Synthesis and Characterization of the Five-Coordinate Sixteen-Electron Manganese(I) Complex $[Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]^-$

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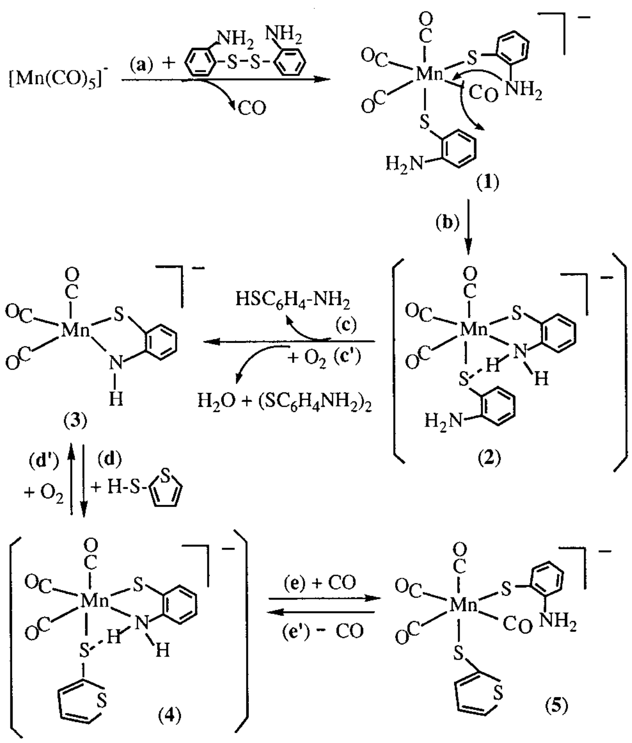
Introduction

The NH···S hydrogen bond which arguably plays a major role in determining the redox potential and the electronic structure of biologically important metalloproteins and metalloenzymes (e.g., iron−sulfur proteins, ferredoxins, and rubredoxins)[1] has been observed in biomimetic structural model complexes.[2]

Recent work in this laboratory has shown that the anionic metal carbonyl fragments ($[Mn(CO)_5]^-$ and $[PhEFe(CO)_4]^-$ (E = Se, Te)) activate the E−E bond of diorganyl dichalcogenides to yield *cis*-$[Mn(CO)_4(ER)_2]^-$ and *fac*-$[Fe(CO)_3(EPh)_3]^-$ complexes which are useful in the syntheses of $(CO)_4Mn(\mu\text{-ER})_2Co(CO)(\mu\text{-ER})_3Mn(CO)_3$ with a unique terminal $Co^{III}-CO$ bond,[3] $[(CO)_3M(\mu\text{-SePh})_3M'(\mu\text{-SePh})_3M(CO)_3]^{-/0}$ (M = Mn, M′ = Co; M = Fe, M′ = Ni, Zn, Cd, Fe) with homoleptic hexaselenolatometal core,[4] and distorted square planar $[Ni(CO)(SPh)_n(SePh)_{3-n}]^-$ (n = 0, 1, 2),[5] the biomimetic nickel-site structure of [NiFeSe] hydrogenases and CO dehydrogenase. In this paper we combine the dichalcogen synthetic technology with the potential for intramolecular H-bonding to synthesize five-coordinate sixteen-electron Mn(I) complex $[Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]^-$ stabilized by S,N π-donation of bidentate $[S-C_6H_4-NH]^{2-}$ ligand. To our knowledge, a few examples of transition-metal carbonyl complexes containing five-coordinate sixteen-electron metal core (d^6) have been reported,[6,7] e.g. $[Mn(CO)_3(DBCat)]^-$ prepared by oxidative substitution of two CO ligands of $[Mn(CO)_5]^-$ by 3,5-di-*tert*-butyl-1,2-benzoquinone,[6a] and $[W(CO)_3(NHC_6H_4NH)]^{2-}$ prepared from $W(CO)_5(THF)$ and 2 equiv of monodeprotonated ligands $[NHC_6H_4NH_2]^-$ by intermolecular deprotonation.[7c]

Scheme 1



Results and Discussion

When a THF solution of 2-aminophenyl disulfide (0.1 mmol, 0.025 g) and $[PPN][Mn(CO)_5]$ (0.1 mmol, 0.073 g) is stirred under N_2, a rapid reaction ensues over the course of 5 min at ambient temperature to give, by what may be described as an oxidative addition/decarbonylation reaction, a thermally unstable, monodentate (S-bonded) *cis*-$[Mn(CO)_4(S\text{-}C_6H_4NH_2)_2]^-$ (**1**) (Scheme 1a), since the IR spectra match those of complex *cis*-$[Mn(CO)_4(SPh)_2]^-$ previously established (by IR and X-ray diffraction).[3,8] As illustrated in Scheme 1b,c, the dark red, five-coordinate, S,N-chelate $[Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]^-$ (**3**) with

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sixteen-electron Mn(I) core was finally isolated as a semisolid from THF−diethyl ether (0.056 g, 73%) after stirring the solution overnight in THF at room temperature. A reasonable reaction sequence accounting for the formation of complex **3** is shown in Scheme 1b,c. The dissociation of a carbonyl ligand resulting from chelate formation of one terminal thiolate ligand Mn^{I}-S-C_6H_4-NH_2 of complex **1** yielded the intermediate *fac*-[$Mn(CO)_3(S\text{-}C_6H_4NH_2)(S\text{-}C_6H_4\text{-}NH_2)]^-$ (**2**) with one anionic [S-$C_6H_4NH_2$] ligand bound to the Mn^{I} metal in a monodentate (S-bonded) manner and the second anionic [S-C_6H_4-NH_2] ligand bound to the Mn^{I} metal in a bidentate manner (S,N-bonded), forming a five-membered chelate ring.[9] The intramolecular N−H···S interaction (cis arrangement of thiolate and NH_2 group in intermediate **2**)[2c,f,7b] and the subsequent elimination of 2-aminothiophenol (the coordination of N atom presumably increases the acidity of amine protons to accelerate the deprotonation of NH_2)[7b,c,10] yielded the five-coordinate complex **3**. The IR spectrum of complex **3** shows two strong CO stretching bands, which supports a facial orientation of three CO ligands. The ^1H and ^{13}C NMR spectra show the expected signals for the S,N chelate $[S\text{-}C_6H_4\text{-}NH]^{2-}$ ligand in a diamagnetic d^6 Mn(I) species. Oxidation chemistry was also successful in the synthesis of complex **3**. Upon contact with dry O_2, the color of reaction mixture immediately turns from orange to dark red in THF/CH_3CN. The IR and ^1H NMR spectra indicated the formation of complex **3** accompanied by byproducts, H_2O and 2-aminophenyl disulfide identified by ^1H NMR (Scheme 1c′). In this oxidative reaction, the Mn(I) was not observed to undergo oxidation, and consequently, the oxidation process is best assigned to the terminal thiolate ligand to yield 2-aminophenyl disulfide via radical ($[S\text{-}C_6H_4\text{-}NH_2]^{\bullet}$) recombination, and the concomitant deprotonation of amine proton of intermediate **2** leads to formation of water.[10]

To further add credibility to the proposed mechanism, a straightforward protonation of complex **3** was conducted. As illustrated in Scheme 1d, the dropwise addition of the excess thiophene-2-thiol to complex **3** in THF under N_2 at ambient temperature led to the formation of an orange yellow solution immediately. The bands at 1973 vs and 1870 s cm^{-1} disappeared, with concomitant formation of a spectrum (ν_{CO} (THF): 1991 vs, 1891 s, 1879 s cm^{-1}) similar to that observed for intermediate **2**, i.e., formation of six-coordinate *fac*-[$Mn(CO)_3(S\text{-}C_4H_3S)(S\text{-}C_6H_4\text{-}NH_2)]^-$ (**4**) (^1H NMR (C_4D_8O): δ 5.53 (br), 4.89 (br) ppm (NH_2)). Attempts to isolate this moderately stable anion **4** was unsuccessful. In common with intermediate **2**, complex **4** is very sensitive, converting to complex **3**, H_2O and di(2-thienyl) disulfide characterized by ^1H NMR, within seconds on exposure to O_2 (Scheme 1d′). Additionally, the ring-opened complex *cis*-[$Mn(CO)_4(S\text{-}C_4H_3S)(S\text{-}C_6H_4NH_2)]^-$ (**5**) (ν_{CO} (THF): 2055 m, 1981 vs, 1959 s, 1916 s cm^{-1}) was obtained upon exposing complex **4** to CO atmosphere in THF at room temperature (Scheme 1e). Apparently, protonation of the amide site of complex **3** labilizes the chelating ligand $[S\text{-}C_6H_4\text{-}NH_2]^-$ and results in the formation of complex **5**. The complete conversion of complex **5** to **4** was observed when removing CO atmosphere under vacuum in THF (Scheme 1e′). The reversibility of CO ligand-binding demonstrates the complexes **4** and **5** are chemically interconvertible.

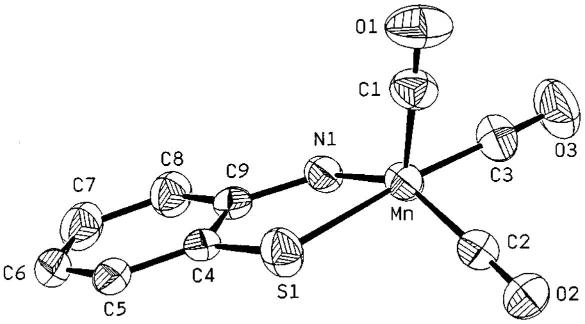

Figure 1. ORTEP drawing and labeling scheme of $[Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]^-$ with thermal ellipsoids drawn at the 50% probability level.

The molecular structure of complex **3** is depicted in Figure 1. Manganese is best described as existing in a distorted tetragonal pyramidal coordination environment with the C(1)O(1) ligand occupying the apex. The Mn^{I}−S distance 2.268(1) Å in the title complex is significantly shorter than the reported Mn^{I}−SPh bond 2.398(1) Å in the *cis*-$[Mn(CO)_4(SPh)_2]^-$,[8] Mn^{II}−SPh bond 2.442(3) Å in the $[Mn(SPh)_4]^{2-}$.[11] The Mn^{I}−N bond distance is 1.889(3) Å, which is also significantly shorter than that in $[Mn^0(CO)_3(TMPO)]$ (TMPO = 2,2,6,6-tetramethylpiperidinyl-1-oxo) (1.981(3) Å),[6b] and in $[Mn^{III}(edt)_2(ImH)]^-$ (edt = ethane-1,2-dithiolate) (2.224(7) Å).[12] This shortening of Mn−S and Mn−N bonds in complex **3** may be attributed to the significantly π-donating ability of the bidentate $[S\text{-}C_6H_4\text{-}NH]^{2-}$ ligand.[7,13]

Experimental Section

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox (Ar gas). Solvents were distilled under nitrogen from appropriate drying agents (ethyl ether from CaH_2; acetonitrile from CaH_2/P_2O_5; hexane and tetrahydrofuran (THF) from Na/benzophenone; ethyl alcohol from CaH_2) and stored in dried, N_2-filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use and transfers to reaction vessels were via stainless steel cannula under N_2 at a positive pressure. The reagents dimanganese decacarbonyl, 2-aminophenyl disulfide, thiophene-2-thiol, bis(triphenylphosphoranylidene)ammonium chloride (Aldrich) were used as received. Infrared spectra were recorded on a spectrometer (Bio-Rad FTS-185) with sealed solution cells (0.1 mm) and KBr windows. In NMR spectra (recorded on a Bruker AC 200 spectrometer), chemical shifts of ^1H and ^{13}C are relative to tetramethylsilane. UV−visible spectra were recorded on a GBC 918 spectrophotometer. Analyses of carbon, hydrogen, and nitrogen were obtained with a CHN analyzer (Heraeus).

Preparation of [PPN][Mn(CO)$_3$(S-C$_6$H$_4$-NH)] (3). [PPN][$Mn(CO)_5$] (0.1 mmol, 0.073 g) and 2-aminophenyl disulfide (0.1 mmol, 0.025 g) dissolved in 5 mL of THF were stirred under nitrogen at ambient temperature. A vigorous reaction occurred immediately with evolution of CO gas. IR spectrum, ν_{CO} (THF) 2050 w, 1965 vs, 1951 m, 1913 m cm^{-1}, indicated the formation of anionic *cis*-[$Mn(CO)_4(S\text{-}C_6H_4NH_2)_2$]. The reaction mixture was stirred overnight at room temperature, and the yellow solution completely converted into a dark red solution. Alternatively, upon contact with dry O_2, the color of

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Table 1. Crystallographic Data of Complex $[Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]^-$

empirical formula	$C_{45}H_{35}O_3N_2P_2SMn$
fw	800.74
cryst syst	triclinic
space group	$P\bar{1}$
λ, Å (Mo Kα)	0.7107
a, Å	9.925(3)
b, Å	14.251(2)
c, Å	14.202(3)
α, deg	89.84(1)
β, deg	88.89(2)
γ, deg	81.60(2)
V, Å^3	1986.8(7)
Z	2
d_{calcd}, g cm^{-3}	1.280
μ, cm^{-1}	5.494
T, °C	25
R^a	0.041
$R_w{}^b$	0.039
GOF^c	1.68

[a] $R = \sum|(F_o - F_c)|/\sum F_o$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum wF_o{}^2]^{1/2}$. [c] GOF $= [\sum[w(F_o - F_c)^2/(M - N)]^{1/2}$ where M = number of reflections and N = number of parameters.

reaction mixture immediately turns from yellow to dark red. After the reaction was completed, diethyl ether was slowly added to precipitate a dark red semisolid. The mother liquor was removed via cannula, and the semisolid was dried under vacuum. The product $[PPN][Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]$, suitable for X-ray crystallography, was recrystallized from vapor diffusion of diethyl ether into concentrated THF solution at −15 °C. The yield was 0.056 g (73%). IR (THF): 1973 vs, 1870 s (CO) cm^{-1}; 3339 br cm^{-1} (N−H). ^{1}H NMR (C_4D_8O): δ 8.98 (br) ppm (N−H), 6.90 (d), 6.60 (t), 6.43 (t) ppm (SC_6H_4). ^{13}C NMR (C_4D_8O): δ 115.04 (s), 115.43 (s), 119.79 (s), 128.65 (s), 133.12 (s), 133.23 (s) ppm ($S\text{-}C_6H_4\text{-}NH$). Absorption spectrum (THF) [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 499 (6639), 403 (9745), 304 (10 400). Anal. Calcd for $C_{45}H_{35}O_3N_2P_2SMn$: C, 67.50; H, 4.41; N, 3.50. Found: C, 67.28; H, 4.64; N, 3.68.

Reaction of $[PPN][Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]$ and Thiophene-2-thiol. A portion (10 μL, 0.11 mmol) of thiophene-2-thiol was added dropwise by syringe into $[PPN][Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]$ (0.08 g, 0.1 mmol) in THF under N_2 at ambient temperature. A vigorous reaction occurred immediately, with the color of reaction mixture turning from dark red to orange yellow, and was monitored with FTIR. The IR spectrum, ν_{CO} (THF) 1991 vs, 1891 s, 1879 s cm^{-1}, having the same pattern as, but differing slightly in position from that of, *fac*-$[Mn(CO)_3(S\text{-}C_6H_4\text{-}NH_2)(S\text{-}C_6H_4\text{-}NH_2)]^-$ (IR, ν_{CO} (THF): 1989 vs, 1887 s, 1883 s cm^{-1}) obtained from reaction of $HSC_6H_4NH_2$ and $[Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]$, indicated the formation of *fac*-$[Mn(CO)_3(S\text{-}C_4H_3S)(S\text{-}C_6H_4\text{-}NH_2)]^-$ (^{1}H NMR (C_4D_8O): δ 5.53 (br), 4.89 (br) ppm (NH_2)). Attempts to isolate this moderately stable *fac*-$[Mn(CO)_3(S\text{-}C_4H_3S)(S\text{-}C_6H_4\text{-}NH_2)]^-$ were unsuccessful. The orange yellow *fac*-$[Mn(CO)_3(S\text{-}C_4H_3S)(S\text{-}C_6H_4\text{-}NH_2)]^-$ solution was stirred under CO atmosphere for 5 min at room temperature. The IR spectrum (ν_{CO} (THF) 2055 m, 1981 vs, 1959 s, 1916 s cm^{-1}) indicated the formation of the ring-opened complex *cis*-$[Mn(CO)_4(S\text{-}C_4H_3S)(S\text{-}C_6H_4NH_2)]^-$. The complete conversion of *cis*-$[Mn(CO)_4(S\text{-}C_4H_3S)(S\text{-}C_6H_4NH_2)]^-$ to *fac*-$[Mn(CO)_3(S\text{-}C_4H_3S)(S\text{-}C_6H_4\text{-}NH_2)]^-$ was observed when removing CO atmosphere under vacuum in THF. Oxidation of complex *fac*-$[Mn(CO)_3(S\text{-}C_4H_3S)(S\text{-}C_6H_4\text{-}NH_2)]^-$ by adding dry O_2 leads to formation of $[Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]^-$ accompanied by byproducts H_2O and di(2-thienyl) disulfide identified by ^{1}H NMR.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]^-$

Mn−S(1)	2.268(1)	Mn−N(1)	1.889(3)
Mn−C(1)	1.753(4)	Mn−C(2)	1.761(4)
Mn−C(3)	1.776(4)	S(1)−C(4)	1.714(4)
N(1)−C(9)	1.375(5)	C(1)−O(1)	1.153(5)
C(2)−O(2)	1.167(5)	C(3)−O(3)	1.156(5)
S(1)−Mn−N(1)	83.42(9)	S(1)−Mn−C(1)	97.37(15)
S(1)−Mn−C(2)	88.55(13)	S(1)−Mn−C(3)	171.13(15)
N(1)−Mn−C(1)	120.34(16)	N(1)−Mn−C(2)	147.98(16)
N(1)−Mn−C(3)	90.84(17)	C(1)−Mn−C(2)	91.37(19)
C(1)−Mn−C(3)	91.36(20)	C(2)−Mn−C(3)	92.83(19)
Mn−S(1)−C(4)	100.16(13)	Mn−N(1)−C(9)	124.19(24)

Crystallography. Crystallographic data for the structure of complex $[PPN][Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]$ are collected in Table 1. Bond distances and angles are collected in Table 2. Crystals of $[PPN][Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]$ used for the X-ray diffraction structural determination were obtained from vapor diffusion of diethyl ether into concentrated THF solution at −15 °C under nitrogen atmosphere. The dark red crystal used for the study had approximate dimensions of 0.60 × 0.50 × 0.20 mm. The crystal was mounted on a glass fiber and quickly coated in epoxy resin at 25 °C. The unit-cell parameters were obtained from 25 reflections with 2θ between 16.40° and 23.22° for product $[PPN][Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]$. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation, $\lambda = 0.7107$ Å, employing the $\theta/2\theta$ scan mode.[14] A φ scan absorption correction was made. Structural determinations were made using the NRCC-SDP-VAX package of programs.[15]

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of $[PPN][Mn(CO)_3(S\text{-}C_6H_4\text{-}NH)]$ is available on the Internet only. Access information is given on any current masthead page.

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