

Preparation of Cobalt Half-Sandwich Complexes with Intramolecular C=C Bond Coordination

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Thermolysis of [1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl]carbonyldiiodocobalt, ($\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$)-Co(CO)₂I₂ (**2**), in boiling octane affords the dimeric diiodide [$(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{CoI}_2$] (**3**) without any interference of the 3-butenyl chain with the cobalt center. **2** reacts with various two-electron ligands L [L = P(OMe)₃, P(OPh)₃, PPh₃, PMe₃, PMe₂Ph, *t*BuNC] to give a series of cobalt(III) com-

plexes of the general formulae ($\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$)Co(L)I₂ (**4–9**). Sodium amalgam reduction of these "open-chain" complexes **4–9** yields novel cobalt(I) complexes containing an intramolecularly coordinated C=C bond ($\eta^5\text{-}\eta^2\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$)Co(L). For L = CO (**12**), P(OMe)₃ (**13**), and P(OPh)₃ (**14**) low-melting crystals are isolated and fully characterized by analytical and spectroscopic methods.

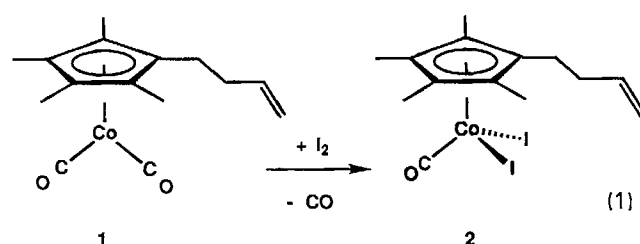
The 16-electron (cyclopentadienyl)cobalt fragment CpCoL (Cp = $\eta^5\text{-C}_5\text{H}_5$; L = two-electron donor) has played an important role in the mechanistic elucidation of several fundamental organometallic transformations such as ligand substitution²⁾, olefin insertion into a metal-alkyl bond³⁾, and alkyne trimerization⁴⁾. Thorough extended Hückel calculations have provided in addition useful insights into the electronic and geometric structure of this coordinatively unsaturated intermediate⁵⁾. Thus, CpCoL offers a soluble "inorganic template" where cobalt-centered reactions of organic substrates can be performed in a well-defined, electronically and sterically tunable ligand sphere. However, complication might arise from uncontrolled participation and/or dissociation of L. Recently, we have designed a new peralkylated cyclopentadienyl ligand that contains a pendent 3-butenyl side chain, viz. $\text{C}_5\text{Me}_4(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{H}$ ⁶⁾. Cobalt half-sandwich complexes bearing this ligand are expected firstly to enable the study of cobalt-olefin interaction in an intramolecular manner within a geometrically constrained ligand environment⁷⁾ and secondly to open access to a conformationally relatively rigid, 16-electron intermediate where the 3-butenyl chain remains coordinated at the cobalt center by virtue of the chelate effect⁸⁾. In this paper we disclose details of the synthesis and characterization of several half-sandwich cobalt complexes containing an intramolecularly coordinated C=C bond. A part of this work has been reported previously¹⁾.

Results and Discussion

We have previously found methods to cleanly coordinate the 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl ligand to the cobalt center using Co₂(CO)₈^{1,6)}. The general strategy

to effect intramolecular coordination of the olefinic bond of the 3-butenyl side chain within a given complex consists of generating a coordinatively unsaturated metal center under mild conditions. We first started probing the coordination capability of the cobalt(III) center before proceeding to the lower valence states.

Oxidation of the readily available dicarbonyl ($\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$)Co(CO)₂ (**1**)¹⁾ with elemental iodine in ether affords in high yields the diiodocarbonyl complex ($\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$)Co(CO)I₂ (**2**) as fairly air-stable, dark violet crystals (Eq. 1).

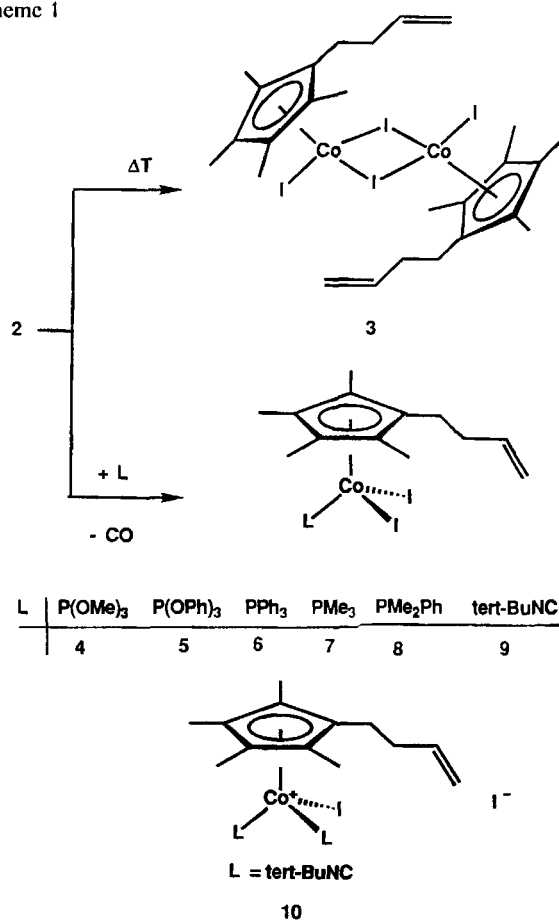


In accord with the overall *C_s* symmetry of the molecule the four ring methyl groups appear as a pair of sharp singlets at $\delta = 1.68$ and 1.78 , and the 3-butenyl group gives rise to an AA'BB'KLM spin system pattern in the ¹H-NMR spectrum. The AA'BB' part due to the aliphatic segment of the side chain consists of two multiplets at $\delta = 1.64$ and 2.34 . The latter exhibiting a triplet-like appearance is assigned to 1-H, while the former is due to 2-H. The three signals of the vinyl part, two close doublets for each of =CH(*trans*) and =CH(*cis*) and a multiplet consisting of ten lines for the methine proton, are centered at $\delta = 4.80$ and 5.39 , respectively. All coupling constants are within the range of values

as expected for a flexible homoallyl group [$J(AA') = J(BB') = 15$, $J(AB') = J(A'B) = 7$, $J_{cis} = 10$, $J_{trans} = 17$, $J_{gem} = 0$ Hz] and have been verified by spectra simulation. The ^{13}C -NMR spectroscopic data are also fully consistent with the structure required. The IR spectrum (KBr) shows an intense $\nu(\text{CO})$ band at 2041 and a weak absorption for $\nu(\text{C}=\text{C})$ at 1640 cm^{-1} . In the solution IR spectrum the $\nu(\text{CO})$ band appears at 2055 cm^{-1} and is comparable to values reported for the $\nu(\text{CO})$ absorption in related cobalt(III) complexes of the type $(\eta^5\text{-C}_5\text{R}_5)\text{Co}(\text{CO})\text{I}_2$ ⁹. Likewise, the carbon monoxide in **2** is easily displaced both in the solid state, as shown by gradual loss of carbon monoxide above 85°C according to thermogravimetric analysis, and in solution, where refluxing in high-boiling hydrocarbon such as octane is sufficient for a quantitative evolution of carbon monoxide from **2**. The product of decarbonylation is straightforwardly identified as the dimeric diiodide $[(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{CoI}_2]_2$ (**3**), which is isolated as greenish black, pentane-insoluble crystals. NMR spectroscopic data are entirely analogous to those of **2**, and the IR spectrum clearly shows an absorption for $\nu(\text{C}=\text{C})$ at 1639 cm^{-1} . Complex **3** is formed exclusively upon decarbonylation of **2** regardless of the solvent, concentration, and temperature applied. Obviously, *intermolecular* coordination of bridging iodide at the cobalt(III) fragment ($\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$)CoI₂ is preferred to *intramolecular* complexation of the C=C bond of the 3-butenyl side chain.

The CO ligand in **2** is also displaced by a series of two-electron donors. While substitution for the less basic ligands

Scheme 1

Table 1. ^1H -NMR spectroscopic data of **2**–**11** (δ , C_6D_6 , 25°C)

Compound	$\text{CH}_3^{\text{a)}$	1-H ₂	2-H ₂	=CH	=CH ₂ ^{b)}	L ^{a)}
2	1.68 1.71	2.31	1.64	5.39	4.80	
3	1.54 1.65	2.57	1.64	5.37	4.77	
4	1.81 (d, 2.9) 1.86 (d, 2.5)	2.57	1.80	5.60	4.91	3.52 (d, 9.8, OCH ₃)
5	1.88 (d, 3.0) 1.96 (d, 3.0)	2.71	1.81	5.54	4.86	6.77, 6.90 7.38 (m, C ₆ H ₅)
6	1.59 1.64	2.26	1.66	5.46	4.82	6.82, 7.08, 7.92 8.15 (m, C ₆ H ₅)
7	1.61 (d, 1.2) 1.68 (d, 1.2)	2.41	1.77	5.53	4.88	1.53 (d, 10.4)
8	1.52 (d, 1.8) 1.53 (d, 1.2)	2.19	1.67	5.48	4.81	1.93 (d, 9.8, OCH ₃) 7.07, 8.01 (m, C ₆ H ₅)
9	1.82 1.89	2.57	1.90	5.57	4.90	1.00 (s, CCH ₃)
10	1.92 2.03	2.67	2.13	5.85	4.99 5.11	1.39 (s, CCH ₃)
11	1.35 1.65	1.88	1.72	5.60	4.88	

^{a)} Multiplicity and $J(\text{P.C})$ in Hz given in parentheses. — ^{b)} For fine structures see text.

Table 2. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopic data of **2–11** (δ , C_6D_6 , 25°C)

Compound	CH_3	Ring-C ^{a)}	C-1 C-2	C-3 C-4	L ^{a)}
2	11.05	100.31	25.85	136.51	208.27
	11.09	101.38 101.99	34.02	116.18	
3	11.31	89.79	26.39	136.98	
	11.59	90.54 91.50	33.17	115.61	
4	11.19	95.63	26.03	137.56	56.62
		(d, 3.7)	33.99	115.51	(d, 8.3, OCH_3)
		97.11			
		(d, 4.6) 98.16			
5	11.37 11.47	96.35	26.27	137.35	121.86, 124.92,
		(d, 3.7)	33.98	115.60	129.50, 153.31
		96.93			(C_6H_5)
		97.65 (d, 4.3)			
6	11.58 11.69	93.59	26.20	137.32	129.56, 130.63,
		95.08	33.47	115.39	134.95, 136.95,
		96.28			(C_6H_5)
7	11.46 11.59	92.84	26.55	137.37	20.38
		(d, 2.5)	34.01	115.69	(d, 34.2, PCH_3)
		94.03			
		(d, 2.9) 95.86			
8	11.20 11.30	92.60	25.87	137.30	21.92 (PCH_3),
		(d, 2.8)	33.61	115.46	130.31, 130.41,
		94.45			132.64, 135.80,
		(d, 2.8) 95.40 (d, 2.8)			(C_6H_5)
9	11.40 11.51	95.63	26.50	137.26	29.95 (CCH_3),
		96.50	34.14	115.73	58.44 (CCH_3),
		97.67			122.60 (CN)
10	12.29 12.62	102.47	25.96	137.60	30.67 (CCH_3),
		102.59	33.90	116.59	59.85 (CCH_3),
		103.35			127.11 (CN)
11	8.63 8.91	94.56	23.80	136.08	— ^{b)}
		95.45	35.29	114.78	
		97.07			

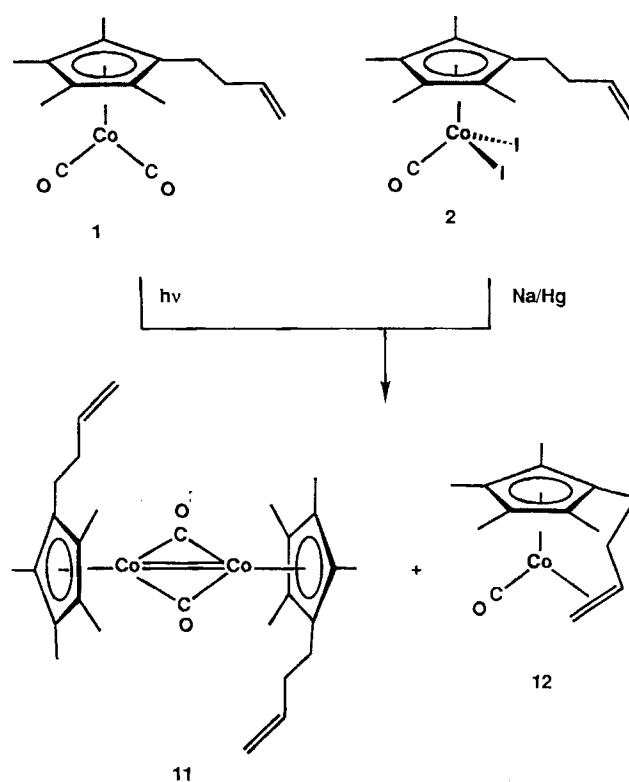
^{a)} Multiplicity and $^2J(\text{P,C})$ in Hz in parentheses. — ^{b)} $\delta(\text{CO})$ not detected.

$\text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$, and PPh_3 can be achieved in refluxing ether, the small basic ligands PMe_3 , PMe_2Ph , and $t\text{BuNC}$ react with **2** at temperatures as low as -78°C . The products of the substitution reactions **4–9** are isolated as fairly air-stable, dark green or black crystals and completely characterized by elemental analysis, NMR, IR spectroscopy as well as mass spectrometry. ^1H - and ^{13}C -NMR spectroscopic data are analogous to those of the parent carbonyl complex **2** and are summarized in Tables 1 and 2. The dramatic difference in the rate of substitution reflects the common observation that both dissociative and associative pathways may be operative depending on the nature of the incoming ligand L^{10} . In the case of $t\text{BuNC}$ the iodo ligand can also be displaced to give ionic $[(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}(t\text{BuNC})_2]\text{I}$ (**10**) as a minor side-product during the formation of neutral **9**. In contrast to the literature report on the failure to prepare $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\text{PPh}_3)_2$ ¹¹, we did not encounter any difficulty in synthesizing **6**.

At the beginning of our studies the dicarbonyl **1** appeared to us as a suitable precursor for the 16-electron fragment

$[(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}(\text{CO})]$ that could be trapped intramolecularly by the $\text{C}=\text{C}$ bond of the side chain. Whereas thermolysis under a variety of conditions gives only moderate yields of the intensely green dimer $[(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}(\mu\text{-CO})]_2$ (**11**) [$\nu(\text{CO}) = 1765\text{ cm}^{-1}$], photolysis of **1** in hexane under rather forcing conditions results in a mixture that contains besides **11** small amounts of a new species characterized by a $\nu(\text{CO})$ absorption at 1959 cm^{-1} . The dimer can be isolated as air-sensitive green crystals and is found to be entirely analogous to $[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\mu\text{-CO})]_2$ ¹², i.e. showing no indication for an interaction of the $\text{C}=\text{C}$ bond with the cobalt center. Since isolation of the new compound from these reaction mixtures proved to be unsuccessful, reductive complexation using **2** as starting material was performed as an alternative (Scheme 2).

Scheme 2



When **2** is treated with a large excess of sodium amalgam in THF at -50°C , a mixture is obtained that consists of the novel chelate complex $(\eta^5\text{-}\eta^2\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}(\text{CO})$ (**12**) and the dimer **11** in a 2:1 ratio. The extremely air-sensitive complex **12** is isolated as highly pentane-soluble brown crystals in moderate yields after careful chromatography on silica gel at lower temperatures. The solution IR spectrum exhibits a single sharp absorption at 1959 cm^{-1} and the solid-state spectrum lacks the $\nu(\text{C}=\text{C})$ mode. In the EI mass spectrum the molecular ion is detected with significant intensity, the main fragmentation pattern being CO elimination from the molecular ion so that the fragment $[(\eta^5\text{-}\eta^2\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}]^+$ presumably has some stability. Both ^1H - and ^{13}C -NMR spectra

Table 3. $^1\text{H-NMR}$ spectroscopic data of **12–15** (δ , C_6D_6 , 25°C)

Compound	$\text{CH}_3^{\text{a)}$	1- H_2	2- H_2	=CH	= CH_2	L ^{a)}	
12	1.67	1.29	2.32	3.58	1.87 ^{b)}		
	1.80		2.92		2.36		
	1.82						
	2.14						
13	1.79	1.56	2.53	3.15	1.62		
	1.88		2.83		1.78		
	1.98				3.27		
	(d, 1.8)						
14	2.37	1.43	2.14	3.04	1.84	(d, 11.6, OCH_3)	
	1.53		2.43		6.82, 7.02,		
	1.80				7.37 (m, C_6H_5)		
	(d, 1.2)						
15	1.81	1.56	2.35	3.27	1.67	7.04, 7.66	
	1.88				1.84		(m, C_6H_5)
	1.02						
	1.40						
	2.06						
	2.57						

^{a)} Multiplicity and $J(\text{P,C})$ in Hz given in parentheses. — ^{b)} ABCDKLM spin system: $J(\text{AB}) = -13.6$, $J(\text{AC}) = 1.1$, $J(\text{AD}) = 9.0$, $J(\text{BC}) = 5.7$, $J(\text{BD}) = 12.6$, $J(\text{CD}) = -14.4$, $J(\text{DK}) = 4.8$, $J(\text{CK}) = 1.1$, $J(\text{KL}) = 12.7$, $J(\text{LM}) = -0.2$, $J(\text{KM}) = 8.7$ Hz.

Table 4. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopic data of **12–14** (δ , C_6D_6 , 25°C)

Compound	CH_3	Ring-C	C-1	C-2	C-3	C-4	L
12	9.76	92.73	18.84	39.75	62.29	39.96	— ^{a)}
	10.86	95.65					
	11.31	97.56					
		100.32					
13^{b)}		101.70					
	10.39	87.73	19.00	40.28	54.35	34.71	49.40
	(d, 1.2)	92.75	(d, 3.0)	(d, 6.7)	(d, 3.7)	(d, 6.7)	(OCH_3)
	10.56	94.84					
	(d, 2.4)	(d, 1.2)					
	11.02	96.17					
(d, 1.2)	(d, 10.4)						
11.99	98.44						
14^{b)}		(d, 5.5)					
	9.97	89.99	18.71	39.79	59.73	38.08	120.82,
	(d, 1.0)	93.68	(d, 3.9)	(d, 7.3)	(d, 2.5)	(d, 5.9)	123.59,
	10.26	95.88					129.41,
	10.85	98.76					152.96
	10.88	(d, 11.2)					(C_6H_5)
(d, 2.0)	99.16						
	(d, 5.4)						

^{a)} $\delta(\text{CO})$ not detected. — ^{b)} Multiplicity and $^nJ(\text{P,C})$ in Hz in parentheses.

(Tables 3, 4) reveal some dramatic change in their appearance consistent with the reduction of C_s to C_1 symmetry upon intramolecular coordination of the 3-butenyl side chain.

Thus, all four ring methyl groups have become inequivalent giving rise to four singlets in the $^1\text{H-NMR}$ spectrum as well as four different methyl resonances and five distinct resonances for the ring carbon atoms in the $^{13}\text{C-NMR}$ spectrum. While the chemical shift difference between the two ring-methyl singlets in the open-chain compounds does not exceed a value of 0.1 ppm (and may be even 0 due to isochrony like in **1**⁶⁾), the difference between the outer most

signals for the methyl groups in **12** is as high as 0.5 ppm. This is ascribed to the fact that each of the four methyl groups resides in a significantly different environment caused by the asymmetry due to the halted rotation of the five-membered ring ligand about the metal-centroid axis. A major change is naturally experienced by the 3-butenyl group of which all the protons are inequivalent and give rise to a seven-spin system of the type ABCDKLM. First, each of the three vinyl protons is significantly shifted upfield as compared to **2**, the terminal *cis* and *trans* protons appearing as doublets centered at $\delta = 2.36$ and 1.87, respectively, and the unique methine proton as a multiplet at $\delta = 3.58$. The four aliphatic protons exhibit a high-order pattern: two of them resonate as well-separated multiplets at $\delta = 2.32$ and 2.92, whereas the two others are detected as a complex multiplet centered at $\delta = 1.29$. We assign the latter signal to 1-H, the protons next to the ring, and the former to those attached to carbon atom 2. The large chemical differences are due to the anisotropic effects caused by the vicinity to the cobalt atom (Figure 1). The connectivity of the 7 protons and their coupling constants have been established by combination of homonuclear decoupling, ^1H , ^1H -, and ^1H , ^{13}C -COSY experiments with spectra simulations. The results are summarized in Table 3. Presently, we are attempting to correlate the conformation with solid state structural data. A detailed conformational analysis on an intramolecularly coordinated $\eta^1:\eta^2$ -pentenyl nickel complex $\text{CpNi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$ has been performed¹³⁾.

The above described reduction of a cobalt(III) complex proves to be a general method for the generation of a coordinatively unsaturated intermediate of the type $(\eta^5\text{-C}_5\text{Me}_5\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{CoL}$ that can be intramolecularly coordinated by the pendent $\text{C}=\text{C}$ bond. Thus, the open-chain cobalt(III) complexes **4–9**, when treated with sodium amalgam in THF at lower temperatures, give in each case the chelate complex. Chelate complexes with PPh_3 and the

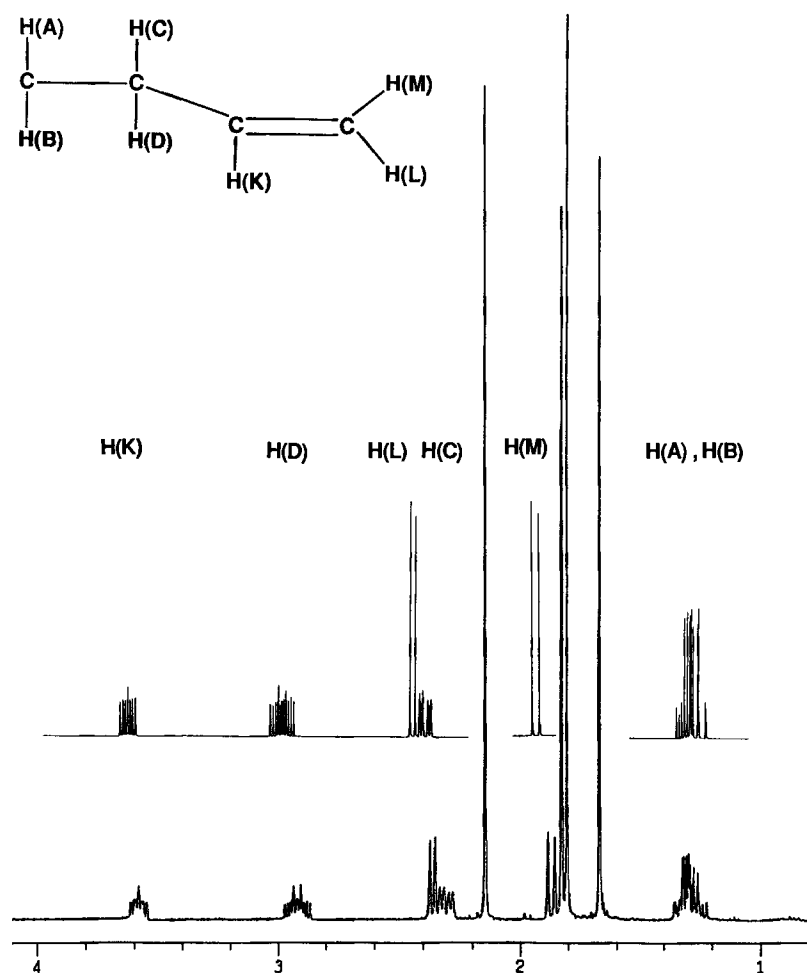


Figure 1. 400-MHz ^1H -NMR spectrum of **12** (δ , C_6D_6 , 25°C) with assignment of the 3-butenyl substituent and the simulated spectrum above

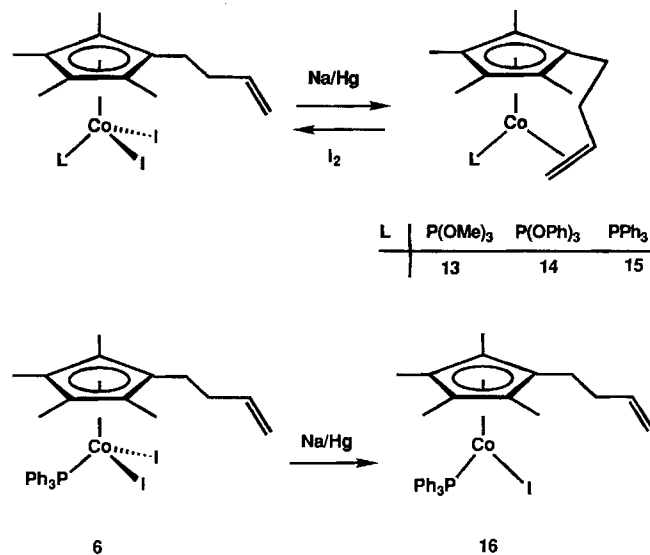
strong bases PMe_3 , PMe_2Ph , and $t\text{BuNC}$ are found to be too thermally labile to be isolated as pure compounds. In addition, their extreme air-sensitivity and low tendency to crystallize cause severe restriction to their handling. Unambiguous evidence for their formation, however, is furnished by ^1H -NMR spectra taken on freshly prepared samples showing diagnostic features for the presence of a chelating ligand. Interestingly, when the reduction of **6** is performed with not large enough an excess of amalgam the paramagnetic cobalt(II) complex **16** is formed in good yield and isolated as brown, thermally robust crystals. Intramolecular $\text{C}=\text{C}$ bond coordination is excluded since the IR spectrum shows the presence of a $\nu(\text{C}=\text{C})$ mode. This type of cobalt(II) half-sandwich complexes has previously been described in some detail for the C_5Me_5 series¹⁴.

Table 5. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopic data (δ , external H_3PO_4 , C_6D_6 , 25°C)

4	135.70	8	11.61
5	121.01	13	176.21
6	30.40	14	147.63
7	6.47	15	69.71

On the other hand, both the phosphite complexes **13** and **14** can be isolated as air-sensitive, pentane-soluble, low-melting red crystals and are fully characterized by elemental

Scheme 3



analysis and by ^1H -, ^{13}C -, ^{31}P -NMR and IR spectroscopic as well as mass spectral methods. Apart from the difference in the nature of L, IR spectroscopic and mass spectral data are analogous to those of the carbonyl derivative **12** as are the very diagnostic overall features of the NMR spectra. Additional proof for the intramolecular C=C bond coordination at the cobalt center is given by the coupling of all the ^1H and ^{13}C nuclei of the vinyl fragment with the phosphorus atom of the phosphite ligand. A particularly noteworthy feature in the ^1H -NMR spectrum of **13** and **14** is that the protons of only one of the four ring methyl groups show a small coupling to the phosphorus atom, while the five ring carbon atoms show a broad range of values for $^2J(\text{P},\text{C})$ in the ^{13}C -NMR spectrum. These observations again reflect a rather rigid conformation in which the phosphite ligand is forced to occupy a specific site within the ligand sphere¹⁵.

Pertinent to the reactivity of the chelate complexes of the above described type is the question about the lability of the intramolecularly coordinated C=C bond. Ethylene ligands in $(\eta^5\text{-C}_5\text{R}_3)\text{Co}(\text{C}_2\text{H}_4)_2$ are considered to be the most labile among conventional two-electron donors, and therefore these complexes serve as good sources for the 14-electron fragment " $(\text{C}_5\text{R}_3)\text{Co}$ "¹⁶. So far we have not found conditions under which clean substitution of merely the olefinic ligand is effected. For instance, the triphenylphosphane complex **15** is directly converted to the dicarbonyl **1** when treated with CO at low temperatures allowing the conclusion that the olefinic double bond is stabilized to a certain degree by virtue of the chelate effect. On the other hand, oxidation of the chelate complexes, e.g. the phosphite complex **14**, with elemental iodine quantitatively yields the open-chain cobalt(III) complex **5**.

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Experimental

All experiments were carried out under dry nitrogen or argon using standard Schlenk technique. Solvents were purified, dried, and distilled under nitrogen. $(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}(\text{CO})_2$ (**1**) was prepared as described in ref.¹⁾ — ^1H NMR: Jeol JNM-GX 270 or 400. — IR: Nicolet 5-DX. — MS: Varian 311 A or Finnigan MAT 90. — Melting points were determined in sealed capillaries.

$[\eta^5\text{-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl}]\text{carbonyl-diiodocobalt}$ (**2**): To a solution of **1** (0.46 g, 1.58 mmol) in 45 ml of ether was added dropwise a solution of iodine (0.35 g, 1.38 mmol) in 25 ml of ether at 0°C and the resulting mixture allowed to warm up to room temp. All volatile compounds were removed in vacuo, and the residue was chromatographed on silica gel (column 10×1 cm). Elution with ether separated a dark violet band which was collected from a greenish grey band containing traces of decarbonylated **3**. Recrystallization from ether/pentane at -30°C gave black crystals; yield 0.61 g (86%). — IR (CH_2Cl_2): $\tilde{\nu} = 2055 \text{ cm}^{-1}$ (CO). — IR (KBr): $\tilde{\nu} = 2041 \text{ cm}^{-1}$ vs (CO), 1640 w (C=C). — EI-MS (70 eV): m/z (%) = 516 (1) [M^+], 488 (1) [$\text{M}^+ - \text{CO}$], 361

(100) [$\text{M}^+ - \text{CO} - \text{I}$], 320 (29) [$\text{M}^+ - \text{CO} - \text{I} - \text{C}_3\text{H}_5$], 234 (18) [$\text{CoC}_{13}\text{H}_{19}^+$], 233 (45) [$\text{CoC}_{13}\text{H}_{18}^+$].

$\text{Bis}[\eta^5\text{-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl}]\text{-di-}\mu\text{-iodo-diiodocobalt}$ (**3**): A suspension of **2** (2.58 g, 5.0 mmol) in 75 ml of octane was heated to reflux for 4 h, during which time the mixture changed its color from dark violet to dark green with concomitant gas evolution. The solvent was removed in vacuo and the residue extracted with 3×25 ml of ether. The extracts were filtered through a pad of kieselguhr and concentrated to a volume of ca. 15 ml. Cooling to -30°C afforded black microcrystals; yield 2.25 g (92%). — IR (KBr): $\tilde{\nu} = 1639 \text{ w cm}^{-1}$ (C=C). — EI-MS (70 eV): m/z (%) = 488 (7) [$\text{M}^+/2$], 361 (100) [$\text{M}^+/2 - \text{I}$], 320 (18) [$\text{M}^+/2 - \text{I} - \text{C}_3\text{H}_5$], 234 (14) [$\text{CoC}_{13}\text{H}_{19}^+$], 233 (39) [$\text{CoC}_{13}\text{H}_{18}^+$].

$[(\eta^5\text{-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl}]\text{diiodo-(trimethyl phosphite)cobalt}$ (**4**): A solution of **2** (1.55 g, 3.0 mmol) in 125 ml of ether was treated with trimethyl phosphite (0.40 g, 3.2 mmol) at room temp. and heated to reflux for 15 h. The dark brown mixture was filtered through a pad of silica gel, concentrated to a volume of 15 ml, and cooled to -30°C to give black crystals; yield 1.43 g (78%). — IR (KBr): $\tilde{\nu} = 1637 \text{ w cm}^{-1}$ (C=C), 1066 s, 1043 s, 1017 s, 791 s, 772 s, 733 s (POMe). — EI-MS (70 eV): m/z (%) = 612 (4) [M^+], 486 (11) [$\text{M}^+ - \text{P(OMe)}_3$], 361 (100) [$\text{M}^+ - \text{P(OMe)}_3 - \text{I}$], 234 (16) [$\text{CoC}_{13}\text{H}_{19}^+$], 233 (42) [$\text{CoC}_{13}\text{H}_{18}^+$].

$[(\eta^5\text{-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl}]\text{diiodo-(triphenyl phosphite)cobalt}$ (**5**): A solution of **2** (1.55 g, 3.0 mmol) in 125 ml of ether was treated with triphenyl phosphite (1.05 g, 3.4 mmol) in a manner analogous to that described for the preparation of **4** to afford 2.30 g (96%) of lustrous black microcrystals. — IR (KBr): $\tilde{\nu} = 1639 \text{ w cm}^{-1}$ (C=C), 1219 s, 1192 vs, 1165 s, 1025 s, 932 vs, 917 vs, 755 vs. — EI-MS (70 eV): m/z (%) = 361 (2) [$\text{M}^+ - \text{P(OPh)}_3 - \text{I}$].

$[(\eta^5\text{-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl}]\text{diiodo-(triphenylphosphane)cobalt}$ (**6**): To a solution of **2** (1.03 g, 2.0 mmol) in 75 ml of ether was added triphenylphosphane (0.53 g, 2.0 mmol) and the mixture heated to reflux for 25 h. The solvent was removed in vacuo and the greenish black residue chromatographed on silica gel (column 10×2 cm) at room temp. With hexane as an eluent unreacted triphenylphosphane was eluted. Further elution with ether/THF (1:2) gave a green band which was collected. The solvent was evaporated and the residue recrystallized from THF/hexane at -30°C to give dark green crystals; yield 1.30 g (87%). — IR (KBr): $\tilde{\nu} = 1640 \text{ m cm}^{-1}$ (C=C). — EI-MS (70 eV): m/z (%) = 361 (1) [$\text{M}^+ - \text{PPh}_3 - \text{I}$], 233 (1) [$\text{CoC}_{13}\text{H}_{18}^+$].

$[(\eta^5\text{-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl}]\text{diiodo-(trimethylphosphane)cobalt}$ (**7**): To a solution of **2** (0.52 g, 1.0 mmol) in 50 ml of ether was added at -78°C trimethylphosphane (0.08 g, 1.0 mmol). The color of the solution instantaneously changed from dark violet to brown. The reaction mixture was allowed to warm up to room temp. over a period of 1 h and then stirred at room temp. for 1 h. All volatiles were removed under vacuum, the residue was washed several times with pentane and dried in vacuo to afford a black powder; yield 0.52 g (91%). — IR (KBr): $\tilde{\nu} = 1639 \text{ m cm}^{-1}$ (C=C), 1276 s, 947 vs, 932 vs (PMe₃). — EI-MS (70 eV): m/z (%) = 564 (1) [M^+], 488 (2) [$\text{M}^+ - \text{PMe}_3$], 361 (100) [$\text{M}^+ - \text{PMe}_3 - \text{I}$], 234 (15) [$\text{CoC}_{13}\text{H}_{19}^+$], 233 (39) [$\text{CoC}_{13}\text{H}_{18}^+$].

$[(\eta^5\text{-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl}]\text{(dimethylphenylphosphane)diiodocobalt}$ (**8**): Applying a procedure analogous to that used for the preparation of **7**, we treated **2** (0.52 g, 1.0 mmol) with dimethylphenylphosphane (0.14 g, 1.0 mmol) and obtained 0.60 g (95%) of a black powder. — IR (KBr): $\tilde{\nu} = 1640 \text{ w cm}^{-1}$ (C=C). — EI-MS (70 eV): m/z (%) = 488 (1) [$\text{M}^+ -$

PMe₂Ph], 361 (100) [M⁺ - PMe₂Ph - I], 234 (16) [CoC₁₃H₁₉], 233 (39), [CoC₁₃H₁₈].

[η^5 -1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl](*tert*-butyl isonitrile)diiodocobalt (**9**): A solution of **2** (0.52 g, 1.0 mmol) was treated at -78°C with *tert*-butyl isonitrile (0.08 g, 1.0 mmol) and allowed to warm up to room temp. over a period of 1 h during which time a color change from dark violet to brown occurred. The reaction mixture was filtered through a pad of silica gel, the dark brown filtrate concentrated to a few ml, and cooled to -78°C after the addition of hexane to give lustrous black needles; yield 0.48 g (84%). - IR (KBr): $\tilde{\nu}$ = 2188 vs cm⁻¹ (CN), 1639 w (C=C). - EI-MS (70 eV): *m/z* (%) = 571 (2) [M⁺], 488 (4) [M⁺ - Me₃CNC], 444 (20) [M⁺ - I], 361 (100) [M⁺ - Me₃CNC - I], 234 (28) [CoC₁₃H₁₉], 233 (70) [CoC₁₃H₁₈].

[η^5 -1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl]bis(*tert*-butyl isonitrile)iodocobalt iodide (**10**): The filter bed from the preparation of **9** as described above was extracted with 3 × 10 ml of THF, the extracts concentrated to 3 ml, followed by addition of ether (3 ml). Cooling to -78°C afforded a brown solid; yield 40 mg (12%). - IR (KBr): $\tilde{\nu}$ = 2200 vs cm⁻¹ (CN), 1639 w (C=C). - FD-MS (THF): *m/z* = 571 (100) [M⁺ - Me₃CNC], 527 (24) [M⁺ - I].

[η^5 : η^2 -1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl]carbonylcobalt (**12**): A solution of **2** (0.78 g, 1.5 mmol) in 50 ml of ether was treated at -50°C with sodium amalgam (1.5%, 38 g, 25 mmol) and allowed to warm up to room temp. over a period of 1 h during which time the color of the mixture changed from dark violet to dark green. After stirring at room temp. for 2 h, NaI was filtered off, the solvent evaporated, and the oily residue chromatographed on silica gel (column 30 × 2 cm) at -20°C. Elution with pentane/toluene (5:1) gave first an orange band followed by a dark green band upon elution with toluene. The first band gave after crystallization at -78°C very air-sensitive red brown crystals; yield 0.21 g (53%). - IR (pentane): $\tilde{\nu}$ = 1959 cm⁻¹ (CO). - EI-MS (70 eV): *m/z* (%) = 262 (29) [M⁺], 234 (100) [M⁺ - CO], 233 (3) [CoC₁₃H₁₈], 192 (82) [CoC₁₀H₁₅].

Bis[η^5 -1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl]di- μ -carbonyldicobalt (Co=Co) (**11**): The green band from the chromatography for **12** as described above afforded after crystallization at -78°C 0.10 g (25%) of air-sensitive green crystals. - IR (pentane): $\tilde{\nu}$ = 1759 cm⁻¹ (CO). - CI-MS (*i*-C₄H₈): *m/z* (%) = 524 (7) [M⁺], 496 (4) [M⁺ - CO], 468 (2) [M⁺ - 2 CO], 290 (22) [M⁺ - CoC₁₃H₁₉], 262 (100) [M⁺ - CoC₁₃H₁₉ - CO], 234 (18) [CoC₁₃H₁₅].

[η^5 : η^2 -1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl](*trime*-thyl phosphite)cobalt (**13**): To a solution of **4** (1.22 g, 2.0 mmol) in 60 ml of ether was added at -50°C sodium amalgam (1.0%, 69 g, 30 mmol) and the reaction mixture allowed to warm up to room temp. over a period of 45 min. After stirring at room temp. for 2 h the solution was decanted off from excess amalgam, and the volatiles were removed in vacuo. The residue was extracted with 3 × 25 ml of pentane, and the extracts were filtered through a pad of kieselguhr. The solvent was distilled off and the oily brown residue chromatographed on silica gel (column 10 × 2 cm) at room temp. Elution with pentane/ether (5:1) gave an orange red band which was collected. Recrystallization from pentane at -78°C afforded air-sensitive red crystals; yield 0.52 g (73%). - EI-MS (70 eV): *m/z* (%) = 358 (28) [M⁺], 327 (3) [M⁺ - OMe], 234 (100) [CoC₁₃H₁₅], 233 (17) [CoC₁₃H₁₈].

[η^5 : η^2 -1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl](*tri*-phenyl phosphite)cobalt (**14**): The reaction of **5** (1.60 g, 2.0 mmol) with sodium amalgam (1.0%, 69 g, 30 mmol) was performed anal-

ogously to the synthesis of **13** and gave 0.89 g (82%) of an orange yellow powder. - EI-MS: *m/z* (%) = 544 (26) [M⁺], 234 (100) [CoC₁₃H₁₉], 233 (7) [CoC₁₃H₁₈].

Table 6. Analytical data

Com- pound	Formula (Mol. mass)		Analysis			M.p. [°C]
			C	H	I	
2	C ₁₄ H ₁₉ CoI ₂ O (516.1)	Calcd.	32.59	3.71	49.18	91
		Found	32.33	3.62	48.50	
3	C ₂₆ H ₃₈ Co ₂ I ₄ (976.1)	Calcd.	31.99	3.92	52.01	155
		Found	31.96	3.97	51.81	
4	C ₁₆ H ₂₈ CoI ₂ O ₃ P (612.1)	Calcd.	31.40	4.61	41.46	75
		Found	31.54	4.76	41.12	
5	C ₃₁ H ₃₄ CoI ₂ O ₃ P (798.3)	Calcd.	46.64	4.29	31.80	125
		Found	46.66	4.33	31.67	
6	C ₃₁ H ₃₄ CoI ₂ P (730.3)	Calcd.	49.62	4.57	33.83	147
		Found	49.51	4.67	33.16	
7	C ₁₆ H ₂₈ CoI ₂ P (564.1)	Calcd.	34.07	5.00	44.99	98
		Found	33.74	4.99	44.63	
8	C ₂₁ H ₃₀ CoI ₂ P (626.2)	Calcd.	40.28	4.83	40.53	110
		Found	40.39	4.79	39.34	
9	C ₁₈ H ₂₈ CoI ₂ N (571.2)	Calcd.	37.85	4.94	44.44 ^{a)}	58
		Found	38.15	5.14	43.75	
10	C ₂₃ H ₃₇ CoI ₂ N ₂ (654.3)	Calcd.	42.22	5.70 ^{b)}	112	
		Found	41.31	5.55		
11	C ₂₈ H ₃₈ Co ₂ O ₂ (524.5)	Calcd.	64.12	7.30	69	
		Found	62.86	7.36		
12	C ₁₄ H ₁₉ CoO (262.2)	Calcd.	64.12	7.30 ^{c)}	57	
		Found	63.92	7.18		
13	C ₁₆ H ₂₈ CoO ₃ P (358.3)	Calcd.	53.63	7.88 ^{d)}	37	
		Found	53.86	7.91		
14	C ₃₁ H ₃₄ CoO ₃ P (544.5)	Calcd.	68.38	6.29 ^{e)}	20	
		Found	68.64	6.61		
16	C ₃₁ H ₃₄ CoIP (623.4)	Calcd.	59.72	5.50	20.36	113
		Found	59.30	5.80	20.12	

^{a)} N: calcd. 2.45, found 2.39. - ^{b)} N: calcd. 4.28, found 4.01. - ^{c)} Co: calcd. 22.48, found 21.70. - ^{d)} Co: calcd. 16.45, found 16.80. - ^{e)} Co: calcd. 10.82, found 10.20.

[η^5 -1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl]iodo(*tri*-phenylphosphane)cobalt (**16**): To a solution of **6** (1.2 g, 1.6 mmol) in 50 ml of toluene was added sodium amalgam (1.5%, 7.5 g, 5 mmol) and the reaction mixture allowed to warm up to room temp. The color gradually changed from dark green to brown. After stirring at room temp. for 4 h the solvent was removed in vacuo, the residue taken up in 30 ml of ether, and the solution filtered through a pad of silica gel. The filtrate was concentrated to ca. 5 ml and after addition of 5 ml of pentane cooled to -78°C to afford air-sensitive dark brown crystals; yield 0.62 g (62%). - IR (KBr): $\tilde{\nu}$ = 1639 w cm⁻¹ (C=C). - EI-MS: *m/z* (%) = 361 (30) [M⁺ - PPh₃], 320 (8) [M⁺ - PPh₃ - C₃H₅], 234 (6) [CoC₁₃H₁₉], 233 (18) [CoC₁₃H₁₈].

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[85/90]