Functionalized Cyclopentadienyl Ligands, VII[1]

Cobalt-Mediated Cyclohexadiene Formation Involving an Intramolecularly Coordinated C = C Bond☆

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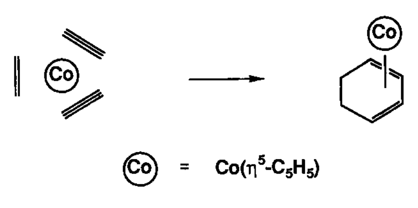
Reaction of $Co(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)(\eta^2\text{-}C_2H_4)$ (**1**) with bis(trimethylsilyl)acetylene gives a substitution product $Co(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)(\eta^2\text{-}Me_3SiC\equiv CSiMe_3)$ (**2**) which simultaneously contains both an η^2-alkene and an η^2-alkyne ligand. With **1** substituted alkynes $R^1C\equiv CR^2$ (R^1 = R^2 = CO_2Me, Ph; R^1 = CO_2Me, R^2 = Ph; R^1 = $SiMe_3$, R^2 = H) react to give cyclohexadiene complexes of the type $Co(\eta^5:\eta^4\text{-}C_5Me_4CH_2CH_2C_6H_3R_4)$ (**4**, **5**, **8**, **9**). This [2+2+2] cycloaddition involves two molecules of an alkyne and the intramolecularly coordinated C = C bond leading to an η^4-bonded cyclohexadiene ligand which is linked to the five-membered ring by a CH_2CH_2 bridge. In the case of diphenylacetylene the cyclobutadiene complex $Co(\eta^5\text{-}C_5Me_4CH_2CH_2CH=CH_2)(\eta^4\text{-}C_4Ph_4)$ (**6**) is formed as a byproduct.

The cobalt-mediated [2+2+2] cycloaddition of two alkynes with an olefin represents a versatile synthetic method by which cyclohexadiene derivatives can be assembled in one step (Scheme 1)[2]. Apart from the intramolecular cyclization of enediynes to give polycyclic skeletons relevant to natural products[3], a variety of substrates containing a C–C double bond including ethene[4a], substituted olefins[4a,b], and several unsaturated heterocycles[4c] can be coupled with alkynes. As a precursor for the transition-metal template cobalt complexes of the type $CpCoL_2$ (Cp = η^5-C_5H_5; L = CO, C_2H_4) are commonly employed in these reactions, the active center presumably being the coordinatively unsaturated 14-electron fragment "CoCp"[2].

Scheme 1



We have been studying the properties of a remarkably conformationally rigid quasi-14-electron fragment $Co(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)$[1b,5] for which we have found a good source in the form of the easily accessible ethene complex $Co(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)(\eta^2\text{-}H_2C=CH_2)$ (**1**)[6]. By using this fragment it was hoped that mechanistic insights into various steps of the C–C bond formation during the cobalt-centered [2+2+2] cycloaddition involving unsaturated organic substrates could be obtained. We describe here the reaction of several substituted alkynes at $Co(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)$. A preliminary communication has recently been published[7].

Results and Discussion

When the ethene complex **1** is treated with bis(trimethylsilyl)acetylene the alkyne complex $Co(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)(\eta^2\text{-}Me_3SiC\equiv CSiMe_3)$ (**2**) is isolated in virtually quantitative yield under various conditions, irrespective of the stoichiometry applied. Compound **2** forms highly pentane-soluble red crystals which melt at 27°C. The results of an X-ray structure determination as published previously[7] show the presence of an (η^2-alkene)(η^2-alkyne)cobalt complex with a trigonal planar geometry around the cobalt(I) center if the five-membered ring ligand is taken as the third monodentate ligand. This structural feature in the solid state is fully consistent with spectroscopic data. Thus, the IR spectrum (KBr) exhibits a relatively intense band for the $\nu(C\equiv C)$ mode at $\tilde{\nu}$ = 1806 cm^{-1} which corresponds to a decrease of ca. 400 cm^{-1} relative to the absorption of free bis(trimethylsilyl)acetylene. This value is typical for alkyne ligands η^2-bonded at an electron-rich transition-metal fragment with pronounced π-back-bonding capability[8]. Both ^1H- and ^{13}C-NMR spectra clearly show the presence of the chiral fragment $Co(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)$[5] in which all diastereotopic groups remain inequivalent up to +80°C. In particular, it is noteworthy that the four methyl resonances appear in an unusually wide region of δ = 0.33–2.03, reflecting a rigid conformation with constrained ligand dynamics even in solution. The two acetylenic carbon atoms resonate at δ = 109.80 and 115.58 and demonstrate that the bis(trimethylsilyl)acetylene ligand in **2** can be classified as a two-electron donor[9].

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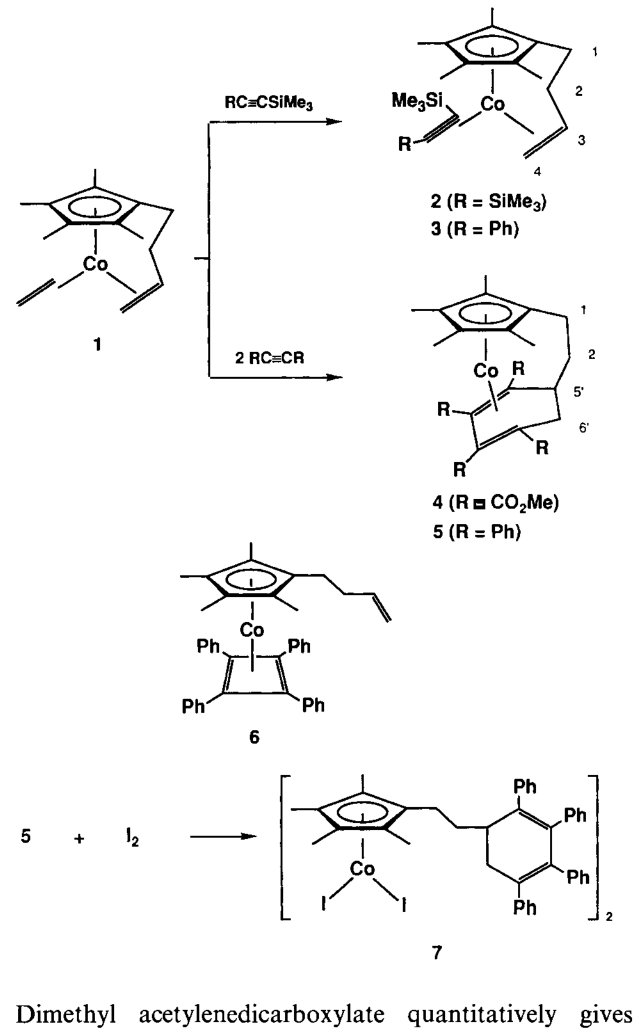
Phenyl(trimethylsilyl)acetylene reacts analogously to give the alkyne complex $Co(\eta^5:\eta^2\text{-}C_5Me_4CH_2CH_2CH=CH_2)(\eta^2\text{-}PhC\equiv CSiMe_3)$ (**3**) as a red oil that, quite surprisingly, consists of only one diastereoisomer. The alkyne ligand gives rise to two ^{13}C-NMR resonances at $\delta = 106.02$ and 118.41 and a medium-intense absorption in the IR spectrum (KBr) at $\tilde{\nu} = 1792\ cm^{-1}$. During chromatographic workup of the reaction mixture traces of a green compound are isolated which according to mass-spectrometric analysis, however, contains two molecules of the alkyne. As will be described below, we assume that this byproduct has the structure of an η^4-cyclohexadiene complex[10].

Scheme 2



Dimethyl acetylenedicarboxylate quantitatively gives brown crystals of the η^4-cyclohexadiene complex **4** which contains a novel bridged ligand system consisting of both a cyclopentadienyl and a cyclohexadiene ring. Spectroscopic data show unambiguously that the formation of the cyclohexadiene ring must have involved the C−C double bond of the 3-butenyl side-chain. In particular, the signals of the former carbon atoms of the vinyl group C-3 and C-4 appear at $\delta = 35.32$ as a doublet and at $\delta = 42.55$ as a triplet, respectively, each showing a coupling constant of $^1J_{C,H} = 126$ Hz. These spectral properties are characteristic for the occurrence of the cycloaddition (Table 1), since they clearly prove that the C−C double bond of the intramolecularly coordinated 3-butenyl chain has been transformed into the aliphatic segment of the cyclohexadiene ring. The signals of the four carbon atoms of the diene part are found between $\delta = 53.94$ and 98.44 and reflect the unsymmetric overall structure of the molecule. No temperature dependence of the NMR spectra is observed suggesting a stable coordination of the cyclohexadiene moiety at the cobalt center which leads to a stereochemically rigid molecule.

Table 1. Selected ^{13}C-NMR data of **2**, **4**, **5**, and **8** (δ, C_6D_6, 25°C); multiplicity and $^1J_{C,H}$[Hz] in parentheses

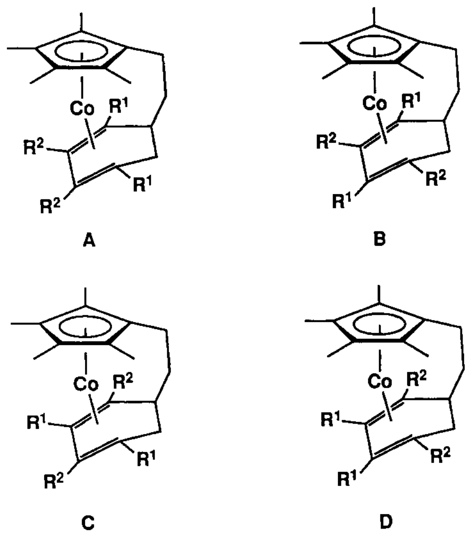
Compound	C-1	C-2	C-3/5'	C-4/6'
2	19.63 (t, 125)	38.84 (t, 126)	62.13 (d, 153)	44.40 (t, 153)
4	18.97 (t, 128)	27.27 (t, 133)	35.32 (d, 126)	42.55 (t, 126)
5	18.31 (t, 127)	28.33 (t, 129)	31.92 (d, 125)	36.71 (t, 127)
8	18.56 (t, 126)	24.63 (t, 129)	34.35 (d, 123)	40.70 (t, 125)

The main product of the reaction of **1** with diphenylacetylene is the cyclohexadiene complex **5** of which the constitution is supported by spectroscopic data and by a single-crystal X-ray structure analysis. Because of the presence of a nonstoichiometric amount of pentane in the lattice and partial disordering of the molecule (statistical distribution of enantiomers) only the overall structure could be found with certainty[6]. It confirms, however, the formation of a cyclohexadiene ring from two diphenylacetylene and the C−C double bond of the 3-butenyl chain. In addition, the oxidation of **5** with iodine at −78°C gives the diiodocobalt(III) derivative **7** with decomplexed cyclohexadiene as black crystals; **7** has been characterized by elemental analysis and spectroscopic methods.

A minor product in the reaction of **1** with diphenylacetylene is shown to be the η^4-cyclobutadiene complex **6**. It is easily identified by the presence of a mirror plane in the molecule suggesting that the 3-butenyl side chain is not coordinated. Moreover, the IR spectrum shows the diagnostic band at $\tilde{\nu} = 1639\ cm^{-1}$ due to $\nu(C=C)$ of the dangling 3-butenyl side-chain. The resonance for the cyclobutadiene carbon atoms are found at $\delta = 72.73$ in the ^{13}C-NMR spectrum. Similar values have been reported for other cyclobutadienecobalt complexes such as $CpCo(\eta^4\text{-}C_4Ph_4)$[12].

With unsymmetrically substituted acetylenes bearing two different substituents R^1 and R^2 it is to be expected that the [2+2+2] cycloaddition reaction would produce four regioisomers each as enantiomeric pair (Scheme 3). Methyl phenylpropiolate, however, yields with **1** a brown powder which according to NMR spectra consists of only two isomeric compounds **8** in equal amounts. When compared to the spectra of **4** and **5** the number of all signals due to the ligand system is doubled. Because of the high complexity of the spectra an unambiguous assignment of the resonances is impossible even with the aid of 2D-NMR techniques. However, in analogy with the formation of regioisomeric cobaltacyclopentadiene complexes by using unsymmetrically substituted alkynes[13], it is assumed that differences in the steric demand of the alkyne substituents R^1 and R^2 govern the product geometry of the cyclohexadiene. In this case differently sized groups would lead to discrimination and thus to selective formation of a certain isomer. In fact, reaction of **1** with trimethylsilylacetylene (R^1 = $SiMe_3$, R^2 = H) leads to the formation of a *single* isomer of **9** according to ^1H- and ^{13}C-NMR spectra. Thus, the ^1H-NMR spectrum of the yellow oil isolated shows only four sharp singlets of equal intensity for the four inequivalent methyl groups of the five-membered ring, while two high-field singlets due to the trimethylsilyl groups are found at $\delta = 0.17$ and 0.31. In the ^{13}C-NMR spectrum those diene carbon atoms which carry a hydrogen atom are observed at $\delta = 60.12$ with $^1J_{C,H} = 157$ and at $\delta = 88.88$ with $^1J_{C,H} = 161$ Hz. The great difference in the chemical shifts suggests that an isomer of the type **B** or **C** has most likely been formed.

Scheme 3



8 (R^1 = CO_2Me, R^2 = Ph)
9 (R^1 = $SiMe_3$, R^2 = H)

In the above reactions of **1** with alkynes it is important to note that the $Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)$ fragment does not give rise to a catalytic trimerization of various alkynes to afford benzene derivatives, whereas with CoCp*, lacking an intramolecularly coordinated C=C bond, this catalytic reaction readily takes place[14]. We have confirmed that the reaction of the alkynes with other sources for the fragment $Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)$ such as $Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)(L)$ (L = PR_3[5]) or $Co(\eta^5{:}\eta^2\text{-}C_5Me_4CH_2CH_2CH{=}CH_2)X/NaHg_x$ (X = halide[5,6]) essentially lead to the same results. Interestingly, the alkyne complex **2** gives with dimethyl acetylenedicarboxylate compound **4** rather than a mixed cyclohexadiene complex. These findings corroborate the postulate that the [2+2+2] cycloaddition of alkynes or the cotrimerization of alkynes with another unsaturated substrate require an easily accessible 14- rather than a 16-electron valence shell[15].

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Experimental

All experiments were carried out under dry nitrogen or argon by using standard Schlenk techniques. Solvents were purified, dried, and distilled under nitrogen. – Melting points were determined in sealed capillaries. – ^1H and ^{13}C NMR: Jeol JNM-GX 400. – IR: Nicolet FT-5-DX. – MS: Varian 311 A, Finnigan MAT 90. – Elemental analyses: Microanalytical Laboratory of the Institute.

[η^2-Bis(trimethylsilyl)acetylene][η^5:η^2-1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl]cobalt (**2**): To a solution of **1** (0.26 g, 1.0 mmol) in 50 ml of hexane was added bis(trimethylsilyl)acetylene (0.17 g, 1.0 mmol) and the mixture heated to reflux for 20 h. The solvent was removed in vacuo and the oily residue extracted with 3 × 20 ml of pentane. After filtration through a pad of silica gel, the filtrate was concentrated and cooled to −78 °C over a period of 3 d to afford dark red cubes; yield 0.35 g (87%), m.p. 27 °C. – ^1H NMR (C_6D_6, 25 °C): $\delta = 0.24$ [d, $^3J_{H,H} = 7.9$ Hz, 1H, 4-H (*Z*)]; 0.33, 0.40 [s, 9H, $Si(CH_3)_3$]; 0.85 (s, 3H, CH_3); 1.30, 1.43 (m, 1H, 1-H_2); 1.61 (s, 3H, CH_3); 1.85 [d, $^3J_{H,H} = 11.6$ Hz, 1H, 4-H (*E*)]; 2.08 (s, 3H, CH_3); 2.14 (m, 2H, 2-H/3-H); 2.72 (s, 3H, CH_3); 3.33 (m, 1H, 2-H). – ^{13}C NMR (C_6D_6, 25 °C): $\delta = 2.07$, 2.37 [q, $^1J_{C,H} = 119$ Hz, $Si(CH_3)_3$]; 8.80, 10.42, 12.48 (q, $^1J_{C,H} = 126$ Hz, CH_3); 19.63 (t, $^1J_{C,H} = 125$ Hz, C-1); 38.84 (t, $^1J_{C,H} = 126$ Hz, C-2); 44.40 (t, $^1J_{C,H} = 153$ Hz, C-4); 62.13 (d, $^1J_{C,H} = 153$ Hz, C-3); 93.21, 94.01, 94.07, 95.17, 98.26 (s, ring C), 109.80, 111.58 (s, C≡C). – IR (KBr): $\tilde{\nu} = 3083\ cm^{-1}$ w, 2981 m, 2951 m, 2915 m, 2860 m, 1806 s, 1473 m, 1456 m, 1449 m, 1378 m, 1245 s, 1222 w, 1023 w, 994 w, 908 m, 854 s, 842 s, 757 m, 692 w. – EI MS: *m/z* (%) = 404 (10) [M^+], 234 (100) [$C_{13}H_{19}Co^+$], 233 (25) [$C_{13}H_{18}Co^+$], 192 (52) [$C_{10}H_{13}Co^+$], 191 (24), [$C_{10}H_{12}Co^+$], 155 (56) [$C_2Si_2(CH_3)_5$], 133 (28) [$C_{10}H_{13}^+$], 97 (33) [$C_2Si(CH_3)_3^+$], 73 (83) [$Si(CH_3)_3^+$].

$C_{21}H_{37}CoSi_2$ (404.6) Calcd. C 62.34 H 9.22 Co 14.56
Found C 62.51 H 9.34 Co 14.20

[η^5:η^2-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl][η^2-phenyl(trimethylsilyl)acetylene]cobalt (**3**): A solution of **1** (0.20 g, 0.75 mmol) in 40 ml of hexane was treated with phenyl(trimethylsilyl)acetylene (0.13 g, 0.75 mmol) and the mixture heated to reflux for 25 h. The solvent was removed in vacuo and the residue chromatographed on alumina (15 × 1.5 cm, 25 °C). With hexane unreacted acetylene was removed. With hexane/toluene (10:1) a red-brown band was eluted and collected to give a red-brown oil; yield 0.11 g (35%). – ^1H NMR (C_6D_6, 25 °C): $\delta = 0.38$ [s, 9H, $Si(CH_3)_3$]; 0.73 [d, $^3J_{H,H} = 7.9$ Hz, 1H, 4-H (*Z*)]; 0.89, 1.33 (s, 3H, CH_3); 1.48, 1.69 (m, 1H, 1-H_2); 1.94 [d, $^3J_{H,H} = 11.6$ Hz, 1H, 4-H (*E*)]; 2.06 (s, 3H, CH_3), 2.21 (m, 1H, 2-H), 2.57 (m, 1H, 3-H), 2.71 (s, 3H, CH_3), 3.42 (m, 1H, 2-H); 7.11 (m, 1H, *p*-H); 7.27 (m, 2H, *m*-H); 8.12 (m, 2H, *o*-H). – $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): $\delta = 1.93$ [$Si(CH_3)_3$]; 8.65, 9.83, 10.42, 12.28 (CH_3); 19.74 (C-1); 39.10 (C-2); 44.39 (C-4); 64.91 (C-3); 90.99, 93.16, 93.73, 95.79, 100.48 (five-membered ring C); 106.02, 118.41 (C≡C), 125.81, 126.28, 126.91, 129.24, 131.10, 131.42 (C_6H_5). – IR (KBr): $\tilde{\nu} = 3080\ cm^{-1}$ w, 3056 w, 2978 m, 2954 m, 2927 m, 2906 m, 2856 m, 1792 m, 1489 m, 1458 w, 1249 m, 1070 w, 1027 w, 913 w, 864 s, 842 s, 757 s, 690 m. – EI MS: *m/z* (%) = 408 (14) [M^+], 234 (100) [$C_{13}H_{19}Co^+$], 192 (25) [$C_{10}H_{13}Co^+$], 174 (17) [$C_6H_5C{\equiv}CSi(CH_3)_3^+$], 159 (67) [$C_6H_5C{\equiv}CSi(CH_3)_2^+$], 133 (31) [$C_{10}H_{13}^+$], 73 (33) [$Si(CH_3)_3^+$].

(η^5:η^4-1-{2-[2,3,4,5-Tetrakis(methoxycarbonyl)-2,4-cyclohexadienyl]ethyl}-2,3,4,5-tetramethylcyclopentadienyl)cobalt (**4**): To a solution of **1** (0.26 g, 1.0 mmol) in 50 ml of hexane was added dimethyl acetylenedicarboxylate (0.29 g, 2 mmol) at room temp. The mixture was heated to reflux for 4 h. All volatiles were removed in vacuo and the residue chromatographed on silica gel (30 × 2 cm). With toluene/ether (5:1) an yellow band of the unreacted ester was removed. With toluene/ether (1:3) as eluent a red-brown band was eluted and collected. Recrystallization from hexane/ether afforded a red-brown powder; yield 0.45 g (88%); m.p. 72°C. – ^{1}H NMR (C_6D_6, 25°C): δ = 0.40 (m, 1 H, 1-H); 1.20, 1.39, 1.43, 1.53 (s, 3 H, CH_3); 1.62 (m, 1 H, 1-H); 1.77, 2.20 (m, 1 H, 2-H); 2.27 (m, 2 H, 6'-H_2); 2.81 (m, 1 H, 5'-H); 3.31, 3.32, 3.58, 3.63 (s, 3 H, CO_2CH_3). – ^{13}C NMR (C_6D_6, 25°C): δ = 8.36, 8.73, 8.82, 9.30 (q, $^{1}J_{C,H}$ = 128 Hz, CH_3); 18.97 (t, $^{1}J_{C,H}$ = 128 Hz, C-1); 27.27 (t, $^{1}J_{C,H}$ = 133 Hz, C-2); 35.32 (d, $^{1}J_{C,H}$ = 126 Hz, C-5'); 42.55 (t, $^{1}J_{C,H}$ = 126 Hz, C-6'); 50.90, 51.02, 52.09, 52.17 (q, $^{1}J_{C,H}$ = 146 Hz, CO_2CH_3); 53.94, 59.88 (s, six-membered ring C); 85.36, 90.89, 91.65 (s, five-membered ring C); 93.34 (s, six-membered ring C); 97.30 (s, five-membered ring C); 98.44 (s, six-membered ring C); 99.84 (s, five-membered ring C); 168.88, 168.90, 173.37, 173.60 (s, CO_2CH_3). – IR (KBr): ṽ = 2951 cm^{-1} m, 2917 m, 2868 m, 1726 vs, 1699 vs, 1436 s, 1382 m, 1355 m, 1318 w, 1268 s, 1231 vs, 1170 s, 1110 m, 1097 m, 1079 m, 1029 w, 998 m, 955 w, 802 w, 770 w, 716 m, 690 m, 621 w. – EI MS: *m/z* (%) = 518 (100) [M^+], 459 (22) [$M^+ - CO_2CH_3$], 400 (19) [$M^+ - 2\,CO_2CH_3$], 133 (11) [$C_{10}H_{13}^+$].

$C_{25}H_{31}CoO_8$ (518.5) Calcd. C 57.92 H 6.02 Co 11.37
Found C 57.79 H 6.29 Co 10.70

{η^5:η^4-1-[2-(2,3,4,5-Tetraphenyl-2,4-cyclohexadienyl)ethyl]-2,3,4,5-tetramethylcyclopentadienyl}cobalt (**5**): A solution of **1** (0.20 g, 0.75 mmol) in 40 ml of hexane was treated with diphenylacetylene (0.27 g, 1.5 mmol) at room temp. and the mixture heated to reflux for 15 h. All volatiles were removed in vacuo, and the residue was chromatographed on alumina (30 × 2 cm, water cooling). With hexane/toluene (5:1) an orange-yellow band was eluted first (**6**). A dark green band was then eluted with neat toluene and collected. Recrystallization from pentane at −78°C afforded black, lustrous crystals; yield 0.25 g (56%), m.p. 184°C. – ^{1}H NMR (C_6D_6, 25°C): δ = 0.75, 0.81 (s, 3 H, CH_3); 1.10 (m, 1 H, 1-H); 1.67, 1.73 (s, 3 H, CH_3); 1.85 (m, 1 H, 1-H); 1.90 (m, 1 H, 2-H); 2.38 (m, 2 H, 6'-H_2); 2.58 (m, 1 H, 5'-H); 2.66 (m, 1 H, 2-H); 6.55 (m, 3 H), 6.70 (m, 2 H), 6.79 (m, 1 H), 6.89 (m, 6 H), 7.14 (m, 3 H), 7.25 (m, 3 H), 8.06 (m, 1 H), 8.33 (m, 1 H) (C_6H_5). – ^{13}C NMR (C_6D_6, 25°C): δ = 8.93, 10.68, 10.81, 11.39 (q, $^{1}J_{C,H}$ = 126 Hz, CH_3); 18.31 (t, $^{1}J_{C,H}$ = 127 Hz, C-1); 28.33 (t, $^{1}J_{C,H}$ = 129 Hz, C-2); 31.92 (d, $^{1}J_{C,H}$ = 125 Hz, C-5'); 36.71 (t, $^{1}J_{C,H}$ = 127 Hz, C-6'); 59.28, 65.99, 84.00 (s, six-membered ring C); 85.45, 87.32, 98.68 (s, five-membered ring C); 98.95 (s, six-membered ring C); 99.96, 102.78 (s, five-membered ring C); 124.15, 124.20, 124.48, 124.53, 125.52, 125.69, 125.76, 125.91, 126.09, 126.55, 126.87, 127.09, 129.69, 129.75, 130.96, 131.01, 131.35, 131.43, 135.38, 135.74, 141.04, 141.19, 142.61, 145.99 (C_6H_5). – IR (KBr): ṽ = 3079 cm^{-1} w, 3053 m, 3021 w, 2954 m, 2931 m, 2904 m, 2890 m, 2873 m, 2847 m, 1597 s, 1492 s, 1461 m, 1442 s, 1377 m, 1265 w, 1071 w, 1028 m, 761 s, 731 s, 700 vs, 591 m, 574 w, 547 w. – EI MS: *m/z* (%) = 590 (75) [M^+], 72 (74) [$C_5H_{12}^+$], 57 (100) [$C_4H_9^+$].

$C_{41}H_{39}Co$ (590.7) Calcd. C 83.37 H 6.65 Co 9.98
Found C 83.42 H 7.49 Co 9.30

[η^5-1-(3-Butenyl)-2,3,4,5-tetramethylcyclopentadienyl](η^4-tetraphenylcyclobutadiene)cobalt (**6**): The first band of the chromatography above afforded 0.11 g (24%) of an orange-yellow oil. – ^{1}H NMR (C_6D_6, 25°C): δ = 1.46, 1.52 (s, 6 H, CH_3); 2.01 (m, 2 H, 2-H_2); 2.13 (t, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, 1-H_2); 4.88 [d, $^{3}J_{H,H}$ = 11.0 Hz, 1 H, 4-H (*Z*)]; 4.92 [d, $^{3}J_{H,H}$ = 17.1 Hz, 1 H, 4-H (*E*)]; 5.69 (m, 1 H, 3-H); 7.05 (m, 12 H, *m*-H, *p*-H); 7.53 (m, 8 H, *o*-H). – ^{13}C{^{1}H} NMR (C_6D_6, 25°C): δ = 9.15, 9.26 (CH_3); 22.68 (C-1); 34.38 (C-2); 72.73 (four-membered ring C); 88.98, 89.84, 92.80 (five-membered ring C); 117.59 (C-4); 125.94 (C-*p*); 128.92 (C-*m*); 136.82 (C-*o*); 138.45 (C-*i*); 138.98 (C-3). – IR (KBr): ṽ = 3079 cm^{-1} w, 3058 w, 3026 w, 2953 m, 2924 m, 2855 m, 1639 w, 1598 s, 1469 s, 1446 m, 1378 w, 1071 w, 1027 w, 912 w, 776 m, 762 m, 747 m, 700 vs, 560 m. – EI MS: *m/z* (%) = 590 (100) [M^+], 549 (8) [$M^+ - C_3H_5$].

$C_{41}H_{39}Co$ (590.7) Calcd. C 83.37 H 6.65
Found C 82.27 H 7.21

Bis(diiodo{η^5-1-[2-(2,3,4,5-tetraphenyl-2,4-cyclohexadienyl)ethyl]-2,3,4,5-tetramethylcyclopentadienyl}cobalt) (**7**): A solution of **5** (0.24 g, 0.4 mmol) in 30 ml of hexane was treated at −78°C with a cooled solution of iodine (0.10 g, 0.40 mmol) in 10 ml of ether. The color of the solution changed from green to dark brown. The reaction mixture was stirred at room temp. for 1 h and the residue chromatographed on silica gel (6 × 2 cm, 25°C). With hexane/ether (1:1) traces of iodine were eluted as a pale violet band. A dark brown band was eluted with ether/dichloromethane (3:1) and collected. Recrystallization from ether/hexane afforded a black powder; yield 0.25 g (73%); m.p. 114°C. – ^{1}H NMR (C_6D_6, 25°C): δ = 1.36, 1.45 (s, 6 H, CH_3); 1.54 (m, 3H); 2.33 (m, 2 H); 2.73 (m, 2 H); 6.75 (m, 4 H), 6.82 (m, 5 H), 6.90 (m, 2 H), 6.99 (m, 3 H), 7.06 (m, 3 H), 7.30 (m, 3 H) (C_6H_5). – ^{13}C{^{1}H} NMR (C_6D_6, 25°C): δ = 11.08, 11.44 (CH_3); 26.33 (C-1); 30.16 (C-2); 43.00, 51.16 (C-3, -4); 96.16, 98.55, 102.83 (five-membered ring C); 125.85, 126.10, 126.56, 126.79, 127.11, 127.58, 128.30, 129.24, 130.25, 131.07, 131.48, 131.92, 139.81, 140.34, 140.74, 142.17 (six-membered ring C, C_6H_5). – IR (KBr): ṽ = 3080 cm^{-1} m, 3074 m, 3053 m, 3021 m, 2956 m, 2943 m, 2922 s, 2853 m, 1654 w, 1637 w, 1599 m, 1491 m, 1467 s, 1440 s, 1421 s, 1375 s, 1072 w, 1013 m, 762 m, 699 vs. – EI MS: *m/z* (%) = 531 (7) [$M^+/2 - 2I - Co$], 254 (100) [I_2^+]. – CI MS: *m/z* (%) = 531 (75) [$M^+/2 - 2I - Co$], 530 (100) [$M^+/2 - 2I - Co - H$], 516 (10) [$M^+/2 - 2I - Co - CH_3$].

$(C_{41}H_{39}CoI_2)_2$ [$(844.5)_2$] Calcd. C 58.31 H 4.66 I 30.05
Found C 58.22 H 4.64 I 29.97

(η^5:η^4-1-{2-[Bis(methoxycarbonyl)diphenylcyclohexadienyl]ethyl}-2,3,4,5-tetramethylcyclopentadienyl)cobalt (**8**): A solution of **1** (0.13 g, 0.5 mmol) in 40 ml of hexane was treated with 0.16 g (1.0 mmol) of methyl phenylpropiolate and the mixture heated to reflux for 15 h. All volatiles were removed in vacuo, and the residue was chromatographed on silica gel (8 × 2 cm, 25°C). A red band was eluted with hexane/ether (1:1). Recrystallization from pentane gave a red powder; yield 0.23 g (84%), m.p. 87°C. – ^{1}H NMR (C_6D_6, 25°C): δ = 0.71 (s, 3 H, CH_3); 0.76 (m, 2 H); 1.31, 1.32 (s, CH_3); 1.39 (m, 2 H); 1.52, 1.57, 1.64 (s, 3 H, CH_3); 1.66 (m, 1 H); 1.70 (m, 1 H); 1.78 (m, 1 H); 1.87 (m, 1 H); 1.97 (s, 3 H, CH_3); 2.24 (m, 3 H); 2.30 (s, 3 H, CH_3); 2.38 (m, 3 H); 2.91, 3.06, 3.31, 3.47 (s,. 3 H, CO_2CH_3); 7.05, 7.25, 7.39, 8.41 (m, 20 H, C_6H_5). – ^{13}C{^{1}H} NMR (C_6D_6, 25°C): δ = 7.45, 8.48, 8.81, 9.71, 9.89, 9.95, 10.43, 10.51 (CH_3); 20.05, 21.30 (C-1); 25.45, 29.84 (C-2); 35.29, 36.32 (C-5'); 39.42, 40.07 (C-6'); 49.97 (CO_2CH_3), 50.65, 51.26 (six-membered ring C), 51.29, 51.46, 51.52 (CO_2CH_3), 55.82, 57.20, 75.12, 79.56 (six-membered ring C); 82.54, 83.44 (five-membered ring C); 85.47 (six-membered ring C); 86.08, 87.86, 88.07 (five-membered ring C); 89.98 (six-membered ring C); 90.52, 94.11, 98.87, 99.99, 100.40 (five-membered ring C); 124.09, 126.26, 126.34, 126.35, 127.04, 127.07, 127.31, 127.36, 128.47, 129.39, 129.79, 133.92, 137.12, 138.63, 139.80, 144.01, 144.21, 144.55, 147.94, 148.17, 149.21, 150.89, 155.25, 155.36 (C_6H_5); 166.47, 170.17, 170.43,

170.76 (CO_2CH_3). – IR (KBr): $\tilde{\nu}$ = 3075 cm^{-1} w, 3053 w, 3020 w, 2993 w, 2944 m, 2924 m, 2902 m, 2857 m, 1718 vs, 1685 s, 1595 w, 1490 m, 1433 s, 1377 w, 1351 s, 1312 w, 1274 w, 1247 m, 1214 vs, 1168 m, 1036 w, 757 m, 700 vs. – EI MS: *m/z* (%) = 554 (10) [M^+], 73 (100) [$C_5H_{13}^+$], 57 (59) [$C_4H_9^+$].

$C_{33}H_{35}CoO_4$ (554.6) Calcd. C 71.47 H 6.36 Co 10.63
Found C 71.30 H 6.48 Co 9.70

(η^5 : η^4-1-{2-[Bis(trimethylsilyl)-2,4-cyclohexadienyl]ethyl}-2,3,4,5-tetramethylcyclopentadienyl)cobalt (**9**): To a solution of **1** (0.20 g, 0.75 mmol) in 40 ml of hexane was added trimethylsilylacetylene (0.15 g, 1.5 mmol) at room temp. The mixture was heated to reflux for 15 h. After removal of the solvent, the residue was chromatographed on alumina (6 × 2 cm, 25°C). A yellow band was eluted with hexane and collected. Evaporation of the solvent afforded a dark yellow oil; yield 0.25 g (75%). – ^{1}H NMR (C_6D_6, 25°C): δ = 0.17, 0.31 [s, 9H, $Si(CH_3)_3$]; 1.04 (m, 1H); 1.33 (m, 1H); 1.37, 1.49, 1.56 (s, 3H, CH_3); 1.62 (m, 1H); 1.78 (s, 3H, CH_3); 1.90 (m, 1H); 2.02 (m, 1H); 2.40 (m, 2H); 2.53 (m, 1H); 2.62 (m, 1H). – ^{13}C NMR (C_6D_6, 25°C): δ = –0.91, 0.96 [q, $^1J_{C,H}$ = 119 Hz, $Si(CH_3)_3$]; 9.96, 11.00, 11.89, 14.13 (q, $^1J_{C,H}$ = 126 Hz, CH_3); 18.56 (t, $^1J_{C,H}$ = 126 Hz, C-1); 24.63 (t, $^1J_{C,H}$ = 129 Hz, C-2); 34.35 (d, $^1J_{C,H}$ = 123 Hz, C-5'); 40.17 (t, $^1J_{C,H}$ = 125 Hz, C-6'); 60.12 (d, $^1J_{C,H}$ = 157 Hz, ring CH); 63.96, 77.88 (s, six-membered ring C); 84.63, 86.28, 88.76 (s, five-membered ring C); 88.88 (d, $^1J_{C,H}$ = 161 Hz, ring CH); 94.40, 95.82 (s, five-membered ring C). – IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} w, 3059 w, 2954 m, 2925 m, 2872 m, 2854 m, 2798 w, 1459 m, 1442 m, 1403 w, 1377 m, 1247 s, 1143 w, 1072 w, 1024 w, 837 vs br, 751 m, 691 w, 630 w. – CI MS: *m/z* (%) = 430 (100) [M^+], 415 (8) [$M^+ - CH_3$], 357 (19) [$M^+ - Si(CH_3)_3$].

$C_{23}H_{39}CoSi_2$ (430.7) Calcd. C 64.15 H 9.13
Found C 64.87 H 9.26

CAS Registry Numbers

1: 132157-56-3 / **2**: 132157-57-4 / **3**: 138667-05-7 / **4**: 138667-06-8 / **5**: 132157-60-9 / **6**: 138667-07-9 / **7**: 138667-08-0 / **8**: 138667-09-1 / **9**: 138693-68-2 / $Me_3SiC{\equiv}CSiMe_3$: 14630-40-1 / $PhC{\equiv}CSiMe_3$: 2170-06-1 / $HC{\equiv}CSiMe_3$: 1066-54-2 / $MeO_2CC{\equiv}CCO_2Me$: 762-42-5 / $PhC{\equiv}CPh$: 501-65-5 / $PhC{\equiv}CCO_2Me$: 4891-38-7

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