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Highly reduced organometallics 52. Synthesis and chemistry of tricarbonylnitrosylmanganate(2 −), $[Mn(CO)_3(NO)]^{2-}$ ☆

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Dedicated to Professor Marcetta Y. Darensbourg for her friendship, support, inspiration and in recognition of her many wonderful contributions to inorganic and organometallic chemistry over the past 30 + years.

Abstract

Treatment of $Mn(CO)_3(NO)(PPh_3)$ in THF at 20°C with excess sodium amalgam, followed by treatment with cryptand 2.2.2, or with two equiv. of potassium tri-*sec*-butylborohydride afforded high isolated yields (≥ 80%) of air sensitive yellow solids identified as $[Na(crypt.2.2.2)]_2[Mn(CO)_3(NO)]$ and $K_2[Mn(CO)_3(NO)]$, respectively. These products contain the only known mixed carbonylnitrosylmetallate dianion, isoelectronic with $[Fe(CO)_4]^{2-}$ and $[Mn(CO)_4]^{3-}$. Reactions of $[Mn(CO)_3(NO)]^{2-}$ with Ph_3SnCl, $Mn(CO)_4(NO)$ and $Fe(CO)_5$, followed by metathesis, provided the new derivatives $[Et_4N][Mn(CO)_3(NO)(SnPh_3)]$, $[PPN]_2[Mn_2(CO)_6(NO)_2]$, and $[PPN]_2[MnFe(CO)_7(NO)]$. On the basis of IR spectral data the latter two have been formulated to contain non-bridged structures analogous to that previously established for the isoelectronic salt $[PPN]_2[Fe_2(CO)_8]$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Manganese complexes; Carbonyl complexes; Nitrosyl complexes; Organotin; Organophosphane complexes

1. Introduction

For several years we have been interested in the synthesis of new mixed carbonylnitrosylmetalates of the general formula $[M(CO)_x(NO)_y]^{z-}$ since these substances could be useful as reagents in the chemical synthesis of new materials as are the closely related carbonylmetalates [1]. Mononuclear metalates containing only CO and NO are quite rare substances. Indeed, when this study was initiated, only two compounds of this type were known, i.e. $[Fe(CO)_3(NO)]^-$ [2] and $[Mn(CO)_2(NO)_2]^-$ [3]. More recently, Gladfelter and co-workers also prepared $[Cr(CO)_4(NO)]^-$ [4] and $[Ru(CO)_3(NO)]^-$ [5], the only carbonylnitrosylmetalate of a second or third row transition metal reported to date. Despite the existence of homoleptic carbonyl metalate di-, tri- and tetra-anions [6] no corresponding highly reduced carbonylnitosylmetalates were previously known. The objective of this present study was to prepare the first dianion of this type. In view of the remarkable thermal stabilities of alkali metal salts of $[Fe(CO)_4]^{2-}$ [7] and $[Mn(CO)_4]^{3-}$ [8], an appropriate initial target was the isoelectronic $[Mn(CO)_3(NO)]^{2-}$, a dianionic analog of Hieber's $[Fe(CO)_3(NO)]^{1-}$ [2]. Herein is presented the first full account of this research, a portion of which has previously appeared as a communication [9].

2. Experimental

2.1. General procedures and starting materials

All operations were carried out under an atmosphere of purified dinitrogen or argon further purified by passage through columns of activated BTS catalyst and molecular sieves. Solutions were transferred by stainless steel cannulas and syringes. Otherwise reactions were

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performed using standard Schlenk techniques [10]. Solvents were freed of impurities by standard procedures and stored under dinitrogen or argon. The following reactants were prepared according to literature procedures: $[Mn(CO)_5(CH_3CN)][BF_4]$ [11] and $[PPN][NO_2]$ [12]. An improved modification of the prior synthesis of $Mn(CO)_3(NO)(PPh_3)$ [13] was developed and is included herein. All other reagents were obtained from commercial sources, made anaerobic when necessary, and used without additional purification. Infrared spectra were recorded on a Perkin–Elmer 283 grating with samples in 0.1 mm sealed NaCl liquid cells or as Nujol mulls between NaCl plates. Melting points are uncorrected and were obtained in sealed capillaries on a Thomas–Hoover Unimelt apparatus. Elemental analyses were obtained by Analytischen Laboratorien, Engelskirchen, Germany.

2.1.1. *$Mn(CO)_3(NO)(PPh_3)$ (**1**)*

A solution of $[PPN][NO_2]$ (1.808 g, 3.10 mmol) in 20 ml of ethanol was added dropwise into solution of $[Mn(CO)_5(CH_3CN)][BF_4]$ (1.00 g, 3.10 mmol) in 10 ml of ethanol. Gas evolution and formation of a red reaction mixture occurred immediately. An IR spectrum of this red solution showed the following bands: ν(CO) 2090 m, 2010 vs. 1970 vs. ν(NO) 1755 cm^{-1}, indicating the formation of $Mn(CO)_4(NO)$ (literature value [14] (cm^{-1}), ν(CO) 2095 m, 2019 vs. 1972 vs; ν(NO) 1759 s). This red solution was then vacuum distilled and condensed into another flask containing PPh_3 (0.810 g, 2.10 mmol) at −196°C. Upon warming to room temperature (r.t.), a solution of $Me_3NO·2H_2O$ (0.35 g, 3.10 mmol) in 20 ml of ethanol was added dropwise with vigorous stirring. Instantaneous gas evolution occurred, accompanied by precipitation of brilliant red crystals of $Mn(CO)_3(NO)(PPh_3)$. The crystals were collected by filtration, washed with 20 ml of cold ethanol and vacuum dried. Yield: 0.68 g (51% based on $[Mn(CO)_5(CH_3CN)][BF_4]$). IR data in THF: ν(CO) 2030 s, 1965 m, 1920 s; ν(NO) 1705 cm^{-1}. Literature value [15] in THF: ν(CO) 2034 s, 1972 m, 1925 s; ν(NO) 1712 cm^{-1}. ^1H NMR (300 MHz, d_6-acetone, 20°C) 7.75–7.26 (m, $P(C_6H_5)_3$) ppm.

2.1.2. *$[Na(cryptand\ 2.2.2)]_2[Mn(CO)_3(NO)]$ (**2**)*

A solution of **1** (0.350 g, 0.812 mmol) in 35 ml of THF was added to sodium amalgam (Na, 0.374 g; Hg, 38 g) and the reaction mixture was stirred for 16 h at r.t. During this time, the red color of **1** changed to a golden yellow. The IR spectrum of this solution in the ν(CO, NO) region showed bands at: 1918 s, 1860 w, 1815 vs br, 1380 m br, 1345 m br cm^{-1}). Filtration of this solution and treatment of the resulting filtrate with cryptand 2.2.2 (1.23 g, 3.25 mmol) resulted in precipitation of **2** as a pale yellow solid. The latter was separated by filtration, washed with THF (20 ml) and dried in vacuo to provide 0.652 g (83%) of (**2**), which gave satisfactory analysis without further purification, m.p. 185°C (w. dec.) IR (silicone fluid mull); ν(CO, NO) 1840 m, 1720 s, 1480 m cm^{-1}. *Anal.* Calc. for $C_{39}H_{72}MnN_5Na_2O_{16}$: C, 48.39; H, 7.50; N, 7.23. Found: C, 48.05; H, 7.61; N, 7.41%.

2.1.3. *$[PPN][Mn(CO)_5]$ (**3**) via reduction of $Mn(CO)_4NO$ by Na–Hg*

To a solid mixture of $[PPN][NO_2]$ (0.904 g, 1.55 mmol) and $[Mn(CO)_5(CH_3CN)][BF_4]$ (0.500 g, 1.55 mmol), 50 ml of THF was added with vigorous stirring to provide a red solution of $Mn(CO)_4NO$ (see the above preparation of **1**). This solution was vacuum distilled into a flask containing excess approximately 0.72% Na–Hg (Na, 0.36 g; Hg, 50 g) at −195°C. After warming to r.t. and stirring for 19 h, the mercury was separated by filtration giving a pale yellow solution. Inspection of its IR spectrum in the ν(CO, NO) region showed the following bands: 1890 s, 1860 s, 1825 w cm^{-1}. This spectrum was superimposable with that of an authentic THF solution of $Na[Mn(CO)_5]$ prepared from Na–Hg reduction of $Mn_2(CO)_{10}$ [16]. Metathesis with [PPN]Cl in THF, filtration and recrystallization from THF–petroleum ether (30–60°C) afforded shiny yellow crystals of $[PPN][Mn(CO)_5]$. Yield: 0.15 g (13%, based on $[Mn(CO)_5(CH_3CN)][BF_4]$). IR(THF): ν(CO) 1890 s, 1855 vs cm^{-1}. Literature value [17] ν(CO) in THF: 1893, 1860 cm^{-1}.

2.1.4. *$K_2[Mn(CO)_3(NO)]$ (**4**)*

2.1.4.1. Reduction of $Mn(CO)_4NO$ by K[sec-Bu_3BH]. To solid $[PPN][NO_2]$ (1.808 g, 3.10 mmol) and $[Mn(CO)_5(CH_3CN)][BF_4]$ (1.00 g, 3.10 mmol) 40 ml of THF was added with vigorous stirring. A red solution of $Mn(CO)_4NO$ was immediately formed as described above. One hour later, the resulting solution was vacuum distilled and condensed into another flask cooled with liquid nitrogen. Upon warming to r.t., this red THF solution of $Mn(CO)_4(NO)$ was treated with 31 ml of 1.0 M THF solution of K[*sec*-Bu_3BH] (31 mmol). The reaction mixture was first stirred at ambient temperature for 30 min while some yellow product precipitated. Then it was heated to reflux for 1.5 h, during which time considerably more yellow precipitate formed. An almost colorless solution remained. The product was collected by filtration, washed with THF (2 × 30 ml) and hexanes (30 ml), and dried in vacuo, to provide 0.48 g (62% yield, based on $[Mn(CO)_5(CH_3CN)][BF_4]$) of a yellow crystalline solid that gave satisfactory analyses for the composition $K_2[Mn(CO)_3(NO)]$. M.p. 176°C (decomp). Fluorolube mull IR spectrum: ν(CO) 1900 m, 1775 sh, 1755 vs; ν(NO) 1440 sh, 1420 s, cm^{-1}. *Anal.* Calc. for $C_3K_2MnNO_4$: C, 14.58; H, 0.00; K, 31.64; Mn, 22.23;

N, 5.66. Found: C, 13.80; H, 0.24; K, 31.97; Mn, 22.00; N, 5.50%.

2.1.4.2. Reduction of $Mn(CO)_3(NO)(PPh_3)$ by K[sec-Bu_3BH]. 27 ml of 1.0 M THF solution of K[*sec*-Bu_3BH] (27.0 mmol) was added to 40 ml of a THF solution of $Mn(CO)_3(NO)(PPh_3)$ (1.16 g, 2.70 mmol). The red color was discharged and yellow insoluble **4** began to form within 15 min of stirring. Three hours later the yellow precipitate was collected by filtration, washed with THF (2 × 30 ml) and hexanes (30 ml), and dried in vacuo. Brilliant yellow crystalline **4** (0.56 g) was obtained in 84% yield. Spectroscopic properties of this compound were identical to those obtained from route a shown above. *Anal.* Calc. for $C_3K_2MnNO_4$: C, 14.58; H, 0.00; N, 5.66. Found: C, 13.18; H, 0.12; N, 5.87%. Almost invariably low carbon analyses were obtained (inexplicably) for **4** obtained by either route a or b.

2.2. $[Et_4N][Mn(CO)_3(NO)SnPh_3]$ (5)

A solution of Ph_3SnCl (0.31 g, 0.81 mmol) in 20 ml of THF was added dropwise into a slurry of **4** (0.20 g, 0.81 mmol), in 15 ml of THF. After 24 h of stirring, an orange solution had formed, which showed the following bands in the ν(CO, NO) region: 1970s, 1900m, 1865s, 1835w, 1645m cm^{-1}. Solvent was then removed by evaporation in vacuo and $[Et_4N]Br$ (0.17g, 0.81 mmol) dissolved in 25 ml of CH_3CN was added. After removing the precipitated KCl and KBr by filtration, Et_2O was added to afford beautiful orange crystals. Further recrystallization from THF–Et_2O gave analytically pure **5**, which was air-stable for an indefinite period of time. Yield: 0.22 g (41%) m.p. 141°C (decomp). *Anal.* Calc. for $C_{29}H_{35}MnN_2O_4Sn$: C, 53.65; H, 5.40; N, 4.32. Found: C, 53.62; H, 5.53; N, 4.25%, IR (CH_3CN): ν(CO) 1975 s, 1895 m, 1860 s; ν(NO): 1640 m cm^{-1}. ^1H NMR (300 MHz, CD_3CN, 20°C): δ 1.20 (t of t, 12H, CH_3 of Et_4N), 3.14 (q, 8H, CH_2 of Et_4N), 7.24–7.74 (m, 15H, $SnPh_3$), ppm.

2.3. $[PPN]_2[Mn_2(CO)_6(NO)_2]$ (6)

2.3.1. From reaction of $K_2[Mn(CO)_3(NO)]$ with $Mn(CO)_4(NO)$

A solution of $Mn(CO)_4(NO)$ in 40 ml of THF was freshly prepared from the reaction of $[Mn(CO)_5(CH_3CN)][BF_4]$ (0.80 g, 2.48 mmol) with $[PPN][NO_2]$ (1.45 g, 2.48 mmol) as described previously. This solution was then added dropwise into a slurry of **4** (0.61g, 2.48 mmol) in 20 ml of THF over a period of 2 h. No apparent change of the reaction mixture was observed during an overnight stirring. The resulting red solution was then filtered into a suspension of [PPN]Cl (5.68 g, 9.89 mmol) in 20 ml of THF. It was allowed to stir for 16 h. Potassium chloride was removed by filtration. Addition of Et_2O to the filtrate produced brilliant orange crystals, characterized as $[PPN]_2[Mn(CO)_6(NO)_2]$. Yield: 0.77 g (40%), m.p. 125°C (decomp), air-stable as a solid for hours. IR spectrum (THF): ν(CO) 1970 m, 1890 s, 1860 s; ν(NO) 1650 w-m, 1610 m cm^{-1}. ^1H NMR (300 MHz, d_6-acetone, 20°C): δ 7.77–7.30 (m, PPN^+). *Anal.* Calc. for $C_{78}H_{60}Mn_2N_4O_8P_4$: C, 66.20; H, 4.27; N, 3.96; P, 8.75. Found: C, 66.07; H, 4.15; N, 3.80; P, 8.79%.

2.3.2. From reaction of $K_2[Mn(CO)_3(NO)]$ with $C_7H_7BF_4$

To a solid mixture of **4** (0.25 g, 1.10 mmol) and tropylium tetrafluoroborate (0.18 g, 1.10 mmol) in a flask was added 25 ml of THF. It was allowed to stir for 5 days. A mixture of yellow solids and orange solution was obtained. A silicone fluid mull IR spectrum of the yellow solids showed bands at 1900 m, 1750 s, and 1420 s cm^{-1}, indicating the presence of **4**. There were also mysterious bands at 2170 m and 1590 s, br cm^{-1}. After filtration, the orange solution was treated with [PPN]Cl (1.45 g, 2.53 mmol). After overnight stirring and filtration, about 20 ml of the THF was removed in vacuo from the orange filtrate. Initial addition of Et_2O caused formation of a white precipitate that was removed by filtration. Further addition of Et_2O afforded a brilliant orange crystalline product, identified as $[PPN]_2[Mn_2(CO)_6(NO)_2]$ by its IR spectrum. (THF): ν(CO) 1970 m, 1980 s, 1860 s; ν(NO) 1650 w-m, 1610 m cm^{-1}, which was superimposable on an IR spectrum of bona fide $[PPN]_2[Mn_2(CO)_6(NO)_2]$ prepared by route a. Yield: 0.10 g (14%).

2.4. $[PPN]_2[MnFe(CO)_7(NO)]$ (7)

2.4.1. From reaction of $K_2[Mn(CO_3(NO)]$ with $Fe(CO)_5$

Iron pentacarbonyl (1.6 ml, 12 mmol) was dissolved in 100 ml of THF. 10 ml of this THF solution (1.2 mmol of $Fe(CO)_5$) was then added dropwise into a slurry of **4** (0.300 g, 1.21 mmol) in 50 ml of THF. All solid **4** was consumed after 17 h of stirring, resulting in a dark brownish-red solution that showed ν(CO,NO) bands at 1965 m, 1955 sh, 1890 s, 1870 s, 1830 m, 1645 m, 1615 m cm^{-1}. After filtration through a medium frit, all solvent and unreacted $Fe(CO)_5$ were removed in vacuo. The resulting oily brownish red solids were redissolved in 50 ml of THF and filtered into a flask containing solid [PPN]Cl (2.08 g, 3.64 mmol). Overnight stirring and filtration, followed by crystallization from THF–Et_2O gave yellow-gold crystals of $[PPN]_2[MnFe(CO)_7(NO)]$, contaminated with a small amount of [PPN]Cl. Further recrystallization from THF–Et_2O gave the pure sample. Yield, 0.46 g (30%) m.p. 155°C (decomp). IR (THF): ν(CO) 1985 m, 1940 w, 1870 vs; ν(NO) 1645 m cm^{-1}; (Nujol) mull): ν(CO) 1985 m, 1970 w, 1910 s, 1875 vs br; ν(NO) 1645 m cm^{-1} (there are also very weak bands at 1610 and 1585 cm^{-1} due to PPN$^+$ ion). ^{1}H NMR (300 MHz, d$_6$-acetone, 20°C) δ 7.80–7.30 (m, phenyl of PPN$^+$); no M–H signals were present. *Anal.* Calc. for $C_{79}H_{60}FeMnN_3O_8P_4$: C, 67.10; H, 4.29; N, 2.97. Found: C, 67.03; H, 4.41; N, 2.79%.

2.4.2. From reaction of $K_2[Mn(CO)_3(NO)]$ with $Fe_2(CO)_9$

A dark purple solution of $Fe_2(CO)_9$ (0.442 g, 1.21 mmol) in 25 ml of THF was added dropwise to a slurry of **4** (0.300 g, 1.21 mmol) in 15 ml of THF with vigorous stirring. Six hours later the original purple solution changed to a dark brownish red reaction mixture. Inspection of the infrared spectrum showed the following bands in the ν(CO, NO) region: 2020 s, 1995 vs, 1965 s, 1955 vs, 1890 vs, 1870 vs, 1830 m, 1645 m, 1615 w cm^{-1} (the first two bands are due to liberated and unreacted $Fe(CO)_5$). THF and $Fe(CO)_5$ were removed under vacuum. The reaction mixture was then redissolved in 50 ml of THF and filtered into a flask containing solid [PPN]Cl (2.50 g, 4.36 mmol). After stirring overnight, the solution was filtered and the compound was precipitated by addition of diethyl ether. Further recrystallization from $CH_3CN–Et_2O$ and $THF–Et_2O$ gave yellowish brown crystals of $[PPN]_2[MnFe(CO)_7(NO)]$. Yield: 0.38 g (25%). The IR spectrum of **5** prepared by this route was superimposable with that of the sample made by route a.

2.4.3. From reaction of $Na_2[Fe(CO)_4]$ with $Mn(CO)_4(NO)$

A solution of $Mn(CO)_4(NO)$ in 40 ml of THF was freshly prepared from the reaction of $[PPN][NO_2]$ (1.70 g, 2.84 mmol) and $[Mn(CO)_5(CH_3CN)][BF_4]$ (0.94 g, 2.84 mmol) as described previously. This solution was then added dropwise with vigorous stirring into a solution of $Na_2[Fe(CO)_4]$ (1.5 dioxane) (1.01 g, 2.84 mmol) in 50 ml of THF. Inspection of the solution spectrum at the end of addition showed the following bands in the ν(CO, NO) region: 1995 m, 1985 m, 1965 m, 1895 s, 1880 s, 1645 m, 1605 w cm^{-1}. The absence of bands due to $Mn(CO)_4(NO)$ indicated that the reaction was complete. The resulting dark brownish red solution was then filtered into a flask containing solid [PPN]Cl (7.37 g, 11.36 mmol). After overnight stirring, filtration and removal of about 60 ml of THF from the dark brownish red filtrate, Et_2O was added to precipitate the compound. Further recrystallization from $THF–Et_2O$ gave brilliant gold crystals of $[PPN]_2[MnFe(CO)_7(NO)]$. Yield 1.63 g (40%). Compound **5** obtained by route c had an identical IR spectrum to those accessed by routes a and b.

3. Results and discussion

3.1. Synthesis of $[Mn(CO)_3(NO)]^{2-}$ via reductions of $Mn(CO)_3(NO)PPh_3$ and $Mn(CO)_4(NO)$

3.1.1. Sodium-amalgam reductions

Although alkali metal or alkali metal–amalgam reductions of homoleptic mono- or di-nuclear metal carbonyls are often good routes to pure carbonylmetalates [18], corresponding reductions of mixed carbonylnitrosylmetal complexes almost invariably result in loss of a nitrosyl group via irreversible and poorly understood processes. For example, $Co(CO)_3(NO)$ and $Fe(CO)_2(NO)_2$ undergo such reductions to provide $[Co(CO)_4]^-$ [19] and $[Fe(CO)_3(NO)]^-$ [20], respectively, as the only isolable products. The fates of the lost NO groups in these reductions remain unknown. Similarly, we found that reduction of $Mn(CO)_4(NO)$ by sodium amalgam gave only a low isolated yield (13%) of microcrystalline $[PPN][Mn(CO)_5]$ after metathesis of the initially formed $Na[Mn(CO)_5]$ with PPN$^+$Cl$^-$ (Eq. (1)). Due to the failure to obtain the desired $Na_2[Mn(CO)_3(NO)]$ from this route via $Mn(CO)_4(NO)$, we decided to examine the corresponding reduction of $Mn(CO)_3(NO)(PPh_3)$ (**1**). The presence of the relatively good donor triphenylphosphane group in complex **1** was expected to make the nitrosyl group in the latter complex more difficult to reduce than that in $Mn(CO)_4(NO)$. However, and perhaps more importantly, it seemed likely that the PPh_3 group would be lost from complex **1**, rather than CO or NO, during reduction. Thus, it has been found that reduction of mononuclear transition metal complexes containing a mixture of good and poor- or non-acceptor ligands usually causes preferential loss of one or more of the weakest acceptor/strongest donor ligands, provided reduction of coordinated ligands does not occur. This synthetic strategy, which has been called 'the reductive labilization method' [6], represents an often unique and rather poorly explored route to unusual highly reduced organometallics/inorganics. It was first introduced several years ago for the syntheses of the 'superreduced' species $Na_4[M(CO)_4]$, M = Cr, Mo, W. The latter could only be accessed in good yield and pure form by reduction of the respective M(CO)$_4$(η^2-TMEDA), TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine with sodium metal in liquid ammonia [21].

$$Mn(CO)_4(NO) + \text{excess Na–Hg} \xrightarrow[-196°C \text{ to } 20°C]{THF} \xrightarrow{[PPN]Cl} [PPN][Mn(CO)_5] + \ldots \quad (1)$$

Reduction of complex **1** by excess Na–Hg in THF at r.t. was a remarkably clean reaction compared to that of $Mn(CO)_4NO$ and provided, after complexation with cryptand 2.2.2, a high isolated yield (83%) of a pale yellow powdery solid, for which satisfactory analyses were obtained as the unsolvated [Na(crypt 2.2.2)]$_2$[Mn(CO)$_3$(NO)] (**2**) (Eq. (2)). Interestingly, **2** is isoelectronic with

$$\mathrm{Mn(CO)_3(NO)(PPh_3)} + \text{excess Na–Hg} \xrightarrow[\text{20°C-PPh}_3]{\text{THF}} \xrightarrow{\text{crypt 2.2.2}} \mathrm{[Na(crypt\ 2.2.2)]_2\text{-}[Mn(CO)_3(NO)]}\downarrow \ 83\% \tag{2}$$

[Na(crypt 2.2.2)]$_2$[Fe(CO)$_4$], which was established by single-crystal X-ray crystallography to contain an essentially undistorted tetrahedral [Fe(CO)$_4$]$^{2-}$ unit [22]. On the basis of IR spectral and derivative data complex **2** is formulated to contain similarly discrete [Mn(CO)$_3$(NO)]$^{2-}$ units of C_{3V} symmetry. This information will be discussed in detail below.

3.2. Potassium tri-*sec*-butylborohydride reductions

Since Fe(CO)$_5$ [23] and Fe(CO)$_4$PPh$_3$ [24] both undergo reduction by potassium tri-*sec*-butylborohydride, K[R$_3$BH], to give high isolated yields of unsolvated K$_2$[Fe(CO)$_4$], the corresponding reductions of Mn(CO)$_3$(NO)L, L = CO, PPh$_3$ were also examined. These reactions provided identical yellow microcrystalline solids of the formulation K$_2$[Mn(CO)$_3$(NO)] (**4**) in 62% (L = CO), and 84% (L = PPh$_3$) isolated yields, respectively (Eq. (3)). IR spectral and chemical reactivity data for complex **4** are completely in accord with the presence of [Mn(CO)$_3$(NO)]$^{2-}$ units in this potassium salt. These data will be discussed in later sections.

$$\mathrm{Mn(CO)_3(NO)L} + 2\mathrm{K[R_3BH]} \xrightarrow[\text{-H}_2\text{,-2BR}_3]{\text{THF}^{a}} \mathrm{K_2[Mn(CO)_3(NO)]}\downarrow + \mathrm{L} \tag{3}$$

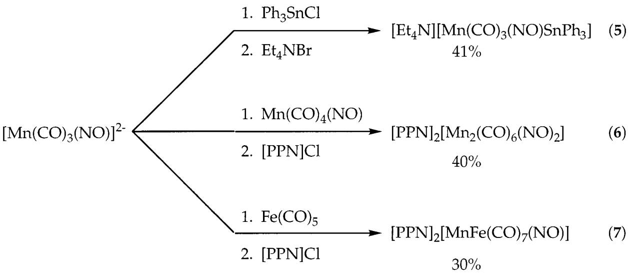
L = CO, PPh$_3$, R = *sec*-Bu, aL = CO, reflux, 1.5 h, yield = 62%; L = PPh$_3$, 20°C, 3 h, yield = 84%.

Interestingly, the reaction of Mn(CO)$_4$(NO) with K[R$_3$BH] required substantially more forcing conditions (reflux in THF) to go to completion than the corresponding one of Mn(CO)$_3$(NO)(PPh$_3$), which proceded efficiently at r.t. Since carbonyls are far more susceptible towards nucleophilic attack than nitrosyl ligands, for a given mixed carbonylnitrosylmetal complex [25], it is believed that Mn(CO)$_3$(NO)L, L = CO, PPh$_3$, initially reacted with [R$_3$BH]$^-$ to generate formyl anions, [Mn(CO)$_2$(NO)L(CHO)]$^-$. Loss of L from the putative formyl intermediates would provide the presently unknown hydride, [Mn(CO)$_3$(NO)H]$^-$, vide infra. The latter would be expected to react with additional [R$_3$BH]$^-$ to afford the observed product [Mn(CO)$_3$(NO)]$^{2-}$, along with hydrogen gas and tri-*sec*-butylborane.

The proposed reaction sequence above is well precedented in the corresponding reactions of Fe(CO)$_5$ [23,26] and Fe(CO)$_4$PPh$_3$ [26] with K[R$'_3$BH], R$'$ = *sec*-Bu [23], O-i-Pr [26], which initially provide the formyl anions, [Fe(CO)$_3$L(CHO)]$^-$, L = CO, PPh$_3$. The latter lose L to provide [Fe(CO)$_4$H]$^-$, which undergoes facile deprotonation by [R$_3$BH]$^-$ to give [Fe(CO)$_4$]$^{2-}$. Loss of L from the formyl iron anions is more facile for L = PPh$_3$ than CO, undoubtedly because the electron rich iron center leads to preferential labilization of the phosphane, which is a better donor and weaker acceptor than CO. We believe the same situation obtains for the proposed manganese analogs and it is this facile

Table 1
Infrared data for carbonylnitrosylmanganese complexes

Compound	Solvent/medium	IR ν(CO)	ν(NO) (cm^{-1})
Mn(CO)$_4$NO	ethanol	2090 s, 2010 vs, 1970 vs	1755 m
Mn(CO)$_3$(NO)PPh$_3$	THF	2030 s, 1965 m, 1920s	1705 m
Na$_2$[Mn(CO)$_3$(NO)]	THF	1918 s, 1860 w, 1815 vs br	1380 m br, 1345 m br
[Na(crypt2.2.2)]$_2$[Mn(CO)$_3$(NO)]	silicone fluid mull	1840 m, 1720 vs	1480 m
K$_2$[Mn(CO)$_3$(NO)]	fluorolube mull	1900 m 1775 sh, 1755 vs br	1440 sh 1420 m
[Et$_4$N][Mn(CO)$_3$(NO)SnPh$_3$]	CH$_3$CN	1975 s 1895 m, 1860 s	1640 m
[PPN]$_2$[Mn$_2$(CO)$_6$(NO)$_2$]	THF	1970 m, 1890 s, 1860 s	1650 w-m 1610 m
[PPN]$_2$[MnFe(CO)$_7$(NO)]	THF	1985 m, 1940 w, 1870 vs br	1645 m



Scheme 1.

loss of PPh_3 that accounts for the mild conditions required for the reaction of $Mn(CO)_3(NO)(PPh_3)$ with $K[R_3BH]$, as depicted above in Eq. (3).

3.3. Infrared spectral properties of $[Mn(CO)_3(NO)]^{2-}$

Infrared data for salts of $[Mn(CO)_3(NO)]^{2-}$ are shown in Table 1. Fluorolube mull spectra of $K_2[Mn(CO)_3(NO)]$ in the ν(CO,NO) region show three main peaks at 1900 (m), 1755 (vs) and 1420 (m) cm^{-1}. In the same region, THF solution spectra of $Na_2[Mn(CO)_3(NO)]$ exhibit principal bands at 1918 (s), 1815 (vs, br), 1380 (m, br), 1345 (m, br) cm^{-1}. The two very low-energy bands for the disodium salt at 1380 and 1345 cm^{-1} are undoubtedly caused by strong interactions between sodium cations and nitrosyl oxygens. To the best of our knowledge, these are the lowest ν(NO) bands previously observed for mononuclear metal nitrosyls. The related $K_3[Mn(CN)_2(NO)_2]$, which likely also contains linear nitrosyls, exhibited ν(NO) values of 1455, 1425 cm^{-1}, the previous lowest energies for metal nitrosyls of this type [27]. The Σ-NO binding is significantly weaker in $K_2[Mn(CO_3(NO)]$ than for $Na_2[Mn(CO)_3(NO)]$. This feature also accounts for the lower ν(CO) values observed for the potassium salt compared to those for $Na_2[Mn(CO)_3(NO)]$ [28]. Addition of cryptand 2.2.2 to THF solutions of the latter species caused the two broad ν(NO) peaks to coalesce into a dramatically sharper one at considerably higher energy, 1480 cm^{-1}. The corresponding ν(CO) peaks also sharpened and moved to lower energies of 1840 m, 1720 vs cm^{-1}. These spectral changes indicate that the complexation of Na^+ by cryptand 2.2.2 substantially (or completely) disrupted the nitrosyl oxygen $-Na^+$ ion pairing interactions and perturbation of the pseudotetrahedral $[Mn(CO)_3(NO)]^{2-}$ unit. Similar trends have been previously reported for the isoelectronic $[Fe(CO)_3(NO)]^-$. For example, infrared spectra of $Na[Fe(CO)_3(NO)]$ in Et_2O, where the nitrosyl oxygen is ion-paired with Na^+, show peaks in the ν(CO,NO) region at 2001, 1900 and 1599 cm^{-1}, while corresponding spectra of $[PPN][Fe(CO_3(NO)]$ in THF, where no such interaction is possible, show peaks at 1978, 1876 and 1645 cm^{-1} [29].

3.4. Reactions of $[Mn(CO)_3(NO)]^{2-}$

Further confirmation of the natures of (**2**) and (**4**) has been obtained by the preparation of appropriate derivatives thereof from the reactions of these species with Ph_3SnCl, $Mn(CO)_4NO$, and $Fe(CO)_5$, all of which also combine with the isoelectronic $[Fe(CO)_4]^{2-}$ to give reasonably robust products, vide infra. The results of these various reactions are shown in Scheme 1.

3.5. $[Mn(CO)_3(NO)(SnPh_3)]^-$

Treatment of slurry of complex **4** with 1 equiv. of Ph_3SnCl in THF at r.t. gave rise to an orange solution. After metathesis with $[Et_4N]Br$ and recrystallizations from CH_3CN-Et_2O and $THF-Et_2O$ a pure orange microcrystalline and thermally robust product (mp: 141°C w dec.). was identified as $[Et_4N][Mn(CO)_3(NO)SnPh_3]$ (**5**), by elemental analyses, IR (Table 1) and ^1H NMR spectra. Crystalline **5** is stable in air for hours at r.t. and forms thermally stable solutions in THF, acetonitrile and acetone. The ν(CO,NO) band shapes and relative intensities are virtually identical to those found for $Mn(CO)_3(NO)(PPh_3)$ (**1**), 2030 (s), 1965 (m), 1920 (s), 1705 (s) cm^{-1}, except the latter are all shifted about 60 cm^{-1} to higher energies. On this basis, it seems likely that $[Mn(CO)_3(NO)SnPh_3]^-$ and $[Mn(CO)_3(NO)PPh_3]$ are also isostructural. The latter species has been shown to have a trigonal bipyramidal structure, where the PPh_3 and NO groups occupy axial and equatorial positions, respectively [30]. The isoelectronic neutral $Fe(CO)_3(NO)SnPh_3$ also has a very similar spectral signature, 2065 (s), 2010 (m), 1980 (s), 1773 (s) cm^{-1} [31], except all corresponding bands have shifted from about 90 to 130 cm^{-1} to higher energy.

3.6. $[Mn_2(CO)_6(NO)_2]^{2-}$ and $[MnFe(CO)_7(NO)]^{2-}$

Since $[Fe(CO)_4]^{2-}$ readily interacts with $Fe(CO)_5$ to provide the dinuclear dianion, $[Fe_2(CO)_8]^{2-}$ [32], corresponding reactions of $[Mn(CO)_3(NO)]^{2-}$ with $Mn(CO)_4(NO)$ and $Fe(CO)_5$ were examined. As shown in the above Scheme, both combinations provide new dinuclear anions, which were isolated as PPN^+, i.e. $[N(Ph_3P)_2]^+$, salts. On the basis of elemental analyses, IR and ^1H NMR spectra, these products were formulated as $[PPN]_2[Mn_2(CO)_6(NO)_2]$ (**6**) and $[PPN]_2[MnFe(CO)_7(NO)]$ (**7**), respectively. Compounds **6** and **7** were isolated in 40 and 30% yields as brilliant orange and golden microcrystals, respectively. Their ^1H NMR spectra confirmed that no metal hydrides were present in significant amounts. Further confirmation of the natures of complexes **6** and **7** were obtained by their independent syntheses as shown below in Eqs. (4) and (5), respectively, where

$$2K_2[Mn(CO)_3(NO)] + 2[C_7H_7][BF_4] \xrightarrow[\text{2. [PPN]Cl-KBF}_4\text{,-KCl,-C}_{14}\text{H}_{14}]{\text{1. 20°C, THF}} \underset{14\%}{[PPN]_2[Mn_2(CO)_6(NO)_2]} \quad (4)$$

$$Mn(CO)_4(NO) + Na_2[Fe(CO)_4] \xrightarrow[\text{2. [PPN]Cl-NaCl}]{\text{1. 20°C, THF}} \underset{40\%}{[PPN]_2[MnFe(CO)_7(NO)]} \quad (5)$$

$[C_7H_7][BF_4]$ is tropylium tetrafluoroborate, a convenient one electron oxidant [34]. Compound **7** was also obtained in 25% isolated yield via the reaction of $K_2[Mn(CO)_3(NO)]$ and $Fe_2(CO)_9$ in THF, followed by metathesis with [PPN]Cl and recrystallizations. IR spectra of complexes **6** and **7** in the ν(CO,NO) region indicate that no bridging ligands are present, as is the case for $[Fe_2(CO)_8]^{2-}$ [33]. Further, the very simple IR patterns observed for compounds **6** and **7** suggest that only one structural isomer of each is present. The remarkable similarity of the ν(CO,NO) spectral signature of compounds **5** and **6** indicate that the local geometry about the manganese atoms in both species are closely related. Indeed, as noted previously, complex **5** and the structurally characterized $Mn(CO)_3(NO)(Ph_3P)$ [30] almost certainly have identical structures. Thus, on the basis of available data, complex **6** is likely to have a structure essentially identical to that of $[Fe_2(CO)_8]^{2-}$, except two of the equatorial carbonyl groups in the latter are replaced by nitrosyl groups. It is well established that nitrosyls have a great preference to occupy equatorial positions in trigonal bipyramidal mixed carbonylnitrosyl complexes, due to their much stronger acceptor abilities compared to carbonyls [35]. Similar arguments suggest that complex **7** and $[Fe_2(CO)_8]^{2-}$ are also isostructural. However, single crystal X-ray structural characterizations of **6** and **7** will be required to corroborate these claims. Unfortunately, attempts to obtain suitable single crystals of these species have so far failed.

3.7. Other reactions of $[Mn(CO)_3(NO)]^{2-}$

Earlier in this article it was suggested that the hydride route to $K_2[Mn(CO)_3(NO)]$ likely involved the intermediate formation of the presently unknown hydride $[Mn(CO)_3(NO)H]^-$. The latter species would be entirely analogous to the neutral $Fe(CO)_3(NO)H$, which decomposes at −45°C and was obtained by protonation of $[Fe(CO)_3(NO)]^-$ [2]. Unfortunately, all attempts to protonate salts of $[Mn(CO)_3(NO)]^{2-}$, even by weak Brønsted acids such as methanol at −78°C, led only to intractable products, which decomposed well below ambient temperature. Also, treatment of $Mn(CO)_4(NO)$ with methanolic Et_4N^+ OH^- gave quite unstable species, which showed no NMR resonances due to metal hydrides. In contrast, corresponding methanolysis of $[Fe(CO)_4]^{2-}$ or hydroxide attack of $[Fe(CO)_5]$ provide high yields of the thermally robust $[Fe(CO)_4H]^-$ [1].

To the best of our knowledge, the only other known reaction of $K_2[Mn(CO)_3(NO)]$ was that recently reported with the chlorogallane, ClGaRR′, R = $(CH_2)_3NMe_2$, R′ = t-Bu. After metathesis, high (88%) yields of the respective [PPN][Mn(CO)$_3$(NO)(GaRR′)] were obtained [36]. This latter report, as well as our studies described herein, demonstrate that $[Mn(CO)_3(NO)]^{2-}$ is an effective nucleophile and a potentially useful reagent for the syntheses of new classes of mixed metal complexes, some of which may find applications in the production of novel alloy-films [36].

4. Conclusions

Our success in obtaining $[Mn(CO)_3(NO)]^{2-}$ by the alkali metal reduction of $[Mn(CO)_3(NO)(Ph_3P)]$ represents another demonstration of the value of the 'reductive labilization method,' vide supra, in the synthesis of unusual organometallic complexes of the transition metals. The same strategy has been employed in the preparation of the previously unknown $[V(CO)_4(NO)]^{2-}$, which cannot be obtained by a direct reduction of $V(CO)_5(NO)$ [37]. Similarly, it is possible that a wide variety of highly reduced carbonylnitrosylmetallates may be available by related reductions, including unusual electronically saturated three coordinate dianions such as $[Mn(NO)_3]^{2-}$, $[Fe(CO)(NO)_2]^{2-}$, and $[Co(CO)_2(NO)]^{2-}$. These are all unknown presently but are isoelectronic with the known species $[Co(CO)_3]^{3-}$ [38]. Since free or coordinated $[NO]^+$ and NO can undergo facile reductive coupling to form the hyponitrite ion, $[N_2O_2]^{2-}$ [39], the existence of highly reduced di- or poly-nitrosyl metalates may be problematic. Indeed, presently the only known mononuclear polynitrosylmetallate anion is $[Mn(CO)_2(NO)_2]^-$ [3]. However, at least in this case, there is no indication from its crystal structure [3,40] that the NO units are involved in a form of 'incipient reductive coupling,' which is well established in certain dicarbonyl metal complexes, such as $Nb(CO)_2(dmpe)_2Cl_2$ [41].

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