PREPARATION OF NEW (η^5-C$_5$H$_4$CH$_3$)Mn(NO)(PPh$_3$) AND (η^7-C$_7$H$_7$)Mo(CO)-(PPh$_3$) COMPLEXES *

D.L. REGER *, D.J. FAUTH and M.D. DUKES

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208 (U.S.A.)

Summary

The complex (η^5-C$_5$H$_4$CH$_3$)Mn(NO)(PPh$_3$)I has been prepared by the reaction of NaI with [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CO)(PPh$_3$)]$^+$ and also by the reaction of [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CO)$_2$]$^-$ with NaI followed by PPh$_3$. This iodide compound reacts with NaCN to yield (η^5-C$_5$H$_4$CH$_3$)Mn(NO)(PPh$_3$)CN which is ethylated by [(C$_2$H$_5$)$_3$O]BF$_4$ to yield [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(PPh$_3$)(CNC$_2$H$_5$)]$^+$. Both [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CO)$_2$]$^-$ and [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(PPh$_3$)(CO)]$^+$ react with NaCN to yield [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CN)$_2$]$^-$. This anion reacts with Ph$_3$SnCl to yield *cis*-(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CN)$_2$SnPh$_3$ and with [(C$_2$H$_5$)$_3$O]BF$_4$ to yield [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CNC$_2$H$_5$)$_2$]$^+$. The reaction of (η^5-C$_5$H$_4$CH$_3$)Mn(NO)(PPh$_3$)I with AgBF$_4$ in acetonitrile yields [(η^5-C$_5$H$_4$CH$_3$)Mn-(NO)(PPh$_3$)(NCCH$_3$)]$^+$. The complex (η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CO)I, produced in the reaction of [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CO)$_2$]$^+$ with NaI, is not stable and decomposes to the dimeric complex (η^5-C$_5$H$_4$CH$_3$)$_2$Mn$_2$(NO)$_3$I for which a reasonable structure is proposed. Similar dimers can be prepared from the other halide salts. The reaction of (η^7-C$_7$H$_7$)Mo(CO)(PPh$_3$)I with NaCN yields (η^7-C$_7$H$_7$)Mo(CO)(PPh$_3$)CN which is ethylated by [(C$_2$H$_5$)$_3$O]BF$_4$ to yield [(η^7-C$_7$H$_7$)-Mo(CO)(PPh$_3$)(CNC$_2$H$_5$)]$^+$. The interaction of this molybdenum halide complex with AgBF$_4$ in acetonitrile and pyridine yields [(η^7-C$_7$H$_7$)Mo(CO)(PPh$_3$)-(NCCH$_3$)]$^+$ and [(η^7-C$_7$H$_7$)Mo(CO)(PPh$_3$)(NC$_5$H$_5$)]$^+$, respectively. Both (η^5-C$_5$H$_4$CH$_3$)Mn(NO)(PPh$_3$)I and (η^7-C$_7$H$_7$)Mo(CO)(PPh$_3$)I are oxidized by NOPF$_6$ to the respective 17-electron cations in acetonitrile at —78°C but revert to the neutral halide complex at room temperature. This result is supported by electrochemical data.

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Introduction

The derivative chemistry of the $(\eta^5\text{-}C_5H_5)Fe(CO)(L)$ system (L = CO, PPh$_3$, P(OPh)$_3$) has been extensive and has proven to be useful for studies ranging from CO and SO$_2$ insertion reactions [1] to alkyl decomposition studies [2] to use as a template for organic synthesis [3]. An important reason that this system has been chosen in many cases is that the starting material for this chemistry, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, is readily available [4].

Two somewhat similar systems, $(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(L)$ and $(\eta^7\text{-}C_7H_7)Mo\text{-}CO(L)$, that also arise from readily available starting materials have not been studied extensively. Of specific interest to us was the derivatization of these two systems starting with the appropriate metal halide, known for the molybdenum case [5] but not for manganese. We have had considerable success recently in carrying out a wide variety of substitution reactions with $(\eta^5\text{-}C_5H_5)\text{-}Fe(CO)(L)I$ complexes [6] and hoped to extend this chemistry to these other two systems. Reported here are the results of that investigation.

Experimental

General

All operations on complexes in solution were carried out under purified nitrogen using freshly distilled degassed solvents. All ^{13}C NMR spectra were run with ^1H decoupling on a Varian CFT-20 spectrometer. Dichloromethane was used as internal reference for the ^{13}C NMR spectra and is assigned a value of 54.00 ppm. Ethanol was also used as an internal reference and is assigned values of 57.45 and 18.02 ppm. Both ^1H and ^{13}C chemical shift data are reported in δ(ppm) from TMS. Infrared spectra were recorded on a Perkin—Elmer model 337. Far infrared spectra were recorded on Perkin—Elmer 621.

Silver tetrafluoroborate and nitrosonium hexafluorophosphate were purchased from Ozark—Mahoning. These solids were stored and weighed for reactions in an inert atmosphere box. The complex $(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$ was a gift from the Ethyl Corporation. The method of King [4] was used to prepare $[(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(CO)_2]PF_6$, $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ and $(\eta^7\text{-}C_7H_7)Mo\text{-}(CO)_2I$ and $(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)I$ was prepared as described by Beall and Houk [5].

$[(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(PPh_3)(CO)]PF_6$ (I)

A mixture of $[(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(CO)_2]PF_6$ (12.0 g, 32.9 mmol) and PPh$_3$ (9.0 g, 34 mmol) in THF (300 ml) was stirred in a 500 ml three-neck flask. Gas evolution was immediate and the starting dicarbonylmanganese complex dissolved as the substitution reaction proceeded. After 30 minutes, orange crystals formed from the now homogeneous solution. This solution was stirred another 30 minutes then cooled to $-20°C$ to complete crystallization. These crystals were collected, washed with hexane (5 × 20 ml), and dried in vacuo (18.3 g, 95%). The infrared spectrum matched that previously reported [7]. ^1H NMR spectrum (acetone-d_6): 7.65, 7.50 (15, multiplets, PPh$_3$) 5.68, 5.19, 5.13 (2,1,1, multiplets, C$_5$H$_4$), 2.15 (3, singlet, CH$_3$). ^{13}C NMR spectrum (CH$_2$Cl$_2$): 223.58 (doublet, J 35.2 Hz, carbonyl carbon), 132.83 (doublet, J 11.2 Hz,

ortho phenyl carbons), 132.40 (singlet, *para* phenyl carbons), 130.68 (doublet, J 49.7 Hz, P-bound carbons), 129.92 (doublet, J 10.6 Hz, *meta* phenyl carbons), 114.64 (singlet, C-CH_3 cyclopentadienyl carbon), 97.38, 95.80, 93.46, 92.74 (singlets, C-H cyclopentadienyl carbons), 12.65 (singlet, methyl carbon).

$(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(PPh_3)I$ (II)

Method A. A mixture of $[(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(CO)(PPh_3)]PF_6$ (2.0 g, 3.3 mmol) and NaI (0.55 g, 3.6 mmol) was stirred in THF (100 ml). After 15 h the solvent was evaporated, the residue extracted with hot toluene (150 ml), and this mixture filtered hot. Evaporation of the toluene followed by recrystallization from an acetone/water mixture (50 ml, 4/1 v/v) yielded brown crystals that were collected, washed with hexane (5 × 20 ml), and dried in vacuo over P_4O_{10} at 100°C (1.23 g, 65%), m.p. 145–146°C.

Method B. A mixture of $[(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(CO)_2]PF_6$ (1.2 g, 3.3 mmol) and NaI (0.55 g, 3.6 mmol) in THF (50 ml) was stirred for 30 minutes then filtered using filter aid. Triphenylphosphine (1.0 g, 3.9 mmol) in THF (10 ml) was added to the filtrate and stirring was continued for 2 h. The solvent was then evaporated and the remaining brown solid purified as in Method A (0.5 g, 82%). (Found: C, 51.83; H, 4.06. $C_{24}H_{22}IMnNOP$ calcd.: C, 52.10; H, 4.01%) IR spectrum (cm^{-1}): ν(NO) 1715 (CH_2Cl_2), 1705 (mull). ^{1}H NMR spectrum ($CDCl_3$): 7.38 (15, broad multiplet, PPh_3), 4.94, 4.61, 3.81 (2, 1, 1, multiplets, C_5H_4), 1.91 (3, singlet, CH_3). ^{13}C NMR spectrum (CH_2Cl_2): 134.04 (doublet, J 55.6 Hz, P-bound carbons), 133.68 (doublet, J 9.8 Hz, *ortho* phenyl carbons), 130.34 (singlet, *para* phenyl carbons), 128.31 (doublet, J 9.6 Hz, *meta* phenyl carbons), 107.30 (singlet, C-CH_3 cyclopentadienyl carbon), 95.89, 97.51, 91.91, 87.06 (singlets, C-H cyclopentadienyl carbons), 13.06 (singlet, methyl carbon).

$(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(PPh_3)CN$ (IV)

A mixture of $(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(PPh_3)I$ (5.53 g, 10.0 mmol) and NaCN (0.98 g, 20 mmol) in ethanol (100 ml) was stirred and heated at 50°C for 30 minutes. The solvent was then evaporated, the residue extracted with boiling CH_2Cl_2 (200 ml), and filtered hot using filter aid. The solvent was slowly evaporated to yield a red powder. Recrystallization of this powder from an acetone/water mixture (100 ml, 3/1 v/v) gave dark red crystals (2.67 g, 59%), m.p. 143–144°C. (Found: C, 66.50; H, 4.96. $C_{25}H_{22}MnN_2OP$ calcd.: C, 66.36; H, 4.90%). IR spectrum (cm^{-1} in CH_2Cl_2): ν(CN) 2095, ν(NO) 1730. ^{1}H NMR spectrum ($CDCl_3$): 7.38, 7.25 (15, singlet, multiplet, PPh_3), 4.80, 4.42, 4.38 (1, 1, 2, multiplets, C_5H_4), 1.92 (3, singlet, CH_3). ^{13}C NMR spectrum (CH_2Cl_2): 146.44 (doublet, J 34.0 Hz, cyanide carbon), 134.34 (doublet, J 44.2 Hz, P-bound carbons), 133.37 (doublet, J 9.9 Hz, *ortho* phenyl carbons), 130.66 (doublet, J 2.4 Hz, *para* phenyl carbons), 128.67 (doublet, J 10.0 Hz, *meta* phenyl carbons), 109.40 (singlet, C-CH_3 cyclopentadienyl carbon), 93.74, 92.69, 91.69, 89.47 (singlets, C-H cyclopentadienyl carbons), 13.10 (singlet, methyl carbon).

$[(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(PPh_3)(CNC_2H_5)]BF_4$

A mixture of $(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(PPh_3)CN$ (1.0 g, 2.2 mmol) and $[(C_2H_5)_3O]BF_4$ (0.55 g, 2.9 mmol) in CH_2Cl_2 (50 ml) was stirred at 0°C. After 20

minutes the solvent was evaporated, the residue extracted with boiling ethanol (50 ml) and filtered hot. Slow cooling to $-20°C$ yielded orange-red crystals which were collected, washed with hexane (3 × 20 ml), and dried in vacuo (0.90 g, 72%), m.p. 211—212°C. (Found: C, 56.81; H, 4.88. $C_{27}H_{27}BF_4MnN_2$-OP calcd.: C, 57.06; H, 4.79%). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(CN)$ 2175, $\nu(NO)$ 1760. ^{1}H NMR spectrum (CDCl$_3$): 7.38, 7.28 (15, singlet, multiplet, PPh$_3$), 5.21, 4.91, 4.74, 4.63 (1, 1, 1, 1, multiplets, C$_5$H$_4$), 3.66, 3.68 (1,1 quartets, J 8.0 Hz, CNCH$_2$), 1.97 (3, singlet, C$_5$H$_4$CH$_3$), 0.99 (3, triplet, J 6.0 Hz, CH$_2$CH$_3$). ^{13}C NMR spectrum (CH_2Cl_2): 172.7 (broad singlet, cyanide carbon), 132.93 (doublet, J 10.4 Hz, *ortho* phenyl carbons), 131.98 (doublet, J 38.5 Hz, P-bound carbons), 131.55 (doublet, J 2.2 Hz, *para* phenyl carbons), 129.34 (doublet, J 10.1 Hz, *meta* phenyl carbons), 106.25 (singlet, C-CH$_3$ cyclopentadienyl carbon), 94.41, 93.66, 92.80, 90.10 (singlets, C-H cyclopentadienyl carbons), 35.80 (singlet, isocyanide methylene carbon), 14.22 (singlet, isocyanide methyl carbon), 12.65 (singlet, cyclopentadienyl methyl carbon).

Na[(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CN)$_2$] (VI)

Method A. A mixture of [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CO)$_2$]PF$_6$ (3.65 g, 10.0 mmol) and NaCN (2.45 g, 50.0 mmol) in ethanol (125 ml) was stirred and heated at 50°C for 12 h. The solution was heated to reflux then filtered using filter aid. Heptane (70 ml) was slowly added to the hot solution. Slow cooling to $-20°C$ yielded a light red powder which was collected, washed with CH_2Cl_2 (4 × 20 ml), and dried in vacuo (2.13 g, 89%), dec. 220°C.

Method B. A mixture of [(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CO)(PPh$_3$)]PF$_6$ (5.99 g, 10.0 mmol) and NaCN (1.47 g, 30.0 mmol) in ethanol (125 ml) was stirred and heated at 50°C for 3 h. Work-up as in Method A gave an identical light red powder (1.8 g, 76%). IR spectrum (cm^{-1}): $\nu(CN)$ 2095, $\nu(NO)$ 1730 (acetone); $\nu(CN)$ 2100, 2095, $\nu(NO)$ 1715 (mull). ^{1}H NMR spectrum (acetone-d_6): 4.63 (4, singlet, C$_5$H$_4$), 1.82 (3, singlet, CH$_3$). ^{13}C NMR spectrum (C$_2$H$_5$OH): 159.0 and 162.0 (broad singlets, cyanide carbons), 108.52 (singlet, C-CH$_3$ cyclopentadienyl carbon), 90.24 (singlet, C-H cyclopentadienyl carbons), 13.46 (singlet, methyl carbon).

(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CN)$_2$SnPh$_3$

A tetrahydrofuran solution (100 ml) of Na[(η^5-C$_5$H$_4$CH$_3$)Mn(NO)(CN)$_2$] (2.39 g, 10.0 mmol) was cooled to 0°C and treated with Ph$_3$SnCl (4.0 g, 10 mmol). After this had been stirred for 5 minutes, the solvent was evaporated, the residue extracted with hot heptane (325 ml) and this mixture filtered hot using filter aid. Cooling the filtrate to $-20°C$ yielded dark red crystals which were collected, washed with hexane and dried in vacuo (3.28 g, 58%), m.p. 94—95°C. (Found: C, 55.00, H, 3.92. $C_{26}H_{22}MnN_3OSn$ calcd.: C, 55.06; H, 3.92%). IR spectrum (cm^{-1}): $\nu(CN)$ 2095, $\nu(NO)$ 1750 (CH_2Cl_2); $\nu(CN)$ 2100 (vs), 2095 (s), $\nu(NO)$ 1740 (vs) (mull). ^{1}H NMR spectrum (CDCl$_3$): 7.89, 7.16 (15, multiplets, PPh$_3$), 4.42 (4, singlet, C$_5$H$_4$), 1.51 (3, singlet, CH$_3$). ^{13}C NMR spectrum (CH_2Cl_2): 166.76, 166.64 (singlets, cyanide carbons), 141.84 (singlet, Sn-bound phenyl carbons), 136.47 (singlet, *ortho* phenyl carbons), 129.35 (singlet, *para* phenyl carbons) 128.59 (singlet, *meta* phenyl carbons), 109.69 (singlet, C-CH$_3$ cyclopentadienyl carbon), 90.48 (singlet, C-H cyclopentadienyl carbons), 13.10 (singlet, methyl carbon).

[(η⁵-C₅H₄CH₃)Mn(NO)(CNC₂H₅)₂]BF₄

A mixture of Na[(η⁵-C₅H₄CH₃)Mn(NO)(CN)₂] (2.39 g, 10.0 mmol) and [(C₂-H₅)₃O]BF₄ (5.70 g, 30.0 mmol) was stirred in CH₂Cl₂ (120 ml). After 45 minutes, the mixture was filtered and the solvent then evaporated. Extraction of the residue with hot ethanol (50 ml) was followed by filtration and the addition of heptane (60 ml) to the warm ethanolic solution. Slow cooling to —20°C yielded dark red crystals which were collected, washed with hexane and dried in vacuo (2.2 g, 61%), m.p. 59—60°C. (Found: C, 38.95; H, 4.79. C₁₂H₁₇BF₄-MnN₃O calcd.: C, 39.92; H, 4.74%). IR spectrum (cm⁻¹ in CH₂Cl₂): ν(CN) 2210, 2190, ν(NO) 1780. ¹H NMR spectrum (CDCl₃): 5.16 (4, complex AB type pattern, C₅H₄), 4.01 (4, quartet, *J* 7.0 Hz, CNCH₂), 1.94 (3, singlet, C₅H₄*CH₃*), 1.45 (6, triplet, *J* 5.9 Hz, CH₂*CH₃*). ¹³C NMR spectrum (CH₂Cl₂): 155.14 (broad, cyanide carbons), 112.44 (singlet, C-CH₃ cyclopentadienyl carbon), 92.32, 91.24, (singlets, C-H cyclopentadienyl carbons), 41.27 (singlet, isocyanide methylene carbons), 14.65 (singlet, isocyanide methyl carbons), 12.88 (singlet, cyclopentadienyl methyl carbon).

(η⁵-C₅H₄CH₃)₂Mn₂(NO)₃I (VII)

A mixture of [(η⁵-C₅H₄CH₃)Mn(NO)(CO)₂]PF₆ (3.65 g, 10.0 mmol) and NaI (3.50 g, 28.4 mmol) in THF (150 ml) was stirred for 40 minutes. The solvent was evaporated and the residue was extracted with boiling heptane (175 ml) and filtered hot. Slow cooling of the filtrate to —20°C yielded dark crystals which were collected and dried in vacuo at 100°C for several hours (0.58 g, 12%), dec. 176°C (with formation of I₂). (Found: C, 29.35; H, 3.02; Mn, 22.38; I, 26.15, N, 8.49; O (by difference), 10.59. C₁₂H₁₄IMn₂N₃O₃ calcd.: C, 29.69; H, 2.91; Mn, 22.65; I, 26.16; N, 8.66; O, 9.89%). IR spectrum (cm⁻¹): ν(NO) 1730, ν(μ-NO) 1520 (mull); ν(Mn—I) 250 (CsBr pellet). ¹H NMR spectrum (CDCl₃): 5.61, 5.43, 5.03, (8, broad singlets, C₅H₄), 2.14, 1.92, (3,3, singlets, CH₃). ¹³C NMR spectrum (CH₂Cl₂): 104.30 (singlet, C-CH₃ cyclopentadienyl carbons), 104.17, 104.00, 103.46, 100.57 (singlets, C-H cyclopentadienyl carbons), 12.42, 12.01, (singlets, methyl carbons).

(η⁵-C₅H₄CH₃)₂Mn₂(NO)₃Br

A mixture of [(η⁵-C₅H₄CH₃)Mn(NO)(CO)₂]PF₆ (3.65 g, 10.0 mmol) and NaBr (1.54 g, 15.0 mmol) in THF (100 ml) was stirred for 6 h then filtered. The solvent was evaporated and the residue extracted with hot heptane (300 ml) and filtered hot. Slow cooling to —20°C yielded dark brown crystals which were collected, washed with hexane (3 × 10 ml), and dried in vacuo (0.53 g, 12%), dec. 150°C (with formation of Br₂). (Found: C, 32.36; H, 3.20; Br, 17.75. C₁₂H₁₄BrMn₂N₃O₃ calcd.: C, 32.90; H, 3.22; Br, 18.24%). IR spectrum (cm⁻¹): ν(NO) 1745, ν(μ-NO) 1530 (mull); ν(Mn—Br) 260 (CsBr pellet). ¹H NMR spectrum (CDCl₃): 5.18, 4.86 (8, broad singlets, C₅H₄), 2.00, 1.80 (3,3, singlets, CH₃). ¹³C NMR spectrum (CH₂Cl₂): 117.51 (singlet, C-CH₃ cyclopentadienyl carbons), 105.06, 104.74, 102.44, 99.67 (C-H cyclopentadienyl carbons), 12.37, 11.93 (singlets, methyl carbons).

The complexes (η⁵-C₅H₄CH₃)₂Mn₂(NO)₃Cl and (η⁵-C₅H₄CH₃)₂Mn₂(NO)₃F could also be prepared in analogous reactions but proved difficult to purify completely. The far-infrared spectra of these complexes show a ν(Mn—Cl) band at 280 cm⁻¹ and a ν(Mn—F) band at 295 cm⁻¹, respectively.

[(η⁵-C₅H₄CH₃)Mn(NO)(PPh₃)(CH₃CN)]BF₄

A mixture of (η⁵-C₅H₄CH₃)Mn(NO)(PPh₃)I (1.0 g, 1.8 mmol) and AgBF₄ (0.40 g, 2.0 mmol) in acetonitrile (40 ml) in an aluminum foil covered flask was stirred for 20 minutes and then filtered using filter aid. The solvent was evaporated to yield a dark solid. Recrystallization of this solid from an ethanol/ heptane mixture (100 ml, 1/1 v/v) yielded dark brown crystals which were collected, washed with hexane, and dried in vacuo, (0.40 g, 40%), m.p. 107— 108°C. IR spectrum (cm⁻¹ in CH₂Cl₂): ν(NO) 1750. ¹H NMR spectrum (CDCl₃): 7.38, 7.19 (15, singlet, multiplet, PPh₃) 5.40, 5.18, 4.68 (1,1,2, multiplets, C₅H₄), 2.03 (3, singlet, C₅H₄*CH₃*), 1.78 (3, singlet, NCCH₃). ¹³C NMR spectrum (CH₂Cl₂): 144.54 (triplet, J(CN) 3.0 Hz, nitrile carbon), 133.16 (doublet, J 10.3 Hz, *ortho* phenyl carbons), 131.39 (singlet, *para* phenyl carbons), 131.12 (doublet, J 45.2 Hz, P-bound carbons), 129.26 (doublet, J 10.1 Hz, *meta* phenyl carbons), 113.24 (doublet, J 1.2 Hz, C-CH₃ cyclopentadienyl carbon), 97.03, 96.24, 92.70, 87.21 (doublet, J 1.7 Hz; singlet; singlet; doublet, J 1.2 Hz; C-H cyclopentadienyl carbons), 12.32 (singlet, cyclopentadienyl methyl carbon), 4.12 (singlet, acetonitrile methyl carbon).

(η⁷-C₇H₇)Mo(CO)(PPh₃)CN

A mixture of (η⁷-C₇H₇)Mo(CO)(PPh₃)I (3.0 g, 5.0 mmol) and NaCN (2.1 g, 43 mmol) was stirred in ethanol (50 ml) at 50°C for 3 h. The resulting brownish-green mixture was filtered and the solvent was evaporated leaving a green solid. Recrystallization of this solid from ethanol/hexane (50 ml, 4/1 v/v) yielded green platelets (2.0 g, 79%), dec. 139—142°C. (Found: C, 63.95; H, 4.47. C₂₇H₂₂MoNOP calcd.: C, 64.42; H, 4.41%). IR spectrum (cm⁻¹ in CH₂-Cl₂): ν(CO) 1945, ν(CN) 2080. ¹H NMR spectrum (CDCl₃): 7.28—7.72 (15, PPh₃), 5.02 (7, C₇H₇).

[(η⁷-C₇H₇)Mo(CO)(PPh₃)(CNC₂H₅)]BF₄

A mixture of (η⁷-C₇H₇)Mo(CO)(PPh₃)CN (0.35 g, 0.70 mmol) and [(C₂-H₅)₃O]BF₄ (0.13 g, 0.70 mmol) was stirred in CH₂Cl₂ (20 ml). Over a 30 minutes period the color of the solution changed from green to red. The solvent was then evaporated, the residue extracted with boiling ethanol (20 ml) and this mixture filtered hot. Upon cooling to −20°C, red-brown crystals precipitated from the solution. These crystals were collected and dried in vacuo (0.26 g, 59%), dec. 221°C. (Found: C, 56.31; H, 4.50. C₂₉H₂₇BF₄MoNOP calcd.: C, 56.24; H, 4.40%). IR spectrum (cm⁻¹ in CH₂Cl₂): ν(CO) 1960, ν(CN) 2160. ¹H NMR spectrum (CDCl₃): 7.15—7.57 (15, multiplet, PPh₃), 5.36 (7, doublet, J 2.0 Hz, C₇H₇), 3.52 (2, quartet, J 7.0 Hz, CH₂), 0.95 (3, triplet, J 7.0 Hz, CH₃).

[(η⁷-C₇H₇)Mo(CO)(PPh₃)(CH₃CN)]BF₄

Acetonitrile (20 ml) was added to a mixture of (η⁷-C₇H₇)Mo(CO)(PPh₃)I (1.00 g, 1.66 mmol) and AgBF₄ (0.32 g, 1.7 mmol). A vigorous reaction was noted and the green-gray solution turned bright green. After 10 minutes of stirring, the solvent was evaporated and the residue extracted with CH₂Cl₂ (4 × 20 ml). This mixture was filtered using filter aid and the CH₂Cl₂ evaporated yielding a green solid. Recrystallization from CH₂Cl₂/hexane (15 ml, 4/1 v/v)

yielded deep green crystals (0.83 g, 83%), dec. 185—188°C. (Found: C, 55.33, H, 4.15. $C_{28}H_{25}BF_4MoNOP$ calcd.: C, 55.56; H, 4.16%). IR spectrum (cm^{-1} in CH_2Cl_2); $\nu(CO)$ 1950. ^{1}H NMR spectrum (CDCl$_3$): 7.48 (15, multiplet, PPh$_3$), 5.33 (7, doublet, J 3.0 Hz, C_7H_7). 1.90 (3, doublet, J 2.0 Hz, CH$_3$).

$[(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)(C_5H_5N)]BF_4$

This compound was prepared as described for $[(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)(CH_3\text{-}CN)]BF_4$ except pyridine (15 ml) was added to the mixture of $(\eta^7\text{-}C_7H_7)Mo\text{-}(CO)(PPh_3)I$ and AgBF$_4$. The work-up described previously yielded a bright green solid. The green solid was dissolved in boiling ethanol (20 ml) and the solution was filtered hot. Cooling to —20°C yielded green crystals which were collected by filtration and dried in vacuo (0.90 g, 85%), m.p. 126—129°C. This solid contained one equivalent of EtOH of crystallization which was liberated at 104°C. (Found: C, 56.84; H, 4.70. $C_{33}H_{33}BF_4MoNO_2P$ calcd.: C, 57.50; H, 4.83%). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(CO)$ 1940. ^{1}H NMR spectrum (acetone-d_6): 8.64 (2, doublet, J 5.0, H 2,6 of pyridine), 6.96—7.79 (18, multiple peaks, PPh$_3$ and H 3,4,5 of pyridine), 5.53 (7, doublet, J 2.0 Hz, C_7H_7), 3.58 (2, quartet, J 7.0, CH$_3$C$\underline{H}_2$OH), 2.89 (1, broad, CH$_3$CH$_2$O$\underline{H}$), 1.12 (3, triplet, J 7.0, C$\underline{H}_3$CH$_2$OH).

Solid state reaction of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ with KBr

A small portion of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ and approximately ten times as much KBr were placed in a small vial along with a ball pestle and the mixture was crushed and mixed with a wiggle bug. A pellet was pressed and the IR spectrum of the metal-CO region was recorded. This spectrum consisted of two peaks of equal intensity and width at 1945 and 1995 cm^{-1}. This pattern indicated a dicarbonyl rather than a tricarbonyl compound. The crushing procedure was repeated and it was noted that although $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ is yellow, the mixture with KBr was green. Apparently, $(\eta^7\text{-}C_7H_7)Mo(CO)_2Br$ had formed in the solid state. This was verified by allowing $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]\text{-}BF_4$ to react with KBr in acetone to form $(\eta^7\text{-}C_7H_7)Mo(CO)_2Br$ and comparing the infrared spectra.

Reaction of $(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)I$, $(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(PPh_3)I$, and $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with NOPF$_6$ in acetonitrile.

The addition of NOPF$_6$ to an acetonitrile solution of $(\eta^7\text{-}C_7H_7)Mo(CO)\text{-}(PPh_3)I$ at —78°C causes a color change of the green solution to an intense blue color. This solution turns green again upon warming to room temperature and the starting molybdenum complex can be reisolated in 60% yield. In a similar manner, a brown acetonitrile solution of $(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(PPh_3)I$ turns green upon addition of NOPF$_6$ at —78°C and upon warming to room temperature the starting material can be reisolated in 90% yield. Conversely, mixing NOPF$_6$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ in acetonitrile leads to the isolation of the known complex $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]PF_6$ in high yield as had been reported previously [8].

Electrochemistry

Cyclic voltammograms were obtained using a Bioanalytical Systems, Inc. Cyclic Voltammetry Instrument, Model CV-1A, with a Hewlett—Packard

Mosely 7035B X-Y Recorder. The potentials were determined using a platinum electrode and referenced against an aqueous saturated calomel electrode. Acetonitrile, carefully distilled twice from P_4O_{10} under a nitrogen atmosphere, was used as a solvent and $[NEt_4]ClO_4$ used as a supporting electrolyte.

   a. *(η^5-$C_5H_4CH_3$)Mn(NO)(PPh$_3$)I.* (η^5-$C_5H_4CH_3$)Mn(NO)(PPh$_3$)I (11.6 mg, 2.10×10^{-5} mol) was added to a solution of acetonitrile (20.0 ml) and $[NEt_4]$-ClO_4 (22.9 mg, 1.00×10^{-4} mol). A scan rate of 150 mV/sec was used over the range from 0.7 to 1.3 V. A reversible one-electron oxidation wave was observed at 1.056 V.

   b. *(η^7-C_7H_7)Mo(CO)(PPh$_3$)I.* (η^7-C_7H_7)Mo(CO)(PPh$_3$)I (12.2 mg, 2.02×10^{-5} mol) was added to a solution of acetonitrile (20.0 ml) and $[NEt_4]ClO_4$ (22.9 mg, 1.00×10^{-4} mol). A scan rate of 150 mV/sec was used over a potential range from 0.6 to 1.3 V. A one-electron oxidation wave was observed at 0.839 V for which the reduction wave was severely depressed. Increasing the scanning rate to 800 mV/sec did not appreciably change the appearance of the wave.

   c. *(η^5-C_5H_5)Fe(CO)(PPh$_3$)I.* (η^5-C_5H_5)Fe(CO)(PPh$_3$)I (10.7 mg, 1.99×10^{-5} mol) was added to a solution of acetonitrile (20.0 ml) and $[NEt_4]ClO_4$ (22.9 mg, 1.00×10^{-4} mol). At a scan rate of 150 mV/sec a one-electron oxidation wave was observed at 0.626 V with a depressed reduction wave when run over the potential range from 0.6 to 1.3 V. Increasing the scanning speed changes the shape of the wave such that it had a normal reversible appearance at 800 mV/sec.

Results and discussion

Monomeric manganese complexes

   The known complex $[(\eta^5$-$C_5H_4CH_3)Mn(NO)(CO)(PPh_3)]PF_6$ (I) was prepared in 94% yield by reaction of PPh$_3$ and $[(\eta^5$-$C_5H_4CH_3)Mn(NO)(CO)_2]PF_6$ in tetrahydrofuran. This preparation gives a slightly better yield than earlier procedures by Brunner [7b] who carried out the reaction in refluxing methanol (90% yield) and James and McCleverty [7a] who used acetone, catalyzing the reaction with a few drops of triethylamine (85% yield). Also, the one-flask room temperature procedure is much simpler than earlier reported syntheses. Complex I crystallizes from the THF solution and can be isolated directly from this reaction mixture.

   The preparation of (η^5-$C_5H_4CH_3$)Mn(NO)(PPh$_3$)I (II) was accomplished by two different procedures. From the reaction of I with sodium iodide for 15 h in THF solution, brown crystals of II can be isolated in 65% yield. A better route for this synthesis is to start with $[(\eta^5$-$C_5H_4CH_3)Mn(NO)(CO)_2]PF_6$, add sodium iodide, and after 30 minutes add triphenylphosphine to yield II in 82% yield. The intermediate in this reaction, (η^5-$C_5H_4CH_3$)Mn(NO)(CO)I (III), could not be isolated (vide infra) but can be observed when infrared spectroscopy is used to monitor the reaction.

   Complex II reacts with NaCN in ethanol to yield (η^5-$C_5H_4CH_3$)Mn(NO)-(PPh$_3$)CN (IV). This complex reacts readily with $[(C_2H_5)_3O]BF_4$ to form the isocyanide complex $[(\eta^5$-$C_5H_4CH_3)Mn(NO)(PPh_3)(CNC_2H_5)]BF_4$ (V).

   A separate resonance is observed for each of the four C-H carbons in the

η^5-$C_5H_4CH_3$ ring in the $^{13}C\{^1H\}$ NMR spectra of II, IV and V. The chiral center at the metal atom renders both pairs of C-H carbons in the ring diastereotopic. This has been observed for chiral indenyliron complexes [9].

The reaction of [(η^5-$C_5H_4CH_3$)Mn(NO)(CO)$_2$]PF$_6$ with excess NaCN yields the dicyanide complex Na[(η^5-$C_5H_4CH_3$)Mn(CO)(CN)$_2$] (VI) as characterized by infrared and NMR data. This material is also produced in the reaction of NaCN with compound I. A 10% yield of the monocyanide complex IV can also be isolated in this latter reaction. Since IV did not react further with NaCN under the reaction condition employed, the PPh$_3$ must be mainly displaced from I in preference to the CO in this reaction with NaCN. This is in contrast to the rather similar reaction of I with NaI to yield II in which CO is displaced by the incoming nucleophile.

The reaction of the anion VI with triphenyltin chloride yields (η^5-$C_5H_4CH_3$)-Mn(NO)(CN)$_2$(SnPh$_3$). The $^{13}C\{^1H\}$ NMR spectrum of this complex shows two cyanide resonances consistent with a *cis*-geometry. The intensities of the cyanide stretching bands in the infrared spectrum confirm this assignment [10].

Although VI does not react with CH$_3$I or C$_6$H$_5$CH$_2$Cl, it does react with [(C$_2$H$_5$)$_3$O]BF$_4$ to yield [(η^5-$C_5H_4CH_3$)Mn(NO)(CNC$_2$H$_5$)$_2$]BF$_4$. The methyl analog of this complex was prepared previously by Treichel et al. by a direct reaction of [(η^5-$C_5H_4CH_3$)Mn(NO)(CO)$_2$]PF$_6$ with methyl isocyanide [11].

Silver(I) assisted substitution reactions have been very successful with many organometallic halides. The reaction of II with AgBF$_4$ in acetonitrile does lead to the formation of [(η^5-$C_5H_4CH_3$)Mn(NO)(PPh$_3$)(NCCH$_3$)]BF$_4$. Unfortunately, similar reactions with olefins in inert solvents, a procedure that has been very successful with the analogous iron compounds [6], did not yield characterizable products.

Dimeric manganese complexes

As mentioned above, the reaction of [(η^5-$C_5H_4CH_3$)Mn(NO)(CO)$_2$]PF$_6$ (I) with NaI yields (η^5-$C_5H_4CH_3$)Mn(NO)(CO)I (III) in solution (ν(CO) 2020 cm^{-1}, ν(NO) 1770 cm^{-1}). Attempts to isolate this compound were not successful because it decomposes to a material for which after crystallization from heptane a total analysis yields the formula (η^5-$C_5H_4CH_3$)$_2$Mn$_2$(NO)$_3$I (VII). This compound has a terminal NO stretch at 1730 cm^{-1}, a bridging NO stretch at 1520 cm^{-1}, and in the far infrared there is a sharp Mn—I terminal stretch at 250 cm^{-1}. The ^1H and ^{13}C NMR spectra of this complex show that the two η^5-C_5H_4-CH$_3$ groups are non-equivalent. Cotton et al. [12] have reported the X-ray crystal structure of an analogous compound, (η^5-C_5H_5)$_2$Mn$_2$(NO)$_3$(NO$_2$), formed surprisingly in the reaction of NO with (η^5-C_5H_5)$_2$Mn. By analogy to this structure and on the basis of the NMR and infrared data, compound VII is formulated as having structure A shown below although a *cis* structure cannot be ruled out.
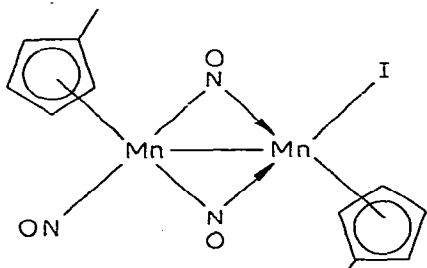
(A)

Analogous reactions yield similar dimeric complexes of the other halides although it was not possible to completely purify the fluoride and chloride complex. The driving force for the formation of these unusual dimers must be quite strong as they certainly form in unexpected reactions.

Molybdenum complexes

The reaction of $(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)I$ (VIII) with an excess of NaCN yields $(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)CN$. This cyanide derivative reacts with $[(C_2H_5)_3O]BF_4$ to yield $[(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)(CNC_2H_5)]BF_4$. Two new compounds $[(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)(NCCH_3)]BF_4$ and $[(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)(NC_5H_5)]BF_4$, were prepared by mixing VIII and $AgBF_4$ in acetonitrile and pyridine, respectively. An analogous reaction in THF saturated with CO yields the known complex $[(\eta^7\text{-}C_7H_7)Mo(CO)_2(PPh_3)]BF_4$ [13] as does the reaction of $(\eta^7\text{-}C_7H_7)Mo(CO)_2I$ with $AgBF_4$ in THF in the presence of excess PPh_3. As with the manganese system, π-olefin complexes could not be prepared from either of these molybdenum halide complexes by standard silver assisted substitution routes.

In the course of preparing the starting materials for this chemistry an interesting reaction was noted. In an attempt to prepare a KBr pellet of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$, a solid state reaction took place yielding $(\eta^7\text{-}C_7H_7)Mo(CO)_2Br$. This reaction has not been reported in the literature, but there is an incorrect report of an infrared spectrum of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ in a KBr pellet. In this report, widely spaced carbonyl absorptions are listed, 2030, 1990 and 1950 cm^{-1} [4]. Of these three absorptions, the two at lower energy are correct for $(\eta^7\text{-}C_7H_7)Mo(CO)_2Br$. The correct carbonyl stretching frequencies of $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ measured in a mull occur at 2072, 2021 and 1997 cm^{-1}.

Oxidation and reduction reactions

The reaction of $NOPF_6$ with low valent metal halides has been a successful method to carry out substitution reactions in other systems [8]. The reaction of both $(\eta^5\text{-}C_5H_4CH_3)Mn(NO)(PPh_3)I$ (II) and $(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)I$ (VIII) with $NOPF_6$ in acetonitrile at $-78°C$ leads to an immediate color change. These solutions return to the color of the starting materials when warmed to room temperature and the starting materials can be reisolated in 90% yield for II and 60% yield for VIII. It is believed that these color changes are due to an oxidation of these complexes to the respective 17-electron cationic species by NO^+ which then regain an electron from the solvent upon warming to room temperature. This contention is supported by electrochemical studies. The cyclic voltammogram of II in acetonitrile shows a reversible one electron oxidation wave at 1.056 V versus a saturated calomel electrode. Complex VIII shows a one electron oxidation wave at 0.839 V in which the reduction wave is severely depressed. Thus, both of these complexes are capable of being oxidized by $NOPF_6$ (reduction potential of ca. 1.4 V versus a saturated calomel electrode [14]). For VIII, the reaction of the oxidized species with the solvent must be more rapid than with II, thus, removing the 17-electron cation from the solution causing the depression of the reduction wave. Interestingly, the cyclic voltammogram of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)I$, run for comparative purposes, shows a depressed reduction wave similar to VIII using a scanning rate of 150

mV/sec, but a normal reversible one electron wave at 0.626 V at a scanning speed of 800 mV/sec. It should be noted that for $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, a complex with a known reduction potential greater than $NOPF_6$ [15], a simple substitution reaction takes place when mixed with $NOPF_6$ in acetonitrile to yield $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]PF_6$ [8].

As metal halides are generally successful starting materials for the preparation of both alkylmetal and metal hydride complexes, many attempts were made to prepare such complexes starting with both II and VIII using a wide variety of reagents. For no reaction was a desired product isolated. In the reaction of n-Bu$_3$Al with VIII a distinct color change was observed and the carbonyl stretching frequency changed from 1930 to 1895 cm^{-1}, an appropriate change for a metal halide converting to an alkylmetal complex [6]. This compound could not be crystallized and decomposed on an alumina chromatography column and thus could not be isolated.

Acknowledgement

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