Cobalt-mediated Two-carbon Ring Expansion of Five-membered Rings. Electrophilic Carbon-Carbon Bond Activation in the Synthesis of Seven-membered Rings

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Supporting Information

Methods. All manipulations on air sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres drybox. Vacuum transfer of volatile reagents was performed at high vacuum ($\leq 10^{-5}$ mm Hg) using a MKS Baratron digital pressure transducer for measurement of gas pressure in known volume bulbs. Toluene, benzene, tetrahydrofuran, diethyl ether, hexane and pentane were distilled from sodium/ benzophenone ketyl or sodium (potassium)/benzophenone ketyl. Reagent grade acetone was degassed and stored under nitrogen with no further purification. Dichloromethane and acetonitrile were distilled from calcium hydride and degassed. Photolysis was carried out using a Hanovia 450 watt high pressure mercury lamp filtered through pyrex. IR spectra were recorded on a Nicolet Magna IR 750 or a Nicolet 20SX spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker (AM-400, AM-360, AM-300, AM-200) or Varian (Unity-500 or Unity-Inova 300) spectrometers. Chemical shifts are reported in ppm relative to external TMS using residual protiated solvent resonances as reference. Mass spectra were obtained on a Kratos MS-50 spectrometer or by positive mode electrospray ionization on a Micromass ZabSpec Hybrid Sector-TOF. FAB mass spectra were recorded on an AEIMS9 spectrometer. Elemental analyses were performed by the University of Alberta Microanalysis Laboratories.

Further Note on Spectroscopic Methods. In ^1H NMR spectral data, values of the coupling constants are either obtained directly from the spectrum, or extracted using standard homonuclear decoupling techniques. Although generally measured to ± 0.1 Hz, J values are self-consistent only to ± 1 Hz. GCOSY denotes the standard COSY experiment, acquired using field gradients. Data for the ^1H - ^1H COSY or GCOSY is presented such that correlations are listed only once. Values of $^1J_{\text{CH}}$ are obtained directly from the gated decoupled spectrum or from the coupled HMQC spectrum. ^1H - ^{13}C HETCORR experiments are recorded at the ^{13}C frequency of the spectrometer, while HMQC and HMBC are recorded at the ^1H frequency.

Numbering scheme for cycloheptadienyl complexes. To aid in tabulation of ^1H NMR spectral information, a common numbering scheme for cycloheptadienyl complexes was devised: the most upfield signal in the ^1H NMR spectrum is assigned to the $\text{H}_{6\text{exo}}$ atom. This signal was identified based on careful correlation of the $J_{\text{H-H}}$ values to the expected Karplus value obtained from the torsional angle between the relevant hydrogen atoms, as determined from X-ray crystallographic structures. In cases where the cycloheptadienyl ligand has a mirror plane, this artifice is maintained and the signals are assigned to the two symmetry related positions.

Materials. $(\text{C}_5\text{Me}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ ¹ and 1,2-dimethylcyclopentadiene² were prepared by published procedures. $(\text{C}_5\text{H}_5)_2\text{Co}$ (cobaltocene) was made by the addition of solid anhydrous CoCl_2 to a solution of NaCp in THF/DME.³ $(\text{C}_5\text{H}_5)_2\text{Co}^+\text{Cl}^-$ was prepared by oxidation of this solution with aqueous HCl and air.³ $(\text{C}_5\text{H}_5)_2\text{Co}^+\text{PF}_6^-$ was precipitated from an aqueous solution of $(\text{C}_5\text{H}_5)_2\text{Co}^+\text{Cl}^-$ using NH_4PF_6 . All cyclopentadienes were distilled before use. $(\text{C}_5\text{H}_5)\text{Co}(\eta^4\text{-exo-alkylcyclopentadiene})$ complexes [$\text{R} = \text{H}$, Me (**4a**), *tert*-Bu (**4b**)] were prepared by addition of NaBH_4 or the appropriate alkylmetal reagents ($\text{M} = \text{Li}$, MgX) to a slurry of $(\text{C}_5\text{H}_5)_2\text{Co}^+\text{X}^-$ in THF at -78°C . Workup consisted of removing the THF solvent in vacuo and trituration of the solid residue with pentane. The pentane extracts were filtered through a Celite pad and evaporated to dryness. These compounds have been prepared previously via very similar procedures.⁴

$(\text{C}_5\text{Me}_5)\text{Co}(\eta^4\text{-cyclohexadiene})$ was prepared by heating a solution of $\text{Cp}^*\text{Co}(\text{C}_2\text{H}_4)_2$ and 1,3-cyclohexadiene in hexane at $65\text{ }^\circ\text{C}$ for 12 h. Sodium dimethylmalonate was prepared by the addition of NaH to a THF solution of dimethylmalonate.

Experimental procedures.

$(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\eta^4\text{-C}_5\text{H}_6)$ **2a** and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4\text{-C}_5\text{Me}_5\text{H})$ **2a'**. To a Schlenk tube was added $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ (0.2364 g, 0.9446 mmol). Pentane (50 mL) was added, and the tube was removed from the drybox. On the Schlenk line, monomeric cyclopentadiene **1a** (0.45 mL, 5 equiv) was added and the tube was cooled to $-30\text{ }^\circ\text{C}$. Photolysis (450W Hanovia, pyrex) was carried out for 1h under a slow nitrogen purge to remove ethylene. After photolysis, the tube was returned to the drybox, the solvent was removed in vacuo, and the residue extracted with pentane (8 mL). The pentane extract was filtered through Celite and then evaporated to dryness. A red-orange solid residue (0.2432 g, 99%) remained, consisting of about a 2:1 mixture of $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\eta^4\text{-C}_5\text{H}_6)$ **2a** and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4\text{-C}_5\text{Me}_5\text{H})$ **2a'**. Depending on photolysis time, this ratio varies from about 1 : 3 to 6 : 1. This mixture was used without further purification or separation. Data for $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4\text{-C}_5\text{Me}_5\text{H})$ **2a'**: IR (hexane cast, cm^{-1}) 3093 (w), 3040 (m), 2949 (s), 2907 (s), 2856 (s), 2721 (s), 1652 (m), 1447 (s), 1378 (s), 1334 (m), 1308 (w), 1236 (w), 1107 (w), 1065 (m), 1027 (m), 1006 (m), 990 (m), 795 (s), 402 (s); ^1H NMR (300 MHz, C_6D_6) δ 4.36 (s, 5H, C_5H_5), 2.48 (q, $J = 6.0$ Hz, 1H, $\text{C}_5\text{Me}_5\text{H}$), 2.10 (s, 6H, Me), 1.18 (s, 6H, Me), 0.28 (d, $J = 6.1$ Hz, 3H, Me); ^{13}C NMR (100 MHz, C_6D_6) δ 89.0, 80.8 (C_5H_5), 56.7, 41.4, 20.4, 15.2, 12.6. MS m/z calculated for $\text{C}_{15}\text{H}_{21}\text{Co}$ (M^+): 260.09753; found: 260.09757 (96%).

MS m/z calculated for $C_{15}H_{19}Co$ ($M^+ - H_2$): 258.08188; found: 258.08223(100%). Data for $(\eta^5-C_5Me_5)Co(\eta^4-C_5H_6)$ **2a**: 1H NMR (300 MHz, C_6D_6) δ 4.75 (t, $J = 1.9$ Hz, 2H, $H_{2,3}$), 2.66 (dt, $J = 13.5, 2.2$ Hz, 1H, H_{5a}), 2.30* (br d, $J = 13.5$ Hz, 1H, H_{5b}), 1.76 (m, 2H, obscured by C_5Me_5 , $H_{1,4}$), 1.74 (s, 15H, C_5Me_5). *This signal appears to have an unresolved triplet coupling of about 1-2 Hz, as determined by shoulders on the doublet peaks.

$(\eta^5-C_5Me_5)Co(\eta^4-MeC_5H_5)$ **2b** and $(\eta^5-MeC_5H_4)Co(\eta^4-C_5Me_5H)$ **2b'**. To a Schlenk tube was added $(\eta^5-C_5Me_5)Co(C_2H_4)_2$ (0.1760 g, 0.7032 mmol). Benzene (50 mL) was added and the tube was removed from the drybox. On the Schlenk line, methylcyclopentadiene **1b** (0.40 mL, 5 equiv) was added and the tube was placed in a cooling bath initially maintained at -30 °C. Photolysis was carried out for 60 min under a nitrogen purge to remove ethylene. After photolysis, the solvent was removed and the residue extracted with pentane (ca. 10 mL) in the drybox. The pentane extract was filtered through Celite and evaporated to dryness. A red-orange oily residue (0.1744 g, 90%) was obtained, which consisted of a about a 1.6 : 1 mixture of $(\eta^5-C_5H_4Me)Co(\eta^4-C_5Me_5H)$ **2b'** and $(\eta^5-C_5Me_5)Co(\eta^4-MeC_5H_5)$ **2b** (mixture of isomers). This mixture was used without further purification or separation. Data for $(\eta^5-C_5H_4Me)Co(\eta^4-C_5Me_5H)$ **2b'**: IR (hexane cast, cm^{-1}) 3035 (m), 2959 (s), 2909 (s), 2704 (m), 1615 (w), 1448 (s), 1374 (m), 1269 (m), 1028 (m), 937 (w), 881 (w), 817 (w), 704 (w); 1H NMR (400 MHz, C_6D_6) δ 4.19 (t, $J = 2$ Hz, 2H, Cp'), 4.13 (t, $J = 2$ Hz, 2H, Cp'), 2.45 (q, $J = 6.1$ Hz, 1H, C_5Me_5H), 1.83 (s, 3H, Cp'), 2.02 (s, 6H, Me), 1.17 (s, 6H, Me), 0.45 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 92.3 (Cp' quaternary), 88.6, 81.7 (Cp'), 80.3 (Cp'), 56.4, 45.0, 20.2, 14.6, 12.1, 10.3

(Cp^tMe). MS m/z calculated for C₁₆H₂₃Co (M⁺): 274.10535 found: 274.11296 (15%). MS m/z calculated for C₁₅H₂₀Co (M⁺-CH₃): 259.08969 found: 259.08967 (100%).

(η^5 -C₅Me₅)Co(η^4 -*tert*-BuC₅H₅) **2c** and (η^5 -*tert*-BuC₅H₄)Co(η^4 -C₅Me₅H) **2c'**. To a Schlenk tube was added (η^5 -C₅Me₅)Co(C₂H₄)₂ (0.1858 g, 0.7424 mmol). Hexane (40 mL) was added, and the tube was removed from the drybox. On the Schlenk line, *tert*-butylcyclopentadiene **1c** (0.27 mL, 3 equiv) was added and the tube was initially maintained at -30 °C. Photolysis was carried out for 40 min under a nitrogen purge to remove ethylene. After photolysis, the solvent was reduced to about 10 mL under reduced pressure and filtered through Celite. After removal of the solvent in vacuo, a red-orange solid residue (0.2326 g, 99%) remained, which consisted of about a 1.3 : 1 mixture of (η^5 -*t*-BuC₅H₄)Co(η^4 -C₅Me₅H) (**2c'**) and isomeric mixture (η^5 -C₅Me₅)Co(η^4 -*t*-BuC₅H₅) **2c**. This mixture was used without further purification or separation. Data for *t*-BuC₅H₄)Co(η^4 -C₅Me₅H) **2c'**. IR (hexane cast, cm⁻¹) 3037 (m), 2956 (s), 2902 (s), 2720 (m), 1634 (w), 1457 (m), 1378 (s), 1362 (m), 1273 (w), 1028 (m), 909 (w), 855 (w), 803 (w), 408 (w); ¹H NMR (400 MHz, C₆D₆) δ 4.06 (br s, 2H, Cp^t), 3.97 (br s, 2H, Cp^t), 2.55 (q, J = 6.0 Hz, 1H, C₅Me₅H), 1.99 (s, 6H, Me), 1.33 (s, 9H, *t*-Bu), 1.11 (s, 6H, Me), 0.36 (d, J = 6.0 Hz, 3H, Me); ¹³C NMR (100 MHz, C₆D₆) δ 88.5, 80.4 (Cp^t), 76.9 (Cp^t), 56.7, 43.0, 32.1 (*t*-Bu), 20.4, 14.9, 12.8. Cp^t ring quaternary and *t*-Bu quaternary carbons were not located. MS m/z calculated for C₁₉H₂₈Co (M⁺-H): 315.15231; found: 315.15225 (64%). MS m/z calculated for C₁₅H₂₀Co (M⁺-*t*-Bu): 259.08969; found: 259.08989 (100%).

Table 1. Comparative ^{13}C NMR Data for η^4 -Pentamethylcyclopentadiene Complexes **2a'**, **2b'**, and **2c'**

Signal	2a'	2b'	2c'
Cp-H	80.8 -- --	81.7 80.3 92.3	80.4 76.9 a
C ₁	56.7	56.4	56.7
C ₂	89.0	88.6	88.5
C ₃	41.4	45.0	43.0
C ₄	20.4	20.2	20.4
C ₅	12.6	12.1	12.8
C ₆	15.2	14.6	14.9
R group	--	10.3	32.1 ^b

^a Quaternary carbon not located. ^b Resonance for the methyl groups of the ^tBu substituent; quaternary carbon not located.

[(η^5 -C₅Me₅)Co(η^5 -3,4-Me₂C₇H₇)]⁺BF₄⁻ **3a.**

In the drybox, the mixture of (η^5 -C₅H₅)Co(η^4 -C₅Me₅H) (**2a**) and its isomer (29.4 mg, 0.113 mmol) was weighed into a Schlenk flask. The flask was removed to the Schlenk line, where degassed dichloromethane (6 mL) was added. The solution was cooled to -78 °C and 2-butyne (44 μ L, 5 equiv) was added. HBF₄•Et₂O (18 μ L, 1.1 equiv) was added and the solution was allowed to slowly warm to room temperature. All volatile material was removed *in vacuo* and the residue was purified by flash chromatography on silica gel, using 7% methanol-dichloromethane as the eluent. An orange band was collected and upon removal of

solvent, an orange solid (32 mg, 70%), pure **3a** by NMR spectroscopy, was obtained. An analytical sample was obtained by recrystallization from dichloromethane/diethyl ether. IR (CH₂Cl₂ cast, cm⁻¹) 2990 (w), 2915 (w), 1489 (w), 1476 (w), 1437 (w), 1385 (m), 1089 (m), 1049 (s), 1032 (s), 518 (w); ¹H NMR (300 MHz, CD₂Cl₂) δ 4.67 (br d, $J_{2-1} = 9.1$ Hz, 1H, H₂), 4.40 (ddd, $J_{1-2} = 8.7$ Hz, $J_{1-7\text{exo}} \approx J_{1-7\text{endo}} = 4.4$ Hz, 1H, H₁), 4.04 (dd, $J_{5-6\text{endo}} = 4.0$ Hz, $J_{5-6\text{exo}} = 7.3$ Hz, 1H, H₅), 2.45 (dddd, $J_{7\text{endo}-7\text{exo}} = 16.7$ Hz, $J_{7\text{endo}-6\text{endo}} = 9.8$ Hz, $J_{7\text{endo}-6\text{exo}} = 8.8$ Hz, $J_{7\text{endo}-1} = 5.3$ Hz, 1H, H_{7endo}), 2.24 (s, 3H, Me₃), 2.00 (s, 3H, Me₄), 2.15-1.95 (m, 1H, H_{6endo}, obscured by Me), 1.77 (s, 15H, C₅Me₅), 1.58 (dddd, $J_{7\text{exo}-7\text{endo}} = 15.9$ Hz, $J_{7\text{exo}-6\text{exo}} = 5.9$ Hz, $J_{7\text{exo}-1} = 3.3$ Hz, $J_{7\text{exo}-2} = 4$ Hz, 1H, H_{7exo}), 0.77 (dddd, $J_{6\text{exo}-6\text{endo}} = 16.5$ Hz, $J_{6\text{exo}-7\text{endo}} = 8.1$ Hz, $J_{6\text{exo}-7\text{exo}} = 5.9$ Hz, $J_{6\text{exo}-5} = 4.2$ Hz, 1H, H_{6exo}); ¹H-¹H COSY (400 MHz, CD₂Cl₂) δ 4.67 (H₂) ↔ δ 2.24 (w, Me₃), δ 2.00 (w, Me₄); δ 4.40 (H₁) ↔ δ 2.45 (H_{7endo}), δ 1.58 (H_{7exo}); δ 4.04 (H₅) ↔ δ 2.07 (H_{6endo}), δ 0.77 (H_{6exo}); δ 2.45 (H_{7exo}) ↔ δ 1.58 (H_{7exo}), δ 0.77 (w, H_{6exo}); δ 2.07 (H_{6endo}) ↔ δ 1.58 (H_{7exo}), δ 0.77 (H_{6exo}); ¹³C NMR (100 MHz, CD₂Cl₂) δ 110.9 (s, C₃), 107.4 (s, C₄), 98.0 (s, C₅Me₃), 97.7 (d, $^1J_{\text{CH}} = 164.2$ Hz, C₂), 93.5 (d, $^1J_{\text{CH}} = 149.7$ Hz, C₁), 87.0 (d, $^1J_{\text{CH}} = 156.3$ Hz, C₅), 35.9 (t, $^1J_{\text{CH}} = 130.2$ Hz, C₇), 30.6 (t, $^1J_{\text{CH}} = 130.0$ Hz, C₆), 19.8 (q, $^1J_{\text{CH}} = 128.3$ Hz, Me₃), 18.6 (q, $^1J_{\text{CH}} = 126.2$ Hz, Me₄), 9.3 (q, $^1J_{\text{CH}} = 128.8$ Hz, C₅Me₅); ¹H-¹³C HETCORR (100 MHz, CD₂Cl₂) δ 97.7 (C₂) ↔ δ 4.67 (H₂); δ 93.5 (C₁) ↔ δ 4.40 (H₁); δ 87.0 (C₅) ↔ δ 4.04 (H₅); δ 35.9 (C₇) ↔ δ 2.45 (H_{7endo}), δ 1.58 (H_{7exo}); δ 30.6 (C₆) ↔ δ 2.07 (H_{6endo}), δ 0.77 (H_{6exo}); δ 19.8 (Me₃) ↔ δ 2.00 (Me₃); δ 18.6 (Me₄) ↔ δ 2.24 (Me₄); δ 9.3 (C₅Me₅) ↔ δ 1.77 (C₅Me₅); Long range ¹H-¹³C HETCORR (100 MHz, CD₂Cl₂) δ 2.24 (Me₃) ↔ δ 97.7 (C₂), δ 107.4 (C₄), δ 110.9 (C₃, strong); δ 2.00 (Me₄) ↔ δ 87.0 (C₅), δ 107.4 (C₄, strong), δ 110.9 (C₃); HMBC (300 MHz, CD₂Cl₂) δ 110.9 (C₃) ↔ δ 4.40 (H₁), δ 4.04 (H₅), δ 2.24 (Me₃), δ 2.00 (Me₄); δ 107.4 (C₄) ↔ δ 4.67 (H₂), δ 4.40 (H₁), δ 4.04 (H₅), δ 2.24 (Me₃), δ 2.00 (Me₄), δ 0.77 (H_{6exo}); δ 97.7 (C₂) ↔ δ 4.04 (H₅), δ 2.45 (H_{7endo}), δ 2.24 (Me₃); δ 93.5 (C₁) ↔ δ 4.67 (H₂), δ 2.45 (H_{7endo}), δ 1.58 (H_{7exo}), δ 0.77 (H_{6exo}); δ 87.0 (C₅) ↔ δ 2.45 (H_{7endo}), δ 2.00 (Me₄), δ 0.77 (H_{6exo}); δ 35.9 (C₇) ↔ δ 4.67 (H₂), δ 4.04 (H₅), δ 0.77 (H_{6exo}); δ 30.6 (C₆) ↔ δ 2.45 (H_{7endo}); δ 19.8 (Me₃) ↔ δ 4.67 (H₂), δ 2.45 (H_{7endo}); δ 18.6 (Me₄) ↔ δ 4.67 (H₂). Analysis calculated for C₁₉H₂₈BCoF₄: C, 56.74; H, 7.02; found: C, 56.842; H, 7.052.

$[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\eta^4\text{-1-(bis(carbomethoxy)methyl)-3,4-dimethylcyclohepta-2,4-diene)}]$. In the drybox, a solution of $[(\text{C}_5\text{Me}_5)\text{Co-}\eta^5\text{-3,4-Me}_2\text{-C}_7\text{H}_7]^+ \text{BF}_4^-$ **3a** (134.8 mg, 0.3351 mmol) in tetrahydrofuran (12 mL) was prepared. To this orange solution, solid sodium dimethylmalonate (86.3 mg, 0.560 mmol, 1.7 equiv) was added and the solution was stirred for 4 h. No obvious color change was observed. At the end of 4 h, the solvent was removed *in vacuo* and the residue extracted with pentane until the extracts were colorless. The combined extracts were filtered through a Celite pad and the solvent was removed *in vacuo*, leaving 108.6 mg (73%) of an orange solid. Crystals suitable for an X-ray diffraction analysis were grown from a saturated solution of pentane cooled slowly from room temperature to -35°C . Full data on this crystal structure is provided as an appendix (vide infra). IR (hexane cast, cm^{-1}) 2978 (m), 2908 (m), 1753 (s), 1734 (s), 1433 (s), 1376 (m), 1285 (m), 1250 (s), 1197 (m), 1149 (s), 1027 (m); ^1H NMR (400 MHz, C_6D_6) δ 3.43 (s, 3H, CO_2Me), 3.27 (s, 3H, CO_2Me), 3.32 (d, $J_{8-1} = 7.4$ Hz, 1H, H_8), 2.31 (dddd, $J_{1-7\text{exo}} = 11.1$ Hz, $\text{H}_{1-8} = 7.4$ Hz, $J_{1-7\text{endo}} = 3.6$ Hz, $J_{1-2} = 1.3$ Hz, 1H, H_1), 2.05-1.95 (m, 2H, $\text{H}_{2,5}$), 1.79 (s, 3H, Me_3), 1.72 (s, 3H, Me_2), 1.68 (s, 15H, C_5Me_5), 1.75-1.65 (m, 1H, obscured by C_5Me_5 , $\text{H}_{6\text{exo}}$), 1.40-1.31 (m, 1H, $\text{H}_{6\text{endo}}$), 1.31-1.25 (m, 1H, $\text{H}_{7\text{endo}}$), 0.69 (qd, $J_{7\text{exo}-1} = J_{7\text{exo}-7\text{endo}} = J_{7\text{exo}-6\text{endo}} = 12.0$ Hz, $J_{7\text{exo}-6\text{exo}} = 3.5$ Hz, 1H, $\text{H}_{7\text{exo}}$); ^1H - ^1H COSY (400 MHz, C_6D_6) δ 3.32 (H_8) $\leftrightarrow$ δ 2.31 (H_1); δ 2.31 (H_1) $\leftrightarrow$ δ 2.0 ($\text{H}_{2,5}$), δ 1.3 ($\text{H}_{7\text{endo}}$), 0.69 ($\text{H}_{7\text{exo}}$); δ 2.0 ($\text{H}_{2,5}$) $\leftrightarrow$ δ 1.70 ($\text{H}_{6\text{exo}}$), δ 1.3 ($\text{H}_{7\text{endo}}$); δ 1.3 ($\text{H}_{7\text{endo}}$) $\leftrightarrow$ δ 0.69 ($\text{H}_{7\text{exo}}$); ^{13}C NMR (100 MHz, C_6D_6) δ 169.2^a (m, CO_2Me), 168.9^a (m, CO_2Me), 89.4 (s, C_5Me_5), 88.7 (s, $\text{C}_{3/4}$), 87.3 (s, $\text{C}_{3/4}$), 60.0 (d, $^1J_{\text{CH}} = 131.6$ Hz, C_8), 53.7^b (br d, $^1J_{\text{CH}} = 141$ Hz, $\text{C}_{2/5}$), 53.6^b (br d, $^1J_{\text{CH}} = 141$ Hz, $\text{C}_{2/5}$), 51.5 (q, $^1J_{\text{CH}} = 146.3$ Hz, CO_2Me), 40.1 (d, $^1J_{\text{CH}} = 131.7$ Hz, C_1), 28.5 (t, $^1J_{\text{CH}} = 124.4$ Hz, C_6), 28.0 (t, $^1J_{\text{CH}} = 124.6$ Hz, C_7), 19.1 (qd, $^1J_{\text{CH}} = 125.2$ Hz, $^2J_{\text{CH}} = 4.6$ Hz, Me_3), 18.5 (qd, $^1J_{\text{CH}} = 125.0$ Hz, $^2J_{\text{CH}} =$

4.3 Hz, Me₂), 9.3 (q, ¹J_{CH} = 125.0 Hz, C₅Me₅). ^aSmall unresolved ²J_{CH} and ³J_{CH} complicate the signal. ^bSignals overlap in gated spectrum. ¹H-¹³C HETCORR (100 MHz, C₆D₆) δ 60.0 (C₈) ↔ δ 3.32 (H₈); δ 53.7/53.6 (C_{2/5}) ↔ δ 2.0 (H_{2/5}); δ 51.5 (CO₂Me) ↔ δ 3.43 (CO₂Me), δ 3.37 (CO₂Me); δ 40.1 (C₁) ↔ δ 2.31 (H₁); δ 28.5 (C₆) ↔ δ 1.70 (H_{6exo}), δ 1.36 (H_{6endo}); δ 28.0 (C₇) ↔ δ 1.25 (H_{7endo}), δ 0.69 (H_{7exo}); δ 19.1 (Me₃) ↔ δ 1.79 (Me₃); δ 18.5 (Me₂) ↔ δ 1.72 (Me₂); δ 9.3 (C₅Me₅) ↔ δ 1.68 (C₅Me₅). MS *m/z* calculated for C₂₄H₃₅CoO₄ (M⁺): 446.18674; found: 446.18633 (59%). Analysis calculated for C₂₄H₃₅CoO₄: C, 64.56; H, 7.90; found: C, 64.655; H, 8.041.

[(η^5 -C₅Me₅)Co(η^5 -2,3,5-Me₃C₇H₆)]⁺ BF₄⁻ **3b.** A solution of (η^5 -C₅H₄Me)Co(η^4 -C₅Me₃H) (**2b'**) and its isomer (0.1327 g, 0.4837 mmol) in degassed dichloromethane (8 mL) was cooled to -78 °C in a dry-ice/acetone bath. 2-Butyne (0.2 mL, 10 equiv) was added by syringe. HBF₄•Et₂O (0.16 mL, 2.2 equiv) was then slowly added. The solution was then allowed to slowly warm to room temperature, with stirring. All volatile material was removed and the residue was purified by flash chromatography on a silica gel column, eluting with 7% methanol/dichloromethane. This yielded **3b** as a dark red powder (0.111 g, 55%). IR (CH₂Cl₂ cast, cm⁻¹) 2993 (m), 2966 (m), 2912 (m), 2884 (m), 1454 (s), 1437 (s), 1384 (s), 1354(m), 1270 (m), 1092 (s), 1053 (vs), 1034 (s), 734 (s), 701 (m), 519 (m); ¹H NMR (400 MHz, CD₂Cl₂) δ 4.80 (br s, 1H, H₄), 3.91 (dd, *J*_{5-6exo} = 7.3 Hz, *J*_{5-6endo} = 4.0 Hz, 1H, H₁), 2.50 (dddd, *J*_{7endo-7exo} = 16.7 Hz, *J*_{7endo-6exo} = *J*_{7endo-6endo} = 7.9 Hz, *J*_{7endo-1} = 4.6 Hz, 1H, H_{7endo}), 2.24 (s, 3H, CH₃), 1.89 (s, 3H, CH₃), 1.68 (s, 15H, C₅Me₅), 1.70-1.60 (m, 2H, H_{6endo}, H_{7exo}, overlaps with C₅Me₅), 1.52 (s, 3H, CH₃), 0.70 (ddd, *J*_{6exo-6endo} = 14.5 Hz, *J*_{6exo-7endo} = 8.1 Hz, *J*_{6exo-7exo} = 5.5 Hz, 1H, H_{6exo}); ¹H-¹H COSY (400 MHz, CD₂Cl₂) δ

3.91 (H₁) $\delta \leftrightarrow \delta$ 2.50 (H_{7endo}), δ 1.67 (H_{6endo,7exo}); δ 2.50 (H_{7endo}) $\delta \leftrightarrow \delta$ 1.67 (H_{6endo,7exo}), δ 0.70 (H_{6exo}); δ 1.67 (H_{6endo,7exo}) $\delta \leftrightarrow \delta$ 0.70 (H_{6exo}); δ 4.80 (H₄) $\delta \leftrightarrow \delta$ 1.52 (w, Me), δ 1.89 (w, Me); ¹³C NMR (100 MHz, CD₂Cl₂) δ 115.7 (s, C₃), 105.6 (s, C₂), 97.4 (d, ¹J_{CH} = 158 Hz, C₄), 96.8 (s, C₅Me₅), 82.7 (d, ¹J_{CH} = 151 Hz, C₁), 38.4 (t, ¹J_{CH} = 130 Hz, C₇), 35.4 (t, ¹J_{CH} = 127 Hz, C₆), 27.6 (q, ¹J_{CH} = 128 Hz, Me), 20.6 (q, ¹J_{CH} = 129 Hz, Me), 18.9 (q, ¹J_{CH} = 129 Hz, Me), 9.0 (q, ¹J_{CH} = 129 Hz, C₅Me₅); ¹H-¹³C HETCORR (100 MHz, CD₂Cl₂) δ 97.4 (C₄) $\leftrightarrow \delta$ 4.80 (H₄); δ 82.7 (C₁) $\leftrightarrow \delta$ 3.91 (H₁); δ 38.4 (C₇) $\leftrightarrow \delta$ 2.50 (H_{7endo}), δ 1.67 (H_{7exo}); δ 35.4 (C₆) $\leftrightarrow \delta$ 1.67 (H_{6endo}), δ 0.70 (H_{6exo}); δ 27.6 (Me) $\leftrightarrow \delta$ 1.52 (Me); δ 20.6 (Me) $\leftrightarrow \delta$ 1.89 (Me); δ 18.9 (Me) $\leftrightarrow \delta$ 2.24 (Me); δ 9.0 (C₅Me₅) $\leftrightarrow \delta$ 1.68 (C₅Me₅). Analysis calculated for C₂₀H₃₀BCoF₄: C, 57.72; H, 7.27; found: C, 57.471; H, 7.481.

[(η^5 -C₅Me₅)Co(η^5 -6-*tert*-Bu-2,3-Me₂C₇H₆)]⁺ BF₄⁻ **3c**. A solution of (η^5 -*tert*-BuC₅H₄)Co(η^4 -C₅Me₅H) (**2c'**) and its isomer (0.1472 g, 0.4652 mmol) in degassed dichloromethane (8 mL) was prepared and cooled under nitrogen to -78 °C using a dry-ice/acetone bath. 2-butyne (0.36 mL, 10 equiv) was then added via syringe. HBF₄·Et₂O (0.15 mL, 2 equiv) was added dropwise with stirring. The solution was then allowed to slowly warm overnight to room temperature. All volatile material was removed *in vacuo* and the residue was purified by flash chromatography on silica gel using 7% methanol/dichloromethane. Complex **3c** was obtained as a red powder (0.107 g, 50%). IR (CH₂Cl₂ cast, cm⁻¹) 3014 (m), 2989 (w), 2955 (s), 2914 (m), 2891 (m), 2868 (m), 2846 (m), 1481 (s), 1432 (m), 1394 (m), 1385 (s), 1365 (m), 1282 (w), 1244 (m), 1136 (w), 1071 (s), 1043 (s), 1033 (s), 976 (m), 839 (m), 733 (m), 520 (m); ¹H NMR (400 MHz, CD₂Cl₂) δ 5.00 (d, *J*_{4,5} = 8.3 Hz, 1H, H₄), 4.15 (dd, *J*_{5,4} = 8.3 Hz, *J*_{5,6} = 5.0 Hz, 1H, H₅), 4.05 (dd, *J*_{1-7endo} = *J*_{1-7exo} = 3.5 Hz, 1H,

H₁), 2.64 (ddd, $J_{7\text{endo}-7\text{endo}} = 16.0$ Hz, $J_{7\text{endo}-6} = 11.8$, $J_{7\text{endo}-1} = 4.0$ Hz, 1H, H_{7endo}), 2.15 (ddd, $J_{7\text{exo}-7\text{endo}} = 16.3$ Hz, $J_{7\text{exo}-6} = 5.3$ Hz, $J_{7\text{exo}-1} = 3.2$ Hz, 1H, H_{7exo}), 2.24 (s, 3H, Me₃), 1.88 (s, 3H, Me₄), 1.76 (s, 15H, C₅Me₅), 0.84 (s, 9H, *t*-Bu), 0.21 (ddd, $J_{6-7\text{endo}} = 11.8$, $J_{6-7\text{exo}} = J_{6-5} = 5.2$ Hz, 1H, H₆); ¹H-¹H COSY (400 MHz, CD₂Cl₂) δ 5.00 (H₄) ↔ δ 4.15 (H₅); δ 4.15 (H₅) ↔ δ 0.21 (H₆); δ 4.05 (H₁) ↔ δ 2.64 (H_{7endo}), δ 2.15 (H_{7exo}); δ 2.64 (H_{7endo}) ↔ δ 2.15 (H_{7exo}), δ 0.21 (H₆); δ 2.15 (H_{7exo}) ↔ δ 0.21 (H₆); ¹³C NMR (100 MHz, CD₂Cl₂) δ 111.7 (s, C₃), 105.7 (s, C₂), 98.1 (s, C₅Me₅), 98.1 (d, ¹J_{CH} = 168.3 Hz, C₄); 94.3 (d, ¹J_{CH} = 152.4 Hz, C₅); 84.6 (d, ¹J_{CH} = 150.5 Hz, C₁); 47.9 (d, ¹J_{CH} = 129.2 Hz, C₆); 44.8 (t, ¹J_{CH} = 127.7 Hz, C₇); 31.8 (s, C₈); 27.3 (q, ¹J_{CH} = 125.3 Hz, *t*-Bu); 21.2 (q, ¹J_{CH} = 129.0 Hz, Me); 18.6 (q, ¹J_{CH} = 129.4 Hz, Me); 9.4 (q, ¹J_{CH} = 128.7 Hz, C₅Me₅); ¹H-¹³C HETCORR (100 MHz, CD₂Cl₂) δ 98.1 (C₄) ↔ δ 5.00 (H₄); δ 94.3 (C₅) ↔ δ 4.15 (H₅); δ 84.6 (C₁) ↔ δ 4.05 (H₁); δ 47.9 (C₆) ↔ δ 0.21 (H₆); δ 44.8 (C₇) ↔ δ 2.64 (H_{7endo}), δ 2.15 (H_{7exo}); δ 27.3 (*t*-Bu) ↔ δ 0.84 (*t*-Bu); δ 21.2 (Me) ↔ δ 1.88 (Me); δ 18.6 (Me) ↔ δ 2.24 (Me); δ 9.4 (C₅Me₅) ↔ δ 1.76 (C₅Me₅); Analysis calculated for C₂₃H₃₆BCoF₄: C, 60.28; H, 7.92; found: C, 60.004; H, 7.766.

[(η^5 -C₅Me₅)Co(η^5 -2,3,5,6-Me₄C₇H₅)]⁺ BF₄⁻ **3d**. To a Schlenk flask was added (C₅Me₅)Co(C₂H₄)₂ (0.1662 g, 0.6641 mmol) and hexane (40 mL). Dimethylcyclopentadiene **1d** (0.188 g, 2.0 mmol, 3 equiv) was added to the solution. The light orange solution was then subjected to photolysis for 1h, under a slight nitrogen purge. The solvent was removed *in vacuo* and the residue was extracted with a small amount of pentane. The red pentane extract was filtered through a pad of Celite and the pentane was removed. A red oily residue (0.1673 g, 87%, if pure mixture of isomers) remained and was used directly in the next step.

To a Schlenk flask was added $(C_5Me_5)Co(\eta^4-C_5H_4Me_2)$ (0.0674 g, 0.234 mmol) and dichloromethane (6 mL) under a nitrogen atmosphere. The solution was cooled to $-78^\circ C$ and 2-butyne (0.18 mL, 10 equiv) was added, followed by $HBf_4 \cdot Et_2O$ (76 μL). The solution was allowed to warm slowly to room temperature over a 12 h period and the solvent was removed. The residue was purified by flash chromatography on silica gel, eluting with 5% methanol/dichloromethane. Complex **3d** was obtained as a red solid (0.034 g, 33%, assuming pure diene complex) was obtained. The 1H NMR spectrum of this material was identical to that of authentic $[(C_5Me_5)Co(2,3,5,6-Me_4-\eta^5-C_7H_5)]^+ BF_4^-$ **3d** prepared from $[3 + 2 + 2]$ cycloaddition of $(C_5Me_5)Co(\eta^3-C_3H_5)(OTf)$ and 2-butyne.⁵

$[(\eta^5-MeC_5H_4)Co(3-tert-Bu-4-MeC_7H_7)]^+ BF_4^-$ **5a**. In the drybox, $(C_5H_5)Co(\eta^4-1-MeC_5H_5)$ **4a** (0.1230 g, 0.6025 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where dichloromethane (10 mL) was added. The solution was cooled to $-78^\circ C$ and 3,3-dimethyl-2-pentyne (0.56 mL, 7 equiv) was added, followed by $HBf_4 \cdot Et_2O$ (0.20 mL, 2.2 equiv). Upon addition of the acid, the color of the solution deepened from orange to dark red. The mixture was allowed to warm to room temperature overnight with stirring. All volatile material was removed *in vacuo* and the residue redissolved in dichloromethane (3 mL). The product was precipitated by addition of diethyl ether (20 mL). Recrystallization from dichloromethane/diethyl ether gave pure **5a** as a red solid (0.1983 g, 85%). IR (CH_2Cl_2 cast, cm^{-1}) 3113 (m), 2968 (s), 1695 (w), 1481 (s), 1456 (s), 1416 (m), 1382 (s), 1344 (w), 1308 (w), 1283 (w), 1241 (w), 1173 (w), 1057 (s), 860 (m), 733 (w), 695 (w), 520 (m), 481 (w), 465 (w); 1H NMR (300 MHz, $CDCl_3$) δ 5.48 (br s, 1H, Cp'), 5.38 (br s, 1H, Cp'), 5.30-5.24 (m, ddd by decoupling, $J_{1-2} = 9.6$

Hz, $J_{1-7\text{endo}} = 3.6$ Hz, $J_{1-7\text{exo}} = 2.0$ Hz, 1H, H_1), 5.20-5.14 (m, 2H, Cp' and H_2), 5.04 (br s, 1H, Cp'), 4.96 (dd, $J_{5-6\text{endo}} = 8.4$ Hz, $J_{5-6\text{exo}} = 5.4$ Hz, 1H, H_5), 2.87 (dddd, $J_{7\text{endo}-7\text{exo}} = 17.4$ Hz, $J_{7\text{endo}-6\text{exo}} = 11.7$ Hz, $J_{7\text{endo}-6\text{endo}} = 8.7$ Hz, $J_{7\text{endo}-1} = 3.6$ Hz, 1H, $H_{7\text{endo}}$), 2.37 (s, 3H, Me_4), 2.08 (s, 3H, Cp' Me), 2.02-1.90 (m, ddddd by decoupling, $J_{7\text{exo}-7\text{endo}} = 17$ Hz, $J_{7\text{exo}-6\text{exo}} = 5.9$ Hz, $J_{7\text{exo}-1} = 2.0$ Hz, $J_{7\text{exo}-6\text{endo}} \approx 0.8$ Hz, $J_{7\text{exo}-2} < 1$ Hz, 1H, $H_{7\text{exo}}$), 1.75-1.65 (m, ddddd by decoupling, $J_{6\text{endo}-6\text{exo}} = 12.5$ Hz, $J_{6\text{endo}-5} = J_{6\text{endo}-7\text{endo}} = 8.3$ Hz, $J_{6\text{endo}-2} = 1.8$ Hz, $J_{6\text{endo}-7\text{exo}} \approx 0.8$ Hz, 1H, $H_{6\text{endo}}$), 1.58 (s, 9H, *t*-Bu), 0.057 (dddd, $J_{6\text{exo}-6\text{endo}} = J_{6\text{exo}-7\text{endo}} = 11.6$ Hz, $J_{6\text{exo}-7\text{exo}} = J_{6\text{exo}-5} = 5.7$ Hz, 1H, $H_{6\text{exo}}$); ^1H - ^1H GCOSY (300 MHz, CDCl_3) δ 5.48 (Cp') $\leftrightarrow$ δ 5.38 (Cp'), δ 5.17 (Cp'), δ 5.04 (Cp'), 2.08 (w, Cp' Me); δ 5.38 (Cp') $\leftrightarrow$ δ 5.17 (Cp'), δ 5.04 (Cp'), 2.08 (w, Cp' Me); δ 5.27 (H_1) $\leftrightarrow$ δ 5.17 (H_2), δ 2.87 ($H_{7\text{endo}}$), 1.95 ($H_{7\text{exo}}$), δ 1.70 ($H_{6\text{endo}}$); δ 5.17 (H_2 , Cp') $\leftrightarrow$ δ 5.04 (Cp'), δ 2.87 ($H_{7\text{endo}}$), δ 2.37 (w, Me_4), 1.95 ($H_{7\text{exo}}$), δ 1.70 ($H_{6\text{endo}}$); δ 4.96 (H_5) $\leftrightarrow$ δ 2.37 (w, Me_4), δ 1.70 ($H_{6\text{endo}}$), δ 0.057 ($H_{6\text{exo}}$); δ 2.87 ($H_{7\text{endo}}$) $\leftrightarrow$ δ 1.95 ($H_{7\text{exo}}$), δ 1.70 ($H_{6\text{endo}}$), δ 0.057 ($H_{6\text{exo}}$); δ 1.95 ($H_{7\text{exo}}$) $\leftrightarrow$ δ 0.057 ($H_{6\text{exo}}$); δ 1.70 ($H_{6\text{endo}}$) $\leftrightarrow$ δ 0.057 ($H_{6\text{exo}}$); ^{13}C NMR (100 MHz, CDCl_3) δ 134.3, 106.4, 104.2, 90.2, 87.9, 87.6, 87.00, 86.98, 86.8, 40.8 (C_7), 36.6, 32.3 (*t*-Bu), 25.35 (Me_4 , C_6), 25.26 (Me_4 , C_6), 13.0 ($\text{C}_5\text{H}_4\text{Me}$); HMQC (300 MHz, CDCl_3 , select data only) δ 90.2-86.8 $\leftrightarrow$ δ 5.8-4.6; δ 40.8 (C_7) $\leftrightarrow$ δ 2.87 ($H_{7\text{endo}}$), δ 1.90 ($H_{7\text{exo}}$); δ 32.3 (*t*-Bu) $\leftrightarrow$ δ 1.58 (*t*-Bu); δ 25.35/25.26 (Me_4 , C_6) $\leftrightarrow$ δ 2.37 (Me_4), δ 1.70 ($H_{6\text{endo}}$), δ 0.057 ($H_{6\text{exo}}$); δ 13.0 ($\text{C}_5\text{H}_4\text{Me}$) $\leftrightarrow$ δ 2.08 ($\text{C}_5\text{H}_4\text{Me}$). Electrospray MS m/z calculated for $\text{C}_{18}\text{H}_{26}\text{Co}$ ($\text{M}^+ - \text{BF}_4^-$): 301.136649; found: 301.135900 (100%). Analysis calculated for $\text{C}_{18}\text{H}_{26}\text{BCoF}_4$: C, 55.70; H, 6.75; found: C, 55.383; H, 6.790.

$[(\eta^5\text{-MeC}_5\text{H}_4)\text{Co}(3\text{-(SiMe}_3)\text{-4-MeC}_7\text{H}_7)]^+ \text{BF}_4^-$ **5b.** In the drybox, $(\text{C}_5\text{H}_5)\text{Co}(\eta^4\text{-1-MeC}_5\text{H}_5)$ **4a** (0.0722 g, 0.354 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where dichloromethane (8 mL) was added. The solution was cooled to -78°C and 1-

(trimethylsilyl)propyne (0.105 mL, 2 equiv) was added, followed by $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (0.115 mL, 2.2 equiv). Upon addition of the acid, the color of the solution deepened from orange to dark red. The mixture was allowed to warm to room temperature overnight, with stirring. All volatile material was removed *in vacuo*. The residue was purified by flash chromatography on silica gel, using 5% methanol/dichloromethane as an eluent. A deep red band was collected and dried to give **5b** as an orange solid (0.1131 g, 85%), pure by spectroscopic and combustion analysis. IR (CDCl_3 cast, cm^{-1}) 3111 (w), 2958 (w), 2263 (w), 1694 (w), 1481 (m), 1455 (m), 1435 (m), 1414 (m), 1381 (w), 1344 (w), 1256 (s), 1056 (s), 916 (m), 842 (s), 763 (m), 727 (m), 647 (w), 624 (w), 520 (m), 409 (m); ^1H NMR (360 MHz, CDCl_3) δ 5.64 (br s, 1H, Cp'), 5.4-5.3 (m, 2H, Cp' and H_1), 5.18 (br s, 1H, Cp'), 5.09 (d, $J_{2-1} = 9.6$ Hz, 1H, H_2), 5.01 (dd, $J_{5-6\text{endo}} = 8.1$ Hz, $J_{5-6\text{exo}} = 5.1$ Hz, 1H, H_5), 4.97 (br s, Cp'), 2.94 (m, dddd by decoupling, $J_{7\text{endo}-7\text{exo}} = 17.5$ Hz, $J_{7\text{endo}-6\text{exo}} = 11.2$ Hz, $J_{7\text{endo}-6\text{endo}} = 8.5$ Hz, $J_{7\text{endo}-1} = 3.9$ Hz, 1H, $\text{H}_{7\text{endo}}$), 2.52 (s, 3H, Me_4), 2.06 (s, 3H, Cp' Me), 2.00 (m, dddd by decoupling, $J_{7\text{exo}-7\text{endo}} = 16.9$ Hz, $J_{7\text{exo}-6\text{exo}} = 5.4$ Hz, $J_{7\text{exo}-1} = \text{small}$, $J_{7\text{exo}-6\text{endo}} = \text{small}$, 1H, $\text{H}_{7\text{exo}}$), 1.85 (m, ddddd by decoupling, $J_{6\text{endo}-6\text{exo}} = 12.2$ Hz, $J_{6\text{endo}-7\text{endo}} = J_{6\text{endo}-5} = 8.3$ Hz, $J_{6\text{endo}-1} < 1$ Hz, $J_{6\text{endo}-7\text{exo}} = 0.8$ Hz, 1H, $\text{H}_{6\text{endo}}$), 0.36 (s, 9H, SiMe_3), 0.15 (m, dddd by decoupling, $J_{6\text{exo}-6\text{endo}} = 12.0$ Hz, $J_{6\text{exo}-7\text{endo}} = 12.0$ Hz, $J_{6\text{exo}-7\text{exo}} = 5.9$ Hz, $J_{6\text{exo}-5} = 5.1$ Hz, 1H, $\text{H}_{6\text{exo}}$); ^1H - ^1H GCOSY (300 MHz, CDCl_3) δ 5.64 (Cp') $\leftrightarrow$ δ 5.37 (Cp'), δ 5.18 (Cp'), δ 4.97 (Cp'), δ 2.06 (w, Cp' Me); δ 5.37 (H_1) $\leftrightarrow$ δ 5.09 (H_2), δ 2.94 (w, $\text{H}_{7\text{endo}}$), δ 2.00 (w, $\text{H}_{7\text{exo}}$), δ 1.85 (w, $\text{H}_{6\text{endo}}$); δ 5.34 (Cp') $\leftrightarrow$ δ 5.18 (Cp'), δ 4.97 (Cp'); δ 5.18 (Cp') $\leftrightarrow$ δ 4.97 (Cp'); δ 5.09 (H_2) $\leftrightarrow$ δ 2.00 (w, $\text{H}_{7\text{exo}}$); δ 5.01 (H_5) $\leftrightarrow$ δ 1.85 ($\text{H}_{6\text{endo}}$), δ 0.15 ($\text{H}_{6\text{exo}}$); δ 2.94 ($\text{H}_{7\text{endo}}$) $\leftrightarrow$ δ 2.00 ($\text{H}_{7\text{exo}}$), δ 1.85 ($\text{H}_{6\text{endo}}$), δ 0.15 ($\text{H}_{6\text{exo}}$); δ 2.00 ($\text{H}_{7\text{exo}}$) $\leftrightarrow$ δ 0.15 ($\text{H}_{6\text{exo}}$); δ 1.85 ($\text{H}_{6\text{endo}}$) $\leftrightarrow$ δ 0.15 ($\text{H}_{6\text{exo}}$). Note that no cross peak was observed for δ 2.00 ($\text{H}_{7\text{exo}}$) $\leftrightarrow$ δ 1.85 ($\text{H}_{6\text{endo}}$). ^{13}C NMR (100 MHz, CDCl_3) δ 121.2 (s, C_3), 104.6 (s, Cp' quaternary), 101.5 (s, C_4), 95.8 (d, $^1J_{\text{CH}} = 167.8$ Hz, C_2), 91.9 (d, $^1J_{\text{CH}} = 154.8$ Hz, C_1), 88.6 (d, $^1J_{\text{CH}} = 159.6$ Hz, C_5), 87.4^a (d, $^1J_{\text{CH}} \approx 180$ Hz, Cp'), 86.4 (d, $^1J_{\text{CH}} = 182.7$ Hz, Cp'), 85.4^b (d, $^1J_{\text{CH}} \approx 183$ Hz, Cp'), 41.3 (t, $^1J_{\text{CH}} = 131.3$ Hz, C_7), 27.0 (t, $^1J_{\text{CH}} = 132.9$ Hz, C_6), 22.6 (q, $^1J_{\text{CH}} = 129.1$ Hz, Me_4), 12.7 (q, $^1J_{\text{CH}} = 129.3$ Hz, Cp' Me), -0.10 (q, $^1J_{\text{CH}} = 120.3$ Hz, SiMe_3). ^aSignal obscured in gated spectrum. ^bTwo carbon signals overlap. HMQC (300 MHz, CDCl_3) δ 95.8 (C_2) $\leftrightarrow$ δ 5.09

(H₂); δ 91.9 (C₁) $\leftrightarrow$ δ 5.35 (H₁); δ 88.6 (C₃) $\leftrightarrow$ δ 5.01 (H₅); δ 87.4 (Cp') $\leftrightarrow$ δ 5.18 (Cp'); δ 86.4 (Cp') $\leftrightarrow$ δ 5.64 (Cp'); δ 85.4 (Cp') $\leftrightarrow$ δ 5.35 (Cp'), δ 4.97 (Cp'); δ 41.3 (C₇) $\leftrightarrow$ δ 2.94 (H_{7endo}), δ 2.00 (H_{7exo}); δ 27.0 (C₆) $\leftrightarrow$ δ 1.85 (H_{6endo}), δ 0.15 (H_{6exo}); δ 22.6 (Me₄) $\leftrightarrow$ δ 2.52 (Me₄); δ 12.7 (Cp' Me) $\leftrightarrow$ δ 2.06 (Cp' Me); δ -0.10 (SiMe₃) $\leftrightarrow$ δ 0.36 (SiMe₃); HMBC (300 MHz, CDCl₃) δ 121.2 (C₃) $\leftrightarrow$ δ 5.01 (H₅), δ 2.52 (Me₄); δ 104.6 (Cp') $\leftrightarrow$ δ 5.64 (Cp'), δ 5.35 (Cp'), δ 5.18 (Cp'), δ 4.97 (Cp'), δ 2.06 (Cp' Me); δ 101.5 (C₄) $\leftrightarrow$ δ 5.09 (H₂), δ 5.01 (H₅), δ 2.52 (Me₄), δ 1.85 (H_{6endo}), δ 0.15 (H_{6exo}); δ 95.8 (C₂) $\leftrightarrow$ δ 5.44 (H₁), δ 2.94 (H_{7endo}); δ 91.9 (C₁) $\leftrightarrow$ δ 5.09 (H₂), δ 2.94 (H_{7endo}), δ 1.85 (H_{6endo}); δ 88.6 (C₅) $\leftrightarrow$ δ 2.52 (Me₄), δ 1.85 (H_{6endo}), δ 0.15 (H_{6exo}); δ 87.4/86.4/85.4^a (Cp') $\leftrightarrow$ δ 5.64 (Cp'), δ 5.35 (Cp'), δ 5.18 (Cp'), δ 2.06 (Cp' Me); δ 41.3 (C₇) $\leftrightarrow$ δ 5.09 (H₂), δ 0.15 (H_{6exo}); δ 27.0 (C₆) $\leftrightarrow$ δ 5.01 (H₅), δ 2.94 (H_{7endo}); δ 22.6 (Cp' Me) $\leftrightarrow$ δ 5.18 (Cp'). ^aCarbon signals unresolved. Electrospray MS *m/z* calculated for C₁₇H₂₆CoSi (M⁺-BF₄): 317.113577; found: 317.113890 (100%). Analysis calculated for C₁₇H₂₆BCoF₄Si: C, 50.51; H, 6.48; found: C, 50.331; H, 6.137.

[(η^5 -MeC₅H₄)Co(3,4-(SiMe₃)₂C₇H₇)]⁺ BF₄⁻ **5c.** In the drybox, (C₅H₅)Co(η^4 -1-MeC₅H₅) **4a** (0.1457 g, 0.7137 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where dichloromethane (15 mL) was added. The solution was cooled to -78 °C and bis(trimethylsilyl)acetylene (0.35 mL, 3 equiv) was added, followed by HBF₄•Et₂O (0.231 mL, 2.2 equiv). Upon addition of the acid, the color of the solution deepened from orange to dark red. The mixture was allowed to warm to room temperature overnight, with stirring. All volatile material was removed *in vacuo* and the residue redissolved in dichloromethane (3 mL). The product was precipitated by addition of diethyl ether (20 mL). Recrystallization from dichloromethane/diethyl ether gave pure **5c** as a light orange solid (0.3104 g, 94%). IR (CH₂Cl₂

cast, cm^{-1}) 3096 (w), 2957 (m), 1482 (m), 1455 (m), 1433 (m), 1254 (m), 1054 (s), 981 (m), 867 (s), 834 (s), 761 (m), 699 (w), 638 (w), 627 (w), 520 (m); ^1H NMR (400 MHz, CDCl_3) δ 5.73 (br s, 1H, Cp'), 5.73-5.68 (m, dddd by decoupling, $J_{1-2} = 10.2$ Hz, $J_{1-7\text{endo}} = 3.6$ Hz, $J_{1-7\text{exo}} = 3.2$ Hz, $J_{1-6\text{endo}} < 1$ Hz, 1H, H_1), 5.40 (br s, 1H, Cp'), 5.23 (dd, $J_{5-6\text{endo}} = 8.1$ Hz, $J_{5-6\text{exo}} = 5.6$ Hz, 1H, H_5), 5.21 (br s, 1H, Cp'), 5.08 (d, $J_{2-1} = 10.2$ Hz, 1H, H_2), 4.90 (br s, 1H, Cp'), 3.09 (m, dddd by decoupling, $J_{7\text{endo}-7\text{exo}} = 18.0$ Hz, $J_{7\text{endo}-6\text{exo}} = 11.8$ Hz, $J_{7\text{endo}-6\text{endo}} = 8.3$ Hz, $J_{7\text{endo}-1} = 3.6$ Hz, 1H, $\text{H}_{7\text{endo}}$), 2.23 (s, 3H, Cp' Me), 2.20 (m, obscured by Me, $J_{\text{obs}} \approx 17$ Hz, dddd by decoupling, $J_{7\text{exo}-7\text{endo}} = 17.1$ Hz, $J_{7\text{exo}-6\text{exo}} = 5.9$ Hz, $J_{7\text{exo}-6\text{endo}} = 2.1$ Hz, $J_{7\text{exo}-1} = 3.2$ Hz, 1H, $\text{H}_{7\text{exo}}$), 1.75-1.65 (m, dddd by decoupling, $J_{6\text{endo}-6\text{exo}} = 11.9$ Hz, $J_{6\text{endo}-7\text{endo}} = 8.3$ Hz, $J_{6\text{endo}-5} = 8.1$ Hz, $J_{6\text{endo}-7\text{exo}} = 2.1$ Hz, 1H, $\text{H}_{6\text{endo}}$), 0.55 (s, 9H, SiMe_3), 0.41 (s, 9H, SiMe_3), 0.042 (dddd, $J_{6\text{exo}-6\text{endo}} = J_{6\text{exo}-7\text{endo}} = 12.6$ Hz, $J_{6\text{exo}-7\text{exo}} = J_{6\text{exo}-5} = 6.3$ Hz, 1H, $\text{H}_{6\text{exo}}$); ^1H - ^1H GCOSY (300 MHz, CDCl_3) δ 5.73 (Cp') $\leftrightarrow$ δ 5.40 (Cp'), δ 5.21 (Cp'), δ 4.90 (Cp'); δ 5.70 (H_1) $\leftrightarrow$ δ 5.08 (H_2), δ 3.09 ($\text{H}_{7\text{endo}}$), δ 2.20 (w, $\text{H}_{7\text{exo}}$), δ 1.70 ($\text{H}_{6\text{endo}}$); δ 5.40 (Cp') $\leftrightarrow$ δ 5.21 (Cp'), δ 4.90 (Cp'); δ 5.23 (H_5) $\leftrightarrow$ δ 1.70 ($\text{H}_{6\text{endo}}$), δ 0.04 ($\text{H}_{6\text{exo}}$); δ 5.21 (Cp') $\leftrightarrow$ δ 4.90 (Cp'); δ 5.08 (H_2) $\leftrightarrow$ δ 2.20 (w, $\text{H}_{7\text{exo}}$); δ 3.09 ($\text{H}_{7\text{endo}}$) $\leftrightarrow$ δ 2.20 ($\text{H}_{7\text{exo}}$), δ 1.70 ($\text{H}_{6\text{endo}}$), δ 0.04 ($\text{H}_{6\text{exo}}$); δ 2.20 ($\text{H}_{7\text{exo}}$) $\leftrightarrow$ δ 0.04 ($\text{H}_{6\text{exo}}$); δ 1.70 ($\text{H}_{6\text{endo}}$) $\leftrightarrow$ δ 0.04 ($\text{H}_{6\text{exo}}$); ^{13}C NMR (100 MHz, CDCl_3 , $^1J_{\text{CH}}$ values obtained from HMQC spectrum) δ 119.9 (s, C_3), 106.8 (s, C_4), 105.0 (s, Cp' ring quaternary), 99.4 (d, $^1J_{\text{CH}} = 168$ Hz, C_2), 95.3 (d, $^1J_{\text{CH}} = 156$ Hz, C_1), 91.7 (d, $^1J_{\text{CH}} = 158$ Hz, Cp'), 88.1 (d, $^1J_{\text{CH}} = 184$ Hz, Cp'), 86.6 (d, $^1J_{\text{CH}} = 182$ Hz, Cp'), 85.0^a (d, $^1J_{\text{CH}} = 186$ Hz, C_5), 84.6 (d, $^1J_{\text{CH}} = 184$ Hz, Cp'), 42.2 (t, $^1J_{\text{CH}} = 128$ Hz, C_7), 26.5 (t, $^1J_{\text{CH}} = 133$ Hz, C_6), 13.5 (q, $^1J_{\text{CH}} = 128$ Hz, Cp' Me), 2.2 (q, $^1J_{\text{CH}} = 117$ Hz, SiMe_3), 1.6 (q, $^1J_{\text{CH}} = 120$ Hz, SiMe_3). ^a J value appears abnormally large. HMQC (300 MHz, CDCl_3) δ 99.4 (C_2) $\leftrightarrow$ δ 5.08 (H_2); δ 95.3 (C_1) $\leftrightarrow$ δ 5.70 (H_1); δ 91.7 (Cp') $\leftrightarrow$ δ 5.21 (Cp'); δ 88.1 (Cp') $\leftrightarrow$ δ 5.40 (Cp'); δ 86.6 (Cp') $\leftrightarrow$ δ 5.73 (Cp'); δ 85.0 (C_5) $\leftrightarrow$ δ 5.23 (H_5); δ 84.6 (Cp') $\leftrightarrow$ δ 4.90 (Cp'); δ 42.2 (C_7) $\leftrightarrow$ δ 3.09 ($\text{H}_{7\text{endo}}$), δ 2.20 ($\text{H}_{7\text{exo}}$); δ 26.5 (C_6) $\leftrightarrow$ δ 1.70 ($\text{H}_{6\text{endo}}$), δ 0.04 ($\text{H}_{6\text{exo}}$); δ 13.5 (Cp' Me) $\leftrightarrow$ δ 2.23 (Cp' Me); δ 2.2 (SiMe_3) $\leftrightarrow$ δ 0.55 (SiMe_3); δ 1.6 (SiMe_3) $\leftrightarrow$ δ 0.41 (SiMe_3). Analysis calculated for $\text{C}_{19}\text{H}_{32}\text{BCoF}_4\text{Si}_2$: C, 49.36; H, 6.98; found: C, 49.192; H, 7.115.

$[(\eta^5\text{-MeC}_5\text{H}_4)\text{Co}(3\text{-tert-BuC}_7\text{H}_8)]^+ \text{BF}_4^-$ **5d** and $[(\text{C}_5\text{H}_5)\text{Co}(1\text{-Me-3-tert-BuC}_7\text{H}_7)]^+ \text{BF}_4^-$. In the drybox, $(\text{C}_5\text{H}_5)\text{Co}(\eta^4\text{-1-MeC}_5\text{H}_5)$ **4a** (0.1463 g, 0.7166 mmol) was weighed into a Schlenk flask and removed to the Schlenk line, where dichloromethane (12 mL) was added. The solution was cooled to -78°C and 3,3-dimethyl-1-butyne (0.62 mL, 7 equiv) was added, followed by $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.23 mL, 2.2 equiv). Upon addition of the acid, the color of the solution deepened from orange to dark red. The mixture was allowed to warm to room temperature overnight with stirring. All volatile material was removed *in vacuo* and the residue redissolved in dichloromethane (3 mL) and filtered through a Celite pad. The product was precipitated by addition of diethyl ether (20 mL). Recrystallization from dichloromethane/ diethyl ether gave an orange powder (0.2364 g, 88%). The product consisted of a 4:1 mixture of $(\text{C}_5\text{H}_4\text{Me})\text{Co}(3\text{-tert-BuC}_7\text{H}_8)$ **5d** and $(\text{C}_5\text{H}_5)\text{Co}(1\text{-Me-3-tert-BuC}_7\text{H}_7)$. Major isomer **5d**: IR (CH_2Cl_2 cast, cm^{-1}) 3114 (m), 2968 (m), 2876 (m), 1497 (w), 1480 (m), 1411 (m), 1374 (m), 1266 (w), 1053 (s), 871 (m), 735 (m), 699 (w), 521 (m), 466 (w); ^1H NMR (300 MHz, CDCl_3) δ 5.51 (t, $J = 1.9$ Hz, 2H, Cp'H), 5.46 (d, $J = 9.0$ Hz, 2H, $\text{H}_{2/4}$), 5.38 (t, $J = 2.0$ Hz, 2H, Cp'), 5.30-5.20 (m, 2H, $\text{H}_{1/5}$), 2.50-2.40 (m, 2H, $\text{H}_{6\text{endo}/7\text{endo}}$), 2.00 (s, 3H, Me), 1.56 (s, 9H, *t*-Bu), 1.25-1.15 (m, 2H, $\text{H}_{6\text{exo}/7\text{exo}}$); ^1H - ^1H GCOSY (300 MHz, CDCl_3) δ 5.51 (Cp') $\leftrightarrow$ δ 5.38 (Cp'); δ 5.46 ($\text{H}_{2/4}$) $\leftrightarrow$ δ 5.25 ($\text{H}_{1/5}$); δ 5.25 ($\text{H}_{1/5}$) $\leftrightarrow$ δ 2.45 ($\text{H}_{6/7\text{endo}}$), δ 1.20 ($\text{H}_{6/7\text{exo}}$); δ 2.45 ($\text{H}_{6/7\text{endo}}$) $\leftrightarrow$ δ 1.20 ($\text{H}_{6/7\text{exo}}$); ^{13}C NMR (100 MHz, CDCl_3) δ 132.7 (C_3), 129.2 (Cp' quaternary), 89.6 ($\text{C}_{2/4}$), 87.5 (Cp'), 87.0 (Cp'), 85.4 ($\text{C}_{1/5}$), 36.5 (*t*-Bu quaternary), 33.7 ($\text{C}_{6/7}$), 31.2 (*t*-Bu), 13.2 (Cp' Me). Data for minor isomer, $[(\text{C}_5\text{H}_5)\text{Co}(1\text{-Me-3-tert-Bu-(1-5)\eta^5\text{-cycloheptadienyl}})]^+ [\text{BF}_4]^-$: ^1H NMR (300 MHz, CDCl_3 , partial data only) δ 5.58 (s, 1H, H_2), 5.43 (s, 5H, Cp), 5.40-5.35 (m, obscured, 2H, $\text{H}_{4/5}$), 2.80 (dddd, $J = 15.9, 8.4, 8.4, 4.5$ Hz, 1H, $\text{H}_{7\text{endo}}$), 2.06-1.92 (m, obscured by Me), 1.84-1.76 (m, obscured by *t*-Bu), 1.84 (s, 3H, Me), 1.58 (s, 9H, *t*-Bu), 0.83 (ddd, $J = 14.1, 8.4, 6.0$ Hz, 1H, $\text{H}_{6\text{exo}}$); ^1H - ^1H GCOSY (300

MHz, CDCl₃) δ 5.58 (H₂) $\leftrightarrow$ δ 5.37 (w, H_{4/5}), δ 1.84 (w, Me); δ 5.37 (H_{4/5}) $\leftrightarrow$ δ 2.80 (H_{7endo}); δ 2.80 (H_{7endo}) $\leftrightarrow$ δ 2.00 (H_{7exo}), δ 1.80 (H_{6endo}), δ 0.83 (H_{6exo}); δ 2.00 (H_{7exo}) $\leftrightarrow$ δ 1.80 (H_{6endo}), δ 0.83 (H_{6exo}); δ 1.80 (H_{6endo}) $\leftrightarrow$ δ 0.83 (H_{6exo}). Analysis calculated for C₁₇H₂₄BCoF₄: C, 54.58; H, 6.47; found: C, 54.614; H, 6.326.

Table 2. Comparative ¹H NMR Spectroscopic Data for Methylcyclopentadienyl-derived η^5 -Cycloheptadienyl Complexes

	5a	5b	5c	5d
H₁ <i>J</i> ₁₋₂	5.27 (m) 9.6 Hz	5.35 (m) 9.6	5.70 (m) 10.2	5.15 (m) 9.0 Hz
H₂ <i>J</i> ₂₋₃	5.17 (m) b	5.09 (d) b	5.08 (d) b	5.46 (d) b
H₄ <i>J</i> ₄₋₅	b	b	b	5.46 (d) 9.0 Hz
H₅ <i>J</i> _{5-6endo} <i>J</i> _{5-6exo}	4.96 (dd) 8.4 5.4	5.01 (dd) 8.1 5.1	5.23 (dd) 8.1 5.6	5.15 (m) a a
H_{6endo} <i>J</i> _{6endo-6exo} <i>J</i> _{6endo-7endo} <i>J</i> _{6endo-7exo}	1.70 (m) 12.5 8.3 0.8	1.85 (m) 12.2 8.3 0.8	1.65 (m) 12.6 8.3 2.1	2.45 (m) a a a
H_{6exo} <i>J</i> _{6exo-7endo} <i>J</i> _{6exo-7exo}	0.06 11.6 5.7	0.15 (m) 12.0 5.9	0.04(dddd) 12.6 5.9	1.20 (m) a a
H_{7endo} <i>J</i> _{7endo-7exo} <i>J</i> _{7endo-1}	2.87 (dddd) 17.4 3.6	2.94 (m) 17.5 3.9	3.09 (m) 18.0 3.6	2.45 (m) a a
H_{7exo} <i>J</i> _{7exo-1}	1.98 (m) 2.0	2.00 (m) small	2.20 (m) 3.2	1.20 (m) a

^a Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. ^b Not applicable due to a non-hydrogen substituent.

$[(\eta^5\text{-}tert\text{-BuC}_5\text{H}_4)\text{Co}(\eta^5\text{-}3\text{-}tert\text{-Bu-4-MeC}_7\text{H}_8)]^+ \text{BF}_4^-$ **6a.** A solution of $(\text{C}_5\text{H}_5)\text{Co}(\eta^4\text{-}1\text{-}tert\text{-BuC}_5\text{H}_5)$ **4b** (46.6 mg, 0.189 mmol) in dichloromethane (4 mL) was cooled to -78°C . To the solution was added 4,4-dimethyl-2-pentyne (0.18 mL, 7 equiv), followed by $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (61.3 mL, 2.2 equiv). The color of the red solution deepened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period. Removal of the solvent was followed by flash chromatography on silica gel using 5% methanol/dichloromethane. Recrystallization from dichloromethane/diethyl ether gave complex **6a** as a light orange powder (57 mg, 70%). IR (CH_2Cl_2 cast, cm^{-1}) 3112 (w), 2964 (m), 1484 (m), 1468 (w), 1384 (w), 1369 (w), 1274 (w), 1242 (w), 1173 (w), 1152 (w), 1054 (s), 904 (w), 858 (w), 733 (w), 694 (w), 520 (w), 488 (w); ^1H NMR (300 MHz, CDCl_3) δ 5.58-5.57 (m, 1H, Cp^i), 5.49 (m, dddd by decoupling, $J_{1-2} = 9.5$ Hz, $J_{1-7\text{endo}} = 4.0$ Hz, $J_{1-7\text{exo}} < 2$ Hz, $J_{1-6\text{exo}} < 2$ Hz, 1H, H_1), 5.33 (dd, $J_{2-1} = 9.5$ Hz, $J_{2-7\text{exo}} = 0.8$ Hz, 1H, H_2), 5.27-5.24 (m, 1H, Cp^i), 5.24-5.20 (m, 1H, Cp^i), 5.10 (dd, $J_{5-6\text{endo}} = 8.4$ Hz, $J_{5-6\text{exo}} = 4.8$ Hz, 1H, H_5), 4.96-4.94 (m, 1H, Cp^i), 2.89 (dddd, $J_{7\text{endo-}7\text{exo}} = 17.3$ Hz, $J_{7\text{endo-}6\text{exo}} \approx J_{7\text{endo-}6\text{exo}} \approx 9$ Hz, $J_{7\text{endo-}1} = 4$ Hz, 1H, $\text{H}_{7\text{endo}}$), 2.41 (s, 3H, Me_4), 1.93 (m, dddd by decoupling, $J_{7\text{exo-}7\text{endo}} = 17.1$ Hz, $J_{7\text{exo-}6\text{exo}} = 6.3$ Hz, $J_{7\text{exo-}1} < 2$ Hz, $J_{7\text{exo-}2} < 2$ Hz, 1H, $\text{H}_{7\text{exo}}$), 1.75-1.65 (m, 1H, $\text{H}_{6\text{endo}}$), 1.63 (s, 9H, C_3 *t*-Bu), 1.40 (s, 9H, Cp^i *t*-Bu), 0.20 (dddd, $J_{6\text{exo-}6\text{endo}} = 12.7$ Hz, $J_{6\text{exo-}7\text{endo}} = 11.5$ Hz, $J_{6\text{exo-}7\text{exo}} = 6.5$ Hz, $J_{6\text{exo-}5} = 7$ Hz, 1H, $\text{H}_{6\text{exo}}$); ^1H - ^1H GCOSY (300 MHz, CDCl_3) δ 5.57 (Cp^i) $\leftrightarrow$ δ 5.24 (Cp^i), δ 5.20 (Cp^i), δ 4.94 (Cp^i); δ 5.49 (H_1) $\leftrightarrow$ δ 5.33 (H_2), δ 2.89 ($\text{H}_{7\text{endo}}$), δ 1.93 ($\text{H}_{7\text{exo}}$), δ 1.65 (w, $\text{H}_{6\text{endo}}$); δ 5.33 (H_2) $\leftrightarrow$ δ 2.41 (Me), δ 1.93 ($\text{H}_{7\text{exo}}$); δ 5.24 (Cp^i) $\leftrightarrow$ δ 5.20 (Cp^i), δ 4.94 (Cp^i); δ 5.10 (H_1) $\leftrightarrow$ δ 2.89 ($\text{H}_{7\text{endo}}$), δ 2.41 (Me_4), δ 1.63 (C_3 *t*-Bu), δ 0.20 (H_{endo}); δ 2.89 ($\text{H}_{7\text{endo}}$) $\leftrightarrow$ δ 1.93 ($\text{H}_{7\text{exo}}$), δ 1.65 (w, $\text{H}_{6\text{endo}}$), δ 0.20 (H_{endo}); δ 1.93 ($\text{H}_{7\text{exo}}$) $\leftrightarrow$ δ 1.65 (w, $\text{H}_{6\text{endo}}$), δ 0.20 (H_{endo}); δ 1.65 ($\text{H}_{6\text{endo}}$) $\leftrightarrow$ δ 0.20 (H_{endo}); ^{13}C NMR (100 MHz, CDCl_3) δ 136.4 (s, C_3), 120.1 (s, Cp^i ring quaternary), 106.5 (s, C_4), 89.3 (dd, $^1J_{\text{CH}} = 167.8$ Hz, $^2J_{\text{CH}} = 9.2$ Hz, C_2), 86.5 (dd,

$^1J_{\text{CH}} = 181.7 \text{ Hz}$, $^2J_{\text{CH}} = 6.1 \text{ Hz}$, Cp^{I}), 85.3^{a} (d, $^1J_{\text{CH}} = 177.7 \text{ Hz}$), 85.2^{a} (d, $^1J_{\text{CH}} = 179.4 \text{ Hz}$), 84.5 (dd, $^1J_{\text{CH}} = 180.3 \text{ Hz}$, $^2J_{\text{CH}} = 5.9 \text{ Hz}$, Cp^{I}), 84.2 (d, $^1J_{\text{CH}} = 157.3 \text{ Hz}$, C_1), 41.1 (t, $^1J_{\text{CH}} = 136.1 \text{ Hz}$, C_7), 36.8 (s, C_3 $t\text{-Bu}$ quaternary), 32.2 (q, $^1J_{\text{CH}} = 127.1 \text{ Hz}$, C_3 $t\text{-Bu}$), 31.6 (s, Cp^{I} $t\text{-Bu}$ quaternary), 31.0 (q, $^1J_{\text{CH}} = 126.2 \text{ Hz}$, Cp^{I} $t\text{-Bu}$), 25.8 (t, $^1J_{\text{CH}} = 132.3 \text{ Hz}$, C_6), 25.6 (q, $^1J_{\text{CH}} = 129.3 \text{ Hz}$, Me_4). ^a2 carbons overlap for one of these signals. C_5 and 2 C's for the Cp ring resonate at these 2 positions. HMQC (300 MHz, CDCl_3) δ 89.3 (C_2) $\leftrightarrow$ δ 5.33 (H_2); δ 86.5 (Cp^{I}) $\leftrightarrow$ δ 5.20 (Cp^{I}); δ 85^a (C_5 , Cp^{I}) $\leftrightarrow$ δ 5.24 (Cp^{I}), δ 5.10 (H_5), δ 4.94 (Cp^{I}); δ 84.5 (Cp^{I}) $\leftrightarrow$ δ 5.57 (Cp^{I}); δ 84.2 (C_1) $\leftrightarrow$ δ 5.49 (H_1); δ 41.1 (C_7) $\leftrightarrow$ δ 2.89 ($\text{H}_{7\text{endo}}$), δ 1.93 ($\text{H}_{7\text{exo}}$); δ 32.2 (C_3 $t\text{-Bu}$) $\leftrightarrow$ δ 1.63 (C_3 $t\text{-Bu}$); δ 31.0 (Cp^{I} $t\text{-Bu}$) $\leftrightarrow$ δ 1.40 (Cp^{I} $t\text{-Bu}$); δ 25.8 (C_6) $\leftrightarrow$ δ 1.65 ($\text{H}_{6\text{exo}}$), δ 0.20 ($\text{H}_{6\text{exo}}$); δ 25.6 (Me_4) $\leftrightarrow$ δ 2.41 (Me_4). ^aUnresolved signals in ^{13}C spectrum. HMBC (300 MHz, CDCl_3) δ 136.4 (C_3) $\leftrightarrow$ δ 5.10 (H_5), δ 2.41 (Me_4), δ 1.63 (C_3 $t\text{-Bu}$); δ 120.1 (Cp^{I} $t\text{-Bu}$ ring quaternary) $\leftrightarrow$ δ 5.57 (Cp^{I}), δ 5.24 (Cp^{I}), δ 5.20 (Cp^{I}), δ 4.94 (Cp^{I}), δ 1.40 (C_3 $t\text{-Bu}$); δ 106.5 (C_4) $\leftrightarrow$ δ 5.33 (H_2), δ 2.41 (Me_4), δ 0.20 ($\text{H}_{6\text{exo}}$); δ 89.3 (Cp^{I}) $\leftrightarrow$ δ 5.57 (Cp^{I}); δ 86.5 (Cp^{I}) $\leftrightarrow$ δ 5.57 (Cp^{I}), δ 5.24 (Cp^{I}), δ 4.94 (Cp^{I}); δ 85^a $\leftrightarrow$ δ 5.57 (Cp^{I}), δ 5.24 (Cp^{I}), δ 5.20 (Cp^{I}), δ 4.94 (Cp^{I}), δ 2.41 (Me_4), δ 0.20 ($\text{H}_{6\text{exo}}$); δ 84^b $\leftrightarrow$ δ 5.24 (Cp^{I}), δ 5.20 (Cp^{I}), δ 4.94 (Cp^{I}), δ 2.89 ($\text{H}_{7\text{endo}}$); δ 41.1 (C_7) $\leftrightarrow$ δ 5.33 (H_2), δ 5.10 (H_5), δ 0.20 ($\text{H}_{6\text{exo}}$); δ 36.8 (C_3 $t\text{-Bu}$ quaternary) $\leftrightarrow$ δ 5.33 (H_2), δ 1.63 (C_3 $t\text{-Bu}$); δ 31.0 (Cp^{I} $t\text{-Bu}$ quaternary) $\leftrightarrow$ δ 1.40 (C_3 $t\text{-Bu}$); δ 25^c $\leftrightarrow$ δ 5.10 (H_5), δ 2.89 ($\text{H}_{7\text{endo}}$). ^aSignals at 85.3 and 85.2 (C_5 and Cp^{I}) overlap. ^bSignals at 84.5 (Cp^{I}) and 84.2 (C_1) overlap. ^cSignals at 25.8 (C_6) and 25.6 (C_{10}) overlap. Analysis calculated for $\text{C}_{21}\text{H}_{32}\text{BCoF}_4$: C, 58.63; H, 7.51; found: C, 58.484; H, 7.729.

$[(\eta^5\text{-tert-BuC}_5\text{H}_4)\text{Co}(\eta^5\text{-3-(Me}_3\text{Si)-4-MeC}_7\text{H}_7)]^+ \text{BF}_4^-$ 6b. In the drybox, $(\text{C}_5\text{H}_5)\text{Co}(\eta^4\text{-1-tert-BuC}_5\text{H}_5)$ **4b** (34.7 mg, 0.141 mmol) was weighed into a Schlenk flask. The compound was

dissolved in degassed dichloromethane (5 mL) and cooled to $-78\text{ }^{\circ}\text{C}$. To the solution was added 1-trimethylsilylpropyne (0.15 mL, 7 equiv), followed by $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (0.46 μL , 2.2 equiv). The color of the red solution deepened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period. The solvent was removed and the crude residue was redissolved in dichloromethane (3 mL) and filtered through a Celite column. Addition of diethyl ether (50 mL) precipitated complex **6b** as an orange solid (45.6 mg, 72%), pure by NMR spectroscopy. Recrystallization from dichloromethane/diethyl ether gave analytically pure orange-red crystals (29.6 mg, 47%). IR (CH_2Cl_2 cast, cm^{-1}) 3113 (w), 2962 (m), 1486 (m), 1468 (m), 1434 (m), 1384 (m), 1266 (m), 1151 (m), 1053 (s), 978 (m), 912 (m), 838 (s), 761 (m), 724 (w), 697 (w), 622 (w), 520 (m); ^1H NMR (400 MHz, CDCl_3) δ 5.67 (br d, dddd by decoupling, $J_{1-2} = 9.3\text{ Hz}$, $J_{1-7\text{exo}} = J_{1-7\text{endo}} = 3.5\text{ Hz}$, $J_{1-6\text{endo}} < 2\text{ Hz}$, 1H, H_1), 5.55-5.40 (m, 2H, Cp^i), 5.46-5.43 (m, 1H, Cp^i), 5.22 (d, $J_{2-1} = 9\text{ Hz}$, 1H, H_2), 5.19 (dd, $J_{5-6\text{endo}} = 8.2\text{ Hz}$, $J_{5-6\text{exo}} = 5.0\text{ Hz}$, 1H, H_5), 5.03-5.00 (m, 1H, Cp^i), 2.99 (m, dddd by decoupling, $J_{7\text{endo}-7\text{exo}} = 17.6\text{ Hz}$, $J_{7\text{endo}-6\text{exo}} = 11.7\text{ Hz}$, $J_{7\text{endo}-6\text{endo}} = 9.7\text{ Hz}$, $J_{7\text{endo}-1} = 3.5\text{ Hz}$, 1H, $\text{H}_{7\text{endo}}$), 2.60 (s, 3H, Me_4), 2.01 (br d, dddd by decoupling, $J_{7\text{exo}-7\text{endo}} = 17.6\text{ Hz}$, $J_{7\text{exo}-6\text{exo}} = 5.8\text{ Hz}$, $J_{7\text{exo}-1} = 3.5\text{ Hz}$, $J_{7\text{exo}-6\text{endo}} < 2\text{ Hz}$, 1H, $\text{H}_{7\text{exo}}$), 1.80 (m, dddd by decoupling, $J_{6\text{endo}-6\text{exo}} = 11.7\text{ Hz}$, $J_{6\text{endo}-7\text{endo}} = 9.7\text{ Hz}$, $J_{6\text{endo}-5} = 8.2\text{ Hz}$, $J_{6\text{endo}-7\text{exo}} < 2\text{ Hz}$, $J_{6\text{endo}-1} = 2\text{ Hz}$, 1H, $\text{H}_{6\text{endo}}$), 1.30 (s, 9H, $\text{Cp}^i\text{'Bu}$), 0.41 (s, 9H, SiMe_3), 0.23 (dddd, $J_{6\text{exo}-6\text{endo}} = J_{6\text{exo}-7\text{endo}} = 11.7\text{ Hz}$, $J_{6\text{exo}-7\text{exo}} = 5.8\text{ Hz}$, $J_{6\text{exo}-5} = 5.0\text{ Hz}$, 1H, $\text{H}_{6\text{exo}}$); ^1H - ^1H GCOSY (300 MHz, CDCl_3) δ 5.67 (H_1) $\leftrightarrow$ δ 5.22 (H_2), δ 2.99 ($\text{H}_{7\text{endo}}$), δ 2.01 ($\text{H}_{7\text{exo}}$), δ 1.80 (w, $\text{H}_{6\text{endo}}$); δ 5.47 (Cp^i) $\leftrightarrow$ δ 5.02 (Cp^i); δ 5.45 (Cp^i) $\leftrightarrow$ δ 5.02 (Cp^i); δ 5.22 (H_2) $\leftrightarrow$ δ 2.60 (w, Me_4), δ 2.01 ($\text{H}_{7\text{exo}}$); δ 5.19 (H_5) $\leftrightarrow$ δ 1.80 ($\text{H}_{6\text{endo}}$), δ 0.23 ($\text{H}_{6\text{exo}}$); δ 2.99 ($\text{H}_{7\text{endo}}$) $\leftrightarrow$ δ 2.01 ($\text{H}_{7\text{exo}}$), δ 1.80 ($\text{H}_{6\text{endo}}$), δ 0.23 ($\text{H}_{6\text{exo}}$); δ 2.01 ($\text{H}_{7\text{exo}}$) $\leftrightarrow$ δ 0.23 ($\text{H}_{6\text{exo}}$); δ 1.80 ($\text{H}_{6\text{endo}}$) $\leftrightarrow$ δ 0.23 ($\text{H}_{6\text{exo}}$); ^{13}C NMR (75 MHz, CDCl_3) δ 122.3 (s, C_3), 119.6 (s, Cp^i ring quaternary), 102.2 (s, C_4), 94.6 (d, $^1J_{\text{CH}} = 164.9\text{ Hz}$, C_2), 89.2 (d, $^1J_{\text{CH}} = 155.4\text{ Hz}$, C_1), 87.7 (d, $^1J_{\text{CH}} = 155.5\text{ Hz}$, C_5), 85.7 (d, $^1J_{\text{CH}} = 183.5\text{ Hz}$, Cp^i), 85.2 (d, $^1J_{\text{CH}} = 180.2\text{ Hz}$, Cp^i), 84.3 (d, $^1J_{\text{CH}} = 182.5\text{ Hz}$, Cp^i), 83.8 (d, $^1J_{\text{CH}} = 178.9\text{ Hz}$, Cp^i), 41.9 (t, $^1J_{\text{CH}} = 130.8\text{ Hz}$, C_7), 31.6 (s, 'Bu quaternary), 30.9 (q, $^1J_{\text{CH}} = 126.9\text{ Hz}$, 'Bu), 27.3 (t, $^1J_{\text{CH}} = 131.1\text{ Hz}$, C_6), 23.3 (q, $^1J_{\text{CH}} = 132.7\text{ Hz}$, Me_4), 0.05 (q, $^1J_{\text{CH}} = 120.1\text{ Hz}$, SiMe_3); HMQC (300 MHz, CDCl_3) δ 94.6 (C_2)

$\leftrightarrow \delta$ 5.22 (H_2); δ 89.2 (C_1) $\leftrightarrow \delta$ 5.67 (H_1); δ 87.7 (C_5) $\leftrightarrow \delta$ 5.19 (H_5); δ 85.7 (Cp^l) $\leftrightarrow \delta$ 5.52 (Cp^l); δ 85.2 (Cp^l) $\leftrightarrow \delta$ 5.44 (Cp^l); δ 84.3 (Cp^l) $\leftrightarrow \delta$ 5.02 (Cp^l); δ 83.8 (Cp^l) $\leftrightarrow \delta$ 5.50 (Cp^l); δ 41.9 (C_7) $\leftrightarrow \delta$ 2.99 (H_{7endo}), δ 2.01 (H_{7exo}); δ 30.9 (t -Bu) $\leftrightarrow \delta$ 1.30 (t -Bu); δ 27.3 (C_6) $\leftrightarrow \delta$ 1.80 (H_{6endo}), δ 0.23 (H_{6exo}); δ 23.3 (Me_4) $\leftrightarrow \delta$ 2.60 (Me_4); δ 0.05 ($SiMe_3$) $\leftrightarrow \delta$ 0.41 ($SiMe_3$); HMBC (300 MHz, $CDCl_3$) δ 122.3 (C_3) $\leftrightarrow \delta$ 5.22 (H_2), δ 5.19 (H_5), δ 2.60 (Me_4); δ 119.6 (Cp^l ring quaternary) $\leftrightarrow \delta$ 5.50 (Cp^l), δ 5.40 (Cp^l), δ 1.30 (t -Bu); δ 102.2 (C_4) $\leftrightarrow \delta$ 5.22 (H_2), δ 2.60 (Me_4), δ 1.80 (H_{6endo}), δ 0.23 (H_{6exo}); δ 94.6 (C_2) $\leftrightarrow \delta$ 2.60 (Me_4); δ 89.2 (C_1) $\leftrightarrow \delta$ 1.80 (H_{6endo}); δ 87.7 (C_5) $\leftrightarrow \delta$ 1.80 (H_{6endo}), δ 0.23 (H_{6exo}); δ 85.7^a, δ 85.2^a, δ 84.3^a, δ 83.8^a $\leftrightarrow \delta$ 5.50 (Cp^l), δ 5.43 (Cp^l), δ 5.00 (Cp^l); δ 41.9 (C_7) $\leftrightarrow \delta$ 5.22 (H_2), δ 5.19 (H_5), δ 2.60 (Me_4), δ 1.80 (H_{6endo}), δ 0.23 (H_{6exo}); δ 30.9 (t -Bu) $\leftrightarrow \delta$ 1.30 (t -Bu); δ 27.3 (C_6) $\leftrightarrow \delta$ 5.19 (H_5); δ 23.3 (Me_4) $\leftrightarrow \delta$ 5.22 (H_2); δ 0.05 ($SiMe_3$) $\leftrightarrow \delta$ 0.41 ($SiMe_3$). Analysis calculated for $C_{20}H_{32}BCoF_4Si$: C, 53.82; H, 7.23; found: C, 53.434; H, 6.884.

^aResolution of these signals is poor.

$[(\eta^5\text{-}tert\text{-BuC}_5\text{H}_4)\text{Co}(\eta^5\text{-}3,4\text{-(Me}_3\text{Si)}_2\text{C}_7\text{H}_7)]^+ \text{BF}_4^-$ **6c**. In the drybox, $(C_5H_5)Co(\eta^4\text{-}1\text{-}tert\text{-BuC}_5\text{H}_5)$ **4b** (102.9 mg, 0.4179 mmol) was weighed into a Schlenk flask. The compound was dissolved in degassed dichloromethane (20 mL) and cooled to -78°C . To the solution was added bis(trimethylsilyl)acetylene (0.47 mL, 5 equiv), followed by $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (0.135 mL, 2.2 equiv). The color of the red solution deepened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period. The solvent was removed and the crude residue was re-dissolved in dichloromethane (5 mL) and filtered through a Celite column. Addition of diethyl ether (100 mL) gave an orange precipitate (165.9 mg, 79%), pure by NMR spectroscopy. Recrystallization from dichloromethane/diethyl ether gave **6c** as orange-red crystals (156.4 mg,

74%). Crystals suitable for X-ray crystallographic analysis were grown by layering diethyl ether on top of a dichloromethane solution. Full data on this crystal structure is provided as an appendix (vide infra). IR (CH₂Cl₂ cast, cm⁻¹) 3116 (w), 2961 (m), 1486 (m), 1457 (m), 1393 (m), 1365 (w), 1254 (s), 1151 (m), 1055 (s), 979 (m), 906 (m), 866 (s), 834 (s), 760 (m), 698 (w), 638 (w), 520 (m); ¹H NMR (400 MHz, CDCl₃) δ 5.94 (br d, $J_{\text{obs}} = 9$ Hz, dddd by decoupling, $J_{1-2} = 9.2$ Hz, $J_{1-7\text{endo}} = J_{1-7\text{exo}} = 3.3$ Hz, $J_{1-6\text{endo}} < 2$ Hz, 1H, H₁), 5.84-5.85 (narrow m, 1H, Cp^b), 5.33 (dd, $J_{5-6\text{endo}} = 8.2$ Hz, $J_{5-6\text{exo}} = 5.2$ Hz, 1H, H₅), 5.28 (d, $J_{2-1} = 9.2$ Hz, 1H, H₂), 5.20-5.22 (narrow m, 1H, Cp^b), 5.07-5.09 (narrow m, 1H, Cp^b), 4.92-4.94 (narrow m, 1H, Cp^b), 3.05 (m, dddd by decoupling, $J_{7\text{endo}-7\text{exo}} = 17.7$ Hz, $J_{7\text{endo}-6\text{endo}} = J_{7\text{endo}-6\text{exo}} = 9.5$ Hz, $J_{7\text{endo}-1} = 3.7$ Hz, 1H, H_{7endo}), 2.08 (br dd, $J_{\text{obs}} = 17.3$, 5.4 Hz, dddd by decoupling, $J_{7\text{exo}-7\text{endo}} = 17.7$ Hz, $J_{7\text{exo}-6\text{exo}} = 6.0$ Hz, $J_{7\text{exo}-1} = 2.7$ Hz, $J_{7\text{exo}-2} < 1$ Hz, 1H, H_{7exo}), 1.72 (br q, $J_{\text{obs}} = 11$ Hz, ddd by decoupling, $J_{6\text{endo}-6\text{exo}} = 12.3$ Hz, $J_{6\text{endo}-7\text{endo}} = J_{6\text{endo}-5} = 8.5$ Hz, $J_{6\text{endo}-1} < 2$ Hz, 1H, H_{6endo}), 1.42 (s, 9H, *t*-Bu), 0.55 (s, 9H, C₃ SiMe₃), 0.41 (s, 9H, C₄ SiMe₃), 0.15 (apparent tt, $J_{6\text{exo}-6\text{endo}} = 12.3$ Hz, $J_{6\text{exo}-7\text{endo}} = 9.5$ Hz, $J_{6\text{exo}-7\text{exo}} = 6.0$ Hz, $J_{6\text{exo}-5} = 5.2$ Hz, 1H, H_{6exo}); ¹H-¹H GCOSY (300 MHz, CDCl₃) δ 5.94 (H₁) ↔ δ 5.28 (H₂), δ 3.05 (H_{7endo}), δ 2.08 (H_{7exo}), δ 1.72 (H_{6endo}); δ 5.84 (Cp^b) ↔ δ 5.20 (Cp^b), δ 5.07 (Cp^b), δ 4.92 (Cp^b); δ 5.33 (H₅) ↔ δ 1.72 (H_{6endo}), δ 0.15 (H_{6exo}); δ 5.28 (H₂) ↔ δ 2.08 (H_{7exo}); δ 5.20 (Cp^b) ↔ δ 5.07 (Cp^b), δ 4.92 (Cp^b); δ 5.07 (Cp^b) ↔ δ 4.92 (Cp^b); δ 3.05 (H_{7endo}) ↔ δ 2.08 (H_{7exo}), δ 1.72 (H_{6endo}), δ 0.15 (H_{6exo}); δ 2.08 (H_{7exo}) ↔ δ 0.15 (H_{6exo}); δ 1.72 (H_{6endo}) ↔ δ 0.15 (H_{6exo}); ¹³C NMR (100 MHz, CDCl₃) δ 121.6 (s, C₃), 120.0 (s, Cp^b ring quaternary), 107.7 (s, C₄), 98.1 (dd, $^1J_{\text{CH}} = 166.0$ Hz, $^2J_{\text{CH}} = 8.9$ Hz, C₂), 91.6 (d, $^1J_{\text{CH}} = 156.3$ Hz, C₁), 88.9 (d, $^1J_{\text{CH}} = 156.2$ Hz, C₅), 86.8 (d, $^1J_{\text{CH}} = 182.0$ Hz, Cp^b), 84.5 (d, $^1J_{\text{CH}} = 181.1$ Hz, Cp^b), 83.0 (d, $^1J_{\text{CH}} = 183.9$ Hz, Cp^b), 82.7 (d, $^1J_{\text{CH}} = 178.1$ Hz, Cp^b), 42.5 (t, $^1J_{\text{CH}} = 130.2$ Hz, C₇), 31.8 (s, ^tBu quaternary), 31.2 (q, $^1J_{\text{CH}} = 126.9$ Hz, ^tBu), 27.1 (t, $^1J_{\text{CH}} = 131.5$ Hz, C₆), 2.07 (q, $^1J_{\text{CH}} = 120.7$ Hz, C₃ SiMe₃), 1.63 (q, $^1J_{\text{CH}} = 119.9$ Hz, C₄ SiMe₃); HMQC (300 MHz, CDCl₃) δ 98.1 (C₂) ↔ δ 5.28 (H₂); δ 91.6 (C₁) ↔ δ 5.94 (H₁); δ 88.9 (C₅) ↔ δ 5.33 (H₅); δ 86.8 (Cp^b) ↔ δ 5.84 (Cp^b); δ 84.5 (Cp^b) ↔ δ 5.07 (Cp^b); δ 83.0 (Cp^b) ↔ δ 4.92 (Cp^b); δ 82.7 (Cp^b) ↔ δ 5.20 (Cp^b); δ 42.5 (C₇) ↔ δ 3.05 (H_{7endo}), δ 2.08 (H_{7exo}); δ 31.2 (^tBu) ↔ δ 1.42 (*t*-Bu); δ 27.1 (C₆) ↔ δ 1.72 (H_{6endo}), δ 0.15 (H_{6exo}); δ 2.07 (C₃ SiMe₃) ↔ δ 0.55

(C₃ SiMe₃); δ 1.63 (C₄ SiMe₃) $\leftrightarrow$ δ 0.41 (C₄ SiMe₃); HMBC (300 MHz, CDCl₃) δ 121.6 (C₃) $\leftrightarrow$ δ 5.33 (H₅), δ 5.28 (H₂); δ 120.0 (Cp^l ring quaternary) $\leftrightarrow$ δ 5.20 (Cp^l), δ 5.07 (Cp^l), δ 4.94 (Cp^l), δ 1.42 (^tBu); δ 107.7 (C₄) $\leftrightarrow$ δ 5.33 (H₅), δ 5.28 (H₂), δ 1.72 (H_{6endo}), δ 0.15 (H_{6exo}); δ 98.1 (C₂) $\leftrightarrow$ δ 3.05 (H_{7endo}); δ 91.6 (C₁) $\leftrightarrow$ δ 3.05 (H_{7endo}), δ 1.72 (H_{6endo}); δ 88.9 (C₅) $\leftrightarrow$ δ 2.08 (H_{7exo}), δ 1.72 (H_{6endo}), δ 0.15 (H_{6exo}); δ 86.8^a, δ 84.5^a, δ 83.0^a, δ 82.7^a (Cp^l) $\leftrightarrow$ δ 5.84 (Cp^l), δ 5.20 (Cp^l), δ 5.07 (Cp^l), δ 4.92 (Cp^l); δ 42.5 (C₇) $\leftrightarrow$ δ 5.33 (H₅), δ 5.28 (H₂), δ 1.72 (H_{6endo}), δ 0.15 (H_{6exo}); δ 31.8/31.2 (^tBu and ^tBu quaternary) $\leftrightarrow$ δ 1.42 (^tBu); δ 27.1 (C₆) $\leftrightarrow$ δ 5.33 (H₅), δ 3.05 (H_{7endo}); δ 2.07 (C₃ SiMe₃) $\leftrightarrow$ δ 0.55 (C₃ SiMe₃); δ 1.63 (C₄ SiMe₃) $\leftrightarrow$ δ 0.41 (C₄ SiMe₃). ^aSignals overlap. Analysis calculated for C₂₂H₃₈BCoF₄Si₂: C, 52.38; H, 7.59; found: C, 52.075; H, 7.586.

[(η^5 -*tert*-BuC₅H₄)Co(η^5 -3-*tert*-BuC₇H₈)]⁺ BF₄⁻ **6d.** In the drybox, (η^5 -C₅H₅)Co(η^4 -1-*tert*-BuC₅H₅) **4b** (0.1005 g, 0.4081 mmol) was weighed into a Schlenk flask. The compound was dissolved in degassed dichloromethane (10 mL) and cooled to -78 °C. To the solution was added 3,3-dimethyl-1-butyne (0.50 mL, 10 equiv), followed by HBF₄·Et₂O (0.13 mL, 2.2 equiv). The color of the red solution deepened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period. Removal of the solvent was followed by flash chromatography on silica gel using 5% methanol/dichloromethane. Crystallization from dichloromethane/diethyl ether gave complex **6d** as a light orange powder (0.112 g, 66%). IR (CH₂Cl₂ cast, cm⁻¹) 3113 (m), 2964 (m), 2910 (w), 2874 (w), 1497 (w), 1484 (w), 1467 (w), 1409 (w), 1398 (w), 1392 (w), 1372 (w), 1280 (w), 1151 (w), 1055 (s), 1035 (s), 904 (w), 857 (w), 837 (w); ¹H NMR (300 MHz, CDCl₃) δ 5.57 (d, J_{2-1} = 8.9 Hz, 2H, H_{2/4}), 5.52 (t, J = 2.2 Hz, 2H, Cp^l), 5.4-5.3 (m, 2H, H_{1/5}), 5.21 (t, J = 2.2 Hz, 2H, Cp^l), 2.5-2.3 (m, 2H, H_{6endo/7endo}), 1.52 (s, 9H, ^tBu), 1.33 (s, 9H, *t*-Bu), 1.2-1.1 (m, 2H, H_{6exo/7exo}); ¹H-¹H GCOSY (300 MHz, CDCl₃) δ 5.57 (H_{2/4}) $\leftrightarrow$

δ 5.35 ($H_{1/5}$); δ 5.52 (Cp^I) $\leftrightarrow$ δ 5.21 (Cp^I); δ 5.35 ($H_{1/5}$) $\leftrightarrow$ δ 2.4 ($H_{6endo/7endo}$), δ 1.15 ($H_{6exo/7exo}$); δ 2.4 ($H_{6endo/7endo}$) $\leftrightarrow$ δ 1.15 ($H_{6exo/7exo}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2 (s, C_3), 121.2 (s, Cp' ring quaternary), 90.0 (d, $^1J_{CH} = 166.5$ Hz, $C_{2/4}$), 85.4 (d, $^1J_{CH} = 156.6$ Hz, $C_{1/5}$), 84.2^a (d, $^1J_{CH} = 181.5$ Hz, Cp^I), 84.0^a (d, $^1J_{CH} = 181.5$ Hz, Cp^I), 36.1 (s, t -Bu, quaternary), 34.1 (d, $^1J_{CH} = 132.6$ Hz, $C_{6/7}$), 31.8 (s, t -Bu quaternary), 31.1 (q, $^1J_{CH} = 127.3$ Hz, t -Bu), 30.7 (q, $^1J_{CH} = 126.3$ Hz, t -Bu).

^aThese carbons overlap in the 1H coupled spectrum. J values are approximate. 1H - ^{13}C HETCORR (100 MHz, $CDCl_3$) δ 90.0 ($C_{2/4}$) $\leftrightarrow$ δ 5.57 ($H_{2/4}$); δ 85.4 ($C_{1/5}$) $\leftrightarrow$ δ 5.35 ($H_{1/5}$); δ 84.2 (Cp^I) $\leftrightarrow$ δ 5.21 (Cp^I); δ 84.0 (Cp^I) $\leftrightarrow$ δ 5.52 (Cp^I); δ 34.1 ($C_{6/7}$) $\leftrightarrow$ δ 2.4 ($H_{6endo/7endo}$), δ 1.15 ($H_{6exo/7exo}$); δ 31.1 (t -Bu) $\leftrightarrow$ δ 1.52 (t -Bu); δ 30.7 (t -Bu) $\leftrightarrow$ δ 1.33 (t -Bu). Analysis calculated for $C_{20}H_{30}BCoF_4$: C, 57.72; H, 7.27; found: C, 57.467; H, 7.021.

$[(\eta^5\text{-}tert\text{-BuC}_5\text{H}_4)\text{Co}(\eta^5\text{-}3,4\text{-Ph}_2\text{C}_7\text{H}_7)]^+ \text{BF}_4^-$ **6e.** A solution of $(C_5H_5)Co(\eta^4\text{-}1\text{-}tert\text{-BuC}_5\text{H}_5)$ **4b** (42.1 mg, 0.171 mmol) in dichloromethane (5 mL) was prepared under nitrogen and cooled to -78°C . To the solution was added diphenylacetylene (0.305 g, 10 equiv), followed by $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (55 μL , 2.2 equiv). The solution darkened immediately upon addition of the acid. The solution was slowly warmed with stirring over a 12 h period. Removal of the solvent was followed by flash chromatography on silica gel using 5% methanol/dichloromethane. Recrystallization from dichloromethane/diethyl ether gave complex **6e** (61 mg, 70%) as a light orange powder. IR (CH_2Cl_2 cast, cm^{-1}) 3110 (w), 3059 (w), 3033 (w), 2965 (w), 2909 (w), 2876 (w), 1485 (w), 1464 (w), 1449 (w), 1420 (w), 1398 (w), 1370 (w), 1273 (w), 1150 (w), 1056 (s), 1036 (s), 1003 (m), 914 (m), 859 (w), 837 (w), 766 (m), 728 (m), 702 (s), 681 (w), 647 (w); 1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, $J = 6.5$ Hz, 2H, H_{Ph}), 7.4-7.4 (m, 2H, H_{Ph}), 7.3-7.15 (m, 6H, H_{Ph}), 6.09 (br s, 1H, Cp^I), 5.9-5.8 (m, 2H, $H_{1,2}$), 5.59 (dd, $J_{5\text{-}6\text{exo}} = 8.4$ Hz, $J_{5\text{-}6\text{endo}} = 4.7$ Hz, 1H,

H_5), 5.41 (br s, 1H, Cp^b), 5.12 (br s, 1H, Cp^b), 4.29 (br s, 1H, Cp^b), 3.21-3.10 (m, 1H, H_{7endo}),
 2.18-2.06 (m, 2H, H_{7exo, 6endo}), 1.30 (s, 9H, *t*-Bu), 0.74-0.65 (m, 1H, H_{6exo}); ¹H-¹H GCOSY (300
 MHz, CDCl₃) δ 7.54 (H_{ph}) ↔ δ 7.45 (H_{ph}); δ 6.09 (Cp^b) ↔ δ 5.41 (Cp^b), δ 5.12 (Cp^b), δ 4.29
 (Cp^b); δ 5.9 (H_{1,2}) ↔ δ 5.8 (H_{1,2}), δ 3.15 (H_{7endo}), δ 2.12 (H_{7exo, 6endo}); δ 5.59 (H₅) ↔ δ 2.12
 (H_{7exo, 6endo}), δ 2.04 (H_{7exo, 6endo}), δ 0.70 (H_{6exo}); δ 5.41 (Cp^b) ↔ δ 5.12 (Cp^b), δ 4.29 (Cp^b); δ 5.12
 (Cp^b) ↔ δ 4.29 (Cp^b); δ 3.15 (H_{7endo}) ↔ δ 2.1 (H_{7exo, 6endo}), δ 0.70 (H_{6exo}); δ 2.1 (H_{7exo, 6endo}) ↔
 δ 0.70 (H_{6exo}); ¹³C NMR (100 MHz, CDCl₃) δ 136.3 (s, C_{ph, ipso}), 136.0 (s, C_{ph, ipso}), 131.3 (dt, ¹J_{CH}
 = 159.6 Hz, ²J_{CH} = 6.1 Hz, C_{ph}), 130.1 (d, ¹J_{CH} = 160.9 Hz, C_{ph}), 129.7 (d, ¹J_{CH} = 162.1 Hz, C_{ph}),
 129.3 (dd, ¹J_{CH} = 163.1 Hz, ²J_{CH} = 7.0 Hz, C_{ph}), 131.3 (dd, ¹J_{CH} = 162.6 Hz, ²J_{CH} = 7.0 Hz, C_{ph}),
 122.5 (s, Cp^b ring quaternary), 119.4 (s, C₃), 110.2 (s, C₄), 94.4 (d, ¹J_{CH} = 169.7 Hz, C₂), 88.9^a (d,
¹J_{CH} = 151.1 Hz, C₁), 88.6^a (d, ¹J_{CH} = 187.3 Hz, Cp^b), 86.2 (d, ¹J_{CH} = 184.6 Hz, Cp^b), 83.2 (d, ¹J_{CH}
 = 182.2 Hz, Cp^b), 81.8 (d, ¹J_{CH} = 153.2 Hz, C₅), 42.2 (t, ¹J_{CH} = 128.6 Hz, C₇), 31.8 (s, 'Bu
 quaternary), 31.0 (q, ¹J_{CH} = 127.6 Hz, 'Bu), 26.9 (t, ¹J_{CH} = 130.2 Hz, C₆). ^aSignals overlap, ¹J_{CH}'s
 are approximate. Most signals from 94.4-81.8 show small unresolved ^{2,3} J_{CH} coupling constants.
 HMQC (300 MHz, CDCl₃) δ 131.3 (C_{ph}) ↔ δ 7.2 (H_{ph}); δ 130.1 (C_{ph}) ↔ δ 7.54 (H_{ph}); δ 129.7
 (C_{ph}) ↔ δ 7.35 (H_{ph}); δ 129.3 (C_{ph}) ↔ δ 7.35 (H_{ph}); δ 128.2 (C_{ph}) ↔ δ 7.2 (H_{ph}); δ 94.4 (C₂) ↔ δ
 5.80 (H₂); δ 88.9 (C₁) ↔ δ 5.84 (H₁); δ 88.6 (Cp^b) ↔ δ 5.12 (Cp^b); δ 88.2 (Cp^b) ↔ δ 4.29 (Cp^b); δ
 86.2 (Cp^b) ↔ δ 5.41 (Cp^b); δ 83.2 (Cp^b) ↔ δ 6.09 (Cp^b); δ 81.8 (C₅) ↔ δ 5.59 (H₅); δ 42.2 (C₇) ↔
 δ 3.15 (H_{7endo}), δ 2.13 (H_{7exo}); δ 31.0 ('Bu) ↔ δ 1.30 ('Bu); δ 26.9 (C₆) ↔ δ 2.13 (H_{6endo}), δ 0.70
 (H_{6exo}); HMBC (300 MHz, CDCl₃) δ 136.3 (C_{ph, ipso}) ↔ δ 7.17 (H_{ph}), δ 5.59 (H₅); δ 136.0 (C_{ph,}
{ipso}) ↔ δ 7.35 (H{ph}), δ 5.8 (H_{1,2}); δ 131.3 (C_{ph}) ↔ δ 7.31 (H_{ph}), δ 7.24 (H_{ph}); δ 130.1 (C_{ph}) ↔ δ
 7.24 (H_{ph}); δ 129.7 (C_{ph}) ↔ δ 7.54 (H_{ph}); δ 129.3 (C_{ph}) ↔ δ 7.37 (H_{ph}), δ 7.33 (H_{ph}); δ 128.2 (C_{ph})
 ↔ δ 7.17 (H_{ph}); δ 122.5 (Cp^b) ↔ δ 6.09 (Cp^b), δ 5.41 (Cp^b), δ 5.12 (Cp^b), δ 4.29 (Cp^b), δ 1.30
 ('Bu); δ 119.4 (C₃) ↔ δ 7.54 (H_{ph}), δ 5.80 (H_{1,2}), δ 5.59 (H₅); δ 110.2 (C₄) ↔ δ 7.25 (H_{ph}), δ 5.80
 (H_{1,2}), δ 2.09 (H_{7exo, 6endo}), δ 2.05 (H_{7exo, 6endo}), δ 0.74 (H_{6exo}); δ 94.4 (C₂) ↔ δ 6.09 (Cp^b), δ 3.15
 (H_{7endo}); δ 88.9/ 88.6/ 88.2 (Cp^b) ↔ δ 6.09 (Cp^b), δ 5.41 (Cp^b), δ 5.12 (Cp^b), δ 4.29 (Cp^b), δ 1.30 (*t*-
 Bu), δ 3.15 (H_{7endo}), δ 2.10 (H_{7exo}); δ 86.2 (Cp^b) ↔ δ 6.09 (Cp^b), δ 5.12 (w, Cp^b), δ 4.29 (Cp^b); δ

83.2 (Cp^l) ↔ δ 5.41 (Cp^l), δ 5.12 (Cp^l), δ 4.29 (Cp^l); δ 81.8 (C₅) ↔ δ 2.10 (H_{7exo,6endo}), δ 2.06 (H_{7exo,6endo}), δ 0.74 (H_{6exo}); δ 42.2 (C₇) ↔ δ 5.9 (H_{1,2}), δ 5.59 (H₅), δ 2.15 (H_{7exo,6endo}), δ 0.74 (H_{6exo}); δ 31.8, 31.0 (tBu and tBu quaternary) ↔ δ 1.30 (tBu); δ 26.9 (C₆) ↔ δ 5.59 (H₅), δ 3.15 (w, H_{7endo}), δ 2.15 (H_{7exo,6endo}). Analysis calculated for C₂₈H₃₀BCoF₄: C, 65.64; H, 5.91; found: C, 65.240; H, 5.854.

[(η^5 -*tert*-BuC₅H₄)Co(η^5 -3,4-Me₂C₇H₇)]⁺ BF₄⁻ **6f.** In the drybox, (C₅H₅)Co(η^4 -1-*tert*-BuC₅H₅) **4b** (0.2059 g, 0.8362 mmol) was weighed into a Schlenk flask. The compound was dissolved in degassed dichloromethane (20 mL) and cooled to -40 °C. To the solution was added HBF₄·Et₂O (0.135 mL, 1.1 equiv). The color of the red solution turned a deep green upon addition of the acid. After stirring 1 min at -40 °C, 2-butyne (0.196 mL, 3 equiv) was added, changing the color of the solution to a dark red. The solution was slowly warmed with stirring to room temperature. A drop of saturated aqueous NaHCO₃ was added and all volatile material was removed *in vacuo*. The crude residue was re-dissolved in dichloromethane and filtered through a Celite column. Addition of diethyl ether gave complex **6f** as an orange-brown precipitate (0.2416 g, 74%), pure by NMR spectroscopy. IR (CH₂Cl₂ cast, cm⁻¹) 3112 (m), 2965 (s), 2875 (m), 1695 (w), 1485 (s), 1463 (m), 1372 (m), 1278 (m), 1152 (m), 1054 (s), 867 (m), 520 (m), 495 (w); ¹H NMR (360 MHz, CDCl₃) δ 5.59-5.55 (m, 1H, Cp^l), 5.41-5.38 (m, Cp^l), 5.36-5.32 (m, 2H, H_{1,2}), 5.25 (dd, *J*_{5-6endo} = 8.1 Hz, *J*_{5-6exo} = 4.4 Hz, 1H, H₅), 5.24-5.22 (m, 1H, Cp^l), 5.10-5.07 (m, 1H, Cp^l), 2.77 (dddd, *J*_{7endo-7exo} = 17.2 Hz, *J*_{7endo-6endo} = *J*_{7endo-6exo} = 9.6 Hz, *J*_{7endo-1} = 4.1 Hz, 1H, H_{7endo}), 2.58 (s, 3H, Me₃), 2.31 (s, 3H, Me₄), 2.00-1.88 (m, *J*_{6endo-6exo} = 13.8 Hz, *J*_{6endo-7endo} = 9.6 Hz, *J*_{6endo-5} = 8.1 Hz, *J*_{6endo-7exo} = 1.9 Hz, 1H, H_{6endo}), 1.76 (m, dddd by decoupling, *J*_{7exo-7endo} = 16.9 Hz, *J*_{7exo-6exo} = 6.1 Hz,

$J_{7\text{exo-1}}$ = small, $J_{7\text{exo-6endo}}$ = 1.9 Hz, 1H, $H_{7\text{exo}}$), 1.30 (s, 9H, *t*-Bu), 0.45 (dddd, $J_{6\text{exo-6endo}}$ = 13.8 Hz, $J_{6\text{exo-7endo}}$ = 10.2 Hz, $J_{6\text{exo-7exo}}$ = 6.3 Hz, $J_{6\text{exo-5}}$ = 4.5 Hz, 1H, $H_{6\text{exo}}$); ^1H - ^1H GCOSY (300 MHz, CDCl_3) δ 5.59 (Cp^{I}) $\leftrightarrow$ δ 5.39 (Cp^{I}), δ 5.23 (Cp^{I}), δ 5.08 (Cp^{I}); δ 5.39 (Cp^{I}) $\leftrightarrow$ δ 5.23 (Cp^{I}), δ 5.08 (Cp^{I}); δ 5.34 ($H_{1,2}$) $\leftrightarrow$ δ 2.77 ($H_{7\text{endo}}$), δ 1.75 ($H_{7\text{exo}}$); δ 5.25 (H_5) $\leftrightarrow$ δ 1.93 ($H_{6\text{endo}}$), δ 0.45 ($H_{6\text{exo}}$); δ 5.23 (Cp^{I}) $\leftrightarrow$ δ 5.08 (Cp^{I}); δ 2.77 ($H_{7\text{endo}}$) $\leftrightarrow$ δ 1.93 ($H_{6\text{endo}}$), δ 1.75 ($H_{7\text{exo}}$), δ 0.45 ($H_{6\text{exo}}$); δ 1.93 ($H_{6\text{endo}}$) $\leftrightarrow$ δ 1.75 ($H_{7\text{exo}}$), δ 0.45 ($H_{6\text{exo}}$); δ 1.75 ($H_{7\text{exo}}$) $\leftrightarrow$ δ 0.45 ($H_{6\text{exo}}$); ^{13}C NMR (100 MHz, CDCl_3) δ 120.2 (s, C_3), 117.3 (s, Cp^{I}), 109.1 (s, C_4), 93.7 (d, $^1J_{\text{CH}}$ = 170.4 Hz, C_2), 87.0^a (d, $^1J_{\text{CH}}$ = 183.3 Hz, Cp^{I}), 86.9^a (d, $^1J_{\text{CH}}$ = 183.3 Hz, Cp^{I}), 85.9 (d, $^1J_{\text{CH}}$ = 158.0 Hz, C_1), 85.5 (d, $^1J_{\text{CH}}$ = 165 Hz, C_5), 84.56^b (d, $^1J_{\text{CH}}$ = 181.7 Hz, Cp^{I}), 84.53^b (d, $^1J_{\text{CH}}$ = 183.3 Hz, Cp^{I}), 39.7 (t, $^1J_{\text{CH}}$ = 131.8 Hz, C_7), 31.5 (s, *t*-Bu quaternary), 30.9 (q, $^1J_{\text{CH}}$ = 127.3 Hz, *t*-Bu), 27.7 (t, $^1J_{\text{CH}}$ = 125.2 Hz, C_6), 23.0 (q, $^1J_{\text{CH}} \approx 125$ Hz, Me_4), 21.5 (q, $^1J_{\text{CH}}$ = 126.9 Hz, Me_3). ^{a,b}Carbon signals overlap in gated spectrum. HMQC (300 MHz, CDCl_3) δ 93.7 (C_2) $\leftrightarrow$ δ 5.34 ($H_{1,2}$); δ 87.0 (Cp^{I}) $\leftrightarrow$ δ 5.08 (Cp^{I}); δ 86.9 (Cp^{I}) $\leftrightarrow$ δ 5.57 (Cp^{I}); δ 85.9 (C_1) $\leftrightarrow$ δ 5.34 ($H_{1,2}$); δ 85.5 (C_5) $\leftrightarrow$ δ 5.25 (H_5); δ 84.6^a (Cp^{I}) $\leftrightarrow$ δ 5.39 (Cp^{I}); δ 84.6^a (Cp^{I}) $\leftrightarrow$ δ 5.23 (Cp^{I}); δ 39.7 (C_7) $\leftrightarrow$ δ 2.77 ($H_{7\text{endo}}$), δ 1.75 ($H_{7\text{exo}}$); δ 30.9 (*t*-Bu) $\leftrightarrow$ δ 1.30 (*t*-Bu); δ 27.7 (C_6) $\leftrightarrow$ δ 1.93 ($H_{6\text{endo}}$), δ 0.45 ($H_{6\text{exo}}$); δ 23.0 (Me_4) $\leftrightarrow$ δ 2.31 (Me_4); δ 21.5 (Me_3) $\leftrightarrow$ δ 2.58 (Me_3); Analysis calculated for $\text{C}_{18}\text{H}_{26}\text{BCoF}_4$: C, 55.70; H, 6.75; found: C, 55.962; H, 6.790. Electrospray MS m/z calculated for $\text{C}_{18}\text{H}_{26}\text{Co}$ ($\text{M}^+ - \text{BF}_4$): 301.136649; found: 301.136128 (100%).

^a Signals are not resolved.

Table 3. Comparative ^1H NMR Spectroscopic Data For (*tert*-BuC₅H₄)Co(η^5 -Cycloheptadienyl) Complexes

	6a	6b	6c	6d	6e	6f
H₁ <i>J</i> ₁₋₂	5.49 (dddd) 9.5 Hz	5.67 (dddd) 9.3 Hz	5.94 (br d) 9.2 Hz	5.35 (m) 8.9 Hz	5.85 (m) a	5.34 (m) a
H₂ <i>J</i> ₂₋₃	5.33 (dd) b	5.22 (d) b	5.28 (d) b	5.57 (d) b	5.85 (m) b	5.34 (m) b
H₃ <i>J</i> ₃₋₄	b	b	b	b	b	b
H₄ <i>J</i> ₄₋₅	b	b	b	5.57 (d) 8.9 Hz	b	b
H₅ <i>J</i> _{5-6endo} <i>J</i> _{5-6exo}	5.10 (dd) 8.4 Hz 4.8 Hz	5.19 (dd) 8.2 Hz 5.0 Hz	5.33 (dd) 8.2 Hz 5.2 Hz	5.35 (m) a a	5.59 (dd) 8.4 Hz 4.7 Hz	5.25 (dd) 8.1 Hz 4.4 Hz
H_{6endo} <i>J</i> _{6endo-6exo} <i>J</i> _{6endo-7endo} <i>J</i> _{6endo-7exo}	1.70 (m) 12.7 Hz 9 Hz a	1.80 (m) 11.7 Hz 9.7 Hz <2 Hz	1.72 (br q) 12.3 Hz 8.5 Hz 0 Hz	2.4 (m) a a a	2.1 (m) ^c a a a	1.95 (m) 13.8 Hz 9.6 Hz 1.9 Hz
H_{6exo} <i>J</i> _{6exo-7endo} <i>J</i> _{6exo-7exo}	0.20 (dddd) 11.5 Hz 6.5 Hz	0.23 (dddd) 11.7 Hz 5.8 Hz	0.15 (tt) 9.5 Hz 6.0 Hz	1.15 (m) a a	0.7 (m) a a b	0.45 (m) 10.2 Hz 6.3 Hz
H_{7endo} <i>J</i> _{7endo-7exo} <i>J</i> _{7endo-1}	2.89 (dddd) 17.3 Hz 4 Hz	2.99 (dddd) 17.6 Hz 3.5 Hz	3.05 (dddd) 17.7 Hz 3.7 Hz	2.4 (m) a a	3.15 (m) a a	2.77 (dddd) 17.2 Hz 4.1 Hz
H_{7exo} <i>J</i> _{7exo-1}	1.93 (m) <2 Hz	2.01 (br d) 3.5 Hz	2.08 (dd) 2.7 Hz	1.15 (m) a	2.1 (m) ^c a	1.76 (m) a

^a Numerical value for the coupling constant was not obtained due to second order character or complexity of the signal. ^b Not applicable due to a non-hydrogen substituent. ^c Signals overlap.

Notes and References

1. (a) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1985**, 23, 15. (b) Nicholls, J. C.; Spencer, J. L. *Inorg. Synth.* **1990**, 28, 278. (c) Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organomet. Chem.* **1981**, 221, C25. For the C₅Me₄Et analogue, see: (d) Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Dalton Trans.* **1979**, 355.
2. (a) Holm, K. H.; Skatteboel, L. *Acta Chem. Scand.* **1984**, B38, 783. (b) Detailed experimental procedures were provided by Professor Neil Boag (personal communication). The compound was prepared from 2,3-dimethyl-1,3-butadiene by conversion to vinyl-1,1-dibromo-2-methyl-2-isopropenylcyclopropane treatment (bromoform/NaO^tBu, -20 °C) followed by anionic vinylcyclopropane rearrangement (MeLi, -78 °C). We thank Professor Boag for his generous assistance.
3. (a) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, 7, 99. (b) Sheats, J. E. *J. Organomet. Chem. Lib.* **1979**, 7, 461.
4. Lehmkuhl, H.; Nehl, H. F. *Chem. Ber.* **1984**, 117, 3443.
5. Dzwiniel, T. D.; Etkin, N. Stryker, J. M. *J. Am. Chem. Soc.* **1999**, 121, 10640.

Appendix 1. Structure Report: Malonate adduct of complex 3a

Compound: $[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}\{\eta^4\text{-(2,3-Me}_2\text{-5-(CH}\{\text{CO}_2\text{Me}\}_2)\text{C}_7\text{H}_7\})]$

Formula: $\text{C}_{24}\text{H}_{35}\text{CoO}_4$

Supervisor: J. M. Stryker

Crystallographer: R. McDonald

Figure 1. Perspective view of the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Co}\{\eta^4\text{-(2,3-Me}_2\text{-5-(CH}\{\text{CO}_2\text{Me}\}_2)\text{C}_7\text{H}_7\})]$ molecule/ion showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters except for those of the $\eta^5\text{-C}_5\text{Me}_5$ group, which are not shown.

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Table 1. Crystallographic Experimental Details

A. Crystal Data

formula	$\text{C}_{24}\text{H}_{35}\text{CoO}_4$
formula weight	446.45
crystal dimensions (mm)	$0.44 \times 0.38 \times 0.22$
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters ^a	
a (Å)	16.4190 (7)
b (Å)	8.6648 (3)
c (Å)	16.2655 (7)
β (deg)	100.458 (4)
V (Å ³)	2275.61 (16)
Z	4
ρ_{calcd} (g cm ⁻³)	1.303
μ (mm ⁻¹)	6.116

B. Data Collection and Refinement Conditions

diffractometer	Siemens P4/RA ^b
radiation (λ [Å])	graphite-monochromated Cu K α (1.54178)
temperature (°C)	-60
scan type	θ - 2θ
data collection 2θ limit (deg)	113.5
total data collected	3158 ($0 \leq h \leq 17$, $0 \leq k \leq 9$, $-17 \leq l \leq 17$)
independent reflections	3036 ($R_{\text{int}} = 0.0362$)

number of observed reflections (<i>NO</i>)	2550 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (<i>SHELXS-86</i> ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-93</i> ^d)
absorption correction method	semiempirical (ψ scans)
range of transmission factors	0.3464–0.1739
data/restraints/parameters	3036 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 262
goodness-of-fit (<i>S</i>) ^e	1.023 [$F_o^2 \geq -3\sigma(F_o^2)$]
final <i>R</i> indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0547
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1416
largest difference peak and hole	0.419 and –0.385 e Å ^{–3}

^aObtained from least-squares refinement of 32 reflections with $58.4^\circ < 2\theta < 59.0^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Siemens.

^cSheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o^2 ; conventional *R*-factors R_1 are based on F_o , with F_o set to zero for negative F_o^2 . The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 , and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o , and *R*-factors based on ALL data will be even larger.

^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0737P)^2 + 4.2221P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

^f $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}, \text{\AA}^2$
Co	0.32212(4)	0.32558(7)	0.14693(4)	0.0255(2)*
O1	0.1062(2)	0.1859(4)	-0.0862(3)	0.0596(11)*
O2	-0.00964(19)	0.3172(4)	-0.0811(2)	0.0490(9)*
O3	0.1076(2)	0.5204(4)	-0.1953(2)	0.0503(9)*
O4	0.0725(2)	0.7003(4)	-0.1095(2)	0.0434(8)*
C1	0.3441(3)	0.5472(5)	0.1293(3)	0.0361(11)*
C2	0.2822(3)	0.5279(5)	0.1812(3)	0.0327(11)*
C3	0.2151(3)	0.4278(5)	0.1501(3)	0.0298(10)*
C4	0.2141(2)	0.3600(5)	0.0687(3)	0.0266(10)*
C5	0.2059(3)	0.4451(5)	-0.0130(3)	0.0284(10)*
C6	0.2446(3)	0.6059(5)	-0.0046(3)	0.0333(10)*
C7	0.3329(3)	0.6062(5)	0.0408(3)	0.0381(11)*
C8	0.2960(4)	0.5910(6)	0.2688(3)	0.0541(14)*
C9	0.1523(3)	0.3774(6)	0.2020(3)	0.0447(12)*
C10	0.1128(3)	0.4587(5)	-0.0501(2)	0.0278(10)*
C11	0.0725(3)	0.3036(5)	-0.0733(3)	0.0322(11)*
C12	-0.0580(4)	0.1788(7)	-0.1003(4)	0.0692(18)*
C13	0.0967(3)	0.5594(5)	-0.1274(3)	0.0319(10)*
C14	0.0629(4)	0.8121(6)	-0.1769(4)	0.0616(16)*
C20	0.3263(3)	0.0887(5)	0.1595(3)	0.0315(11)*
C21	0.3585(3)	0.1556(5)	0.2382(3)	0.0321(11)*
C22	0.4259(3)	0.2493(6)	0.2284(3)	0.0391(11)*
C23	0.4369(3)	0.2386(6)	0.1435(3)	0.0416(12)*
C24	0.3757(3)	0.1390(5)	0.1006(3)	0.0375(12)*
C25	0.2542(3)	-0.0211(6)	0.1407(3)	0.0485(13)*
C26	0.3248(4)	0.1302(6)	0.3166(3)	0.0516(14)*
C27	0.4788(3)	0.3419(6)	0.2964(4)	0.0647(18)*
C28	0.5038(4)	0.3150(7)	0.1054(5)	0.078(2)*
C29	0.3659(4)	0.0880(7)	0.0118(3)	0.0643(17)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3. Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Co	C1	1.984(4)	C3	C4	1.444(6)
Co	C2	1.987(4)	C3	C9	1.511(6)
Co	C3	1.977(4)	C4	C5	1.504(6)
Co	C4	2.009(4)	C5	C6	1.528(6)
Co	C20	2.063(4)	C5	C10	1.542(6)
Co	C21	2.100(4)	C6	C7	1.504(6)
Co	C22	2.068(4)	C10	C11	1.516(6)
Co	C23	2.040(4)	C10	C13	1.515(6)
Co	C24	2.048(4)	C20	C21	1.417(6)
O1	C11	1.196(5)	C20	C24	1.431(6)
O2	C11	1.337(5)	C20	C25	1.507(6)
O2	C12	1.441(6)	C21	C22	1.405(6)
O3	C13	1.199(5)	C21	C26	1.496(6)
O4	C13	1.332(5)	C22	C23	1.427(7)
O4	C14	1.450(6)	C22	C27	1.508(7)
C1	C2	1.443(6)	C23	C24	1.410(7)
C1	C7	1.508(6)	C23	C28	1.509(7)
C2	C3	1.422(6)	C24	C29	1.491(7)
C2	C8	1.504(6)			

Table 4. Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	Co	C2	42.61(19)	C2	C1	C7	128.4(4)
C1	Co	C3	75.86(18)	Co	C2	C1	68.6(2)
C1	Co	C4	85.84(18)	Co	C2	C3	68.6(2)
C1	Co	C20	166.84(19)	Co	C2	C8	125.8(3)
C1	Co	C21	138.20(18)	C1	C2	C3	116.4(4)
C1	Co	C22	104.59(19)	C1	C2	C8	120.7(4)
C1	Co	C23	99.26(19)	C3	C2	C8	122.2(4)
C1	Co	C24	127.5(2)	Co	C3	C2	69.4(2)
C2	Co	C3	42.05(18)	Co	C3	C4	69.9(2)
C2	Co	C4	75.41(17)	Co	C3	C9	125.8(3)
C2	Co	C20	149.01(18)	C2	C3	C4	117.0(4)
C2	Co	C21	119.14(17)	C2	C3	C9	122.7(4)
C2	Co	C22	112.20(19)	C4	C3	C9	119.9(4)
C2	Co	C23	133.4(2)	Co	C4	C3	67.6(2)
C2	Co	C24	170.16(19)	Co	C4	C5	124.0(3)
C3	Co	C4	42.49(17)	C3	C4	C5	126.5(4)
C3	Co	C20	117.20(18)	C4	C5	C6	113.5(4)
C3	Co	C21	115.86(17)	C4	C5	C10	107.8(3)
C3	Co	C22	139.43(19)	C6	C5	C10	109.3(3)
C3	Co	C23	175.08(19)	C5	C6	C7	113.2(4)
C3	Co	C24	143.72(19)	C1	C7	C6	114.0(4)
C4	Co	C20	102.73(17)	C5	C10	C11	112.7(4)
C4	Co	C21	131.06(17)	C5	C10	C13	112.4(3)
C4	Co	C22	169.56(18)	C11	C10	C13	107.5(3)
C4	Co	C23	138.75(19)	O1	C11	O2	123.3(4)
C4	Co	C24	105.85(18)	O1	C11	C10	127.2(4)
C20	Co	C21	39.78(17)	O2	C11	C10	109.4(4)
C20	Co	C22	67.01(18)	O3	C13	O4	124.0(4)
C20	Co	C23	67.69(18)	O3	C13	C10	124.8(4)
C20	Co	C24	40.73(17)	O4	C13	C10	111.1(4)
C21	Co	C22	39.39(18)	Co	C20	C21	71.5(3)
C21	Co	C23	67.31(18)	Co	C20	C24	69.1(3)
C21	Co	C24	67.68(17)	Co	C20	C25	126.7(3)
C22	Co	C23	40.66(19)	C21	C20	C24	108.4(4)
C22	Co	C24	67.95(19)	C21	C20	C25	126.3(4)
C23	Co	C24	40.3(2)	C24	C20	C25	125.2(4)
C11	O2	C12	116.9(4)	Co	C21	C20	68.7(2)
C13	O4	C14	116.3(4)	Co	C21	C22	69.1(3)
Co	C1	C2	68.8(2)	Co	C21	C26	127.2(3)
Co	C1	C7	118.2(3)	C20	C21	C22	107.8(4)

Table 4. Selected Interatomic Angles (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C20	C21	C26	125.1(4)	Co	C23	C28	126.4(4)
C22	C21	C26	127.1(4)	C22	C23	C24	108.3(4)
Co	C22	C21	71.5(3)	C22	C23	C28	126.8(5)
Co	C22	C23	68.6(3)	C24	C23	C28	124.9(5)
Co	C22	C27	126.8(4)	Co	C24	C20	70.2(2)
C21	C22	C23	108.2(4)	Co	C24	C23	69.5(3)
C21	C22	C27	125.9(5)	Co	C24	C29	127.7(3)
C23	C22	C27	125.9(5)	C20	C24	C23	107.1(4)
Co	C23	C22	70.7(3)	C20	C24	C29	125.7(5)
Co	C23	C24	70.1(3)	C23	C24	C29	127.1(5)

Table 5. Anisotropic Displacement Parameters (U_{ij} , Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	0.0253(4)	0.0282(4)	0.0227(4)	0.0014(3)	0.0036(3)	-0.0002(3)
O1	0.050(2)	0.041(2)	0.082(3)	-0.0257(19)	-0.006(2)	0.0032(18)
O2	0.0339(19)	0.051(2)	0.064(2)	-0.0211(18)	0.0134(16)	-0.0122(16)
O3	0.068(2)	0.056(2)	0.0273(19)	0.0055(17)	0.0100(17)	0.0138(19)
O4	0.052(2)	0.0349(19)	0.041(2)	0.0065(15)	0.0035(16)	0.0092(15)
C1	0.032(3)	0.032(3)	0.039(3)	-0.002(2)	-0.007(2)	-0.008(2)
C2	0.040(3)	0.029(2)	0.027(2)	-0.005(2)	-0.001(2)	0.004(2)
C3	0.032(2)	0.031(2)	0.026(2)	0.0038(19)	0.0063(19)	0.008(2)
C4	0.025(2)	0.030(2)	0.025(2)	0.0064(19)	0.0044(18)	0.0000(19)
C5	0.031(2)	0.032(2)	0.023(2)	-0.0027(19)	0.0060(18)	0.0038(19)
C6	0.035(3)	0.035(2)	0.029(2)	0.008(2)	0.005(2)	-0.001(2)
C7	0.036(3)	0.033(3)	0.046(3)	0.006(2)	0.007(2)	-0.007(2)
C8	0.070(4)	0.050(3)	0.039(3)	-0.013(3)	-0.002(3)	0.003(3)
C9	0.045(3)	0.060(3)	0.033(3)	0.006(2)	0.016(2)	0.008(3)
C10	0.034(2)	0.031(2)	0.019(2)	-0.0049(19)	0.0066(18)	0.004(2)
C11	0.037(3)	0.038(3)	0.020(2)	-0.003(2)	-0.0006(19)	-0.003(2)
C12	0.058(4)	0.073(4)	0.080(5)	-0.027(3)	0.022(3)	-0.029(3)
C13	0.030(2)	0.038(3)	0.027(3)	0.001(2)	0.003(2)	0.001(2)
C14	0.074(4)	0.044(3)	0.067(4)	0.024(3)	0.013(3)	0.012(3)
C20	0.037(3)	0.029(2)	0.029(3)	0.0022(19)	0.007(2)	0.004(2)
C21	0.036(3)	0.035(3)	0.024(2)	0.003(2)	0.0031(19)	0.004(2)
C22	0.032(3)	0.039(3)	0.043(3)	0.007(2)	-0.003(2)	0.005(2)
C23	0.034(3)	0.037(3)	0.057(3)	0.016(2)	0.017(2)	0.008(2)
C24	0.048(3)	0.041(3)	0.026(3)	0.009(2)	0.013(2)	0.016(2)
C25	0.054(3)	0.032(3)	0.058(3)	-0.002(2)	0.005(3)	-0.006(2)
C26	0.065(4)	0.060(3)	0.033(3)	0.007(3)	0.016(3)	0.010(3)
C27	0.045(3)	0.058(4)	0.075(4)	-0.006(3)	-0.033(3)	0.002(3)
C28	0.046(3)	0.078(5)	0.119(6)	0.046(4)	0.040(4)	0.013(3)
C29	0.111(5)	0.052(3)	0.037(3)	0.007(3)	0.033(3)	0.020(3)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*}c^{*}U_{23} + 2hla^{*}c^{*}U_{13} + 2hka^{*}b^{*}U_{12})]$$

Table 6. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}, \text{\AA}^2$
H1	0.3978	0.5800	0.1626	0.043
H4	0.1805	0.2643	0.0621	0.032
H5	0.2330	0.3836	-0.0517	0.034
H6A	0.2424	0.6495	-0.0606	0.040
H6B	0.2116	0.6726	0.0254	0.040
H7A	0.3544	0.7119	0.0417	0.046
H7B	0.3661	0.5424	0.0095	0.046
H8A	0.3447	0.6566	0.2778	0.065
H8B	0.3041	0.5062	0.3084	0.065
H8C	0.2480	0.6508	0.2767	0.065
H9A	0.1120	0.3096	0.1692	0.054
H9B	0.1244	0.4674	0.2190	0.054
H9C	0.1803	0.3229	0.2512	0.054
H10	0.0850	0.5065	-0.0073	0.033
H12A	-0.1163	0.2029	-0.1043	0.083
H12B	-0.0416	0.1034	-0.0563	0.083
H12C	-0.0486	0.1369	-0.1531	0.083
H14A	0.0452	0.9101	-0.1573	0.074
H14B	0.0217	0.7756	-0.2233	0.074
H14C	0.1154	0.8255	-0.1954	0.074
H25A	0.2451	-0.0493	0.0820	0.058
H25B	0.2049	0.0284	0.1532	0.058
H25C	0.2661	-0.1131	0.1747	0.058
H26A	0.2781	0.0599	0.3053	0.062
H26B	0.3068	0.2279	0.3362	0.062
H26C	0.3676	0.0861	0.3591	0.062
H27A	0.5211	0.3964	0.2733	0.078
H27B	0.5050	0.2731	0.3404	0.078
H27C	0.4445	0.4157	0.3192	0.078
H28A	0.5383	0.3778	0.1472	0.093
H28B	0.4786	0.3797	0.0590	0.093
H28C	0.5375	0.2365	0.0853	0.093
H29A	0.3185	0.0196	-0.0011	0.077
H29B	0.4154	0.0338	0.0035	0.077
H29C	0.3573	0.1774	-0.0246	0.077

Appendix 2. Structure Report: Complex 6c

Compound: $[(\eta^5\text{-C}_5\text{H}_4'\text{Bu})\text{Co}\{\eta^5\text{-C}_7\text{H}_7(\text{SiMe}_3)_2\}][\text{BF}_4]\cdot\text{CHCl}_3$

Formula: $\text{C}_{23}\text{H}_{39}\text{BCl}_3\text{CoF}_4\text{Si}_2$ ($\text{C}_{22}\text{H}_{38}\text{BCoF}_4\text{Si}_2\cdot\text{CHCl}_3$)

Supervisor: J. M. Stryker

Crystallographer: R. McDonald

Figure 1. Perspective view of the $[(\eta^5\text{-C}_5\text{H}_4'\text{Bu})\text{Co}\{\eta^5\text{-C}_7\text{H}_7(\text{SiMe}_3)_2\}]^+$ complex ion (**6c**) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters except for methyl hydrogens, which are not shown.

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Table 1. Crystallographic Experimental Details

A. Crystal Data

formula	$\text{C}_{23}\text{H}_{39}\text{BCl}_3\text{CoF}_4\text{Si}_2$
formula weight	623.81
crystal dimensions (mm)	$0.55 \times 0.06 \times 0.06$
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters ^a	
a (Å)	10.0706 (15)
b (Å)	11.0942 (19)
c (Å)	13.396 (2)
α (deg)	92.638 (13)
β (deg)	96.004 (12)
γ (deg)	95.300 (13)
V (Å ³)	1479.8 (4)
Z	2
ρ_{calcd} (g cm ⁻³)	1.400
μ (mm ⁻¹)	0.968

B. Data Collection and Refinement Conditions

diffractometer	Siemens P4/RA ^b
radiation (λ [Å])	graphite-monochromated Mo K α (0.71073)
temperature (°C)	-60
scan type	$\theta-2\theta$
data collection 2θ limit (deg)	50.0
total data collected	5511 ($0 \leq h \leq 11$, $-13 \leq k \leq 13$, $-15 \leq l \leq 15$)

independent reflections	5186 ($R_{\text{int}} = 0.0450$)
number of observed reflections (NO)	3047 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson search/structure expansion (<i>DIRDIF-96</i> ^c)
refinement method	full-matrix least-squares on F^2 (<i>SHELXL-93</i> ^d)
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9442–0.6179
data/restraints/parameters	5186 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 307
goodness-of-fit (S) ^e	1.016 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices ^f	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0695
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1296
largest difference peak and hole	0.517 and -0.449 e Å ⁻³

^aObtained from least-squares refinement of 36 reflections with $20.2^\circ < 2\theta < 24.7^\circ$.

^bPrograms for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Siemens.

^cBeurskens, P. T.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Garcia Granda, S.; Gould, R. O.; Israel, R.; Smits, J. M. M. (1996). The *DIRDIF-96* program system. Crystallography Laboratory, University of Nijmegen, The Netherlands.

^dSheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted R -factors wR_2 and all goodnesses of fit S are based on F_o^2 ; conventional R -factors R_1 are based on F_o , with F_o set to zero for negative F_o^2 . The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1 , and is not relevant to the choice of reflections for refinement. R -factors based on F_o^2 are statistically about twice as large as those based on F_o , and R -factors based on ALL data will be even larger.

^e $S = [\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0296P)^2 + 1.4394P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$).

^f $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters*(a) atoms of $[(\eta^5\text{-C}_5\text{H}_4^t\text{Bu})\text{Co}\{\eta^5\text{-C}_7\text{H}_7(\text{SiMe}_3)_2\}]^+$*

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
Co	0.20994(8)	0.35306(7)	0.30654(6)	0.0247(2)*
Si1	0.40346(18)	0.60246(15)	0.21911(13)	0.0327(4)*
Si2	0.01992(18)	0.59107(16)	0.18749(13)	0.0332(4)*
C1	0.3310(6)	0.3506(5)	0.1894(4)	0.0310(15)*
C2	0.2745(6)	0.4631(5)	0.1997(4)	0.0242(13)*
C3	0.1304(6)	0.4573(5)	0.1920(4)	0.0261(14)*
C4	0.0509(6)	0.3433(5)	0.2001(4)	0.0306(15)*
C5	0.0942(6)	0.2263(5)	0.2048(5)	0.0367(16)*
C6	0.1793(7)	0.1641(5)	0.1361(5)	0.0437(18)*
C7	0.2801(7)	0.2571(6)	0.1036(4)	0.0443(18)*
C10	0.3538(7)	0.7382(5)	0.2888(5)	0.0450(18)*
C11	0.5610(7)	0.5627(6)	0.2893(5)	0.056(2)*
C12	0.4408(7)	0.6381(6)	0.0891(5)	0.0488(19)*
C13	0.0811(7)	0.7046(6)	0.1003(5)	0.052(2)*
C14	-0.1491(6)	0.5291(6)	0.1283(5)	0.055(2)*
C15	-0.0003(7)	0.6599(5)	0.3133(4)	0.0411(17)*
C20	0.2475(6)	0.2411(5)	0.4249(4)	0.0248(13)*
C21	0.1285(6)	0.3000(5)	0.4338(4)	0.0303(15)*
C22	0.1622(7)	0.4266(6)	0.4435(4)	0.0390(17)*
C23	0.3017(7)	0.4487(5)	0.4364(4)	0.0400(18)*
C24	0.3524(6)	0.3343(5)	0.4235(4)	0.0315(15)*
C25	0.2637(6)	0.1077(5)	0.4373(5)	0.0337(15)*
C26	0.2814(8)	0.0956(6)	0.5518(5)	0.054(2)*
C27	0.1402(7)	0.0236(5)	0.3941(5)	0.0482(19)*
C28	0.3875(7)	0.0708(6)	0.3920(5)	0.053(2)*

(b) tetrafluoroborate ion atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
F1	-0.1761(4)	0.1819(3)	0.3622(3)	0.0546(11)*
F2	-0.3526(4)	0.2693(4)	0.2936(3)	0.0781(14)*
F3	-0.3080(5)	0.2789(4)	0.4592(3)	0.0825(15)*
F4	-0.1693(4)	0.3859(3)	0.3682(3)	0.0548(11)*
B	-0.2522(8)	0.2797(7)	0.3711(6)	0.0388(19)*

(c) solvent chloroform atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
Cl1	-0.2370(2)	0.1136(2)	0.06444(17)	0.0889(8)*
Cl2	-0.4623(3)	-0.0139(2)	0.1391(2)	0.1004(9)*
Cl3	-0.2014(3)	-0.0961(2)	0.17474(19)	0.1177(11)*
C99	-0.2909(7)	0.0302(6)	0.1614(5)	0.052(2)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3. Selected Interatomic Distances (Å)*(a) within $[(\eta^5\text{-C}_5\text{H}_4\text{tBu})\text{Co}\{\eta^5\text{-C}_7\text{H}_7(\text{SiMe}_3)_2\}]^+$*

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Co	C1	2.086(5)	Si2	C15	1.857(6)
Co	C2	2.042(5)	C1	C2	1.425(7)
Co	C3	2.100(5)	C1	C7	1.526(8)
Co	C4	2.021(5)	C2	C3	1.439(7)
Co	C5	2.094(6)	C3	C4	1.448(8)
Co	C20	2.084(5)	C4	C5	1.408(8)
Co	C21	2.054(5)	C5	C6	1.507(8)
Co	C22	2.094(6)	C6	C7	1.492(8)
Co	C23	2.078(6)	C20	C21	1.429(7)
Co	C24	2.042(6)	C20	C24	1.411(8)
Si1	C2	1.915(6)	C20	C25	1.519(7)
Si1	C10	1.870(6)	C21	C22	1.411(8)
Si1	C11	1.858(7)	C22	C23	1.418(9)
Si1	C12	1.871(6)	C23	C24	1.421(8)
Si2	C3	1.935(6)	C25	C26	1.538(8)
Si2	C13	1.863(6)	C25	C27	1.529(8)
Si2	C14	1.857(7)	C25	C28	1.523(8)

(b) within the tetrafluoroborate ion

Atom1	Atom2	Distance	Atom1	Atom2	Distance
F1	B	1.393(8)	F3	B	1.359(8)
F2	B	1.365(8)	F4	B	1.384(8)

(c) within the solvent chloroform molecule

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Cl1	C99	1.733(7)	Cl3	C99	1.740(7)
Cl2	C99	1.741(7)			

Table 4. Selected Interatomic Angles (deg)*(a) within $[(\eta^5\text{-C}_5\text{H}_4\text{tBu})\text{Co}\{\eta^5\text{-C}_7\text{H}_7(\text{SiMe}_3)_2\}]^+$*

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	Co	C2	40.4(2)	C21	Co	C22	39.7(2)
C1	Co	C3	71.2(2)	C21	Co	C23	67.1(3)
C1	Co	C4	87.2(2)	C21	Co	C24	67.3(2)
C1	Co	C5	79.5(2)	C22	Co	C23	39.7(2)
C1	Co	C20	118.6(2)	C22	Co	C24	67.2(2)
C1	Co	C21	158.5(2)	C23	Co	C24	40.3(2)
C1	Co	C22	151.4(3)	C2	Si1	C10	116.8(3)
C1	Co	C23	113.7(3)	C2	Si1	C11	110.0(3)
C1	Co	C24	98.8(2)	C2	Si1	C12	104.4(3)
C2	Co	C3	40.6(2)	C10	Si1	C11	106.3(3)
C2	Co	C4	76.2(2)	C10	Si1	C12	111.4(3)
C2	Co	C5	95.4(2)	C11	Si1	C12	107.7(3)
C2	Co	C20	151.2(2)	C3	Si2	C13	110.3(3)
C2	Co	C21	159.8(2)	C3	Si2	C14	106.7(3)
C2	Co	C22	120.7(2)	C3	Si2	C15	113.7(3)
C2	Co	C23	100.4(2)	C13	Si2	C14	105.1(3)
C2	Co	C24	114.1(2)	C13	Si2	C15	112.8(3)
C3	Co	C4	41.1(2)	C14	Si2	C15	107.6(3)
C3	Co	C5	75.6(2)	Co	C1	C2	68.1(3)
C3	Co	C20	168.1(2)	Co	C1	C7	114.3(4)
C3	Co	C21	129.0(2)	C2	C1	C7	121.8(5)
C3	Co	C22	107.7(2)	Co	C2	Si1	127.6(3)
C3	Co	C23	116.2(2)	Co	C2	C1	71.5(3)
C3	Co	C24	149.6(2)	Co	C2	C3	71.9(3)
C4	Co	C5	40.0(2)	Si1	C2	C1	114.5(4)
C4	Co	C20	129.2(2)	Si1	C2	C3	128.9(4)
C4	Co	C21	104.2(2)	C1	C2	C3	116.5(5)
C4	Co	C22	111.1(3)	Co	C3	Si2	134.6(3)
C4	Co	C23	144.1(3)	Co	C3	C2	67.5(3)
C4	Co	C24	169.2(2)	Co	C3	C4	66.5(3)
C5	Co	C20	98.8(2)	Si2	C3	C2	127.8(4)
C5	Co	C21	97.3(2)	Si2	C3	C4	111.3(4)
C5	Co	C22	128.7(3)	C2	C3	C4	120.5(5)
C5	Co	C23	164.1(3)	Co	C4	C3	72.4(3)
C5	Co	C24	132.1(2)	Co	C4	C5	72.8(3)
C20	Co	C21	40.4(2)	C3	C4	C5	128.3(6)
C20	Co	C22	67.3(2)	Co	C5	C4	67.3(3)
C20	Co	C23	67.5(2)	Co	C5	C6	111.8(4)
C20	Co	C24	40.0(2)	C4	C5	C6	128.6(6)

Table 4. Selected Interatomic Angles (continued)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C5	C6	C7	108.4(5)	C21	C22	C23	107.7(5)
C1	C7	C6	110.9(5)	Co	C23	C22	70.7(3)
Co	C20	C21	68.7(3)	Co	C23	C24	68.5(3)
Co	C20	C24	68.4(3)	C22	C23	C24	107.4(6)
Co	C20	C25	137.1(4)	Co	C24	C20	71.6(3)
C21	C20	C24	106.2(5)	Co	C24	C23	71.2(3)
C21	C20	C25	126.6(5)	C20	C24	C23	109.4(5)
C24	C20	C25	126.0(5)	C20	C25	C26	104.5(5)
Co	C21	C20	70.9(3)	C20	C25	C27	113.5(5)
Co	C21	C22	71.6(3)	C20	C25	C28	111.2(5)
C20	C21	C22	109.2(5)	C26	C25	C27	107.6(5)
Co	C22	C21	68.6(3)	C26	C25	C28	109.9(5)
Co	C22	C23	69.6(3)	C27	C25	C28	110.0(5)

(b) within the tetrafluoroborate ion

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
F1	B	F2	108.4(6)	F2	B	F3	108.7(6)
F1	B	F3	110.4(6)	F2	B	F4	111.1(6)
F1	B	F4	108.6(6)	F3	B	F4	109.7(6)

(c) within the solvent chloroform molecule

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
Cl1	C99	Cl2	110.6(4)	Cl2	C99	Cl3	110.5(4)
Cl1	C99	Cl3	109.8(4)				

Table 5. Anisotropic Displacement Parameters (U_{ij} , Å²)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	0.0300(5)	0.0227(4)	0.0219(4)	0.0010(3)	0.0033(4)	0.0056(4)
Si1	0.0330(11)	0.0306(10)	0.0350(10)	0.0014(8)	0.0075(8)	0.0015(8)
Si2	0.0358(11)	0.0371(11)	0.0300(10)	0.0074(8)	0.0079(8)	0.0134(9)
C1	0.031(4)	0.038(4)	0.029(3)	0.006(3)	0.013(3)	0.013(3)
C2	0.030(4)	0.029(3)	0.015(3)	0.004(2)	0.007(3)	0.007(3)
C3	0.034(4)	0.029(3)	0.016(3)	-0.002(2)	0.006(3)	0.005(3)
C4	0.030(4)	0.036(4)	0.024(3)	0.006(3)	-0.005(3)	0.001(3)
C5	0.033(4)	0.034(4)	0.040(4)	-0.006(3)	-0.004(3)	0.000(3)
C6	0.061(5)	0.030(4)	0.039(4)	-0.004(3)	0.001(4)	0.007(3)
C7	0.065(5)	0.040(4)	0.029(4)	-0.004(3)	0.010(3)	0.010(4)
C10	0.054(5)	0.036(4)	0.042(4)	-0.006(3)	0.006(4)	-0.008(3)
C11	0.045(5)	0.056(5)	0.064(5)	0.004(4)	0.001(4)	-0.002(4)
C12	0.051(5)	0.046(4)	0.050(5)	0.001(3)	0.018(4)	-0.001(4)
C13	0.057(5)	0.056(5)	0.051(5)	0.024(4)	0.022(4)	0.020(4)
C14	0.052(5)	0.066(5)	0.052(5)	0.008(4)	0.002(4)	0.026(4)
C15	0.055(5)	0.036(4)	0.036(4)	0.002(3)	0.014(3)	0.018(3)
C20	0.029(3)	0.027(3)	0.018(3)	0.005(2)	0.001(3)	0.004(3)
C21	0.031(4)	0.038(4)	0.025(3)	0.014(3)	0.004(3)	0.010(3)
C22	0.061(5)	0.039(4)	0.021(3)	0.002(3)	0.011(3)	0.020(4)
C23	0.071(5)	0.019(3)	0.024(3)	-0.005(3)	-0.012(3)	-0.003(3)
C24	0.031(4)	0.036(4)	0.026(3)	0.004(3)	-0.002(3)	0.004(3)
C25	0.032(4)	0.027(3)	0.042(4)	0.009(3)	0.000(3)	0.008(3)
C26	0.089(6)	0.030(4)	0.043(4)	0.013(3)	0.003(4)	0.004(4)
C27	0.054(5)	0.029(4)	0.059(5)	0.011(3)	0.000(4)	-0.006(3)
C28	0.056(5)	0.031(4)	0.072(5)	0.004(4)	0.001(4)	0.015(4)
F1	0.048(3)	0.035(2)	0.081(3)	-0.008(2)	0.001(2)	0.0136(19)
F2	0.069(3)	0.064(3)	0.094(4)	-0.016(3)	-0.032(3)	0.021(2)
F3	0.106(4)	0.072(3)	0.072(3)	-0.013(2)	0.049(3)	-0.016(3)
F4	0.051(3)	0.034(2)	0.080(3)	-0.001(2)	0.021(2)	-0.0045(19)
B	0.036(5)	0.037(5)	0.041(5)	-0.009(4)	0.005(4)	0.002(4)
Cl1	0.0908(18)	0.0969(18)	0.0742(16)	0.0375(14)	0.0007(13)	-0.0239(14)
Cl2	0.0861(19)	0.0942(19)	0.119(2)	-0.0010(16)	0.0330(16)	-0.0233(15)
Cl3	0.187(3)	0.0950(19)	0.0808(18)	0.0090(15)	0.0002(19)	0.081(2)
C99	0.077(6)	0.039(4)	0.040(4)	0.001(3)	0.008(4)	0.001(4)

The form of the anisotropic displacement parameter is:

$$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^{*c^{*}}U_{23} + 2hla^{*c^{*}}U_{13} + 2hka^{*b^{*}}U_{12})]$$

Table 6. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}, \text{\AA}^2$
H1	0.4284	0.3542	0.2110	0.037
H4	-0.0360	0.3514	0.2268	0.037
H5	0.0334	0.1690	0.2374	0.044
H6A	0.2248	0.1016	0.1715	0.052
H6B	0.1227	0.1252	0.0773	0.052
H7A	0.2393	0.2980	0.0465	0.053
H7B	0.3558	0.2173	0.0815	0.053
H10A	0.2715	0.7626	0.2550	0.054
H10B	0.4245	0.8041	0.2908	0.054
H10C	0.3397	0.7181	0.3569	0.054
H11A	0.5911	0.4923	0.2559	0.067
H11B	0.5447	0.5444	0.3573	0.067
H11C	0.6295	0.6305	0.2912	0.067
H12A	0.3600	0.6592	0.0507	0.059
H12B	0.4720	0.5678	0.0565	0.059
H12C	0.5097	0.7058	0.0928	0.059
H13A	0.1698	0.7409	0.1269	0.062
H13B	0.0201	0.7672	0.0939	0.062
H13C	0.0853	0.6648	0.0349	0.062
H14A	-0.1416	0.4924	0.0622	0.066
H14B	-0.2070	0.5941	0.1219	0.066
H14C	-0.1869	0.4683	0.1699	0.066
H15A	0.0866	0.6932	0.3462	0.049
H15B	-0.0391	0.5984	0.3538	0.049
H15C	-0.0591	0.7242	0.3058	0.049
H21	0.0375	0.2585	0.4355	0.036
H22	0.0993	0.4889	0.4521	0.047
H23	0.3542	0.5291	0.4401	0.048
H24	0.4473	0.3219	0.4171	0.038
H26A	0.2924	0.0120	0.5660	0.065
H26B	0.2027	0.1202	0.5803	0.065
H26C	0.3601	0.1472	0.5812	0.065
H27A	0.1568	-0.0600	0.4043	0.058
H27B	0.1220	0.0345	0.3227	0.058
H27C	0.0635	0.0428	0.4278	0.058
H28A	0.3954	-0.0146	0.4009	0.063
H28B	0.4667	0.1183	0.4254	0.063
H28C	0.3791	0.0852	0.3208	0.063
H99	-0.2736	0.0817	0.2246	0.063