of doublets at δ 5.2 and 5.0 (J_{HH} = 7.3 Hz) in 60% yield, along with several unidentified species. After 24 h, the doublets at δ 5.2 and 5.0 were replaced by the characteristic resonance of the μ-acetyl cluster **5** (83% yield) at δ 2.58.[15] IR monitoring of the reaction of **2** with $BF_3{\cdot}Et_2O$ showed immediate loss of the ketene ν_{CO} stretch and the formation of a new species with ν_{CO} (CH_2Cl_2) bands at 2107 (w), 2066 (s), 2033 (w), 2018 (s), and 1999 (w) cm^{-1}.

Crystal and Molecular Structure of [PPN][$Os_3(CO)_{11}(CH_2C\{O\}OCH_3)$] (4). A crystal of **4** was cleaved from a much larger and well-formed specimen and was mounted with epoxy cement on a glass fiber. The crystal, data collection, and refinement parameters are contained in Table I. Unit-cell parameters were obtained from the least-squares fit of the angular settings of 25 reflections (22 ° ≤ 2θ ≤ 29°) which contained Friedel related reflections to check optical and diffractometer alignment. The intensity data were processed with a profile-fitting routine to improve the accuracy in the measurement of weak reflections and corrected for a 2% linear decay, *Lp* effects, and absorption (empirical, six-parameter ellipsoid model, 252 data).

The structure was solved by direct methods and completed by a series of difference Fourier syntheses. The equatorial plane of Os(2) is disordered about an approximate, perpendicular mirror plane containing the axial carbonyl groups (5 and 7), C(14), and the midpoint of the Os(1)–Os(3) bond. The methylene carbon atom of the $-CH_2C(O)OCH_3$ group, C(12), and the carbon atom of the carbonyl group, C(6), are superimposed, as are the terminal methyl groups, C(14), of the two acetate orientations. These atoms were refined at full occupancy. The atoms O(6), O(12), O(13), and C(13) were paired with their primed counterparts, and their occupancies were collectively refined; the sum of the primed and unprimed sets was constrained to unit occupancy. The unprimed set occupancy is 72 (1)%; this is the set shown in Figure 1.

The six phenyl rings of the PPN$^+$ ion were constrained to rigid, planar hexagons (d(C–C) = 1.395 Å) with calculated hydrogen atom contributions. No hydrogen atom contributions were included for the minor orientation of the disordered $CH_2C(O)OCH_3$ group but were for the major one. All non-hydrogen atoms (except for the 28%—occupied primed atoms) were refined with anisotropic temperature factors.

All programs and sources of the scattering factors are included in the P3 and SHELXTL (version 5.1) program libraries distributed by the Nicolet Corp., Madison, WI. Atomic coordinates are given in Table II and selected bond distances and angles in Table III. Tables of structure factors, complete bond lengths and angles, and anisotropic temperature factors were previously supplied as supplementary material to ref 11.

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Registry No. **1**, 85883-28-9; **2**, 93923-21-8; **3**, 96395-20-9; **4**, 103477-25-4; **5**, 91312-92-4; **6**, 103438-79-5; **7**, 103438-81-9; $OS_3(CO)_{12}$, 15696-40-9; $CH_3C(O)N$-n-Bu_2, 1563-90-2; $CH_3C(O)NH$-n-Bu, 1119-49-9; Os, 7440-04-2.

Kinetics, Stereochemistry, and Mechanism of the Interconversions of Cobaltaoxanorbornadiene and Cobaltacyclopentene Complexes

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The metallaoxanorbornadiene complexes 1-(cyclopentadienyl)-1-cobalta-5,7-dicarbomethoxy-3-methoxy-2-oxa-6-R-norbornadiene (**1a**, R = phenyl; **1b**, R = carbomethoxy) reacted with $P(C_6H_5)_3$, $P(OCH_3)_3$, $(CH_3)_3CNC$, $P(n\text{-}C_4H_9)_3$, and $n\text{-}C_3H_7NH_2$ to afford the ligand-substituted cobaltacyclopentene complexes **2**–**6**, respectively. No evidence was seen for activation of the coordinated ester group in **1**. The equilibrium positions for the interconversion of cobaltacyclopentene/cobaltaoxanorbornadiene complexes were determined as a function of temperature. Thermodynamic data established that the formation of **1** was driven entirely by entropy. Kinetic measurements showed the reaction of **1** and ligand to be first order in both **1** and the ligand. Activation parameters for the reaction of **1** with $P(C_6H_5)_3$ and $(CH_3)_3CNC$ were consistent with an associative mechanism in which the entering ligand displaced the coordinated ester group. Ligands attacked from the face of the metallacycle opposite the coordinated ester group. Isomeric complexes with ligand on the same face as the coordinated ester group were obtained in low yield as kinetic products of preparative scale reactions when the concentration of ligand was high and the steric bulk of the ligand was low. These complexes were observed only when intermolecular trapping of a coordinatively unsaturated cobaltacyclopentene intermediate became competitive with intramolecular trapping by the ester group. The results establish that cobaltaoxanorbornadiene complexes are the kinetically important intermediates in the reactions of cobaltacyclopentenes.

During an investigation in our laboratories of the reactivity of metallacyclopent-2-ene complexes, we discovered a novel class of [2.2.1]-cobaltacyclic complexes, **1**, which we refer to as cobaltaoxanorbornadienes.[1] These complexes formally result from ligand substitution reactions in which the carbonyl oxygen of a metallacycle β-ester substituent displaces triphenylphosphine from the metal center of a cobaltacyclopent-2-ene complex, **2** (eq 1). The only precedent for substitution of an ester group for a phosphine ligand is found in the formation of $(\eta^5\text{-}C_5H_5)\text{-}\overline{Ru[C(CO_2CH_3)CHC(OCH_3)O]}[P(C_6H_5)_3]$ from $(\eta^5\text{-}C_5H_5)\text{-}Ru[\eta^1\text{-}C(CO_2CH_3)CH(CO_2CH_3)][P(C_6H_5)_3]_2$.[2] Reactions

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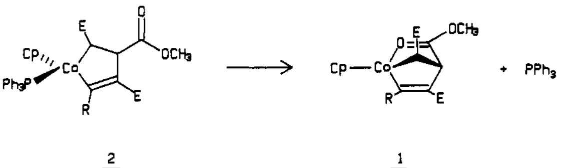
[1] Stolzenberg, A. M.; Scozzafava, M.; Foxman, B. M. *Organometallics* 1987, *6*, 769.

[2] Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* 1974, 106.



(1)

2 1

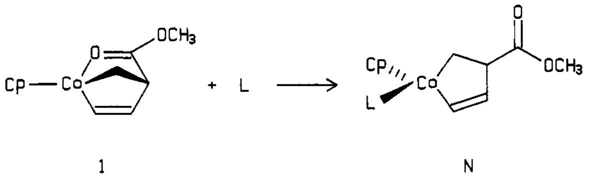
a: R = Ph, E = CO$_2$CH$_3$

b: R = E = CO$_2$CH$_3$

leading to 1 result in inversion of the configuration of the chiral cobalt atom. The carbonyl oxygen atom coordinates to cobalt solely on the face of the metallacycle that was opposite the phosphine.

Several features of the structure of **1a** suggested to us that the coordinated ester group should be reactive. A Co(III)-coordinated ester structural unit also occurs in Co(III)-chelated glycine ester complexes.[3-5] The metal-coordinated acyl groups of these complexes are activated toward hydrolysis and aminolysis.[3-7] Rate increases of 10^7 over that of an uncoordinated ester have been reported. The similarity of the frequencies of the IR band of the coordinated esters in the glycine ester complexes[3,4] and in 1 suggested that the acyl group of 1 might also be activated by coordination to a metal. On the other hand, cleavage of the cobalt–oxygen bond appeared likely. The X-ray structure of **1a**[1] established that the bond lengths and angles in the organic portion of the [2.2.1] ring system are remarkably similar to those in norbornadiene, implying the existence of considerable ring strain. In addition, the cobalt–oxygen bond length was longer than expected and the cobalt atom was relatively exposed.

Several examples of cleavage of the cobalt–oxygen bond were discovered in our initial investigation of the reactivity of these complexes.[1] 1 reacted with stoichiometric quantities of a number of ligands to form substitutionally related cobaltacyclopentene complexes (eq 2). Addition of



(2)

1 N

N = 3, L = P(OCH$_3$)$_3$
4, (CH$_3$)$_3$CNC
5, P(C$_4$H$_9$)$_3$

the ligand occurred solely from the face of the metallacycle opposite the coordinated oxygen for all but the least sterically demanding ligands. In all cases, the newly formed cobaltacyclopentene was in equilibrium with the cobaltaoxanorbornadiene. The position of equilibrium appeared to vary considerably with ligand.

A third type of reactivity for 1 that appeared possible included reactions of the imbedded metallacyclopentene ring. Reactions of this type have been reported for cobaltacyclopentene complexes. **2a** reacted with acrylonitrile and alkynes to yield (η^5-C$_5$H$_5$)Co(η^4-diene) and -(η^4-cyclohexadiene) complexes, respectively.[8] A kinetic investigation of the reaction with diphenylacetylene demonstrated that the initial step involved loss of triphenylphosphine.[8] Two complexes were potential intermediates in the reaction. The first was the coordinatively unsaturated cobaltacyclopentene complex that results from dissociation of phosphine from **2a**. The second was the coordinatively saturated (η^5-C$_5$H$_5$)Co(η^2-dimethyl maleate)(η^2-methyl phenylpropiolate) complex formed by the scission of the cobaltacyclopentene ring of the former. Our isolation of **1a** under conditions that should have led to the above complexes establishes that both either are less stable than **1a** or are kinetically inaccessible. We have further observed that reaction of diphenylacetylene with **1a** yields products identical with those of the reaction with **2a**.[9] Thus, cobaltaoxanorbornadiene complexes either are in equilibrium with or must be the kinetically significant intermediate in the reactions of cobaltacyclopentenes.

In this paper, we describe a detailed study of the kinetics and stereochemical outcome of the reaction of 1 with a variety of ligands. On the basis of this evidence, a mechanism is proposed for the interconversion of cobaltaoxanorbornadiene and cobaltacyclopentene complexes. Measurements of the temperature dependence of the equilibrium constants for these reactions reveal that the formation of cobaltaoxanorbornadiene is entirely entropy driven. Finally, the reactivity of the coordinated ester group is examined for evidence of acyl activation upon coordination.

Experimental Section

Materials. Metallaoxanorbornadiene complexes,[1] substituted metallacyclopentenes **2–5**,[1,8] and (η^5-C$_5$H$_5$)Ru[C(CO$_2$CH$_3$)-CHC(OCH$_3$)O][P(C$_6$H$_5$)$_3$][2] were prepared by literature methods and were recrystallized prior to use in kinetic and/or equilibrium experiments. Trimethyl phosphite and tri-*n*-butylphosphine were vacuum distilled before use. All other ligands were of reagent grade and were used without further purification. Toluene and benzene were distilled from sodium benzophenone ketyl and stored under N$_2$ in a drybox.

Physical Measurements. Samples of less than 100 mg were weighed to a precision of ±10 μg on a Mettler Gram-atic microgram balance. UV–vis spectra were recorded on a Perkin-Elmer Lambda 4C spectrophotometer interfaced with a Perkin-Elmer 7300 computer. A Haake A81 constant temperature circulating water bath was used to control the temperature (±0.25 °C) of kinetic and equilibrium experiments. ^{1}H and ^{13}C NMR spectra were determined on a Varian XL-300 spectrometer. Chemical shifts are reported in parts per million relative to TMS (δ). Benzene-d_6 and CDCl$_3$ were used as secondary internal standards in ^{13}C NMR spectra. IR spectra were recorded on a Perkin-Elmer Model 683 equipped with a data station.

Sample Handling. The cobalt complexes included in this investigation were generally air-stable as solids but underwent slow aerobic decomposition in solution in the absence of an excess of ligand. Equilibrium experiments, preparative reactions, and chromatographic procedures were performed anaerobically. Inert atmosphere manipulations were carried out under a nitrogen or argon atmosphere in a Vacuum/Atmospheres Co. drybox or by Schlenk techniques. Kinetic experiments were conducted aerobically. Decomposition of complexes was demonstrated to be negligible during these experiments because of their short time scales (minutes) and the presence of large excesses of ligand. In all cases, solid cobalt compounds were weighed out in air on a microgram balance, placed under vacuum, and brought into the drybox. Stock solutions of metallaoxanorbornadiene complexes and of substituted cobaltacyclopentene complexes **2–5** were prepared by using dry, degassed toluene. Stock solutions of ligands

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[3] Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 4539.

[4] Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6032.

[5] Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 5701.

[6] Baraniak, E.; Buckingham, D. A.; Clark, C. R.; Moynihan, B. H.; Sargeson, A. M. *Inorg. Chem.* **1986**, *25*, 3466.

[7] Buckingham, D. A.; Clark, C. R. *Inorg. Chem.* **1986**, *25*, 3478.

[8] Wakatsuki, Y.; Katsuyuki, A.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123.

[9] Stolzenberg, A. M.; Scozzafava, M., unpublished observations.

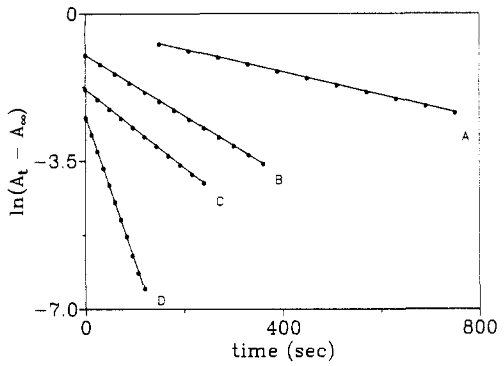

Figure 1. Plots of ln $(A_t - A_\infty)$ vs. time for the reactions of **1a** with PPh_3 in toluene at several different temperatures: (A) 5.0 °C, $[PPh_3]$ = 169 mM; (B) 25.0 °C, $[PPh_3]$ = 53.6 mM; (C) 40.0 °C, $[PPh_3]$ = 2.04 mM; (D) 55.8 °C, $[PPh_3]$ = 1.02 mM. For clarity, only every second data point (every fourth data point for (d)) is shown.

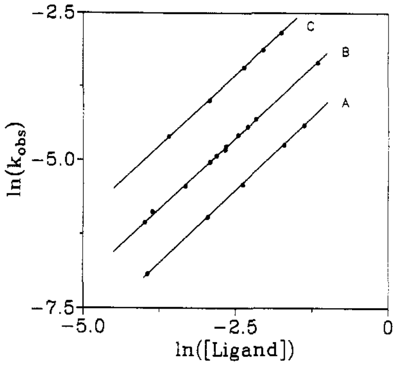

Figure 2. Plots of ln (k_{obsd}) vs. ln ([ligand]) for the reactions of 1 with PPh_3 and $(CH_3)_3CNC$ in toluene at 25.0 °C: (A) **1b**, PPh_3; (B) **1a**, PPh_3; (C) **1a**, $(CH_3)_3CNC$.

Table I. Rate Constants for the Reaction of 1 with L in Toluene

Co complex	ligand	T, °C	10^2k_1, s^{-1} M^{-1}	10^6k_{-1}, s^{-1}
1a	PPh_3	5.0	1.54 ± 0.08	
		15.0	4.45 ± 0.04	
		25.0	12.2 ± 1.0	50 ± 9
		40.0	45.8 ± 0.7	
		55.0	170 ± 9	
	$(CH_3)_3CNC$	5.0	4.52 ± 0.24	
		15.0	15.0 ± 0.3	
		25.0	35.2 ± 1.1	1.4 ± 0.4
		35.0	92.5 ± 2.0	
	$P(OCH_3)_3$	25.0	4.98 ± 0.50	2.7 ± 0.7
	$P(n\text{-}Bu)_3$	25.0	6.70 ± 0.10	2.8 ± 0.5
1b	PPh_3	15.0	1.82 ± 0.03	
		25.0	4.95 ± 0.09	1.2 ± 0.4
		35.0	13.2 ± 0.1	
		45.0	30.6 ± 0.3	
		55.0	68.3 ± 0.6	

Table II. Activation Parameters for the Reaction of 1 with L in Toluene

	1a		**1b**
	PPh_3	$(CH_3)_3CNC$	PPh_3
E_A[a]	16.9 ± 0.3	16.8 ± 0.8	17.0 ± 0.6
$\Delta H^{\ddagger}$[a]	16.3 ± 0.3	16.2 ± 0.8	16.4 ± 0.6
$\Delta S^{\ddagger}$[b]	−8.0 ± 1.2	−6.1 ± 3.3	−9.4 ± 2.9

[a] Reported in kcal mol^{-1}. [b] Reported in cal mol^{-1} K^{-1}.

used in kinetics experiments were typically prepared under aerobic conditions. Solutions used in kinetics experiments were freshly prepared each working day. Those of the cobalt complexes were stored under anaerobic conditions and were checked for decomposition prior to use.

Kinetic Experiments. Kinetic data for the reactions of 1 with various ligands were obtained spectrophotometrically by monitoring the absorbance of the reaction solution as a function of time. The monitored wavelengths were near the λ_{max} of either the starting complex 1 or the product cobaltacyclopentene and were chosen to maximize the absorbance change during the course of the reaction. The absorbance due to added ligand was determined to be insignificant at the wavelengths where the reaction was monitored. When solutions of the pure complexes were used, the molar extinction coefficients of both the starting metallaoxanorbornadiene and the product metallacycles **2**–**5** were determined to a precision of 0.1–0.3%.[1] (Addition of an excess of the appropriate ligand to solutions of **2**–**5** was necessary to suppress dissociation of ligand during these measurements.) Independent knowledge of the extinctions and of initial concentrations in the reaction solutions permitted a check on the validity of the kinetic data. In general, agreement of calculated and observed initial and final absorbances was excellent.

In a typical experiment, a solution of known volume and concentration of the appropriate ligand was placed in a 1.000-cm quartz cuvette. The cuvette was inserted into a water-jacketed cell holder in the sample compartment of the spectrophotometer. The cell holder was connected to the Haake circulating bath. An anaerobic stock solution of 1 was stored inside the circulating bath. After both solutions had reached thermal equilibrium, a predetermined volume of the stock solution of 1 was added to the ligand solution and the resulting solution was rapidly mixed. The initial absorbance reading was typically obtained ca. 15 s after mixing. The reaction was monitored at regular intervals for 4–8 $t_{1/2}$'s (3–30 min depending on reaction rate).

Kinetic data were obtained at regular temperature intervals between 5 and 55 °C. At temperatures below ambient, the spectrophotometer sample compartment was purged with dry nitrogen and the initial data collection was delayed to minimize the effects of condensation on the cuvette. The concentration of 1 ranged from 5×10^{-4} to 25×10^{-4} M, and that of the ligands ranged from 1×10^{-2} to 30×10^{-2} M. The ratio of the ligand concentration, [L], to [1] varied from 33 to 200, sufficient to ensure pseudo-first-order kinetic behavior in the event that the reaction rate depended upon [L].

Figure 1 shows typical first-order rate plots for the formation of the substituted metallacycle **2a** from **1a** and triphenylphosphine. Rate plots of this and other reactions were linear for at least 4 half-lives. Observed rate constants were obtained from weighted nonlinear least-squares fits of the log $(A_t - A_\infty)$ vs. time. Weighted nonlinear least-squares analysis of log k_{obsd} vs. log [L], Figure 2, established that the full rate law was second order (see below). Data (absorbance vs. time) from at least three replicate experiments were used to calculate a second-order rate constant for each unique combination of 1 and ligand concentrations. (Data from individual experiments are reported in the supplementary material.) Rate constants from 4 to 12 combinations of 1 and ligand concentrations were averaged to calculate the rate constant at a given temperature, Table I. The errors in the rate constants are reported as the standard deviation from the mean value. Activation parameters for the reactions of 1 with PPh_3 and $(CH_3)_3CNC$ were calculated with the Eyring equation by using a weighted nonlinear least-squares analysis, Table II.

Equilibrium Experiments. The position of equilibrium for the dissociation of complexes **2**–**5** to 1 and the corresponding ligand was determined spectrophotometrically. Anaerobic conditions were necessary, especially at elevated temperatures, owing to the sensitivity of the complexes to air oxidation over the 3–6 h time period required to reach equilibrium. Starting concentrations of the metallacycles were ca. 1.5×10^{-3} M. In the case of **2a**, added PPh_3 was present in concentrations ranging from 0 to 1.5×10^{-3} M. In all other cases, addition of ligand caused near total suppression of the dissociation reaction. Equilibrium constants are reported in Table III. Thermodynamic parameters for the dissociation of **2a** were calculated by weighted nonlinear least-squares fits of log K vs. $1/T$, Table IV. All errors are reported as standard deviations.

Preparative Scale Reactions. Reaction of 1a with $P(OCH_3)_3$. A solution of **1a** (40 mg, 0.093 mmol) in dry benzene (20 mL) was prepared under N_2. Trimethyl phosphite (58 mg, 55 μL, 0.93 mmol) was added via syringe to the stirred solution. After 24 h, the reaction solution was reduced to dryness and the residue

Table III. Equilibrium Constants for the Dissociation of Cobaltacyclopentene to the Corresponding Ligand and Cobaltaoxanorbornadiene

		10^5K_{eq},[a] M, at the following temp (°C)					
	L	15.0	25.0	35.0	40.0	50.0	60.0
2a	PPh_3	20 ± 4	41.0 ± 7	86 ± 11	120 ± 10	240 ± 40	349 ± 7
2b	PPh_3		2.4 ± 0.7				
3a	$P(OCH_3)_3$		5.5 ± 1.2				
4a	$(CH_3)_3CNC$		0.41 ± 0.11				
5a	$P(n\text{-}Bu)_3$		4.1 ± 0.8				

[a] Toluene as solvent.

Table IV. Thermodynamic Parameters for the Reaction 2a ⇄ 1a + PPh$_3$ in Toluene

$\Delta H_m°$	11.6 ± 0.5	kcal mol^{-1}
$\Delta S_m°$	23.6 ± 1.6	cal mol^{-1} deg^{-1}
$\Delta G_m°$[a]	4.2 ± 0.6	kcal mol^{-1}

[a] At T = 38 °C.

was purified by chromatography on a silica column (1 × 12 cm). Elution with 100:1 CH_2Cl_2/THF gave a pale green band of unreacted **1a**. Elution with 100:3 CH_2Cl_2/THF afforded an orange band containing the major product (**3a-1**). Reduction of this eluate to dryness and recrystallization in toluene/hexane gave 40 mg of **3a-1** (88% yield). A small amount of an isomeric minor product (**3a-2**) was obtained from the column on further elution. Upon reduction of this eluate to dryness, a crude yield of 1 mg of **3a-2** (2% yield) was obtained. The compound was not further purified. Insufficient material was available for an elemental analysis of **3a-2**. **3a-1** has been reported previously.[1] NMR spectral data for the latter complex is included in Tables V and VI for purposes of comparison with **3a-2**.

Reaction of 3a-1 with P(OCH$_3$)$_3$. A solution of **3a-1** (35 mg, 0.063 mmol) and $P(OCH_3)_3$ (52 mg, 49 μL, 0.42 mmol) in benzene (15 mL) was allowed to stir overnight. The orange color of the solution remained unchanged. An aliquot (2 mL) was taken and was reduced to dryness. The residue was redissolved in $CDCl_3$ and was examined by ^1H NMR spectroscopy. No signals characteristic of the minor isomer, **3a-2**, were observed. In addition, chromatography on silica gel TLC plates (5:1 CH_2Cl_2/THF) gave no indication of the formation of **3a-2**. After 6 days, the remaining solution was worked up as described above. **3a-1** (30 mg) was recovered as well as ca. 1 mg of **3a-2**.

Reaction of 1a with (CH$_3$)$_3$CNC. **1a** (40 mg, 0.093 mmol) and $(CH_3)_3CNC$ (60 mg, 81 μL, 0.72 mmol) were dissolved in dry benzene and allowed to stir. The solution rapidly changed color from green to red. After 3 h, the solution was reduced to dryness and the residue was purified by chromatography on a silica column (1.5 × 12 cm, 50:1 CH_2Cl_2/THF). A small band of unreacted starting material eluted first. It was followed by the major orange band containing **4a-1**. This band was collected and reduced to dryness. The residue was recrystallized from toluene/hexane to yield 36 mg of the known complex **4a-1** (76% yield). Further elution of the column with 25:1 CH_2Cl_2/THF gave a pale orange band, which contained 4 mg of the isomeric minor product **4a-2** (a crude yield of 8%). **4a-2**: IR (CH_2Cl_2) ν 2171 (s, C≡N), 1734 (s, C=O), 1693 cm^{-1} (s, br, C=O). Insufficient material was

Table V. ^1H NMR Spectra Data[a,b]

	η^5-C_5H_5	OCH_3	ring protons			ligand
3a-1[c]	4.69	3.81, 3.61, 3.31	3.79 (dd)	$^3J_{HH}$ = 8.0	J_{PH} = 1.2	3.63 (d, 9 H, $POCH_3$)
			3.25 (dd)		J_{PH} = 9.0	J_{PH} = 10.7
3a-2	4.64	4.29, 3.59, 3.52	4.83 (dd)	$^3J_{HH}$ = 11.4	J_{PH} = 2.7	3.85 (d, 9 H, $POCH_3$)
			4.29 (dd)		J_{PH} = 4.7	J_{PH} = 10.5
4a-1[c]	4.59	3.80, 3.62, 3.37	3.81 (d)	$^3J_{HH}$ = 7.6		1.56 (s, 9 H, t-CH_3)
			3.37 (d)			
4a-2	4.86	3.78, 3.64, 3.60	3.77 (d)	$^3J_{HH}$ = 9.0		1.57 (s, 9 H, t-CH_3)
			3.27 (d)			
6a[d]	4.16	3.59, 3.46, 3.18	4.84 (d)	$^3J_{HH}$ = 9.5		2.77 (m, 1 H, NH)
			4.51 (d)			2.21 (m, 1 H, NH)
						2.12 (m, 2 H, CH_2)
						1.93 (m, 2 H, CH_2)
						0.69 (t, 3 H, CH_3)
						$^2J_{HH}$ = 7.5

[a] δ. All coupling constants are reported in Hz. Spectra were recorded in $CDCl_3$ unless otherwise noted. [b] Phenyl proton multiplets are omitted from the table. [c] Reference 1. [d] In C_6D_6.

Table VI. ^{13}C NMR Spectral Data[a]

	η^5-C_5H_5	ring[b] sp^2	ring[b] sp^3	OCH_3	C=O	aromatic	ligand
3a-1[c,d]	89.2 (2.9[e])	α: 154.3 (2.0[e])	α: 18.6 (2.90[e])	51.6	182.2	128.3–124.7	52.8 (7.0[e]) ($POCH_3$)
				50.5	176.3 (2.0)		
		β: 139.5	β: 56.1 (3.3[f])	50.3	161.3		
3a-2	89.8	α: not obsd	α: 30.4	50.9	181.6	129.8–123.7	54.5 (9.7[e])
				50.3	2CO's not obsd		
		β: not obsd	β: 57.5	49.8			
4a-1[c,d]	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 [$C(CH_3)$]
		β: 138.4	β: 55.7	50.4	161.1		
4a-2	89.0	α: 148.3	α: 23.4	51.7	182.0	128.2–125.4	59.2 [$C(CH_3)_3$]
				50.9	176.4		30.6 [$C(CH_3)_3$]
		β: 138.7	β: not obsd	50.4	175.3		
6a	87.3	α: 153.0	α: 15.3	51.9	182.6	129.1–122.9	52.9 (NCH_2)
				50.3	179.1		26.7 (CH_2)
		β: 142.1	β: 56.0	50.2	160.8		11.0 (CH_3)

[a] δ (J_{CP}, Hz). All spectra recorded in C_6D_6 unless otherwise noted. [b] Carbons in metallacyclopentene ring. [c] Reference 1. [d] In $CDCl_3$. [e] $^2J_{CP}$. [f] $^3J_{CP}$.

available for an elemental analysis. NMR spectral data for **4a-1**[1] is included in Tables V and VI for purposes of comparison with **4a-2**.

Reaction of 4a-1 with $(CH_3)_3CNC$. **4a-1** (3 mg, 0.006 mmol) and 131 μL of a 0.044 M solution (in $CDCl_3$) of $(CH_3)_3CNC$ (0.006 mmol) were dissolved in $CDCl_3$ (0.75 mL). The reaction was monitored by ^1H NMR spectroscopy. After 24 h, no indication of conversion of **4a-1** to **4a-2** was observed. Excess $(CH_3)_3CNC$ (11 mg, 15 μL, 130 mmol) was added to the solution. No evidence of the formation of **4a-2** was observed by ^1H NMR spectroscopy during the next 72 h.

Reaction of 1a with *n*-Propylamine. Compound **1a** (45 mg, 0.105 mmol) and excess *n*-propylamine (50 μL, 0.610 mmol) were dissolved in 15 mL of dry benzene, and the resulting solution was stirred for 20 h. The color of the solution gradually changed from green to reddish brown. ^1H NMR spectroscopy of the reaction solution indicated a 3:1 mixture of **6a**/**1a**. The solution was reduced to dryness, and the residue was purified by chromatography on a silica column (1 × 10 cm). Elution with 1:1:98 THF/*n*-propylamine/benzene afforded a brown major band which, on reduction to dryness and crystallization from toluene/hexane, gave brown needlelike crystals of the *n*-propylamine-substituted cobaltacyclopentene **6a** (45 mg, 88%). (Elution with a 1% *n*-propylamine solution increased the yield of isolated product.) Further elution gave a green-brown colored minor band which contained a mixture of **1a** and **6a**. **6a**: mp 121–122.5 °C; IR ($CHCl_3$) ν 3244 (br, w, NH), 1726 (s, C=O), 1680 cm^{-1} (br, s, C=O). Anal. Calcd for $C_{24}H_{30}CoNO_6$: Co, 12.09; C, 59.13; H, 6.22; N, 2.87. Found: Co, 12.26; C, 58.96; H, 6.59; N, 2.97.

Results

Reactivity at the Cobalt–Oxygen Bond. (a) Kinetics. The reactions of metallaoxanorbornadiene complexes with added ligands (eq 2) proceed by the microscopic reverse of the mechanism for ligand dissociation from metallacyclopentene complexes. Equivalent mechanistic information could be obtained in principle from an examination of either reaction. In practice, only the reactions of **1** with added ligand readily lend themselves to the type of detailed kinetic investigations that are necessary to obtain data of high precision. For these reactions the ratio of ligand to complex can be varied over a considerable range, the net chemical change required to reach equilibrium is generally large, and the reaction can be initiated at a definite point in time by the rapid mixing of two reactants rather than the dissolution of one.

The reactions of **1** with the ligands PPh_3, $P(n\text{-}C_4H_9)_3$, $P(OCH_3)_3$, and $(CH_3)_3CNC$ were examined in toluene solution under pseudo-first-order conditions. A [L]:[**1**] ratio between 33 and 200 was employed. The presence of excess ligand suppressed ligand dissociation reactions, increased the stability of the reaction systems, and resulted in considerable simplification of the data analysis.

Kinetic data for the above reactions were obtained by UV–vis spectrophotometry. Isosbestic points were observed in full-wavelength spectra throughout the course of these reactions. This is consistent with (but not unequivocal proof of) the presence of significant quantities of only two independent absorbing species in solution. The majority of reactions were monitored at a single wavelength. These wavelengths were near the λ_{max} of either the starting complex **1** or the product cobaltacyclopentene and were chosen to maximize the absorbance change during the course of the reaction. First-order plots of ln $(A_t - A_\infty)$ vs. t, Figure 1, established that the reaction is first order in [**1**] over at least 4–6 half-lives. Observed rate constants, k_{obsd}, were obtained from weighted nonlinear least-squares fits of the above function.

The order of the reaction in [L] was determined from the slope of plots of ln k_{obsd} vs. ln [L], Figure 2. Data were obtained at several concentrations of ligand ranging over 1–2 orders of magnitude. The slopes of these lines, Table VII, are all very close to 1.000. With the exception of the result for $(CH_3)_3CNC$, the results are statistically indistinguishable (less than 3σ) from 1.000 (see below, however). Thus, on the basis of the kinetic evidence, the overall rate law is strictly second order.

Table VII. Slope of the Plot of ln k_{obsd} vs. ln [L] for the Reaction of 1 with L in Toluene

	ligand	slope
1a	PPh_3	0.963 ± 0.018
	$P(OCH_3)_3$	0.989 ± 0.005
	$(CH_3)_3CNC$	0.967 ± 0.006
	$P(n\text{-}Bu)_3$	1.000 ± 0.010
1b	PPh_3	0.989 ± 0.005

Second-order rate constants, k_1, were calculated by dividing k_{obsd} by the appropriate ligand concentration. Data from at least three replicate experiments were used to calculate rate constants for each unique combination of [**1**] and [L]. (The data are available in the supplementary material.) Individual rate constants from 4 to 12 combinations of [**1**] and [L] were averaged to calculate the rate constant for a given temperature, Table I.

Kinetic measurements were made for the PPh_3 and $(CH_3)_3CNC$ reaction systems at intervals of approximately 10 °C between 5 and 55 °C. Activation parameters were determined from the plot of ln k_1 vs. $1/T$ and application of the Eyring equation and are reported in Table II. The reactions of both **1a** and **1b** have positive ΔH^* and negative ΔS^*. These observations are fully consistent with the associative mechanism suggested by the rate law.

The data in Table I establish that the nature of the entering ligand and of the substituents on the metallacycle affect the rate of reaction. Rate constants decreased by a factor of 7 on going from the nucleophilic t-$(CH_3)_3CNC$ to the less basic $P(OCH_3)_3$. Replacement of the phenyl α-substituent in **1a** with CO_2CH_3 in **1b** resulted in a three-fold decrease in rate constant for reaction with $P(C_6H_5)_3$. The sense of the change was opposite that expected on the basis of steric effects. Thus, the difference resulted either from electronic effects or from a lesser strain energy for **1b** (more stable ground state). A similar decrease in rate was observed for phosphine dissociation from the analogous cyclopentadienylcobaltacyclopentadiene phosphine complexes.[10] The diminished rate was attributed to a decrease in the electron density on the cobalt atom upon introduction of a stronger electron-withdrawing substituent on the cobaltacyclopentadiene ring and a concomitant strengthening of the Co–P bond. By extention, the Co–O bond in **1b** is expected to be stronger than in **1a**.

(b) Equilibria. Equilibrium was attained by allowing solutions of the complexes **2**–**5** to dissociate to **1** and the corresponding ligand. The position of the equilibrium was determined spectrophotometrically. Equilibrium constants for the dissociation reactions, K_{eq}, are reported in Table III.

The reaction system for **2a** was the best behaved of all the systems that we investigated. Over a wide temperature range, equilibrium was attained in a reasonably short time period. The net change in absorbance was large enough that precise values of K_{eq} could be obtained. The extent of dissociation for other complexes was significantly smaller than for **2a**. Hence, K_{eq} for these reactions were less precise. In addition, the approach to equilibrium for these complexes was rather slow. In some cases decom-

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(10) Yasufuku, K.; Hamada, A.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1980**, *102*, 4363.

position was significant on the time scale of the experiment. Both problems were accentuated at temperatures below 25 °C. Competing reactions became important for **3a** and **4a** at elevated temperatures. Thus, a full series of measurements covering a broad temperature range was not attempted for complexes other than **2a**.

Thermodynamic parameters were determined for the conversion of **2a** to **1a**, Table IV. The reaction is endothermic. Formation of the metallaoxanorbornadiene is driven entirely by the positive entropy change. At least two factors contribute to the endothermicity of the reaction: the strain energy of the [2.2.1] ring system of **1a** and the substitution of a presumably weak Co–O bond for a stronger Co–P bond. The magnitude of ΔS for this reaction is consistent with that expected upon formation of two species from a single starting compound.

Comparison of K_{eq} values at 25 °C for the series of substituted cobaltacyclopentene complexes established the following order for the extent of ligand dissociation from the cobalt center: $PPh_3 > P(n\text{-}Bu)_3 \simeq P(OCH_3)_3 > (CH_3)_3CNC$. Both ligand size and basicity affect the extent of ligand dissociation. *tert*-Butyl isocyanide is the hardest base and has the smallest cone angle[11] of the ligand series. It has the highest affinity for the cobalt complex. Triphenylphosphine, a softer base with a large cone angle (145°), has an equilibrium constant for dissociation 2 orders of magnitude greater than that of $(CH_3)_3CNC$. The K_{eq} values for $P(n\text{-}Bu)_3$ and $P(OCH_3)_3$ are statistically indistinguishable. They occupy an intermediate position owing to the competing influences of basicity ($P(n\text{-}Bu)_3 > P(OCH_3)_3$) and size (cone angles: $P(n\text{-}Bu)_3$, 132°; $P(OCH_3)_3$, 107°).

Rate constants for the dissociation of ligands from **2–5**, k_{-1}, were calculated from measured K_{eq} and k_1 and are included in Table I. The k_{-1} for **2b** and for **3–5a** were nearly identical within experimental error (3σ). This result is surprising if the mechanism is a simple dissociation of the ligand. If so, the activation energy should be dominated by the Co–ligand bond energy. There is no reason to suspect that the Co–ligand bond energies of the four complexes are the same. In contrast to the above, the k_{-1} for **2a** is roughly 25 times greater than for the other complexes.

(c) Preparative Scale Reactions. The slopes of the plots of ln k_{obsd} vs. ln [L], Figure 2 and Table VII, established that the orders of the reaction with respect to [L] were within 3σ of 1.000 (see above). One exception was $(CH_3)_3CNC$, which had an order slighlty less than 1.000. We were somewhat concerned, however, by the observation that most of the other slopes were approximately 2σ *less* than 1.000 rather than scattered uniformly about this value. Deviations from unit slope, if real, could be indicative either of a decrease in the activity coefficients of the ligands or of the significance of other reaction pathways at high ligand concentration.

We have investigated previously the reaction of the four ligands under consideration here with **1** on a preparative scale.[1] In each case, equimolar quantities of complex and ligand reacted to yield only one product. In contrast, reactions with excesses of the sterically nondemanding ligands acetonitrile and thiocyanate led to the formation of two isomeric metallacyclic products. This observation and our concern over the possibility of deviations from unity in the order of rate law with respect to [L] led us to investigate the reaction of **1** with excesses of the above ligands.

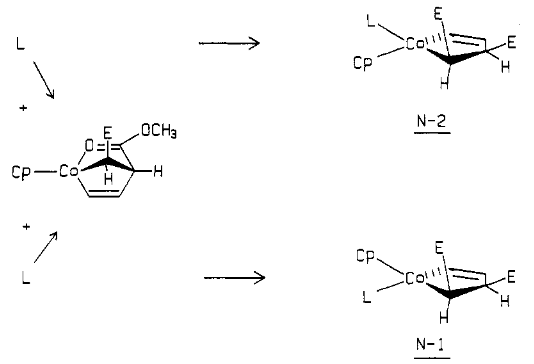

Figure 3. Diastereoisomers of ligand-substituted cobaltacyclopentene complexes resulting from coordination of ligand on both nonequivalent faces of the metallacycle.

Reaction of **1a** with 10 equiv of $P(OCH_3)_3$ gave rise to two products. The major product **3a-1**, isolated in 88% yield, was the product that we previously characterized.[1] A minor product of the same stoichiometry, **3a-2**, was isolated in ca. 1% yield. The isomeric products **4a-1** and **4a-2** were isolated in 76% and 8% yields, respectively, from the reaction of **1** with excess $(CH_3)_3CNC$. Again, the major product was the one that we previously had isolated.[1] Only one product was observed in the reactions of **1** with gross excess of PPh_3, $P(p\text{-tol})_3$, and $P(n\text{-}Bu)_3$. Apparently, the formation of the minor product is sensitive to the steric bulk of the ligand rather than its donor properties.

The existence of two isomeric cobaltacyclopentene acetonitrile complexes suggested to us that small ligands were able to coordinate to cobalt on either of the two nonequivalent faces of the metallacycle, Figure 3. Larger ligands were constrained to bind on the less hindered face that bore the two dimethyl maleate derived protons. This resulted in inversion of configuration at cobalt relative to that in **1**. The observations in the previous paragraph and the ^1H and ^{13}C NMR data for **3a-1**, **3a-2**, **4a-1**, and **4a-2**, Tables V and VI, respectively, are entirely consistent with this view. The spin systems observed in the NMR spectra of each pair of isomers were identical, as in the case of the two acetonitrile complexes. Spectra differed only in the chemical shifts and coupling constants observed for these spin systems. One of the most telling pieces of evidence was the ligand phosphorus–metallacycle ring proton coupling constant. A strong dependence of the magnitude of J_{PH} on the directions of the proton on the α-carbon has been noted in cobaltacyclopentene complexes.[1,8,12] A large coupling constant was observed when the phosphorus-containing ligand coordinated to cobalt on the proton-bearing face of the metallacycle. It was gratifying that the major product **3a-1** had one metallacycle proton with a large J_{PH}. Both metallacycle protons of minor isomer **3a-2** had small J_{PH}, suggesting that $P(OCH_3)_3$ displaced the coordinated ester group of **1** with *retention* of configuration at cobalt. Other notable differences in the ^1H NMR spectra of **3a-2** included a nearly 1 ppm deshielding of the metallacycle protons, a larger J_{HH}, and nearly equal chemical shifts of two of the three methoxy groups. Analogous differences were noted for **4a-2** and one of the acetonitrile complexes.[1] The significant changes in chemical shifts can be rationalized to result from the major differences in interatomic distances in the two isomers. The increase in J_{HH} may be more indicative of conformational changes resulting from the decrease in steric bulk on the proton-bearing face rather than being indicative of

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[11] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[12] Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1970**, *21*, 431.

ligand coordination on the ester-bearing face (see below).

The minor isomers **3a-2** and **4a-2** could be secondary products that result from displacement by a second ligand molecule of the coordinated ligand of the initially formed major isomer. If the entering ligand attacks the cobalt center from the face of the metallacycle opposite the original ligand, the minor product will result. To address this point, the major isomer **3a-1** was reacted with a 10-fold excess of $P(OCH_3)_3$ overnight, a time interval typical for a preparative scale reaction in this system. No isomerization of **3a-1** to **3a-2** was detected. However, after 6 days at room temperature, **3a-2** was observed in solution. (**3a-1** equilibrates with **1a** over this period of time.) **4a-2** was not observed after 3 days when **4a-1** was reacted with 10 equiv of $(CH_3)_3CNC$. (The reaction of **1** and $(CH_3)_3CNC$ is complete in less than an hour.) Clearly, formation of the minor isomers from the reaction of the major isomer and excess ligand is much too slow to account for observed distribution of products in the reactions of **1**. Thus, the minor isomers are true kinetic products. Formation of these complexes must be accounted for in any mechanism proposed.

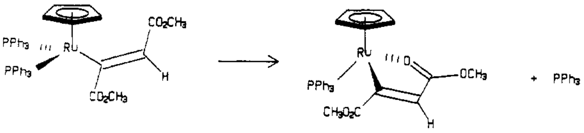
Examination of the Reactivity of the Coordinated Esters. (a) Cobaltaoxanorbornadiene Complexes. The activation of Co(III)-chelated glycine ester complexes toward hydrolysis and aminolysis was discussed in the introduction. The presence of a common Co(III)-coordinated ester structural unit and the similarity of the frequencies of the IR bands of the coordinated esters in the glycine ester complexes and in **1** led us to consider the possibility that the coordinated ester in **1** was similarly activated. Thus, we sought evidence of aminolysis and alkoxide exchange reactions for the coordinated ester.

Reaction of **1a** with 6 equiv of *n*-propylamine yielded a single new complex, **6a**. Analytical and spectroscopic data, Tables V and VI, unequivocally established that the amine had displaced the coordinated ester from cobalt rather than reacting with it to form an amide. The IR band near 1610 cm^{-1} that is characteristic of the coordinated ester[1,3,4] was absent in the spectrum of **6a**. Furthermore, amide N–H and CO bands were not observed. The ^1H NMR spectra of **6a** established that all three ester methoxy groups were retained. Finally, the observed ring proton J_{HH} of 9.5 Hz was much too large for a cobaltaoxanorbornadiene complex but was appropriate for a cobaltacyclopentene complex.

The magnitude of this coupling constant in **6a** is in the range typical of the minor stereoisomer of the substituted cobaltacyclopentene complexes (ligand syn to ester-bearing face of the metallacycle). We do not suggest that **6a** has this stereochemistry, however. The hydrogen bonding between the coordinated amine and the adjacent ester groups that is possible in this stereoisomer would seem unlikely to be sufficiently exothermic to shift the equilibrium totally in favor of this more sterically congested isomer. It is possible that a decrease in the steric bulk of the ligand (or the absence of a ligand) on the proton-bearing face of the metallacycle permits access to a conformation with a large J_{HH}.

An unidentified red product was formed in low yield upon reaction of **1a** and 400 equiv of *tert*-butyl alcohol at reflux in benzene for 44 h. The product eluted faster than **1a** but spontaneously reverted to **1a** on the column, upon standing (in the absence of excess *tert*-butyl alcohol), and when taken to dryness. Thus, we were at best able to obtain mixtures of **1a** and the new complex. The ^1H NMR spectrum of the mixture in $CDCl_3$ clearly established that the unidentified complex still had three carbomethoxy groups (at 3.84, 3.83, and 3.61 ppm). This observation eliminated the possibility that a transesterification reaction had occurred. The presence of a η^5-C_5H_5 group (4.84 ppm), and a *tert*-butyl group (1.27 ppm) with appropriate integrations suggested that the product was a labile *tert*-butyl alcohol substituted cobaltacyclopentene complex. Transesterification was not promoted by the presence of base. A brown solid was produced when **1a** and *tert*-butyl alcohol were reacted in benzene in the presence of a small amount of potassium *tert*-butoxide. The solid was insoluble in most organic solvents and was not eluted from silica with even the most polar solvents. This behavior is inconsistent with that expected for a neutral *tert*-butoxy-substituted cobaltaoxanorbornadiene complex. Most likely, the potassium salt of a *tert*-butoxy-substituted cobaltacyclopentene complex has formed.

(b) $(\eta^5\text{-}C_5H_5)\overline{Ru[C(CO_2CH_3)CHC(OCH_3)O}][P(C_6H_5)_3]$ (7). The reaction leading to the formation of complex **7** (eq 3) has the appearance of being reversible.[2]



(3)

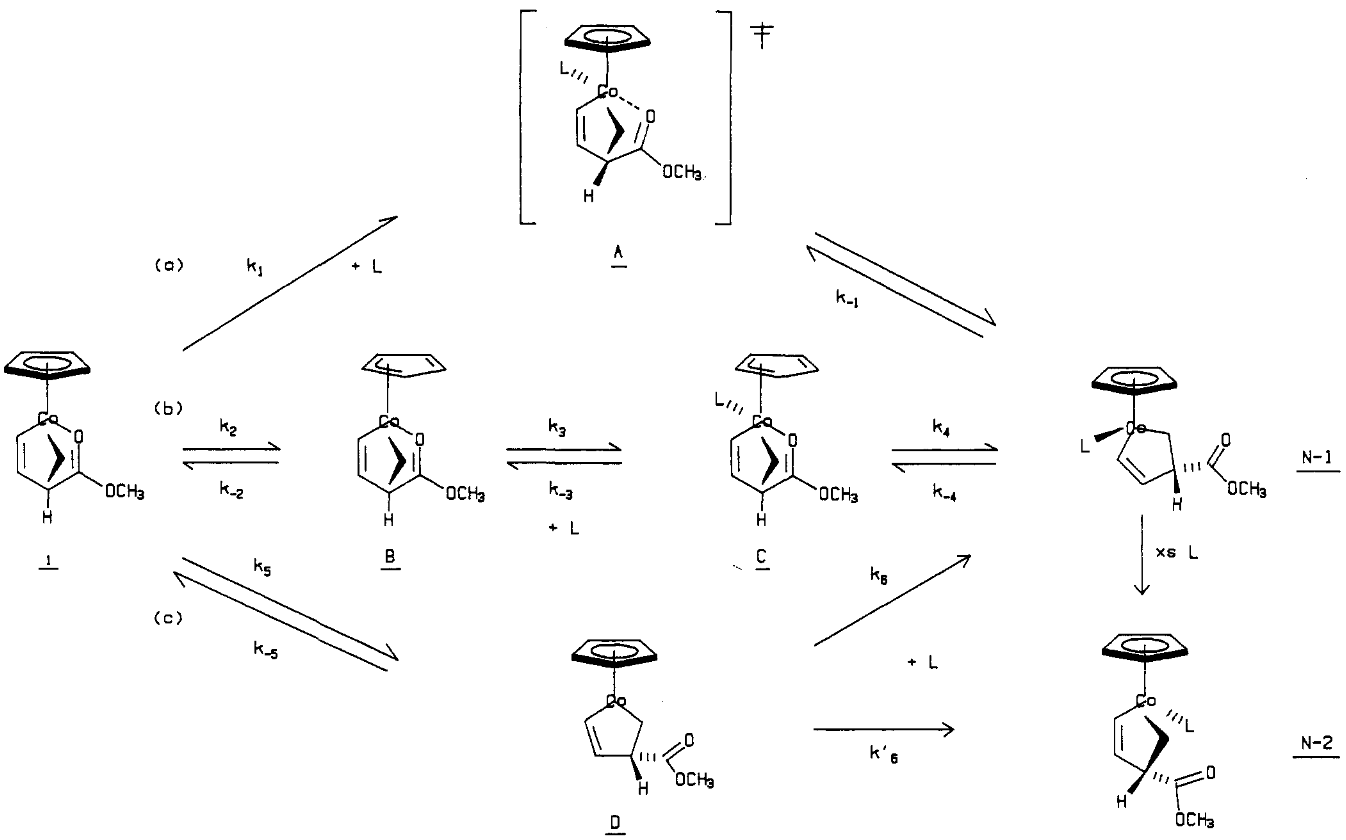
Elevated temperatures drive the loss of phosphine and formation of this ester-coordinated complex. Excluding the cobaltacyclopentene/cobaltaoxanorbornadiene systems, the ruthenium system is the only example of ligand substitution of an ester for a phosphine. We were curious whether the cobalt and ruthenium systems were related on a mechanistic level. Thus, the reactions of **7** with phosphine and isocyanide ligands were investigated.

Two equivalents of $P(C_6H_5)_3$ were reacted with **7** in benzene. No reaction was detectable after 2 days at reflux. Roughly 25% of **7** was converted $(\eta^5\text{-}C_5H_5)Ru[\eta^1\text{-}C(CO_2CH_3)CH(CO_2CH_3)][P(C_6H_5)_3]_2$ after 4 days at reflux in toluene, however. The reaction of 1 equiv of $(CH_3)_3CNC$ with **7** in benzene solution led cleanly but slowly to a single product. Conversion was 50% complete after about 120 h at room temperature. The product was tentatively identified as $(\eta^5\text{-}C_5H_5)Ru[\eta^1\text{-}C(CO_2CH_3)CH(CO_2CH_3)][P(C_6H_5)_3][(CH_3)_3CNC]$ on the basis of its ^1H NMR spectrum: 4.99 $(\eta^5\text{-}C_5H_5)$, 2.93, 3.51 (OCH_3), 0.94 ppm $((CH_3)_3C)$. In contrast, the reaction of equivalent amounts of $P(n\text{-}C_4H_9)_3$ and **7** resulted in only a 15% conversion to two products after 120 h at room temperature. The ^{31}P NMR spectrum of these products unequivocally established that neither minor product is the expected η^1-vinyl, mixed bis(phosphine) complex. The behavior of **7** in the three reaction systems demonstrates that the Ru–O bond is quite inert. Thus, we chose not to investigate the kinetics of these reactions.

The rather low frequency of the IR band[2] of the coordinated ester (1586 cm^{-1}) in **7** prompted us to examine aminolysis and alkoxide exchange reactions of the coordinated ester. Complex **7** was reacted with 14 equiv of *n*-propylamine or of *tert*-butyl alcohol in benzene solution. No evidence of alkoxide exchange or of aminolysis of the coordinated ester was detected after 24 h at 60 °C.

The only site of attack by nucleophiles on **1** was the cobalt center. The lability of the cobalt–oxygen bond precluded effective activation of the coordinated ester group. On the other hand, the results for **7** demonstrated that an inert metal–oxygen bond and a low frequency for the IR band of the coordinated carbonyl are not sufficient conditions for activation. These observations suggest that the impressive activation of the bound acyl in Co(III)–glycine ester complexes is a consequence of both the rather

Scheme I



high charge density of the small Co(III) iron (hard acid) and the inertness of the metal–oxygen bond in these complexes.

Discussion

Three mechanisms for the reaction of 1 with added ligands are outlined in Scheme I. In mechanism (a), the entering ligand directly attacks the metal center and displaces the coordinated carbonyl group. The rate law for this associative mechanism, (eq 4), is first order in both

$$-\mathrm{d}[1]/\mathrm{d}t = k_1[1][\mathrm{L}] \qquad (4)$$

complex and in ligand under all conditions. In mechanism (b), the C_5H_5 group slips from η^5 to η^3, opening a coordination site for addition of a ligand. Dissociation of the carbonyl group and recoordination of the slipped C_5H_5 group results in formation of the product. The form of the rate law for this mechanism depends upon which step is rate limiting. Three rate laws and the corresponding rate-determining steps are presented in eq 5–7. (Equation

$$-\mathrm{d}[1]/\mathrm{d}t = k_2[1] \quad (1 \text{ to B}) \qquad (5)$$

$$-\mathrm{d}[1]/\mathrm{d}t = k_2k_3[1][\mathrm{L}]/(k_{-2} + k_3[\mathrm{L}]) \quad (\text{B to C}) \qquad (6)$$

$$-\mathrm{d}[1]/\mathrm{d}t = k_2k_3[1][\mathrm{L}]/k_{-2}k_{-3} \quad (\text{C to N}) \qquad (7)$$

7 assumes that the equilibrium concentrations of B and C are not perturbed significantly by the conversion of C to N.) Finally, in mechanism (c) the coordinatively unsaturated intermedate D is formed by reversible dissociation of the coordinated carbonyl group. Intermolecular trapping of the intermediate D by external ligand leads to formation of one of the metallacyclopentene complexes 2–5. The steady-state rate law for this dissociative (D) process is given in eq 8. The rate law will become first

$$-\mathrm{d}[1]/\mathrm{d}t = k_5k_6[1][\mathrm{L}]/(k_{-5} + k_6[\mathrm{L}]) \qquad (8)$$

order in [1] and independent of [L] when intermolecular trapping of intermediate D is much more rapid than intramolecular trapping by the carbonyl; i.e., $k_6[\mathrm{L}] \gg k_{-5}$.

Our kinetic data established that the rate law for eq 2 was second order, that the rate constant varied with the entering ligand, and that $\Delta S^{\ddagger}$ was negative. Mechanism (c), when operating in a first-order regime, is clearly inconsistent with these observations, as is mechanism (b) when the first step is rate limiting (i.e. eq 5 pertains). Mechanisms (b) and (c) can be ruled out entirely on other grounds. The rate law for these mechanisms can be second order when the later steps are rate limiting. Kinetically significant quantities of intermediates B and C or D would accumulate in this event. No evidence for these complexes was detected during NMR or UV–vis experiments. Given the form of the rate laws in eq 6–8 and the experimentally determined rates, a demonstrable consequence of assuming that the steady-state concentration of intermediate complex(es) was too small to detect (<1%) is that complexes B, C, and/or D exchange rapidly with 1.[13] The line widths of the ^{1}H NMR resonances due to 1 would be broad. This was not observed. Thus, the associative mechanism (a) is operative in these reactions.

Although the kinetic evidence is completely consistent with mechanism (a), nonkinetic evidence exists which suggests that another mechanism is important. A second

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[13] Consider the case for mechanism b with the conversion of B to C representing the rate limiting step. If the reaction is second order, then $k_{-2} \gg k_3[\mathrm{L}]$. Assume that k_{-2} = at least 100 $k_3[\mathrm{L}]$. The rate law will reduce to rate = $k_2k_3[\mathbf{1a}][\mathrm{L}]/k_{-2}$, and the observed second-order rate constant = k_2k_3/k_{-2}. If we assume that we could detect the presence of 1% B, then the failure to observe B implies that $k_2/k_{-2} < 100$ and that $k_3 > 100\ k_{\mathrm{obsd}} = 12.2\ \mathrm{s^{-1}\ M^{-1}}$ at 25 °C. Maintenance of second-order kinetics when $[\mathrm{PPh_3}] = 0.318$ M, the highest concentration investigated, then places a lower limit on k_{-2} of 388 s^{-1}. Given the previous assumptions, this implies that $k_2 = 3.88\ \mathrm{s^{-1}}$, sufficiently fast that the ^{1}H NMR spectrum of 1 should show evidence of exchange broadening. This is not observed.

product complex was isolated in rather low yield from preparative scale reactions when the concentration of the ligand was high relative to [1] and the steric bulk of the ligand was low. The minor product was identified as a stereoisomer of the major product. It differed from the major isomer in that the ligand was coordinated to cobalt on the face of the metallacycle that bore the ester groups. None of the minor isomer was produced when equivalent quantities of 1 and ligand were reacted. The failure to observe evidence of the minor isomers in the kinetic experiments (i.e. preservation of isosbestic points) is understandable given the low yields of these products and the close similarity of their UV–vis spectra to those of the major product.

The existence of the minor isomer is not in itself inconsistent with mechanism (a). In the presence of excess ligand, mechanism (d) (Scheme I) could become operative. The possibility that the minor isomers were secondary products was eliminated, however. The conversion of major isomers **3a-1** and **4a-1** to their respective minor isomers **3a-2** and **4a-2** by reaction with an excess of the appropriate ligand was much too slow to account for the yield of minor isomers in the reactions of **1** with ligand. In fact, the rate of isomerization suggested that conversion proceeded via the intermediacy of **1**. Thus, the minor isomers are true kinetic products.

The above observations establish that two reaction mechanisms operate at high ligand concentrations. The second mechanism cannot have a bimolecular rate law like mechanism (a). An increase in ligand concentration cannot affect the relative proportions of the reaction proceeding through two competing second-order channels. The observations are consistent with operation of the dissociative mechanism (c). The partioning of the intermediate D depends upon the relative trapping efficiencies of the ester carbonyl and of the external ligand. Because of the high effective concentration of the carbonyl group, intramolecular trapping is extremely efficient. No net reaction will occur by mechanism (c) at low ligand concentration. At high external ligand concentration some intermolecular trapping can occur. In this regime the reaction begins to change from first to zero order in [L]; i.e., $k_{-5} \approx k_6[\mathrm{L}]$. k_5 is not then required to be large. Thus, line broadening in the ^{1}H NMR spectrum of **1** due to dissociation of the coordinated ester group need not be detectable.

Unlike the ester carbonyl, external ligand can attack the cobalt atom of D from either face of the metallacycle. Approach from the direction of the face bearing the protons is expected to be preferred on steric grounds. Only the least bulky ligands can approach from the direction of the ester-bearing metallacycle face. The minor isomer so produced provides the only visible evidence of the existence of this pathway. The major isomer produced by this path will be indistinguishable from that produced via mechanism (a). Thus, the proportion of the reaction proceeding by this pathway is at least twice as great as the yield of the minor isomer. The isolated yields of products from the reaction of **1a** and $(CH_3)_3CNC$, the ligand that is best able to trap intermediate D, suggest that roughly 20% or less of the reaction proceeds by the dissociative pathway.

The loss of ligand from the cobaltacyclopentene complexes **2–5** must proceed by the microscopic reverse of the mechanism for the reaction of **1** with ligand. Our evidence establishes that the major pathway for formation of cobaltaoxanorbornadiene complexes **1** is the reverse of mechanism (a), intramolecular attack of the ester carbonyl group on the cobalt atom of the cobaltacyclopentene. The role of the coordinatively unsaturated metallacyclopentene complex D in this reaction must be relatively minor. These results contrast sharply with the mechanisms determined for ligand substitution in a variety of coordinatively saturated $(\eta^5\text{-}C_5H_5)Co$ phosphine complexes.[10,14,15] Kinetic evidence has established that both $(\eta^5\text{-}C_5H_5)Co(PPh_3)_2$[15] and $(\eta^5\text{-}C_5H_5)Co[C_4(CH_3)_4](PPh_3)$[10,14] react via dissociative mechanisms.

The kinetics of the reactions of **2a** with diphenylacetylene or with acrylonitrile involve the initial loss of phosphine ligand.[8] This observation led to a proposal that coordinatively unsaturated cobaltacyclopentene complexes or related η^2-alkene, η^2-alkyne complexes are intermediates in these reactions. Our results demonstrate that this proposal is untenable. Such intermediates are minor species in solution at best. It is extremely unlikely that they participate in the above reactions, even if present. Trapping of these intermediates by such weak, bulky ligands as alkenes and alkynes cannot be expected to compete with intramolecular trapping by the β-ester group. Thus, cobaltaoxanorbornadiene complexes are the kinetically significant intermediates in the reactions of cobaltacyclopentenes. Efforts are currently underway in our laboratories to develop the reactivity of the imbedded cobaltacyclopentene ring in **1**.[9]

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Registry No. **1a**, 106800-02-6; **1b**, 106800-03-7; **2a**, 53559-30-1; **2b**, 69896-30-6; **3a-1**, 106800-07-1; **3a-2**, 110170-96-2; **4a-1**, 106800-09-3; **4a-2**, 110170-95-1; **5a-1**, 106800-04-8; **5a-2**, 110170-97-3; **6a**, 110096-60-1; **7**, 52462-44-9; $(\eta^5\text{-}C_5H_5)Ru[\eta^1\text{-}C(CO_2CH_3)CH(CO_2CH_3)][P(C_6H_5)_3]_2$, 52520-60-2; $(\eta^5\text{-}C_5H_5)Ru[\eta^1\text{-}C(CO_2CH_3)CH(CO_2CH_3)][P(C_6H_5)_3][(CH_3)_3CNC]$, 110096-59-8; $P(OCH_3)_3$, 121-45-9; $(CH_3)_3CNC$, 7188-38-7; $P(n\text{-}C_4H_9)_3$, 998-40-3; PPh_3, 603-35-0; *n*-propylamine, 107-10-8; *tert*-butyl alcohol, 75-65-0.

Supplementary Material Available: Tables of rate constants for the reactions of **1** with ligands at each unique combination of concentrations and temperature (6 pages). Ordering information is given on any current masthead page.

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(14) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* 1977, *99*, 1666.

(15) Janowicz, A. H.; Bryndza, H. E.; Bergman, R. G. *J. Am. Chem. Soc.* 1981, *103*, 1516.