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SYNTHESIS AND REACTIONS OF SOME NEW THIOCARBOXAMIDO COMPLEXES OF MANGANESE AND MOLYBDENUM CARBONYLS

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Summary

Several thiocarboxamido complexes of manganese and molybdenum have been prepared by the reactions of metal carbonyl anions with dimethylthiocarbamoyl chloride, Me_2NCSCl. In these complexes the thiocarboxamido group is thought to be bound to the metal through both the carbon and sulfur atoms, acting as a three-electron donating ligand. The sulfur atom can be methylated without altering this mode of bonding. Reactions of some of these complexes with triphenylphosphine are described.

Introduction

Although reactions of carbonylmetallate anions and various carbamoyl chlorides have been used as a general route to carboxamidometal carbonyl derivatives [1], analogous reactions with thiocarbamoyl chlorides had not been reported prior to this work. Such reactions should offer a convenient route to thiocarboxamidometal complexes, including a number of compounds not available from the other reactions. Herein we describe studies on these reactions. A prior communication of our work has appeared [2].

When we began these studies, there were two previous reports of thiocarboxamido complexes. The species $C_5H_5Fe(CO)_2CSNHR$ (R = Me, Et) were obtained [3] from the appropriate primary amine and the thiocarbonyl complex $C_5H_5Fe(CO)_2(CS)^+$; and addition of HS^- to a coordinated isocyanide in $[Pt(CNMe)_2(PPh_3)_2](BF_4)_2$ was reported [4] to give $[Pt(CSNHMe)(CNMe)(PPh_3)_2]BF_4$. Subsequent to our work a number of additional thiocarboxamido complexes have been described. These include: (a) various $MX(CSNMe_2)(Phos)_2$ species (M = Pd, Pt; X = Cl, I; Phos = PPh_3, PPh_2Me) obtained from oxidative addition of dimethylthiocarbamoyl chloride to zerovalent $M(Phos)_4$ complexes followed in some cases by halide exchange; $[PdCl(CSNMe_2)P(OMe)_3]_2$, obtained by the analogous reaction with $Pd[P(OMe)_3]_4$;

$[M_2(CSNMe_2)_2(Phos)_4](BF_4)_2$, (M = Pd, Pt), obtained from $MCl(CSNMe_2)(Phos)_2$ and aqueous HBF_4 [5]; (b) the nickel complex, $NiCl(CSNMe_2)(PPh_3)_2$ also obtained by a route involving oxidative addition [6]; and (c) $[Mo(CSNPr_2)(S_2CNPr_2)S]_2$, obtained from a rearrangement of the dipropyl thiocarbamate ion with molybdenum(II) acetate [7].

Results and discussion

Reactions of dimethylthiocarbamoyl chloride and various carbonylmetallate anions gave the following products in good yield: $Mn(CO)_4CSNMe_2$ (from $Mn(CO)_5^-$); $Mn(CO)_3(PPh_3)CSNMe_2$ (from $Mn(CO)_4PPh_3^-$); and $C_5H_5Mo(CO)_2CSNMe_2$ (from either $C_5H_5Mo(CO)_3^-$ or $C_5H_5Mo(CO)_2PPh_3^-$). These stoichiometries, which lack one carbonyl from the formulation that would be predicted assuming that the thiocarboxamido group is a simple one electron donor and that the EAN rule* is obeyed, were established using a variety of data. Analyses were generally appropriate though distinction between this formula and a formula having an additional carbonyl was not possible. For the compounds not containing a triphenylphosphine, mass spectrometry gave a parent peak of the correct mass number. In addition, the pattern of absorptions associated with $\nu(CO)$ were in accord with the assigned stoichiometry and stereochemistry. Thus for $Mn(CO)_4CSNMe_2$ four $\nu(CO)$ absorptions at 2079s, 2056s, 1992s and 1941s cm^{-1} were observed; this pattern is quite similar to that seen for *cis*-$M(CO)_4L_2$ species but inappropriate for a $M(CO)_5X$ species, for which one expects peaks at about 2100w, 2000vs, and 1990s. Two $\nu(CO)$ absorptions, rather than three, were observed for $C_5H_5Mo(CO)_2CSNMe_2$.

In view of the previous report of a thiocarboxamido group serving as a ligand bridging between two metals [5], it was important to establish molecular weight data. This was done both by mass spectrometry and osmometric measurements on solutions; together these results leave little doubt about the monomeric nature of these complexes.

Given the data at hand, one has either the choice of postulating a non-EAN formulation for these species; or alternatively, one could allow both carbon and sulfur to coordinate to the metal, in which case the $CSNMe_2$ group would formally become a three electron donor. Our distinct preference is toward the latter structure. Non-EAN rule complexes, particularly having so simple a stoichiometry, are rare. Moreover one would anticipate with such a structure a substantial tendency to add another ligand to become coordinately saturated; this apparently does not happen. The formulation containing a chelating $CSNR_2$ ligand receives additional support from the subsequent structural determination of $[Mo(CSNPr_2)(S_2CNPr_2)S]_2$ by X-ray crystallography [7]. In this compound the $CSNR_2$ group functions in the same capacity.

The structures proposed for these thiocarboxamido complexes is reminiscent of the structure proposed for metal complexes of CS_2 [8 - 13]; in these latter species carbon and one sulfur coordinate to a single metal. Formally, CS_2

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* EAN rule = effective atomic number rule.

in these compounds is functioning as a two electron donor however, in contrast to the behavior as three electron donors suggested here.

The NMR spectra of the thiocarboxamido species show two methyl proton resonances, indicating that the methyl groups are not equivalent. This fact can best be accommodated by assuming substantial carbon—nitrogen multiple bond character; this implies delocalization of the π electron system over the sulfur—carbon—nitrogen framework. Equivalence of the methyl groups is prevented by the restriction of rotation of the carbon—nitrogen bond. The observation of restricted rotation around the carbon—nitrogen bond in σ-bonded carboxamido and thiocarboxamido complexes was noted earlier [5].

The complexes $C_5H_5Mo(CO)_2CSNMe_2$ and $Mn(CO)_3(PPh_3)CSNMe_2$ react with $[Me_3O]BF_4$ to give the ionic complexes $[C_5H_5Mo(CO)_2C(SMe)NMe_2]^+$ (eventually isolated as the PF_6^- salt) and $[Mn(CO)_3(PPh_3)C(SMe)NMe_2]BF_4$ respectively. Proton NMR spectra of these species show a new methyl resonance but otherwise little difference from the spectra of the precursors. The methyl groups on nitrogen remain non-equivalent. Infrared spectra are also little changed. The values of ν(CO) are shifted to higher frequency as expected with the overall charge of the complex; thus for the molybdenum species carbonyl absorptions are seen at 2006s and 1935s cm^{-1}, in contrast to values of 1934s and 1841s cm^{-1} measured for $C_5H_5Mo(CO)_2CSNMe_2$. In addition there is a shift to higher frequency of a strong peak associated with the thiocarboxamido group [3] from about 1570 to about 1620 cm^{-1}.

Methylation at nitrogen would seem to be ruled out by the NMR data since a species derived by such a reaction would presumably have equivalent methyl groups, with restriction in rotation of a carbon—nitrogen single bond being unlikely. In a sense, this result is surprising. It is known that protonation of many carboxamidometal complexes occurs at nitrogen with consequent loss of NHR_2 (or $NH_2R_2^+$ in acid solution) and generation of a metal carbonyl complex [14]. However such reactions are apparently not general for thiocarboxamido species; attempted protonation by HBF_4 of $MCl(CSNMe_2)L_2$ species [5] was accompanied by HCl loss and formation of the ionic dinuclear complexes $[M_2(CSNMe_2)_2L_4]^{2+}$. In contrast, protonation of the species $C_5H_5Fe(CO)_2CSX$, (X = OR, SR, NHMe) does cleave the group [15] to give a thiocarbonyl derivative, $[C_5H_5Fe(CO)_2CS]^+$.

The only apparent alternatives to methylation at nitrogen would be methylation either at sulfur or at the carbon of the thiocarboxamido group. The latter would yield a metal complex of the ligand dimethylthioacetamide, $MeCSNMe_2$. We cannot entirely rule out this possibility at present, and indeed there are analogous complexes known, including a number of nickel, palladium and platinum derivatives $ML_2(R_2C{=}X)$; (X = S, O, NH; R = CF_3) [16,17]. In these species the $R_2C{=}X$ group bonds to the metal utilizing the π electrons of the C=X group; this ligand is formally a two electron donor. If the complexes in question did indeed have such a ligand group they would be coördinately unsaturated; again we are predisposed against this prediction since the compounds are not inclined to add an additional ligand.

The other possible structure, involving alkylation at sulfur, is suggested by the formulas given above for these species. The alkylation at sulfur would not be expected to substantially influence either the geometry or the electronic structure of the complex.

If indeed this proposed structure is correct, another interesting contrast ought to be made. It appears that the same sort of ligand group is seen in at least one other instance, the complex $[Pt(CNMe)_2\{C(SEt)NHMe\}_2](PF_6)_2$ [18]. However in this instance the C(SEt)NHMe groups are bonded to the metal only through carbon; the ligand is thus of the carbenoid type.

Reactions of the compounds $Mn(CO)_4CSNMe_2$ and $[(C_5H_5)Mo(CO)_2$-$C(SMe)NMe_2]PF_6$ and triphenylphosphine were carried out. In each instance the reaction occurred with carbonyl displacement, rather than with displacement of the thiocarboxamido ligand or with addition.

Experimental

Various starting materials, including $Mn_2(CO)_8(PPh_3)_2$ [19] and $C_5H_5Mo(CO)_2(PPh_3)I$ [20], were prepared as described in the literature. Dimethylthiocarbamoyl chloride was obtained from the Aldrich Chemical Company.

All reactions were carried out under a nitrogen atmosphere. Tetrahydrofuran was distilled from lithium aluminium hydride and benzene was distilled from calcium hydride before use. Dichloromethane was dried over silica gel. Other solvents were used as obtained but were saturated with nitrogen before use.

Carbonyl stretching frequencies were recorded in solution using a Perkin—Elmer model 421 high-resolution spectrophotometer. Other regions of the infrared spectrum were recorded as Nujol or Fluorolube mulls with a Beckman IR-10 spectrophotometer. Proton NMR data were obtained using a Varian T-60 spectrometer. Molecular weights were determined, when possible, by mass spectroscopy (using an AEI MS-902 mass spectrometer) or using a Mechrolab vapor pressure osmometer. Analyses were carried out by the Meade Microanalytical Laboratory, Amherst, Mass.

Preparation of $Mn(CO)_4CSNMe_2$

A solution of $Na[Mn(CO)_5]$ was prepared by reducing 8.00 g of $Mn_2(CO)_{10}$ (20.2 mmol) in 400 ml of tetrahydrofuran with excess sodium amalgam. The solution was cooled to −78°C and a solution of 5.00 g $ClCSNMe_2$ (40.4 mmol) in 50 ml of tetrahydrofuran was added. The mixture was allowed to warm to room temperature overnight, and the solvent was removed. The residue was recrystallized twice from tetrahydrofuran at −78°C. The product was obtained as brown crystals, mp. 120 - 121°C. Yield, 6.45 g (25.3 mmol, 62.7%).

Anal.: Found: C, 33.9; H, 2.36; N, 4.78; S, 11.1; mol. wt., 255 (mass spec.). $C_7H_6NSO_4Mn$ calcd. C, 32.9; H, 2.35; N, 5.48; S, 12.2%; mol. wt., 255.

Infrared data: ν(CO) ($CHCl_3$): 2079s, 2056s, 1992s, 1941s cm^{-1}. Other bands: 2940w, 1684m, 1638s, 1570s, 1443w, 1402s, 1243m, 1169s, 1020s, 908s, 761s, 720w, 677s, 649s, 626s cm^{-1}.

NMR data: ($CDCl_3$) τ6.54, singlet, NCH_3(1); 6.80, singlet, NCH_3(2).

Preparation of $Mn(CO)_3(PPh_3)CSNMe_2$

(A). A solution of $Na[Mn(CO)_4PPh_3]$ was prepared by the reduction of 8.67 g $Mn_2(CO)_8(PPh_3)_2$ (10.1 mmol) in 500 ml of tetrahydrofuran with excess sodium amalgam. The solution was cooled to −78°C and a solution of $ClCSNMe_2$ was added. The mixture was allowed to warm to room temperature overnight. The solvent was then removed and the residue was chromatographed over alumina. One yellow band eluted with benzene. The product was obtained as orange-yellow crystals from toluene–heptane, m.p. 148 - 150°C. Yield, 7.50 g (15.35 mmol, 76.0%).

(B). The same product was obtained by the reaction of 0.60 g of $Mn(CO)_4CSNMe_2$ (2.36 mmol) with 0.68 g of triphenylphosphine (2.59 mmol) in 75 ml of benzene at room temperature for 72 h. The product was worked up as above. Yield, 0.54 g (1.105 mmol, 46.9%).

Anal.: Found: C, 58.5; H, 4.26; N, 2.91; P, 6.58; S, 7.26; mol. wt., 455 (osmometry). $C_{24}H_{21}NSO_3PMn$ calcd.: C, 58.9; H, 4.29; N. 2.86; P, 6.34; S, 6.54%; mol. wt., 489.

Infrared data: ν(CO) ($CHCl_3$): 2005s, 1926s, 1885s cm^{-1}. Other bands: 2924vw, 1642vw, 1572s, 1475s, 1426s, 1392s, 1219vw, 1163w, 1079w, 908m, 814s, 735m, 713vw, 684m, 656m, 625m, 605m cm^{-1}.

NMR data: ($CDCl_3$) τ2.64, multiplet, C_6H_5; 6.73, singlet, NCH_3(1), 7.05, singlet, NCH_3(2).

Preparation of $C_5H_5Mo(CO)_2CSNMe_2$

(A). A solution of $Na[C_5H_5Mo(CO)_3]$ was prepared by reducing 10.0 g of $[C_5H_5Mo(CO)_3]_2$ (20.2 mmol) in 500 ml of tetrahydrofuran with excess sodium amalgam. The solution was cooled to −78°C and a solution of 5.00 g of $ClCSNMe_2$ (40.4 mmol) in 50 ml of tetrahydrofuran was added. The solution was allowed to warm to room temperature overnight, the solvent was removed, and the residue was chromatographed over alumina. 1/3 chloroform/hexane eluted a pink band of $[C_5H_5Mo(CO)_3]_2$ (0.20 g, 0.202 mmol, 2% recovery). 1/2 chloroform/hexane eluted an orange band of the product, which was obtained as red-brown crystals from heptane, m.p. 110 - 111°C. Yield, 9.10 g 29.9 mmol, 75.5%).

(B). The same product was obtained by the reaction of $Na[C_5H_5Mo(CO)_2PPh_3]$ (produced by the reduction of 12.23 g of $C_5H_5Mo(CO)_2(PPh_3)I$ (20.2 mmol) in 500 ml of tetrahydrofuran with excess sodium amalgam) with 2.50 g of $ClCSNMe_2$ (20.2 mmol) as described above. Yield, 4.15 g (13.62 mmol), 67.5%).

Anal.: Found: C, 39.4; H, 3.74; N, 4.29; S, 11.6; mol. wt., 305 (mass spec.). $C_{10}H_{11}NSO_2Mo$ calcd.: C, 39.3; H, 3.60; N, 4.59; S, 10.5%; mol. wt., 305.

Infrared data: ν(CO) ($CHCl_3$): 1934s, 1841s cm^{-1}. Other bands: 2920vw, 1573s, 1447w, 1414w, 1399m, 1226m, 1167s, 1010m, 1002m, 915m, 840w, 820w(sh), 812s, 797s, 615m cm^{-1}.

NMR data: ($CDCl_3$) τ4.58, singlet, C_5H_5; 6.27, singlet, NCH_3(1); 6.40, singlet, NCH_3(2).

Preparation of $[Mn(CO)_3(PPh_3)C(SMe)NMe_2]BF_4$

A solution of 2.01 g of $Mn(CO)_3(PPh_3)CSNMe_2$ (4.12 mmol) was stirred with 0.67 g of $[Me_3O]BF_4$ (4.53 mmol) in 100 ml of dichloromethane for 18 h. The solvent was then removed and the residue was washed with water and with ether and then recrystallized from acetone—ether. The product was obtained as yellow crystals, m.p. 172 - 174°C. Yield, 1.81 g (2.60 mmol, 63.3%).

Anal.: Found: C, 50.8; H, 4.13; N, 2.31; P, 5.25; S, 5.51. $C_{25}H_{21}NSO_3$-PBF_4Mn calcd.: C, 50.8; H, 4.06; N, 2.37; P, 5.24; S, 5.41%.

Infrared data: ν(CO) (acetone): 2050s, 1983s, 1942s cm^{-1}. Other bands: 1622s, 1566w, 1480m, 1438m, 1409w, 1306w, 1279w, 1203w, 1181w, 1159m, 1088s, 1050vs, 1020(sh), 991m, 781m, 752m, 745m, 714w, 600m, 890m, 665vw, 641m, 619m, 601m cm^{-1}.

NMR data: (acetone-d_6) τ2.56, multiplet, C_6H_5; 6.25, singlet, NCH_3(1); 6.39, singlet, NCH_3(2); 7.52, singlet, SCH_3.

Preparation of $[C_5H_5Mo(CO)_2C(SMe)NMe_2]PF_6$

A mixture of 1.37 g of $C_5H_5Mo(CO)_2CSNMe_2$ (4.44 mmol) and 0.726 g of $[Me_3O]BF_4$ (4.88 mmol) was stirred in 100 ml of dichloromethane for 18 h. The solvent was removed and the residue was dissolved in water. The product was precipitated as the hexafluorophosphate salt by the addition of an aqueous solution of NH_4PF_6. The product was obtained as orange crystals from acetone—ether, m.p. 168 - 169°C. Yield, 1.52 g (3.25 mmol, 73.4%).

Anal.: Found: C, 28.4; H, 3.02; N, 3.03; S, 4.59. $C_{11}H_{14}NSO_2PF_6Mo$ calcd.: C, 29.0; H, 3.01; N, 3.01; S, 6.88%.

Infrared data: ν(CO) (acetone): 2006s, 1935s cm^{-1}. Other bands: 3122m, 1616s, 1555m, 1446m, 1420m, 1400s, 1342w, 1322m, 1204s, 1155s, 1030m, 1001m, 965m, 835vs, 772(sh), 715(sh) cm^{-1}.

NMR data: (acetone-d_6) τ3.98, singlet, C_5H_5; 5.97, singlet, NCH_3(1); 6.07, singlet, NCH_3(2); 7.65, singlet, SCH_3.

Preparation of $[C_5H_5Mo(CO)(PPh_3)C(SMe)NMe_2]PF_6$

This compound was obtained by irradiating a solution of 1.00 g of $[C_5H_5Mo(CO)_2C(SMe)NMe_2]PF_6$ (2.14 mmol) and 0.62 g of triphenylphosphine (2.36 mmol) in 50 ml of acetone for 25 h (GE H100 PSP44-4 lamp, Pyrex flask). The solvent was removed and the residue was washed with ether and recrystallized from acetone—ether. Bright red crystals of the product formed slowly at —20°C, m.p. 191 - 193°C. Yield, 0.30 g (0.43 mmol, 20.1%).

Anal.: Found: C, 47.8; H, 4.22; N, 1.80; P, 8.75; S, 4.57. $C_{28}H_{29}NSP_2$-OF_6Mo calcd.: C, 48.0; H, 4.15; N, 2.00; P, 8.86; S, 4.58%.

Infrared data: ν(CO) (acetone): 1895s cm^{-1}. Other bands: 3135vw, 3065vw, 2939vw, 2875vw, 1714vw, 1590s, 1552s, 1480m, 1435s, 1397s, 1309m, 1215w, 1183w, 1154s, 1089s, 1064m, 1039vw, 1019w, 1002vw, 995vw, 920w, 834vs, 784w, 752m, 742m, 720w, 694s cm^{-1}.

NMR data: (acetone-d_6) τ2.50, multiplet, C_6H_5; 4.47, singlet, C_5H_5, 6.12, singlet, NCH_3(1); 6.22, singlet, NCH_3(2); 8.15, singlet, SCH_3.

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