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FULL PAPER

A five-coordinate, sixteen-electron manganese(I) complex $[Mn(CO)_3(S,S–C_6H_4)]^-$ stabilized by S,S π-donation from chelating $[S,S–C_6H_4]^{2-}$

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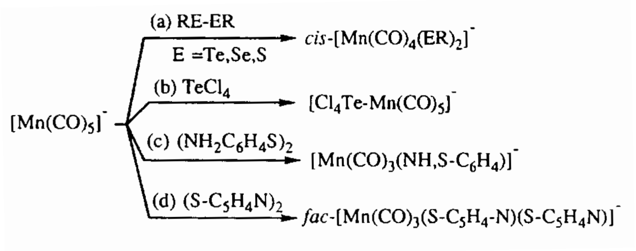
The five-coordinate, sixteen-electron manganese(I) complex $[N(PPh_3)_2][Mn(CO)_3(S,S–C_6H_4)]$ **1** was prepared from reaction of $[N(PPh_3)_2][Mn(CO)_3(NH,S–C_6H_4)]$ and 1,2-benzenedithiol *via* the hexacoordinate intermediate *fac*-$[Mn(CO)_3(S–C_6H_4SH)(NH_2,S–C_6H_4)]^-$. Alternatively, oxidative addition of 1,2-benzenedithiol to $[Mn(CO)_5]^-$, followed by a Lewis acid–base reaction, with evolution of H_2 gas (identified by gas chromatography), led to formation of the coordinatively-unsaturated complex **1**. In contrast, reaction of bis(2-pyridyl) disulfide and $[N(PPh_3)_2][Mn(CO)_5]$ afforded hexacoordinate *fac*-$[N(PPh_3)_2][Mn(CO)_3(S–C_5H_4–N)(S–C_5H_4N)]$ **2**, with one anionic $[S–C_5H_4N]^-$ ligand bound to Mn^I in a monodentate (S-bonded) manner and the other $[S–C_5H_4–N]^-$ ligand bound in a bidentate manner (S,N-bonded). Complexes **1** and **2** have been characterized in solution by infrared spectroscopy and in the solid state by X-ray crystallography. The strong π-donating ability of the bidentate $[S,S–C_6H_4]^{2-}$ ligand stabilizes the unsaturated complex **1** which has short Mn^I–S bond lengths of 2.230(1) Å (average) as a result. The existence of one π and two σ bonds between the $[Mn(CO)_3]^+$ and $[S,S–C_6H_4]^{2-}$ fragments, based on qualitative frontier molecular orbital analysis, also indicates that the lone-pair electrons are delocalized around the sulfur-manganese-sulfur system stabilizing the five-coordinate complex **1**. The IR carbonyl stretching frequencies and the Mn^I–S bond distances of complexes **1** and $[N(PPh_3)_2][Mn(CO)_3(NH,S–C_6H_4)]$ suggest that the relative π-donating ability of the bidentate ligands is $[NH,S–C_6H_4]^{2-} > [S,S–C_6H_4]^{2-}$. The Mulliken atomic charges derived from Hartree–Fock calculations roughly quantify the charge distribution in the complex $[Mn(CO)_3(NH,S–C_6H_4)]^-$ ($\delta(N) = -1.14$; $\delta(S) = -0.43$; $\delta(Mn) = 1.14$), and supports the premise that the reactions of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ with electrophiles (1,2-benzenedithiol, thiophene-2-thiol, 1,2-ethanedithiol) occur at the more electron-rich amide site, yielding charge-controlled, collision complexes.

Introduction

Anionic metal carbonyls are known to function as nucleophiles and show a range of reactivity that depends on the metal, its oxidation state, its substituents and the ligand environment.[1]

Recently, application of the anionic metallic fragment $[Mn(CO)_5]^-$ to the preparation of manganese chalcogenolates proved a successful approach in this direction, *i.e.* oxidative addition of diorganyl dichalcogenides to the low-valent manganese carbonyl fragment $[Mn(CO)_5]^-$ led to formation of *cis*-$[Mn(CO)_4(ER)_2]^-$ (E = Te, Se, S; R = phenyl) [Scheme 1(a)].[2]



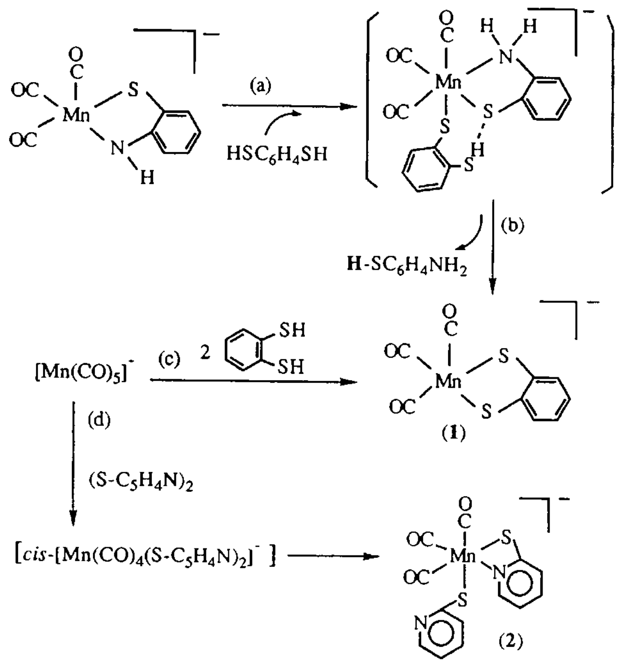
Scheme 1

In addition, $[Mn(CO)_5]^-$ may also serve as a lone-pair-electron donor. Coordinative addition of $[Mn(CO)_5]^-$ to $TeCl_4$ led to formation of a discrete chlorotellurate, $[Cl_4Te–Mn(CO)_5]^-$ [Scheme 1(b)].[3] Very recently, the five-coordinate, sixteen-electron Mn^I complex $[Mn(CO)_3(NH,S–C_6H_4)]^-$ was prepared by combining the dichalcogen synthetic methodology with the potential for intramolecular H-bonding, *via* the reaction of $[Mn(CO)_5]^-$ with 1 equiv. of 2-aminophenyl disulfide [Scheme 1(c)].[4] By way of contrast, the six-coordinate Mn^I complex *fac*-$[Mn(CO)_3(S–C_5H_4–N)(S–C_5H_4N)]^-$ **2** was isolated and structurally characterized from the reaction of $[Mn(CO)_5]^-$ and bis(2-pyridyl) disulfide [Scheme 1(d)]. In an effort to examine the reaction chemistry of the coordinatively-unsaturated complex $[Mn(CO)_3(NH,S–C_6H_4)]^-$, we report herein a study of the conversion of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ to five-coordinate, sixteen-electron $[Mn(CO)_3(S,S–C_6H_4)]^-$ **1**, stabilized by the bidentate S,S π-donation of the $[S,S–C_6H_4]^{2-}$ ligand. Unsaturated $[Mn(CO)_3(S,S–C_6H_4)]^-$ was also obtained from the reaction of 2 equiv. of 1,2-benzenedithiol with $[Mn(CO)_5]^-$. To our knowledge, only a few examples of d^6 transition metal carbonyl complexes containing five-coordinate sixteen-electron metal cores have been reported,[5,6] *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,[5a] and $[W(CO)_3(NHC_6H_4NH)]^{2-}$ prepared from $W(CO)_5(thf)$ and 2 equiv. of the monodeprotonated ligand $[NHC_6H_4NH_2]^-$ by intermolecular deprotonation.[6c]

Results and discussion

Synthesis

As illustrated in Scheme 2(a,b), treatment of 1 equiv. of $[N(PPh_3)_2][Mn(CO)_3(NH,S–C_6H_4)]$ with 1,2-benzenedithiol in



Scheme 2

thf led to the formation of the five-coordinate sixteen-electron manganese(I) complex $[N(PPh_3)_2][Mn(CO)_3(S,S–C_6H_4)]$ **1** stabilized by incorporation of the π-donating chelate $[S,S–C_6H_4]^{2-}$ and ejection of $HS-C_6H_4-NH_2$, identified by NMR. Alternatively, complex **1** was also obtained when 2 equiv. of 1,2-benzenedithiol was added to $[N(PPh_3)_2][Mn(CO)_5]$ and the solution was stirred overnight in thf at ambient temperature [Scheme 2(c)]. The dark red-purple complex **1** is soluble in common organic solvents, such as thf, MeCN and CH_2Cl_2, and can be crystallized by vapor diffusion of diethyl ether–hexane into a concentrated thf solution at −15 °C under nitrogen. No decomposition was observed on stirring complex **1** in thf solution at ambient temperature for 2 days. In contrast, protonation of complex **1** by 2-aminothiophenol was not successful in synthesising $[Mn(CO)_3(NH,S–C_6H_4)]^-$. The coordinatively-unsaturated complex **1** is completely unreactive toward CO: **1** remains unchanged when treated with 1 atm (101 325 Pa) CO in thf at room temperature. This is in contrast to the observation that catecholate tungsten(0) tricarbonyl and catecholate tungsten(0) tetracarbonyl are readily interconvertible.[6g] The six-coordinate Mn^I complex *fac*-$[N(PPh_3)_2][Mn(CO)_3(S–C_5H_4–N)(S–C_5H_4N)]$ **2**, with one anionic $[S–C_5H_4N]^-$ ligand bound to Mn^I in a monodentate (S-bonded) manner and the second $[S–C_5H_4–N]^-$ bound in a bidentate manner (S,N-bonded), was obtained from the reaction of $[Mn(CO)_5]^-$ and 1 equiv. of bis(2-pyridyl) disulfide [Scheme 2(d)]. The air-stable complex **2** was isolated as an orange–yellow semi-solid from thf–diethyl ether, and is soluble in thf, MeCN and CH_2Cl_2.

Characterization in solution

The IR spectrum of complex **1** shows two strong CO stretching bands, 1986vs and 1887s cm^{-1} (thf), which suggests facial orientation of the three CO ligands.[4] The ^1H and ^{13}C NMR spectra show the expected signals for the $[S,S–C_6H_4]^{2-}$ ligand in a diamagnetic d^6 Mn^I species. The electronic spectrum of complex **1** is dominated by ligand-to-metal charge-transfer bands at approximately 349, 400, 502 and 552 nm. Complex **2** exhibits a three-band pattern in the ν(CO) region of its IR spectrum, at 1994vs, 1901s and 1882s cm^{-1} (thf), which is consistent with a tricarbonyl derivative of pseudo C_{3v} symmetry.[7] The ^1H and ^{13}C NMR spectra are consistent with the presence of low-spin octahedrally coordinated d^6 Mn^I.

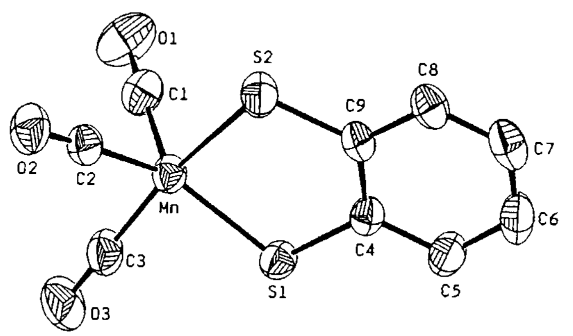


Fig. 1 ORTEP drawing and labeling scheme for anionic $[Mn(CO)_3(S,S–C_6H_4)]^-$ with thermal ellipsoids drawn at the 30% probability level.

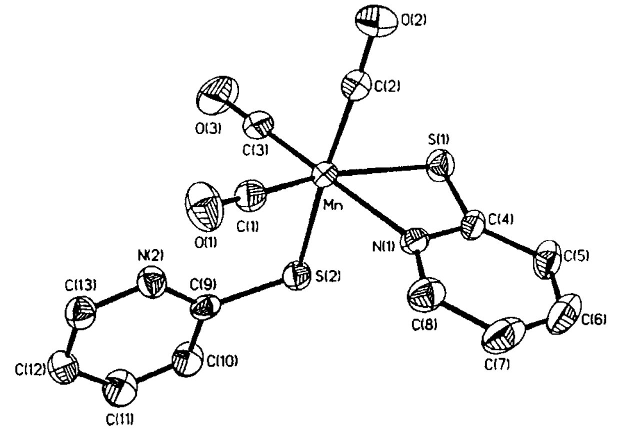


Fig. 2 ORTEP drawing and labeling scheme for anionic *fac*-$[Mn(CO)_3(S–C_5H_4–N)(S–C_5H_4N)]^-$ with thermal ellipsoids drawn at the 30% probability level.

Structures

A definitive assignment of the structure of complex **1** was obtained by X-ray crystallography; the structure of the $[Mn(CO)_3(S,S–C_6H_4)]^-$ unit in the $[N(PPh_3)_2]^+$ salt is shown in Fig. 1. The geometry about manganese is intermediate between square pyramidal and trigonal bipyramidal, with the bite angle of the chelating $[S–C_6H_4–S]^{2-}$ ligand being 87.81(4)°. The five-membered chelate ring MnS_2C_2 is almost planar, with a deviation from planarity of 0.02 Å. The interesting feature of complex **1** is the asymmetry in the Mn^I–S bond lengths (2.211(1) and 2.248(1) Å), which shows a difference of 0.036 Å. The significantly shorter Mn^I–S bonds [2.230(1) Å (average)] in complex **1**, as compared to the reported 2.398(1) Å for the Mn^I–SPh bond in *cis*-$[Mn(CO)_4(SPh)_2]^-$,[8] were attributed to the strong π-donating ability of the bidentate $[S,S–C_6H_4]^{2-}$ ligand which stabilizes the unsaturated complex **1**.[6,9] The Mn^I–S distances [2.230(1) Å (average)] in complex **1** are shorter than the reported 2.268(1) Å Mn^I–S bond in the analogue $[Mn(CO)_3(NH,S–C_6H_4)]^-$.[4] The Mn^I–CO bonds, which average 1.767(4) Å, in compound **1** are comparable to the Mn^I–CO distances [1.763(4) Å (average)] in $[Mn(CO)_3(NH,S–C_6H_4)]^-$.[4]

The X-ray crystal structure of complex **2** is shown in Fig. 2. The Mn^I–S distances of 2.380(1) and 2.445(1) Å in complex **2** are significantly longer than those in five-coordinate, coordinatively-unsaturated complex **1** [average 2.230(1) Å]. The Mn^I–N(1) bond distance is 2.028(3) Å, which is also significantly longer than that in $[Mn(CO)_3(NH,S–C_6H_4)]^-$ [1.889(3) Å].[4] The bond angles at the Mn^I center are considerably distorted from the idealized octahedral limits due to the presence of the four-membered N,S-chelate ring, a characteristic apparent in the internal chelate angle, S–Mn–N of 68.30(8)°.[10]

Discussion

A reasonable reaction sequence accounting for the formation of complex **1** is shown in Scheme 2(a,b). Protonation of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ with 1,2-benzenedithiol in thf under N_2 at ambient temperature led to formation of the unstable six-coordinate intermediate *fac*-$[Mn(CO)_3(S–C_6H_4SH)(NH_2,S–C_6H_4)]^-$. Attempts to detect this extremely unstable intermediate by FTIR were unsuccessful. Presumably, the intramolecular S–H···S interaction (*cis* arrangement of thiolate and SH groups in the intermediate),[11] and the subsequent elimination of 2-aminothiophenol yielded the stable five-coordinate, sixteen-electron complex **1**. Apparently, protonation of the amide site of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ labilizes the chelating ligand $[NH,S–C_6H_4]^{2-}$ and results in the formation of complex **1**. Alternatively, complex **1** was also obtained when 2 equiv. of 1,2-benzenedithiol were added to $[N(PPh_3)_2][Mn(CO)_5]$ and the solution was stirred overnight in thf at ambient temperature [Scheme 2(c)]. Presumably, oxidative addition of $H–SC_6H_4SH$ to $[Mn(CO)_5]^-$, leading to the intermediate $[Mn(CO)_4(H)(S–C_6H_4SH)]^-$, is followed by a Lewis acid–base reaction (the second equiv. of 1,2-benzenedithiol reacts with $[Mn(CO)_4(H)(S–C_6H_4SH)]^-$) with evolution of H_2 gas, identified by gas chromatography. Further intermolecular deprotonation of the $[S–C_6H_4SH]^-$ ligand bound to the Mn^I center by free anionic $[S–C_6H_4SH]^-$,[6d] and subsequent dissociation of a carbonyl ligand as a result of chelation led to formation of complex **1**.[6d,8] However, the presumed intermediate $[Mn(CO)_4(H)S–C_6H_4(SH)]^-$ was not observed spectroscopically, even at −20 °C.

In contrast, protonation of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ by 1,2-ethanedithiol in thf under N_2 at ambient temperature led to the formation of an orange–yellow solution immediately. A three-band pattern in the ν(CO) region of the IR spectrum at 1980vs, 1899s and 1885s cm^{-1} (thf) was assigned to the formation of six-coordinate *fac*-$[Mn(CO)_3(S–(CH_2)_2SH)(NH_2,S–C_6H_4)]^-$, isolated as a semi-solid. In order to add further credibility to the formation of the six-coordinate intemediate *fac*-$[Mn(CO)_3(S,NH_2–C_6H_4)(S–C_6H_4SH)]^-$ in the proposed mechanism [Scheme 2(a)] and of six-coordinate *fac*-$[Mn(CO)_3(S–(CH_2)_2SH)(NH_2,S–C_6H_4)]^-$ in the protonation reaction, the analogous six-coordinate Mn^I complex **2** was isolated and structually characterized from the reaction of $[Mn(CO)_5]^-$ and 1 equiv. of bis(2-pyridyl) disulfide [Scheme 2(d)]. The proposed mechanism, shown in Scheme 2(d), involves oxidative addition of bis(2-pyridyl) disulfide to $[Mn(CO)_5]^-$, possibly *via* the intermediate *cis*-$[Mn(CO)_4(S–C_5H_4N)_2]^-$.[2,8]

Ab initio calculations

In order to investigate the conversion of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ to complex **1** [Scheme 2(a,b)], *ab initio* quantum chemistry computations were also performed. The Gaussian 94 suite of programs were used.[12] The geometries of the four species, $[Mn(CO)_3(NH,S–C_6H_4)]^-$, $[SH–C_6H_4–SH]$, complex **1** and $[NH_2–C_6H_4–SH]$ were fully optimized, firstly at the Hartree–Fock level where a 6-311G basis set for Mn and a 6-31G basis set (set 1) for other atoms were used. The frequency analyses on the optimized structures were performed at this level of theory. All four molecules were identified as genuine minima, the vibrational frequencies (scaled by 0.89) were later used in calculating thermal corrections to the reaction energetics (298 K). The structures were then further optimized at the MP2 level of theory. Selected geometrical parameters of complex **1** are compared with those obtained from X-ray diffraction data (Table 1). The bond distances and bond angles predicted at the MP2 level of theory compare reasonably well with the experimental results. One exception is the predicted bond angle S(1)–Mn–C(1), which differs from the experimental value by more than 10°. A possible explanation for such a deviation is that the prediction is based on gas-phase molecules, while the experimental structures were determined using crystals. Computations revealed that the energy surface is relatively insensitive to the orientation of the $S,S–C_6H_4$ ring. Basis set truncation and correlated level of theory applied could also affect the prediction.

Table 1 Selected bond distances (Å) and angles (°) for (a) **1**[a] and (b) **2** determined *via* X-ray diffraction

(a) Complex **1**

Mn–S(1)	2.211(1) [2.217]	Mn–S(2)	2.248(1) [2.260]
Mn–C(1)	1.750(4) [1.670]	Mn–C(2)	1.781(3) [1.688]
Mn–C(3)	1.770(3) [1.670]	C(1)–O(1)	1.157(4) [1.220]
C(2)–O(2)	1.154(4) [1.221]	C(3)–O(3)	1.159(4) [1.234]
S(1)–Mn–S(2)	87.81(4) [89.2]	S(1)–Mn–C(1)	117.96(11) [130.4]
S(1)–Mn–C(2)	149.67(11) [144.6]	S(1)–Mn–C(3)	86.34(11) [87.9]
S(2)–Mn–C(1)	98.57(12) [92.5]	S(2)–Mn–C(2)	88.76(10) [94.2]
S(2)–Mn–C(3)	170.02(12) [177.1]	C(1)–Mn–C(2)	92.35 (15) [84.8]
C(1)–Mn–C(3)	91.31(16) [89.7]	C(2)–Mn–C(3)	92.21(15) [88.0]
Mn–S(1)–C(4)	107.01(8) [107.5]	Mn–S(2)–C(9)	106.28(11) [106.6]

(b) Complex **2**

Mn–S(1)	2.445(1)	Mn–S(2)	2.380(1)
Mn–C(1)	1.790(4)	Mn–C(2)	1.773(4)
Mn–C(3)	1.775(4)	C(1)–O(1)	1.152(4)
C(2)–O(2)	1.165(4)	C(3)–O(3)	1.160(4)
Mn–N(1)	2.028(3)		
S(1)–Mn–S(2)	84.84(4)	S(1)–Mn–C(1)	163.17(12)
S(1)–Mn–C(2)	87.06(11)	S(1)–Mn–C(3)	103.47(13)
S(1)–Mn–N(1)	68.30(8)	S(2)–Mn–C(1)	97.86(11)
S(2)–Mn–C(2)	170.76(12)	S(2)–Mn–C(3)	86.07(12)
S(2)–Mn–N(1)	87.62(7)	N(1)–Mn–C(1)	95.13(14)
N(1)–Mn–C(2)	93.51(13)	N(1)–Mn–C(3)	170.08(14)
Mn–S(1)–C(4)	77.74(11)	Mn–S(2)–C(9)	113.74(12)

[a] Numbers in brackets are geometrical parameters predicted at the MP2/set 1 level of theory.

Table 2 Predicted reaction enthalpy for the conversion of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ to complex **1**

Method[a]	ΔE	ΔH(0 K)	ΔH(298 K)
HF/set 1// HF/set 1	−38.2	−35.6	−36.1
MP2/set 1// MP2/set 1	−14.5	−11.9	−12.3
MP2/set 2// MP2/set 1	−14.2	−11.6	−12.1

[a] Set 1: 6-311G on Mn, 6-31G on H, C, N, O, S; set 2: 6-311G* on Mn, 6-31G* on C, N, O, S.

Energetics were evaluated using the MP2 method with extra polarization functions on each atom (6-311G* on Mn, and 6-31G* on other atoms, named set 2). The theoretical predictions for the energetics of reaction are summarized in Table 2. Significant electron correlation effects have been observed for the reaction enthalpy: the magnitude of the reaction energy and enthalpy (ΔE and ΔH) is reduced by more than 20 kcal mol^{-1} at the correlated MP2 level. Introducing zero-point vibrational energy corrections (from the HF method) reduces the energy difference by another 2.6 kcal mol^{-1}, while adding the temperature correction raises this difference by about 0.5 kcal mol^{-1}. The effect of adding an extra set of polarization functions to the heavy atoms is minor. The reaction enthalpy (ΔH) for the conversion of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ to complex **1** [Scheme 2(a,b)] is −12.1 kcal mol^{-1} at 298 K. This result is supportive of the observation that the chemical conversion is not reversible experimentally.

The calculated Mulliken charge distributions on the N, S and Mn atoms of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ are −1.14, −0.43 and 1.14 respectively. The charge distribution on Mn of complex **1**

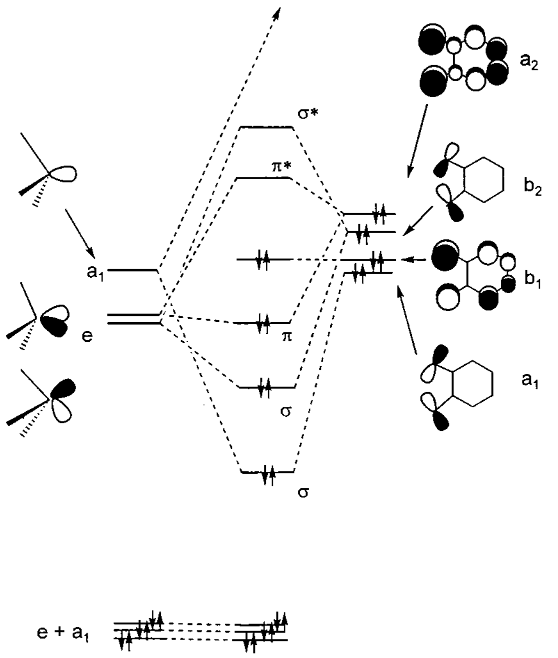


Fig. 3 Frontier molecular orbital (MO) analysis for $[N(PPh_3)_2][Mn(CO)_3(S,S–C_6H_4)]$.

is 1.02. Thus both $[Mn(CO)_3(NH,S–C_6H_4)]^-$ and complex **1** can be accurately described as Mn^I complexes.

Attempts to compute the energies of the species using density functional theory (DFT) were made. However, serious convergence difficulties were encountered while trying to evaluate these energies. All attempts to overcome these were unsuccessful.

A qualitative analysis using the frontier molecular orbitals (MOs) of complex **1** is illustrated in Fig. 3. The $[Mn(CO)_3]^+$ fragment was kept within the C_{3v} point group, while the $[S,S–C_6H_4]^{2-}$ anionic precursor has C_{2v} symmetry. The model complex has C_s symmetry despite the optimized structure being slightly distorted from C_s. Three unoccupied MOs (a_1 and e) of the $[Mn(CO)_3]^+$ fragment interact with the three highest occupied $[S,S–C_6H_4]^{2-}$ MOs having proper symmetry (a_1, b_2 and a_2). Two of these interactions form σ bonds, and one interaction results in a π bond. The b_1 MO in $[S,S–C_6H_4]^{2-}$ is nonbonding. The stability of complex **1** is attributed to these three MO interactions.

Summary

Protonation of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ by 1,2-benzenedithiol and 1,2-ethanedithiol yielded complex **1** and *fac*-$[Mn(CO)_3(S–(CH_2)_2SH)(NH_2,S–C_6H_4)]^-$ respectively. The calculated Mulliken atomic charge distribution in the complex $[Mn(CO)_3(NH,S–C_6H_4)]^-$ supports the hypothesis that the reactions of $[Mn(CO)_3(NH,S–C_6H_4)]^-$ with electrophiles (1,2-benzenedithiol, 1,2-ethanedithiol) occur at the more electron-rich amide site to yield charge-controlled, collision complexes. In contrast, reaction of bis(2-pyridyl) disulfide and $[N(PPh_3)_2][Mn(CO)_5]$ afforded the hexacoordinate complex **2**. The Mn^I–S bond angles, and carbonyl stretching frequencies (ν(CO) 1986vs and 1887s cm^{-1} (thf) for complex **1** *vs.* 1973vs and 1870s cm^{-1} (thf) for $[Mn(CO)_3(NH,S–C_6H_4)]^-$) of complexes **1** and $[Mn(CO)_3(NH,S–C_6H_4)]^-$ unequivocally indicate that the relative π-donating ability of the bidentate ligands investigated here is $[NH,S–C_6H_4]^{2-} > [S,S–C_6H_4]^{2-}$.[13] The existence of two σ and one π bond between the $[Mn(CO)_3]^+$ and $[S,S–C_6H_4]^{2-}$ fragments, based on qualitative frontier molecular orbital analysis, also indicates that one lone-pair of electrons is delocalized around the sulfur–manganese–sulfur chelate stabilizing the five-coordinate complex **1**, *i.e.* the additional donation of charge from $[S,S–C_6H_4]^{2-}$ effectively means that there are more than 16 electrons around Mn^I (the total electron count around Mn^I amounts to 18 electrons instead of 16 electrons), and this explains the unusual stability of complex **1**. The hexacoordinate metal centre as well as the long Mn^I–S and Mn^I–N bond distances of complex **2**, compared to the five-coordinate complexes **1** and $[Mn(CO)_3(NH,S–C_6H_4)]^-$, reflect the fact that bidentate $[S–C_5H_4N]^-$ may not serve as a strong π-donating ligand.

Experimental

Manipulations, reactions and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glove-box (argon gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH_2; acetonitrile from $CaH_2–P_2O_5$; methylene chloride from P_2O_5; hexane and tetrahydrofuran (thf) from sodium–benzophenone) 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, 1,2-benzenedithiol, bis(2-pyridyl) disulfide, bis(triphenylphosphoranylidene)ammonium chloride, 1,2-ethanedithiol (Lancaster/Aldrich) were used as received. Infrared spectra were recorded on a Bio-Rad FTS-185 spectrometer with sealed solution cells (0.1 mm) and KBr windows. NMR spectra were recorded on a Bruker AC 200 spectrometer; ^1H and ^{13}C chemical shifts being relative to tetramethylsilane. UV/VIS spectra were taken on a GBC 918 spectrophotometer. Gas chromatography was carried out on a Shimadzu GC-3BT with a Shimadzu R-11 recorder. Analyses made use of the thermal conductivity detector (TCD); nitrogen was the carrier gas, the column was OV-17 (5%) on Chromosorb W, 80/100 mesh, 6 ft × 1/8 in stainless steel tubing. Analyses of carbon, hydrogen and nitrogen contents were obtained with a Heraeus CHN analyzer.

Preparations

Reaction of 1,2-benzenedithiol and $[N(PPh_3)_2][Mn(CO)_3(NH,S–C_6H_4)]$. Initially, 1,2-benzenedithiol (0.2 mmol, 24 μL) was added dropwise to a solution containing 0.16 g (0.2 mmol) of $[N(PPh_3)_2][Mn(CO)_3(NH,S–C_6H_4)]$ in thf (5 cm^3).[4] After stirring the reaction solution for 30 min at room temperature, diethyl ether was added to precipitate the dark red-purple solid $[N(PPh_3)_2][Mn(CO)_3(S,S–C_6H_4)]$ **1**. The stable product **1** was washed twice with thf–diethyl ether and dried under vacuum. Crystals suitable for X-ray crystallography were grown by vapor diffusion of diethyl ether into a concentrated thf solution of **1** at −15 °C. Yield 0.151 g (92%). IR (thf): ν(CO) 1986vs, 1887s cm^{-1}. ^1H NMR (CD_3CN): δ 6.99, 7.89 (br, $S,S–C_6H_4$). ^{13}C NMR (CD_3CN): δ 134.49, 133.27, 133.15, 133.03, 130.40, 130.23 and 130.14. UV/VIS (thf): λ_{max}/nm ($\varepsilon/M^{-1}\ cm^{-1}$) 349(2079), 400(4569), 502(2109) and 552(1556). Found: N, 1.83; C, 66.17; H, 4.27. Calc. for $C_{45}H_{34}O_3P_2NS_2Mn$: N, 1.75; C, 66.13; H, 4.16%).

Reaction of 1,2-benzenedithiol and $[N(PPh_3)_2][Mn(CO)_5]$. $[N(PPh_3)_2][Mn(CO)_5]$[14] (0.2 mmol, 0.147 g) dissolved in thf (3 cm^3) was stirred under N_2 and 1,2-benzenedithiol (0.4 mmol, 48 μL) added dropwise at room temperature. After stirring overnight, the volume of the solution was reduced to 2 cm^3 and the dark red-purple product precipitated by addition of diethyl ether (15 cm^3). The thermally stable product was isolated by removing the solvent. Yield of $[N(PPh_3)_2][Mn(CO)_3(S,S–C_6H_4)]$ (**1**) 0.130 g (80%). IR (thf): ν(CO) 1986vs, 1887s cm^{-1}, consistent with the formation of $[N(PPh_3)_2][Mn(CO)_3(S,S–C_6H_4)]$.

***fac*-$[N(PPh_3)_2][Mn(CO)_3(S–(CH_2)_2SH)(NH_2,S–C_6H_4)]$.** 1,2-Ethanedithiol (0.2 mmol, 18 μL) was added dropwise to a solution containing 0.16 g (0.2 mmol) of [N(PPh$_3$)$_2$][Mn(CO)$_3$(NH,S–C$_6$H$_4$)] in thf (3 cm^3). The reaction mixture was stirred for 10 min at ambient temperature and hexane added to precipitate the yellow-brown semi-solid (76% yield). The product was washed with hexane twice and dried under vacuum. IR (thf): ν(CO) 1980vs, 1899s, 1885s cm^{-1}. ^{1}H NMR (C$_4$D$_8$O): δ 4.78 (br, NH$_2$), 3.03–2.75 (m, SCH$_2$CH$_2$), 2.25 (s, SH), 6.68, 6.45 (m, C$_6$H$_4$).

***fac*-[N(PPh$_3$)$_2$][Mn(CO)$_3$(S–C$_5$H$_4$–N)(S–C$_5$H$_4$N)] 2.** Bis(2-pyridyl) disulfide (0.4 mmol, 0.088 g) was added to a solution containing 0.308 g (0.4 mmol) of [N(PPh$_3$)$_2$][Mn(CO)$_5$] in tetrahydrofuran (5 cm^3). After stirring the reaction mixture overnight at room temperature, diethyl ether was added to precipitate the orange-yellow semi-solid *fac*-[N(PPh$_3$)$_2$][Mn(CO)$_3$(S–C$_5$H$_4$–N)(S–C$_5$H$_4$N)] **2**. The stable product **2** was washed twice with thf–diethyl ether and dried under vacuum. Crystals suitable for X-ray crystallography were grown by vapor diffusion of diethyl ether into a concentrated thf solution of **2** at −15 °C. Yield 0.320 g (89%). IR (thf): ν(CO) 1994vs, 1901s, 1882s cm^{-1}. ^{1}H NMR (CD$_3$COCD$_3$): δ 8.05, 7.88, 7.29, 7.11 (d, SC$_5$H$_4$N), 7.01, 6.55, 6.49 (t, SC$_5$H$_4$N) and 7.72–7.58 (m, Ph). ^{13}C NMR (CD$_3$COCD$_3$): δ 114.68, 115.55, 127.13, 129.27, 130.25, 130.39, 130.52, 133.12, 133.23, 133.35, 133.90, 134.59, 148.22 and 151.21. UV/VIS (thf): λ_{max}/nm (ε/M^{-1} cm^{-1}) 384(4599). Found: N, 4.76; C, 65.39; H, 4.20. Calc. for C$_{49}$H$_{38}$O$_3$P$_2$N$_3$S$_2$Mn: N, 4.68; C, 65.55; H, 4.27%).

Ab initio calculations

The Gaussian 94 suite of programs[12] was used in the study of several complexes. The geometries of these species were fully optimized using analytic gradients at the Hartree–Fock (HF) and MP2 levels of theory. At the stationary points, vibrational frequency analysis was performed. The computed vibrational frequencies were used to verify whether these structures are genuine minima on the potential energy surfaces. These frequencies were also used in calculating thermal corrections to enthalpies (up to 298 K). The 6-311G basis set on Mn, and the 6-31G basis sets on other atoms were used in geometry optimizations (set 1). An extra set of polarization functions were added to atoms other than hydrogen (6-311G* on Mn and 6-31G* on C, N, O, and S, named set 2) for the most elaborate energy calculations using MP2.

Crystallography

Crystallographic data for complexes **1** and **2** are collected in Table 3. The crystals of **1** and **2** chosen for the X-ray diffraction studies measured 0.55 × 0.50 × 0.45 mm and 0.23 × 0.20 × 0.15 mm, respectively. Each crystal was mounted on a glass fiber and quickly coated in epoxy resin. Unit-cell parameters for complex **1** were obtained by least-squares refinement from 25 reflections with 2θ between 19.00 and 28.82°. Least-squares refinement of the positional and anisotropic thermal parameters for all non-hydrogen and fixed hydrogen atom contributions was based on F. Diffraction measurements were carried out on a Nonius CAD 4 diffractometer with graphite-monochromated Mo-Kα radiation employing the $\theta/2\theta$ scan mode.[15] A φ scan absorption correction was made. The NRCC-SDP-VAX package of structure solution programs was employed[16] and atomic scattering factors were obtained from ref. 17. Diffraction measurements for complex **2** were carried out at 22 °C on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ 0.7107 Å) and θ between 1.38 and 25.00°. Least-squares refinement of the positional and anisotropic thermal parameters for all non-hydrogen and fixed hydrogen atom contributions was based on F^2. A SADABS[18] absorption correction was made. The SHELXTL[19] structure refinement program was employed. Selected bond distances and angles are listed in Table 1.

Table 3 Crystallographic data for complexes **1** and **2**

	1	**2**
Formula	C$_{45}$H$_{34}$NO$_3$P$_2$S$_2$Mn	C$_{49}$H$_{38}$N$_3$O$_3$P$_2$S$_2$Mn
M	817.77	897.82
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	10.030(3)	14.7936(2)
b/Å	14.259(2)	10.2732(2)
c/Å	14.396(3)	29.6377(2)
α/°	88.62(2)	
β/°	80.50(2)	92.567(1)
γ/°	89.76(2)	
V/Å^3	2030.1(8)	4499.75(11)
Z	2	4
d_{calc}/g cm^{-3}	1.338	1.325
μ/cm^{-1}	5.273	5.02
T/°C	25	22
R	0.036[a]	0.051
R_w	0.034[b]	
R_{WF^2}		0.095[c]
GOF	1.56	1.044

[a] $R = \Sigma|(F_o - F_c)|/\Sigma F_o$; [b] $R_w = [\Sigma\omega(F_o - F_c)^2/\Sigma\omega F_o^2]^{\frac{1}{2}}$; [c] $R_{WF^2} = \{\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma[\omega(F_o^2)^2]\}^{\frac{1}{2}}$.

CCDC reference number 186/1463.

See http://www.rsc.org/suppdata/dt/1999/2393/ for crystallographic files in .cif format.

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