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SYNTHESIS AND REACTIVITY OF BRIDGING THIOLATO-MANGANESE CARBONYL COMPLEXES, $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$

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Summary

The yellow-orange complexes $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ (R = Ph, Me, Bu^t) have been prepared by several routes, including: (1) reactions of $Et_4N[MnBr_2(CO)_4]$ with Bu_3SnSR; (2) reactions of $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ with either Bu_3SnSR, RSH, or NaSPh; and (3) reactions of $Mn_2(\mu\text{-}X)_2(CO)_8$ (X = Br, SPh) with NaSPh, followed by metathesis using $[Et_4N]Cl$. The complex $Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$ can be converted to $Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$ by reaction with PhSH in the presence of either a base (pyridine) or an acid (CF_3CO_2H or CH_3CO_2H). These bridging thiolate complexes, $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$, undergo reactions with $[Me_3O]BF_4$ (or other electrophilic reagents) to give $[Mn(CO)_3(\mu\text{-}SR)]_4$; if the same reactions are carried out in the presence of CO, $Mn_2(\mu\text{-}SR)_2(CO)_8$ is the product. Similarly, reactions of $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ with $[Me_3O]BF_4$ in the presence of a phosphine (PMe_3, dppm) produce the phosphine substituted species, *cis*-$Mn_2(\mu\text{-}SR)_2(CO)_6(PMe_3)_2$ and $Mn_2(\mu\text{-}SR)_2(CO)_6(\mu\text{-}dppm)$; the former is converted upon heating to the known species $Mn_2(\mu\text{-}SR)_2(\mu\text{-}CO)(CO)_4(PMe_3)_2$.

A survey of organothiolate derivatives of manganese carbonyl reveals that most attention has been accorded to three groups of compounds: $Mn(SR)(CO)_5$, $Mn_2(\mu\text{-}SR)_2(CO)_8$, and $[Mn(\mu\text{-}SR)(CO)_3]_4$ [1]. Conspicuously absent are several groups of anionic complexes including those having the formula $[Mn_2(\mu\text{-}SR)_3(CO)_6]^-$, the subject of this paper, where we describe the preparation of several of these complexes, isolated as tetraethylammonium salts. We have also reported reactions of these species with various electrophilic reagents in the presence and absence of molecules capable of acting as ligands, and contrasted the chemical behavior of these complexes, with that of the structurally similar compounds $Et_4N[Mn_2(\mu\text{-}X)_3(CO)_6]$, (X = Cl, Br) [2,3].

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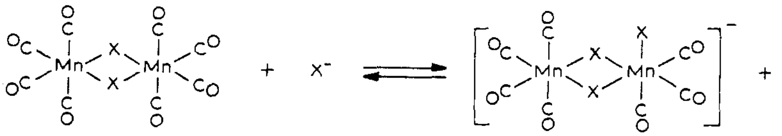
Discussion

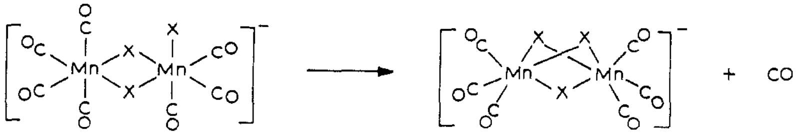
Anionic complexes of the formula $[Mn_2(\mu\text{-}X)_3(CO)_6]^-$ ($X = Cl$, Br), having structures similar to the compounds prepared in this study, have been known for some time. First prepared inadvertently in low yield by photolysis of $[Et_4N]Cl$ and $Mn_2(CO)_{10}$ [2], these compounds are best obtained by reactions of $MnX(CO)_5$ and $[Et_4N]X$ in a 2/1 molar ratio in $CHCl_3$ at reflux [3]. Analogous halorhenium complexes have also been characterized [4,5] as have the isoelectronic species $[M_2(\mu\text{-}X)_3(CO)_6]^{3-}$ ($M = Cr$, Mo, W; $X = F$, Cl, Br, I) [6,7]. Two related complexes with bridging thiolate groups are known. The first is $[Fe_2(\mu\text{-}SMe)_3(CO)_6]BF_4$, prepared first by oxidation of $Fe_2(\mu\text{-}SMe)_2(CO)_6$ [8] and more recently prepared in our laboratories from this precursor and $[Me_2SSMe]BF_4$ [9]. The second is the species $[Ru_2(\mu\text{-}SEt)_3(\eta\text{-}C_6H_6)_2]BPh_4$, recently reported in this journal [10].

Since numerous analogues are known, it seemed likely that the compounds $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ would exist as stable species if a route for their synthesis could be found. In fact, such syntheses proved to be no problem; virtually every logical reaction appears to lead to these compounds. We have reported six different reactions for the preparation of these compounds in this paper. Three involve exchange of bromide ion in $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ using different thiolate reagents including mercaptans (PhSH and Bu^tSH), benzenethiolate ion (PhS^-), and the organotin derivatives Bu^n_3SnSR ($R = Ph$, Bu^t, Me). Organotin reagents have been used in previous instances for the conversion of $MnX(CO)_5$ to $Mn_2(\mu\text{-}SR)_2(CO)_8$ and $[Mn(\mu\text{-}SR)(CO)_3]_4$ [11,12,13]. We have also prepared the title compounds from the reactions of $Et_4N[MnBr_2(CO)_4]$ with Bu_3SnSR ($R = Ph$, Bu^t) and from reactions between $Mn_2(\mu\text{-}X)_2(CO)_8$ ($X = Br$, SPh) and NaSPh, the tetraethylammonium salt being formed subsequently by metathesis with $[Et_4N]Cl$. Given their availability, the organotin thiolate reagents are probably the simplest to use for these syntheses and provide the best yields of products, usually greater than 90%. However none of the other procedures is particularly complicated. The rather straightforward synthesis of these species accords with our initial assessment concerning their stable existence.

Minimal discussion on the mechanism of formation of the halide bridged species $[Mn_2(\mu\text{-}X)_3(CO)_6]^-$ has appeared. There is evidence that the mononuclear species $[MnX_2(CO)_4]^-$ are present in reactions of $MnX(CO)_5$ with $[Et_4N]X$ and the intermediacy of these complexes in these syntheses has been suggested [3]. This may be so, but the observation of such species in the reaction probably misdirects attention from key steps which occur subsequently. We suggest that the two reactions show in eq. 1 and 2 may also be significant steps.



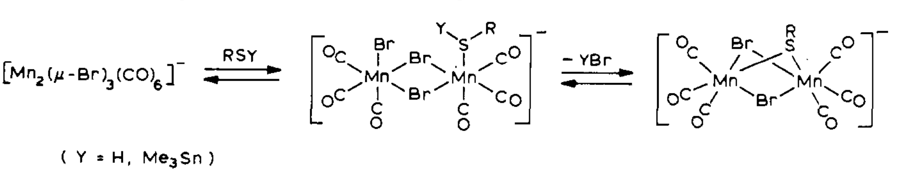
(1)



(2)

The important intermediates in these reactions are the dimeric species $Mn_2(\mu\text{-}X)_2(CO)_8$ (X = Br, Cl, SR). The halide bridged dimeric species are known to be easily formed from $MnX(CO)_5$ [14] and also from $[MnX_2(CO)_4]^-$ [15]. Once formed they could enter the sequence shown above. Initial reaction of $Mn_2(\mu\text{-}X)_2(CO)_8$ with X^-, as given in eq. 1, is suggested to produce the complex $[Mn_2X(\mu\text{-}X)_2(CO)_7]^-$. These species have not previously been reported; however, related complexes are known in the case of rhenium [16]. Subsequent loss of CO and conversion of the X^- group in a bridging ligand gives the product.

Most of the syntheses reported here may be understood in terms of either these reactions or similar reactions in which ligands other than CO are involved (L replacing the X^- group in reaction 1, or in place of CO in the reverse reaction in eq. 2). For example, conversion of $[Mn_2(\mu\text{-}Br)_3(CO)_6]^-$ to $[Mn_2(\mu\text{-}SR)_3(CO)_6]^-$ could occur by initial coordination via a sulfur lone pair of Me_3SnSR or RSH to $[Mn_2(\mu\text{-}Br)_3(CO)_6]^-$, breaking one of the bridging groups (the reverse of reaction 2), followed by elimination of Br^-, HBr, or Me_3SnBr and reformation of a triply-bridged species (eq. 3). A similar process could occur using PhS^-, with initial coordination of this reagent followed by elimination of Br^-. Repeated three times, this would effect complete conversion of $[Mn_2(\mu\text{-}Br)_3(CO)_6]^-$ to the corresponding thiolate complex.



(3)

This proposed mechanism suggests that one ought to be able to obtain the complexes $Et_4N[Mn_2(\mu\text{-}X)_2(\mu\text{-}Y)(CO)_6]$, ($X \neq Y$), by appropriate choice of reaction conditions. We have not yet isolated such species pure although one example has been detected in an instance described below. Failure to isolate these intermediates must be a consequence of the relative rates of each step. Studies on this problem are continuing.

A very slow reaction occurs between $Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$ and excess (11/1 mole ratio) PhSH in acetone at reflux to produce $Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$. The infrared spectrum was monitored to follow the progress of the reaction; the $\nu(CO)$ values of starting material (1975s, 1885vs, br) and product (1997s, 1910s, br) are clearly distinguishable. In the course of this reaction a sharp $\nu(CO)$ absorption at an intermediate value (1985 cm^{-1}) is also seen; presumably this is due to an intermediate species $Et_4N[Mn_2(\mu\text{-}SBu^t)_n(\mu\text{-}SPh)_{3-n}(CO)_6]$, with $n = 1$ or 2. After 7 days approximately 33% of the starting material had reacted to give the final product plus a small amount of the intermediate. We believe that this reaction will eventually reach completion, since catalyzed reactions do so (vide infra). The reverse reaction, between $Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$ and Bu^tSH, does not occur in the presence or absence of a catalyst. Apparently there is a thermodynamic preference in the $[Mn_2(\mu\text{-}X)_3(CO)_6]^-$ series in the order PhS > Bu^tS > Br as bridging groups in these complexes.

The reaction between $Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$ and PhSH is more rapid when a base (pyridine) is added to the system. The room temperature reaction, using an excess of pyridine, reaches completion in 3 days. Addition of pyridine may serve simply to generate some PhS^- which is a more nucleophilic reagent than PhSH. Alternatively, it may be that pyridine adds reversibly to $Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$ converting a bridging -SBu^t group to a terminal ligand and facilitating its exchange. Such a reaction has an analogy in the chemistry of $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ which has been shown to react with bases (pyridine, PMe_3) with cleavage of the bridging groups (vide infra). It should be noted, however, that the same reactions with $Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$ must be energetically unfavorable since no cleavage products are detectable in reactions of these species over prolonged periods of time.

Catalysis of the exchange reaction by acids (CH_3CO_2H or CF_3CO_2H) is rather more spectacular, complete conversion to product occuring in 15 min, room temperature (1.0 equiv. acid). Initial protonation at the sulfur of the bridging thiolate group to give an intermediate complex with a bridging mercaptan ligand is proposed. This ligand should be easily displaced by other ligands including PhSH; loss of a proton and reformation of the thiolate bridging linkage accomplishes the net exchange of PhS^- for Bu^tS^-.

We have extended this study to reactions in which other ligands are involved, and have also experimented with other electrophilic reagents such as $[Me_3O]BF_4$. If $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ complexes are treated with a stoichiometric quantity of $[Me_3O]BF_4$ in the presence of CO, there is rapid and complete conversion to $Mn_2(\mu\text{-}SR)_2(CO)_8$ and RSMe. In the absence of added CO, the tetramers $[Mn(\mu\text{-}SR)(CO)_3]_4$ are formed. Addition of $Ph_2PCH_2PPh_2$ (dppm) and acid to $Et_4[Mn_2(\mu\text{-}SR)_3(CO)_6]$ complexes give $Mn_2(\mu\text{-}SR)_2(CO)_6$(dppm) while similar reactions using PMe_3 give *cis*-$Mn_2(\mu\text{-}SR)_2(CO)_6(PMe_3)_2$. Several complexes having the formula *cis*-$Mn_2(\mu\text{-}SR)_2(CO)_6(PMe_3)_2$ ($R = Me$, H, $SnMe_3$) have been reported previously [17], although a different synthetic route was involved in this earlier work. There is also mention of an isomer with *trans*-phosphines (*trans*-$Mn_2(\mu\text{-}SR)_2(CO)_6(PPh_3)_2$; R = Me, *p*-tol[18]) but this formulation may be suspect. The ν(CO) data on these species are quite similar to data on the complexes $Mn_2(\mu\text{-}SR)_2(\mu\text{-}CO)(CO)_4(PMe_3)_2$, which are readily obtained by heating *cis*-$Mn_2(\mu\text{-}SR)_2(CO)_6(PMe_3)_2$.

We have also demonstrated that similar reactions occur using $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$. Electrophilic reagents like Ag^+ or $[Me_3O]^+$ react with this species in the presence of CO to give first $Mn_2(\mu\text{-}Br)_2(CO)_8$ and then $MnBr(CO)_5$. As in reactions of the thiolate species, addition of the electrophile to the bridging halide ion is presumed to be the initial step in this sequence. The new bridging group (either MeBr or AgBr) is then readily lost, with addition of CO to the coordinately unsaturated intermediate giving the observed product.

Bases such as PMe_3 and pyridine (but not CO) react directly with $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$, forming $MnBr(CO)_3(L)_2$ ($L = PMe_3$, py) complexes in good yield. The formation of these products contrasts to the inertness of the related thiolate complexes, $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ toward these ligands. This result emphasizes the lower stability of the bridging halide functionality relative to bridging thiolate groups in this type of system.

Experimental

Preparations of $Mn_2(\mu\text{-}Br)_2(CO)_8$, [19], $Mn_2(\mu\text{-}SR)_2(CO)_8$ ($R = Me$, Bu^t, Ph) [12], $Et_4N[MnBr_2(CO)_4]$ [20], $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ [3], and Bu_3SnSR ($R = Me$,

Bu^t, Ph) [21] were carried out according to literature directions. Other compounds were commercial samples. Solvents were dried before use. All manipulations were carried out under N_2 as a precautionary measure.

Infrared data were obtained using a Beckman 4230 spectrometer. ^1H NMR spectra were recorded on an IBM-WP-200 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ *complexes (R = Ph,* Bu^t*, Me)*

A. From $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ *and* Bu_3SnSR. Typically, a solution of $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ (1.60 g, 2.5 mmol) and 10.0 mmol of the tin compound in 50 ml methanol was heated at reflux for 1 h. After cooling, the solvent volume was reduced to about 10 ml; the product precipitated as an orange powder upon standing at −20°C. This solid was filtered, dried and recrystallized from CH_2Cl_2/Et_2O.

$Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$: 92%, m.p. 192°C. Anal. Found: C, 52.52; H, 4.77; S, 13.27. $C_{32}H_{35}NO_6S_3Mn_2$ calcd.: C, 52.24; H, 4.80; S, 13.07%. IR (CH_2Cl_2): ν(CO) 1997s, 1918s, 1908sh cm^{-1}. ^1H NMR (acetone-d_6): 1.32t (int. 12); 3.40q (int. 8); 7.19m, 8.05m (int. 15) ppm.

$Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$: 91%; m.p. > 250°C decomp. Anal. Found: C, 46.34; H, 6.91; S, 14.35. $C_{26}H_{47}NO_6S_3Mn_2$ calcd.: C, 46.08; H, 6.99; S, 14.19%. IR (CH_2Cl_2): ν(CO) 1975s, 1885vs,br. ^1H NMR (acetone-d_6): 1.35 t (int., 12), 1.47s (int. 27); 3.50q (int. 8) ppm.

$Et_4N[Mn_2(\mu\text{-}SMe)_3(CO)_6]$: 65%; m.p. 175°C decomp. Anal. Found: C, 36.89; H, 5.25; S, 17.74. $C_{17}H_{29}NO_6S_3Mn_2$ calcd.: C, 37.16; H, 5.32; S, 17.51%. IR (CH_2Cl): ν(CO) 1982s, 1890vs,br. ^1H NMR (CD_2Cl_2): 1.38t (int. 12); 2.30s,br (int. 9); 3.28q (int. 8) ppm.

B. From $Et_4N[MnBr_2(CO)_4]$ *and* Bu_3SnSR. A solution containing 2.9 g (4.4 mmol) of $Et_4N[MnBr_2(CO)_4]$ and 8.8 mmol of Bu_3SnSR in 80 ml methanol was heated at reflux for 1 h. After cooling, the reaction mixture was processed as described above. Isolated yields of $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$: R = Ph, 87%; R = Bu^t, 83%; R = Me, 50%.

C. From $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ *and RSH (R = Ph,* Bu^t*).* A ten-fold excess of the appropriate thiol (5 mmol) was added to a solution of 0.32 g (0.50 mmol) of $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ in 50 ml methanol. The solution was heated at reflux (R = Ph, 0.5 h; R = Bu^t, 2.0 h), and then cooled. Saturated aqueous $NaHCO_3$ (~ 1 ml) was added to neutralize HBr present; after mixing for several minutes the solution was filtered and then evaporated under vacuum. The sticky residue (which contained some H_2O) was extracted with CH_2Cl_2, and this solution was dried over $MgSO_4$. Evaporation under vacuum left an orange solid which was crystallized from CH_2Cl_2/Et_2O. Isolated yields of $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$: R = Ph, 70%; R = Bu^t, 63%.

D. From $Mn_2(\mu\text{-}Br)_2(CO)_8$ *and NaSPh.* A solution containing 0.12 g (0.25 mmol) of $Mn_2(\mu\text{-}Br)_2(CO)_8$ and 0.26 g (2.0 mmol) NaSPh in 50 ml methanol was heated at reflux for 2 h. After cooling, 1.0 g $[Et_4N]Cl$ was added. The product, $Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$, precipitated immediately. It was filtered, dried, and recrystallized from CH_2Cl_2/Et_2O; 49% yield.

E. From $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ *and NaSR (R = Ph,* Bu^t*).* A mixture of $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ (0.16 g, 0.25 mmol) and NaSPh (0.26 g, 2.0 mmol) in 50 ml methanol was heated for 1 h. After cooling, 1.0 g $[Et_4N]Cl$ was added. Evaporation of the solvent left an orange solid, which was extracted into CH_2Cl_2. This solution was extracted with several ml H_2O and dried over $MgSO_4$. Addition of Et_2O to the dry CH_2Cl_2 solution caused precipitation of the product. Isolated yields of $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$: R = Ph, 52%: R = Bu^t, 44%.

F. From $Mn_2(\mu\text{-}SPh)_2(CO)_8$ and NaSPh. A solution of 0.14 g (0.25 mmol) $Mn_2(\mu\text{-}SPh)_2(CO)_8$ and 0.26 g (2.0 mmol) NaSPh in 50 ml methanol was heated at reflux for 2 h. After cooling, 1.0 g $[Et_4N]Cl$ was added to the dark solution, causing the orange product to precipitate. This was filtered and recrystallized; yield, 54%.

Conversion of $Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$ to $Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$

A. Using PhSH only (uncatalyzed reaction). A solution of 0.30 g (0.44 mmol) $Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$ and 0.50 ml (5 mmol) PhSH in 50 ml acetone was heated at reflux. Periodically a small sample of the solution was removed and its infrared spectrum was recorded, to monitor the progress of the reaction (ν(CO) for reactant: 1975s, 1885vs cm^{-1}; ν(CO) for product: 1997s, 1910s,br cm^{-1}). An intermediate species with ν(CO) 1985 cm^{-1} was detected also. After 7 days the reaction was judged to be about 33% complete, based on infrared intensities.

B. Using PhSH and pyridine. A solution of 0.15 g (0.22 mmol) $Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$, 0.25 ml (2.5 mmol) PhSH, and 0.5 ml (6 mmol) of pyridine in 50 ml acetone was heated at reflux. Periodically, samples were removed and the infrared spectrum recorded to monitor the progress of the reaction. The reaction reached completion after 3 days and no decomposition was evident.

C. Using PhSH and CF_3CO_2H. To a solution of 0.15 g (0.22 mmol) $Et_4N[Mn_2(SBu^t)_3(CO)_6]$ in 50 ml acetone was added 0.05 ml CF_3CO_2H. The orange solution immediately became more red in color, and an infrared spectrum showed ν(CO) absorption at 1990 cm^{-1} (m). Addition of 0.5 ml (5 mmol) of PhSH at this point caused an immediate change of color back to orange. After about 30 min, 1.0 ml saturated aqueous $NaHCO_3$ was added, the solution was evaporated and the residue extracted into CH_2Cl_2. The CH_2Cl_2 solution was dried and the product precipitated by addition of Et_2O; an 83% yield of product was isolated.

Attempted reaction of $Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$ and Bu^tSH

A solution of 0.16 g (0.21 mmol) $Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$, 0.5 ml (6 mmol) pyridine, and 2.0 ml (18 mmol) Bu^tSH in 50 ml acetone was heated at reflux for 5 days. An infrared spectrum of the reaction mixture indicated that no reaction had occurred.

Reactions of $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ with $[Me_3O]BF_4$

Solid $[Me_3O]BF_4$ (0.75 g, 0.5 mmol) was added to a solution of 0.38 g (0.5 mmol) $Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$ in 50 ml CH_2Cl_2. The color of the solution changed immediately from orange to red, and then gradually turned to yellow-orange. After 30 min the solvent was removed in vacuo. The residue remaining was dissolved in Et_2O. The solution was filtered; slow evaporation of the solvent precipitated the product, $[Mn(\mu\text{-}SPh)(CO)_3]_4$; yield 0.25 g, ~ 100%; identified by IR (ν(CO) 2021s, 1951m cm^{-1}) and m.p. 228°C (dec.)

A preparation of $[Mn(\mu\text{-}SMe)(CO)_3]_4$ was carried out in the same manner.

Reactions of $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ with several ligands in the presence and absence of $[Me_3O]BF_4$

A. With CO. Carbon monoxide was bubbled through a solution of 0.25 mmol $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ (R = Ph, Bu^t) in 50 ml CH_2Cl_2 for one hour. No color change was evident at this time, and the infrared spectrum indicated no reaction had occurred. At this time 0.04 g (0.27 mmol) of $[Me_3O]BF_4$ was added. Stirring and CO addition was continued for 30 min. An infrared spectrum of this solution showed that complete conversion to the known complexes $Mn_2(\mu\text{-}SR)_2(CO)_8$ had occurred.

B. With PMe_3. A solution containing 0.17 g (0.25 mmol) $Et_4N[Mn_2(\mu\text{-}SBu^t)_3(CO)_6]$ and 0.2 ml (2.0 mmol) PMe_3 in 50 ml MeCN was heated at reflux for 7 days. No reaction was evident, based on an infrared spectrum of the reaction mixture, although the presence of some dark insoluble solids at this point indicated some decomposition had occurred.

To solutions of 0.25 mmol $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$ (R = Ph, Bu^t, Me) in 50 ml CH_2Cl_2 were added 0.04 g (0.27 mmol) $[Me_3O]BF_4$. The color changed from orange to red. After 20 min a 0.05 ml (0.5 mmol) sample of PMe_3 was added. Stirring was continued for 30 min then the solvent was removed in vacuo. The solid residue was extracted with Et_2O and the white Et_4NBF_4 filtered away from the orange solution. This was collected and evaporated in vacuo. Addition of a small amount of Et_2O and cooling caused formation of orange crystals. Recrystallization of the product *cis*-$Mn_2(\mu\text{-}SR)_2(CO)_6(PMe_3)_2$, was accomplished using Et_2O. Repeated recrystallizations were required to remove the difficult to separate $[Mn(\mu\text{-}SR)(CO)_3]_4$ which was also formed.

Similar results were obtained when CF_3CO_2H replaced $[Me_3O]BF_4$ as the electrophile in this reaction.

cis-$Mn_2(\mu\text{-}SPh)_2(CO)_6(PMe_3)_2$. Yield 28%; m.p. 182°C, Anal. Found: C, 44.68; H, 5.74. $C_{24}H_{28}O_6P_2S_2Mn_2$ calcd.: C, 44.46; H, 4.35%. IR ($CHCl_3$): ν(CO) 2015s, 1996s, 1936m, 1914s, 1902s cm^{-1}.

cis-$Mn_2(\mu\text{-}SBu^t)_2(CO)_6(PMe_3)_2$. Yield 59%; m.p. > 300°C (dec.). Anal. Found: C, 39.10; H, 6.06. $C_{20}H_{36}O_6P_2S_2Mn_2$ calcd.: C, 39.47; H, 5.97%. IR ($CHCl_3$): ν(CO) 2010s, 1990s, 1932m, 1913s, 1901s cm^{-1}.

cis-$Mn_2(\mu\text{-}SMe)_2(CO)_6(PMe_3)_2$. Yield 36% m.p. 136°C. Anal. Found: C, 31.99; H, 4.60. $C_{14}H_{24}O_6P_2S_2Mn_2$ calcd.: C, 32.05; H, 4.61%. IR ($CHCl_3$): ν(CO) 2020s, 1995s, 1936m, 1910sh, 1900s cm^{-1}.

C. With dppm. Reactions of $Et_4N[Mn_2(\mu\text{-}SR)_3(CO)_6]$, $[Me_3O]BF_4$ and dppm were carried out in the same manner as described above (for the reaction using PMe_3). The products characterized are listed below.

$Mn_2(\mu\text{-}SPh)_2(CO)_6$(dppm). Yield 61%; m.p. 237°C. Anal. Found: C, 58.14; H, 4.29. $C_{43}H_{32}O_6P_2S_2Mn_2$ calcd.: C, 58.62; H, 3.66%. IR (CH_2Cl_2): ν(CO) 2020m, 2008s, 1953s, 1943sh, 1918s cm^{-1}.

$Mn_2(\mu\text{-}SBu^t)_2(CO)_6$(dppm). Yield 84%; m.p. 191°C. Anal. Found: C, 55.10; H, 4.73. $C_{39}H_{40}O_6P_2S_2Mn_2$ calcd.: C, 55.70; H, 4.80%. IR (hexane): ν(CO) 2020m, 2005s, 1945m, 1937m, 1920s cm^{-1}.

$Mn_2(\mu\text{-}SMe)_2(CO)_6$(dppm). Yield 54%; m.p. 192°C. Anal. Found: C, 52.65; H, 3.92. $C_{33}H_{28}O_6P_2S_2Mn_2$ calcd.: C, 52.37; H, 3.73%. IR (hexane): ν(CO) 2038w, 2020s, 2003s, 1950s, 1937m, 1922s cm^{-1}.

Conversion of cis-$Mn_2(\mu\text{-}SR)_2(CO)_6(PMe_3)_2$ to $Mn_2(\mu\text{-}SR)_2(\mu\text{-}CO)(CO)_4(PMe_3)_2$

A solution of 0.16 g (0.25 mmol) of *cis*-$Mn_2(\mu\text{-}SPh)_2(CO)_6(PMe_3)_2$ in 25 ml acetone (or MeCN or THF) was heated at reflux for 2 h. The solution was allowed to cool and solvent removed in vacuo leaving a purple solid. This was recrystallized from CH_2Cl_2/hexane to give a pure sample of the product, 0.14 g, 85% yield; m.p. 164–165°C (dec.).

Anal. Found: C, 44.91; H, 4.89. $C_{24}H_{28}O_6P_2S_2Mn_2$ calcd.: C, 44.51; H, 4.55%. IR ($CHCl_3$); ν(CO) 1985vs, 1947s, 1905m, 1805wbr cm^{-1}.

A similar procedure was used to convert orange *cis*-$Mn_2(\mu\text{-}SMe)_2(CO)_6(PMe_3)_2$ to the dark red $Mn_2(\mu\text{-}SMe)_2(\mu\text{-}CO)(CO)_4(PMe_3)_2$ in 82% yield; m.p. 235°C (dec.)

Anal. Found: C, 31.62; H, 4.93. $C_{14}H_{24}O_6P_2S_2Mn$ calcd.: C, 31.32; H, 4.76%. IR ($CHCl_3$): ν(CO) 1982s, 1941s, 1898s, 1803w cm^{-1}.

It is also possible to carry out these conversions in solution at room temperature over a 3 day period.

Reactions of $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ with CO in the presence of $[Me_3O]BF_4$ or $AgBF_4$

Carbon monoxide was bubbled through a solution containing 0.16 g (0.25 mmol) of $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ in 50 ml CH_2Cl_2 for 2 h (ambient temperature). No reaction occurred according to infrared spectra monitoring. One equivalent of either $[Me_3O]BF_4$ or $AgBF_4$ was then added. The infrared spectrum changed with starting material bands decreasing and new absorptions due to $Mn_2(\mu\text{-}Br_2)(CO)_8$ appearing. Complete conversion of this new species occurred in 45 min. Further monitoring revealed a conversion of this species to $MnBr(CO)_5$ during the next 45 min. Solvent was removed at this point and the residue was extracted with $CHCl_3$. Filtration, followed by addition of hexane to the filtrate and evaporation yielded $MnBr(CO)_5$ (80–90% yield).

Reaction of $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ with other ligands

A. With PMe_3. To a solution of 0.33 g (0.5 mmol) $Et_4N[Mn_2(\mu\text{-}Br)_3(CO)_6]$ in 50 ml methanol was added 0.025 ml (2.4 mmol) PMe_3. After stirring the mixture for 1 h. solvent was evaporated in vacuo. The solid residue was extracted with Et_2O. The Et_2O solution was filtered and the volume reduced to 1.0 ml. Hexane was then added; cooling (−20°C) caused crystals of known $MnBr(CO)_3(PMe_3)_2$ to precipitate (67% yield).

B. With pyridine. A similar reaction using pyridine was run in methanol. Heating at reflux for 4 h was required. After cooling and workup similar to that described in the PMe_3 reaction, the known product $MnBr(CO)_3(py)_2$ was isolated.

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