

Site Selectivity in Substitution Reactions of Heterobinuclear (CO)₄Ru(μ-PPh₂)Co(CO)₃(Ru-Co): Synthesis and Characterization of Terminal Anionic Hydrido and Halo Complexes [Et₄N][(X)(CO)₃Ru(μ-PPh₂)Co(CO)₃]. X-ray Structure of [Et₄N][(H)(CO)₃Ru(μ-PPh₂)Co(CO)₃]

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The synthesis and characterization of a series of heterobinuclear phosphido-bridged anionic complexes, [M][(X)(CO)₃Ru(μ-PPh₂)Co(CO)₃] (M = Et₄N, X = H, **2**; M = [(Ph₃P)₂N], X = I, **3a**; M = [(Ph₃P)₂N], X = Br, **3b**), are described. These products result from site-specific substitution of a carbonyl group on the ruthenium atom of (CO)₄Ru(μ-PPh₂)Co(CO)₃ (**1**) by a hydride or halide ion at the axial-cis and equatorial-trans positions, respectively. The molecular structure of [Et₄N][(H)(CO)₃Ru(μ-PPh₂)Co(CO)₃] (**2**) has been determined by X-ray diffraction. Crystal data: RuCoPO₆NC₂₈H₃₁, monoclinic crystals, space group *Cc* with *a* = 8.185 (1) Å, *b* = 22.621 (3) Å, *c* = 15.865 (2) Å, β = 98.67 (1)°, and *Z* = 4. The structure was solved and refined to *R* and *R_w* values of 0.035 and 0.043, respectively, by using 2302 observed reflections. In the phosphido-bridged heterobinuclear anion a terminal hydride occupies an axial site on ruthenium trans to a CO group and cis to the phosphido bridge with the latter supporting a strong Ru-Co bond (Ru-Co = 2.737 (1) Å). The reactions of the hydrido anion **2** toward MeI, H⁺, Ph₃P, and Ru₃(CO)₁₂ are discussed.

Introduction

There is growing evidence that for some catalytic processes, mixed-metal systems may be more effective than their monometallic components. Thus, selectivity for cobalt-catalyzed methanol homologation is substantially improved by additions of ruthenium derivatives.¹ Another notable example is the beneficial influence of added rhodium on the conversion of synthesis gas to ethylene glycol in the presence of ruthenium(III) acetylacetonate/tetra-butylphosphonium bromide catalysts² where maximum glycol productivity is achieved at Ru:Rh ratios of 1. Unfortunately, metal center cooperativity and the promotional effects of one metal on another are poorly understood phenomena even at the most fundamental level of discrete, well-characterized binuclear complexes.

For simple carbonyl substitution processes in heterobinuclear molecules several recent observations³⁻⁷ imply

preferential substitution at one metal site: at Re in (Re-Mn(CO)₁₀)₂,^{3b} at Mn and Re in (C₅H₅)₂(CO)₂FeM(CO)₅ (M = Mn, Re),⁴ and at Ru in RuCo(μ-PPh₂)(CO)₇.⁵ Earlier work indicated substitution at Co in (C₅H₅)₂(CO)₂FeCo(CO)₆⁶ and MnCo(CO)₉.⁷ Some of these results, taken at face value, might not be predictable per se from the chemistry of the mononuclear fragments. In the case of (CO)₄Ru(μ-PPh₂)Co(CO)₃,⁵ the isolated *thermodynamic* products of reactions with phosphines indicate a preference for CO monosubstitution at ruthenium whereas in an ostensibly similar Fe-Co system, (CO)₄Fe(μ-AsMe₂)Co(CO)₃, phosphine or phosphite addition initially occurs at the 5-coordinate cobalt site with Fe-Co bond cleavage,^{3a,8} the iron-substituted species (L)(CO)₃Fe(μ-AsMe₂)Co(CO)₃ being produced by subsequent CO loss, Fe-Co bond reformation, and isomerization. More recent studies on (CO)₄Fe(μ-PPh₂)Co(CO)₃ have shown that addition at the cobalt site with Fe-Co bond cleavage (L = P(OMe)₃, PPh₃), precedes thermal or photochemical conversion to the thermodynamic iron-monosubstituted products.⁹ The mechanism of isomerization from (CO)₄Fe(μ-PPh₂)Co(CO)₂L to the

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iron substituted isomer is unknown.

In order to shed further light on cooperativity effects influencing the mechanisms of these reactions and the thermodynamic stabilities of products, we have examined the reactions of $(\text{CO})_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (**1**) with anionic nucleophiles. In this paper we describe the synthesis and characterization of a series of anionic complexes $[(\text{X})\text{-}(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]^-$ ($\text{X} = \text{H, Br, I}$) resulting from CO displacement at the ruthenium atom of **1** together with an X-ray structural study of $[\text{Et}_4\text{N}][(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]$ (**2**). A communication 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 and ether, CaH_2 for hexane, $\text{Mg}(\text{OMe})_2$ for methanol, and P_2O_5 for CH_2Cl_2) and nitrogen saturated prior to use. Chromatographic separations were made on thick layer plates of Merck silica gel.

Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 225 instrument using either Nujol mulls or cyclohexane solutions in matched 0.5-mm NaCl cells. ^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 . ^{13}C NMR spectra were recorded either on a JEOL FX-900, operating at 20.45 MHz, or on a Bruker WP-80, operating at 20.115 MHz, spectrometer. ^{31}P spectra were proton noise decoupled, and shifts are reported relative to external 85% H_3PO_4 . ^1H and ^{13}C shifts are relative to Me_4Si . Microanalyses were obtained from the CNRS laboratory, Villeurbanne, France.

Syntheses. $[\text{Et}_4\text{N}][(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]$ (**2**). To a suspension of $(\text{CO})_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (**1**)¹⁰ (1 mmol, 0.54 g) in 70 mL of THF was added, under nitrogen, an excess of NaBH_4 (5 mmol, 0.19 g). The reaction mixture was stirred at room temperature for 2 h. After filtration on a frit, the solvent was removed under vacuum and a solution of tetraethylammonium chloride (1.5 mmol, 0.25 g) in 20 mL of methanol was added to the residue. The mixture was stirred for 5 min at room temperature; red crystals of **2** formed immediately and were separated by filtration (0.34 g, 53%).

2: mp 80–82 °C. IR (THF): $\nu(\text{CO})$ 2048 (m), 1983 (m), 1963 (s), 1942 (w), 1903 (m) cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (32.38 MHz, CD_2Cl_2 , 213 K): δ (ppm) 186.5 (s). ^1H NMR (80 MHz, CD_2Cl_2 , 303 K): δ (ppm) 7.4 (m, Ph), -9.25 (d, Ru-H, $^2J_{\text{HP}} = 22.3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.45 MHz, CD_2Cl_2 , 300 K): δ (ppm) 215.1 (d, $\text{Co}(\text{CO})_3$, $^2J_{\text{PC}} = 6.8$ Hz), 207.3 (d, Ru-CO (eq-trans), $^2J_{\text{PC}} = 46.2$ Hz), 203.1 (s, Ru-CO (eq-cis)), 198.3 (d, Ru-CO (ax-cis), $^2J_{\text{PC}} = 7.7$ Hz), 147.3 (d, P-C(Ph), $^1J_{\text{PC}} = 30.8$ Hz), 145.6 (d, P-C(Ph), $^1J_{\text{PC}} = 25.6$ Hz), 134.3 (d, ortho-C(Ph), $^2J_{\text{PC}} = 23.1$ Hz), 133.8 (d, ortho-C(Ph), $^2J_{\text{PC}} = 23.9$ Hz). ^{13}C NMR (20.45 MHz, CD_2Cl_2 , 300 K): δ (ppm) 215.1 (d), 207.3 (dd, Ru-CO (eq-trans), $^2J_{\text{CH}} = 6.8$ Hz), 203.1 (d, Ru-CO (eq-cis), $^2J_{\text{CH}} = 6.0$ Hz), 198.3 (d, Ru-CO (ax-cis), $^2J_{\text{CH}} = 27.8$ Hz).

$[\text{PPN}][(\text{I})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]$ (**3a**). (i) **From 1 and KI.** To a stirred solution of complex **1**¹⁰ (1 mmol, 0.54 g) in 60 mL of THF, at room temperature and under nitrogen, were added successively 1 mmol (0.17 g) of potassium iodide and 1 mmol (0.11 g) of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$. After 1 h of stirring at room temperature the solution was filtered on a frit and the solvent was evaporated under vacuum. The residue and a solution of 1.5 mmol (0.86 g) of $(\text{Ph}_3\text{PNPPH}_3)\text{Cl}[(\text{PPN})\text{Cl}]$ in 60 mL of dichloromethane were stirred for 5 min. The red complex **3a** crystallized on addition of hexane to the filtered dichloromethane solution; **3a** was obtained in 71% yield (0.84 g).

(ii) **From 1 and CH_3I .** Into 60 mL of THF were successively introduced 1 mmol (0.54 g) of complex **1**,¹⁰ 1.6 mmol (0.1 mL) of methyl iodide, and, on stirring at room temperature, 1 mmol (0.11 g) of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$. After 1 h of stirring followed by filtration, solvent evaporation, dissolution in a solution of 1.5 mmol

(0.86 g) of $(\text{PPN})\text{Cl}$ in 60 mL of dichloromethane, a second filtration, and crystallization in a dichloromethane-hexane mixture, complex **3a** was obtained in 92% yield (1.08 g).

(iii) **From 2 and CH_3I .** A suspension of the salt **2** (1 mmol, 0.64 g) in 60 mL of THF was prepared under nitrogen. An excess of methyl iodide (1.6 mmol, 0.1 mL) was added. The mixture was stirred for 1.5 h at room temperature, and after filtration the solvent was evaporated. Treatment of the residue by stirring with a solution of $(\text{PPN})\text{Cl}$ (1.5 mmol (0.86 g) in 60 mL of dichloromethane) for 5 min, followed by filtration and crystallization, in a dichloromethane-hexane mixture, led to the isolation of 45% (0.53 g) of **3a**.

Anal. Calcd for $\text{C}_{54}\text{H}_{40}\text{ICoNO}_6\text{P}_3\text{Ru}$ (**3a**): C, 55.20; I, 10.76; P, 7.88. Found: C, 55.53; I, 9.81; P, 8.11. IR (Nujol): $\nu(\text{CO})$ 2070 (w), 2045 (vs), 2004 (s), 1977 (s), 1947 (s), 1913 (vs), 1898 (vs) cm^{-1} . ^{31}P NMR (CD_2Cl_2 , 32.38 MHz, 193 K): δ (ppm) 190.7 (s, $\mu\text{-PPh}_2$), 21.2 (s, PPN). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.115 MHz, CD_2Cl_2 , 193 K): δ (ppm) 212.0 (d, $\text{Co}(\text{CO})_3$, $^2J_{\text{PC}} = 7.1$ Hz), 199.2 (d, Ru-CO (ax-cis), $^2J_{\text{PC}} = 8.5$ Hz), 198.8 (s, Ru-CO (eq-cis)).

$[\text{PPN}][(\text{Br})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]$ (**3b**). Complex **1**¹⁰ (1 mmol, 0.54 g) and 1 mmol of potassium bromide (0.12 g) were stirred in 70 mL of THF. One equivalent of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ (0.11 g) was then added. The mixture was stirred at room temperature for 1 h. The solution was filtered, the solvent removed under vacuum and the residue was stirred with a solution of 1.5 mmol (0.86 g) of $(\text{PPN})\text{Cl}$ in 40 mL of methanol. The red complex **3b** precipitated, was isolated by filtration after 5 min, washed twice with 10 mL of cold methanol, dried under vacuum, and isolated in 41% yield.

Anal. Calcd for $\text{C}_{54}\text{H}_{40}\text{BrCoNO}_6\text{P}_3\text{Ru}$ (**3b**): P, 8.20; Br, 7.06. Found: P, 8.45; Br, 7.62. IR (Nujol): $\nu(\text{CO})$ 2073 (w), 2045 (w), 2006 (s), 1974 (s), 1944 (s), 1910 (s), 1896 (vs) cm^{-1} . ^1H NMR (CDCl_3 , 80 MHz, 300 K): δ (ppm) 7.52–8.10 (m, C_6H_5). ^{31}P NMR (CD_2Cl_2 , 32.38 MHz, 193 K): δ (ppm) 185.3 (s, $\mu\text{-PPh}_2$), 21.3 (s, PPN).

$(\text{Ph}_3\text{P})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (**4**). Complex **2** (0.3 g, 0.46 mmol) was dissolved in 60 mL of dry THF, 0.4 mmol (0.12 g) of triphenylphosphine was first added, and then on stirring a slight excess of HPF_6 (0.48 mmol) was introduced. After 6 h of stirring the THF was evaporated and crystallization of the product in dichloromethane-ether afforded 35% of the dark red complex **4**.⁵ ^{31}P NMR (CD_2Cl_2 , 32.38 MHz, 193 K): trans isomer, δ (ppm) 183.5 (d, $\mu\text{-PPh}_2$), 32.5 (s, PPh_3 , $^2J_{\text{PP}} = 104$ Hz); cis isomer, δ (ppm) 170.3 (s, $\mu\text{-PPh}_2$), 37.2 (PPh_3).

$\text{Ru}_3(\mu\text{-H})_2(\mu\text{-PPh}_2)_2(\text{CO})_8$ (**5**). Complex **2** (0.3 g, 0.46 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (0.46 mmol, 0.28 g) in 70 mL of THF were reacted at 60 °C for 12 h. After filtration and evaporation of the solvent, the products were chromatographed on a thick layer of silica gel (eluant hexane). $\text{Ru}_3(\text{CO})_{12}$ was eluted first, followed by complex **5**, which was crystallized in a dichloromethane-hexane mixture and obtained in 12% yield (0.05 g). Complex **5** was identified by its infrared and NMR spectra as $\text{Ru}_3(\mu\text{-H})_2(\mu\text{-PPh}_2)_2(\text{CO})_8$.¹³

X-ray Analysis. Crystallographic Data, Collection, and Reduction. Single crystals of **2** were grown from methanol at -5 °C. A suitable crystal of dimensions 0.22 × 0.22 × 0.27 mm was glued to a glass fiber and mounted on a eucentric goniometer head for space group determination and unit cell measurement. The crystal was centered on a $\text{P}2_1$ diffractometer, and the Syntex autoindexing and cell refinement routines were used to derive accurate unit cell parameters. An inspection of diffraction data revealed systematic absences hkl , $h+k=2n+1$, and $h0l$, $l=2n+1$, consistent with the monoclinic space groups Cc or $C2/c$. As shown by the subsequent solution and refinement of the structure Cc was the correct space group. With $Z=4$ and space group $C2/c$, the molecule would be required to have either a center of symmetry or a twofold axis, neither of which are reasonable for this heterobinuclear species. Intensity data were collected as indicated in Table I by using $\text{Mo K}\alpha$ radiation. Intensities of two standard reflections, 008 and 400, monitored every 100 measurements varied by only $\pm 2\%$ during data collection. Diffraction intensities were corrected for Lorentz and polarization

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Table I. Crystal Data, Intensity Collection, Reduction, and Refinement for $[\text{Et}_4\text{N}][(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPH}_2)\text{Co}(\text{CO})_3] (2)$

formula	$\text{RuCoPO}_6\text{NC}_{26}\text{H}_{31}$
mol wt	644.58
cryst class	monoclinic
cryst color, habit	red prisms
space group	<i>Cc</i>
<i>a</i> , Å	8.185 (1)
<i>b</i> , Å	22.621 (3)
<i>c</i> , Å	15.865 (2)
β , deg	98.67 (1)
<i>V</i> , Å ³	2903.9 (7)
<i>Z</i>	4
ρ_{calcd} , g cm ⁻³	1.474
<i>F</i> (000)	1312
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	11.96
cryst size, mm	0.22 × 0.22 × 0.27
transmissn factors	0.70–0.80
radiatn	graphite monochromated ($\lambda = 0.710$ 69 Å), Mo K α
<i>T</i> (K)	297 ± 1
2 θ range (deg)	3.2–50
octants data	<i>h, k, ± l</i>
scan speed, deg min ⁻¹	2.93–29.30
scan width, deg	0.8° below K α_1 to 0.8° above K α_2
stds (every 100 measurements)	0.08; 400
variance of stds	±2%
reflectns measd	2572
reflectns obsd (<i>I</i> > 3 σ (<i>I</i>))	2302
<i>R</i> (metal atom only)	0.195
<i>R</i> (isotropic)	0.071
final <i>R</i>	0.035
<i>R</i> _w	0.043
<i>w</i> ⁻¹	2.22 – 0.058 <i>F</i> _o + 0.001 39 <i>F</i> _o ²
max residuals, e Å ³	0.6

effects but not absorption due to the low value of $\mu_{\text{MoK}\alpha}$ (11.96 cm⁻¹) and the equidimensional crystal and reduced to structure factors in the normal way.

Solution and Refinement of the Structure. The structure was solved by Patterson and Fourier techniques using the full set of 2302 observed reflections. The ruthenium, cobalt, and phosphorus atoms were readily located in a Patterson map and all other non-hydrogen positions in subsequent Fourier syntheses. Refinement of non-hydrogen positional and isotropic temperature coefficients gave an *R* value ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.071. With anisotropic coefficients, several further cycles of refinement reduced *R* to 0.045. At this point it was evident that the tetraethylammonium cation was slightly disordered. A difference Fourier map clearly revealed a peak of 0.4 e Å⁻³ consistent with the presence of a terminal hydride on the ruthenium atom. Although positions of several phenyl ring hydrogen atoms were also located because of the limitations of the data set and cation disorder, hydrogen atoms on the anion were not included nor refined in subsequent structure factor calculations. Convergence was achieved at *R* = 0.035 with *R*_w ($R_w = [\sum w(|F_o| - |F_c|)^2] / \sum w(F_o)^2$)^{1/2} = 0.043. The function minimised in least squares refinement was $\sum w(|F_o| - |F_c|)^2$. In the final cycles a weighting scheme $w^{-1} = 2.22 - 0.058|F_o| + 0.001 39 |F_o|^2$ was introduced. In a final difference map the largest peaks were at a level of 0.6 e Å⁻³ in the region of the disordered cation. Around the metal atoms, peaks and troughs of electron density were at the level of ±0.3 e Å⁻³. Refinement in space group *Cc* with *h* and *l* indices reversed (*hkl* instead of *hkl*) made no significant difference in the *R* value nor in the positions of any atoms. All calculations were carried out on IBM 4341 systems in the Department of Computer Services, University of Waterloo using a menu of programs described elsewhere.¹⁴ Neutral atom scattering factors were taken from ref 15 with corrections for anomalous dispersion for Co and Ru included. All refinements used the full matrix. Table II lists atomic positions, and Tables III and IV list a se-

Table II. Atomic Positional Parameters (×10⁴) for $[\text{Et}_4\text{N}][(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPH}_2)\text{Co}(\text{CO})_3] (2)$

atom	<i>x</i>	<i>y</i>	<i>z</i>
Ru	0	863.0 (3)	0
Cc	2509.8 (15)	1662.1 (5)	-3.2 (8)
P	1765.2 (23)	127.4 (8)	1119.4 (12)
C(1)	-2470 (9)	1897 (3)	-33 (5)
C(21)	-1741 (11)	-114 (4)	768 (7)
C(3)	-519 (10)	485 (5)	-1868 (5)
C(4)	4140 (12)	2714 (3)	725 (6)
C(5)	5009 (10)	852 (4)	-503 (7)
C(6)	523 (10)	2116 (4)	-1501 (5)
C(1)	-1577 (9)	1515 (4)	-22 (5)
C(2)	-1122 (12)	263 (4)	459 (7)
C(3)	-350 (11)	643 (4)	-1183 (6)
C(4)	3503 (12)	2304 (4)	443 (7)
C(5)	4032 (10)	1169 (4)	-313 (6)
C(6)	1274 (11)	1923 (4)	-903 (6)
C(7)	3175 (9)	793 (3)	1834 (5)
C(8)	4874 (10)	813 (4)	1841 (6)
C(9)	5920 (12)	468 (5)	2414 (7)
C(10)	5254 (11)	85 (4)	2963 (6)
C(11)	3564 (11)	69 (4)	2946 (6)
C(12)	2550 (10)	414 (3)	2395 (5)
C(13)	971 (10)	1725 (3)	1924 (5)
C(14)	-681 (10)	1672 (4)	2057 (6)
C(15)	-1283 (13)	2045 (5)	2648 (6)
C(16)	-222 (15)	2434 (5)	3130 (6)
C(17)	1384 (15)	2472 (4)	3013 (6)
C(18)	2021 (11)	2130 (4)	2415 (5)
N	3734 (9)	1269 (3)	5563 (5)
C(19)	4496 (17)	1708 (4)	4973 (8)
C(20)	5602 (22)	1381 (7)	4377 (10)
C(21)	5045 (15)	886 (5)	6068 (8)
C(22)	6391 (16)	1244 (6)	6674 (9)
C(23)	2868 (16)	1672 (5)	6121 (8)
C(24)	1958 (18)	1317 (6)	6760 (10)
C(25)	2537 (16)	848 (4)	5022 (8)
C(26)	1103 (16)	1144 (6)	4474 (9)
H(1)	1550	450	0

Table III. Bond Lengths (Å) for $[\text{Et}_4\text{N}][(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPH}_2)\text{Co}(\text{CO})_3] (2)$

Ru–Co	2.737 (1)	Ru–P	2.307 (2)
Ru–C(1)	1.957 (8)	Ru–C(2)	1.848 (10)
Ru–C(3)	1.920 (9)	Ru–H(1)	1.58
Co–P	2.157 (2)	Co–C(4)	1.761 (10)
Co–C(5)	1.795 (9)	Co–C(6)	1.724 (9)
P–C(7)	1.843 (8)	P–C(13)	1.832 (8)
C(1)–O(1)	1.131 (10)	C(2)–O(2)	1.140 (13)
C(3)–O(3)	1.134 (13)	C(14)–O(4)	1.222 (13)
C(5)–O(5)	1.148 (13)	C(6)–O(6)	1.138 (13)
C(7)–C(8)	1.390 (11)	C(8)–C(9)	1.389 (13)
C(9)–C(10)	1.397 (14)	C(10)–C(11)	1.380 (12)
C(11)–C(12)	1.358 (12)	C(12)–C(7)	1.387 (11)
C(13)–C(14)	1.405 (12)	C(14)–C(15)	1.404 (14)
C(15)–C(16)	1.383 (15)	C(16)–C(17)	1.358 (17)
C(17)–C(18)	1.398 (13)	C(18)–C(13)	1.393 (11)
N–C(19)	1.557 (14)	N–C(21)	1.511 (14)
N–C(23)	1.519 (15)	N–C(25)	1.534 (14)
C(19)–C(20)	1.586 (21)	C(21)–C(22)	1.573 (18)
C(23)–C(24)	1.567 (19)	C(25)–C(26)	1.509 (18)

lection of bond lengths and angles, respectively. All other data (Table S1, thermal parameters, and Table S2, structure factors) are available as, supplementary material.

Results and Discussion

Synthesis and Characterization of $[\text{Et}_4\text{N}][(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPH}_2)\text{Co}(\text{CO})_3] (2)$. The addition of hydride to neutral homopolymetallic carbonyl complexes has already been shown to constitute a route, via carbonyl substitution, to anionic clusters containing a bridging hydrido ligand. A representative example was given by the reaction of sodium borohydride with $\text{Ru}_3(\text{CO})_{12}$ which led to the cluster anion $[\text{Ru}_3(\mu\text{-H})(\text{CO})_{11}]^-$,¹⁶ an efficient

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Table IV. Bond Angles (deg) for $[\text{Et}_4\text{N}][(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2\text{Co}(\text{CO})_3)](2)$

Co-Ru-P	49.74 (5)	Co-Ru-C(1)	89.7 (2)
Co-Ru-C(2)	154.6 (3)	Co-Ru-C(3)	99.8 (2)
Co-Ru-H(1)	78	P-Ru-C(1)	92.7 (2)
P-Ru-C(2)	106.3 (3)	P-Ru-C(3)	147.1 (2)
P-Ru-H(1)	80	C(1)-Ru-C(2)	101.2 (3)
C(1)-Ru-C(3)	100.2 (3)	C(1)-Ru-H(1)	167
C(2)-Ru-C(3)	100.7 (4)	C(2)-Ru-H(1)	91
C(3)-Ru-H(1)	81	Ru-Co-P	54.71 (5)
Ru-Co-C(4)	147.8 (3)	Ru-Co-C(5)	98.2 (2)
Ru-Co-C(6)	83.2 (3)	P-Co-C(4)	100.2 (3)
P-Co-C(5)	105.4 (3)	P-Co-C(6)	128.3 (3)
C(4)-Co-C(5)	108.9 (4)	C(4)-Co-C(6)	103.2 (4)
C(5)-Co-C(6)	109.4 (4)	Ru-P-Co	75.55 (5)
Ru-P-C(7)	120.0 (2)	Ru-P-C(13)	120.9 (2)
Co-P-C(7)	121.4 (2)	Co-P-C(13)	121.3 (2)
C(7)-P-C(13)	98.9 (3)	Ru-C(1)-O(1)	179.0 (3)
Ru-C(2)-C(2)	176.5 (4)	Ru-C(3)-O(3)	176.3 (4)
Co-C(4)-C(4)	179.7 (4)	Co-C(5)-O(5)	179.4 (4)
Co-C(6)-C(6)	176.4 (4)		
P-C(7)-C(8)	121.3 (3)	P-C(7)-C(12)	120.0 (3)
C(12)-C(7)-C(8)	118.7 (4)	C(7)-C(8)-C(9)	120.3 (5)
C(8)-C(9)-C(10)	119.7 (5)	C(9)-C(10)-C(11)	119.2 (4)
C(10)-C(11)-C(12)	120.8 (5)	C(11)-C(12)-C(7)	121.2 (4)
P-C(13)-C(14)	120.5 (3)	P-C(13)-C(18)	119.7 (3)
C(18)-C(13)-C(14)	119.8 (5)	C(13)-C(14)-C(15)	119.5 (5)
C(14)-C(15)-C(16)	119.8 (5)	C(15)-C(16)-C(17)	120.3 (6)
C(16)-C(17)-C(18)	121.6 (5)	C(17)-C(18)-C(13)	118.9 (5)
C(19)-N-C(21)	111.5 (6)	C(19)-N-C(23)	103.4 (6)
C(19)-N-C(25)	109.8 (6)	C(21)-N-C(23)	113.1 (6)
C(21)-N-C(25)	106.4 (6)	C(23)-N-C(25)	112.6 (6)
N-C(19)-C(20)	112.2 (6)	N-C(21)-C(22)	113.9 (5)
N-C(23)-C(24)	112.3 (6)	N-C(25)-C(26)	114.9 (5)

catalyst for a variety of reaction.¹⁷ The case of access to the simple heterobimetallic complex $(\text{CO})_4\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (**1**),¹⁰ via the reaction of $\text{RuCl}_2(\text{PPh}_2\text{H})(p\text{-cymene})$ with $\text{Co}_2(\text{CO})_8$, offered the possibility of studying its reaction with borohydride in an effort to probe site selectivity toward attack by hydride ion. Several reaction pathways can be envisaged for **1**: attack at cobalt or ruthenium with CO displacement; Ru-Co bond cleavage and H^- addition; reaction at the phosphido bridge. Numerous examples of the conversion of a phosphido bridge into a terminal PPh_2H ligand are now known.¹⁸ Previous studies^{5,12,19} of carbonyl substitution reactions of complex **1** by phosphorus groups have indicated that the phosphido bridge is maintained and that mono- and disubstitution take place at the ruthenium atom. Substitution at the cobalt atom of **1** was only observed with bis(diphenylphosphino)methane (dppm),¹² affording the double-bridged complex $(\text{CO})_2\text{Ru}(\mu\text{-dppm})(\mu\text{-PPh}_2)\text{Co}(\text{CO})_2$ as well as the chelate isomer $(\text{CO})_2(\text{dppm})\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$, and with phosphite groups when two phosphite ligands are already bonded to the ruthenium atom, giving $(\text{CO})_2\{\text{P}(\text{OR})_3\}_2\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_2\{\text{P}(\text{OR})_3\}$.¹⁹

On reaction, a red solution of **1** mmol of **1** in THF with excess (5 mmol) of NaBH_4 resulted in a gradual change in color to orange. After 2 h the infrared spectrum no longer exhibited the 2107 cm^{-1} band characteristic of **1**. Metathetical exchange of the Na^+ cation with a solution

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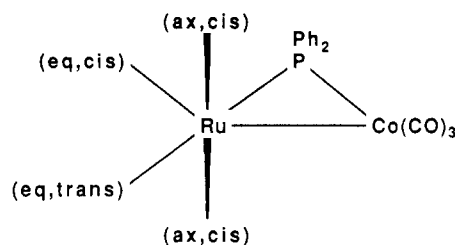
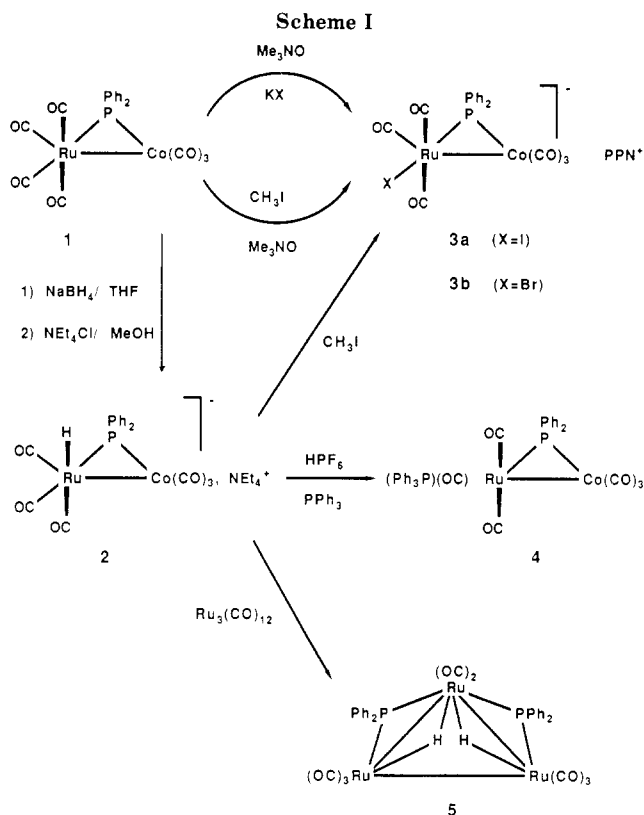


Figure 1. Stereochemical assignments at the octahedral ruthenium site defined relative to the Ru, P, Co plane (axial, equatorial) and the phosphido bridge (cis, trans).



of tetraethylammonium chloride in methanol led to the precipitation of the orange anionic complex **2** in 53% yield (Scheme I).

The infrared spectrum of **2** indicated the presence of terminal carbonyls only. The ^{31}P NMR spectrum at 213 K showed a singlet at δ 185.5, consistent with the presence of a phosphido group bridging the Ru-Co bond.^{5,10} The ^1H NMR spectrum of **2** at 303 K showed a sharp doublet at δ -9.25 (1 H), with a $^2J_{\text{PH}}$ value of 22.3 Hz. This sharp doublet at room temperature indicates that the hydride ligand in **2** is bonded only to the ruthenium atom because a hydrogen nucleus directly linked to cobalt gives a broad signal at 297 K due to the ^{59}Co quadrupole.²⁰

The stereochemistry of complex **2** was unambiguously established by ^{13}C NMR studies. Relative equatorial (eq) and axial (ax) positions of ligands at the Ru sites are given with respect to the equatorial $\text{Ru}(\mu\text{-P})\text{Co}$ plane and cis and trans positions with respect to the phosphido-bridged phosphorus atom^{5,12} according to Figure 1.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** provided unequivocal evidence for the nonequivalence of the phenyl groups linked to the phosphorus atom. For instance the carbon nuclei bonded to the phosphorus nucleus give doublet signals at δ 147.3 ($^1J_{\text{PC}} = 30.8$ Hz) and 145.6 ($^1J_{\text{PC}} = 25.6$

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Table V. Comparison of Carbonyl ^{13}C NMR Data of Complexes 1, 2, and 3a^c

		CO-Co	CO-Ru		
			eq, trans	eq, cis	ax, cis
1: ^a $^{13}\text{C}\{^1\text{H}\}^b$	δ (ppm)	208.0 (d)	197.0 (d)	190.6 (6)	192.8 (d)
	$^2J_{\text{PC}}$ (Hz)	6.9	39.8	...	13.7
2: $^{13}\text{C}\{^1\text{H}\}^c$	δ (ppm)	215.1 (d)	207.3 (d)	203.1 (s)	198.3 (d)
	$^2J_{\text{PC}}$ (Hz)	6.8	46.2	...	7.7
2: $^{13}\text{C}^c$	δ (ppm)	215.1 (d)	207.3 (dd)	203.1 (d)	198.3 (dd)
	$^2J_{\text{HC}}$ (Hz)	...	6.8	6.0	27.8
3a: $^{13}\text{C}\{^1\text{H}\}^b$	δ (ppm)	212.0 (d)	...	198.9 (s)	199.2 (d)
	$^2J_{\text{PC}}$ (Hz)	7.1	8.5

^a in CD_2Cl_2 solution at 193 K. ^b 20.115 MHz. ^c 20.45 MHz.

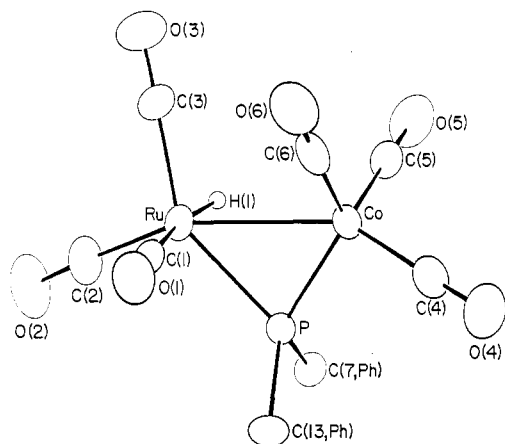


Figure 2. The molecular structure of the anion $[(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]^-$ of 2.

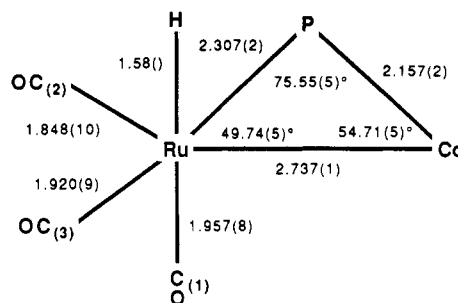
H_z). This is consistent with nonequivalent faces of the $\text{Ru}(\mu\text{-P})\text{Co}$ plane and with an axial-cis position of the hydride on the ruthenium atom.

The comparison of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2 with that of complex 1 allows the assignment of the carbonyl resonances (Table V). The doublet at the lower field was shown to be due to the three carbon nuclei bonded to the cobalt atom.^{10b} For the upfield signals corresponding to the carbonyl nuclei bonded to the ruthenium atom, their assignment was based on the value of the coupling constants corresponding to the sequence:^{10b} $^2J_{\text{P-C}(\text{eq-trans})} \gg ^2J_{\text{P-C}(\text{ax-cis})} \gg ^2J_{\text{P-C}(\text{eq-cis})} \approx 0$. Consequently in the spectrum of 2 (Table V), the resonances at δ 207.3 (d, $^2J_{\text{P-C}} = 46.2$ Hz), 203.1 (s), and 198.3 (d, $^2J_{\text{P-C}} = 7.7$ Hz) correspond to the carbonyls at the equatorial-trans, equatorial-cis, and axial-cis positions, respectively. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2 shows a coupling of the proton with each of these three carbonyl carbon nuclei. The larger value of the coupling constant $^2J_{\text{H-C}}$ observed for the ax-cis carbonyl carbon (27.8 Hz) indicates that the hydride has a position trans to this carbonyl and therefore occupies the axial-cis position with respect to the $\text{Ru}(\mu\text{-P})\text{Co}$ plane. As complex 2 was the first example of a heterobinuclear Ru-Co derivative containing a terminal hydride,¹¹ an X-ray diffraction study of 2 was undertaken and led to the confirmation of its stereochemistry established by NMR.

Description and Discussion of the Structure of 2.

An ORTEP plot of the molecular structure of the complex anion 2, looking down on the $\text{Ru}, \text{P}, \text{Co}$ plane, is shown in Figure 2. Complex 2 is formed by two 15-electron $\text{HRu}(\text{CO})_3$ and $\text{Co}(\text{CO})_3$ moieties held together by the phosphido bridge and a Ru-Co bond. The short Ru-Co distance in 2 (2.737 (1) Å) is consistent with a strong metal-metal interaction and leads to an acute Ru-P-Co angle (75.55 (5)°). Significant structural features of 2 are compared to those of a closely related complex, $(\text{Ph}_3\text{P})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (4)⁵ in Figure 3.

Structure of 2



Structure of 4

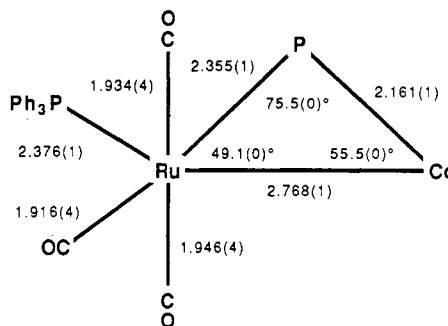


Figure 3. A comparison of structural parameters for $(\text{Et}_4\text{N})-[(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]$ (2) and $(\text{Ph}_3\text{P})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (4).

There is a significant change in stereochemistry at the cobalt from $(\text{Ph}_3\text{P})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ to the anion $[(\text{H})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3]^-$. Thus in the former the largest bond angle subtended at the cobalt atom is $\text{P}(1)\text{-Co-C}(6)$ ($140.9(1)^\circ$) with $\text{C}(6)\text{-O}(6)$ very approximately trans to the phosphido bridge. In the anion of 2, however, the largest angle at cobalt is $\text{Ru-Co-C}(4)$ ($147.8(3)^\circ$), placing the carbonyl group $\text{C}(4)\text{-O}(4)$ trans to the Ru-Co bond. The cobalt stereochemistry thus more closely approaches that of a trigonal bipyramid in 2 than in 4. Alternatively, if the metal-metal vector is ignored, the cobalt geometry in both molecules could be described as distorted tetrahedral.

The coordination geometry around the ruthenium atom is almost octahedral. The hydrogen atom $\text{H}(1)$ and the $\text{C}(1)\text{-O}(1)$ carbonyl occupy axial sites perpendicular to the $\text{Ru}, \text{P}, \text{Co}$ plane and are approximately trans to one another ($\text{H}(1)\text{-Ru-C}(1) = 167(1)^\circ$). It is noteworthy that the terminal hydride exerts a strong trans influence on the Ru-C(1) bond with the Ru-C(1) bond length (1.957 (8) Å) significantly longer than any of the other Ru-Co distances

in 2 and 4, including those mutually trans in 4 (Figure 3). The Ru–H bond length (1.58 Å) is marginally longer than the terminal Ru–H distance of 1.40 (5) Å observed for the binuclear Ru–Rh compound $\text{RuRhH}_2(\mu\text{-H})(\text{dppm})_2$ (1.40 (5) Å),²¹ but it is doubtful whether much chemical significance can be attached to X-ray determined terminal Ru–H distances in view of the large estimated standard deviations. Other Ru–H bond lengths recently reported (Ru–H(1) = 1.654 Å in $\text{Ru}_2\text{H}_4\text{N}_2(\text{PPh}_3)_4$,²² Ru(1)–H(1_r) = 1.648 (71) and Ru(2)–H(2_r) = 1.720 (57) Å in $\text{Ru}_2\text{H}_4(\text{PMe}_3)_6$,²³ Ru–H = 1.58 (15) Å in *cis*- $\text{H}_2\text{Ru}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{C}_6\text{H}_6$,²⁴ Ru–H = 1.67 (7) Å in $\text{H}_2\text{Ru}_2(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2[\text{Me}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Me})\text{CH}_2]_2$ ²⁵ illustrate the range of values for terminal ruthenium–hydrogen distances. On the other hand, the terminal Ru–H distance in 2 is below the range normally found for hydrides bridging two ruthenium atoms. A typical comparison with $[(\mu\text{-H})\text{Ru}_2(\text{CO})_6(\mu\text{-CHC}(\text{Ph})\text{NEt}_3)(\mu\text{-PPh}_2)]\text{-PF}_6$ where Ru–H distances of 1.77 (4) and 1.94 (4) Å have been reported.²⁶

Synthesis and Characterization of [PPN][(X)(CO)₃Ru(μ-PPh₂)Co(CO)₃] (X = I (3a), Br (3b)). Halides have been shown to be catalysts for the substitution by neutral ligands of carbonyls in mononuclear²⁷ and polynuclear²⁸ complexes. Furthermore, iodide has been used as a promoter for methanol homologation catalyzed by ruthenium cobalt systems.¹ Since the formation of complex 2 indicated the possibility of accessing anionic Ru–Co complexes by carbonyl substitution reactions, we investigated the synthesis of Ru–Co complexes containing halides from derivative 1. When complex 1 and potassium iodide were heated in THF and at reflux, no apparent reaction took place. We have shown that Me_3NO , a carbonyl displacing reagent, allows the selective substitution of one carbonyl of 1 in THF at room temperature. In the presence of triphenylphosphine the only derivative obtained (in 92% yield) was $(\text{Ph}_3\text{P})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ (4). In an analogous way, complex 1 with 1 equiv of Me_3NO and potassium iodide in THF reacts at room temperature to give a red salt which was isolated by cation exchange after treatment with (PPN)Cl in 71% yield and identified as 3a (Scheme I). Complex 1 reacts in THF with 1 equiv of Me_3NO in the presence of potassium bromide affording, after treatment with (PPN)Cl, complex 3b in 40% yield.

The infrared spectra of complexes 3a and 3b are closely similar and exhibit only terminal carbonyl absorption bands. The elemental analyses are consistent with the substitution of one carbonyl of 1 by one halide ligand. The ³¹P NMR spectra show one singlet at low field (δ 190.7 (3a) and 185.5 (3b)) which is sharp only at 193 K. This is compatible with retention of the phosphido group bridging the Ru–Co bond.²⁹ A comparison of the ¹³C{¹H} NMR

spectrum of 3a with spectra of complexes 1 and 2 (Table V) establishes that the halide is located on the ruthenium atom in the equatorial-trans position in the ¹³CO(Ru) resonance region; the doublet with a large ²J_{PC} coupling constant characteristic of the equatorial-trans carbonyl carbon nucleus is absent from the spectrum of 3a. The similarity observed between the infrared spectrum of 3a and 3b suggests that in 3b the bromide ligand is also located at the equatorial-trans position on the ruthenium atom.

Treatment of 1 with Me_3NO in THF leads to a red intermediate which was not isolable but was presumed to be $(\text{CO})_3(\text{THF})\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$ on the basis of its infrared and ³¹P NMR spectra³⁰ and its reactivity under mild conditions with triphenylphosphine leading to 4 or with halides affording complexes 3. We have examined the reactivity of this intermediate toward methyl iodide, a reaction which a priori should lead to oxidative addition or capture of halide. Complex 1 reacts with 1 equivalent of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in THF and CH_3I affording, after only 1 h of stirring and treatment with (PPN)Cl, a quantitative yield of complex 3a. This reaction which is assisted by the presence of liberated trimethylamine, from the reduction of Me_3NO by a carbonyl ligand, constitutes the best way to produce the iodo complex.

Reactivity of Complex 2. As an anion containing a terminal hydride, two reaction pathways available to 2 are loss of a hydride ion, to generate, in the presence of a suitable coordinating ligand, neutral substitution products of 1, or attack by electrophiles E⁺ giving neutral derivatives with H and E in the coordination sphere. The chemical behavior of 2 was first investigated by its reaction with methyl iodide in THF. A reaction slowly took place at room temperature affording a red salt which after 3 h and exchange of the ammonium counterion by treatment with (PPN)Cl afforded a 75% yield of complex 3a. Although the mechanism of formation of 3a in this reaction is unknown, the two most plausible possibilities are nucleophilic displacement of I[−] from CH_3I by a hydride ion of 2 creating a vacant coordination site for attachment of iodide anion or alternatively formation of an intermediate methyl hydride, $(\text{H})(\text{Me})(\text{CO})_3\text{Ru}(\mu\text{-PPh}_2)\text{Co}(\text{CO})_3$, which subsequently loses methane by reductive elimination and coordinates an iodide anion to afford 3a.

The formation of 3a either from 2 and CH_3I or from 1 and KI or CH_3I demonstrates that the equatorial-trans stereochemistry of 3a does not depend on the nature of the leaving ligand (CO from 1 or H[−] from 2) but on the nature of the incoming ligand (X[−] to 3a or H[−] to 2).

Protonation of ruthenium hydride complexes has been shown recently to give molecular hydrogen–ruthenium complexes³¹ which by facile loss of the molecular hydrogen ligand liberates a vacant coordination site allowing the coordination of a two-electron ligand. Protonation of the bimetallic complex 2 by HPF_6 in THF did not allow the observation of a proton adduct but immediately leads to a red intermediate similar to that obtained from 1 and Me_3NO . Complex 2 is inert toward triphenylphosphine at room temperature, but in the presence of 1 equiv of HPF_6 leads to derivative 4, which exists in solution as the eq-trans and eq-cis isomers⁵ (Scheme I). The transfor-

(30) The infrared spectrum in THF shows only terminal carbonyl absorption bands at 2081 (s), 2046 (m), 2020 (vs), 1995 (s), 1933 (m) cm^{-1} . The ³¹P NMR spectrum (32.38 MHz, 193 K) in a mixture of THF (2 mL) and of toluene-*d*₆ (0.3 mL) gives a single line at δ 147.2, which is consistent with a phosphido group bridging a Ru–Co bond.^{5,10}

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mation 2 → 4 shows that on protonation 2 leads selectively under mild conditions to monosubstitution products of precursor 1.

Finally, we have examined whether complex 2 could transfer its hydride to another substrate, namely, Ru₃(C-O)₁₂ (ref 16) as a possible route to cluster anions or used to elaborate other phosphido-bridged polynuclear complexes. Complex 2 was reacted with 1 equiv of Ru₃(CO)₁₂ at 60 °C, and after chromatography a small amount (12%) of the hydrido cluster Ru₃(μ-H)₂(μ-PPh₂)₂(CO)₈ (5) was isolated (Scheme I). This complex 5 was produced previously in better yields by simple thermolysis of Ru₃(PPh₂H)₂(CO)₁₀.¹³ Nevertheless the formation of 5 indicates the possibility of transfer of the RuH(PPh₂)(CO)_n unit by cleavage of the Ru-Co bond of 2.

Conclusion

Displacement of a carbonyl group of (CO)₄Ru(μ-PPh₂)Co(CO)₃ by anionic hydride or halide donors leads to thermodynamic products in which regiospecific sub-

stitution of CO at the ruthenium site has occurred. For the anion [(H)(CO)₃Ru(μ-PPh₂)Co(CO)₃]⁻ the hydride occupies an axial cis site with respect to the Ru(μ-P)Co plane and the phosphido bridge whereas for [(X)(CO)₃Ru(μ-PPh₂)Co(CO)₃]⁻ the halide has an equatorial trans configuration. Thus the present results serve to confirm the previous observations on CO substitution in 1 by tertiary phosphines, namely, that the stable products of substitution have the Lewis base coordinated at the ruthenium site.

Acknowledgment. We are grateful to NSERC (Canada) and CNRS and MEN (France) for financial support of this research.

Registry No. 1, 82544-75-0; 2, 95392-70-4; 3a, 118142-02-2; 3b, 118142-04-4; cis-4, 99094-59-4; trans-4, 99094-58-3; 5, 87552-32-7; Ru₃(CO)₁₂, 15243-33-1; Co, 7440-48-4; Ru, 7440-18-8.

Supplementary Material Available: A table of thermal parameters (1 page); a listing of structure factors (14 pages). Ordering information is given on any current masthead page.

Coordination Chemistry of Siloles: Synthesis, Reactions, and Stereochemistry of Silicon-Substituted (η^4 -2,5-Diphenylsilacyclopentadiene)transition-metal Complexes.¹ Crystal Structure of Dicarboxyl[phenyl(η^4 -exo-1-methyl-2,5-diphenylsilacyclopentadien-1-yl)oxy]carbene]iron

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New silicon-monosubstituted and -disubstituted (η^4 -2,5-diphenylsilacyclopentadiene)transition-metal complexes are described. These complexes undergo a variety of substitution reactions at silicon, in which the exo leaving groups showed enhanced reactivity. The stereochemistry of substitution reactions at silicon with nucleophiles (RMgX, LiAlH₄, ROH, H₂O) differs significantly from that established for optically active silanes. (η^4 -1-Chloro-2,5-diphenylsilacyclopentadiene)tricarbonyliron complexes undergo displacement at silicon with complete retention at both exo and endo positions. These observations are discussed in terms of electronic factors. Reactions of the endo-chloro derivative with organolithiums resulted in the formation of new carbene complexes; the crystal structure of dicarbonyl[phenyl(η^4 -exo-1-methyl-2,5-diphenylsilacyclopentadien-1-yl)oxy]carbene]iron is reported. In the case of the exo-chloro isomer, the reaction course depends on the nature of the solvent and of the organolithium reagent; either attack at silicon or at a carbonyl ligand was observed.

Introduction

Transition-metal complexes of nonfunctional siloles are well-known,^{2,3} and in all complexes reported thus far the silole functions as an η^4 -ligand. Still unreported, however,

is the generation or detection of a (η^5 -silacyclopentadienyl)metal complex. One route could be, in principle, the reaction of a silicon functional coordinated η^4 -silole.

In terms of substitution and reaction at coordinated siloles, previous studies have been carried out by Sakurai et al.³ and Jutzi et al.⁴ and suggested that the reacting group at silicon must be exo to the metal center. However the experiments were restricted to a few exo isomers of (η^4 -2,3,4,5-tetraphenylsilacyclopentadiene)transition-metal

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