

Synthesis of a Cobalt Half-Sandwich Complex with Intramolecular C–C Double-Bond Coordination

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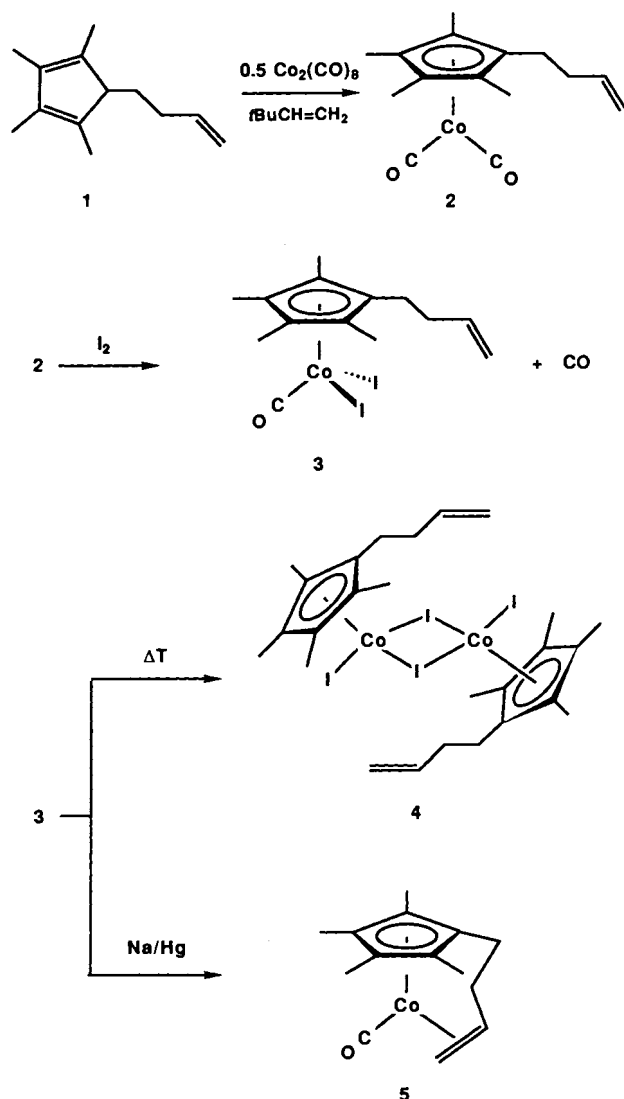
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The synthesis of 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl cobalt complexes without and with intramolecular C–C double-bond coordination is reported.

Olefin coordination at organocobalt fragments has long been of fundamental importance in the context of cobalt-catalyzed olefin



transformations such as hydrogenation, isomerization, and hydroformylation²⁾. We have recently described a new peralkylated cyclopentadienyl ligand with a pendant 3-butenyl side-chain, viz. 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadiene¹⁾, $\text{C}_5\text{Me}_4(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{H}$ (1), that was designed to enable the study of C–C double-bond coordination at a transition-metal center in an *intramolecular* manner. Herein, we wish to report the synthesis of some new cobalt complexes bearing this ligand, including the first example of a complex with the 3-butenyl side-chain intramolecularly coordinated to the cobalt center by the olefinic double bond.

The low-melting, highly air-sensitive dicarbonyl derivative ($\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$) $\text{Co}(\text{CO})_2$ (2), readily available from the reaction of $\text{Co}_2(\text{CO})_8$ with 1 in neat 3,3-dimethyl-1-butene according to a procedure described by Buzinkai and Schrock³⁾, can be cleanly oxidized with elemental iodine in ether to give the iodo(carbonyl) complex ($\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$) $\text{Co}(\text{CO})\text{I}_2$ (3) in high yield. 3 is isolated as dark violet crystals and fully characterized by elemental analysis and NMR- and IR-spectroscopic as well as EI mass-spectrometric methods. In the solution IR spectrum the $\tilde{\nu}(\text{CO})$ band appears at 2055 cm^{-1} and is comparable to the value reported for related ($\eta^5\text{-C}_5\text{R}_4$) $\text{Co}(\text{CO})\text{I}_2$ complexes ($\text{R} = \text{H}$: $\tilde{\nu} = 2080^4)$; $\text{R} = \text{Me}$: $\tilde{\nu} = 2060 \text{ cm}^{-1}$ ⁵⁾). Thermogravimetric analysis of crystalline 3 shows gradual loss of carbon monoxide above 85°C . When 3 is refluxed in heptane for 2 h, carbon monoxide is smoothly evolved, and the dimeric complex [$(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{CoI}_2$]₂ (4) is formed as black, pentane-insoluble crystals in virtually quantitative yield. NMR- and IR-spectroscopic data clearly show that the 3-butenyl substituent of the ring ligand in 4 is not affected during the decarbonylation reaction. Evidently, bridging iodide is a better ligand for the trivalent cobalt center than is a C–C double bond of the side chain. Thermally induced nucleophilic substitutions of the CO ligand in 3 with various two-electron donors L such as triphenylphosphine, trimethyl phosphite, or *tert*-butylisocyanide cleanly give three-legged piano-stool molecules of general formula ($\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$) $\text{Co}(\text{L})\text{I}_2$ and also leave the olefin moiety completely intact⁶⁾.

Reduction of the iodo(carbonyl) derivative 3 with sodium amalgam generates the formally 16-electron species " $(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}(\text{CO})$ " that is trapped intramolecularly by the C–C double bond of the 3-butenyl side-chain to yield the chelate complex ($\eta^5\text{-}\eta^2\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$) $\text{Co}(\text{CO})$ (5). The highly reactive intermediate is apparently long-lived enough to give rise to some side reactions leading to dicarbonyl 2 and intense green dinuclear dicarbonyl [$(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}$]₂($\mu\text{-CO}$)₂ (6), as judged by solution IR spectroscopy of the reaction mixture⁷⁾. Chromatographic separation of this mixture proved to be not satisfactory, repeated crystallizations from pentane at -78°C , however, yielded

analytically pure **5** as brown, thermally unstable extremely air-sensitive crystals in moderate yield. **5** is characterized by NMR and IR spectroscopy as well as EI mass spectrometry. While the IR spectrum exhibits a strong $\tilde{\nu}(\text{CO})$ band at 1959 cm^{-1} and lacks any absorptions assignable to $\tilde{\nu}(\text{C}=\text{C})$ at ca. 1640 cm^{-1} , ^1H - and ^{13}C -NMR spectra clearly reveal the intramolecular coordination of the olefinic double bond of the 3-butenyl substituent. The Figure compares the ^1H -NMR spectrum of **3** with that of **5**. Noteworthy features include the inequivalence of all four methyl groups of the five-membered ring due to the loss of C_s symmetry and a significant up-field shift of the three resonances for the olefinic protons of the 3-butenyl group, caused by complexation of the C—C double bond at the monovalent cobalt center. In addition, the larger chemical shift difference for the geminal *cis* and *trans* protons indicates that each of them is residing in significantly different chemical environments.

We expect a novel reactivity pattern for chelate complexes such as **5** and are presently studying their reactions with small molecules. A few similar transition-metal complexes with intramolecularly coordinated C—C double bond have been described in the literature^{8–10}.

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Experimental

[η⁵-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl]dicarbonylcobalt (2): A solution of octacarbonyldicobalt (0.56 g, 1.65 mmol) and **1**¹⁾ (0.88 g, 5.00 mmol) in 15 ml of 3,3-dimethyl-1-butene was refluxed for 1 h. All volatiles were removed in vacuo, the oily residue was taken up in 25 ml of pentane and filtered through a pad of silica gel. The solvent was distilled off and the remaining oil crystallized from pentane at -78°C to give brown red crystals; yield 0.66 g (70%), mp 0°C . — IR (pentane): $\tilde{\nu} = 2009\text{ cm}^{-1}$ vs, $1950\text{ vs}(\text{CO})$. — ^1H NMR (C_6D_6 , 25°C): $\delta = 1.58$ (s, 12H, CH_3), 2.00 (m, 2H, 2- H_2), 2.24 (m, 2H, 1- H_2), 4.93 [m, 1H, = $\text{CH}_2(\text{cis})$], 4.96 [m, 1H, = $\text{CH}_2(\text{trans})$], 5.68 (m, 1H, =CH). — $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C): $\delta = 10.33, 10.36$ (CH_3), 25.04 (C-1), 36.03 (C-2), 96.36, 97.06, 100.90 (ring-C), 115.25 (C-4), 137.83 (C-3), 208.52 (CO). — EI MS (70 eV): m/z (%) = 262 (27) [$\text{M}^+ - \text{CO}$], 234 (100) [$\text{M}^+ - 2\text{CO}$], 192 (79) [$\text{CoC}_{10}\text{H}_{15}$], 133 (67) [$\text{C}_{10}\text{H}_{15}$].

$\text{C}_{15}\text{H}_{19}\text{CoO}_2$ (290.3) Calcd. C 62.07 H 6.60
Found C 61.99 H 6.70

[η⁵-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl]carbonyldiiodocobalt (3): To a solution of **2** (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 volatiles were removed in vacuo and the residue chromatographed on silica gel (column $10 \times 1\text{ cm}$). Elution with ether separated a dark violet band which was collected from a greenish grey band containing traces of decarbonylated **4**. Recrystallization from pentane at -30°C gave black crystals; yield 0.61 g (86%), mp 91°C . — IR (CH_2Cl_2): $\tilde{\nu} = 2055\text{ cm}^{-1}$ (CO); (KBr): $\tilde{\nu} = 2041\text{ cm}^{-1}$ vs (CO), $1640\text{ w}(\text{C}=\text{C})$. — ^1H NMR (C_6D_6 , 25°C): $\delta = 1.64$ (m, 2H, 2- H_2), 1.68 (s, 6H, CH_3), 1.71 (s, 6H, CH_3), 2.31 (m, 2H, 1- H_2), 4.80 (m, 2H, = CH_2), 5.39 (m, 1H, =CH). — $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C): $\delta = 11.05, 11.09$ (CH_3), 25.85 (C-1), 34.02 (C-2), 100.31, 101.38, 101.99 (ring-C), 116.18 (C-4), 136.51 (C-3), 208.27 (CO). — EI MS (70 eV): m/z (%) = 516 (1) [M^+], 448 (1) [$\text{M}^+ - \text{CO}$], 361 (100) [$\text{M}^+ - \text{CO} - \text{I}$], 320 (29) [$\text{M}^+ - \text{CO} - \text{I} - \text{C}_3\text{H}_5$].

$\text{C}_{14}\text{H}_{19}\text{CoI}_2\text{O}$ (516.1) Calcd. C 32.59 H 3.71 I 49.18
Found C 32.33 H 3.62 I 48.50

Bis[η⁵-1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl]tetraiododicobalt (4): A suspension of **3** (0.38 g, 0.75 mmol) in 100 ml of heptane was heated to reflux for 2 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 $3 \times 10\text{ ml}$ ether. The extracts were filtered through a pad of silica gel and concentrated to ca. 5 ml. Cooling to -30°C afforded 0.28 g (77%) of black microcrystals; mp 155°C . — IR (KBr): $\tilde{\nu} = 1639\text{ m cm}^{-1}$ (C=C). — ^1H NMR (C_6D_6 , 25°C): $\delta = 1.54$ (s, 6H, CH_3), 1.64 (m, 2H, 2- H_2), 1.65 (s, 6H, CH_3), 2.57 (m, 2H, 1- H_2), 4.77 (m, 2H, = CH_2), 5.37 (m, 1H, =CH). — $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C): $\delta = 11.31, 11.59$ (CH_3), 26.39 (C-1), 33.17 (C-

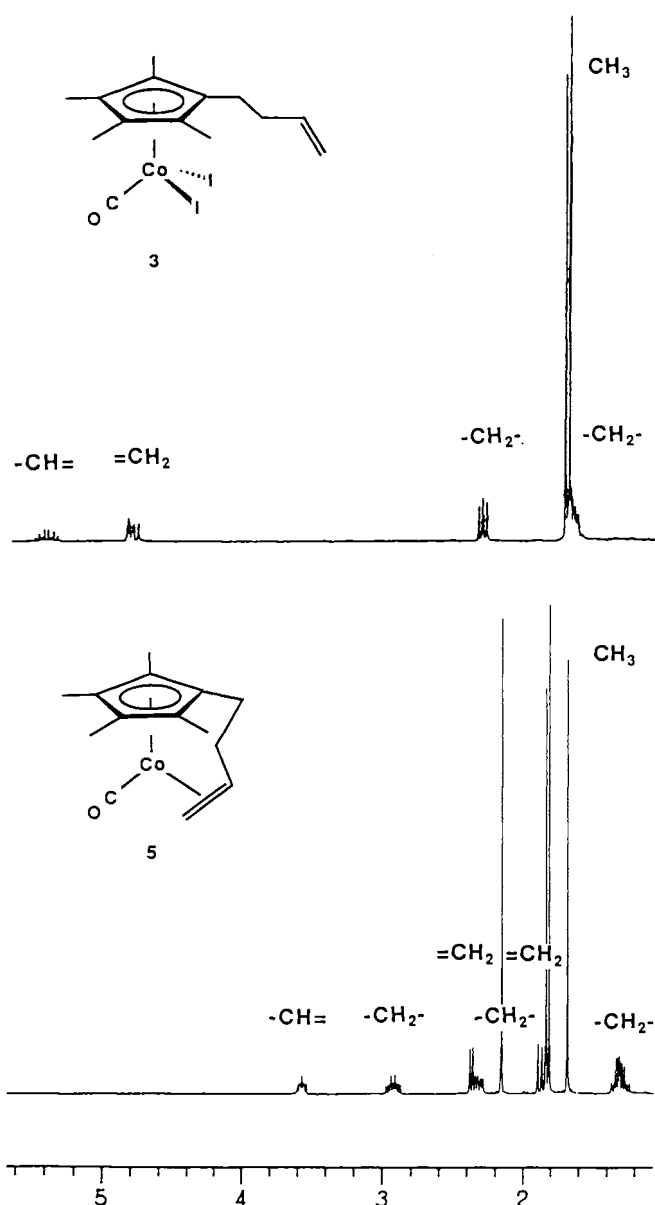


Figure. 400-MHz ^1H -NMR spectrum of $(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}(\text{CO})\text{I}_2$ (**3**) and of $(\eta^5\text{-}\eta^2\text{-C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Co}(\text{CO})$ (**5**) in C_6D_6 at 25°C [$\delta(\text{ppm})$]

Functionalized Cyclopentadienyl Ligands, II

2), 89.79, 90.54, 91.50 (ring-C), 115.61 (C-4), 136.98 (C-3). — EI MS (70 eV): m/z (%) = 488 (7) [$M^+/2$], 361 (100) [$M^+/2 - I$], 320 (18) [$M^+/2 - I - C_3H_5$].

$C_{13}H_{19}CoI_2$ (488.0) Calcd. C 31.99 H 3.92 I 52.01
Found C 31.96 H 3.97 I 51.81

[η^5 : η^2 -1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl]carbonylcobalt (**5**): To a solution of **3** (0.78 g, 1.5 mmol) in 50 ml of ether was added sodium amalgam (1.5%; 38.0 g, 25.0 mmol) at -50°C . The mixture was allowed to warm up to room temp. and stirred for 2 h. After filtration through a pad of kieselguhr and removal of the solvent in vacuo, the residue was taken up in pentane and cooled to -78°C . Repeated recrystallizations of the crude product from pentane at -78°C afforded pale brown crystals; yield 0.18 g (46%), mp 50°C (dec.). — IR (pentane): $\tilde{\nu} = 1959\text{ cm}^{-1}$ (CO). — $^1\text{H NMR}$ (C_6D_6 , 25°C): $\delta = 1.29$ (m, 2H, 1-H₂), 1.67, 1.80, 1.82 (s, 3H, CH₃), 1.87 [d, $^3J(\text{H,H}) = 12\text{ Hz}$, 1H, =CH₂], 2.14 (s, 3H, CH₃), 2.32 (m, 1H, 2-H), 2.36 [d, $^3J(\text{H,H}) = 8\text{ Hz}$, 1H, =CH₂], 2.92 (m, 1H, 2-H), 3.58 (m, 1H, =CH). — $^{13}\text{C NMR}$ ($C_6D_5CD_3$, 25°C): $\delta = 9.76$, 10.86, 11.31 [q, $^1J(\text{C,H}) = 127\text{ Hz}$, CH₃], 18.84 [q, $^1J(\text{C,H}) = 127\text{ Hz}$, C-1], 39.75 [t, $^1J(\text{C,H}) = 126\text{ Hz}$, C-2], 39.96 [t, $^1J(\text{C,H}) = 158\text{ Hz}$, =CH₂], 62.29 [d, $^1J(\text{C,H}) = 154\text{ Hz}$, =CH], 92.73, 95.65, 97.56, 100.32, 101.70 (s, ring-C). — EI MS (70 eV): m/z (%) = 262

(29) [M^+], 234 (100) [$M^+ - \text{CO}$], 192 (82) [$\text{CoC}_{10}\text{H}_{13}$], 133 (67) [$\text{C}_{10}\text{H}_{13}$].

$C_{14}H_{19}CoO$ (262.2) Calcd. C 64.12 H 7.30 Co 22.48
Found C 63.92 H 7.18 Co 21.70

CAS Registry Numbers

1: 119859-30-2 / 2: 119862-39-4 / 3: 121571-80-0 / 4: 121596-26-7 /
5: 121571-81-1 / $\text{Co}_2(\text{CO})_8$: 10210-68-1 / $t\text{BuCH}=\text{CH}_2$: 558-37-2

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