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Reactions of Manganese Formyl Complexes with Electrophiles

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Summary: Reactions of manganese formyl complexes in the series $Mn(CO)_3LL'CHO$ [**2a**, L = L′ = $P(OPh)_3$, *mer*,trans; **2b**, L = CO, L′ = $P(OPh)_3$, cis; **2c**, L = CO, L′ = PPh_3, cis; **2d**, L = L′ = PPh_3, *mer*,trans] with electrophiles have been investigated. Compounds **2a–c** yield metallacyclic complexes, **3a–c**, as major products when treated with protonic acids; the structures of **3a**, $Mn(CO)_3[P(OPh)_3][P(OPh)_2(o\text{-}OC_6H_4CH_2)]$, and **3c**, $Mn(CO)_4[(PPh_2)(o\text{-}C_6H_4CH_2)]$, have been established by X-ray crystallography. Compound **2d** yields hydroxymethylidene cation complexes after protonation with strong acids. Reaction of **2d** with methyl triflate yields the corresponding methoxymethylidene cation complex, but **2c** is converted to the methoxymethyl derivative. The same derivative is formed by treating **2c** with HBF_4 in the presence of methanol.

The possible intermediacy of catalyst-bound formyls in syngas transformations has prompted efforts to prepare and study the chemistry of transition-metal formyl complexes.[1] Reactions of these complexes with electrophiles, particularly protonic acids, have shown much diversity; both organic products (formaldehyde and methanol) and organometallic products (hydroxymethylidene, methyl, and methylidene-bridged complexes) resulting from further transformations of the formyl ligands have been observed.[2] The possible relevancy of such reactions to CO reductions on metal surfaces has also been noted.[2d,e] We report here reactions of phosphine- and phosphite-substituted manganese formyl complexes with protonic acids which lead to new metallacylic compounds as well as the first isolable hydroxymethylidene complexes of a first-row transition metal. Also, we have demonstrated each stage of the conversion of a formyl to a substituted methylene ligand in electrophile-promoted reactions.

The manganese formyls $Mn(CO)_3LL'CHO$ were prepared by reductions of the corresponding metal carbonyl cations as shown in eq 1.

$$\begin{array}{lcl} [Mn(CO)_4LL']BF_4 & \xrightarrow{Et_4NBH_4} & Mn(CO)_3LL'CHO \\ \mathbf{1a},\ L = L' = P(OPh)_3;\ trans & & \mathbf{2a},\ \mathit{mer},trans \\ \mathbf{1b},\ L = CO,\ L' = P(OPh)_3 & & \mathbf{2b},\ cis \\ \mathbf{1c},\ L = CO,\ L' = PPh_3 & & \mathbf{2c},\ cis \\ \mathbf{1d},\ L = L' = PPh_3;\ trans & & \mathbf{2d},\ \mathit{mer},trans \end{array} \qquad (1)$$

Compounds **2a**[3] and **2d**[4] have been characterized previously; the spectral properties of our products are in agreement with those reported earlier. Compound **2c** has been characterized by its spectral properties.[5] Compound **2b** was not isolated but was converted to products immediately after it was formed; its IR spectrum is consistent with its formulation.[6]

Addition of **2a** to excess CF_3COOH in CH_3CN at 0 °C afforded, after workup, a 35% yield of metallacycle **3a**, $Mn(CO)_3[P(OPh)_3][P(OPh)_2(o\text{-}OC_6H_4CH_2)]$, which showed a doublet of doublets for the methylene protons at δ 2.12 and a doublet of doublets at δ 4.27 for the methylene carbon.[7] The molecular structure of **3a** has been established by X-ray crystallography.[8] Similar reaction of **2b** with CF_3COOH afforded metallacycle **3b**, $Mn(CO)_4[P(OPh)_2(o\text{-}OC_6H_4CH_2)]$ (41%), which has been characterized spectroscopically; **3b** showed a doublet at δ 2.00 for the methylene protons and a doublet at δ 2.96 for the methylene carbon.[7] Compounds **3a** and **3b** represent the first examples of this class of metallacyclic complexes.

Reaction of formyl complex **2c** with excess CF_3COOH at −78 °C afforded **1c**·TFA (45%) and three additional compounds: metallacycle **3c**, $Mn(CO)_4[(PPh_2)(o\text{-}C_6H_4CH_2)]$ (23%),[9] compound **4**, $Mn(CO)_4(PPh_3)CH_2OC(O)CF_3$ (22%),[10] and compound **5**, *cis*-$Mn(CO)_4(PPh_3)COOCF_3$ (trace).[11] The spectral properties of **3c** are similar to those of $Mn(CO)_4[(PPh_2)(o\text{-}C_6H_4CHOH)]$ reported recently by Gladysz et al.[12] Reaction of **2c** with HBF_4·

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[1] Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

[2] (a) Collman, J. P.; Winter, S. R. *J. Am. Chem. Soc.* **1973**, *95*, 4089. (b) Casey, C. P.; Newmann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395. (c) Wong, W.-K.; Tam, W.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5440. (d) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278. (e) Steinmetz, G. R.; Morrison, E. D.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 2559.

[3] (a) Berke, H.; Huttner, G.; Scheidsteger, O.; Weiler, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 735. (b) Berke, H.; Weiler, G.; Huttner, G.; Orama, O. *Chem. Ber.* **1987**, *120*, 297. (c) Compound **2a** was prepared by treatment of **1a** in CH_3CN at room temperture with a molar equivalent of Et_4NBH_4. The mixture was then chilled to 0 °C to complete precipitation of **2a**. The product was isolated by filtration under N_2 (95% yield); the melting point of **2a** is 107–109 °C dec.

[4] (a) Weiler, G.; Huttner, G.; Zsolnai, L.; Berke, H. *Z. Naturforsch., B. Anorg. Chem., Org. Chem.* **1987**, *42B*, 203. (b) Compound **2d** was prepared by treating a saturated solution of **1d** in 1:1 CH_3CN/CH_3OH at 0 °C with a molar equivalent of Et_4NBH_4. Precipitation of **2d** began immediately and was complete within 1 min. The product was quickly collected by filtration under N_2 (96% yield; mp 99–102 °C dec).

[5] Compound **2c** was prepared by treating a saturated solution of **1c** in CH_3OH at −40 °C with a molar equivalent of Et_4NBH_4. Precipitation of **2c** began immediately; after about 1 min the product was collected by filtration under N_2 (88% yield; mp 134–135 °C dec); its IR spectrum (Nujol mull) showed ν_{CO} 2065 (m), 1975 (s), 1965 (s), 1945 (s), and 1605 (m) cm^{-1}. IR (DRIFTS) showed 2720 and 2575 (both weak) cm^{-1} for the ν_{CHO}. ^1H and ^{13}C data for **2c** are provided in the supplementary material.

[6] Compound **2b** was prepared by treatment of a solution of **1b** in 1:1 CH_2Cl_2/hexane at −40 °C with a molar equivalent of Et_4NBH_4. Reaction was complete after 45 min; the IR spectrum showed ν_{CO} at 2070 (w), 1980 (s), 1960 (sh, m), and 1590 (m) cm^{-1}.

[7] Compound **3a**: mp 108.5–110 °C. Anal. Calcd for $C_{40}H_{31}O_9P_2Mn$; C, 62.19; H, 4.05; P, 8.02. Found: C, 61.83; H, 4.14; P, 7.96. Compound **3b**: mp 86–89 °C. IR and ^1H and ^{13}C NMR spectral data for both metallacycles are provided in the supplementary material.

[8] The space group for **3a** is $P2_1/n$ with a = 15.977 (8) Å, b = 26.554 (10) Å, C = 8.523 (6) Å, β = 87.12 (5)°, R_1 = 0.039, and R_2 = 0.049. Further details are provided in the supplementary material.

[9] The molecular structure of **3c** has been confirmed by X-ray diffraction techniques: space group $P2_1/c$, a = 13.519 (2) Å, b = 8.295 (1) Å, c = 18.199 (2) Å, β = 90.82 (1)°, R = 0.029, R_w = 0.033. Anal. Calcd for $C_{23}H_{16}O_4PMn$: C, 62.46; H, 3.65; P, 7.00. Found: C, 62.25; H, 4.02; P, 7.18. The melting point of **3c** is 127.5–128 °C. IR and ^1H, ^{13}C, and ^{31}P NMR spectral data for **3c** are provided in the supplementary material.

[10] Compound **4**: mp 99–99.5 °C; IR (hexane) ν_{CO} 2070 (s), 2000 (s), 1977 (vs), 1950 (s), 1770 (m) cm^{-1}. Anal. Calcd for $C_{25}H_{17}F_3O_6PMn$: C, 53.98; H, 3.08; P, 5.57. Found: C, 54.23; H, 2.87; P, 5.70. ^1H, ^{13}C, and ^{31}P NMR spectral data are provided in the supplementary material.

[11] Compound **5** has been prepared previously: Bannister, W. D.; Booth, B. L.; Hazeldine, R. N.; Loader, P. L. *J. Chem. Soc. A* **1971**, 930.

[12] (a) Vaughn, G. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 5608. (b) Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1462.

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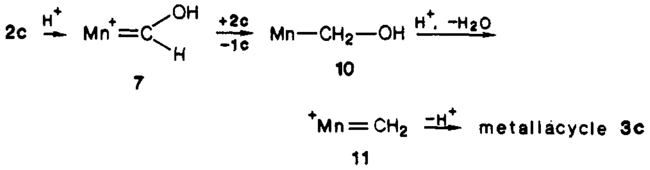
Scheme I



Me_2O at 0 °C afforded only the metallacycle **3c** and cation **1c**·BF_4. In aqueous THF-containing methanol, HBF_4 converted **2c** to *cis*-$Mn(CO)_4(PPh_3)CH_2OCH_3$ (**6**),[13] in addition to cation **1c**·BF_4; this appears to be the first instance of conversion of a formyl complex to an alkoxymethyl complex promoted by acid. Treatment of **4** or **6** with HBF_4·Me_2O afforded metallacycle **3c** in high yields.

The behavior of formyl complex **2d** provides further information about the probable steps in the reactions of the other formyl complex with electrophiles. Treatment of **2d** with HBF_4·Me_2O at −78 °C afforded a 92% yield of a product formulated as the hydroxymethylidene complex, *mer,trans*-$[Mn(CO)_3(PPh_3)_2CHOH]BF_4$ (**7**·BF_4).[14] Similar treatment of **2d** with *p*-toluenesulfonic acid afforded **7**·OTs (OTs = *p*-toluenesulfonate) in 88% yield; the spectral properties of this complex are quite similar to those of **7**·BF_4. Hydroxymethylidene complexes are still very rare;[15] the first such compound was characterized by Gladysz[2c,15a] a few years ago, and several others have been identified since then. Compounds **7**·BF_4 and **7**·OTs appear to be the first hydroxymethylidene complexes of a first-row transition metal to be isolated, although other such complexes have been observed at low temperatures.[15c,d,e] When treated with Et_3N, compound **7**·BF_4 reverts to formyl complex **2d** as Ibers has noted for a related iridium complex.[15b]

Treatment of **2d** with $CF_3SO_3CH_3$ afforded the corresponding, but much more stable, methoxymethylidene cation, *mer,trans*-$[Mn(CO)_3(PPh_3)_2CHOCH_3]SO_3CF_3$ (**8**),[16] in 85% yield. Reaction of **8** with an equimolar amount of formyl complex **2d** afforded a 78% yield of the known methoxymethyl complex, *mer,trans*-$Mn(CO)_3(PPh_3)_2CH_2OCH_3$ (**9**)[13] and a 91% yield of cation **1d**·OTf (OTf = trifluoromethanesulfonate). Reaction of formyl complex **2c** with $CF_3SO_3CH_3$ proceeds directly to methoxymethyl complex **6** (and cation **1c**·OTf); we have not yet been able to stop this reaction at the methoxymethylidene cation stage.

These results demonstrate each stage of the electrophile-promoted conversions of a formyl to a substituted methylene ligand as suggested in previous work.[1,2d,15f] On this basis, the sequence shown in Scheme I is suggested to illustrate the pathway by which metallacyclic compounds **3a–c** are formed;[17] the maximum possible yield of metallacycle is 50%. The high reactivity of formyls **2a** and **2b** and the ready cyclization of presumed intermediates analogous to **11** have not yet allowed the isolation of any intermediates from these complexes. However, we are not yet able to generate a metallacycle from **2d**; thus the systems are very sensitive to changes in the steric and electronic environment about the metal center.

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Supplementary Material Available: Tables of crystallographic experimental details, positional and thermal parameters, and bond lengths and angles, an ORTEP perspective view of **3a**, and spectral data for compounds **2c**, **3a–c**, **7**, and **8** (16 pages); a listing of structure factors (13 pages). Ordering information is given on any current masthead page.

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[13] Pelling, S.; Botha, C.; Moss, J. R. *J. Chem. Soc., Dalton Trans.* **1983**, 1495.

[14] Compound **7**·BF_4 showed IR ν_{CO} (CH_2Cl_2) at 2045 (w), 1960 (s), and 1940 (s) cm^{-1}, ^1H and ^{13}C NMR spectral data are in the supplementary material.

[15] (a) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141. (b) Lilga, M. A.; Ibers, J. A. *Organometallics* **1985**, *4*, 590. (c) Catheline, D.; Lapinte, C.; Astruc, D. *C. R. Acad. Sc. Paris* **1985**, t.301, Serie II, 479. (d) Guerchais, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1986**, 663. (e) Asdar, A.; Lapinte, C. *J. Organomet. Chem.* **1987**, *327*, C33. (f) Barratt, D. S.; Cole-Hamilton, D. J. *J. Organomet. Chem.* **1986**, *306*, C41.

[16] Compound **8** showed IR ν_{CO} (CH_2Cl_2) at 2050 (w) and 1965 (s) cm^{-1}; ^1H, ^{13}C and ^{31}P NMR spectral data are in the supplementary material. The molecular structure of the CH_2Cl_2 solvate of **8** has been confirmed by X-ray diffraction techniques: space group *Pbca*, $a = 18.952$ (3) Å, $b = 19.730$ (9) Å, $c = 23.458$ (6) Å, current $R = 0.067$.

[17] The last step in Scheme I is similar to that suggested for a cyclometalation reaction; see: Hoskins, S. V.; Rickard, C. E. F.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1000.