2080 *Organometallics* 1988, *7*, 2080–2081

# Synthesis and Chemical Characterization of $[Mn(\eta\text{-}C_5H_5)(CO)_2]^{2-}$

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*Received February 26, 1988*

*Summary:* Naphthalenide reduction of $[Mn(\eta\text{-}C_5H_5)(CO)_2(py)]$ (**1**) gives $[Mn(\eta\text{-}C_5H_5)(CO)_2]^{2-}$ ($\mathbf{2}^{2-}$), which reacts with $Ph_3PbCl$ to give $[Mn(\eta\text{-}C_5H_5)(CO)_2PbPh_3]^-$ ($\mathbf{4}^-$, from 1 equiv) or $[Mn(\eta\text{-}C_5H_5)(CO)_2(PbPh_3)_2]$ (**3**, from excess). Addition of $H_2O$ (1 equiv) to $\mathbf{2}^{2-}$ gives $[Mn(\eta\text{-}C_5H_5)(CO)_2H]^-$ ($\mathbf{5}^-$), and excess $NH_4PF_6$ gives unstable $[Mn(\eta\text{-}C_5H_5)(CO)_2H_2]$ (**6**).

Monoanionic cyclopentadienyl carbonylmetalates such as $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$,[3-6] $[Cr(\eta\text{-}C_5H_5)(CO)_3]^-$,[3,5,6] $[Mo(\eta\text{-}C_5H_5)(CO)_3]^-$,[3-6] and $[W(\eta\text{-}C_5H_5)(CO)_3]^-$ [3,5,6] are valuable intermediates in organometallic synthesis, but the $[M(\eta^5\text{-}C_5H_5)(CO)_3]^{2-}$ complexes of the group 5 metals (M = V,[7a,b] Nb,[7c] and Ta[7c]) are the sole examples of more highly reduced dianionic cyclopentadienylcarbonylmetalates. Reactions that might have produced others, such as Na/HMPA or Na/Hg reduction of $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$,[8] $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$,[8,9] or $[Rh(\eta^5\text{-}C_5H_5)(CO)_2]$,[10] lead primarily to products formed by $C_5H_5^-$ loss (except for the formation of $[\{Co(\eta^5\text{-}C_5H_5)(CO)\}_2]^{-}$ [9]). Our synthesis of the benzene-substituted carbonylmetalate $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$ by naphthalenide reduction of a precursor containing a donor ligand which is a poor $\pi$-acceptor[11] suggested that a similar strategy could provide access to dianionic carbonylmetalates with cyclopentadienyl ligands, and we now wish to report the synthesis of $[Mn(\eta\text{-}C_5H_5)(CO)_2]^{2-}$ and the chemical characterization of this dianion as summarized in Scheme I. With recent reports on the synthesis of $[Ti(\eta^5\text{-}C_5H_5)(CO)_4]^-$,[12] cyclopentadienylcarbonylmetalates are now known for all the 3d metals from Ti to Fe.

The substrate for reduction was $[Mn(\eta\text{-}C_5H_5)(CO)_2(py)]$ (**1**), prepared by addition of pyridine (py) to $[Mn(\eta\text{-}C_5H_5)(CO)_2(THF)]$ in THF.[13] A solution of **1** (0.05 g, 0.20 mmol) was treated dropwise with 2.3 mL of a 0.17 M solution of $NaC_{10}H_8$ (2 equiv) in THF (25 mL) at −78 °C to give a dark brown-red solution. IR spectra revealed that the carbonyl absorptions of **1** (1925 s, 1850 s $cm^{-1}$) had been replaced by bands at 1685 s, 1600 s, and 1550 vs $cm^{-1}$, together with weak bands at 1870 and 1785 $cm^{-1}$ (see below). Assignment of the three principal bands to $Na_2[Mn(\eta\text{-}C_5H_5)(CO)_2]$ ($Na_2$**2**) was confirmed by addition of excess $Ph_3PbCl$[14] (0.23 g, 0.49 mmol) at −78 °C to give a solution with bands at 1930 m and 1890 s $cm^{-1}$ from which the bisadduct $[Mn(\eta\text{-}C_5H_5)(CO)_2(PbPh_3)_2]$ (**3**)[15] could be isolated as the *dia* isomer[16,17] in high yield—THF removal gave an orange oil from which spectroscopically pure **3** (0.17 g, 0.16 mmol 83%) was obtained by addition of pentane (25 mL) to concentrated (5 mL) toluene extracts.

An intermediate monoadduct could be prepared by addition of 1 equiv of $Ph_3PbCl$ (0.14 g, 0.29 mmol) to a solution of $\mathbf{2}^{2-}$ (from 0.075 g, 0.29 mmol, of **1**) at −78 °C. IR spectra indicated replacement of $\mathbf{2}^{2-}$ with a species with bands at 1885 s and 1795 s $cm^{-1}$, consistent with formulation as $[Mn(\eta^5\text{-}C_5H_5)(CO)_2PbPh_3]^-$. The $Na^+$ counterion was metathesized by room temperature addition of $Et_4NBr$ (0.065 g, 0.31 mmol). After 1 h the THF was removed under vacuum and the solid washed with $Et_2O$ (2 × 20 mL) and redissolved in THF (20 mL). Golden yellow needles of pure $Et_4N[Mn(\eta\text{-}C_5H_5)(CO)_2PbPh_3]$ ($[NEt_4]$**4**)[18] (0.12 g, 0.161 mmol, 55%) crystallized after addition of a layer of $Et_2O$ (20 mL) to the filtered, concentrated (10 mL) solution. Excess $Ph_3PbCl$ converts $\mathbf{4}^-$ to **3** in THF in 65% recrystallized yield.

The three-band IR spectrum of $Na_2$**2** in THF is consistent with perturbation of the local symmetry by ion-pairing effects.[19] This is supported by IR spectra of precipitates obtained by addition of dibenzo-18-crown-6 or the cryptand Kryptofix 222 to a THF solution of $Na_2$**2**—these contained only two peaks attributable to $\mathbf{2}^{2-}$, at 1735 s and 1600 s $cm^{-1}$.[20] Solid samples of $Na_2$**2**,[21] obtained as brown powders by solvent removal at room temperature and washed with pentane, also had two band

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[14] In this system $Ph_3PbCl$ gives higher yields of adducts than the $Ph_3SnCl$ electrophile which we and others have used to characterize other reactive carbonylmetalates (see ref 11 and references therein). $Ph_3PbCl$ adducts of carbonylmetalates have been reported previously by Ellis and others: (a) Ellis, J. E.; Hentges, S. G.; Kalina, D. G.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79–93. (b) Ellis, J. E.; Faltynek, R. A. *J. Chem. Soc., Chem. Commun.* **1975**, 966–967. (c) Ellis, J. E.; Faltynek, R. A. *J. Am. Chem. Soc.* **1977**, *99*, 1801–1808. (d) Ellis, J. E.; Barger, P. T.; Winzenburg, M. L. *J. Chem. Soc., Chem. Commun.* **1977**, 686–687. (e) Ellis, J. E.; Fjare, K. L.; Hayes, T. G. *J. Am. Chem. Soc.* **1981**, *103*, 6100–6106. (f) Patil, H. R. H.; Graham, W. A. *Inorg. Chem.* **1966**, *5*, 1401–1405.

[15] IR (THF, $\nu_{CO}$): 1930 m, 1890 s $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 7.70–7.30 (m, 30 H, $PbPh_3$), 4.95 (s, 5 H, $C_5H_5$). $^{13}C\{^1H\}$ NMR (benzene-$d_6$): $\delta$ 223.0 (s, CO), 184.3, 137.7, 129.7, 128.5 (all s, $PbPh_3$), 82.8 (s, $C_5H_5$). Analytical samples were recrystallized from THF/pentane as red orange needles. Anal. Calcd for $C_{43}H_{35}MnO_2Pb_2$: C, 49.04; H, 3.35. Found (Galbraith, Knoxville TN): C, 48.69; H, 3.52.

[16] The distinction between diagonal and lateral isomers was made by established procedures[17] in which the angle $2\theta$ between the two CO ligands was calculated to be ca. 113° from the relationship $I_{asym}/I_{sym} = \tan^2 \theta$.

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[18] IR (THF, $\nu_{CO}$): 1880 s, 1810 s $cm^{-1}$. $^1H$ NMR (acetone-$d_6$): $\delta$ 7.70–6.90 (m, 15 H, $PbPh_3$), 4.32 (s, 5 H, $C_5H_5$). $^{13}C\{^1H\}$ NMR (acetone-$d_6$): $\delta$ 236.8 (s, CO), 168.5, 139.2, 128.3, 125.7 (all s, $PbPh_3$), 78.5 (s, $C_5H_5$). Resonances characteristic of the tetraethylammonium counterion were observed with the appropriate intensities. Anal. Calcd for $C_{33}H_{40}MnNO_2Pb$: C, 53.24; H, 5.37; N, 1.88. Found: (Multichem Lab., Lowell, MA): C, 53.15; H, 5.45; N, 1.88.

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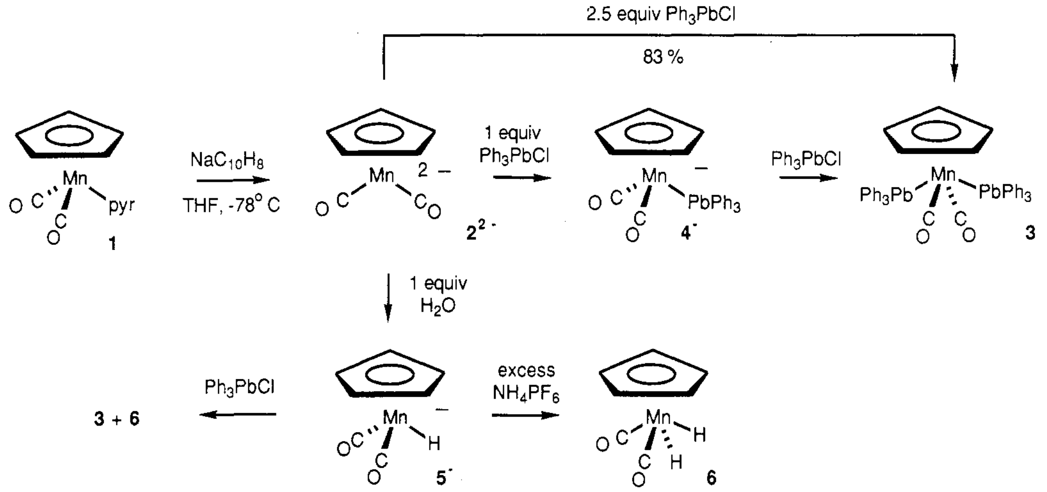
[20] Additional peaks at 1860 and 1770 $cm^{-1}$ indicated contamination by $[Mn(\eta\text{-}C_5H_5)(CO)_2H]^-$ (see below) which precluded definitive characterization of these salts of $\mathbf{2}^{2-}$.

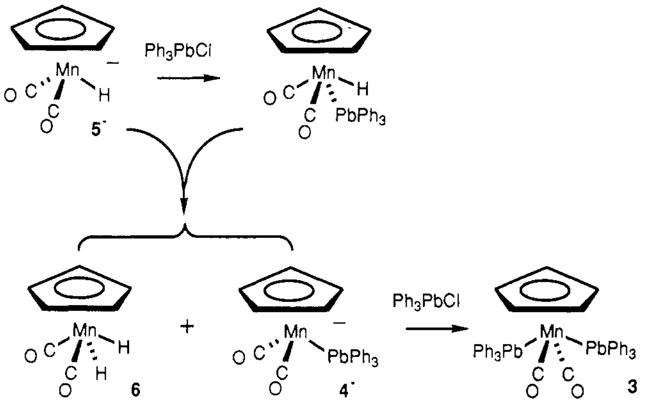
[21] The solid sodium salt is only sparingly soluble in THF and is extremely air- and water-sensitive. It can be stored for days under $N_2$ (IR), and slurries of the solid in THF will react with $Ph_3PbCl$ to give **3**.

0276-7333/88/2307-2080\$01.50/0

### Scheme I



### Scheme II



IR spectra with carbonyl absorptions at 1680 vs (br) and 1580 s (br) cm$^{-1}$. Ion-pairing effects have been observed with the isoelectronic monoanion $[Fe(\eta\text{-}C_5H_5)(CO)_2]^-$,[22] and dianionic $2^{2-}$ should be even more prone to such effects.

The similarity of the weak 1870 and 1785 cm$^{-1}$ absorptions in solutions of $Na_2$**2** to those of $[Re(\eta^5\text{-}C_5H_5)(CO)_2H]^-$ [23] suggested contamination of the $2^{2-}$ by small quantities of $[Mn(\eta\text{-}C_5H_5)(CO)_2H]^-$ ($5^-$). This was confirmed by the protonation of $2^{2-}$ (from 0.075 g, 0.29 mmol, of **1**) with 1 equiv of $H_2O$[24] (5 μL, 0.29 mmol) at −78 °C to give a yellow solution with an IR spectrum identical with that assigned to $5^-$. After addition of $Et_4NBr$ (0.061 g, 0.29 mmol) the solution was stirred at room temperature for 1 h and then filtered to give a yellow solution from which pure crystalline $NEt_4[Mn(\eta\text{-}C_5H_5)(CO)_2H]$ ($[NEt_4]$**5**)[25] was obtained by addition of pentane (15 mL) to the concentrated (5 mL) solution. The independent characterization of $5^-$ confirms the identification of $2^{2-}$ and demonstrates that this preparation is not subject to the ambiguities which clouded early reports of $[Re(\eta\text{-}C_5H_5)(CO)_2]^{2-}$.[23]

Dianion $2^{2-}$ could be diprotonated by addition of excess $NH_4PF_6$ (0.144 g, 0.883 mmol) to a solution of $Na_2$**2** (from 0.075 g, 0.294 mmol, of **1**). This gave a solution with carbonyl absorptions at 1972 s and 1910 s cm$^{-1}$ assigned to $[Mn(\eta\text{-}C_5H_5)(CO)_2H_2]$ (**6**) on the basis of $^1H$ NMR spectra.[26] Complex **6** is much less stable than the Re analogue[23,27] and could not be isolated. Solutions in THF-$d_8$ decomposed in 5 h to mixtures of several species including $[Mn(\eta\text{-}C_5H_5)(CO)_3]$ ($^1H$ NMR). In $CD_3CN$ **6** gives a single ($\eta$-$C_5H_5$) containing species, presumed to be $[Mn(\eta\text{-}C_5H_5)(CO)_2(NCCD_3)]$.

Bergman has reported that $[Re(\eta\text{-}C_5H_5)(CO)_2H]^-$ reacts with MeI to give a mixture of $[Re(\eta\text{-}C_5H_5)(CO)_2(Me)_2]$ and $[Re(\eta\text{-}C_5H_5)(CO)_2H_2]$,[23a] and $5^-$ reacts analogously with $Ph_3PbCl$ in THF (IR), presumably by the mechanism shown in Scheme II, to give a 1.5:1 mixture of **3** and **6** ($^1H$ NMR in THF-$d_8$). This is in reasonable agreement with the suggested stoichiometry and the instability of **6**.

Attempts to prepare $[Re(\eta\text{-}C_5H_5)(CO)_2]^{2-}$, the Re analogue of $2^{2-}$, by deprotonation of $[Re(\eta\text{-}C_5H_5)(CO)_2H_2]$ have been unsuccessful,[23b] and it has been suggested that this reflects the inherent electronic instability of $d^8$ two-legged piano stools.[28] Although $2^{2-}$ is very basic, our results do indicate that, at least with 3d metals, $d^8$ two-legged piano stools are accessible on a synthetically useful scale and that alternate approaches to $[Re(\eta\text{-}C_5H_5)(CO)_2]^{2-}$ may be successful.

**Acknowledgment.** We thank the National Science Foundation for financial support through Grant CHE-8722424 to N.J.C.

**Registry No.** **1**, 12088-91-4; $Na_2$**2**, 115731-41-4; **3**, 115731-42-5; $[Et_4N]$**4**, 115731-44-7; $[Et_4N]$**5**, 115731-46-9; **6**, 115731-47-0; $Ph_3PbCl$, 1153-06-6.

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(24) $NH_4PF_6$ can also be used as the proton source.

(25) IR (THF, $\nu_{CO}$): 1860 s, 1770 s cm$^{-1}$. $^1H$ NMR (acetonitrile-$d_3$): δ 4.21 (s, 5 H, $C_5H_5$), −12.15 (s, 1 H). $^{13}C\{^1H\}$ NMR (acetonitrile-$d_3$): δ 241.0 (s, CO), 78.7 (s, $C_5H_5$). Resonances characteristic of the tetraethylammonium counterion were observed with the appropriate intensity. Analytically pure samples were obtained as yellow cubes by slow removal of solvent from a THF solution of **5**. Anal. Calcd for $C_{15}H_{26}MnNO_2$: C, 58.62; H, 8.53; N, 4.55. Found (Multichem Lab., Lowell, MA): C, 58.10; H, 8.47; N, 4.53.

(26) $^1H$ NMR data for **6** were most conveniently obtained from a solution prepared by addition of $CF_3COOH$ to $5^-$ in THF-$d_8$: δ 4.67 (s, 5, $C_5H_5$), −12.62 (s, 2, MnH).

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