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Cationic η^3-butadienyl complexes of chromium and manganese

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Experimental

$[(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)Cr(CO)_2(\eta^3\text{-}H_2CC(Me)C{=}CH_2)]BF_4$ 2. A mixture of compound **1** (256 mg,1 mmol), isopropenylacetylene (132 mg, 2 mmol), $HBF_4{\cdot}OEt_2$ (0.14 ml, 1 mmol) and 120 ml of Et_2O was irradiated (quartz apparatus with a cooling jacket using DRL 125 mercury lamp (125 W) for 4 min. An orange precipitate was separated and recrystallized from CH_2Cl_2–Et_2O. Yield 282 mg (74%). ^{1}H NMR ([$^2H_6$]acetone) δ: 6.80 (d, 1H, =CH_a, J_{ab} 4.8 Hz), 6.40 (s, 3H, H_{Ar}), 6.09 (d, 1H, =CH_b, J_{ba} 4.8 Hz), 3.80 (s, 1H, H_{syn}), 3.14 (br.s, 1H, H_{anti}), 2.32 (s, 9H, Me_{Ar}), 1.49 (s, 3H, Me). $^{13}C\{^1H\}$ NMR ([$^2H_6$]acetone, 75.5 MHz) δ: 237.4 (br.s, CO), 179.2 (s, =C=), 120.3 (s, $C_{Ar}Me$), 110.8 (s, =CH_2), 107.3 (s, $C_{Ar}H$), 83.3 (s, $C_{All}Me$), 58.7 (s, CH_2(All)), 22.1 (s, Me_{All}), 19.2 (s, Me_{Ar}). IR (CH_2Cl_2, ν/cm^{-1}): 2012 (vs, ν_{CO}), 1974 (vs, ν_{CO}). Found (%): C, 50.48; H, 5.10. Calc. for $C_{16}H_{19}BCrF_4$ (%): C, 50.40; H, 5.02.

Irradiation of 1 with isopropenylacetylene and aqueous HBF_4. Following procedure analogous to synthesis of complex **2,** the use of **1** (256 mg,1 mmol), isopropenylacetylene (132 mg, 2 mmol), 48% aqueous HBF_4 (0.25 mL, 1 mmol) yielded a mixture of **2** and **3** (19:1 according to ^{1}H NMR data).Yield 130 mg. ^{1}H NMR ([$^2H_6$]acetone) δ: for **2:** 6.85 (d, 1H, =CH_a, J_{ab} 4.8 Hz), 6.42 (s, 3H, H_{Ar}), 6.12 (d, 1H, =CH_b, J_{ba} 4.8 Hz), 3.80 (s, 1H, H_{syn}), 3.20 (br.s, 1H, H_{anti}), 2.30 (s, 9H, Me_{Ar}), 1.53 (s, 3H, Me); for **3**: 6.38 (s, 3H, H_{Ar}), 5.12 (br.s, OH), 3.85 (s, 1H, H_{syn}), 2.64 (s, 1H, H_{anti}), 2.38 (s, 9H, Me_{Ar}), 2.18 (s, 3H, Me_{syn}), 0.86 (s, 3H, Me_{anti}). IR (CH_2Cl_2, ν/cm^{-1}): for 2: 2012 (vs, ν_{CO}), 1974 (vs, ν_{CO}), for **3**: 1976 (vs, ν_{CO}), 1930 (vs, ν_{CO}).

$[(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)Cr(CO)_2(\eta^3\text{-}H_2CCHC{=}CH_2)]BF_4$ 4. This complex was prepared similarly to **2** using **1** (256 mg,1 mmol), vinylacetylene (104 mg, 2 mmol), $HBF_4{\cdot}OEt_2$ (0.14 ml, 1 mmol). Yield 117 mg (32%). ^{1}H NMR ([$^2H_6$]acetone) δ: 6.76 (dd, 1H, =CH_a, J_{ab} 5.0 Hz, ^4J 2.9 Hz), 6.60 (s, 3H, H_{Ar}), 6.15 (dd, 1H, =CH_b, J_{ba} 5.0 Hz, ^4J 2.9 Hz), 4.51 (ddt, 1H, H_{centr}, $^3J_1$ 11.3 Hz, $^3J_2$ 8.3 Hz, ^4J 2.9 Hz), 3.98 (d, 1H, H_{syn}, ^3J 9.0 Hz), 2.44 (s, 9H, Me_{Ar}), 1.73 (d, 1H, H_{anti}, ^3J 11.4 Hz). IR (CH_2Cl_2, ν/cm^{-1}): 1996 (vs, ν_{CO}), 1947 (vs, ν_{CO}). Found (%): C, 49.18; H, 4.70. Calc. for $C_{15}H_{17}BCrF_4$ (%): C, 49.05; H, 4.67.

Complex **4** was prepared by the same procedure using allenylcarbinol instead of vinylacetylene. Yield (32%). IR (CH_2Cl_2, ν/cm^{-1}): 1996 (vs, ν_{CO}), 1947 (vs, ν_{CO}).

[η^5-$C_5H_5Mn(CO)_2$(η^3-$H_2CCHC{=}CH_2$)]BF_4 7. A mixture of compound **5** (204 mg, 1 mmol), allenylcarbinol (140 mg, 2 mmol) and 120 ml of C_6H_6 was irradiated for 30 min. The resulting solution was concentrated to *ca* 5 ml, filtered through silica and evaporated to dryness. ^{1}H NMR spectra (C_6D_6) showed a presence of three isomers **6a - 6c** (**6a**/**6b**/**6c** = 75/11/14). For **6a** δ: 6.40 (dd, 1H, *H*HC=, ^4J 3.1 Hz, ^2J 1.9 Hz), 5.72 (dd, 1H, H*H*C=, ^4J 3.1 Hz, ^2J 1.9 Hz), 4.03 (s, 5H, Cp), 3.96 (dd, 1H, C*H*H, ^3J 5.5 Hz, ^2J 11.4 Hz), 3.17 (dd, 1H, CH*H*, ^2J 11.4 Hz, ^3J 8.3 Hz), 2.64 (m, 1H, =CH, ^4J 3.1 Hz), 1.6 (br.s, 1H, OH); for **6b** δ: 6.13 (m, 1H, =CH), 4.34 (d, 2H, CH_2, ^3J 5.6 Hz), 4.00 (s, 5H, Cp): for **6c** δ: 7.00 (m, 1H, =CH), 4.65 (d, 2H, CH_2, ^3J 6.8 Hz), 4.10 (s, 5H, Cp). The NMR sample was evaporated, dried, the residue was solved in 5 ml of Et_2O, cooled to –20 ºC and $HBF_4{\cdot}OEt_2$ (0.14 ml, 1 mmol) added. A yellow precipitate was separated and recrystallized from CH_2Cl_2–Et_2O. Yield 92 mg (30%). IR ($MeNO_2$, ν/cm^{-1}): 2048 (vs, ν_{CO}), 2004 (vs, ν_{CO}). Product represents a mixture of *exo*/*endo* isomers **7a** and **7b** (7/1 according ^{1}H NMR data).

For **7a**: ^{1}H NMR ([$^2H_3$]$MeNO_2$) δ: 6.79 (d, 1H, =CH_a, J_{ab} 6.6 Hz), 6.04 (d, 1H, =CH_b, J_{ba} 6.6 Hz), 5.66 (s, 5H, Cp), 5.19 (m, 1H, H_{centr}), 4.41 (d, 1H, H_{syn}, ^3J 7.4 Hz), 2.555 (d, 1H, H_{anti}, ^3J 12.2 Hz); for **7b**: ^{1}H NMR ([$^2H_3$]$MeNO_2$) δ: 6.69 (d, 1H, =CH_a, J_{ab} 6 Hz), 5.82 (d, 1H, =CH_b, J_{ba} 6 Hz), 5.61 (s, 5H, Cp), 4.71 (d, 1H, H_{syn}, ^3J 7 Hz), 3.68 (d, 1H, H_{anti}, ^3J 12 Hz). IR ($MeNO_2$, ν/cm^{-1}): 2048 (vs, ν_{CO}), 2004 (vs, ν_{CO}). Found (%): C, 43.05; H, 3.50. Calc. for $C_{11}H_{10}BF_4MnO_2$ (%): C, 43.32; H, 3.28.

[η^5-$C_5H_5Mn(CO)_2$(η^3-$H_2CCHC{=}CH_2$)]BF_4 7. A mixture of (**5**) (204 mg, 1 mmol) and 120 ml of THF was irradiated for 1 h and allenylcarbinol (140 mg, 2 mmol) added. After stirring for 1h at room temperature the resulting solution was evaporated and recrystallized from Et_2O–hexane to afford **6a**. Yield 78 mg (32 %). ^{1}H NMR (C_6D_6) δ: 6.39 (dd, 1H, *H*HC=, ^2J 1.9 Hz, ^4J 3.0 Hz), 5.71 (dd, 1H, H*H*C=, ^2J 1.9 Hz, ^4J 3.0 Hz), 4.02 (s, 5H, Cp), 3.94 (dd, 1H, C*H*H, ^2J 11.0 Hz, ^3J 5.9 Hz), 3.17 (dd, 1H, CH*H*, ^2J 11.0 Hz, ^3J 8.9 Hz), 2.62 (m, 1H, =CH, ^4J 3.0 Hz), 1.45 (br.s, 1H, OH). The NMR sample was evaporated to dryness, solved in 3 ml of Et_2O and dropped to cooled (–20 ºC) solution of $HBF_4{\cdot}OEt_2$ (0.14 ml, 1 mmol) in 3 ml of Et_2O. After stirring for 1h at room temperature the forming precipitate was filtered off and dried *in vacuo*. Yield 79 mg (81 %) of **7.** ^{1}H NMR and IR spectra are identical to those for the sample from the previous procedure.

(η^6-1,3,5-$Me_3C_6H_3$)Cr(CO)$_2$(η^2-H_2C=C=CMe_2) 8. $NaBH_4$ (40 mg, 1 mmol) was added to a water solution of **2** (190 mg, 0.5 mmol) under vigorous stirring until the colourless aqueous layer. Organic solution was separated, washed with water and dried over Na_2SO_4. The volatile materials were removed. Recrystallization of the residue from hexane afforded orange crystals of **8** (118 mg, 80%). ^{1}H NMR (C_6D_6) δ: 4.44 (s, 3H, H_{Ar}), 2.39 (t, 3H, =CMe*Me*, ^5J =1.7 Hz), 2.29 (t, 3H, =C*Me*Me, ^5J = 2.2 Hz), 1.72 (s, 9H, Me_{Ar}), 1.35 (septet, 2H, =CH_2, ^5J = 1.9 Hz). IR (hexane, ν/cm^{-1}): 1928 (vs, ν_{CO}), 1879 (vs, ν_{CO}). Found (%): C, 65.05; H, 6.70. Calc. for $C_{16}H_{20}CrO_2$ (%): C, 64.85; H, 6.80.

[(η^6-1,3,5-$Me_3C_6H_3$)Cr(CO)$_2$(η^2-H_2C=C=$CHCH_2PPh_3$)]BF_4 9. PPh_3 (144 mg, 0.55mmol) in Et_2O (3 ml) was added to a suspension of **4** (183 mg, 0.5 mmol) in Et_2O (5 ml), followed by stirring for 2 h. The yellow precipitate was recrystallized from CH_2Cl_2–Et_2O. Yield 218 mg (68%). ^{1}H NMR (CD_2Cl_2) δ: 7.57-7.58 (m, 15H, Ph), 5.51 (m, 1H, =CH). 5.12 (s, 3H, H_{Ar}), 4.28 (dd, 2H, CH_2, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 12.8 Hz), 2.01 (s, 9H, Me), 0.67 (dd, 2H, =CH_2, $^4J_{HH}$ =2.7, $^5J_{HP}$ =5.8 Hz). IR (CH_2Cl_2, ν/cm^{-1}): 1920 (vs, ν_{CO}), 1860 (vs, ν_{CO}). Found (%): C, 63.15; H, 4.90. Calc. for $C_{34}H_{32}BF_4CrO_2P$ (%): C, 63.65; H, 5.03.

[η^5-C_5H_5Mn(CO)$_2$(CO)$_2$(η^2-H_2C=C=$CHCH_2PPh_3$)]BF_4 10. This complex was prepared similarly to **9** using **7** (102 mg, 0.33mmol), PPh_3 (92 mg, 0.35 mmol) and 5 ml of Et_2O. The yellow powder was separated, solved in CH_2Cl_2 and filtered hrough silica pad cooled to –40 ºC. Solvent was removed *in vacuo* and the residue crystallized from CH_2Cl_2–Et_2O. Yield 117 mg (58%). ^{1}H NMR (CD_2Cl_2) δ: 7.74-8.08 (m, 15H, Ph), 5.48(br.dd, 1H, =CH*H*), 5.09 (dd, 1H, =C*H*H, $^2J_{HH}$ ~ $^4J_{HP}$ ~2.5 Hz), 4.94 (s, 5H,Cp), 4.59 (ddd, 1H, C*H*H), 3.21 (ddd, 1H, =CH, $^3J_{HH}$ ~ 2, $^2J_{HH}$ = 15.2, $^2J_{HP}$ =12.9 Hz), 3.21 (ddd, 1H, CH*H*, $^3J_{HH}$ = 9.2, $^2J_{HH}$ = 15.2, $^2J_{HP}$ = 12.9 Hz), 2.70 (m, 1H, =CH, $^4J_{HH}$ = 2.5, $^3J_{HH}$ =8.6 Hz). IR ($MeNO_2$, ν/cm^{-1}): 1986 (vs, ν_{CO}), 1924 (vs, ν_{CO}). Found (%): C, 56.95; H, 3.79. Calc. for $C_{29}H_{25}BF_4MnO_2P$ (%): C, 57.30; H, 4.15.