were not obtained. However, a sample in which all of the starting complex had been converted to the product mixture showed bands at 2080 (m), 2010 (vs), 2000 (vs), 1983 (m, sh), and 1943 (vs) cm^{-1} which may be assigned to the two products of eq 8.

Reaction of $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ with HCl. A rapid (~1 h) color change from burgundy to amber occurs when $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ is stirred with a 3-fold excess of dimethylacetamide–hydrogen chloride at 25 °C in toluene solution. Removal of toluene and washing with hexane gave a yellow solid which showed IR bands (CH_2Cl_2) at 2040 (s), 1988 (s), 1982 (s, sh), and 1925 (s) cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of this yellow solid shows groups of resonances which can be assigned to two principal compounds which integrate in an approximate 3:1 ratio. Although neither of these compounds have been obtained in a pure form, their spectroscopic properties imply that they are isomers of $RuCoH(Cl)(\mu\text{-}PPh_2)(CO)_4(PPh_3)_2$. The ^{31}P NMR spectra have been particularly informative and, as noted above, resonances in the δ 50–70 chemical shift region can be attributed to Co-bound PPh_3 ligands, whereas those in the δ 25–30 spectral region are assigned to PPh_3 attached to Ru. The major product shows a doublet of doublets at δ 167.5 ($J_{^{31}P_{\mu}-^{31}P_{Ru}}$ = 213 Hz, $J_{^{31}P_{\mu}-^{31}P_{Co}}$ = 90 Hz) attributable to a bridging PPh_2 group, a doublet at δ 64.6 ($J_{^{31}P_{Co}-^{31}P_{\mu}}$ = 90 Hz) assignable to PPh_3 on Co, and a doublet at δ 23.3 ($J_{^{31}P_{Ru}-^{31}P_{\mu}}$ = 213 Hz) due to a PPh_3 on Ru. A small coupling of ~4 Hz is observed between the terminal phosphines on the

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(26) (a) Petersen, J. L.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186. (b) Carty, A. J.; MacLaughlin, S. A.; Taylor, N. J. *J. Organometal. Chem.* **1981**, *204*, C27. (c) Carty, A. J. *Adv. Chem. Ser.* **1982**, *No. 196*, 163. (d) Garrou, P. *Chem. Rev.* **1981**, *81*, 229. (e) Johannsen, G.; Stelzer, O. *Chem. Ber.* **1977**, *110*, 3438.

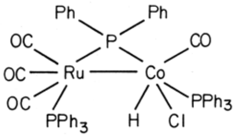
(27) (a) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. (b) Abrahamson, H. B.; Frazier, C. C.; Ginley, D. S.; Gray, H. B.; Lilienthal, J.; Tyler, D. R.; Wrighton, M. S. *Inorg. Chem.* **1977**, *16*, 1554. (c) Madach, T.; Vahrenkamp, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 573. (d) Honrath, U.; Vahrenkamp, H. *Ibid.* **1979**, *34B*, 1190. (e) Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 4908. (f) Madach, T.; Vahrenkamp, H. *Chem. Ber.* **1980**, *113*, 2675.

(28) Kosolopoff, G. M.; Maier, L. "Organic Phosphorus Compounds"; Wiley-Interscience: New York, 1972; Vol 1.

separate metal nuclei. The minor product shows a doublet of doublets at δ 152.6 ($J_{^{31}P_\mu-^{31}P_{Ru}}$ = 22 Hz, $J_{^{31}P_\mu-^{31}P_{Co}}$ = 87 Hz), a doublet at δ 66.2 ($J_{^{31}P_{Co}-^{31}P_\mu}$ = 87 Hz), and a doublet at δ 32.8 ($J_{^{31}P_{Ru}-^{31}P_\mu}$ = 22 Hz) which can be respectively assigned to a bridging PPh$_2$ ligand, PPh$_3$ on Co, and PPh$_3$ on Ru. A ~5-Hz coupling is also observed between the two terminal PPh$_3$ ligands.

The ^{1}H NMR spectrum of this mixture shows a doublet of doublets at δ −9.3 ($J_{^1H-^{31}P_\mu} \simeq J_{^1H-^{31}P_{Co}} \simeq$ 30 Hz) and a doublet of doublet of doublets at δ −10.5 ($J_{^1H-^{31}P_\mu} \simeq J_{^1H-^{31}P_{Co}} \simeq$ 33 Hz, $J_{^1H-^{31}P_{Ru}}$ = 56 Hz) in an overall relative intensity of ~3:1. The assignment of the coupling constants given above was confirmed by selectively decoupling the phenyl protons and analyzing the ^{31}P–^{1}H coupling in the ^{31}P spectrum. For example, the phosphorus on Ru in the minor isomer appears as a doublet at δ 32.8 in the ^{31}P{^{1}H} spectrum but splits into a doublet of doublets in the ^{31}P-{C$_6$H$_5$} decoupled spectrum with $J_{^{31}P_{Ru}-^1H}$ = 56 Hz.

The NMR spectra do not allow a definitive determination of the structures of these products. However, the downfield positions of the μ-PPh$_2$ resonances imply a metal–metal bond in both.[26] Since the initial complex is coordinatively saturated, addition of HCl with maintenance of the Ru–Co bond can only occur if one CO ligand is lost. Thus both compounds are formulated as isomers of RuCoH(Cl)(μ-PPh$_2$)(CO)$_4$(PPh$_3$)$_2$. Consider the major isomer first. The hydride couples only to PPh$_3$ on Co and to the μ-PPh$_2$ bridge, but not to PPh$_3$ on Ru. The three structures which appear most reasonable and which are consistent with the NMR data are shown in **4**–**6**, but we have no basis to distinguish among these. Since the hydride ligand in the minor isomer couples to both terminal phosphines it must bridge the Ru–Co bond. Reasonable structures for the minor isomer are **7** and **8**, but the present data do not allow an unambiguous assignment to be made.



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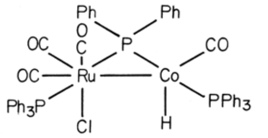

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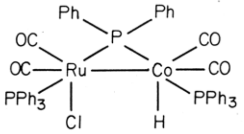

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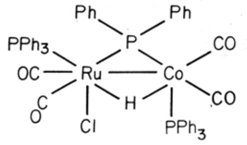

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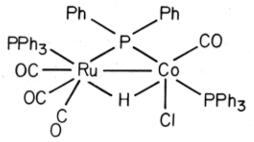


8

Crystal and Molecular Structure of RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$. An ORTEP drawing of RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ is shown in Figure 2. Pertinent bond length and bond angle data are given in Tables IV and V. The geometry about ruthenium is pseudooctahedral with Ru coordinated by PPh$_3$, three terminal carbonyls, the phosphido bridge, and the cobalt. Cobalt is coordinated by one PPh$_3$, two terminal carbonyls, the phosphido bridge, and Ru. The Ru–Co bond length is 2.750 (1) Å consistent with the presence of a single metal–metal bond. It is slightly longer than that found in [Ru$_3$Co(CO)$_{13}$]$^-$ (average 2.618 Å)[6] and [Ru$_2$Co$_2$(CO)$_{13}$] (average 2.677 (2) Å).[7] The Ru–Co bond length and Ru–P$_\mu$–Co angle (74.6 (1)°) are not substantially different from the corresponding Fe-Co bond lengths and the Fe–P$_\mu$–Co angles in FeCo(μ-PMe$_2$)(CO)$_7$ (2.666 (3) Å, 75.2 (1)°)[29a] and FeCo(μ-AsMe$_2$)(CO)$_7$ (2.703 (6) Å, 72.5 (2)°).[29b] These latter complexes have been formulated as having donor–acceptor Fe → Co metal–metal bonds with Fe contributing two electrons to the Co nucleus in each complex.[29]

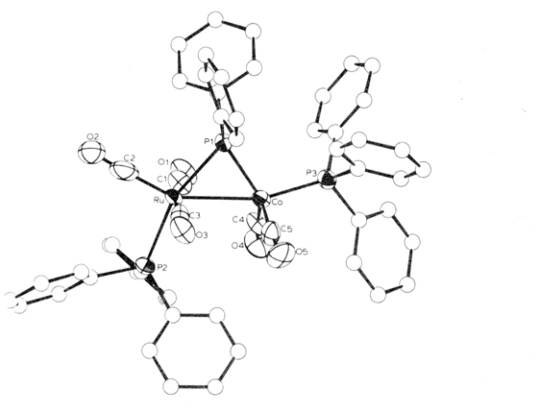
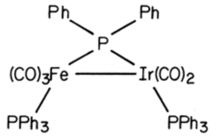


Figure 2. An ORTEP drawing of the structure of RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$. Thermal ellipsoids are drawn at the 25% probability level.

An interesting aspect of the structure of RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ is the cis arrangement of the PPh$_3$ ligand on Co with respect to the phosphido bridge while the PPh$_3$ on Ru is trans to the bridging ligand. This contrasts with the ligand arrangement in the isoelectronic complexes FeRh(μ-PPh$_2$)(CO)$_5$(PEt$_3$)$_2$ and FeIr(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ in which ^{31}P NMR spectra and an X-ray structural analysis of the FeIr complex show both PPh$_3$ ligands to be trans to the bridging ligand.[25a] The mutually trans arrangement in **9** appears to lead to severe steric congestion below the metal–metal vector as evidenced by the rather long 2.959 (1)-Å Fe–Ir bond length. We suggest that the different structures of the isoelectronic RuCo and FeIr complexes is a consequence of the increased tendency for Co to achieve an 18-valence-electron configuration via formation of a strong metal–metal bond. Numerous 16-valence-electron complexes of Ir(I) are known but relatively few for Co(I).[30a] Apparently a trans arrangement of all phosphines prevents a strong metal–metal interaction and thus the Ru–Co complex adopts the cis configuration.



9

Discussion

One of the most interesting aspects of this study is the facile synthesis of the phosphido-bridged complex RuCo(μ-PPh$_2$)(CO)$_5$(PPh$_3$)$_2$ simply upon stirring the reagents Na[Co(CO)$_4$] and RuHCl(CO)(PPh$_3$)$_3$ at or near room temperature. The complex presumably forms via elimination of benzene, which was detected by chromatography, through coupling of the hydride ligand with a phenyl group from one of the PPh$_3$ ligands. Such coupling reactions do

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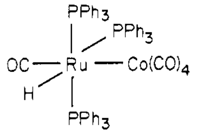
[29] (a) Keller, E.; Vahrenkamp, H. *Chem. Ber.* **1977**, *110*, 430. (b) *Ibid.* **1976**, *109*, 229.

[30] (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980. (b) Uhlig, E., Walther, D. *Coord. Chem. Rev.* **1980**, *33*, 1 and references cited therein.

have precedent.[30,31] For example, $Ir_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_3)_2$ forms via apparent elimination of benzene upon heating $IrH(CO)(PPh_3)_3$ (eq 9).[31] Also, Carty and co-workers[32] have recently demonstrated the H_2-induced loss of benzene from $Ru_3H(\mu\text{-}PPh_2)(CO)_9$ which converts the doubly bridging $\mu\text{-}PPh_2$ ligand into a triply bridging $\mu_3\text{-}PPh$ ligand (eq 10). The most likely mechanism for formation of the observed $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ complex is via the formation of an initial Ru–Co metal–metal bonded intermediate such as that shown.

$$2IrH(CO)(PPh_3)_3 \xrightarrow{150\text{–}190\ ^\circ C} Ir_2(\mu\text{-}PPh_2)_2(CO)_2(PPh_3)_2 + 2C_6H_6 \quad (9)$$

$$Ru_3H(\mu\text{-}PPh_2)(CO)_9 \xrightarrow{H_2,\ 80\ ^\circ C} Ru_3H_2(\mu_3\text{-}PPh)(CO)_9 + C_6H_6 \quad (10)$$

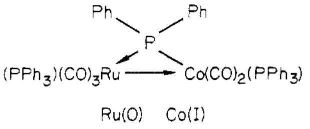


Steric congestion around the Ru center could serve to force H–Ph coupling to lead to benzene and to the PPh_2-substituted species.

Of possible relevance to this study is the recent report by Pez and co-workers[33] of the preparation of $K_2[Ru_2H_4(\mu\text{-}PPh_2)(PPh_3)_3]$ via the reaction of $[RuHCl(PPh_3)_2]_2$ with $K[C_{10}H_8]$ at low temperature. Although the structure of the latter complex has not been completely resolved, spectroscopic studies clearly show the presence of a $\mu\text{-}PPh_2$ ligand bridging two Ru centers. As in our reaction, a phosphido-bridged complex forms by treating a hydridochlororuthenium complex with an alkali-metal salt of a reducing agent, although $Na[Co(CO)_4]$ is a far weaker reducing agent than is $K[C_{10}H_8]$. However, the mechanisms of these two reactions leading to the $RuCo(\mu\text{-}PPh_2)$ and $Ru_2(\mu\text{-}PPh_2)$ complexes may not be at all similar since treatment of PPh_3 itself with strong reducing agents is well-known to lead to cleavage of the phosphorus–phenyl bonds, e.g., eq 11.[34] Coordinated PPh_3 should be even more susceptible to this type of reaction and thus Pez's[33] synthesis of $[Ru_2H_4(\mu\text{-}PPh_2)(PPh_3)_3]^{2-}$ may proceed through reduction of a coordinated PPh_3 by $K[C_{10}H_8]$. An analogous reaction seems less likely for $Na[Co(CO)_4]$.

$$PPh_3 + Li \xrightarrow{THF} LiPPh_2 + LiPh \quad (11)$$

Although $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ can be viewed as having a donor–acceptor metal–metal bond between Ru(0) and Co(I) centers, **10**, analogous to the formulations given for $FeCo(\mu\text{-}AsMe_2)(CO)_7$[27] and $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$,[25a] an alternative description would have the complex possessing a direct covalent single metal–metal bond between Ru(I) and Co(0) centers, **11**. The latter actually appears more consistent with the X-ray structural analysis. The data in Table IV show that the $Ru\text{–}P_1(\mu\text{-}PPh_2)$ distance is 0.051 Å shorter than the $Ru\text{–}P_2(PPh_3)$ distance, suggesting a strong covalent bond between Ru and the $\mu\text{-}PPh_2$ ligand, with the latter serving as the anionic ligand to balance the Ru^+ charge. In contrast, the $Co\text{–}P_1$ and $Co\text{–}P_3$ distances are identical within experimental error (Table IV). These results are in sharp contrast to data obtained for $FeIr(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ where a comparison of metal–phosphorus bond lengths clearly indicates an Fe(0)–Ir(I) formulation with the $IrP(PPh_2)$ length (2.292 (2) Å) significantly shorter than the $Ir\text{-}P(PPh_3)$ length (2.349 (2) Å).[25a]



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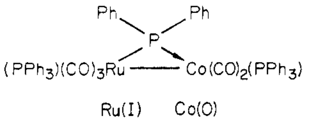
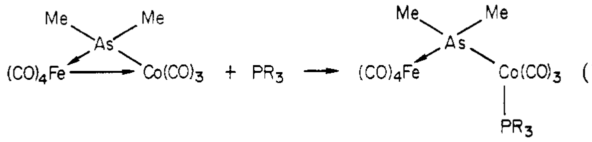


11

It is interesting that $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ and $FeCo(\mu\text{-}AsMe_2)(CO)_7$ show significantly different reactivity properties. The latter complex has been shown to undergo ready displacement of its donor–acceptor metal–metal bond by nucleophilic PR_3 ligands, e.g., eq 12.[35] The Fe–Co bonds in the substituted products can be reformed by thermally inducing CO dissociation. Multiple repetition of these steps combined with migration of the L ligands from Co to Fe leads to $FeCo(\mu\text{-}AsMe_2)(CO)_5(PR_3)_2$ complexes with one PR_3 ligand on each metal, analogous to $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$. The key point to recognize in these reactions is that PR_3 ligands cleave the metal–metal bond to give readily observable open intermediates. The latter require additional energy input to dissociate CO to reform the Co–Fe bond. In contrast, open intermediates are not observed in the substitution reactions of CO for PPh_3 in $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$. It could be argued that the RuCo complex undergoes substitution in a manner analogous to the FeCo complex but that the unbonded intermediates are far less stable and readily dissociate CO to reform the metal–metal bond. On the other hand, substitution could proceed by an entirely different path involving initial dissociation of PPh_3 to give a coordinatively unsaturated intermediate which then adds CO. Detailed kinetic studies will of course be necessary to distinguish between these two reaction paths.



(12)

Summary

The new phosphido-bridged complex $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ has been prepared and structurally characterized. The complex arises from the reaction of $RuHCl(CO)(PPh_3)_3$ with $Na[Co(CO)_4]$. The phosphido bridge apparently forms via coupling of the hydride ligand with a phenyl substituent of a PPh_3 ligand to give benzene and a PPh_2-substituted species. The new complex is remarkably robust as neither CO nor HCl induces fragmentation or bridge cleavage. Reaction with HCl leads to two isomers of $RuHCl(\mu\text{-}PPh_2)(CO)_4(PPh_3)_2$ which have been spectroscopically characterized, whereas reaction with CO leads to progressive substitution of CO for PPh_3.

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Registry No. 1, 82544-73-8; **2**, 82544-74-9; **3**, 82544-75-0; $RuH(Cl)(CO)_2(PPh_3)_2$, 56144-64-0; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $Na[Co(CO)_4]$, 14878-28-5; $RuHCl(CO)(PPh_3)_3$, 16971-33-8; Ru, 7440-18-8; Co, 7440-48-4.

Supplementary Material Available: Tables of derived parameters for the rigid-group atoms of $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ (Table A) and structure factors for $RuCo(\mu\text{-}PPh_2)(CO)_5(PPh_3)_2$ (Table B) and the $^{31}P\{^1H\}$ NMR spectrum (Figure A) of a mixture of **2** and **3** (11 pages). Ordering information is given on any current masthead page.

Electrochemical Study of the Oxidative Cleavage of Cobalt–Polyolefin Compounds in Strongly and Weakly Coordinating Solvents

Jerry Moraczewski and William E. Geiger*

Department of Chemistry, University of Vermont, Burlington, Vermont 05405

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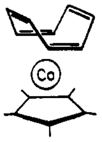
The oxidation of four cobalt–polyolefin compounds has been studied by direct-current polarography, cyclic voltammetry, and controlled potential coulometry. The compounds studied were (η^5-cyclopentadienyl)- or (η^5-permethylcyclopentadienyl)cobalt compounds of either cyclooctadiene (COD) or cyclooctatetraene (COT). In CH_3CN each compound underwent an irreversible oxidation which resulted in cleavage of the polyolefin ligand and production of cobaltocenium ion, Cp_2Co^+, and Co^{2+}. The reaction was quantitative, and an n value of 1.5 e was measured in agreement with this. In dichloromethane, the cyclooctadiene compounds (COD)CoCp and $(COD)Co(C_5Me_5)$ gave one-electron reversible oxidations, and an ESR spectrum of $(COD)Co(C_5Me_5)^+$ was obtained. As the cation radicals decomposed, COD was liberated. Oxidation of either (COT)CoCp or $(COT)Co(C_5Me_5)$ was irreversible, but cleavage of the Co–COT bond was not responsible for the irreversibility. An unidentified intermediate was formed which reacted over about a 1-h time scale to eventually liberate COT and form Cp_2Co^+.

Introduction

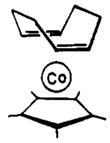
The oxidation of metal–π-olefin complexes has received attention as attempts have been made to activate such complexes toward nucleophilic attack. Strong oxidizing agents such as Br_2 or Ce^{4+} usually result in oxidative cleavage of the metal–carbon bonds and have been used for years as reagents to liberate a polyolefin from a metal–polyolefin complex.[1] The more recent work of Connelly and co-workers has shown that milder chemical oxidants (e.g., NO^+ or diazonium ions) which produce cation radicals of metal π complexes often lead to compounds in which the polyolefin remains bonded to the metal in a rearranged form. Their studies of the oxidation of iron–cyclooctatetraene compounds have been particularly noteworthy.[2,3]

We became interested in studying the oxidation of cobalt–polyolefin compounds as an outgrowth of our earlier work on these compounds, in which a one-electron *reduction* led to isomerization of the metal–olefin bond.[4] The question then arose as to the nature of the metal–hydrocarbon bond in *electron-deficient*, 17-electron, compounds which might be anodically generated from the neutral starting materials and the ultimate fate of the hydrocarbon as well. The electrochemical results which follow show that cation radicals can be generated by one-electron oxidation of cyclooctadiene (COD) compounds of cyclopentadienylcobalt but that their cyclooctatetraene (COT) analogues undergo rapid reaction to form intermediates in which the COT ring has most likely rearranged, while still remaining bonded to the metal. Ultimately, both $(COD)CoCp^+$ and the Co–COT^+ intermediate decompose to yield the free olefin and cobaltocenium ion, Cp_2Co^+. After this work was completed, a cyclic voltammetry study of cobalt π complex oxidations appeared[5] which included data on one of the four compounds reported below. Our conclusions concerning the oxidation mechanism of (COD)CoCp are in agreement with those reported by Koelle.[5] The four compounds studied are shown in **1**–**4**.



— = H (**1**)

— = CH_3 (**2**)



— = H (**3**)

— = CH_3 (**4**)

Experimental Section

Electrochemical techniques, compound preparation, and other experimental factors were as previously described.[4] The supporting electrolyte was 0.1 M Bu_4NPF_6, and potentials are reported vs. the aqueous saturated calomel electrode (SCE). Bulk electrolysis experiments and transfer of electrolyzed solutions to

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(6) Slope of the plot of $-E$ vs. log $[i/(i_d - i)]$, which is 59 mV for a one-electron reversible wave.

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