literature for other lithium enolates.[55] The reaction in eq 18, however, gave a similar but not identical spectrum with bands at 1602 (w), 1579 (s), and 1559 (m) cm^{-1}. Differences were observed both in band positions and in relative intensities. This indicates that the reaction in eq 18 does not simply give loss of vanadocene and a lithium enolate; there are enough similarities in the band positions, however, to prompt us to assign the spectrum to the vanadium enolate. A monomeric formulation is indicated for clarity in eq 18, but this species is very likely dimeric or oligomeric in solution. Its lifetime in solution (hours at room temperature) precludes further structural analysis, although it is isolable as a free-flowing black powder. When analogous infrared studies were carried out for the addition of BuLi to vanadocene ketene, they showed no evidence for an intermediate vanadium hydride (as in **5**, Scheme I); this corroborates the suggestion that vanadium enolate is the first long-lived species on the reaction path.

Conclusions. The studies described herein were undertaken to gain a more complete understanding of the ability of ketenes to bind to transition-metal centers via C=O complexation. They indicate that the formation of such complexes with unsymmetrical ketenes occurs wth a very high degree of facial selectivity, higher than that exhibited by smaller organic nucleophiles. However, the associative substitution of the triethylphosphine ligand on molybdenocene suggests that such reactions go via a straightforward attack by the electron-rich metal center at the ketene central carbon; in that sense, the metallic nucleophiles appear to behave in a manner similar to carbon nucleophiles. Further, it is clear that even though such bonding should place a substantial amount of electron density in the ketene LUMO, C=O bound ketenes are still capable of undergoing nucleophilic attack. The use of unsymmetrical ketenes allos us to define this as an internal attack mediated by the metal. This is particularly important with respect to any potential Fischer–Tropsch ketene C–C and C–H bond-forming reactions, since incoming hydrides or alkyls would presumably also be delivered from the surface of the catalyst. Subsequent attack of the resulting enolate nucleophiles on other ketenes could form the basis for an anionic ketene polymerization leading to several C–C bond formations; the anionic polymerization of ketenes has been reported.[56] However, this does not address the question of whether there is a sufficient population of ketenes on the catalyst surface to support such a polymerization process, and this issue remains in doubt. Likewise, there may be some synthetic use for the vanadocene enolates reported herein since other metallocene enolates undergo highly stereospecific Aldol condensations with aldehydes;[57] the reactions described herein constitute one means of preparing such enolates with high *Z* specificity. Lastly, we note that we have observed behavior by later transition-metal–ketene complexes similar to that reported here, and these results will be communicated separately.

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Registry No. **1**, 113161-87-8; **2**, 113161-88-9; **3**, 76173-79-0; O=C=CEtPh, 20452-67-9; Cp_2V, 1277-47-0; O=C=CMePh, 3156-07-8; $Cp_2Mo(PEt_3)$, 63672-65-1; $Cp_2Mo(O{=}C{=}CPhEt)$, 113161-89-0; $O{=}C{=}CPh_2$, 525-06-4.

Supplementary Material Available: Drawings of **2** and tables of crystal and diffractometer data, bond distances, bond angles, and positional and thermal parameters (12 pages); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

(56) (a) Yoshida, K.; Yamashita, Y. *Makromol. Chem.* **1967**, *100*, 175–185. (b) Nadzhimutdinov, S. H.; Cherneva, E. P.; Kargin, V. A. *Vysokomol. Soedin, Ser. B9* **1967**, 480–485; *Chem. Abstr.* **1967**, *67*, 100431.

(57) (a) Evan, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980**, *21*, 3975–3978. (b) Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1980**, *21*, 4607–4610. (c) Hoffman, R. W.; Kitrich, K.; Froech, S.; Cremer, D. *Tetrahedron* **1985**, *41*, 5517–5524.

Carbon–Carbon Bond-Forming Reactions of Cobaltacyclopentene/Cobaltaoxanorbornadiene Complexes with Isocyanides, Carbon Monoxide, and Alkynes

Maryrose Scozzafava and Alan M. Stolzenberg*

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

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Reaction of $(\eta^5\text{-}C_5H_5)\overline{Co[C(R)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)}][P(C_6H_5)_3]$ (R = C_6H_5, **2a**; R = CO_2CH_3, **2b**) with isocyanides, CO, and diphenylacetylene (DPA) afforded 1-amino-1,3-cyclopentadienes, cyclopent-2-enones, and $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}1,3\text{-cyclohexadiene})$ complexes, respectively. The related [2.2.1]-metallabicyclic cobaltaoxanorbornadiene complexes **1a** and **1b** reacted with the same reagents to afford identical products. Reactions with isocyanides and CO proceeded in two distinct steps: (1) coordination of the reactant to cobalt to form a new ligand-substituted cobaltacyclopentene complex and (2) insertion of the reactant into the metallacycle, followed by reductive elimination. Intermediates were not detected in the reactions with DPA. However, the isolation of isomeric η^4-*cis*-5,6-dicarbomethoxy-1,3-cyclohexadiene complexes with CpCo coordinated on different faces of the diene suggested the intermediacy of a metallacycloheptadiene complex. Kinetic measurements established that the reaction of **1a** with DPA was first order with respect to both reagents. A rate constant for the reaction of **2a** with DPA was calculated from our data and the known equilibrium constant between **2a**, **1a**, and $P(C_6H_5)_3$. The agreement of the calculated rate with a published rate for the reaction confirmed that **1a** is the kinetically significant intermediate in the carbon–carbon bond-forming reactions of **2a**.

The participation of metallacyclic complexes in carbon–carbon bond-forming reactions has created extensive interest in these complexes.[1] Our interest in the reactivity of metallacyclopent-2-ene complexes[2,3] has been prompted

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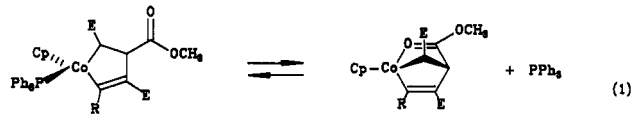
by the rich chemistry of the closely related metallacyclopentadiene complexes. The latter play a major role in alkene and alkyne oligomerization[1,4] and have been utilized in the preparation of arenes,[5,6] dienes,[6-8] substituted pyridines,[9-12] cyclic ketones,[13,14] and a variety of heterocyclic compounds.[15-18] In contrast, the reactivity of metallacyclopentene complexes has received scant attention. $CpCo(\eta^4$-diene) and $CpCo(\eta^4$-cyclohexadiene) complexes were obtained from the reactions of (η^5-cyclopentadienyl)cobaltacyclopentene complexes with acrylonitrile and alkynes, respectively.[19] Analogous results were obtained with (η^5-indenyl)rhodacyclopentene complexes.[20] In the only other reported reaction of metallacyclopentenes, cyclopentenones were produced by carbonylation of zirconacyclopentenes.[21,22]

Our initial investigations of metallacyclopentene chemistry focused on reactivity at the metal center of known $(\eta^5\text{-}C_5H_5)Co[C(R)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)][P(C_6H_5)_3]$ complexes[19] (R = C_6H_5, **2a**; R = CO_2CH_3, **2b**) that have syn metallacycle ring protons. In the course of the investigation, we discovered a novel class of [2.2.1]-metallabicyclic complexes, **1**, which we have named cobaltaoxanorbornadienes.[2] These complexes result from intramolecular ligand substitution reactions in which the carbonyl oxygen of a metallacycle β-ester substituent displaces triphenylphosphine from the metal center of **2** (eq 1).[3] Both **1** and **2** reacted with a variety of ligands to



(1)

2 **1**

a: R = Ph, E = CO_2CH_3

b: R = E = CO_2CH_3

afford ligand-substituted metallacyclopentene complexes **3** (eq 2).[2,3] For all but the least sterically demanding

(2)

1 or **2**

L = PR_3, $P(OR)_3$, RNH_2, RNC, CH_3CN

R = Ph or E

ligands, coordination to the chiral cobalt center in **3** occurred solely from the face of the metallacycle bearing the syn protons. This was the same face to which the phosphine in **1** had been coordinated. The stereochemical outcome and the observed second-order kinetics of formation of **3** from **1** and ligand[3] ruled out dissociative mechanisms or the direct displacement of phosphine by external ligand as significant mechanistic pathways in the chemistry of **2**. All available evidence suggested that cobaltaoxanorbornadiene complexes are the kinetically significant intermediates in the reactions of cobaltacyclopentenes.

Here we turn our attention to the reactivity of the metallacyclopentene ring in **1** and **2**. Details of the reactions of these complexes with isocyanides, CO, and alkynes are presented in this paper. Identical organic products were obtained from either **1** or **2**. The reaction of **2a** with diphenylacetylene, DPA, was thoroughly reinvestigated. Kinetic data for the reaction of **1a** with DPA were determined. Both the form and rate constants of the rate law reported for reaction of **2a** and DPA[19] were consistent with a proposed mechanism that involved **1a**. Two previously unreported products of this reaction provided further insight into the mechanism.

Table I. ^{1}H NMR Data for Organic Compounds[a]

complex	CO_2CH_3	ring protons	phenyl	other ligands
4a	3.90	4.84 (d, ^4J = 1.5)	7.31–7.22	9.34 (br, 1 H, NH)
	3.76			1.09 (s, 9 H, $C(CH_3)_3$)
	3.57			
4b[b]	3.79	3.22 (d, ^4J = 1.3)		8.99 (br, 1 H, NH)
	3.53			0.71 (s, 9 H, $C(CH_3)_3$)
	3.43			
8a	3.98	4.39 (d, ^4J = 1.5)	7.12–6.49	9.44 (br, 1 H, NH)
	3.83			1.52 (s, 6 H, $2CH_3$)
	3.50			
10a[c]	3.24	4.84 (d, ^3J = 3.9)	7.40–7.01	
	3.21	3.75 (d)		
	3.17			
13a	3.76	4.41 (d, ^3J = 7.1)[d]	7.71–6.70	
	3.69	4.10 (d)		
	3.43			
14a	3.88[e]		7.15–6.54	
	3.50			

[a] δ (J_{HH}, Hz). Spectra were recorded in $CDCl_3$ solution unless otherwise noted. [b] C_6D_6 solution. [c] C_6D_6 solution with $^1/_2$% acetic acid. [d] Deviates slightly from a first-order system. [e] Integrates for 6 H.

Experimental Section

General Comments. All manipulations were carried out under a nitrogen atmosphere by use of Schlenk techniques or in a Vacuum/Atmospheres Co. drybox. Benzene, toluene, THF, and hexane were distilled from sodium benzophenone ketyl and stored under N_2 in a drybox. Metallaoxanorbornadiene complexes and substituted metallacyclopentenes were prepared by literature

(1) Chappell, S. D.; Cole-Hamilton, D. J. *Polyhedron* **1982**, *1*, 739.
(2) Stolzenberg, A. M.; Scozzafava, M.; Foxman, B. M. *Organometallics* **1987**, *6*, 769.
(3) Stolzenberg, A. M.; Scozzafava, M. *Organometallics* **1987**, *6*, 2214.
(4) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, Chapter 52.
(5) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.
(6) Suzuki, H.; Itoh, K.; Ishii, Y.; Simon, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8494.
(7) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1977**, *139*, 169.
(8) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1978**, *149*, 385.
(9) Vitulli, G.; Bertozzi, S.; Vignali, M.; Lazzaroni, R.; Salvadori, P. *J. Organomet. Chem.* **1987**, *326*, C33.
(10) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 505.
(11) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1978**, 1278.
(12) Wakatsuki, Y.; Yamazaki, H. *Tetrahedron Lett.* **1973**, 3383.
(13) Grubbs, R. H.; Miyashita, A. *J. Organomet. Chem.* **1978**, *161*, 371.
(14) Wakatsuki, Y.; Nomura, O.; Tone, H.; Yamazaki, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1344.
(15) Yasufuku, K.; Hamada, A.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1980**, *102*, 4363.
(16) Wakatsuki, Y.; Kuramitsu, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549.
(17) Flynn, S. T.; Hasso-Henderson, S. E.; Parkins, A. W. *J. Mol. Catal.* **1985**, *32*, 101.
(18) Hong, P.; Yamazaki, H. *Synthesis* **1977**, 50.
(19) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123.
(20) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648.
(21) (a) Erker, G.; Kropp, K. *J. Organomet. Chem.* **1980**, *194*, 45. (b) Erker, G. *Accts. Chem. Res.* **1984**, *17*, 103.
(22) (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *105*, 2568. (b) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, 2829.

Table II. ^{13}C NMR Data for Organic Compounds[a,b]

complex	ring sp^2	ring sp^3	OCH_3	C=O	other ligands
4a	C_3: 174.8 (1.8[c])	C_5: 54.3 (146.7)	52.3[e]	167.2 (3.9[c])	54.3 ($C(CH_3)_3$)
	C_4: 146.3 (5.2[d])		51.1[e]	165.9 (3.9[c])	29.8 (125.7, $C(CH_3)_3$)
	C_1: 118.8 (6.5[d])		51.0[e]	162.8 (4.0[c])	
	C_2: 99.0 (2.5[c])				
4b[f]	C_3: 170.1	C_5: 38.3 (131.1)	51.9[e]	166.8	52.8 ($C(CH_3)_3$)
	C_4: 148.6	(1.9[g])	50.8[e]	166.2	28.7 (127.0, $C(CH_3)_3$)
	C_1: 112.4		50.6[e]	166.3	
	C_2: 101.0				
8a	C_3: *h*	C_5: 55.3	52.5	*h*	27.2 (CH_3)
	C_4: *h*		51.4		27.1 (CH_3)
	C_1: 116.9		51.3		
	C_2: 103.8				
10a[f]	153.0	55.5	52.6	170.3	197.4 (ketone C=O)
	144.9	48.5	52.3	165.0	
			51.7	*h*	
13a	145.2	49.1	52.5	171.2	137.8[i]
	139.8	46.6	52.4	170.8	135.0[i]
	138.3		51.3	168.7	*h*
	138.1				
14a			53.0	168.1	144.9,[i] 141.2[i]
			52.3	166.2	137.6,[i] 137.4,[i] 134.3[i]

[a] δ ($^1J_{CH}$, Hz). All spectra were recorded in $CDCl_3$ solution unless otherwise noted. [b] Phenyl signals are omitted from the table. [c] $^3J_{CH}$. [d] $^2J_{CH}$. [e] $146 \leq {}^1J_{CH} \leq 147$. [f] In C_6D_6 solution. [g] $^4J_{CH}$. [h] Not observed. [i] Ipso phenyl.

methods.[2,19] All other solvents and reagents were of reagent or HPLC grade and were used without further purification. Chromatography was carried out on silica (Baker 3405) and under a nitrogen atmosphere where noted.

Infrared spectra were recorded on a Perkin-Elmer Model 683 spectrophotometer equipped with a data station. ^1H 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. ^1H and ^{13}C NMR spectral data for organic compounds are compiled in Tables I and II, respectively. All other spectroscopic data are found in the Experimental Section. Materials used for kinetic experiments were weighed to a precision of ± 10 μg on a Mettler Gram-atic microgram balance.

Reactions with Isocyanides. 1-(*N*-*tert*-Butylamino)-5-phenyl-2,3,4-tricarbomethoxy-1,3-cyclopentadiene Monohydrate (4a). (i) **1a** (75 mg, 0.175 mmol) was dissolved in 15 mL of dry, degassed toluene. *tert*-Butyl isocyanide (44 mg, 59 μL, 0.526 mmol) was added, and the green solution immediately turned orange-yellow, the characteristic color of the *tert*-butyl isocyanide substituted metallacycle **5a**. The solution was heated at 80 °C under a nitrogen atmosphere for 24 h and gradually became yellow-brown. The solution was cooled and reduced to dryness. The residue was purified by chromatography on silica. Elution with 100:1 CH_2Cl_2/THF gave an initial yellow band that was collected and reduced to dryness. The residue was recrystallized from toluene/hexane to give 41 mg of the title compound **4a** (58% yield). Further elution with 25:1 CH_2Cl_2/THF gave an orange band which was collected and reduced to dryness. The residue was recrystallized from toluene/hexane to afford 7 mg of the previously reported[2] **5a** (8% yield). **4a**: mp 129–134 °C; IR (CH_2Cl_2) ν 3260 (w, N—H), 3210 (w, N—H), 1750 (s, C=O), 1690 (s br, C=O), 1655 cm^{-1} (s br, H-bonded C=O); MS (EI), *m/e* (% abundance, assignment) 387 (48.7, M), 356 (32.6, M – OCH_3), 331 (94.0, M – Bu[$(CH_3)_2C{=}CH_2$]), 299 (66.2, M – Bu – CH_3OH), 272 (95.7, M – Bu – CO_2CH_3), 240 (100.0, M – Bu – CH_3OH – CO_2CH_3), 180 (79.8, M – Bu – CO_2CH_3 – Ph). Anal. Calcd for $C_{21}H_{25}NO_6 \cdot H_2O$: C, 62.22; H, 6.73; N, 3.46. Found: C, 62.17; H, 6.30; N, 3.47. H_2O by Karl-Fisher titration: calcd, 4.44; found, 0.92.

(ii) **2a** (100 mg, 0.145 mmol) was dissolved in 10 mL of dry, degassed toluene. *tert*-Butyl isocyanide, *t*-BuNC (36 mg, 49 μL, 0.435 mmol), was added. The solution was heated under an N_2 atmosphere near the reflux temperature of toluene for 24 h. Workup and purification were carried out as described in (i) for the reaction of **1a** with *t*-BuNC. Recrystallization from toluene/hexane afforded 27 mg of **4a** (41% yield).

1-(*N*-*tert*-Butylamino)-2,3,4-tricarbomethoxy-1,3-cyclopentadiene (4b). **1b** (75 mg, 0.182 mmol) was dissolved in 20 mL of dry, degassed toluene. *tert*-Butyl isocyanide (80 mg, 110 μL, 0.971 mmol) was then added. The green solution was heated under a nitrogen atmosphere near the reflux temperature of toluene for 7 days. The solution changed in color from green to orange, the characteristic color of the cobaltacycle intermediate **5b**, and then to yellow-brown. A blue solid plated out onto the glassware. The solution was cooled and reduced to dryness, and the residue was purified by chromatography under an N_2 atmosphere. Elution on silica with 100:1 benzene/THF yielded several minor pale red bands which preceded the light yellow band of the title complex **4b**. The yellow eluate was collected and reduced to dryness. The residue was recrystallized from a toluene/hexane solution to afford 23 mg (43% yield). Further elution with 20:1 benzene/THF afforded an orange solution, **6b**, which was reduced to dryness and characterized by NMR and IR.[23] **4b**: mp 128.0–129.5 °C; IR (CH_2Cl_2) ν 3290 (w, N—H), 1740 (s, C=O), 1718 (s, C=O), 1702 (s, C=O), 1665 cm^{-1} (s, H-bonded C=O). Anal. Calcd for $C_{15}H_{21}NO_6$: C, 57.96; H, 6.81. Found: C, 58.34; H, 7.03. **6b**: ^1H NMR ($CDCl_3$) δ 4.33; IR (CH_2Cl_2) ν 2978 (m), 1740 (s), 1710 (s), 1665 (s), 1574 (s), 1476 (w), 1461 (w), 1438 (s), 1208 (br, s), 1112 cm^{-1} (m).

(η^5-C_5H_5)Co[$C(C_6H_5)C(CO_2CH_3)CH(CO_2CH_3)CH(CO_2CH_3)$][CN{2,6-$(CH_3)_2C_6H_3$}] (7a). A solution of **1a** (31 mg, 0.072 mmol) in 20 mL of dry, degassed toluene was stirred with 2,6-dimethylphenyl isocyanide (12 mg, 0.093 mmol) for 15 min. The color changed from green to red. An aliquot (ca. 2 mL) was taken from the solution, reduced to dryness, and redissolved in $CDCl_3$ in preparation for NMR spectroscopy. All spectroscopic characterization was carried out at −10 °C to prevent further reaction to form the insertion product **8a**. Due to the high reactivity of this intermediate, it could not be isolated and was observed only in solution: ^1H NMR ($CDCl_3$) δ 7.21–7.08 (m, 8 H, Ph), 4.73 (s, 5 H, Cp), 3.87 (d, 1 H, ^3J = 7.6 Hz, α-ring proton), 3.83 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.61 (d, 1 H, ^3J = 7.6 Hz, β-ring proton), 3.36 (s, 3 H, OCH_3), 2.47 (s, 6 H, CH_3); an additional signal at δ 5.30 (s, unassigned) was also observed; ^{13}C NMR ($CDCl_3$) δ 181.6 (CO), 175.8 (CO), 161.0 (CO), 153.7 (α-sp^2-ring carbon), 138.6 (β-sp^2-ring carbon), 134.9, 129.0, 125.3 (2, 6, and ipso Ph), 128.4–123.7 (Ph), 90.9 (Cp), 55.5 (β-sp^3-ring carbon), 51.8 (OCH_3), 50.8 (OCH_3), 50.6 (OCH_3), 22.5 (α-sp^3-ring carbon), 18.9 (CH_3); an additional signal was observed at δ 53.5 (unassigned); IR (CH_2Cl_2) ν 2114 (s, C≡N), 1735 (s, C=O), 1697 cm^{-1} (br, s, C=O).

1-(*N*-(2,6-Dimethylphenyl)amino)-5-phenyl-2,3,4-tricarbomethoxy-1,3-cyclopentadiene (8a). **1a** (31 mg, 0.072 mmol) was dissolved in 15 mL of dry, degassed toluene. 2,6-Dimethylphenyl isocyanide (12 mg, 0.093 mmol) was added, and

(23) A analogous species was observed in solution during the synthesis of **4a** but was not isolated.

the solution was stirred at room temperature for 8 h. The color changed from green to red, the characteristic color of cobaltacycle intermediate **7a**, and then to yellow-brown. Thin-layer chromatography on silica (10:1 CH_2Cl_2/THF) indicated the disappearance of the starting materials and the appearance of several new compounds. The solution was reduced to dryness, and the residue was purified by chromatography on silica with 100:1 CH_2Cl_2/THF. Initial elution yielded two unidentified yellow bands containing OCH_3 peaks, followed by a yellow band containing the title compound **8a**. The eluant was reduced to dryness, and the residue was recrystallized from toluene/hexane to yield 6 mg (19% yield) of **8a**. It was not possible to obtain samples of **8a** of sufficient purity for elemental analysis: mp 147–150 °C; IR (CH_2Cl_2) ν 3280 (br w, N—H), 1745 (s, C=O), 1710 (s, C=O), 1670 cm^{-1} (s, H-bonded C=O).

Reactions with CO. 2-Phenyl-3,4,5-tricarbomethoxycyclopent-2-enone (10a). (i) CO was bubbled for 6 h at room temperature through a solution of **1a** (50 mg, 0.117 mmol) in 15 mL of dry, degassed toluene. The solution was then allowed to stir under a CO atmosphere for an additional 15 h. A color change from green to red was observed. A trap to trap distillation of the solvent from the solution on a high vacuum line afforded a brown residue and an orange-red solution, which contained sublimed $CpCo(CO)_2$ in toluene. The toluene was evaporated by bubbling CO through the solution warmed to 40 °C in an H_2O bath. The orange-red liquid that remained had ^1H NMR and IR properties identical with those of $CpCo(CO)_2$. The brown residue was purified by chromatography on silica under an N_2 atmosphere. Elution with 10:1 benzene/THF afforded an orange band containing **9a**, which reverted quickly back to **1a** on standing in a non-CO-saturated solution. Further elution with THF gave a slow-moving and broad yellow band that contained the title compound **10a** (25 mg, 64% yield). Attempts to crystallize the compound were not successful. Initial ^1H NMR spectroscopy of **10a** showed only broad indistinquishable peaks. However, addition of $^1/_2$% acetic acid sharpened the signals considerably (see text). **9a**: ^1H NMR ($CDCl_3$) δ 7.42–7.11 (m, 5 H, Ph), 4.87 (s, 5 H, Cp), 3.89 (d, 1 H, ^3J = 7.0 Hz, ring proton), 3.84 (s, 3 H, OCH_3), 3.79 (d, 1 H, ^3J = 7.0 Hz, ring proton), 3.63 (s, 3 H, OCH_3), 3.38 (s, 3 H, OCH_3); IR (C_6H_6) ν 2022 (s, C≡O), 1744 (s, C=O), 1696 cm^{-1} (s br, C=O). **10a**: IR ($CHCl_3$) ν 1740 (s, C=O), 1725 cm^{-1} (s, C=O); MS (EI), *m/e* (% abundance, assignment) 332 (26.1, M), 300 (100, M – CH_3OH), 272 (41.9, M – CH_3OH – CO), 268 (78.2, M – $2CH_3OH$), 257 (68.1, M – CH_3OH – CH_3O), 241 (31.2, M – CH_3OH – CO_2CH_3), 213 (44.7, M – $2CO_2CH_3$). Calcd (abundance): M (26.1), M + 1 (4.9), M + 2 (0.8). Found (abundance): M (26.1), M + 1 (4.5), M + 2 (0.7).

(ii) **2a** (10 mg, 0.014 mmol) was dissolved in dry, degassed $CDCl_3$ (0.75 mL) and transferred to an NMR tube. The solution was frozen, and the headspace above it was evacuated and filled with 674 mmHg of CO (0.045 mmol). The reaction was monitored by ^1H NMR over 5 days. **9a** was observed after 15 min and its concentration increased over the following 22 h. A new signal at δ 5.03 ($CpCo(CO)_2$) grew in at 30 h and continued to increase in intensity. The formation of **10a** increased steadily during the following 4-day period, concurrent with the decrease of **9a**.

(η^5-C_5H_5)Co[C(CO_2CH_3)C(CO_2CH_3)CH(CO_2CH_3)CH(C-O_2CH_3)](CO) (9b). CO was bubbled for 4 h through a solution of **1b** (40 mg, 0.097 mmol) in 20 mL of dry, degassed toluene. The green solution was allowed to stir under a CO atmosphere for an additional 24 h and gradually turned lemon yellow. An aliquot (ca. 2 mL) containing the title complex **9b** was taken from the solution and reduced to dryness. The residue was redissolved in C_6D_6 in preparation for NMR spectroscopy. All spectroscopic characterizations were carried out immediately as **9b** slowly reverted to **1b** on standing in non-CO-saturated solution. **9b**: ^1H NMR (C_6D_6) δ 4.77 (s, 5 H, Cp), 3.89 (d, ^3J = 7.2 Hz, 1 H, ring proton), 3.68 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3), 3.52 (d, ^3J = 7.2 Hz, 1 H, ring proton), 3.25 (s, 3 H, OCH_3), 3.23 (s, 3 H, OCH_3); ^{13}C NMR (C_6D_6) δ 178.7 (CO), 174.2 (CO), 165.6 (CO), 159.6 (α-sp^2-ring carbon), 140.8 (β-sp^2-ring carbon), 92.5 (Cp), 55.2 (β-sp^3-ring carbon), 51.8 (OCH_3), 51.4 (OCH_3), 51.0 (OCH_3), 23.8 (α-sp^3-ring carbon); one C≡O carbon and one C=O carbon were not observed; IR (CH_2Cl_2) ν 2045 (s, C≡O), 1736 (s br, C=O), 1710 cm^{-1} (s, C=O).

Reactions with Diphenylacetylene. Reaction of 2a with Diphenylacetylene. 2a (100 mg, 0.145 mmol) was dissolved in 10 mL of dry, degassed benzene. Diphenylacetylene (258 mg, 1.45 mmol) was added, and the solution was stirred at room temperature under a nitrogen atmosphere for 3 days. The solution was reduced to dryness, and the residue was purified by chromatography on silica. Elution with 100:1 CH_2Cl_2/THF afforded an orange-red band of the anti isomer of (η^5-C_5H_5)Co(η^4-*cis*-1,2,3-triphenyl-4,5,6-tricarbomethoxy-1,3-cyclohexadiene) (**11a-2**; 14 mg, 16% yield) followed closely by the syn isomer **11a-1** (48 mg, 54% yield). (For explanation of stereochemistry, see text.) A red band containing an unknown CpCo-containing compound, **12a** (2 mg), was eluted next. On further elution with 10:1 CH_2Cl_2/THF, unreacted **2a** (18 mg, 18%) was recovered. All eluates were reduced to dryness, and the residues were recrystallized from toluene/hexane to afford the products in the stated yields. **11a-1**: ^1H NMR spectra in $CDCl_3$ was identical with the reported literature values;[19] ^1H NMR (C_6H_6) δ 7.45–6.73 (m, 15 H, Ph), 5.43 (s, 5 H, Cp), 3.52 (s, 3 H, OCH_3), 3.21 (d, ^3J = 9.6 Hz, 1 H, ring proton), 3.12 (s, 3 H, OCH_3), 3.01 (s, 3 H, OCH_3), 2.62 (d, ^3J = 9.6 Hz, 1 H, ring proton); the pair of doublets assigned to the ring protons showed slight deviations from a first order system; at lower fields, the system is observed as an AB quartet; ^{13}C NMR (C_6H_6) δ 174.7 (CO), 172.4 (CO), 172.3 (CO), 144.0 (C_2 or C_3), 138.5 (C_3 or C_2), 138.6–126.0 (Ph), 98.6 (C_1 or C_4), 97.0 (C_4 or C_1), 85.9 (Cp), 54.3 (C_6 or C_5), 51.4 (OCH_3), 51.0 (OCH_3), 50.9 (OCH_3), 49.0 (C_5 or C_6). **(11a-2)·$C_6H_5CH_3$**: mp 204–206 °C; ^1H NMR (C_6H_6) δ 7.68–6.87 (m, 20 H, Ph), 4.62 (s, 5 H, Cp), 4.25 (d, ^3J = 12.5 Hz, 1 H, ring proton), 3.85 (d, ^3J = 12.5 Hz, 1 H, ring proton), 3.38 (s, 3 H, OCH_3), 3.15 (s, 3 H, OCH_3), 3.03 (s, 3 H, OCH_3), 2.31 (s, 3 H, CH_3 of toluene of crystallization); the pair of doublets assigned to the ring protons showed slight deviations from a first-order system; ^{13}C NMR (C_6H_6) δ 174.7 (CO), 171.4 (CO), 171.1 (CO), 145.0 (C_2 or C_3), 138.9 (C_3 or C_2), 137.9–125.3 (Ph), 100.8 (C_1 or C_4), 99.8 (C_4 or C_1), 57.0 (C_6 or C_5), 51.5 (OCH_3), 51.1 (OCH_3), 50.6 (OCH_3), 49.4 (C_5 or C_6); IR ($CHCl_3$) ν 1751 (s br, C=O), 1729 (s br, C=O), 1685 cm^{-1} (s, C=O). Anal. Calcd for $C_{35}H_{31}O_6Co·C_7H_8$: C, 72.19; H, 5.64. Found: C, 71.97; H, 5.86. **12a**: ^1H NMR (C_6D_6) δ 7.62–6.75 (m, 15 H, Ph), 4.48 (s, 5 H, Cp), 3.67 (s, 3 H, OCH_3), 3.34 (s, 3 H, OCH_3), 3.12 (s, 3 H, OCH_3); IR ($CHCl_3$) ν 1710 (s br, C=O), 1691 cm^{-1} (s br, C=O).

Reaction of 1a with Diphenylacetylene. A solution of **1a** (25 mg, 0.058 mmol) and diphenylacetylene (103 mg, 0.580 mmol) in 15 mL of dry, degassed benzene was stirred for several days at room temperature. Workup as described for reaction of **2a** with diphenylacetylene gave the identical products and comparable product distribution.

Release of η^4-Cyclohexadiene Ligand by Oxidation of 11a-2 with $CuCl_2·H_2O$. A chilled solution of $CuCl_2·H_2O$ (71 mg, 0.416 mmol) in 3 mL of CH_3CN was slowly added to a stirred, cooled (0 °C) solution of **11a-2** (42 mg, 0.069 mmol) in 5 mL of CH_3CN. The mixture was stirred for 15 min at 0 °C during which time the color turned from red to deep green. The solution was reduced to dryness. The residue was redissolved in Et_2O (20 mL), extracted with H_2O, and dried over Na_2SO_4. The resulting solution was reduced to a pale pink oil (25 mg) which contained both **13a** and **14a** in a 20:1 ratio. (When decomposition was carried out with $(NH_4)_2Ce(NO_3)_6$, the product distribution was 2:3 **13a**/**14a**.) The mixture was air-sensitive, converting completely to **14a** upon standing or upon chromatography. Therefore, analytically pure **13a** was not isolated. **13a** was characterized in solution. The mixture was allowed to stand for several days, effecting the complete conversion to **14a**. The solution was reduced to dryness, and **14a** was recrystallized from a CH_2Cl_2/Et_2O solution (12 mg, 36% yield). **14a** had the same NMR and IR spectra and melting point as an authentic sample of 1,2,3-tricarbomethoxy-4,5,6-triphenylbenzene; see below. **13a**: MS (EI), *m/e* (% abundance, assignment) 482 (41, M), 391 (50, M – CO_2CH_3 – CH_3OH), 379 (32, M – CCO_2CH_3 – CH_3OH), 347 (100, M – CCO_2CH_3 – $2CH_3OH$). Found (abundance): M (40.9), M + 1 (13.2), M + 2 (2.8). Calcd (abundance): M (40.9), M + 1 (13.5), M + 2 (2.7). **14a**: mp 210–212 °C.

1,2,3-Tricarbomethoxy-4,5,6-triphenylbenzene (14a). The title compound was prepared by a Diels–Alder addition of 2-carbomethoxy-3,4,5-triphenylcyclopentadienone and dimethyl acetylenedicarboxylate.[24] The literature procedure for the

preparation of the cyclopentadienone from benzil and methyl benzylacetoacetate called for the use of an ethanolic sodium ethoxide solution. The ^1H NMR spectrum of the cyclopentadienone prepared in this manner established that a significant degree of transesterification of the methyl ester to an ethyl ester had occurred under these conditions. This observation explained the low melting point of the arene product that had been reported in the literature.[24] The use of methanolic sodium methoxide in the preparation of the cyclopentadienone prevented undesired transesterification. The arene obtained from the reaction of pure cyclopentadienone and dimethyl acetylenedicarboxylate was recrystallized from methanol to afford 510 mg of analytically pure arene (41% yield): mp 213–214 °C (lit.[24] mp 200 °C); IR (Nujol) ν 1755 (s, C=O), 1724 cm^{-1} (s, C=O). Anal. Calcd for $C_{30}H_{24}O_6$: C, 74.98; H, 5.04. Found: C, 75.16; H, 5.21.

Release of η^4-Cyclohexadiene Ligand by Oxidation of 11a-1 with CuCl·H_2O. **11a-1** (30 mg, 0.050 mmol) in 5 mL of CH_3CN was treated with CuCl·H_2O (54 mg, 0.30 mmol) in 3 mL of CH_3CN as described previously. A pale pink oil that contained two products was isolated. The mixture in the oil had the spectroscopic properties expected for a mixture of **13a** and **14a**; see above.

Kinetic Experiments. Sampling Handling. The cobalt complexes included in this investigation were generally air-stable as solids but underwent slow aerobic decomposition. Sample preparation was carried out under an inert atmosphere in a Vacuum/Atmospheres Co. drybox, and kinetic experiments were conducted anaerobically. In a typical run, the cobalt complex and diphenylacetylene (DPA) were weighed out in air on a microgram balance and transferred to a 2-mL volumetric flask. The flask was placed under vacuum and brought into the drybox where a solution was prepared by using dry, degassed benzene-d_6. Equal 0.6-mL portions of the stock solution and ca. 3 μL of a 1.410 M CH_2Cl_2 solution in benzene-d_6 (used as an internal standard) were pipetted into three NMR tubes. The NMR tubes immediately were placed in either a constant temperature water bath at 25 ± 0.1 °C or the temperature-controlled (at 25 °C) NMR probe where they remained for the duration of the experiment. Temperature variations occurred while the samples were transferred from the bath to the probe and while the NMR probe was maintained at a temperature close to the ambient temperature. An error of ±1.0 °C was a reasonable estimate of these temperature variations.

Data Acquisition. The reaction of **1a** with DPA was followed by integration of the cyclopentadienyl peaks of **1a**, **11a-1**, **11a-2**, and **12a**. Added methylene chloride was used as an internal integration standard. The time of solution preparation was recorded as t_0. If the rate of reaction was fast ($t_{1/2} \leq 2$ h), the sample was placed directly in the NMR probe. For slower rates of reaction ($t_{1/2}$ = 2–8 h), the sample was placed in a Haake circulating bath until immediately prior to data acquisition. The initial reading was typically obtained 15–30 min after mixing. The reaction was monitored at regular intervals for 2–6 $t_{1/2}$'s (4–30 h depending on reaction rate). A pulse delay of 20 s was used to improve the accuracy of integration.

Kinetic data were obtained for a range of [**1a**] and [DPA]. The concentration of **1a** ranged from 3×10^{-3} to 13×10^{-3} M and that of DPA from 0.1028 to 0.3980 M. The ratio [DPA]/[**1a**] was approximately 40 in all experiments. This ensured pseudo-first-order kinetics in the event that the reaction depended on [DPA].

Figure 1 shows a typical first-order rate plot for the consumption of **1a** in the reaction of **1a** and DPA to form the products **11a-1**, **11a-2**, and **12a**. Rate plots were linear for the duration of the experiment (2–6 $t_{1/2}$'s). Observed rate constants were obtained from the weighted nonlinear least-squares fits of the log $[I(\mathbf{1a})/I(CH_2Cl_2)]_t$ vs time, where $I(\mathbf{1a})$ = integration of the Cp signal of **1a** and $I(CH_2Cl_2)$ = integration of the CH_2Cl_2 signal. Weighted nonlinear least-squares analysis of log k_{obsd} vs log [DPA] established that the full rate law was second order (see below). Data from two to three replicate experiments were used to calculate a second-order rate constant for each unique combination of **1a** and DPA. Rate constants from all experiments were averaged to calculate the rate constant for the reaction at 25 °C.

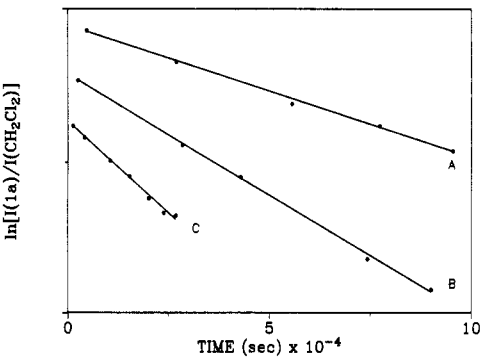


Figure 1. Plots of ln $[I(\mathbf{1a})/I(CH_2Cl_2)]$ vs time for the reaction of **1a** with DPA in benzene: (A) [DPA] = 0.103 M, (B) [DPA] = 0.199 M, and (C) [DPA] = 0.343 M. $I(\mathbf{1a})$ and $I(CH_2Cl_2)$ are the integrated intensities of the Cp peak of **1a** and the peak for added CH_2Cl_2 (integration standard), respectively. The y axis is arbitrary because varying amounts of CH_2Cl_2 were used in the different experiments.

Results and Discussion

The metallaoxanorbornadiene (**1**) and metallacyclopentene (**2**) complexes that were used in this investigation were substituted with electron-withdrawing groups on the metallacycle ring. The presence of these substituents was a consequence of the manner in which **2** were synthesized: reaction of CpCo(η^2-alkyne)(PPh_3) complexes with alkenes. Unactivated alkenes did not react with the alkyne complex. When the alkyne did not contain an electron-withdrawing substituent, i.e. diphenylacetylene, the alkene simply displaced the alkyne from the metal.[25] As a result of the limited range of suitable alkenes and alkynes, the chemistry of the cobaltacyclopentene and cobaltaoxanorbornadiene systems developed here is not readily generalizable. However, investigations of the reactivity of available complexes provide valuable information about the scope of the reactivity and reaction mechanisms of both classes of metallacycle.

In this paper, we describe the reactions of **1** and **2** with isocyanides, carbon monoxide, and alkynes. These led to the formation of aminocyclopentadienes, cyclopentenones, and η^4-cyclohexadiene complexes, respectively. The products still carried the electron-withdrawing substituents of the cyclopentene ring of the parent metallacycle. These groups complicated the isolation and characterization of the products. The spin systems of the substituents (typically carbomethoxy groups) did not couple. Although it was possible to establish the presence and identity of the substituents, the geometric relationships of these groups were difficult to determine. Additionally, the organic products were often difficult to isolate. They underwent rapid decomposition, rearrangement, or oxidation. Often, the product isolated from the reaction mixture was not the initial product.

Reactions with Isocyanides. **1a** reacted with *tert*-butyl isocyanide (*t*-BuNC) to yield the 1-amino-1,3-cyclopentadiene **4a**. The reaction proceeded in two discrete steps. In the initial step, *t*-BuNC coordinated to the cobalt of **1a** to form an isocyanide-substituted cobaltacyclopentene, **5a**. **5a** was a stable, isolable compound and was previously characterized.[2] No further reaction occurred at room temperature. However, at elevated temperatures **5a** was converted to **4a**. Reaction of **2a** with *t*-BuNC afforded **4a** in comparable yields.

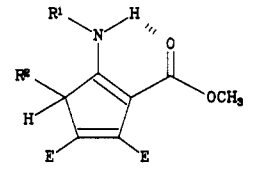
The ^1H NMR spectrum of **4a** (Table I) established that three carbomethoxy groups, one *tert*-butyl group, one

(24) Ried, W.; Wagner, R. *Liebigs Ann. Chem.* **1970**, *741*, 181.

(25) Yamazaki, H.; Hagihari, N. *J. Organomet. Chem.* **1970**, *21*, 431.

phenyl group, and two coupled protons were present. This suggested that the carbon portion of the metallacycle ring and one *tert*-butyl isocyanide were incorporated into the product. The mass spectrum confirmed that this was the exact stoichiometry: no other groups were present.

Spectroscopic evidence established a 1-amino-1,3-cyclopentadiene structure for **4a**. The chemical shifts,



4a, R^1 = t-Bu, R^2 = Ph

4b, R^1 = t-Bu, R^2 = H

8a, R^1 = 2,6-$(CH_3)_2C_6H_3$, R^2 = Ph

coupling constant, and line widths of the two proton peaks were distinctive for this structure. The shift of the upfield peak (δ 4.84) was typical of a cyclopentadienyl proton. The other peak was broad and shifted significantly downfield (δ 9.34). This was consistent with the presence of a strongly hydrogen-bonded proton on the *tert*-butylamine substituent. A good candidate for the donor in the hydrogen bond was the carbonyl oxygen atom of a carbomethoxy substituent on a carbon β to the amine. The cyclopentadienyl proton was also assigned to a carbon β to the amine as the 1.5-Hz coupling of the two protons was typical of a four-bond coupling.

The ^{13}C NMR spectrum of **4a** (Table II) was consistent with the proposed structure. Peaks characteristic of an α,β-unsaturated amine (enamine) were observed at δ 118.8 and 99.0. Three other ring carbons were observed, two sp^2 carbons at δ 174.8 and 146.3 and a sp^3 carbon at δ 54.3. Proton-coupled spectra established that only the latter was directly attached to a proton. Its doublet (^1J = 146.7 Hz) collapsed upon irradiation at 4.84 ppm in single-frequency proton-decoupling experiments. The ^{13}C spectrum was unaffected by irradiation at 9.34 ppm, confirming that the low-field proton was bound to a heteroatom. The ring sp^2 and quaternary enamine carbons were assigned on the basis of the magnitude of their long-range coupling with the cyclopentadienyl proton.

Additional evidence for a hydrogen-bonded amine proton was provided by the characteristic N–H stretching band[26] observed at 3290–3269 cm^{-1} in the IR spectrum of **4a**. Furthermore, a strong band at 1670–1655 cm^{-1} was assigned to the coupled bending (E_1) modes of C=O and C=C groups in a β-ester-substituted α,β-unsaturated amine (enamine).[26,27]

Given the constraints above, placement of substituents around the aminocyclopentadiene ring is straightforward provided that no change had occurred in the connectivity of the metallacycle fragment. The β-carbomethoxy enamine structure fragment requires a 1,2-double bond and a 2-carbomethoxy group. The cyclopentadienyl proton must therefore be on C-5. Finally, the connectivity of the metallacyclic precursor dictates that the phenyl substituent is also on C-5.

One consequence of the proposed structure of **4a** is that both protons must be exchangeable. Attempts to effect exchange by shaking a $CDCl_3$ or C_6D_6 solution of **4a** with D_2O or D_2O/NaOD were unsuccessful. However, addition of a few drops of D_2O/NaOD to a solution of **4a** in DMSO-d_6 effected the rapid exchange of the amine proton with deuterium. Concurrently, the doublet of the cyclopentadienyl proton at δ 4.84 collapsed to a singlet. At longer times, the cyclopentadienyl proton exchanged with deuterium, too.

Most reactions of isocyanides with metallacyclic[14,28] or acetylinic[29] complexes lead to products containing imine groups. It is conceivable that the initial product of the reaction of **1a** and *t*-BuNC was a cyclopentenylimine which then tautomerized to afford the isolated enamine complex **4a**. However, enamines are usually not the stable tautomer for primary amines.[30] The presence of the carbomethoxy substituents and the α,β-double bond in the imine may alter the situation, though. The carbomethoxy group on C-2 participates in the hydrogen bond with the amine hydrogen and can stabilize the partial negative charge that develops on this carbon in one of the enamine resonance structures. Similarly, migration of the α,β-double bond in the imine to the 3,4-position of the enamine permits vinylogous stabilization of the enamine by the carbomethoxy group on C-4.

A third product was detected in the reaction of **1a** with *t*-BuNC. A small quantity of this product, **6b**, was isolated from the analogous reaction of **1b**. The ^1H NMR spectrum of **6b** consisted of a single peak at δ 4.33. It would appear that the product contains one or more equivalent CpCo fragments and is a cobalt-containing product of the reaction. The known trinuclear cluster $[(\eta^5\text{-}C_5H_5)Co(CO)]_3$, which forms from coordinatively unsaturated $(\eta^5\text{-}C_5H_5)Co$ intermediates generated by the photolysis of $(\eta^5\text{-}C_5H_5)\text{-}Co(CO)_2$[31,32] or the decomposition of $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2\text{-}(CH_3)_2$,[33] has a simple ^1H NMR spectrum like that of **6b**.[31-33] However, **6b** is not $[(\eta^5\text{-}C_5H_5)Co(CO)]_3$. The single peaks of the cluster and of **6b** have significantly different chemical shifts. Furthermore, the IR spectra of **6b** and the cluster[32c] were not identical. The spectrum of **6b** had bands with frequencies suggestive of bridging CO or RNC groups (?!)[34] but was otherwise uninformative. In the absence of further spectroscopic or analytical information, a structure cannot be proposed for **6b**.

Variation of the metallacycle or isocyanide used in these reactions affected the rate of reaction and the nature of the products. Reaction of *t*-BuNC with **2a** afforded the same products as described above. However, the reaction proceeded at a much slower rate. This was due to inhibition by free PPh_3 which accumulated as the reaction progressed. Free PPh_3 competes with *t*-BuNC for a coordination site on the metal. We have shown that ligand substitution reactions are faster in general for **1a** than for **2a**.[2]

The reaction of 2,6-dimethylphenyl isocyanide (2,6-DMI) with **1a** was complete after 24 h at room temperature.

(26) Dabrowski, J. *Spectrochim. Acta* **1963**, *19*, 475.
(27) Dürbeck, H. W.; Dukkta, L. L. *Tetrahedron* **1973**, *29*, 4285.
(28) Yamazaki, H.; Wakatsuki, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1239.
(29) (a) Yamazaki, H.; Aoki, K.; Yamamoto, Y.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1975**, *97*, 3546. (b) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1986**, 1193. (c) Wakatsuki, Y.; Miya, S.; Yamazaki, H.; Ikuta, S. *J. Chem. Soc., Dalton Trans.* **1986**, 1201. (d) Wakatsuki, Y.; Miya, S.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1986**, 1207.
(30) House, H. O. *Modern Synthetic Reactions, 2nd ed.*; W. A. Benjamin: Reading, MA, 1972; pp 570–575 and references therein.
(31) King, R. B. *Inorg. Chem.* **1966**, *5*, 2227.
(32) (a) Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4998. (b) Vollhardt, K. P. C.; Bercaw, J. E.; Bergman, R. G. *J. Organomet. Chem.* **1975**, *97*, 283. (c) Bailey, W. I., Jr.; Cotton, F. A.; Jamerson, J. D.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 3131.
(33) Schore, N. E.; Ilenda, C.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 7436.
(34) Note however the absence of proton resonances appropriate for an alkyl group on a bridging isonitrile ligand.

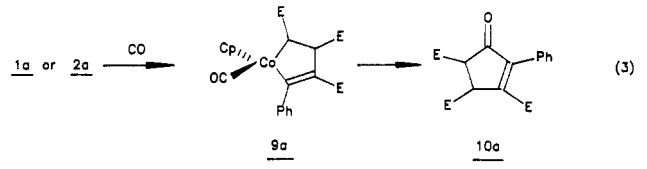
Unlike reactions with *t*-BuNC, the reaction with 2,6-DMI did not progress through two well-defined stages. An isocyanide-coordinated cobaltacyclopentene, **7a**, was observed as an intermediate during the reaction, but the only isolable product was the aminocyclopentadiene **8a**. Isolation of **7a** was precluded by its conversion to **8a**.

1a and **2a** reacted with isocyanides under milder conditions than **1b** and **2b**, respectively. Analogous variations in reaction rates were observed for reactions with CO (see below). Similarly, rates of reaction of cobaltacyclopentadiene complexes with phosphites to form 1-alkoxyphosphole oxide complexes decreased with increased electron-withdrawing capacity of the ring substituents.[15] The reduction in rate was attributed to stronger Co–ligand interactions in relatively electron-poor cobalt complexes. This slowed both the substitution and insertion steps. Our investigation of the substitution reactions of cobaltacyclopentene complexes are consistent with this interpretation.[3]

The increased substitution of the metallacycle ring in **1b** with electron-withdrawing groups affected the stability of the aminocyclopentadiene product. The ^{1}H NMR and ^{13}C NMR spectra of the product that was isolated, **4b**, established that one of the carbomethoxy substituents of the parent metallacycle had been lost during the reaction. The observation in the coupled ^{13}C NMR spectrum of a triplet ($^1J_{CH}$ = 131 Hz) at δ 38.3, which was doubled by long-range coupling to the amine proton, established that the carbomethoxy group on C-5 had been lost.

Decarboxylation of the expected product would yield a cyclopentadienide complex. Related heavily substituted cyclopentadienides have been reported and are quite stable. Tetra-*n*-butylammonium pentacarbomethoxycyclopentadienide was not protonated in aqueous solution by concentrated HCl.[35] Cyano-substituted cyclopentadienides have measured pK_a values between −7 and −9.[36] Decarboxylation did not occur in **4a**, which has a phenyl substituent at C-5. This may imply that decarboxylation occurs specifically at C-5 in these aminocyclopentadiene systems. Alternatively, the milder reaction conditions required for preparation of **4a** may not be sufficiently severe for decarboxylation to occur.

Reactions with CO. **1a** and **2a** were reacted with excess CO under mild conditions. Both reactions yielded product mixtures that contained the cyclopentenone **10a** as the major product and lesser amounts of the CO-substituted cobaltacyclopentene **9a** and $CpCo(CO)_2$ (eq 3). In both cases, color changes suggested that there were two distinct phases to the reaction.



(3)

The reaction of **2a** with CO was monitored by ^{1}H NMR. **9a** formed initially and was the only product until the bulk of **2a** had been consumed. Subsequently, $CpCo(CO)_2$ and **10a** appeared in increasing concentration and **9a** began to disappear. Prior coordination of CO to cobalt appears to be necessary for formation of the cyclopentenone. The concurrent appearance of $CpCo(CO)_2$ and **10a** suggests that excess CO released the cyclopentenone product from the metal center.

The nonvolatile residue from the crude product of preparative-scale reactions of **1a** and CO was worked up by chromatography. **9a** was isolated from the column but was stable only under a CO-saturated atmosphere. Apparently, a weak Co–CO interaction favored reversion of **9a** to **1a** in the absence of CO. Reversion was complete within 1 h.

Because **9a** could not be isolated as an analytically pure solid, it was characterized by spectroscopic means. The presence of a terminal CO ligand was confirmed by a band in the IR spectrum at 2022 cm^{-1}. The ^{1}H NMR spectrum of **9a** was entirely characteristic of cobaltacyclopentene complexes.[2,3] The 7.0-Hz coupling of the ring protons was within the range observed for the normal stereoisomer of ligand-substituted cobaltacyclopentene complexes.[3] In this stereoisomer, ligands coordinate on the less hindered of the two inequivalent faces of the metallacyclopentene ring, the face bearing the syn ring protons. The other stereoisomer, which can be prepared from **1** with high concentrations of sterically nondemanding ligands, has more highly deshielded ring protons and larger $^3J_{HH}$ values than the normal stereoisomer. CO did not form detectable amounts of the second stereoisomer. The weakness of the Co–CO bond in **9** and the limited solubility of CO in benzene may both contribute to this outcome. The lability of **9a** prevented us from obtaining ^{13}C data. However, the ^{13}C NMR spectrum obtained for the somewhat more inert **9b** was consistent with the cobaltacyclopentene structure of these materials.

Elution of **10a** from silica columns required polar solvents. The strong interaction of **10a** with silica caused the band to tail. Addition of $^1/_2$% (v/v) acetic acid to the eluant decreased the elution time and sharpened the band considerably. Evaporation of the eluate afforded **10a** as a noncrystallizable oil. The mass spectrum of the oil established a molecular weight of 332 for **10a**, in agreement with the molecular formula of $C_{17}H_{16}O_7$ that would be obtained by construction of a cyclopentenone from CO and the metallacycle ring.

As might be expected for a cyclopentenone with several carbomethoxy substituents, the ^{1}H NMR spectrum of **10a** was broadened by keto–enol tautomerization and/or other exchange processes. Three closely spaced methoxy peaks and two coupled ring proton peaks, which appeared as partially resolved doublets, were observed. The upfield doublet (δ 3.75) was appreciably broader, suggesting that it was closest to the ketone carbonyl group. Addition of $^1/_2$% protio-acetic acid to a benzene-d_6 solution of **10a** caused slight changes in the chemical shifts and sharpened the spectrum considerably. It was then apparent that peaks characteristic of an enol tautomer were absent. When larger amounts of acetic acid-d_1 were added to benzene-d_6 solutions of **10a**, both proton peaks collapsed to singlets. With time, the protons exchanged with deuterium at roughly comparable rates. Exchange was 85% complete after 20 min in the presence of a 30-fold excess of acid.

The ^{13}C NMR spectrum confirmed the cyclopentenone structure of **10a**. The most notable feature of the spectrum was the ketone C=O peak at δ 197.4. No evidence was seen for the presence of an enol tautomer of **10a**. The two signals at δ 55.5 and 48.3 were assigned to the sp^3 carbons in the cyclopentenone ring. The enol form should have only one sp^3 carbon. Only two signals attributable to sp^2 carbons of the cyclopentenone ring were observed. The enol form should have four.

Changing the C-5 ring substituent of **1** affected the course of its reaction with CO. **1b** reacted with CO at room

(35) Cookson, R. C.; Henstock, J. B.; Hudec, J.; Whitear, B. R. D. *J. Chem. Soc. C* **1967**, 1986.
(36) Webster, O. W. *J. Am. Chem. Soc.* **1966**, *88*, 3046.

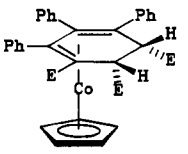
temperature to form **9b**, which in the absence of CO also reverted to **1** on standing. As alluded above, **9b** was longer lived than **9a** under an N_2 atmosphere and was, therefore, more completely characterized. Its properties were comparable to those of **9a**. Unlike **9a**, **9b** did not react further at room temperature to afford a cyclopentenone product, even after several days under a CO atmosphere. Heating a CO-saturated solution of **9b** to 80–100 °C led to reaction, as evidenced by the isolation of $CpCo(CO)_2$ from the reaction mixture. However, no cyclopentenone was detected in the reaction mixture. Apparently, conditions sufficient to induce CO insertion reactions are sufficient to induce further reaction or decomposition of the cyclopentenone product.

The formation of cyclopentenones from CO and **1** or **2** and synthetic routes to **1** and **2** combine to provide a formal synthesis of cyclopentenones from alkene, alkyne, and CO. The net reaction is identical with that of the Pauson–Khand reaction, which is an actual synthesis of cyclopentenones from these three components in the presence of $Co_2(CO)_8$.[37-39] The first step of the Pauson–Khand reaction is alkyne complexation to form the well-known hexacarbonyldicobalt–alkyne species. Although no other intermediates have been isolated or observed during the reaction, assembly of the three components has been hypothesized to occur on a bimetallic intermediate.[38b,39b] The developing cyclopentenone moiety bridges and is stabilized by the two metal centers. Our results demonstrate that two adjacent metal centers are not required to accomplish this chemistry.

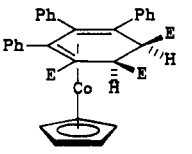
Reactions with Diphenylacetylene. We have reexamined the previously investigated[19] reaction of **2a** with DPA. Contrary to published results, three products, **11a-1**, **11a-2**, and **12a**, were isolated from the reaction. **11a-1** was spectroscopically identical with the product reported in the literature. Identical products were obtained in comparable yields from the reaction of **1a** with DPA.

We initially entertained the possibility that **11a-2** and **12a** were intermediates along the reaction pathway to the final product **11a-1**. For this to be true, a reaction pathway leading from these complexes to **11a-1** must exist. Accordingly, purified samples of **11a-2** and **12a** were subjected to conditions approximating those experienced during the reaction. Solutions of **11a-2** in benzene-d_6 were unchanged after being heated for 24 h at 65 °C under an inert atmosphere and after being heated for 30 h at 50 °C in the presence of a 50-fold excess of DPA. Solutions of **12a** in benzene were nearly completely reacted after being heated at 45 °C for 24 h. Two unidentified products were cleanly obtained (one Cp containing, the other not). **11a-1** was not detected, however. Thus, **11a-2** and **12a** are products of the reaction rather than intermediates on the path to **11a-1**. We confirmed this conclusion by monitoring the progress of the reaction by NMR (see below).

An elemental analysis of **11a-2** established that it had the same empirical formula as **11a-1** (excluding the toluene of solvation in the former complex). These two isomeric complexes had ^1H and ^{13}C NMR spectra with identical spin systems and proton integrations but somewhat different chemical shifts and coupling constants. The major isomer **11a-1** had a C_5H_5 peak at δ 5.43, ring proton peaks at δ 3.21 and 2.62, and $^3J_{HH}$ = 9.6 Hz. The minor isomer **11a-2** had a more shielded C_5H_5 group (δ 4.62), deshielded ring protons (δ 3.89 and 3.52), and larger coupling constant ($^3J_{HH}$ = 12.5 Hz). The relationships of the chemical shifts and the magnitude of the coupling constants for the two isomers of **11a** are precisely the same as those observed for the two isomers of (η^5-C_5H_5)Co(η^4-5,6-*cis*-dicarbomethoxy-1,3-cyclohexadiene) complexes.[7] The only difference between these isomers was the face of the cyclohexadiene ring that was coordinated to cobalt. Furthermore, comparison of the NMR parameters of **11a** to those of a structurally characterized η^4-cyclohexadiene complex[7] established that isomer **11a-1** has the two *cis*-carbomethoxy groups on the same face of the cyclohexadiene as the cobalt (syn). Therefore, isomer **11a-2** is the anti isomer.[40] This assignment agrees with the stereochemistry of **11a-1** that was depicted in a line drawing in ref 19. Interconversion of **11a-1** and **11a-2** would not be facile under the conditions investigated above.

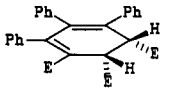


11a-1

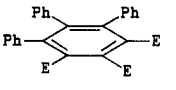


11a-2

Decomplexation reactions should yield identical cyclohexadienes from **11a-1** and **11a-2**, if, as we suggest, the two isomers differ only with respect to the face of the cyclohexadiene that is coordinated by cobalt. Both **11a-1** and **11a-2** afforded the cyclohexadiene compound *cis*-1,2,3-triphenyl-4,5,6-tricarbomethoxy-1,3-cyclohexadiene (**13a**) when oxidized by $CuCl_2 \cdot H_2O$. The spectroscopic properties of **13a** obtained from either complex were identical.



13a



14a

13a was air-sensitive and was easily oxidized to the hexasubstituted benzene compound **14a**. Indeed, some **14a** was always present in the product of the $CuCl_2$ oxidation. Because of our inability to separate these compounds and obtain an analytically pure sample of **13a**, we decided to convert **13a** to **14a**, a known compound, and characterize the latter. Reaction of **11a** with the stronger oxidant Ce^{4+} led to the isolation of a 3:2 mixture of **14a** and **13a**, respectively. Complete conversion of **13a** to **14a** was effected by prolonged air exposure or by chromatography on silica.

In order to confirm the anticipated substitution pattern of **14a** obtained from **11a** (and by inference the substitution patterns of **13a** and **11a**), we prepared an authentic sample of 1,2,3-tricarbomethoxy-4,5,6-triphenylbenzene by the Diels–Alder reaction of 5-carbomethoxy-2,3,4-triphenyl-2,4-cyclopentadienone with dimethyl acetylenedicarboxylate.[24] The literature procedure for the synthesis of the cyclopentadienone called for condensation of benzil and methyl benzylacetoacetate in the presence of ethanolic sodium ethoxide. We found that this led to partial transesterification of the methyl ester to an ethyl ester and consequently to impure **14a**. In fact, the melting point that

(37) (a) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E.; Foreman, M. I. *J. Chem. Soc., Perkin Trans. 1* **1973**, 977. (b) Khand, I. U.; Pauson, P. L. *J. Chem. Soc., Perkin Trans. 1* **1976**, 30. (c) Billington, D. C.; Pauson, P. L. *Organometallics* **1982**, *1*, 1560. (d) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.

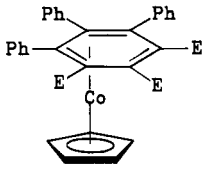
(38) (a) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477. (b) Magnus, P.; Principe, L. M. *Tetrahedron Lett.* **1985**, *26*, 4851.

(39) (a) Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436. (b) La Belle, B. E.; Knudsen, M. J.; Olmstead, M. M.; Hope, H.; Yanuck, M. D.; Schore, N. E. *J. Org. Chem.* **1985**, *50*, 5215. (c) Schore, N. E.; Knudsen, M. J. *J. Org. Chem.* **1987**, *52*, 569.

(40) In the terminology of ref 7, **11a-1** is the exo isomer and **11a-2** the endo isomer. Endo and exo were defined with reference to the stereochemistry of the cyclohexadiene ring rather than to the position relative to cobalt.

we determined for **14a** prepared from **11a** was 13–14 °C higher than the reported melting point[24] of **14a**. This discrepancy was eliminated by use of methanolic sodium methoxide in the synthesis of the cyclopentadienone compound. **14a** prepared in this manner and from **11a** had identical melting points and NMR and IR spectra.

The ^{1}H NMR spectrum of **12a**, the third reaction product, established that it contained one C_5H_5 group, three inequivalent carbomethoxy substituents, a phenyl substituent, and one diphenylacetylene. No ring protons were detected. One possible structure for **12a** that is consistent with the NMR spectrum is an (η^5-C_5H_5)Co-(η^4-arene) complex of **14a**. The substitution pattern of



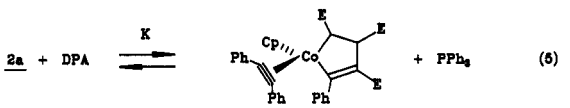
12a

the arene gives rise to several inequivalent ways of coordinating the arene in an η^4 fashion. The new C_5H_5-containing product observed in the ^{1}H NMR spectrum of **12a** after heating could represent a migration of the (η^5-C_5H_5)Co group to a different η^4-binding site.

A Kinetic Study of the Reaction of 1a with Diphenylacetylene. Wakatsuki et al. investigated the kinetics of the reaction of **2a** and DPA.[19] The observed rate law in benzene at 24.4 °C is described by eq 4. The initial

$$\frac{d[\mathbf{11a\text{-}1}]}{dt} = \frac{k_2K[\mathbf{2a}][DPA]}{[PPh_3]} \qquad k_2K = 2.8 \times 10^{-8}\ s^{-1} \quad (4)$$

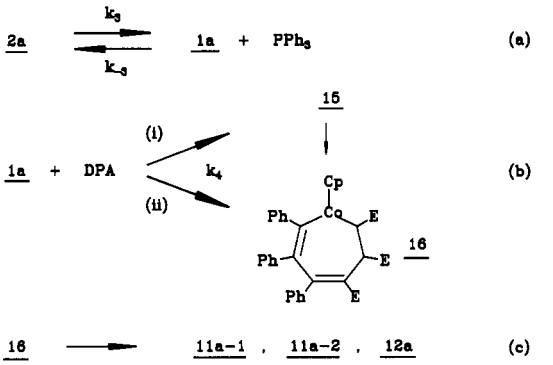
step in the proposed mechanism, eq 5, was equilibration of **2a** and free DPA with an alkyne-coordinated cobaltacyclopentene and free PPh_3. In the rate-determining step, eq 6, the coordinated alkyne inserted into the metallacycle



15

ring to afford a metallacycloheptadiene intermediate, which collapsed rapidly to the product η^4-cyclohexadiene complex. Neither the alkyne-complexed metallacycle nor the metallacycloheptadiene was actually observed during the course of the reaction. However, reasonable precedents exist for invoking metallacycloheptadiene intermediates. They have been proposed previously in the (η^5-indenyl)-RhL_2-assisted cyclotrimerization reactions of alkynes with alkenes[20] and in the metal-catalyzed cyclotrimerization reactions of alkynes.[41,42] (Actually, two parallel reaction pathways have been demonstrated for the latter reactions: (i) insertion of the alkyne into a metal–carbon bond to form a metallacycloheptatriene intermediate and (ii) a direct Diels–Alder reaction of the alkyne with the diene moiety of the cyclopentadiene ring to generate a [2.2.1]-bicyclic intermediate.[41]) Although metallacycle complexes with coordinated alkynes were not observed, prior coordination of the alkyne to the metal center generally has been assumed in these reactions.[6,20,41,42]

Scheme I



Wakatsuki's discussion did not elaborate on the mechanism by which **2a** and DPA react to form the alkyne-coordinated cobaltacyclopentene complex, eq 5. Two mechanisms that would typically be considered for a transformation of this type are phosphine dissociation and direct displacement of phosphine by alkyne. The results of our investigations of the kinetics and mechanisms of ligand substitution reactions of cobaltacyclopentene and cobaltaoxanorbornadiene complexes[2,3] rule out both of the above mechanisms and strongly suggest that **1** is a mechanistically important intermediate in the reactions of **2**. The majority of the reaction proceeds via β-ester-assisted displacement of the phosphine–i.e. formation of **1**. Phosphine dissociation was shown to be a relatively minor pathway in the reactions of **2**. Substitution by the phosphine dissociative pathway occurs only with high concentrations of sterically nondemanding ligands, requirements not met by DPA in the reactions under consideration here. Finally, direct displacement is ruled out by the observed stereochemistry of ligand substitution products. Substitution with larger ligands always leads to retention of configuration at cobalt rather than the inversion required by a direct displacement of phosphine.

We examined the possibility that **1a** was the intermediate in the reaction of **2a** with DPA. The resulting mechanism is outlined in Scheme I. A preequilibrium is established between **2a** and **1a** and free PPh_3. The alkyne then reacts in an associative manner with **1a**. Either (i) a discrete alkyne-coordinated cobaltacyclopentene complex, **15**, is formed and then converted to a cobaltacycloheptadiene intermediate, **16**,[43] on alkyne insertion into a metal–carbon bond, or (ii) the alkyne inserts directly into a cobalt–carbon bond without prior complexation to form **16**. Rapid reductive elimination yields the products. The rate-determining step in case i could be formation either of **15** or of **16**. With the assumption of steady-state conditions for **1a** (i.e., formation of **15** is rate determining) the rate law for the consumption of **2a** is

$$\frac{-d[\mathbf{2a}]}{dt} = \frac{k_3k_4[\mathbf{2a}][DPA]}{k_{-3}[PPh_3] + k_4[DPA]} \quad (7)$$

We have previously determined the rate constant k_{-3} in a series of independent experiments.[3] Even qualitative estimates of the rate of reaction of **1a** with DPA establish that $k_4[DPA] \ll k_{-3}[PPh_3]$, especially if PPh_3 is added as in Wakatsuki's experiments. Equation 7 then reduces to

$$\frac{-d[\mathbf{2a}]}{dt} = \frac{k_4K_3[\mathbf{2a}][DPA]}{[PPh_3]} \quad (8)$$

(41) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* 1977, *99*, 1666.
(42) Jolly, P. W.; Wilke, G. *The Organic Chemistry of Nickel*; Academic: New York; 1975; Vol. 2, Chapter 2.

(43) The alkyne could insert into either cobalt–carbon bond. We have arbitrarily picked one of the possible cobaltacycloheptadiene complexes in our drawing of **16**.

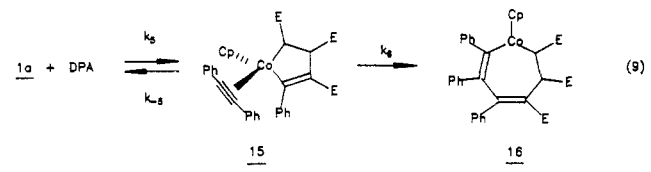
where $K_3 = k_3/k_{-3}$ and k_4 is the rate constant for the reaction of **1a** and DPA to form the observed products. This is exactly the form of the rate law determined by Wakatsuki. Equivalent rate laws are obtained if formation of **16** is assumed to be rate determining (see below).

Three things must be true if our proposed mechanism is correct. First, the reactions of **1a** and of **2a** with DPA must give identical products in identical yields (unless phosphine somehow affects the partitioning of products). Second, the reaction of **1a** and DPA must have a second-order rate law. Third, the product of K_3, which we have previously determined,[3] and k_4 must be the same as Wakatsuki's observed rate constant. The first point was demonstrated above. The determination of the rate law and rate constant for reaction of **1a** and DPA is described below.

The reaction of **1a** with DPA was examined in benzene at 25 °C. A 40-fold excess of DPA was used to reduce the system to pseudo-first-order kinetics, which resulted in considerable simplification of the data analysis. The extent of reaction was determined by integration of the Cp peaks of **1a**, **11a-1**, **11a-2**, and **12a**, which were standardized against an internal CH_2Cl_2 integration. No signals other than those attributed to the starting materials and these products were observed during the course of the reaction, which established the absence of any other species in significant concentrations.

A plot of ln $[I(\mathbf{1a})/I(CH_2Cl_2)]_t$ vs time, where $I(\mathbf{1a})$ = integration of **1a** and $I(CH_2Cl_2)$ = integration of CH_2Cl_2, both at time t, established that the reaction is first order in [**1a**] (Figure 1). A weighted nonlinear least-squares fit of the above function provided the observed rate constant, k_{obsd}. Data were obtained over a 4-fold concentration range of DPA. A plot of ln (k_{obsd}) vs ln ([DPA]) established a first-order dependency of the reaction on [DPA]. At 25 °C, the slope of the line was $(9.6 \pm 0.6) \times 10^{-1}$, which is within 1σ of 1.0. On the basis of kinetic evidence the overall rate law is second order. Thus, the second point has now been established. Division of k_{obsd} by [DPA] provided the second-order rate constant, k_4, for the loss of **1a**. The reaction of **1a** and DPA at 25 °C gave $k_4 = (2.39 \pm 0.13) \times 10^{-4}$ s^{-1} M^{-1}. The overall rate equation for the reaction of **2a** with DPA will be determined and compared to Wakatsuki's results below.

The observed second-order kinetics for the reaction of **1a** and DPA are consistent with four possible mechanisms. In the first mechanism, **1a** reacts with DPA to form the alkyne-coordinated metallacycle **15**; see Scheme I, eq b(i). In this case, k_4 represents the rate of formation of **15**. Reactions affording **16** and the products occur after the rate-determining step and do not affect the rate expression. Alternatively, the alkyne may insert directly into a cobalt–carbon bond of the cyclopentene ring without prior coordination to afford **16**; see Scheme I, eq b(ii). Again, reaction to afford products occurs rapidly after **16** is formed. In this case, k_4 is the rate constant for formation of **16**. In the third mechanism, a preequilibrium is established between **1a**, DPA, and **15**. The equilibrium is required to be sufficiently rapid so as not to be perturbed by the subsequent reaction of **15** to **16** (eq 9). As in the



(9)

first two cases, **16** reacts rapidly to form product. The rate expression for eq 9 is

$$\frac{-d[\mathbf{1a}]}{dt} = \frac{k_5k_6[\mathbf{1a}][DPA]}{k_{-5} + k_6} \tag{10}$$

15 is never present in sufficient concentration to be observed by ^{1}H NMR spectroscopy. Hence, the equilibrium favors **1a** and free DPA. This implies that $k_6 \ll k_{-5}$ and eq 10 reduces to

$$\frac{-d[\mathbf{1a}]}{dt} = k_6K_5[\mathbf{1a}][DPA] \tag{11}$$

where $K_5 = k_5/k_{-5}$ and $k_6K_5 = k_4$. The last second-order mechanism involves a direct addition of DPA to the carbon part of the metallacycle in **1a**, analogous to the direct Diels–Alder addition demonstrated in some cyclotrimerization reactions of alkynes.[41] We reject this mechanism since it cannot account for the two isomers of **11a**. As discussed above, bulky ligands approach the metal center of **1a** exclusively from the exposed face. If DPA approach is limited to one side of the metallacycle, only one isomer would be observed. Our data did not allow us to differentiate between the other three possibilities.

The proposed metallacycloheptadiene intermediate **16**, which is common to the first three mechanisms, provides a rationalization for the presence and relative abundance of the two isomeric η^4-cyclohexadiene complexes, **11a**. **16** has two inequivalent faces, owing to the two *cis*-carbomethoxy substituents on the sp^3 carbons of the ring. During reductive elimination, the cobalt can move onto either of the two inequivalent faces of the evolving cyclohexadiene to generate **11a-1** or **11a-2**. The partitioning of **16** between the two isomers is due to kinetic, not thermodynamic, factors. This was demonstrated by the failure of the individual isomers to reestablish the 3:1 syn:anti isomer ratio when subjected to conditions approximating the original reaction conditions. The preference for the syn isomer could result from stabilization of the cobalt atom by the carbomethoxy substituents on C-5 and C-6 in the transition state leading to reductive elimination. The existence of 1 is evidence for such stabilizing cobalt–oxygen interactions. The anti isomer, with the C-5 and C-6 carbomethoxy substituents on the face opposite the cobalt atom, does not have this type of interaction available to it.

The rate law that we defined for the reaction of **2a** and DPA was cast in terms of the disappearance of **2a**. Wakatsuki's rate law was defined in terms of the rate of formation of **11a-1**. The presence of three products prevent a direct comparison of our rate constants. In order to directly compare our results with those of Wakatsuki, it was necessary to calculate the rate of formation of **11a-1** from our data. The relative proportions of all three products remained constant within error during the course of the reaction. This suggested that the products were formed after the transition state by partitioning of a common intermediate. From the discussion above, **11a-1** and **11a-2** can readily be seen to form from the intermediate **16**. We cannot establish that **12a** also formed directly from **16** because its structure is unknown. In the interests of simplification, however, we decided to treat **12a** as if it had been formed from **16**. With this assumption, the rate constant for formation of **11a-1** from **1a**, k_7, was simply k_4 times the mole fraction of **11a-1** in the product mixture. A value of $(1.6 \pm 0.13) \times 10^{-4}$ s^{-1} M^{-1} was calculated for k_7. The overall rate constant for the formation of **11a-1** from **2a** and DPA is the product of K_3 and k_7. The measured value[3] of K_3 is $(4.1 \pm 0.7) \times 10^{-4}$ M. Thus, k_7K_3 has

a value of (6.6 ± 1.3) × 10^{-8} s^{-1}.

The rate constant of 2.8 × 10^{-8} s^{-1} reported by Wakatsuki lies just within the 3σ error range of our measurement. Agreement may be better than it would appear. Some preliminary observations of ours suggest that the temperature dependence of the rate is significant. Our experiments were conducted at 25 °C, slightly above the temperature of Wakatsuki's experiments. Error estimates were not reported in the earlier work. The error is likely to be of the same magnitude as in our experiments, or larger. The greatest uncertainty in Wakatsuki's number, however, is that it is not clear what was actually measured. No mention was made of the two minor products, **11a-2** and **12a**, both of which should have been readily observed. Obviously, the contribution of these products to the kinetics and to the mechanism was not explicitly considered. The description of their experiment simply stated that the reaction was followed by monitoring the intensity change of the cyclopentadienyl resonances.[19] Since the cyclopentadienyl resonances of **2a** and **11a-1** disappear and appear at different rates, it is impossible to be certain that the reported rate constant actually pertains to the appearance of **11a-1** rather than the disappearance of **2a**. Although we are uncertain, we assume that is was the former of these two possibilities.

Given the difficulties discussed above, we believe that the overall rate constants for the reaction of DPA with **2a** determined in the two experiments are in substantial agreement. The third point has now been established. Thus, all available evidence favors the mechanism in Scheme I. **1a** is the reactive intermediate in the chemistry of **2a**.

Conclusions. This work has demonstrated that the metallacyclic ring of cobaltacyclopentene complexes **2** reacts with several unsaturated reagents to afford cyclic organic products. Cobaltaoxanorbornadiene complexes **1**, which are in equilibrium with **2**, give identical products with these reagents. Coordination of the reagent prior to insertion into the metallacycle ring was demonstrated in two of three cases investigated and was highly probable in the third case. The kinetics of the reaction of **1a** with DPA confirmed that **1** is the kinetically significant intermediate in the reactions of **2**.

The chemistry of cobaltacyclopentene and cobaltaoxanorbornadiene complexes that we have developed here and in previous papers[2,3] is specific to complexes with β-carbomethoxy groups. However, no evidence exists that the β-carbomethoxy group plays a role in the mechanism(s) by which ligand-substituted cobaltacyclopentene complexes yield organic products. Thus, insertion reactions of the cobaltacyclopentene ring could be of general utility if a more general route to cobaltacyclopentenes complexes were developed.

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Registry No. **1a**, 113158-74-0; **1b**, 106800-03-7; **2a**, 53559-30-1; **4a**, 113087-70-0; **4b**, 113087-72-2; **5a**, 106800-09-3; **5b**, 106800-10-6; **7a**, 113087-73-3; **8a**, 113087-71-1; **9a**, 113087-76-6; **9b**, 113087-75-5; **10a**, 113087-74-4; **11a**$^{-1}$, 65167-38-6; **11a**$^{-2}$, 65139-31-3; **13a**, 113109-01-6; **14a**, 30268-70-3; $CpCo(CO)_2$, 12078-25-0; CO, 630-08-0; *tert*-butyl isocyanide, 7188-38-7; 2,6-dimethylphenyl isocyanide, 2769-71-3; diphenylacetylene, 501-65-5; 2-carbomethoxy-3,4,5-triphenylcyclopentadienone, 30268-68-9.

Synthesis of Hexacarbonyl Derivatives of Group 5 Metals and Electron-Transfer Processes. Crystal and Molecular Structure of Tetracarbonyl(1,2-bis(diphenylphosphino)ethane)iodotantalum

Fausto Calderazzo,*† Guido Pampaloni,† Giancarlo Pelizzi,‡ and Francesca Vitali‡

Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy, and Istituto di Chimica Generale and Centro CNR Strutturistica Diffrattometrica, Università di Parma, Viale delle Scienze, 43100 Parma, Italy

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Vanadium, niobium, and tantalum hexacarbonylmetalate(–I) derivatives of several heterocyclic nitrogen bases, $R_nB[M(CO)_6]_n$ (R = H, Me; n = 1, 2), have been synthesized. In some cases an electron transfer from the hexacarbonylmetalate to the protonated or methylated BR_n^{n+} cation has been observed. Pyridinium halides react with $Na[M(CO)_6]$ (M = Nb, Ta) in the presence of 1 equiv of 1,2-bis(diphenylphosphino)ethane (diphos) to give high yields of the halo tetracarbonyl derivatives $MX(CO)_4$(diphos). The red-orange $TaI(CO)_4$(diphos) complex has been studied by X-ray diffraction methods. Crystal data: space group $P2_1/n$; M_r 818.3; a = 14.864 (10) Å, b = 9.875 (7) Å, c = 19.335 (13) Å; β = 105.61 (2)°; U = 2733 (3) Å^3; Z = 4; D_{calcd} = 1.988 g cm^{-3}; $F(000)$ = 1568; μ(Mo Kα) = 52.4 cm^{-1}. The geometry of the seven-coordinate tantalum atom is best described as a capped trigonal prism with the iodide ligand in the capping position. By reaction of $Na[Ta(CO)_6]$ with 1 equiv of hydrogen chloride and diphos in toluene, the hydride $TaH(CO)_4$(diphos) has been isolated in good yield.

Introduction

Since their discovery in late fifties to early sixties,[1] the binary metal carbonyl derivatives of group 5 metals represent an interesting area of research as far as their synthesis and chemical properties are concerned. For example, the neutral species of vanadium(0), $V(CO)_6$ (no neutral

† Università di Pisa.
‡ Università di Parma.

(1) (a) Natta, G.; Ercoli, R.; Calderazzo, F.; Alberola, A.; Corradini, P.; Allegra, A. *Atti Accad. Naz. Lincei, Rend. Cl. Sci. Mat. Fis. Nat.* **1959**, *27* [8], 107. (b) Ercoli, R.; Calderazzo, F.; Alberola, A. *J. Am. Chem. Soc.* **1960**, *82*, 2966. (c) Werner, R. P. M.; Podall, H. E. *Chem. Ind. (London)* **1961**, 144.

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