in the rate-determining step occurs between H-Sn (60 kcal mol^{-1}) and H-Si (77 kcal mol^{-1}). In the former case CO dissociation from $CH_3C(O)Co(CO)_3PPh_3$ is rate limiting and in the latter oxidative addition is rate limiting.

Experimental Section

Materials. THF and 2-ethoxyethyl ether were distilled from Na/benzophenone prior to use. $HSnBu_3$, $HSnPh_3$, $HSiEt_3$, and $HSiPh_3$ were obtained from Aldrich and used without further purification. These compounds were stored under N_2 at 0 °C. $HCo(CO)_4$,[24] $HCo(CO)_8PBu_3$,[25] $HCo(CO)_3PPh_3$,[25] $CH_3C(O)Co(CO)_3PPh_3$,[26] and $CH_3C(O)Mn(CO)_5$[23] were synthesized according to standard literature procedures.

Kinetic Experiments. All manipulations were carried out under N_2 with standard Schlenk procedures. In a typical reaction known amounts of $CH_3C(O)Co(CO)_3PPh_3$ and HMR_3 were dissolved in known volumes of THF in separate flasks in a vacuum Atmospheres Corp. inert-atmosphere box. The sealed flasks were removed from the box and cooled to 0 °C. The $CH_3C(O)Co(CO)_3PPh_3$ and HMR_3 solutions were transferred via syringe into a Pyrex tube approximately 15 cm in height at 1.0 cm in diameter equipped with a septum and stopcock. The solution (0 °C) was then gently purged with CO and maintained under a constant pressure of CO. The tube was then placed in a temperature bath thermostated ±0.5 °C of the desired reaction temperature. After thermal equilibration (15 min) an initial IR spectrum was obtained (= 0 min). Following this IR spectra were recorded as a function of time. The rate of $CH_3C(O)Co(CO)_3PPh_3$ disappearance was determined by monitoring the acyl absorption at 1690 cm^{-1}. The liquid products were analyzed with a Hewlett-Packard Model 5880 gas chromatograph equipped with a $20 \times {}^1/_8$ in., 60/80 mesh Chromosorb 101 column. The following program was utilized: initial temperature = 80 °C; 6 °C/min increase for 12 min followed by 8.0 °C/min increase up to a final temperature of 290 °C.

In the initial part of the reaction the amount of acetaldehyde found corresponded well to the amount of $CH_3C(O)Co(CO)_3PPh_3$ reacted. In some cases toward the end of the reaction ethanol was observed presumably a result of reduction of acetaldehyde by HMR_3. Similar procedures were utilized for the reaction of $CH_3C(O)Mn(CO)_5$ with HMR_3. The products $R_3MCo(CO)_3PPh_3$[20,27] and $R_3MMn(CO)_5$[28] were determined by their characteristic IR spectra.

A description of the high-pressure infrared equipment including the high-pressure infrared cell and spectrometer together with the usual operation procedure has already appeared.[29]

Registry No. $CH_3C(O)Co(CO)_3PPh_3$, 14054-68-3; $CH_3C(O)Mn(CO)_5$, 13963-91-2; $HSnBu_3$, 688-73-3; $HSnPh_3$, 892-20-6; $HSiEt_3$, 617-86-7; $HSiPh_3$, 789-25-3; acetaldehyde, 75-07-0.

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New Synthetic Strategies for Organometallic Complexes with Thiolate Ligands

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Reactions between several carbonylmetalate anions (PPN[$Mn(CO)_5$] and PPN[$M(CO)_3(\eta\text{-}C_5H_5)$]; $PPN^+ = Ph_3PNPPh_3^+$; M = Mo, W) and organic disulfides (RSSR; R = Ph, Me, CF_3) initially give the metal thiolate complexes $Mn(SR)(CO)_5$ and $M(SR)(CO)_3(\eta\text{-}C_5H_5)$. The tungsten species are stable and isolable. The molybdenum and manganese compounds are not stable; the former rapidly lose CO and form thiolate bridge dimers (a known reaction) while the later is converted, within this reaction system, to a mixture of $Mn_2(\mu\text{-}SR)_2(CO)_8$ and PPN[$Mn_2(\mu\text{-}SR)_3(CO)_6$]. Reactions between these carbonylmetalate anions and [Me_2SSMe]BF_4 yield the same mononuclear metal thiolate complexes which, when appropriate, lose CO and dimerize. If an excess of this sulfonium reagent is present, a further reaction may also occur to produce unstable complexes with monodentate organic disulfide ligands ([$Mn(CO)_5(RSSR)$]$^+$ and [$M(RSSR)(CO)_3(\eta\text{-}C_5H_5)$]$^+$). The reaction of PPN[$W(CO)_3(\eta\text{-}C_5H_5)$] with [$W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)$]$BF_4$ gives $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$. This reaction is much faster than the reaction of PPN[$W(CO)_3(\eta\text{-}C_5H_5)$] with MeSSMe, indicating that coordination of the disulfide to the metal has substantially enhanced its reactivity toward nucleophilic attack.

Introduction

Metal carbonyl complexes with thiolate (RS^-) ligands form a well-defined subset among organometallic compounds.[1] Generally in these compounds the thiolate group is found to function as a bridging ligand linked to two or three metal atoms. Complexes with terminal thiolate ligands are also encountered although they are often unstable relative to CO loss and formation of thiolate-bridged dimeric species. Known manganese carbonyl thiolate complexes include $Mn(SR)(CO)_5$, $Mn_2(\mu\text{-}SR)_2(CO)_8$, $Mn_4(\mu_3\text{-}SR)_4(CO)_{12}$,[2] and [$Mn_2(\mu\text{-}SR)_3(CO)_6$]$^-$, the last series of complexes being recently prepared in our research labs[3] and elsewhere.[4] Thiolate derivatives of

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(1) The last general review in this area is quite old, see: Abel, E. W.; Crosse, B. C. *Organomet. Chem. Rev.* **1967**, *2*, 443.

(2) A summary of references to these compounds is provided in: Treichel, P. M. In "Comprehensive Organometallic Chemistry"; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: London, 1982; Vol. 3, pp 103-110.

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cyclopentadienylcarbonylmolybdenum and -tungsten are primarily of two general types with formulas $M(SR)(CO)_3(\eta\text{-}C_5H_5)$ and $M_2(\mu\text{-}SR)_2(CO)_4(\eta\text{-}C_5H_5)_2$ (M = Mo, W).[5] In addition, the compound $Mo_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2(\eta\text{-}C_5H_5)_2(Mo{=}Mo)$ was recently described in a communication.[5i] Examples of the molybdenum thiolate complexes $Mo_2(\mu\text{-}SR)_4(\eta\text{-}C_5H_5)_2$, which lack carbonyl groups, are also known.[6]

Traditional routes for the synthesis of metal carbonyl thiolate complexes utilize reactions of disulfides, mercaptans, and the thiolate anion with various metal carbonyl precursors. Tin thiolate species like Me_3SnSR have also been found to be useful as donors of the thiolate group in a number of recent studies.

We find it convenient to classify the traditional preparations of thiolate metal complexes into two different general classes. The first class involves reactions of metal carbonyl precursors with organic disulfides, RSSR. These reactions are likely to have radical mechanisms and involve oxidation of the metal. They may also be classified as nonpolar to distinguish them from the second group. Two examples are listed (eq 1 and 2). A few examples that

$$[W(CO)_3(\eta\text{-}C_5H_5)]_2 + PhSSPh \rightarrow 2W(SPh)(CO)_3(\eta\text{-}C_5H_5) \qquad \text{(1)[5a]}$$

$$2W(CO)_6 + PhSSPh \rightarrow W_2(\mu\text{-}SPh)_2(CO)_8 \qquad \text{(2)[7]}$$

utilize mercaptans as reagents might well be included with this class, in that the reactions appear nonpolar in character and involve metal oxidation. The formation of $Fe_2(\mu\text{-}SR)_2(CO)_6$ from $Fe_3(CO)_{12}$ and RSH is a long known example of such a reaction.[8] The second class of reactions utilizes either a thiolate anion (RS^-) or a reagent capable of providing a thiolate anion such as R'_3SnSR or RSH. In this group the thiolate group replaces another ligand such as CO or a halide ion. Such reactions, illustrated by eq 3 and 4, do not generally involve formal metal oxidation.

$$2MnBr(CO)_5 + 2RSY \rightarrow Mn_2(\mu\text{-}SR)_2(CO)_8 + 2YBr + 2CO \qquad (3)$$

$$Y = H,\text{[9]}\ Me_3Sn\text{[10]}$$

$$M(CO)_6 + NaSH \xrightarrow[-NaCl]{[PPN]Cl} PPN[M(SH)(CO)_5] + CO \qquad (4)$$

$$M = Cr, Mo, W;\ PPN = Ph_3PNPPh_3^+\ \text{[11]}$$

A few reactions for synthesis of metal thiolate complexes do not clearly fall within these two categories. The reaction of a metal carbonyl hydride and a disulfide[5h] could be a radical reaction (no mechanistic information being available), but this reaction does not produce formal oxidation at the metal. An alternate mechanism, involving nucleophilic attack by a metal species on the disulfide, can also be envisioned; this point will receive further discussion below. Similar reactions are the major topic of this paper. We will propose this type of reaction as a third general mechanistic route of synthesis for metal thiolate complexes. An interesting reference has appeared which reports the addition of a disulfide to the metal–metal triple bond in $[Mo(CO)_2(\eta\text{-}C_5H_5)]_2$, forming $[Mo(\mu\text{-}SR)(CO)_2(\eta\text{-}C_5H_5)]_2$.[5c] This example suggests a useful method for future development. There are also numerous reactions in which one thiolate group is exchange for another. We recently described[3] the conversion of $Et_4N[Mn_2(\mu\text{-}SBu)_3(CO)_6]$ to $Et_4N[Mn_2(\mu\text{-}SPh)_3(CO)_6]$, and other examples of this type of reaction are also known.[12] Finally there are reactions in which substituent groups on sulfur are exchanged; the conversion of $Mn_2(\mu\text{-}SSnMe_3)_2(CO)_8$ to $Mn_2(\mu\text{-}SH)_2(CO)_8$ is such an example.[13]

As indicated above, this paper introduces a third general synthetic method for the synthesis of metal thiolate complexes. This method takes advantage of the nucleophilicity of anionic metal carbonyl species, using these reagents to effect nucleophilic cleavage of the sulfur–sulfur bond in disulfides. Similarily, metal carbonyl anions effect sulfur–sulfur cleavage in the reagent $[Me_2SSMe]BF_4$. This reagent is known to be useful in synthetic chemistry as a donor of the electrophilic MeS^+ group, but from a mechanistic point of view this reaction is similar to disulfide cleavage by nucleophiles.

Experimental Section

The following starting materials were prepared according to procedures given in the literature: $PPN[Mn(CO)_5]$,[14] $PPN[Mo(CO)_3(\eta\text{-}C_5H_5)]$,[14] $[Me_2SSMe]BF_4$.[15] The preparation of $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ was carried out in a manner similar to that used for the molybdenum compound. Disulfides (RSSR; R = Ph, Me, CF_3) were obtained commercially and were used without further purification. Solvents were dried by using standard methods. All manipulations were carried out under dry nitrogen.

Infrared spectra were recorded on a Beckman Model 4230 spectrophotometer, and ^1H NMR spectra were obtained with IBM WP-270 or IBM WP-200 spectrometers. High-resolution mass spectra were obtained with an AEI-MS-902 mass spectrometer. Melting points (uncorrected) were determined on a Thomas-Hoover apparatus. Elemental analyses were performed by the Galbraith Laboratory, Knoxville, TN.

Infrared spectra (ν(CO) region) were recorded on small samples removed periodically from the reaction mixture. This procedure allowed us to monitor the progress of the reaction vs. time and also permitted detection of long-lived intermediates. Two sequences of spectra are presented in Figure 1 to illustrate the data on these reactions.

Reactions of Metal Carbonyl Anions with RSSR. $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ and PhSSPh. A solution of $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ (0.40 g, 0.46 mmol) and PhSSPh (0.20 g, 0.92 mmol) in 100 mL of CH_2Cl_2 was stirred at ambient temperature. Infrared spectra indicated that complete conversion of the reactants to $W(SPh)(CO)_3(\eta\text{-}C_5H_5)$ occurred in 10 min. The solvent was evaporated under reduced pressure. Chromatography

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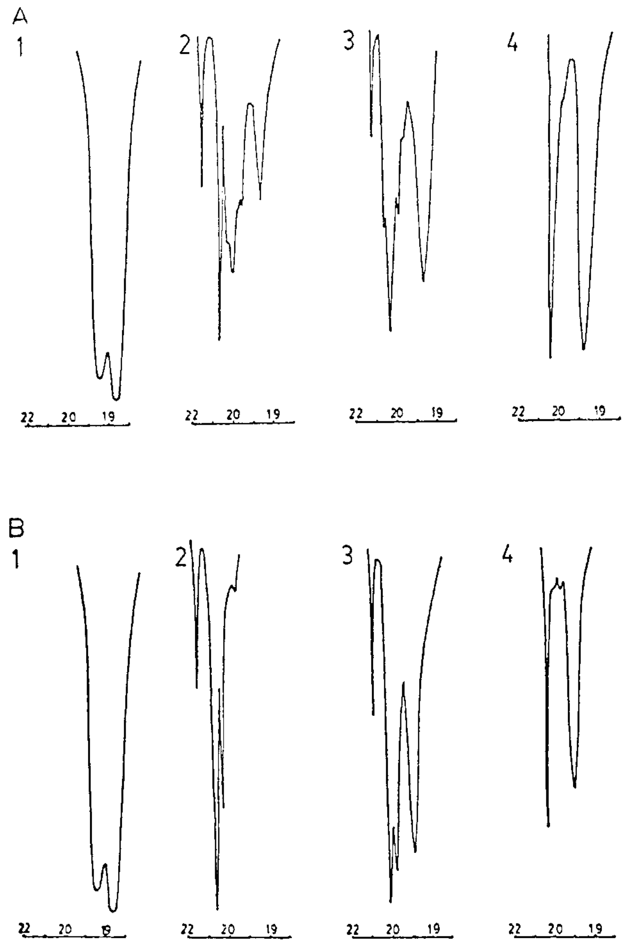

Figure 1. Sequences of infrared spectra for reactions of PPN[$Mn(CO)_5$] with disulfides, in CH_2Cl_2. A: 1, PPN[$Mn(CO)_5$]; 2, 9 min after mixing PPN[$Mn(CO)_5$] and PhSSPh (primarily $Mn(SPh)(CO)_5$ plus some PPN[$Mn_2(\mu\text{-}SPh)_3(CO)_6$]); 3, solution warmed to room temperature, ~7 min ($Mn_2(\mu\text{-}SPh)_2(CO)_8$ + PPN[$Mn_2(\mu\text{-}SPh)_3(CO)_6$]); 4, after 90 min (PPN[$Mn_2(\mu\text{-}SPh)_3(CO)_6$]). B: 1, PPN[$Mn(CO)_5$]; 2, 2 min after mixing PPN[$Mn(CO)_5$] and CF_3SSCF_3, 0 °C ($Mn(SCF_3)(CO)_5$); 3, after 12 h (PPN[$Mn(\mu\text{-}SCF_3)_2(CO)_4$] and PPN[$Mn_2(\mu\text{-}SCF_3)_3(CO)_6$]); 4, after 24 h (PPN[$Mn_2(\mu\text{-}SCF_3)_3(CO)_6$]).

of the residue on a 2.5 cm × 7 cm neutral alumina column using Et_2O as eluent gave a single red band which was collected. Evaporation of solvent followed by recrystallization from hexane yields 0.20 g of $W(SPh)(CO)_3(\eta\text{-}C_5H_5)$ (100% yield).

This compound is known,[5a] but details concerning its purification and properties were not included in the previous reference. We report: decomp without melting ~95 °C: ν(CO) 2034 s, 1947 s, br cm^{-1} ($CHCl_3$); ^{1}H NMR δ 7.06–7.50 (m, C_6H_5), 5.70 (s, C_5H_5); a mass spectrum parent peak at *m/e* 441.9859 ($^{12}C_{14}{}^1H_{10}{}^{16}O_3{}^{32}S^{184}W$, *m/e* 441.9858).

PPN[$W(CO)_3(\eta\text{-}C_5H_5)$] and CF_3SSCF_3. This reaction was carried out in similar manner; the instantaneous color change from yellow to red upon mixing indicated a very fast reaction which was confirmed by IR data. Workup in the manner described above gave known[5d] $W(SCF_3)(CO)_3(\eta\text{-}C_5H_5)$ in 70% yield (melts with CO loss at 115–120 °C (lit. 105–108 °C)): ν(CO) 2048 s, 1968 sh, 1950 s, br cm^{-1} (CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 5.73 (s, C_5H_5).

PPN[$W(CO)_3(\eta\text{-}C_5H_5)$] and MeSSMe. This reaction was carried out in similar manner, except that 34 h was required to effect complete reaction. The product, $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$, obtained in 70% yield, is a known species:[5h] ν(CO) 2028 s, 1924 vs, b cm^{-1}; ^{1}H NMR δ 5.58 (s, C_5H_5), 1.94 (s, SCH_3).

PPN[$Mo(CO)_3(\eta\text{-}C_5H_5)$] and PhSSPh. The reactants were mixed as described in the previous examples. Carbonyl stretching frequencies due to starting material disappeared in about 20 min and were replaced by ν(CO) absorbances at 2039 vs, 1923 sh, 1953 vs, and 1822 w cm^{-1}. The two major absorptions correspond closely to values reported for monomeric $Mo(SR)(CO)_3(\eta\text{-}C_5H_5)$ species and indicate the presence of $Mo(SPh)(CO)_3(\eta\text{-}C_5H_5)$ as the primary product. With continued stirring at room temperature for 5.5 h, the intensity of the ν(CO) absorption at 2039 cm^{-1} slowly decreased while a peak at 1870 cm^{-1} due to $[Mo(\mu\text{-}SPh)(CO)_2(\eta\text{-}C_5H_5)]_2$ increased in intensity in the spectrum. Solvent was removed by using a rotary evaporator and the residue chromatographed on Florosil by using CH_2Cl_2 to elute a red-brown band. The solvent was removed from this band and the residue recrystallized from CH_2Cl_2/hexane; yield ~50%. This compound decomposes readily to yield species that lack CO groups. This fact may explain a lack of data on this compound which has been reported in the literature in several previous instances.[5c,g,i]

PPN[$Mo(CO)_3(\eta\text{-}C_5H_5)$] and CF_3SSCF_3. These reactants were stirred for 2 h at room temperature to effect complete reaction to give $Mo(SCF_3)(CO)_3(\eta\text{-}C_5H_5)$. The solvent was removed by evaporation under a stream of nitrogen and the product purified by chromatography on alumina and crystallization: yield 80%; mp 82–84 °C (lit.[5d] 70–74 °C); ν(CO) 2048 s, 1970 vs, b cm^{-1} (CH_2Cl_2); ^{1}H NMR δ 5.63 (s, C_5H_5). This compound is known to lose CO readily[5d] so it is important to avoid both higher temperatures and prolonged handling of this compound during workup.

PPN[$Mo(CO)_3(\eta\text{-}C_5H_5)$] and MeSSMe. A solution of these reactants in CH_2Cl_2 was stirred at room temperature for 48 h. At this time an infrared spectrum indicated that a very small amount of $Mo(SMe)(CO)_3(\eta\text{-}C_5H_5)$ and $[Mo(\mu\text{-}SMe)(CO)_2(\eta\text{-}C_5H_5)]_2$ were present, along with unreacted starting material.

PPN[$Mn(CO)_5$] and PhSSPh. This reaction and other reactions reported for PPN[$Mn(CO)_5$] are quite complicated. Eventually this reaction was carried out at four temperatures (−78, −26, 0, and 22 °C). Reactions at −26 and 22 °C are described below, the latter because it provided convenient synthetic methodology and the former because it provided definitive information on reaction intermediates. The 1:2 stoichiometry used in the 22 °C reaction provided excess PhSSPh, the ratio of Mn:S in the product being 2:3. A 1:1 stoichiometry, as was used in the −26 °C reaction, gave a lower yield of this product, but the reaction was otherwise similar.

22 °C (Ambient Temperature). A solution of 0.20 g (0.92 mmol) of PhSSPh in 25 mL of CH_2Cl_2 was added to a solution of 0.34 g (0.46 mmol) of PPN[$Mn(CO)_5$] in 75 mL of CH_2Cl_2 and the mixture stirred for 2 h. The infrared spectrum at this point indicated that conversion to the product PPN[$Mn_2(\mu\text{-}SPh)_3(CO)_6$] was complete. The solvent was then removed by evaporation under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 and placed on an alumina column. Elution with CH_2Cl_2 gave a single yellow band which was collected. Evaporation followed by crystallization of the residue from CH_2Cl_2/Et_2O gave the yellow-orange crystalline product PPN[$Mn_2(\mu\text{-}SPh)_3(CO)_6$] in 53% yield (0.28 g): mp with decomp 185–186 °C; ν(CO) 1994 s, 1910 s, b cm^{-1} (CH_2Cl_2). The tetraethylammonium salt of this anionic complex is known.[3]

−26 °C. Solutions containing equimolar amounts of PPN[$Mn(CO)_5$] and PhSSPh were cooled to −26 °C and then mixed, and the reaction mixture was maintained at this temperature. Samples were removed periodically and infrared spectra taken. (This procedure took about 2 min, and the solution temperature rapidly warmed to ambient temperature in the cell.) An initial spectrum at ~1 min showed that starting material had completely reacted, and the major product was $Mn(SPh)(CO)_5$ with ν(CO) at 2126 m, 2038 vs, and 2004 s cm^{-1}. Additional smaller peaks at 1986 s, 1963 s, and 1918 m cm^{-1} were also seen; the last peak is probably due to $[Mn_2(\mu\text{-}SPh)_3(CO)_6]^-$. The spectrum changed with the $Mn(SPh)(CO)_5$ absorptions growing and then declining slightly, the $[Mn_2(\mu\text{-}SPh)_3(CO)_6]^-$ absorptions increasing, and the other two peaks disappearing. The spectrum stabilizes after about 35 min, and no further changes were detected for the next 19 h. At this point the reaction mixture was allowed to warm to room temperature. During this warming process absorptions due to $Mn_2(\mu\text{-}SPh)_2(CO)_8$ at 2079 m, 2022 s, 2006 m, 1970 s cm^{-1} grew and then diminished while the absorptions due to $[Mn_2(\mu\text{-}SPh)_3(CO)_6]^-$ (1994 s, 1910 s, b cm^{-1}) continued to grow and eventually became the major peaks in the solution. A sequence of IR spectra showing the progress of this reaction are given in Figure 1A.

PPN[$Mn(CO)_5$] and CF_3SSCF_3. These reactants PPN[$Mn(CO)_5$] (0.20 g, 0.27 mmol) and CF_3SSCF_3 (0.13 g, 0.62 mmol) were stirred in 50 mL of CH_2Cl_2 at room temperature. Complete formation of $Mn(SCF_3)(CO)_5$ had occurred within the time required to take an infrared spectrum (1–2 min). Within the next 90 min, however, the absorptions due to $Mn(SCF_3)(CO)_5$ at 2142 w, 2052 vs, and 2018 m cm^{-1} were replaced by new absorptions at 2088 w, 2008 vs, 1988 s, and 1944 s cm^{-1}. The reaction may be stopped at this point. Evaporation of the solvent gave a crude product which was purified by chromatography (alumina, CH_2Cl_2 eluent) and crystallization from CH_2Cl_2/Et_2O. It was tentatively identified as $PPN[Mn(SCF_3)_2(CO)_4]$: yield 62%, mp 154–155 °C. Because of the instability (facile conversion to $PPN[Mn_2(\mu\text{-}SCF_3)_3(CO)_6]$) a good analysis could not be obtained.

If the reaction is not interrupted after 90 min but allowed to continue for an additional 8 h, this product converts completely to $PPN[Mn_2(\mu\text{-}SCF_3)_3(CO)_6]$. This yellow, air-stable product was isolated and purified by chromatography and crystallization: yield 40%; mp 160–163 °C; $\nu(CO)$ 2018 vs, 1944 s, b cm^{-1} in CH_2Cl_2. Anal. Found (Calcd): C, 47.96 (48.27); H, 2.87 (2.70); S, 8.59 (8.59%).

Infrared spectra portraying the progress of this reaction are shown in Figure 1B.

$PPN[Mn(CO)_5]$ and MeSSMe. Dichloromethane was not used for this reaction because it reacts with $PPN[Mn(CO)_5]$ to an appreciable extent during the several hours needed for this reaction. Instead THF was chosen as a solvent. The solution of reactants was stirred for 17 h. Filtration, followed by evaporation of the filtrate, yielded a residue. Chromatography on alumina with ether yielded a single band. This was collected and solvent removed. Crystallization of the solid residue from CH_2Cl_2/Et_2O gave the yellow orange product $PPN[Mn_2(\mu\text{-}SMe)_3(CO)_6]$ in 45% yield: mp with decomp 160–170 °C; $\nu(CO)$ 1984 s 1899 s, b cm^{-1} (CH_2Cl_2). The tetraethylammonium salt of this anionic complex is known.[3]

Reactions of Metal Carbonyl Anions with $[Me_2SSMe]BF_4$. $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ and $[Me_2SSMe]BF_4$. A solution of 0.10 g (0.51 mmol) of $[Me_2SSMe]BF_4$ in 20 mL of MeCN was added to a solution of 0.45 g (0.52 mmol) of $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$. The reaction was complete immediately (<1 min). Solvent was removed in vacuo and the residue dissolved in CH_2Cl_2 and placed on an alumina chromatographic column. A single red-orange band, eluting with CH_2Cl_2, was collected and the solvent removed. Crystallization by slow evaporation of Et_2O/hexane gave the product $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$ in 81% isolated yield. The identification was made from IR, ^1H NMR, and melting point data.[5a,h]

If this reaction is carried out with >1:1 mole ratios of $[Me_2SSMe]BF_4$: $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$, a second reaction is observed. The product of this reaction is $[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$ ($\nu(CO)$ 2060 s, 1980 sh, 1968 s cm^{-1} (CH_2Cl_2)). The reaction between $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$ and $[Me_2SSMe]BF_4$ to form this product requires less than 5 min to reach completion. This compound and related species will be discussed elsewhere.

$PPN[Mo(CO)_3(\eta\text{-}C_5H_5)]$ and $[Me_2SSMe]BF_4$. This reaction (1:1 mole ratio) was best carried out by adding a dilute solution of $[Me_2SSMe]BF_4$ dropwise to the solution of the molybdenum complex. Rapid addition (producing locally high concentrations of $[Me_2SSMe]BF_4$) has an adverse effect, increasing the amount of non-carbonyl-containing side products. As in the previous example, the reaction appeared to occur on mixing. An IR spectrum at this point indicated that $Mo(SMe)(CO)_3(\eta\text{-}C_5H_5)$ was the initial product ($\nu(CO)$ 2056 m, 1948 sh, 1941 s, br cm^{-1} (MeCN)). There are several references to this compound describing it as unstable with respect to CO loss[5g] and indicating loss of CO on evaporation of solvent in vacuo.[5e] On the basis of this latter reference, we proceeded to evaporate solvent by using a rotary evaporator. The solid remaining was chromatographed on Florosil using CH_2Cl_2, a single brown band eluting. This was collected and solvent evaporated. Recrystallization from Et_2O/CH_2Cl_2 produced 0.05 g of $Mo_2(\mu\text{-}SMe)_2(CO)_4(\eta\text{-}C_5H_5)_2$ (37%) as dark crystals; identification was based on similarity of IR ($\nu(CO)$ 1965 s, 1947 s, 1877 s, 1869 s, 1852 m, sh cm^{-1} (C_6H_{12})), ^1H NMR, and melting point data with literature values.[5h]

If more than 1 equiv of $[Me_2SSMe]BF_4$ is used or if $[Me_2SSMe]BF_4$ is added to a solution containing $Mo(SMe)(CO)_3(\eta\text{-}C_5H_5)$, a second reaction occurs to form $[Mo(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$. The formation of this compound is much more rapid than the formation of $Mo_2(\mu\text{-}SMe)_2(CO)_4(\eta\text{-}C_5H_5)_2$. The product is unstable, however, decomposing upon attempts to isolate it to give residues which contain no identifiable carbonyl-containing species. Identification of this species is based on the similarity of the $\nu(CO)$ absorptions with $\nu(CO)$ values for the tungsten analogue ($\nu(CO)$ 2070 s, 1998 sh, 1976 s, br cm^{-1} (CH_2Cl_2)).

$PPN[Mn(CO)_5]$ and $[Me_2SSMe]BF_4$. Dropwise addition of a solution of 0.10 g (0.51 mmol) of $[Me_2SSMe]BF_4$ in 20 mL of MeCN to a solution of 0.37 g (0.51 mmol) of $PPN[Mn(CO)_5]$ in 50 mL of MeCN was carried out. An infrared spectrum at this point indicated that $Mn_2(\mu\text{-}SMe)_2(CO)_8$ was the only carbonyl-containing product. Workup of the reaction mixture using chromatography (alumina, CH_2Cl_2) and crystallization from hexane gave the product, a known species,[5h] in 75% yield. It was identified by comparison of IR, ^1H NMR, and melting point data with literature values.

If this reaction is carried out at lower temperature (0, −26 °C), it is possible to detect $Mn(SMe)(CO)_5$ as the initial product of this reaction. At 0 °C, for example, one sees $\nu(CO)$ bands for this species that reach a maximum intensity about 4 min after mixing; these bands then decrease with a concurrent increase in the absorptions due to $Mn_2(\mu\text{-}SMe)_2(CO)_8$. Conversion of monomer to dimer is complete in about 10 min.

In experiments using excess $[Me_2SSMe]BF_4$, $Mn(SMe)(CO)_5$ is initially formed, but conversion to a new species with $\nu(CO)$ at 2095 w, 2027 s, 2014 vs, 2006 sh, and 1961 cm^{-1} follows rapidly. This species, which we assume to be $[Mn(CO)_5(MeSSMe)]BF_4$, is unstable; it decomposes rapidly to non-carbonyl-containing products.

$PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ and $[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$. A solution of $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ (0.25 g, 0.29 mmol) in 20 mL of CH_2Cl_2 was added rapidly to a slurry of 0.15 g (0.29 mmol) of $[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$ in 30 mL of CH_2Cl_2. The reaction occurred upon mixing to give a clear red-orange solution. Workup of this reaction mixture as described earlier gave 0.12 g of $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$ (60% yield). Surprisingly, no other products were detected in infrared spectra of the solution of reactants. Identification was based on IR, ^1H NMR, and melting point data.

Discussion

A new procedure for synthesis of organometallic complexes with thiolate ligands is described in this paper. This is a general route that appears not to have been identified previously despite extensive work on this class of compounds. It has advantages in certain instances over the traditional methods previously used for the synthesis of certain of these species. The method involves nucleophilic displacement of the group Y in a species RSY, using metal carbonyl complexes known to have nucleophilic character. The simplest example of such a reaction is the displacement of RS^- from a disulfide. The general reaction is given in eq 5.

$$m^- + RSSR \rightarrow mSR + RS^- \qquad (5)$$

Our efforts here have been directed to study of the reactions of three anionic metal carbonyls $[W(CO)_3(\eta\text{-}C_5H_5)]^-$, $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$, and $[Mn(CO)_5]^-$. These species are easily prepared; salts of these anions with the bis(triphenylphosphine)nitrogen(1+) cation ($[Ph_3PNPPh_3]^+$, general abbreviated PPN^+) are crystalline species that are easily handled. The anionic complexes are known to act as nucleophiles;[16] indeed this property is much exploited in organometallic chemistry for other synthetic purposes such as the formation of alkyl- and acyl metal carbonyl species.[16] Many other anionic metal carbonyls are known to function as nucleophiles, and there

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(16) Good summaries of such reactions are found in most organometallic chemistry references books; for example, see: Lukehart, C. M. "Fundamental Transition Metal Organometallic Chemistry"; Brooks-Cole Publishing: Belmont, CA, 1985.

have been several studies defining relative nucleophilicities of members of this group.[17] We believe that the examples chosen here, involving metal species of low to average nucleophilicities can be extended to the other known anionic metal carbonyls, making this a route of broad and general synthetic applicability for thiolate metal complexes.

Among the various thiolate reagents RSY that are applicable in this type of reaction the disulfides, RSSR, are the most significant since many organic disulfides are commercially available. Cleavage of disulfides by nucleophiles is a well-known phenomenon[18] which was extensively studied prior to 1950. Predictably, the rate of nucleophilic cleavage of disulfides is enhanced if the organic group of the disulfide is electron withdrawing. In this study (RSSR; R = Ph, CF_3, Me), nucleophilic cleavage was found to be rapid for CF_3SSCF_3 and PhSSPh but quite slow with MeSSMe.

For the general procedure employed here, dichloromethane is a convenient solvent. The organometallic reactants are soluble, and one can easily follow the progress of these reactions by monitoring the ν(CO) absorptions in the infrared spectrum using this solvent. The initial nucleophilic cleavage reaction is often rapid at room temperature, and a qualitative assessment of these systems indicates complete conversions in such cases. Reactions with MeSSMe took considerably longer. This tended to lead to lower product yields and/or difficulty due to side reactions.

The tungsten species $W(SR)(CO)_3(\eta\text{-}C_5H_5)$ are stable and isolable from the reaction mixture in high yield by a simple sequence involving chromatography and crystallization (eq 6). The compounds prepared here are known species.

$$PPN[W(CO)_3(\eta\text{-}C_5H_5)] + RSSR \rightarrow W(SR)(CO)_3(\eta\text{-}C_5H_5) + [PPN]SR \quad (6)$$

The molybdenum species $Mo(SR)(CO)_3(\eta\text{-}C_5H_5)$ are known to be unstable with respect to CO loss and dimerization. We isolated $Mo(SCF_3)(CO)_3(\eta\text{-}C_5H_5)$ for which this process is least rapid. Monomeric $Mo(SPh)(CO)_3(\eta\text{-}C_5H_5)$ was cleanly formed according to IR data in a short time from $PPN[Mo(CO)_3(\eta\text{-}C_5H_5)]$ and PhSSPh. This compound is known to lose CO rapidly, so we chose to isolate $Mo_2(\mu\text{-}SPh)_2(CO)_4(\eta\text{-}C_5H_5)_2$, which was formed cleanly from the monomeric species when the reaction mixture was allowed to stand several hours. The reaction between $PPN[Mo(CO)_3(\eta\text{-}C_5H_5)]$ and MeSSMe was very slow, with only a small amount of the reaction being concluded in a 48-h period.

Reactions of $PPN[Mn(CO)_5]$ with these disulfides proceeded in predictable fashion to give the monomer species $Mn(SR)(CO)_5$ as initial products. It is possible to stop the reaction at this point if the reaction is run at a low temperature. When the solutions are warmed, however, two further reaction sequences take place. One sequence starts with a well-known reaction, CO loss and dimerization of the metal thiolate residue to form $Mn_2(\mu\text{-}SR)_2(CO)_8$. This product reacts in turn with [PPN]SPh to give $PPN[Mn_2(\mu\text{-}SR)_3(CO)_6]$. This behavior is also known;[3] the reaction is much slower than the initial dimerization, however, so it is easy to observe the intermediate species. The second reaction sequence produces an intermediate that we believe to be $PPN[Mn(SR)_2(CO)_4]$, based on an infrared pattern which is similar to that for known species $[MnX_2(CO)_4]^-$. In one instance (with R = CF_3) we were able to isolate an impure samples of this complex. However, the reactivity of these species is apparently appreciable; they are readily converted to $PPN[Mn_2(\mu\text{-}SR)_3(CO)_6]$. This latter species becomes the only product of $PPN[Mn(CO)_5]$–RSSR reactions which are run over longer periods of time. They are easily isolated as crystalline solids in moderate yields.

As noted above, this is apparently a new method for the synthesis of metal carbonyl thiolates. However there may be a mechanistic similarity to the reaction of metal carbonyl hydride and disulfides, a known procedure for synthesis of these compounds.[5h] In these reactions one can envision an initial equilibrium between the protonic metal carbonyl "hydride" and the anion, with disulfide functioning as the base to deprotonate the former species. Reaction of the anion with excess disulfide (or for that matter with the protonated disulfide) would give the product species.

A useful extension to this synthetic methodology for metal carbonyl thiolate complexes is provided by another RSY reagent, the species $[Me_2SSMe]BF_4$. This species is often characterized as a donor of the electrophilic group MeS^+.[19] Reactions involving MeS^+ donation are mechanistically similar to the reactions described above, however, in that they involve nucleophilic displacement of a group bonded to the RS^+ group, which in this instance is molecular Me_2S. Dimethyl sulfide is, of course, a better leaving group than RS^-, and consequently, reactions of this species are much faster.[18] It should be possible to use this reagent in reactions with weakly nucleophilic species that do not react with disulfides. Furthermore, difficulties caused by the presence of RS^- such as were encountered in the reactions of $PPN[Mn(CO)_5]$ should not be a problem. Dimethyl sulfide is a weaker base, and it is also volatile and can easily escape the system.

The comparison of rates of nucleophilic displacement in reactions with MeSSMe and $[Me_2SSMe]BF_4$ is easily made. For example the reaction of the former species with $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ requires 34 h. With $[Me_2SSMe]BF_4$, the quantitative formation of $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$ took place in the time required for mixing. Likewise, the reaction of $[Me_2SSMe]BF_4$ with $PPN[Mo(CO)_3(\eta\text{-}C_5H_5)]$ to form $Mo(SMe)(CO)_3(\eta\text{-}C_5H_5)$ was very fast whereas little reaction of the molybdenum complex with MeSSMe occurred in 48 h at room temperature. Use of $[Me_2SSMe]BF_4$ rather than MeSSMe in a reaction of $PPN[Mn(CO)_5]$ at room temperature produced an excellent yield of $Mn_2(\mu\text{-}SMe)_2(CO)_8$; $PPN[Mn_2(\mu\text{-}SMe)_3(CO)_6]$, the isolated product of the $PPN[Mn(CO)_5]$–MeSSMe reaction, was not seen.

The use of $[Me_2SSMe]BF_4$ is accompanied by several limitations, however. The first is that there are not many reagents of this type known; indeed only this species and $[Et_2SSEt]BF_4$ appear to be well characterized at this time. These reagents are not commercially available, and a several step synthesis is required for their preparation. The most serious limitation, however, is that when an excess of this reagent is present, a second subsequent reaction occurs. This is the rapid transfer of the RS^+ group in the excess reagent to any basic site in the product. In the case of metal thiolate species, the initial products in these systems, this means adding the RS^+ group to the lone pair of the thiolate ligand, thereby forming a complex with

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a dialkyl disulfide ligand. This type of product often has, predictably, a rather low stability to ligand loss and when this is so decomposition of this product is the direct consequence.

The formation and properties of metal complexes having disulfide ligands is an interesting subject. We defer a discussion of this chemistry to a subsequent paper.

One additional result merits comment, in that it portends some further interesting study. This concerns the reaction between $[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$ and $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ which occurs according to 7. The

$$[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4 + PPN[W(CO)_3(\eta\text{-}C_5H_5)] \rightarrow 2W(SMe)(CO)_3(\eta\text{-}C_5H_5) + [PPN]BF_4 \quad (7)$$

rapid formation of the product must come about from nucleophilic attack on the coordinated disulfide ligand. Two alternative reactions, displacement of a ligand in the cation by the nucleophilic anion or electron transfer, do not appear to be a significant factor since $[W(CO)_3(\eta\text{-}C_5H_5)]_2$ is not seen as a product. Significantly the reaction is much faster (complete upon mixing) than the reaction of $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$ and MeSSMe (34 h for completion). In effect, coordination of the metal group to the disulfide has caused the ligand to be much more susceptible to nucleophilic cleavage; or if one prefers, the $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$ group is a better leaving group than SMe^-. Enhanced rates of nucleophilic cleavage upon coordination of a metal ion to a disulfide is a known phenomenon in the biochemical area; metal ions such as Hg^{2+}, Ag^+, and $MeHg^+$ greatly enhance rates of cleavage of disulfide linkages.[20] A similar result was recently documented in cobalt(III) coordination chemistry.[21] It seems desirable to look further at this interesting reaction of a coordinated ligand.

Registry No. $PPN[W(CO)_3(\eta\text{-}C_5H_5)]$, 100312-14-9; $W(SPh)(CO)_3(\eta\text{-}C_5H_5)]$, 12110-93-9; $W(SCF_3)(CO)_3(\eta\text{-}C_5H_5)]$, 35828-05-8; $W(SMe)(CO)_3(\eta\text{-}C_5H_5)$, 12108-26-8; $PPN[Mo(CO)_3(\eta\text{-}C_5H_5)]$, 67486-18-4; $Mo(SPh)(CO)_3(\eta\text{-}C_5H_5)$, 100312-15-0; $[Mo(\mu\text{-}SPh)(CO)_2(\eta\text{-}C_5H_5)]_2$, 12115-34-3; $Mo(SCF_3(CO)_3(\eta\text{-}C_5H_5)$, 35828-04-7; $Mo(SMe)(CO)_3(\eta\text{-}C_5H_5)$, 12108-24-6; $[Mo(M\text{-}SMe)(CO)_2(\eta\text{-}C_5H_5)]_2$, 12112-22-0; $PPN[Mn(CO)_5]$, 52542-59-3; $PPN[Mn_2(\mu\text{-}SPh)_3(CO)_6]$, 100334-04-1; $Mn(SPh)(CO)_5$, 100312-16-1; $Mn_2(\mu\text{-}SPh)_2(CO)_8$, 21240-14-2; $Mn(SCF_3)(CO)_5$, 50979-57-2; $PPN[Mn(SCF_3)_2(CO)_4]$, 100312-18-3; $PPN[Mn_2(\mu\text{-}SCF_3)_3(CO)_6]$, 100312-20-7; $PPN[Mn_2(\mu\text{-}SMe)_3(CO)_6]$, 100312-21-8; $[W(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$, 100312-23-0; $[Mo(MeSSMe)(CO)_3(\eta\text{-}C_5H_5)]BF_4$, 100312-25-2; $Mn_2(\mu\text{-}SMe)_2(CO)_8$, 21321-38-0; $Mn(SMe)(CO)_5$, 66672-68-2; $Mn(CO)_5(MeSSMe)]BF_4$, 100312-27-4; PhSSPh, 882-33-7; CF_3SSCF_3, 372-64-5; MeSSMe, 624-92-0; $[Me_2SSMe]BF_4$, 5799-67-7.

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Synthesis, Structure, and Reactivity of Some (σ-Allenyl)- and (σ-Prop-2-ynyl)palladium(II) Complexes

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Prop-2-ynylic halides, $R^1R^2CXC{\equiv}CR^3$ (**1**, X = Cl, Br), react with $Pd[PPh_3]_4$ to yield pure *trans*-(σ-allenyl)bis(triphenylphosphine)palladium(II) halides, $R^1R^2C{=}C{=}CR^3Pd[PPh_3]_2X$ (**3**), when R^3 is hydrogen. The acetylenic isomers *trans*-$R^3C{\equiv}CCR^1R^2Pd[PPh_3]_2X$ (**4**) are obtained pure when R^3 is a bulky group, e.g., *t*-C_4H_9 and $(CH_3)_3Si$, and R^1 and R^2 are both hydrogen. A mixture of both isomers is formed when R^3 is methyl and R^1 and R^2 are both hydrogen. Prop-2-ynylic acetates, $R^1R^2CXC{\equiv}CR^3$ (**1**, X = OAc), can also be used to prepare the palladium(II) complexes, but salts like zinc or lithium chloride must be present to let the conversion proceed. The formation of **3** from **1** takes place with anti stereoselectivity. In a number of cases adducts **3** have been prepared by reaction of allenic halides, $R^1R^2C{=}C{=}CR^3X$ (**2**, X = Cl, Br), with $Pd[PPh_3]_4$. This reaction occurs with inversion of configuration of the allenyl moiety. The reactivity of adducts **3** and **4** was studied by reacting them with organozinc compounds, R^4ZnX'. The reactions preferentially lead to allenes, $R^1R^2C{=}C{=}CR^3R^4$. The acetylenic isomers arise when the R^3 group is very bulky.

Introduction

In a series of investigations we and others have shown that prop-2-ynylic halides and esters and α-acetylenic oxirans as well as 1-haloallenes are converted smoothly into substituted allenes, $-\dot{C}{=}C{=}\dot{C}\text{-}R$, in which R is an unsaturated group, by reaction with an appropriate organometallic reagent, R–M, in the presence of $Pd[PPh_3]_4$ as a catalyst.[1] In this way allenes could be prepared, in which the R group is aryl, 1-alkenyl, 1,2-alkadienyl, 1-alkynyl, and 1,3-alkadiynyl.

It has been assumed that (σ-allenyl)palladium(II) complexes are intermediates in these reactions, an assumption which is not unreasonable as such complexes are known,

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