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Metallacyclopentene/Metallaoxanorbornadiene Chemistry. Synthesis, Characterization, and Reactivity of 1-(Cyclopentadienyl)-1-cobalta-2-oxanorbornadiene Complexes

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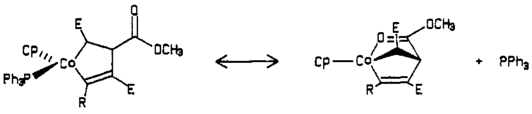
Reaction of $(\eta^5\text{-}C_5H_5)\overline{Co[C(R)C(CO_2CH_3)CH(CO_2CH_3)C}H(CO_2CH_3)][P(C_6H_5)_3]$ ($R = C_6H_5$, **1a**; $R = CO_2CH_3$, **1b**) with silver salts or sulfur resulted in loss of triphenylphosphine to yield new metallabicyclic complexes **2a** and **2b**, respectively. The structure of 1-(cyclopentadienyl)-1-cobalta-5,7-dicarbomethoxy-3-methoxy-2-oxa-6-phenylnorbornadiene (**2a**), $C_{21}H_{21}O_6Co$, was determined by X-ray diffraction. The complex crystallized in the orthorhombic space group *Pbca* with $a = 27.445$ (5) Å, $b = 8.826$ (2) Å, $c = 16.261$ (3) Å, and $Z = 8$. The structure was refined by full-matrix least squares to $R = 0.054$. The [2.2.1] ring system of **2a** is formed from the cobaltacyclopentene **1a** by coordination to cobalt of the carbonyl oxygen atom from the ester on the β-sp^3 carbon. Oxygen coordinates to cobalt solely on the opposite face of the cobaltacyclopentene from the phosphine ligand, resulting in inversion of the configuration of the chiral cobalt atom. Angles within the metallabicyclic complex are comparable to those in norbornadiene and imply the existence of considerable ring strain. Phosphines, phosphites, isocyanides, nitriles, and thiocyanate react cleanly with **2a** and **2b** to afford ligand-substituted cobaltacyclopentene complexes, many of which are not readily accessible from **1a** or **1b**. Ligands other than acetonitrile and thiocyanate add to **2** only from the face opposite the coordinated oxygen. ^1H and ^{13}C NMR characteristics of cobaltacyclopentenes and cobaltaoxanorbornadienes are presented.

Introduction

Metallacyclic complexes play important roles in transition-metal-promoted reactions of unsaturated hydrocarbons. Metallacyclopent-2-ene complexes have been implicated in a number of cooligomerization reactions of alkenes with alkynes catalyzed by cobalt,[1] rhodium,[2–4] and molybdenum[5] complexes. Three classes of metallacyclopentene complexes have been isolated and characterized to date. A series of cobaltacyclopentene complexes were obtained by reaction of activated alkenes with $(\eta^5\text{-}C_5H_5)Co(\eta^2\text{-alkyne})(PPh_3)$.[6] Reaction of several different pyridines with the η^2-alkene η^2-alkyne complex $[Rh(Me_3CCOCHCOCMe_3)(C_2H_4)(CF_3C{\equiv}CCF_3)]$ afforded rhodacyclopentene complexes.[7,8] Finally, benzometallacyclopentene complexes have been isolated from the reaction of ethylene with benzyne complexes $(\eta^5\text{-}C_5H_5)M(C_6H_4)(CH_3)_2$ (M = Nb, Ta).[9]

The reactivity of metallacyclopentenes has not been examined in detail. The sole investigation of this topic reported the reactions of one of the cobaltacyclopentene complexes with acrylonitrile and alkynes to yield diene and cyclohexadiene complexes, respectively.[6] By way of contrast, the reactivity of metallacyclopentane and metallacyclopentadiene complexes has been extensively investigated. These complexes play a central role in alkene and alkyne oligomerization[10,11] and have been exploited in the syntheses of arenes,[12] dienes,[13,14] substituted pyridines,[15–17] cyclic ketones,[18,19] and a range of heterocyclic compounds.[20,21] The diversity and richness of the chemistry of these metallacycles suggest that the development of interesting and synthetically useful metallacyclopentene-based chemistry is highly probable.

In this paper we describe our initial investigations of the reactivity of metallacyclopentene complexes. We have found that several known cobaltacyclopentene complexes[6] are in equilibrium (eq 1) with cobaltaoxanorbornadiene



(1)

1 2

a: R = Ph, E = CO_2CH_3

b: R = E = CO_2CH_3

complexes, novel [2.2.1] metallabicyclic complexes. The syntheses and structural characterization of these cobaltaoxanorbornadiene complexes are reported. Preparation of ligand-substituted metallacyclopentene complexes from both classes of metallacycles is described.

Experimental Section

General Comments. All manipulations were carried out under a nitrogen atmosphere by use of Schlenk techniques or in a

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Table I. ^{1}H NMR Spectral Data[a,b]

complex	η^5-C_5H_5	CO_2CH_3	ring protons		other ligands
2a	4.50	3.75, 3.74, 3.33	3.80 (d) 3.74 (d)[c]	$^3J_{HH}$ = 2.0	
2b	4.91	3.99, 3.81, 3.80, 3.67	4.06 (d) 3.68 (d)	$^3J_{HH}$ = 2.0	
3a	4.62	3.82, 3.58, 3.29	3.80 (dd)[d] 2.74 (dd)[e]	$^3J_{HH}$ = 8.7, J_{PH} = 1.2 J_{PH} = 12.6	1.78 (m, 6 H, PCH_2–) 1.31 (m, 12 H, CH_2CH_2) 0.91 (m, 9 H, CH_3)
3b	4.72	3.76, 3.74, 3.57, 3.55	3.68 (dd)[d] 2.62 (dd)[e]	$^3J_{HH}$ = 8.2, J_{PH} = 1.2 J_{PH} = 12.3	1.82 (m, 6 H, PCH_2–) 1.40 (m, 12 H, CH_2CH_2) 0.91 (m, 9 H, CH_3)
4a	4.65	3.79, 3.53, 3.29	3.62 (dd)[d] 3.38 (dd)[e]	$^3J_{HH}$ = 8.1, J_{PH} = 1.5 J_{PH} = 13.3	2.37 (s, 9 H, *p*-CH_3)
5a	4.69	3.81, 3.61, 3.31	3.79 (dd)[d] 3.25 (dd)[e]	$^3J_{HH}$ = 8.0, J_{PH} = 1.2 J_{PH} = 9.0	3.63 (d, 9 H, $POCH_3$) J_{PH} = 10.7
5b	4.84	3.76, 3.57,[f] 3.56	3.77 (dd)[d] 3.20 (dd)[e]	$^3J_{HH}$ = 7.9, J_{PH} = 1.5 J_{PH} = 13.8	3.70 (d, 9 H, $POCH_3$) J_{PH} = 10.5
6a	4.59	3.80, 3.62, 3.37	3.81 (d) 3.37 (d)	$^3J_{HH}$ = 7.6	1.56 (s, 9 H, *t*-CH_3)
6b	4.94	3.79, 3.69, 3.39, 3.26	4.27 (d) 3.58 (d)	$^3J_{HH}$ = 7.5	0.99 (s, 9 H, *t*-CH_3)
7a	4.50	3.71, 3.66, 3.61	4.97 (d) 4.06 (d)	$^3J_{HH}$ = 9.5	
8a[g]	4.53	3.53, 3.51, 3.27	4.98 (d) 4.04 (d)	$^3J_{HH}$ = 9.6	
8a′[g]	4.48	3.64, 3.63, 3.27	3.65 (d)[h] 3.21 (d)	$^3J_{HH}$ = 7.1	

[a] δ (J_{HH}, Hz). Spectra were recorded in $CDCl_3$ solution at room temperature unless otherwise noted. [b] Phenyl proton multiplets are omitted from the table. [c] Doublet partially obscured by the methoxy resonance. [d] On carbon β to metal, see text. [e] On carbon α to metal, see text. [f] Integrated intensity of 6 H. [g] CD_3CN solution. [h] Doublet partially obscured by the methoxy peak at 3.64 ppm.

Vacuum/Atmospheres Co. drybox. Benzene and hexane were distilled from sodium benzophenone ketyl prior to use. (n-C_4H_9)$_3$P and $(CH_3O)_3P$ were purified by vacuum distillation. All other solvents and reagents were of reagent or HPLC grade and were used without further purification. Chromatography was carried out under a nitrogen or argon atmosphere either on alumina (Woelm N, grade 1) or on silica (Baker 3405).

Absorption spectra were recorded on a Perkin-Elmer Lambda 4C spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer Model 683 spectrophotometer equipped with a data station. ^{1}H and ^{13}C NMR spectra were determined on a Varian XL-300 spectrometer. Proton-coupled ^{13}C spectra were obtained routinely. Mass spectra were obtained on a Hewlett-Packard 5985 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories.

$(\eta^5\text{-}C_5H_5)Co(\eta^2\text{-}C_6H_5C{\equiv}CCO_2CH_3)[P(C_6H_5)_3]$,[22] $(\eta^5\text{-}C_5H_5)Co(CH_3O_2CC{\equiv}CCO_2CH_3)[P(C_6H_5)_3]$,[23] $(\eta^5\text{-}C_5H_5)Co[C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)][P(C_6H_5)_3]$[6] (**1a**), and $(\eta^5\text{-}C_5H_5)Co[C(CO_2CH_3)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)][P(C_6H_5)_3]$[6] (**1b**) were prepared by literature methods. ^{1}H and ^{13}C NMR spectra of these and other complexes are collected in Tables I and II, respectively.

Syntheses of Cobaltaoxanorbornadiene Complexes. 1-(Cyclopentadienyl)-1-cobalta-5,7-dicarbomethoxy-3-methoxy-2-oxa-6-phenylnorbornadiene (2a). (i) Elemental sulfur (28 mg, 0.87 mmol), **1a** (300 mg, 0.435 mmol), and 75 mL of dry benzene were placed in a Schlenk flask. The mixture was gradually warmed over the course of $^1/_2$ h to 60 °C. During this time interval the color changed from red to green. The reaction mixture was concentrated under reduced pressure and purified by chromatography on an alumina column (2 × 17 cm). Elution with 50:1 benzene/ethyl acetate gave a colorless eluate that on concentration and addition of low boiling petroleum ether gave crystals of a material with NMR, IR, and MS identical with those of authentic triphenylphosphine sulfide (88 mg, 69% yield). Further elution of the column with 9:1 benzene/ethyl acetate afforded a green solution. Evaporation of the solution and recrystallization of the resulting residue from benzene/hexane solution gave green-black crystals of the title compound **2a** (37 mg, 21% yield): mp 115–117 °C; UV–vis (C_7H_8) λ_{max} 465.1 nm ($10^{-3}\epsilon_M$ 1.094 M^{-1} cm^{-1}), 597.3 (0.449); IR (KBr) ν 1685 (s, C=O), 1677 (s, C=O), 1606 cm^{-1} (s, C=O); MS (EI), m/e (% abundance, assignment) 428 (87, M^+), 305 (45, $C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)$ = chain), 273 (18, chain – CH_3OH), 245 (31, chain – CO_2CH_3 – H), 213 (56, chain – CH_3OH – CO_2CH_3 – H), 129 (35, chain – 3 CO_2CH_3), 124 (100, $(\eta^5\text{-}C_5H_5)Co$). Anal. Calcd for $C_{21}H_{21}CoO_6$: Co, 13.76; C, 58.88; H, 4.95. Found: Co, 13.67; C, 58.73; H, 4.77.

(ii) Silver trifluoromethanesulfonate (193 mg, 0.75 mmol), **1a** (500 mg, 0.73 mmol), and 250 mL of dry benzene were reacted for 48 h during which time the color turned from red to green. The solution was concentrated and the residue purified by chromatography on a silica column (3 × 15 cm). Elution with 50:1 methylene chloride/THF separated a small amount of **1a** from the main green band. The latter was collected and reduced to dryness. Recrystallization of the residue as in (i) afforded 249 mg (78% yield) of a material identical with that described in (i).

1-(Cyclopentadienyl)-1-cobalta-3-methoxy-2-oxa-5,6,7-tricarbomethoxynorbornadiene (2b). (i) Complex **2b** can be prepared from **1b** and elemental sulfur by the procedure described above for **2a**. The product was identified by NMR but was not isolated. NMR spectra were identical with that of material obtained in (ii), below.

(ii) Silver trifluoromethanesulfonate (206 mg, 0.80 mmol), **1b** (500 mg, 0.75 mmol), and 175 mL of dry benzene were reacted at 60 °C for 48 h. The reaction mixture was concentrated and purified by chromatography on a silica column (3 × 15 cm). A red band of **1b** was eluted first with 20:1 benzene/THF. The main green band followed closely. Recrystallization of the residue of the green band from benzene/hexane afforded 133 mg (44% yield) of **2b**: mp 153–157 °C dec; UV–vis (C_7H_8) λ_{max} 465.6 nm ($10^{-3}\epsilon_M$ 1.202 M^{-1} cm^{-1}), 580.0 (0.379); IR ($CHCl_3$) ν 1690 (s br, C=O), 1676 (s, C=O), 1615 cm^{-1} (s, C=O). Anal. Calcd for $C_{17}H_{19}CoO_8$: C, 49.77; H, 4.67. Found: C, 49.76; H, 4.69.

Syntheses of Substituted Cobaltacyclopentenes. $(\eta^5\text{-}C_5H_5)Co[C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)][P(n\text{-}C_4H_9)_3]$ (3a). (i) Tri-n-butylphosphine (14.5 μL, 0.058 mmol) was added to a solution of 25 mg of **2a** (0.058 mmol) in 10 mL of benzene. The resulting solution was stirred at room temperature for 16 h. Concentration of the red solution was followed by chromatography on a silica column (1 × 15 cm). The major product was eluted as an orange band with 50:1 methylene

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Table II. ^{13}C NMR Spectral Data^{a,b}

complex^c	η^5-C_5H_5	ring^d sp^2	ring^d sp^3	OCH_3^{e}	C=O	aromatic	ligand
[M]MPP^f	83.1			51.5	not obsd	134.7 [39^g]	89.9 (alkyne)
						133.9–127.4	89.4
[M]DMADC^f	83.8			51.4	164.2	134.8 [40^g]	95.9 (alkyne)
						134.4–128.1	95.8
[M]MF^f	85.5 [2.0^k]			50.8	187.5	134.8 [10^g]	40.8 [2.8] (alkene)
				50.1	178.9 [2.1]	129.4–127.5	31.1 [2.9]
1a^h	89.8 (178) (7.0^j)	α: 153.6	α: 19.7^i [12.0^k]	51.8	183.5	136.0 [41^g]	
				50.7	176.8	133.5–128.5	
		β: 141.0 (5.0^j)	β: 56.0 (150)	50.3	160.2		
1b	89.5 [2.0^k]	α: 159.5 [4.4^k]	α: 22.5 [11.0^k]	51.6	182.5		
				51.3	175.9 [1.8]		
		β: 140.9	β: 55.9 [2.5^l]	50.4	175.4		
				50.2	175.3		
2a^h	85.1 (179) (6.6^j)	α: 154.4 (8.0^m)	α: 41.6 (152) (5.7^j)	55.8	189.4	131.1–121.6	
				51.3	182.5		
		β: 159.9^n	β: 56.3 (148)	51.0	169.6		
2b	84.2 (180) (6.4^j)	α: 133.2	α: 44.6 (153) (5.8^j)	56.0	191.7		
				51.7	189.1		
		β: 159.3	β: 56.6 (146)	51.6	181.4		
				51.2	178.5		
3a	88.2 [2.2^k]	α: 154.7 [2.3^k]	α: 17.0 [16.4^k]	51.6	186.6	137.1–124.8	26.5 [4.5] (CH_2)
				50.4	176.3 [1.8]		26.1 [2.3] (CH_2)
		β: 139.5 [1.5^l]	β: 56.4	50.1	161.2		24.6 [11.6] (CH_2)
							13.7 (CH_3)
3b	87.8 [2.0^k]	α: 159.6 [4.3^k]	α: 17.8 [14.5^k]	51.7	182.1		27.2 [3.8] (CH_2)
				51.3	177.4 [2.0]		25.8 [24.8] (CH_2)
		β: 138.8	β: 55.2 [2.2^l]	51.1	175.1		24.6 [12.1] (CH_2)
				50.1	175.0		13.8 (CH_3)
4a	89.9 [2.1^k]	α: 154.2 [2.1^k]	α: 19.7 [7.0^k]	51.6	183.4	140.3–123.7	21.4 (p-CH_3)
				50.4	176.8 [2.9]		
		β: 141.7	β: 56.6	50.0	160.2 [4.1]		
5a	89.2 [2.9^k]	α: 154.3 [2.0^k]	α: 18.6 [29.0^k]	51.6	182.2	128.3–124.7	52.8 [7.0^k]
				50.5	176.3 [2.0]		
		β: 139.5	β: 56.1 [3.3^l]	50.3	161.3		
5b	84.6 [2.1^k]	α: 159.7 [5.0^k]	α: 19.9 [24.7^k]	51.8	187.3		53.4 [7.6^k]
				51.4	181.7		
		β: 139.5	β: 55.5 [4.3^l]	51.1	176.4 [2.8]		
				50.3	175.1 [1.9]		
6a	90.2	α: 154.1	α: 22.9	51.6	181.7	128.1–123.1	58.4 $C(CH_3)_3$
				50.6	175.7		30.7 $C(CH_3)_3$
		β: 138.4	β: 55.7	50.4	161.1		
6b	89.3 (180) (7.0^j)	α: 159.9	α: 23.0 (141) (6.0^j)	51.7	181.2		58.5 (2.0^j) $C(CH_3)_3$
				51.4	176.7		30.5 (2.0^j) $C(CH_3)_3$
		β: 137.9 (5.0^j)	β: 55.0 (133) (2.0^j)	51.2	175.4		
				50.5	174.7		
7a	86.4	α: 152.8	α: 19.7	52.6	185.8	128.5–124.5	
				51.8	176.8		
		β: 141.1	β: 57.2	51.6	166.4		
8a and **8a'**^{p}	89.9, 89.8	α: 155.6, 155.5	α: 26.1, 20.0	51.6	183.6	128.5–124.6	
				51.5	182.2		
		β: not obsd	β: 57.5	50.8	176.5		
				50.7	175.5		
				50.6	161.3		
				50.5	155.6		

[a] δ (J_{CH}, Hz) [J_{CP}, Hz]. [b] All spectra recorded at 19 °C in $CDCl_3$ solution, unless noted otherwise. [c] Abbreviations: [M] = (η^5-C_5H_5)Co[$P(C_6H_5)_3$]; MPP, $C_6H_5C{\equiv}CCO_2CH_3$; DMADC, $CH_3O_2CC{\equiv}CCO_2CH_3$; MF, dimethyl fumarate. [d] Carbons in or derived from metallacyclopentene ring. [e] $145 \le {}^1J_{CH} \le 152$ Hz. [f] C_6D_6 solution. [g] $^1J_{CP}$. [h] Recorded at −30 °C. [i] CH coupling not observed. [j] $^2J_{CH}$. [k] $^2J_{CP}$. [l] $^3J_{CP}$. [m] $^3J_{CH}$. [n] May be doublet in proton-coupled spectrum due to long-range coupling, see text. [o] CD_3CN solution. [p] Data present for both diastereomers present in solution, see text.

chloride/THF. A minor yellow impurity band immediately preceded the desired band. The orange eluate was taken to dryness under reduced pressure and the residue was recrystallized from benzene/hexane solution to afford 27 mg of **3a** (74% yield): mp 130–131 °C; UV-vis (C_7H_8) λ_{max} 425 nm ($10^{-3}\epsilon_M$ 1.316 M^{-1} cm^{-1}); IR ($CHCl_3$) ν 1725 (s, C=O), 1685 cm^{-1} (s br, C=O). Anal. Calcd for $C_{33}H_{48}CoO_6P$: C, 62.85; H, 7.67. Found: C, 62.73; H, 7.61.

(ii) Tri-n-butylphosphine (2.5 mg) was added to a solution of 10 mg of **1a** in 0.75 mL of $CDCl_3$ in an NMR tube (1:1.3 phosphine:**1a**). The reaction was monitored by ^{1}H NMR spectroscopy. After 72 h, integration of Cp peaks indicated that the ratio of **3a**:**1a** was 2:1. **3a** was not isolated. No other species were detected.

(η^5-C_5H_5)Co[C(CO_2CH_3)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)][P(n-C_4H_9)$_3$] (3b). Complex **3b** was prepared in 92% yield from tri-n-butylphosphine and **2b** by the method described above in (i) for **3a**: mp 138–140 °C; UV-vis ($CHCl_3$) λ_{max} 421 nm; IR ($CHCl_3$) ν 1725 (s, C=O), 1690 cm^{-1} (s br, C=O). Anal. Calcd for $C_{29}H_{46}CoO_8P$: C, 56.85; H, 7.58. Found: C, 57.32; H, 7.58.

(η^5-C_5H_5)Co[C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)][P(p-$CH_3C_6H_4$)$_3$] (4a). Complex **4a** was prepared from tri-p-tolylphosphine and **2a** in 93% yield by the method described above in (i) for **3a**: mp 192–194 °C; UV-vis ($CHCl_3$) λ_{max} 457 nm, 511 (sh); IR ($CHCl_3$) ν 1745 (s br, C=O), 1660 cm^{-1} (s br, C=O). Anal. Calcd for $C_{42}H_{42}CoO_6P$: C, 68.84; H, 5.79. Found: C, 68.51; H, 5.89.

(η^5-C_5H_5)Co[C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)][P(OCH_3)$_3$] (5a). (i) Complex **5a** was prepared from trimethyl phosphite and **2a** in 55% yield by the method described above in (i) for **3a**: mp 185–185.5 °C; UV–vis (C_7H_8) λ_{max} 395 nm ($10^{-3}\epsilon_M$ 1.338 M^{-1} cm^{-1}), 468 (0.586, sh); IR ($CHCl_3$) ν 1725 (s, C=O), 1685 cm^{-1} (s br, C=O). Anal. Calcd for $C_{24}H_{30}CoO_9P$: C, 52.18; H, 5.48. Found: C, 52.49; H, 5.52.

(ii) **1a** (10 mg) and 2.2 mg of trimethyl phosphite in 0.75 mL of $CDCl_3$ were reacted in an NMR tube (1:1.5 **1a**:phosphite). After 72 h of reaction, integration of the Cp peaks indicated that the ratio of **5a**:**1a** was 4:1. No other species were detected in the solution.

$(\eta^5\text{-}C_5H_5)\overline{Co[C(CO_2CH_3)C(CO_2CH_3)CH(CO_2CH_3)C}H(CO_2CH_3)][P(OCH_3)_3]$ (5b). Complex **5b** was prepared in 68% yield from trimethyl phosphite and **2b** by the method described in (i) for **5a**: mp 123–124 °C; UV–vis ($CHCl_3$) λ_{max} 397 nm, 560 (sh); IR (CH_2Cl_2) ν 1730 (s, C=O), 1695 cm^{-1} (s br, C=O). Anal. Calcd for $C_{20}H_{28}CoO_{11}P$: C, 44.91; H, 5.29. Found: C, 45.20; H, 5.38.

$(\eta^5\text{-}C_5H_5)\overline{Co[C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)C}H(CO_2CH_3)][CNC(CH_3)_3]\cdot{}^1/_3H_2O$ (6a). (i) *tert*-Butyl isocyanide (7.9 μL, 5.8 mg, 0.07 mmol) was reacted with 30 mg of **2a** (0.07 mmol) in 15 mL of benzene. The solution turned bright red after being stirred at room temperature for 45 min. The solution was reduced in volume. Addition of hexane afforded 24 mg of orange crystals of **6a** (68% yield): mp 141–142 °C; UV–vis (C_7H_8) λ_{max} 404 nm ($10^{-3}\epsilon_M$ 1.369 M^{-1} cm^{-1}), 465 (0.546, sh); IR ($CHCl_3$) ν 2160 (s, C≡N), 1731 (s, C=O), 1692 cm^{-1} (s, C=O); MS (EI), *m/e* (% abundance, assignment) 511 (37, M^+), 455 (21, M − C_4H_8), 446 (15, M − Cp), 428 (58, M − $CNC(CH_3)_3$), 305 (30, $C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)$ = chain), 245 (13, chain − CO_2CH_3 − H), 213 (15, chain − CO_2CH_3 − H − CH_3OH), 187 (13, chain − 2 CO_2CH_3), 151 (100, CpCoCN), 124 (53, CpCo). Anal. Calcd for $C_{26}H_{30}CoNO_6\cdot{}^1/_3H_2O$: C, 60.37; H, 5.99; Co, 10.91; water (by Karl Fisher titration), 1.16. Found: C, 60.37; H, 5.90; Co, 11.39; water (Karl Fisher), 1.54.

(ii) *tert*-Butyl isocyanide (16.4 μL, 12 mg, 0.145 mmol) was added to a solution of **1a** (100 mg, 0.149 mmol) in 30 mL of benzene. The solution was heated in a 50 °C oil bath for 5 h, during which time the color turned from red to amber yellow. The solution volume was reduced in volume and was applied to a silica column (2 × 12 cm). Elution with 20:1 benzene/THF served to separate a small amount of **1a** from the main yellow band of **6a**. The solvent was removed in vacuo, and the residue was recrystallized from benzene/hexane to give 59 mg of **6a** (77% yield) identical with that obtained from (i) above.

$(\eta^5\text{-}C_5H_5)\overline{Co[C(CO_2CH_3)C(CO_2CH_3)CH(CO_2CH_3)C}H(CO_2CH_3)][CNC(CH_3)_3]$ (6b). (i) **6b** (29 mg, 67% yield) was prepared from 35 mg of **2b** (0.085 mmol) and 7.1 mg of *tert*-butyl isocyanide (0.085 mmol) in 20 mL of benzene according to method (i) for **6a**: mp 134–135 °C; UV–vis ($CHCl_3$) λ_{max} 407 nm, 471 (sh); IR ($CHCl_3$) ν 2170 (s, C≡N), 1725 (s, C=O), 1690 cm^{-1} (s br, C=O). ^1H NMR spectra established that the crystalline solid contained roughly 0.2 equiv of benzene. The benzene was not removed by heating in a vacuum. Anal. Calcd for $C_{22}H_{28}CoNO_8\cdot{}^1/_5C_6H_6$: C, 54.73; H, 5.79. Found: C, 54.69; H, 5.88.

(ii) *tert*-Butyl isocyanide (25 μL, 19 mg, 0.223 mmol) was added to a solution of 50 mg of **1b** (0.074 mmol) in 10 mL of dry benzene. The solution was heated in a 75 °C oil bath for 8 h. The solution was orange at the end of the reaction period. The solvent was removed in vacuo, and the residue was purified by chromatography on a silica column (1.5 × 10 cm). The red-orange band containing product was separated from the red band containing **1b** by elution with 20:1 methylene chloride/THF. The solvent of the product band was removed in vacuo, and the residue was recrystallized from benzene/hexane to afford red crystals of **6b** (30 mg, 82% yield) that were identical with those obtained by part (i).

$K[(\eta^5\text{-}C_5H_5)\overline{Co[C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)C}H(CO_2CH_3)](SCN)]$ (7a). **2a** (25 mg, 0.057 mmol) and KSCN (15 mg, 0.160 mmol) were reacted in 15 mL of methylene chloride for 3 days at room temperature. The mixture gradually changed in color from green to brown. The mixture was reduced in volume and filtered rapidly through a small bed of silica to remove unreacted KSCN. The solvent of the filtrate was removed in vacuo, and the residue was recrystallized from benzene/hexane to afford 16 mg (55% yield) of a brown solid, which was a mixture of **7a** and a small amount of **2a**. Efforts to prepare analytically pure **7a** were unsuccessful. Attempts to purify **7a** by recrystallization and/or column chromatograpy served only to increase the proportion of **2a** in the mixture: UV–vis ($CHCl_3$) λ_{max} 461 nm, 553 (sh); IR ($CHCl_3$) ν 2116 (s, SCN), 1717 (s, C=O), 1679 (s, C=O), 1671 cm^{-1} (s, C=O). Preparation of **7a** from **1a** failed.

Analogues of **7a** with different counterions were prepared in an attempt to obtain an analytically pure material. These complexes provide evidence that interactions of K^+ with the ester oxygen atoms and the thiocyanate group are important in stabilizing **7a** relative to **2a**. Reaction of $CHCl_3$ (or $CDCl_3$) solutions of **7a** isolated as above with one equivalent of 18-crown-6 ether resulted in significant changes in the IR and ^1H NMR spectra: IR ($CHCl_3$) ν 2122 (s, SCN), 1730 (s, C=O), 1681 cm^{-1} (s, C=O); ^1H NMR ($CDCl_3$) 5.04, 3.99 (ring protons, 1 H, $^3J_{HH}$ = 8.5 Hz), 3.62, 3.59, 3.38 ppm (OCH_3, 3 H). Solutions of the crown ether analogue of **7a** revert to **2a** on standing. Preparation of a tetraethylammonium analogue of **7a** was attempted by direct reaction of **2a** with tetraethylammonium thiocyanate. This reaction was more rapid—the color of the homogeneous solution changed from green to brown in a few hours. A gross mixture of several products resulted. One had ^1H NMR features consistent with a ligand-substituted metallacyclopentene (but different than **7a**).

$(\eta^5\text{-}C_5H_5)\overline{Co[C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)C}H(CO_2CH_3)](CH_3CN)$ (8a and 8a′). (i) **2a** was dissolved in acetonitrile to afford a red solution. The ^1H NMR spectrum of a CD_3CN solution established that **2a** had been completely converted to nearly equal amounts of two new complexes, **8a** and **8a′**. Attempts to isolate these complexes by slow evaporation or by precipitation led only to recovery of **2a**.

(ii) **1a** was insoluble in neat acetonitrile. The ^1H NMR spectra of **1a** taken in 2:1 (v/v) $CDCl_3$/CD_3CN showed that only about 10% of **1a** was converted to **8a** and **8a′** at long reaction times. A trace of **2a** was also present.

X-ray Structure Determination. A suitable crystal of **2a** was obtained by vapor diffusion of hexane into a benzene solution of the complex. A somewhat irregularly shaped crystal was mounted under nitrogen in a 0.4-mm capillary tube. Preliminary Weissenberg photographs exhibited systematic absences (*0kl*, *k* = 2*n* + 1; *h0l*, *l* = 2*n* + 1; *hk0*, *h* = 2*n* + 1) and symmetry indicative of the orthorhombic space group *Pbca*. Most operations on the Syntex $P2_1$ diffractometer and XTL structure determination system were carried out as described previously.[24,25] Details of the structure analysis are presented in Table III.

The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering were included in the calculations for the cobalt atom.[26] After least-squares refinement using isotropic temperature factors, features on an electron density difference Fourier map indicated that several atoms (Co, O(1), O(2), O(4), O(5), O(6), C(12), C(14) through C(21)) required further refinement using anisotropic temperature factors. Owing to a relatively low data/parameter ratio (about 8:1) and the lack of substantial features on further difference Fourier maps, no additional atoms were refined by using anisotropic temperature factors. At the conclusion of this level of refinement (*R* = 0.072) a difference Fourier map revealed the positions of nearly all of the hydrogen atoms. All non-methyl hydrogen atoms were included in their idealized positions based on a C–H bond length of 0.95 Å. The program METHYL was used to generate "best fit" positions for the three sets of methyl hydrogen atoms. These hydrogen atom positons (also with fixed bond lengths of 0.95 Å) were included as fixed contributions to F_c in subsequent least-squares refinement cycles. Their values were updated following each cycle. Final atomic coordinates are presented in Table IV. Thermal parameters and hydrogen atom coordinates have been deposited with the supplementary material.

Results and Discussion

Formation and Characterization of Cobaltaoxanorbornadiene Complexes. Complexes **1a** and **1b** are

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[24] Foxman, B. M. *Inorg. Chem.* **1978**, *17*, 1932.

[25] Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113.

[26] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101, 148–150.

Table III. Data for the X-ray Diffraction Study of $(C_5H_5)Co(C_{16}H_{16}O_6)$

(A) Crystal Data at 21 (1) °C

cryst system: orthorhombic
$Z = 8$
space group: *Pbca* [D_{2h}^{15}; No. 61]
crystal size: 0.42 × 0.28 × 0.25 mm
a = 27.445 (5) Å
fw 428.14
b = 8.826 (2) Å
ρ_{obsd} = 1.44 (1)[a] g cm^{-3}
c = 16.261 (3) Å
ρ_{calcd} = 1.448 g cm^{-3}
V = 3939.5 Å^3
μ = 9.4 cm^{-1} (Mo Kα)

cell constant determination: 12 pairs of ±(hkl) and refined 2θ, ω, and χ values in the range $24 \leq |2\theta| \leq 26°$
(λ, (Mo Kα_1) = 0.710 73 Å)

(B) Measurement of Intensity Data

radiatn: Mo Kα, graphite monochromator
reflctns measd: $+h$, $+k$, $+l$ (to $2\theta = 47°$)
scan type, speed: ω–2θ, 1.46–3.91°/min
scan range: symmetrical, $[2.0 + \Delta(\alpha_2 - \alpha_1)]°$
bkgd measurement: stationary, for one-quarter of scan time at each of the scan limits
no. of reflctns measd: 2907
std reflctns: 020, 600, 006 measd after each 50 reflctns; variation $< \pm 3\sigma(I)$ for each
automatic recentering: after every 1000 reflctns
statistical informatn: R_s = 0.040

(C) Solution and Refinement with 1665 Data for Which $F > 3.92\sigma(F)$

weighting of reflctns: as before,[b] p = 0.035
soln: Patterson, difference Fourier, routine
refinement:[c] full-matrix least squares, with anisotropic temperature factors for Co and certain C and O atoms (see text); isotropic temperature factors for fixed H atoms; secondary extinction parameter, $g = 2.9\ (4) \times 10^{-7}$; R = 0.054; R_w = 0.062; SDU = 1.16; R (structure factor calcn with all 2907 reflctns) = 0.119
final difference map: 1 peak, 0.41 e/Å^3 near Co; 5 other peaks, 0.34 e/Å^3 near phenyl carbon atoms; remainder random and ≤0.3 e/Å^3
weighting scheme analysis: no systematic dependence on magnitude of $|F_o|$, $(\sin\theta)/\lambda$, or indices

[a] Measured by neutral bouyancy in KI/H_2O. [b] Foxman, B. M.; Mazurek, H. *Inorg. Chem.* **1979**, *18*, 113 and references therein. [c] $R_s = \sum(\sigma(|F_o|)/\sum|F_o|$; $R_{av} = \sum|I - I_{av}|/\sum I$; $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$; SDU $= \{\sum w[|F_o| - |F_c|]^2/(m - n)\}^{1/2}$, where m (= 1665) is the number of observations and n (= 189) is the number of parameters.

air and thermally stable solids. Solutions of **1a** in benzene or chloroform discolor on standing under nitrogen at room temperature for several hours, turning from red to red-brown. ^{1}H NMR spectra of the red-brown solution reveal the formation of a small quantity of a new complex (**2a**) with distinctive cyclopentadienyl, methoxy, and olefinic protons resonances (Table I). The extent of conversion of **1a** and **2a** was substantially increased (to near 50%) upon heating the solution to 80 °C for 36 h. When cooled to room temperature, the original ratio of peak intensities in the spectrum was reestablished. Formation of **2a** was completely suppressed by the addition of excess triphenylphosphine.

The observations above suggest that the phosphine ligand of **1a** dissociates to establish an equilibrium between **1a**, triphenylphosphine, and **2a**. The ^{31}P NMR spectrum of **1a** provided direct evidence for dissociation: a small peak at −5.5 ppm due to unbound triphenylphosphine was observed in addition to the major peak for **1a** at 50.7 ppm. Furthermore, three spots were observed when the discolored solution of **1a** was subjected to TLC on silica. A red and a colorless spot had R_f values identical with those of **1a** and triphenylphosphine, respectively. The existence of the third green spot suggested that **2a** was sufficiently stable to be isolated.

Table IV. Atomic Parameters for 2a

atom	*x*	*y*	*z*
Co	0.10189 (3)	0.12574 (11)	0.01812 (6)
O(1)	0.2007 (2)	0.5528 (6)	−0.0568 (3)
O(2)	0.1794 (2)	0.4860 (7)	−0.1823 (3)
O(3)	0.05174 (14)	0.2438 (5)	−0.0441 (3)
O(4)	0.0457 (2)	0.3571 (6)	−0.1666 (3)
O(5)	0.1104 (2)	−0.1768 (6)	−0.1270 (4)
O(6)	0.0588 (2)	−0.0029 (6)	−0.1751 (3)
C(1)	0.1464 (2)	0.2972 (7)	0.0070 (4)
C(2)	0.1505 (2)	0.3377 (7)	−0.0722 (4)
C(3)	0.1211 (2)	0.2361 (7)	−0.1298 (4)
C(4)	0.1267 (2)	0.0776 (8)	−0.0946 (4)
C(5)	0.1681 (2)	0.3763 (8)	0.0777 (4)
C(6)	0.2118 (3)	0.3304 (8)	0.1128 (4)
C(7)	0.2318 (3)	0.4093 (9)	0.1794 (5)
C(8)	0.2083 (3)	0.5302 (9)	0.2107 (5)
C(9)	0.1648 (3)	0.5767 (10)	0.1790 (5)
C(10)	0.1450 (3)	0.5003 (9)	0.1116 (5)
C(11)	0.1779 (2)	0.4639 (8)	−0.1095 (4)
C(12)	0.2266 (3)	0.6799 (9)	−0.0904 (5)
C(13)	0.0693 (2)	0.2781 (7)	−0.1115 (4)
C(14)	−0.0033 (3)	0.4003 (10)	−0.1473 (6)
C(15)	0.0950 (3)	−0.0310 (9)	−0.1379 (5)
C(16)	0.0795 (3)	−0.2921 (10)	−0.1616 (9)
C(17)	0.1329 (5)	0.031 (2)	0.1180 (11)
C(18)	0.0946 (8)	0.111 (2)	0.1441 (6)
C(19)	0.0543 (4)	0.048 (2)	0.1089 (9)
C(20)	0.0668 (6)	−0.071 (2)	0.0593 (8)
C(21)	0.1166 (6)	−0.0809 (14)	0.0662 (9)

Initial attempts to isolate **2a** entailed the use of elemental sulfur to trap dissociated phosphine. As expected, triphenylphosphine sulfide and **2a** were isolated from the reaction of **1a** and sulfur. Yields of **2a** were small (20%), however, owing to decomposition of **1a** in the presence of sulfur. An alternative method that employed silver salts as phosphine traps[27] afforded **2a** in 78% isolated yield. Although **1b** does not dissociate to as great an extent as **1a**, a complex (**2b**) related to **2a** can be obtained from **1b** by either method. Yields of **2b** are smaller and reaction conditons are more vigorous, however.

Analytical data and the ^{1}H NMR and mass spectra of **2a** confirmed that the stoichiometry of **2a** differs from that of **1a** by loss of triphenylphosphine. Solutions of **2a** reacted surprisingly slowly with added triphenylphosphine to reform **1a**. Furthermore, **2a** is air-stable as a solid or in solution. The inertness of **2a** toward oxygen and the slow rate of reaction with triphenylphosphine strongly suggest that **2a** is coordinatively saturated. Thus, the coordinatively unsaturated (cyclopentadienyl)cobaltacyclopentene complex that results from simple loss of phosphine from **1a** is not a likely structure for **2a**. Two more probable structures for **2a** include a cobalt(I) η^2-dimethyl maleate η^2-methyl phenylpropiolate complex formed by scission of the cobaltacyclopentene ring and a Co(III) metallabicyclic complex formed as a result of ligation of one of the ester group substituents of the original metallacyclopentene to the metal center. While rare, several examples of η^2-alkene η^2-alkyne complexes have been reported.[4,5,8,28,29] The existence of a structure of this type could suggest that the equilibrium between metallacyclopentenes and their precursor η^2-alkene η^2-alkyne complexes favors the latter in coordinatively unsaturated systems.

Spectroscopic data for complexes **2a** and **2b** were not consistent with that expected for η^2-alkene η^2-alkyne

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(29) Howden, M. E.; Kemmitt, R. D. W.; Schilling, M. D. *J. Chem. Soc., Dalton Trans.* **1980**, 1716.

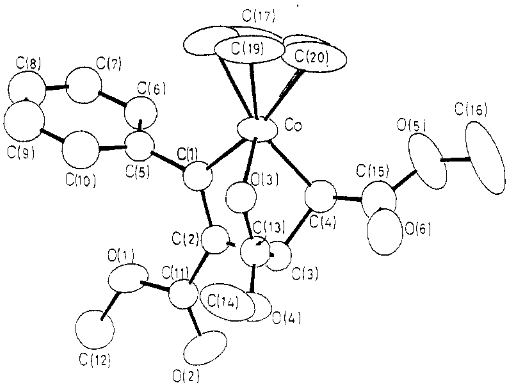

Figure 1. ORTEP diagram of **2a**. The bond between C(2) and C(3) is partially obscured by C(13).

Table V. Bond Lengths (Å) for 2a

Co–O(3)	2.001 (4)	C(1)–C(5)	1.471 (9)
Co–C(1)	1.954 (6)	C(2)–C(3)	1.527 (9)
Co–C(4)	2.002 (7)	C(2)–C(11)	1.475 (9)
Co–C(17)	2.02 (2)	C(3)–C(4)	1.519 (9)
Co–C(18)	2.06 (1)	C(3)–C(13)	1.500 (9)
Co–C(19)	2.09 (1)	C(4)–C(15)	1.47 (1)
Co–C(20)	2.09 (2)	C(5)–C(6)	1.387 (9)
Co–C(21)	2.03 (1)	C(5)–C(10)	1.38 (1)
O(1)–C(11)	1.320 (8)	C(6)–C(7)	1.40 (1)
O(1)–C(12)	1.435 (9)	C(7)–C(8)	1.35 (1)
O(2)–C(11)	1.201 (8)	C(8)–C(9)	1.36 (1)
O(3)–C(13)	1.235 (8)	C(9)–C(10)	1.40 (1)
O(4)–C(13)	1.307 (8)	C(17)–C(18)	1.34 (2)
O(4)–C(14)	1.434 (9)	C(17)–C(21)	1.37 (2)
O(5)–C(15)	1.366 (10)	C(18)–C(19)	1.36 (2)
O(5)–C(16)	1.44 (1)	C(19)–C(20)	1.37 (2)
O(6)–C(15)	1.188 (9)	C(20)–C(21)	1.37 (2)
C(1)–C(2)	1.343 (9)		

complexes. The IR spectra of both complexes lacked bands in the frequency region typical of coordinated alkynes, but each had a characteristic intense band near 1610 cm^{-1}. This frequency agrees well with the reported C$=$O stretching frequencies for chelated esters in [Co(en)$_2$(glyOR)]$^{3+}$, where glyOR is a glycine ester,[30,31] and in dimeric palladiacyclopentadiene complexes.[32] ^{1}H and ^{13}C NMR data, which are discussed later in the paper, were also inconsistent with an η^2-alkene η^2-alkyne complex. The data were suggestive of a metallabicyclic ester chelated complex but were not sufficient to conclusively establish this new structure type or to identify the group that provided the new ligand to the cobalt atom. Thus, the structure of **2a** was determined by X-ray diffraction techniques.

Structure of 2a. Crystals of **2a** consist of discrete molecular units with no intermolecular distance smaller than the sum of van der Waals radii. The molecular structure of **2a** and the numbering scheme of non-hydrogen atoms are shown in Figure 1. Atomic coordinates are listed in Table IV. Important bond lengths and angles are listed in Tables V and VI, respectively.

Table VI. Selected Bond Angles (deg) for 2a

O(3)–Co–C(1)	88.9 (2)	C(10)–C(5)–C(1)	120.1 (6)
O(3)–Co–C(4)	83.2 (2)	C(7)–C(6)–C(5)	120.7 (6)
C(1)–Co–C(4)	82.3 (3)	C(8)–C(7)–C(6)	120.0 (7)
C(11)–O(1)–C(12)	116.9 (6)	C(9)–C(8)–C(7)	120.9 (8)
C(13)–O(3)–Co	107.9 (4)	C(10)–C(9)–C(8)	119.5 (8)
C(13)–O(4)–C(14)	117.2 (6)	C(5)–C(10)–C(9)	121.1 (7)
C(15)–O(5)–C(16)	115.8 (7)	O(1)–C(11)–O(2)	121.9 (6)
C(2)–C(1)–C(5)	126.2 (6)	O(1)–C(11)–C(2)	115.1 (6)
C(2)–C(1)–Co	110.3 (4)	O(2)–C(11)–C(2)	123.0 (6)
C(5)–C(1)–Co	123.3 (4)	O(3)–C(13)–O(4)	123.1 (6)
C(3)–C(2)–C(11)	117.5 (5)	O(3)–C(13)–C(3)	119.1 (6)
C(3)–C(2)–C(1)	112.9 (5)	O(4)–C(13)–C(3)	117.7 (6)
C(11)–C(2)–C(1)	129.6 (6)	O(5)–C(15)–O(6)	121.4 (7)
C(4)–C(3)–C(13)	104.4 (5)	O(5)–C(15)–C(4)	111.6 (6)
C(4)–C(3)–C(2)	104.8 (5)	O(6)–C(15)–C(4)	126.9 (7)
C(13)–C(3)–C(2)	103.5 (5)	C(18)–C(17)–C(21)	109 (1)
C(15)–C(4)–Co	111.9 (5)	C(19)–C(18)–C(17)	107 (1)
C(15)–C(4)–C(3)	111.0 (6)	C(20)–C(19)–C(18)	111 (1)
Co–C(4)–C(3)	96.6 (4)	C(21)–C(20)–C(19)	105 (1)
C(6)–C(5)–C(10)	117.7 (6)	C(17)–C(21)–C(20)	109 (1)
C(6)–C(5)–C(1)	122.1 (6)		

The results of the X-ray diffraction study confirm that **2a** has a metallabicyclic ester chelate structure, as suggested by the spectroscopic data. The cobaltacyclopentene ring of **1a**, Co–C(1)–C(2)–C(3)–C(4), remains intact in **2a**. Coordination of O(3), the carbonyl oxygen atom of the carbomethoxy group on C(3), to the cobalt atom results in formation of a novel [2.2.1] metallabicyclic ring sytem. The cobalt atom occupies a bridgehead site and the ester oxygen atom is at the 2-position. We will refer to the class of complexes represented by **2a** as metallaoxanorbornadienes, given the structural analogy of these complexes to norbornadiene.

The ligands in **2a** are disposed about the cobalt atom in a three-legged piano-stool arrangement. Bond lengths and angles within the Cp ring and between Cp carbon atoms and the cobalt atom are normal. The Co–C(1) bond length of 1.954 (6) Å in **2a** is not significantly different from the Co–C(sp^2) bond lengths of 1.947 (11) Å in **1a**[6] and slightly shorter than 1.995 (11) and 1.993 (11) Å in cyclopentadienyl(triphenylphosphine)tetrakis(pentafluorophenyl)cobaltacyclopentadiene.[33] In contrast, the Co–C(4) bond length of 2.002 (7) Å in **2a** is significantly shorter than the corresponding Co–C(sp^3) bond length of 2.097 (12) Å in **1a**[6] but is comparable to the average Co–C(sp^3) bond lengths found in the cobaltacyclopentanes cyclopentadienyl(triphenylphosphine)cobaltacyclopentane,[34] **10**, and cyclopentadienyl(triphenylphosphine)-1,4-dicyanocobaltacyclopentane (2.024 (4) and 2.027 (4) Å, respectively).[35] Comparisons with inorganic Co(III) ketone complexes[36-39] suggest that the 2.001 (4) Å Co–O(3) bond length may be longer than expected. Typical Co(III)–O(sp^2) bond lengths in these complexes range from 1.888 (4) Å in tris(acetylacetonato)cobalt(III)[36] to 1.919 (5) Å in Co(dmho)$_3$.[37] (dhmo is the monoanion of 5,5-dimethylcyclohexane-1,2,3-trione 2-oxime.) While inorganic cobalt complexes that have hard oxygen and nitrogen ligands are not strictly comparable to organometallic cobalt complexes that have softer carbon atom containing ligands, the dissimilarity is unlikely to account for the 0.09–0.12 Å difference in bond lengths. In fact, the bond length in **2a** is

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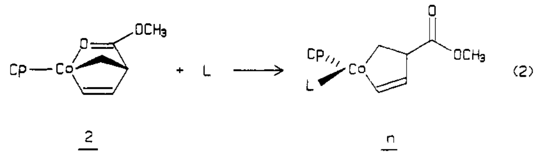
approaching the 2.055 (7) Å bond length of the Co(II) complex Co(acac)$_2$·2H$_2$O.[40] The C(1)–Co–C(4) bond angle in **2a** is similar to the corresponding angles in **1a**[6] and **10**.[34]

The cobaltaoxanorbornadiene ring system and the ester and phenyl substituents of **2a** appear to be normal if only the bond lengths in these groups are considered. Bond angles, on the other hand, provide evidence for considerable strain within the cobaltaoxanorbornadiene system and illustrate the substantial changes that occur upon conversion of **1a** to **2a**. Many angles in **2a** close down to accommodate coordination of the chelating ester group and therefore are smaller than the analogous angles in **1a**. The Co–C(1)–C(2) angle of 110.3 (4)° has decreased considerably from 115.6 (8)° in **1a**. The concomitant increase of the C(2)–C(1)–C(5) angle from 122.3 (9)° in **1a** to 126.2 (6)° in **2a** establishes that the phenyl ring has pivoted away from the double bond and toward the cobalt atom. The Co–O(3)–C(13) angle of 107.9 (4)° is less than the 120° angle that should provide for optimal interaction of the sp^2 oxygen atom nonbonding lone pair with the cobalt atom. The angles about C(3), the bridgehead carbon, have closed down from 108.0 (9)° or greater in **1a** to an average value of 104.3° in **2a**. The decrease of the Co–C(4)–C(3) angle from 107.5 (7)° in **1a** to 96.6 (4)° in **2a** is even more dramatic. With the exception of the angles about the cobalt atom, most angles in **2a** are indistinguishable from the angles in typical organic [2.2.1] ring systems.[41,42]

The metallacyclopentane and -pentene ring fragments in **1a**, **2a**, and **10** are not planar. In **10**, one of the carbon atoms β to the cobalt atom is out of the plane of the other four metallacycle atoms and is considerably closer to the cobalt atom than the other β-carbon atom.[34] In **1a**, the α sp^3 carbon atom is displaced 0.561 Å in the direction of the phosphine ligand from the plane defined by the two sp^2 carbon atoms and their four substituent atoms.[43] Deviations from planarity are even greater in **2a**. The displacement of the α sp^3 carbon atom, C(4), from the analogous six-atom plane has increased to 0.935 (7) Å (in the direction away from O(3)). The plane of the phenyl ring is approximately perpendicular (82–85°) to the six-atom plane in both **1a**[43] and **2a**.

The cobalt atom in **1a** is chiral. In the only known diastereomer of this complex, triphenylphosphine is coordinated to the metal on the same side of the metallacyclopentene ring as the two cis hydrogen atoms.[6] The ester groups on C(3) and C(4) are constrained to lie on the opposite face of the metallacycle ring from the phosphine. Not surprisingly, coordination of the ester on C(3) results in inversion of configuration at the cobalt atom, as evidenced by the change of the dihedral angle defined by the plane of the Cp ring and the six atom olefin plane from 33.6°[43] in **1a** to 103.7° in **2a**. The large angle between these planes in **2a** and the absence of bulky ligands on the face of the metallacycle plane away from the chelated ester leaves the cobalt atom relatively exposed to the approach of ligands from this direction. In contrast, the cobalt atom in **1a** is well-shielded by the surrounding ligands.

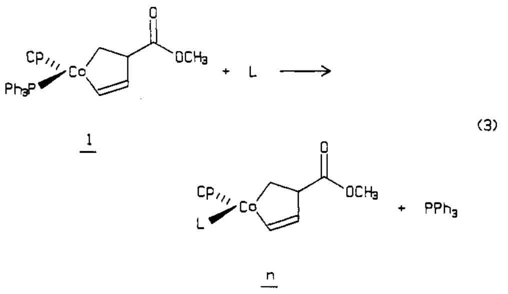
Ligand Substitution Reactivity. Several features of the structure of **2a** suggested to us that displacement of the coordinated ester group by other ligands should be facile. These features included the long Co–O(3) bond length, the small bond angles within the [2.2.1] ring system, and the relatively exposed cobalt atom. We examined the reactions of **2a** and **2b** with tri-*n*-butylphosphine (**3**), tri-*p*-tolylphosphine (**4**), trimethyl phosphite (**5**), *tert*-butyl isocyanide (**6**), thiocyanate (**7**), and acetonitrile (**8**) (eq 2)



n = 3, L = $P(C_4H_9)_3$
4, $P(p\text{-}C_6H_4CH_3)_3$
5, $P(OCH_3)_3$
6, $CNC(CH_3)_3$
7, SCN^-
8, CH_3CN

(metallacycle ring substituents are omitted for clarity). In most cases, reaction at room temperature of equimolar quantities of these complexes and the above ligands resulted in near quantitative formation of substituted metallacyclopentene complexes **3** through **8**, **a** and **b**, respectively. These were isolated in moderate to excellent yields. NMR data for these complexes are collected in Tables I and II and are discussed below.

Complexes **3** through **6** can also be obtained by direct reaction of **1a** or **1b** with the appropriate ligand (eq 3).



These reactions require excesses of ligand and are typically run at elevated temperature, however. Both can lead to the formation of undesired side products. Most of the direct substitution reactions of **1** reach an equilibrium in which significant quantities of **1** remain. Purification by chromatography is necessary to separate the product, unreacted **1**, and triphenylphosphine. Thiocyanate and acetonitrile do not compete effectively with triphenylphosphine. Thus, **7** and **8** cannot be obtained by this route.

Each of the above ligands, with the exception of acetonitrile, reacts with near stoichiometric quantities of **2** or **1** to yield only one of the two possible diastereomers of the product complex. The similarities of the phosphorus–proton coupling constants of all phosphine- and phosphite-containing complexes, see below, and consideration of steric effects imply that the ligands in **3** through **6** bind to cobalt on the face of the metallacyclopentene ring opposite the coordinated ester group. Thus, the net substitution reaction of **2** is stereospecific and results in inversion of configuration at cobalt.

2a does not react to any appreciable extent with 1 equiv of acetonitrile. Large excesses of acetonitrile (neat solvent) react with **2a** to form nearly equal quantities of two different complexes, **8a** and **8a′** (more abundant and less abundant, respectively). The steric demands (cone angle) of acetonitrile are quite small. A reasonable interpretation of the existence of two complexes is that in one acetonitrile coordinates to cobalt on the same face of the metallacyclopentene ring as the displaced ester group. The atypical diastereomer could be a secondary product that

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results from displacement by a second acetonitrile molecule of the acetonitrile ligand in the initially formed normal diastereomer of **8a**.

NMR Spectra of Cobaltacyclopentenes and Cobaltaoxanorbornadienes. ^1H and ^{13}C NMR data for complexes 1 through 8 and other selected complexes are presented in Tables I and II. Data for phenyl proton multiplets were not included in Table I. These resonances provide little information beyond establishing that rotation of the phenyl group is slow on the NMR time scale. An examination of the data reveals a number of features that are characteristic of cobaltacyclopentenes and cobaltaoxanorbornadienes and that permit the two classes of complexes to be distinguished by spectroscopic means.

The ^1H NMR spectra of the cobaltacyclopentenes and cobaltaoxanorbornadienes reported in this paper are similar in their gross features (ignoring the resonances due to the additional ligand in the former). There is little spin-spin coupling in these systems owing to the isolation of most of the individual spin systems. The size of the phosphorus–proton couplings in **1a** and **1b** were used by others to assign the positions of the metallacycle ring protons relative to the cobalt atom.[6] The protons on the α-carbons (corresponding to C(4) in **2a**) were assigned to peaks with $J_{PH} = 14$ Hz. J_{PH} of protons on β-carbons (corresponding to C(3) in **2a**) was 2 Hz. We observe a similar pattern of coupling constants in complexes **3** through **5** and have assigned protons accordingly.

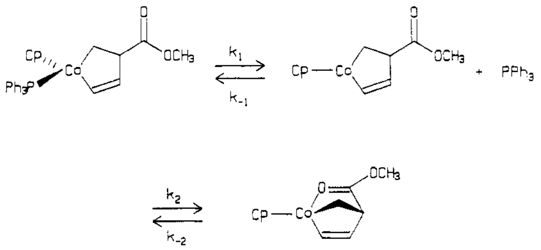
The most striking difference in the ^1H NMR spectra of the two classes of complexes is the magnitude of the vicinal coupling constant of the metallacycle ring protons. Cobaltacyclopentene complexes have coupling constants that range from 7.1 to 8.7 Hz, a reasonable value for cisoid protons on a five-membered ring. In contrast, the coupling constant in cobaltaoxanorbornadiene complexes **2a** and **2b** is 2.0 Hz. This small value is a consequence of the large changes in the conformation of the metallacyclopentene ring moiety that occur upon formation of the [2.2.1] ring system. The H(3)–C(3)–C(4)–H(4) dihedral angle in **2a** is 75°. A minimal coupling constant is predicted for this angle by the Karplus relationship.

Complexes **7a** and **8a** have somewhat atypical ^1H NMR properties. The chemical shifts and vicinal coupling constants of the metallacycle ring protons are larger (9.6 Hz) than those of other cobaltacyclopentenes. The difference in chemical shifts of ring protons in **8a** and **8a′** is about 0.9 ppm. Acetonitrile and thiocyanate both have small steric demands. It is tempting to speculate that **7a** and **8a** may be diastereomers in which the ligand binds to cobalt on the same face as the coordinated ester in **2**.

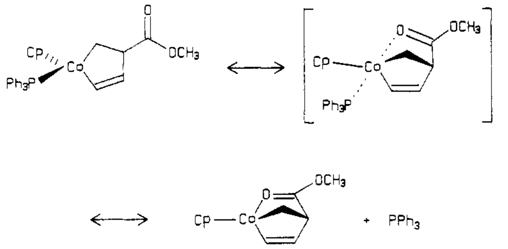
The ^{13}C chemical shifts of metallacycle carbons in cobaltacyclopentenes are significantly different than those in cobaltaoxanorbornadienes. The shifts readily distinguish both classes from simple cobalt(I) alkene and alkyne complexes. Representative ^{13}C data for the latter complexes are included in Table II for purposes of comparison.

Several features of the ^{13}C NMR spectra of cobaltaoxanorbornadiene complexes are distinctive. The shifts of typical methoxy carbons fall in a narrow range about 51 ppm. Both **2a** and **2b** have on methoxy carbon that resonates at 56 ppm. In addition, one carbonyl carbon is found at about 190 ppm in these complexes, substantially downfield from most other ester carbonyl carbons in the complexes in Table II. The unusual methoxy and carbonyl carbons probably are those of the coordinated ester group. The Cp carbons of **2a** and **2b** are about 4 ppm upfield of the analogous carbons in cobaltacyclopentene complexes with a few exceptions. Finally, the peak assigned to C(2) in **2a** was observed to be a narrow doublet in ^1H-coupled spectra. The splitting results from long range coupling with the proton on C(3). Similar long-range coupling was not observed in **2b**, however, owing to a poor signal to noise ratio for the C(2) peak.

Scheme I



Scheme II



The Implications of Metallaoxanorbornadienes. Loss of triphenylphosphine from metallacyclopentene **1a** or **1b** results in formation of cobaltaoxanorbornadiene complex **2a** or **2b**. The existence and stability of these complexes must be considered something of a surprise, given the evidence of strain within the [2.2.1] ring system and the length of the Co–O bond. Nonetheless, the existence of these complexes implies that the 16-electron cobaltacyclopentene complexes and the coordinatively saturated $CpCo(\eta^2\text{-alkene})(\eta^2\text{-alkyne})$ complexes of the same stoichiometry are even less stable or are kinetically inaccessible.

The reaction $(\eta^5\text{-}C_5H_5)Co(\eta^2\text{-}CH_3O_2CC{\equiv}CCO_2CH_3)(PPh_3)$ with dimethyl maleate to form cobaltacyclopentene **1b** and reaction of cobaltacyclopentene **1a** with diphenylacetylene to form a cyclohexadiene complex have been investigated.[6] Kinetic evidence suggested that the initial step was loss of triphenylphosphine in both cases. Loss could occur either by a dissociative mechanism or by an associative reaction of the complex with the entering ligand. The authors suggested a coordinatively saturated $CpCo(\eta^2\text{-alkene})(\eta^2\text{-alkyne})$ complex and a 16-electron cobaltacyclopentene complex as intermediates in the first reaction. These would be potential intermediates in the second reaction, too, if phosphine loss occurs by a dissociative mechanism.

The results of our investigation raises questions about the interpretation of the kinetic data for the above reactions. Could the kinetically significant loss of phosphine be assisted by coordination of the ester carbonyl oxygen atom? Are the intermediates metallaoxanorbornadiene complexes? Are η^2-alkene η^2-alkyne complexes relevant to cobaltacyclopentene chemistry? Fortunately, the existence of isolable metallaoxanorbornadiene complexes provide a remarkable opportunity to answer such questions.

Metallaoxanorbornadiene complexes can be envisioned to arise from cobaltacyclopentene complexes by one of two mechanisms. In the first (Scheme I), reversible dissociation of phosphine from **1** forms a coordinatively unsaturated metallacyclopentene. Intramolecular reaction of the β-ester carbonyl oxygen atom with the cobalt atom affords the product. In the second mechanism, the metallaoxanorbornadiene results from direct attack of the β-ester carbonyl oxygen atom on the cobalt atom of the initial metallacyclopentene (Scheme II). Cobaltaoxanorbornadienes must be considered as intermediates in the reactions of cobaltacyclopentenes if the second mechanism is correct and the rate of this reaction is sufficiently fast. The mechanism of the reaction of **2** with ligands to reform **1** must be the microscopic reverse of the formation of **2**. Study of the reactions of **2** will provide considerable information about the mechanism of cobaltacyclopentene reactions and may permit the determination of several fundamental rate constants for the system. Furthermore, such reactions provide a means of preparing cobaltacyclopentene complexes substituted with potentially reactive ligands that are inaccessible from **1**. Investigations of the reactions of these complexes will afford a test of whether prior coordination of a ligand is necessary for reaction with cobaltacyclopentenes. Several of these points are currently being investigated in our laboratories.

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Registry No. **1a**, 53559-30-1; **1b**, 69896-30-6; **2a**, 106800-02-6; **2b**, 106800-03-7; **3a**, 106800-04-8; **3b**, 106800-05-9; **4a**, 106800-06-0; **5a**, 106800-07-1; **5b**, 106800-08-2; **6a**, 106800-09-3; **6b**, 106800-10-6; **7a**, 106800-11-7; **8a**, 106800-12-8; **8a′**, 106862-51-5.

Supplementary Material Available: Tables of thermal parameters and atomic parameters for hydrogen atoms for **2a** (2 pages); a listing of observed and calculated structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

Nucleophilic Additions to Carbonyl Ligands on Tetracobalt Clusters. Formation of Polynuclear Formyl and Carbene Complexes

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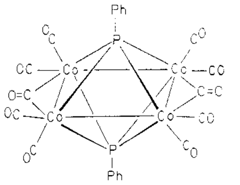
The tetracobalt cluster $Co_4(CO)_{10}(\mu_4\text{-}PPh)_2$ (I) undergoes facile reductive decarbonylation to afford the bridged hydride $Co_4(CO)_9(PPh)_2(\mu\text{-}H)^-$ in quantitative yields upon the treatment with various types of borohydrides at 25 °C. However, when the reductions are carried out at −78 °C, a transient intermediate can be detected and its structure shown to be the corresponding formyl derivative $Co_4(CO)_9(PPh)_2CHO^-$ (III) from its IR spectrum and ^1H and ^{13}C NMR spectra. The formation of the formyl intermediate III is confirmed by deuterium-labeling studies, and its spontaneous decarbonylation to the μ-hydride is described. Nucleophilic addition to a CO ligand as a route to the formyl intermediate is demonstrated by the generation of the corresponding acyl analogues in excellent yields following the treatment of I with methyl- and *n*-butyllithium. The formyl and acetyl tetracobalt clusters are efficiently trapped by O-alkylation with methyl triflate to afford the carbene derivatives $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)H]$ and $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$, respectively. Nucleophilic addition to I followed by alkylation to afford these tetracobalt carbene derivatives is thus analogous to the behavior of the triosmium cluster $Os_3(CO)_{12}$ recently reported by Kaesz and co-workers. The acid-catalyzed 1,2-elimination of methanol from the carbene cluster $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$ yields the vinylidene cluster $Co_4(CO)_9(PPh)_2(\mu\text{-}C{=}CH_2)$, which is also produced in high yields when the acetyl cluster is treated with trifluoroacetic anhydride. The molecular structures of $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$ and the vinylidene derivative are established by X-ray crystallography. $Co_4(CO)_9(PPh)_2[\mu\text{-}C(OMe)Me]$ crystallizes in the monoclinic space group $P2_1/c$ with a = 16.465 (2) Å, b = 23.987 (3) Å, c = 15.775 (2) Å, β = 112.61 (1)°, V = 5752 Å^3, and Z = 8. $Co_4(CO)_9(PPh)_2(\mu\text{-}C{=}CH_2)$ crystallizes in the monoclinic space group $P2_1/n$ with a = 9.954 (1) Å, b = 12.865 (3) Å, c = 10.270 (1) Å, β = 98.88 (1)°, V = 1299 Å^3, and Z = 2. Reactivity studies of the formyl and the various carbene ligands bound to the tetracobalt cluster are described.

Introduction

Polynuclear clusters with contiguous metal centers that can promote the multisite activation of substrates may be suitable models for carbon monoxide reduction.[1,2] The synthesis and reactivity of polynuclear metal clusters that contain formyl, alkyl, hydrido, and alkylidene ligands continue to attract interest as reactive intermediates.[3,4] Among such polynuclear clusters, we have focused our attention on the bicapped tetracarbonyl carbonyl I since



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