Reactions of the SH^- and S^{2-} Groups in $W(CO)_5(SH)^-$ and μ-$S[W(CO)_5]_2^{2-}$

Richard G. W. Gingerich and Robert J. Angelici*

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received March 26, 1979*

Abstract: The mononuclear $W(CO)_5(SH)^-$ and SH^- bridged binuclear μ-$HS[W(CO)_5]_2^-$ complexes have been prepared by reaction of SH^- with $W(CO)_6$. The $W(CO)_5(SH)^-$ complex reacts with acetic anhydride and 2,4-dinitrophenyl acetate to give the thioacetate complex, $MeC(=O)SW(CO)_5^-$. The reactivity of the SH^- group is also demonstrated by the reaction of this complex with aliphatic ketones and aromatic aldehydes to yield thioketone, $W(CO)_5(S{=}CR_2)$, and thioaldehyde, $(ArCHS)W(CO)_5$, complexes of these otherwise unstable organic molecules. While the SH^- group in μ-$HS[W(CO)_5]_2^-$ is considerably less reactive, deprotonation with strong base gives an S^{2-}-bridged dimer, μ-$S[W(CO)_5]_2^{2-}$, which readily reacts with halo compounds, E-Cl, to give the corresponding sulfur-bridged complexes, μ-E-$S[W(CO)_5]_2^-$, where E = Me_3Sn, MeHg, MeC(=O), $PhCH_2$, or Ph_2P. All of the new compounds have been characterized spectroscopically.

Introduction

Although few were known until recently,[1] complexes containing H_2S,[2,3] SH^-,[4] and S^{2-} ligands[5] have now become of considerable interest. Activity in this area stems from the novelty of these complexes and their potential for serving as models for biological systems.[1] Still lacking, however, are studies of the reactivity of these sulfur groups in metal complexes.[2,6]

In the present paper, we report reactions of $W(CO)_5(SH)^-$ and μ-$S[W(CO)_5]_2^{2-}$ which demonstrate that the SH^- and S^{2-} groups in these complexes are highly reactive and allow the preparation of new and unusual sulfur-coordinated ligands.

Results and Discussion

Preparation and Properties of $M(CO)_5(SH)^-$, M = Cr, Mo, or W, and μ-$HS[W(CO)_5]_2^-$. The $M(CO)_5(SH)^-$ complexes were prepared by the direct reaction of $M(CO)_6$ with $[(Ph_3P)_2N][SH]$:

$$M(CO)_6 + [(Ph_3P)_2N]SH \rightarrow [(Ph_3P)_2N][M(CO)_5(SH)] + CO \quad (1)$$

Infrared, ^1H and ^{13}C NMR spectra, and solution conductivities are consistent with their formulation as octahedral $M(CO)_5(SH)^-$ complexes. The ν(CO) frequencies (2056 w, 1912 vs, 1843 m cm^{-1}) of $[(Ph_3P)_2N][W(CO)_5(SH)]$ are significantly lower than those (2064 w, 1923 s, 1902 sh cm^{-1})[7] of the analogous hydroxo complex, [dibenzo-18-crown-6-K]-$[W(CO)_5(OH)]$, suggesting that the more polarizable SH^- group is a stronger electron donor than OH^-. Although the tungsten complex was prepared previously as the $[Et_4N]$-$[W(CO)_5(SH)]\cdot CH_2Cl_2$ salt from $W(CO)_5(SH_2)$,[2] the synthesis shown in eq 1 gives the product in much higher yield (93%). The solid tungsten compound was stable in air for over 1 month; the yellow chromium analogue developed a green coloration in air within 4 h, while $[(Ph_3P)_2N][Mo(CO)_5(SH)]$ was too unstable to be isolated pure.

The mechanism of reaction 1 cannot involve rate-determining CO dissociation from $W(CO)_6$ because this dissociation is known[8] to proceed much more slowly than reaction 1. To confirm this, we observed that there is no reaction between $W(CO)_6$ and Ph_3P under the conditions (refluxing THF for 1 h) of reaction 1. This suggests that reaction 1 involves nucleophilic attack of SH^- on the complex, analogous to that proposed[9] for the I^- reaction with $W(CO)_6$ or $W(CO)_5(CS)$ to give $W(CO)_5I^-$ or *trans*-$W(CO)_4(CS)I^-$.

In an attempt to prepare the known[2] $W(CO)_5(SH_2)$ by protonation of $W(CO)_5(SH)^-$, 0.055 mmol of $[(Ph_3P)_2N]$-$[W(CO)_5(SH)]$ and 0.023 mmol of CF_3SO_3H were reacted in 0.6 mL of $CDCl_3$ in an NMR tube. An ^1H NMR spectrum of the solution showed the formation of μ-$HS[W(CO)_5]_2^-$ (τ 11.74, 32% yield) (see below) and H_2S (τ 9.20)[10] according to the equation

$$2[W(CO)_5(SH)]^- + CF_3SO_3H \rightarrow \mu\text{-}HS[W(CO)_5]_2^- + H_2S + CF_3SO_3^- \quad (2)$$

We found no evidence for the formation of $W(CO)_5(SH_2)$.

The most convenient and highest yield (84%) route to μ-$HS[W(CO)_5]_2^-$ was that involving the reaction of $W(CO)_6$ and NaSH in refluxing diglyme/THF according to the equation

$$2W(CO)_6 + NaSH \rightarrow Na[\mu\text{-}HS[W(CO)_5]_2] + 2CO \quad (3)$$

The complex anion was isolated as the $[Et_4N][\mu$-$HS[W(CO)_5]_2]$ salt. Reaction stoichiometry did not dictate the nature of the product since equimolar NaSH and $W(CO)_6$ reaction mixtures gave μ-$HS[W(CO)_5]_2^-$ exclusively with no evidence for $W(CO)_5(SH)^-$. The yellow solid $[Et_4N][\mu$-$HS[W(CO)_5]_2]$ is stable under vacuum but develops a green coloration when exposed to air for 12 h.

The binuclear anion, μ-$HS[W(CO)_5]_2^-$, is believed to have the structure in which the sulfur atom bridges both $W(CO)_5$ moieties. This is analogous to the structure of μ-$I[Cr(CO)_5]_2^-$, which has been established by an X-ray investigation,[11] and also to that proposed for the μ-$RS[W(CO)_5]_2^-$ complexes (R = CH_3, CH_2Ph, or Ph).[12] The pattern of six ν(CO) absorptions in the infrared spectrum of μ-$HS[W(CO)_5]_2^-$ is very similar to that of the above two complexes. The ^{13}C NMR spectrum of $[Et_4N][\mu$-$HS[W(CO)_5]_2]$ shows only two types of ^{13}CO groups, assignable to the cis and trans CO ligands in the equivalent $W(CO)_5$ moieties. In the ^1H NMR spectrum, the HS proton is observed downfield (τ 11.70) from that (τ 12.93) of $W(CO)_5(SH)^-$, which suggests that the additional $W(CO)_5$ group in μ-$HS[W(CO)_5]_2^-$ reduces electron density at the HS proton.

Reactions of $W(CO)_5(SH)^-$. Although the free SH^- ion is a well-known nucleophile,[13] very little is known about the reactivity of coordinated SH^-. That the SH^- ligand in $W(CO)_5(SH)^-$ is indeed reactive is shown by its room temperature reaction with acetic anhydride to give the corresponding thioacetate complex in 68% yield after 30 min:

$$W(CO)_5(SH)^- + (MeCO)_2O \rightarrow MeC(=O)SW(CO)_5^- + MeCO_2H \quad (4)$$

Similarly, it reacts with 2,4-dinitrophenyl acetate to give the product in 48% yield:

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$$W(CO)_5(SH)^- + 2,4\text{-}(NO_2)_2C_6H_3O_2CMe \rightarrow MeC(=O)SW(CO)_5^- + (NO_2)_2C_6H_3OH \quad (5)$$

However, no reaction occurred with phenyl or ethyl acetate, and reaction with acetyl chloride gave $W(CO)_5Cl^-$.[14] Although reactions 4 and 5 could proceed via SH^- dissociation from $W(CO)_5(SH)^-$, followed by SH^- reaction with the acylating agent and then recombination of the resulting $MeC(=O)S^-$ with the complex to give the product, evidence indicates that the SH^- group does not dissociate sufficiently rapidly from $W(CO)_5(SH)^-$ to allow the reaction to proceed by this pathway. For example, $[(Ph_3P)_2N][W(CO)_5(SH)]$ reacts with equimolar Ph_3P in THF at room temperature to give only 25% yield of $W(CO)_5(Ph_3P)$ even after 48 h. Thus it appears that the coordinated SH^- group behaves as the nucleophile in reactions 4 and 5.

The $[(Ph_3P)_2N][MeC(=O)SW(CO)_5]$ complex is most readily prepared by direct reaction of $W(CO)_6$ and $[(Ph_3P)_2N][MeC(=O)S]$ in refluxing THF. Its infrared, ^1H and ^{13}C NMR spectra, and solution conductivity are consistent with a structure in which the thioacetate ligand is monodentate coordinating through the sulfur atom. The $\nu(C{=}O)$ absorption of the coordinated ligand is observed at 1604 cm^{-1} in the infrared spectrum of the compound in a KBr pellet.

The $[(PPh_3)_2N][W(CO)_5(SH)]$ complex also reacts rapidly with ketones upon addition of acid to give thioketone complexes according to the equation

$$W(CO)_5(SH)^- + R_2C{=}O + 2CF_3SO_3H \rightarrow W(CO)_5(S{=}CR_2) + H_2O + CF_3SO_3^- \quad (6)$$

Magnesium sulfate was added to absorb the H_2O formed in these reactions. When 0.556 mmol of $[(Ph_3P)_2N][W(CO)_5(SH)]$ and excess $MgSO_4$ were added to 15 mL of acetone, there was no reaction; however, on addition of 1.2 mmol of CF_3SO_3H, the mixture immediately darkened, and a 24% yield of $W(CO)_5(S{=}CMe_2)$ was isolated by filtering, evaporating the solution to dryness, and subliming the red product crystals from the residue. The product was identical with that prepared by another route.[15] If the acetone was diluted with THF, the yield was reduced substantially. Also if only 1 mol of acid per mol of $W(CO)_5(SH)^-$ was used, only a 14% yield of $W(CO)_5(S{=}CMe_2)$ was obtained.

Using methyl ethyl ketone or cyclohexanone instead of acetone in reaction 6 gave low yields (~10%) of $W(CO)_5(S{=}CMeEt)$ and $W(CO)_5(S{=}CC_5H_{10})$, respectively. These compounds were not isolated but identified by the similarity of their infrared spectra to that of $W(CO)_5(S{=}CMe_2)$.[15] While yields of aliphatic thioketone complexes prepared by reaction 6 are lower than those obtained from the reaction of $W(CO)_5I^-$, H_2S, $AgBF_4$, and ketone,[15] it does provide a new route to these unusual complexes which may be applied to the increasing number of available SH^- complexes.

Since most aliphatic thioketones cannot be isolated at room temperature because of their rapid oligomerization to polythianes,[16,17] their stabilization as ligands in metal complexes is of particular interest. Still less stable are aromatic and aliphatic thioaldehydes.[16,17] Metal complexes with thioaldehyde ligands are only known where the thioaldehyde is part of a chelating β-ketone–aldehyde or β-dialdehyde type of ligand.[18] We have now found that monodentate aromatic thioaldehyde complexes can be prepared by a reaction which is very similar to that used in the preparation of the thioketone complexes described above:

$$W(CO)_5(SH)^- + p\text{-}YC_6H_4CHO + CF_3SO_3H \rightarrow (p\text{-}YC_6H_4CHS)W(CO)_5 + H_2O + CF_3SO_3^- \quad (7)$$

where Y = Me_2N, MeO, or Me. Like the thioacetone complex preparation, there was no reaction between $W(CO)_5(SH)^-$ and the aldehyde until the acid was added, whereupon the solution immediately turned the purple color of the complexes in solution. Yields of the three complexes ranged from 32 to 52%. Following the same procedure, thioaldehyde complexes could not be isolated from reactions with the following aldehydes: PhCHO, p-ClC_6H_4CHO, p- or m-$O_2NC_6H_4CHO$, MeCHO, or $(CH_2{=}CH)CHO$. Although the mechanism of reaction 7 is unknown, it appears that only benzaldehydes with electron-releasing substituents undergo the reaction under the conditions described.

One of these complexes, $(p\text{-}MeOC_6H_4CHS)W(CO)_5$, could also be prepared from the corresponding Schiff base:

$$W(CO)_5(SH)^- + (p\text{-}MeOC_6H_4)CH{=}NPh + 2CF_3SO_3H \rightarrow (p\text{-}MeOC_6H_4CHS)W(CO)_5 + PhNH_3^+CF_3SO_3^- + CF_3SO_3^- \quad (8)$$

The addition of 1.13 mmol of CF_3SO_3H to a solution of 0.56 mmol of $[(Ph_3P)_2N][W(CO)_5(SH)]$ and 0.57 mmol of $(p\text{-}MeOC_6H_4)CH{=}NPh$ in 10 mL of THF gave, on workup, a 9% yield of the thioaldehyde product. The utility of this method is limited in this system since we found that significant amounts of thioaldehyde complexes were not formed with the following Schiff bases: PhCH=NPh, p-$O_2NC_6H_4CH{=}NPh$, p-$Me_2NC_6H_4CH{=}NPh$, MeCH=NBu-t, or $Me_2C{=}NOH$.

The solid thioaldehyde complexes, $(p\text{-}YC_6H_4CHS)W(CO)_5$, are stable under vacuum and upon short exposure to air. In solution their UV–visible absorptions are extremely intense with extinction coefficients ranging up to 47 800 M^{-1} cm^{-1}. Spectral data for the complexes are consistent with coordination of the ligand to the metal through the sulfur atom as was found for the thioketone complexes.[15,19] In the ^1H NMR spectra of the complexes, the formyl proton of the thioaldehyde ligand is observed in the range τ −1.11 to −0.58. Although these resonances are at unusually low field, they are comparable to those (τ −1.11 to −0.15) of the thioaldehyde group in organic compounds stabilized by α,β unsaturation.[20] In spite of the expected W-S-C angular bonding,[15] there is no evidence in the NMR spectra of the complexes which indicates the presence of isomers with the aryl group syn or anti to the tungsten atom. This suggests that either only one isomer is present or the two isomers interconvert rapidly.

In attempts to prepare $W(CO)_5L$ complexes of other thiocarbonyl ligands, $(H_2N)_2C{=}O$, ethyl acetate, and $MeC(=O)NH_2$ were reacted with $W(CO)_5(SH)^-$ and CF_3SO_3H; however, in each case only $[(Ph_3P)_2N][\mu\text{-}HS[W(CO)_5]_2]$ was isolated in high yield (~80%) according to eq 2. There was no evidence for thiocarbonyl ligand complexes.

Reactions of μ-$S[W(CO)_5]_2^{2-}$. The lower field position (see above) of the SH proton in μ-$HS[W(CO)_5]_2^-$ as compared to that in $W(CO)_5(SH)^-$ suggests that there is less electron density on the sulfur in the binuclear complex. This conclusion is also supported by the observation that μ-$HS[W(CO)_5]_2^-$ does not react with 2,4-dinitrophenyl acetate under conditions in which $W(CO)_5(SH)^-$ reacts rapidly according to eq 5. This lower nucleophilicity may be attributed both to the reduced electron density on the sulfur and to steric effects of the larger binuclear complex.

Consistent with a lower electron density on the sulfur, the SH proton in μ-$HS[W(CO)_5]_2^-$ is much more acidic than that of $W(CO)_5(SH)^-$. Thus a yellow THF solution of μ-$HS[W(CO)_5]_2^-$ turns the green color characteristic of μ-$S[W(CO)_5]_2^{2-}$ on reaction with equimolar NaOEt. In contrast, $[(Ph_3P)_2N][W(CO)_5(SH)]$ is not deprotonated even by a tenfold excess of NaOEt in THF. Nor does it give $W(CO)_5S^{2-}$ upon treatment with such strong bases as NaH or LiMe. The acidity of the SH proton of μ-$HS[W(CO)_5]_2^-$

appears to be intermediate between that of EtOH ($pK_a = 18$)[21] and MeOH ($pK_a = 16$)[21] since equimolar NaOMe in MeOH does not deprotonate the binuclear complex.

The μ-S[W(CO)$_5$]$_2^{2-}$ complex was most readily prepared by reaction with NaH in THF:

$$[Et_4N][\mu\text{-HS}[W(CO)_5]_2] + NaH \rightarrow Na[Et_4N][\mu\text{-S}[W(CO)_5]_2] + H_2 \quad (9)$$

One mole of H_2 gas per mol of complex was evolved and identified by gas chromatography. An infrared spectrum of the green product solution showed ν(CO) absorptions at 2051 (vw), 2038 (w), 1930 (sh), 1908 (vs), and 1852 cm^{-1} (m) with a pattern very similar to that of μ-HS[W(CO)$_5$]$_2^-$ except the positions of the peaks are approximately 20 cm^{-1} lower in the deprotonated complex. Reaction of the THF solution of μ-S[W(CO)$_5$]$_2^{2-}$ with O_2 in a sealed tube resulted in decomposition of the complex within 1.5 h. The addition of 15 equiv of H_2O to a THF solution of μ-S[W(CO)$_5$]$_2^{2-}$ at room temperature gave μ-HS[W(CO)$_5$]$_2^-$ quantitatively. Owing to its sensitivity to O_2 and H_2O, μ-S[W(CO)$_5$]$_2^{2-}$ was not isolated, but its reactions were studied in situ.

Unlike μ-HS[W(CO)$_5$]$_2^-$, the μ-S[W(CO)$_5$]$_2^{2-}$ complex behaved as a strong nucleophile toward electrophilic halo compounds:

$$\mu\text{-S}[W(CO)_5]_2^{2-} + E\text{-}Cl \rightarrow \mu\text{-E-S}[W(CO)_5]_2^- + Cl^- \quad (10)$$

where E = Me_3Sn, MeHg, MeC(=O), $PhCH_2$, or Ph_2P. The reaction of $PhSO_2Cl$ with μ-S[W(CO)$_5$]$_2^{2-}$ proceeded with the evolution of SO_2 gas to give a low yield (7%) of the known[12] μ-PhS[W(CO)$_5$]$_2^-$. The compounds are stable indefinitely under vacuum but decompose slowly in air. All of the compounds were characterized by their elemental analyses and infrared and ^{1}H NMR spectra. Their infrared spectra in the ν(CO) region all show the same pattern observed for μ-HS[W(CO)$_5$]$_2^-$, which supports structures in which the sulfur bridges both tungsten atoms. The ^{13}C NMR spectrum of μ-MeC(=O)S[W(CO)$_5$]$_2^-$ shows that the W(CO)$_5$ groups are equivalent as required by the sulfur-bridged structure. This latter complex may also be conveniently prepared in good yield (78%) from MeC(=O)SW(CO)$_5^-$ and W(CO)$_5$(acetone), generated from W(CO)$_5$I$^-$ and Ag^+ in acetone solvent:

$$MeC(=O)SW(CO)_5^- + W(CO)_5(\text{acetone}) \rightarrow MeC(=O)S[W(CO)_5]_2^- \quad (11)$$

The structure of μ-Ph_2PS[W(CO)$_5$]$_2^-$ was of interest because Lindner and Meier[22] showed that the reaction of Cr(CO)$_5$PMe_2S$^-$ with Cr(CO)$_5$(THF) gives Me_2P-S[Cr(CO)$_5$]$_2^-$, a complex suggested to have the structure in which the P and S atoms are coordinated to different Cr(CO)$_5$ groups, Cr-P-S-Cr. However, μ-Ph_2PS[W(CO)$_5$]$_2^-$ appears to have a sulfur-bridged structure based on its IR spectrum noted above, which is different than that[22] reported for Me_2PS[Cr(CO)$_5$]$_2^-$. In addition, the ^{31}P NMR spectrum of [Et_4N][μ-Ph_2PS[W(CO)$_5$]$_2$] in acetone-d_6 shows a strong absorption at δ −35.5 downfield from the H_3PO_4 external standard flanked by satellites separated by 242 Hz due to coupling with ^{183}W. The spectrum, which was unaffected by temperature over the range 200–300 K, is consistent with sulfur bridging of the two W(CO)$_5$ groups. A W-P-S-W structure would have given a five-line ^{31}P NMR spectrum.

In an attempt to prepare clusters with more than two metals, 2 equiv of μ-S[W(CO)$_5$]$_2^{2-}$ was reacted with 1 equiv of $PdCl_2(PPh_3)_2$ at room temperature. Only W(CO)$_5$(PPh_3) and W(CO)$_5$Cl$^-$ were identified as the major products of the reaction. Reactions of μ-S[W(CO)$_5$]$_2^{2-}$ with SCl_2 and NOCl did not give identifiable products. No reaction occurred between equimolar μ-S[W(CO)$_5$]$_2^{2-}$ and p-$Me_2NC_6H_4CHO$ in THF at 25 °C; however, on addition of 2 equiv of CF_3SO_3H, the mixture immediately turned purple and a 19% yield of (p-$Me_2NC_6H_4CHS$)W(CO)$_5$ was isolated. There was no evidence for a binuclear product with a bridging thioaldehyde ligand.

Experimental Section

General. Solution infrared spectra were obtained employing Perkin-Elmer 237 and 337 spectrophotometers. Band positions were calibrated with the 2147-cm^{-1} band of CO(g) and were accurate to within 3 cm^{-1}. A Beckman IR 4250 spectrophotometer was used for solid-phase spectra. ^{1}H NMR spectra were obtained with Varian A-60, Perkin-Elmer R 20B, and Varian HA-100 spectrometers. Peak positions are reported in τ (ppm) relative to tetramethylsilane (Me_4Si) internal standard. A Bruker HX-90E Fourier transform spectrometer employing proton decoupling was used to acquire ^{13}C and ^{31}P NMR spectra. Deuterated solvents served as the internal lock, and peak positions are reported in δ (ppm) relative to Me_4Si for the ^{13}C NMR spectra. Tris(acetylacetonate)chromium(III) (25 mg) was added to the sample solutions to improve the relative intensities[23] of the carbonyl carbon absorptions. Phosphorus-31 resonances are reported in δ (ppm) relative to phosphoric acid, an external standard.

Visible spectra were obtained on a Cary 14 spectrophotometer. Conductivity measurements were observed employing an Industrial Instruments Conductivity Bridge Model RC 16B2 and were made at 25.00 ± 0.05 °C on 10^{-4} M solutions.

The qualitative H_2 determination was performed on a Varian Aerograph Series 1700 gas chromatograph. Retention times of the unknown sample and a control sample of H_2 were identical, 440 s, with an argon gas flow of 13 cm^3/min through a Poropak Q column (5 ft × 1/4 in. o.d.) with the oven at 105 °C.

Reaction flasks were dried at 110 °C for at least 12 h and flushed with nitrogen immediately before use. Manipulations of reaction mixtures and residues were performed under an atmosphere of N_2.

Diglyme was dried over Drierite for 24 h, refluxed over copper(I) chloride for 2 h, and distilled from CaH_2 under an atmosphere of N_2. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ and stored under N_2. Absolute ethanol (EtOH) was distilled from CaH_2 and stored under N_2. Diethyl ether and hexanes were stored over activated, type 4A molecular sieves and purged with a stream of N_2. Water was distilled prior to use. Methylene chloride (CH_2Cl_2) and acetonitrile (MeCN) were stored over activated, type 4A molecular sieves.

Sodium hydrogen sulfide (NaSH) was prepared by the method of Eibeck.[24] Schiff bases, t-BuN=CMeH[25] and PhN=CPhH,[26] were prepared by the referenced methods. The N-(para-substituted benzylidene)aniline compounds, p-YC_6H_4CH=NPh, were obtained using the procedures of Tabei and Saitou.[27] Hydrogen sulfide (H_2S) was passed through a P_4O_{10} drying tube. All other reagents and solvents were used as received.

Preparations of [(Ph_3P)$_2$N][M(CO)$_5$(SH)], M = Cr, Mo, or W. To a 50-mL flask were successively added 0.151 g (2.7 mmol) of NaSH, 10 mL of EtOH, and 1.15 g (2.00 mmol) of [(Ph_3P)$_2$N]Cl. The mixture was stirred for 1.5 h giving a white suspension (NaCl). Volatile components of the suspension were removed in vacuo. Then 20 mL of THF and 2.1 mmol of M(CO)$_6$, where M = Cr, Mo, or W, were added to the residue. The flask was fitted with a reflux condenser, a drying tube that contained Drierite, and a gas displacement apparatus for measuring the amount of CO evolved. The mixture was refluxed until 1.8 mmol of CO had been liberated (~1 h). Filtering the yellow reaction mixture and then diluting the resultant filtrate with diethyl ether and hexanes mixtures gave the products. Only [(Ph_3P)$_2$N][Mo(CO)$_5$(SH)] could not be isolated as a solid. The compounds were characterized as follows.

[(Ph_3P)$_2$N][Cr(CO)$_5$(SH)]. IR (CH_2Cl_2): 2044 (w) cm^{-1}, 1914 (vs), 1849 (m). ^{1}H NMR (acetone-d_6): τ 2.35 (m), Ph; 14.67 (s), SH. ^{13}C NMR (acetone-d_6): −224.3 (s), trans CO; −219.4 (s), cis CO; −127.5 ppm (m), Ph. Visible maxima (MeCN): 380 nm (401 M^{-1} cm^{-1}), 370 (481), 362 (552). Λ (MeCN) = 119 cm^2 Ω^{-1} M^{-1}. Mp: 133–136 °C. Yield: 73%. Anal. ($C_{41}H_{31}CrNO_5P_2S$) C, H.

[(Ph_3P)$_2$N][Mo(CO)$_5$(SH)]. IR (THF): 2037 (w) cm^{-1}, 1967 (sh), 1913 (vs), 1846 (m). ^{1}H NMR ($CDCl_3$): τ 2.50 (m), Ph; 13.38 (s), SH.

[(Ph_3P)$_2$N][W(CO)$_5$(SH)]. IR (CH_2Cl_2): 2056 cm^{-1} (w), 1912 (vs), 1843 (m). ^{1}H NMR ($CDCl_3$): τ 2.50 (m), Ph; 12.93 (s), SH. ^{13}C NMR ($CDCl_3$): −203.4 (s), trans CO; −199.8 (s), cis CO; −130.5

ppm (m), Ph. Visible maxima (MeCN): 447 nm (506 M^{-1} cm^{-1}), 385 (1280). Λ (MeCN) = 114 cm^2 Ω^{-1} M^{-1}. Mp: 116–119 °C. Yield: 93%. Anal. ($C_{41}H_{31}NO_5P_2SW$) H, S; C: calcd, 54.99; found, 54.50.

Preparation of [Et_4N][μ-HS[$W(CO)_5$]$_2$]. A suspension of 0.179 g (3.19 mmol) of NaSH, 2.27 g (6.46 mmol) of $W(CO)_6$, 10 mL of diglyme, $(CH_3OCH_2CH_2)_2O$, and 3 mL of THF in a 50-mL flask attached to a reflux condenser, a Drierite drying tube, and a gas displacement apparatus was heated (~120 °C) until 6.12 mmol of CO was evolved (~2 h). After the resulting brown mixture was cooled to room temperature, 300 mL of an aqueous [Et_4N]Br (2.51×10^{-2} M, 7.53 mmol) solution was added. The resulting yellow precipitate was filtered off and repeatedly recrystallized from hot $CHCl_3$ to give transparent yellow needles of the product. IR (CH_2Cl_2): 2068 cm^{-1} (sh), 2056 (w), 1969 (sh), 1933 (vs), 1908 (sh), 1859 (m). ^1H NMR ($CDCl_3$): τ 6.72 (q), CH_2; 8.58 (t), CH_3; 11.70 (s), SH. ^{13}C NMR (CD_3CN): −201.2 (s), trans CO; −199.3 (s), cis CO; −51.8 (s), CH_2; −6.4 ppm (s), CH_3. Visible maxima (MeCN): 448 nm (929 M^{-1} cm^{-1}), 377 (2760). Λ (MeCN) = 142 cm^2 Ω^{-1} M^{-1}. Mp: 110–113 °C dec. Yield: 84%. Anal. ($C_{18}H_{21}NO_{10}SW_2$) C, H; S: calcd, 3.95; found, 4.40.

Preparations of [$(Ph_3P)_2N$][MeC(=O)SW$(CO)_5$]. Method A. To a 50-mL flask fitted with a reflux condenser, Drierite drying tube, and a gas displacement apparatus was added 3.12 g (5.09 mmol) of [$(Ph_3P)_2N$][MeC(=O)S] (obtained as a precipitate upon mixing aqueous solutions of [$(Ph_3P)_2N$]Cl and Na[MeC(=O)S]), 1.80 g (5.11 mmol) of $W(CO)_6$, and 30 mL of THF. The mixture was refluxed (~3 h) until 4.90 mmol of CO had been evolved and then suction filtered while still hot. The yellow product precipitated in 82% yield from the filtrate upon addition of pentane. IR (CH_2Cl_2): 2060 cm^{-1} (w), 1968 (sh), 1917 (vs), 1854 (m). ^1H NMR ($CDCl_3$): τ 2.50 (m), Ph; 7.55 (s), Me. ^{13}C NMR ($CDCl_3$): −206.2 (s), SC(=O); −204.9 (s), trans CO; −199.5 (s), cis CO; −126.7 (m), Ph; −34.4 ppm (s), Me. Visible maxima (MeCN): 418 nm (921 M^{-1} cm^{-1}), 377 (1550). Λ (MeCN) = 126 cm^2 Ω^{-1} M^{-1}. Mp: 145–149 °C. Anal. ($C_{43}H_{33}NO_6P_2SW$) C, H.

Method B. A drop (~0.5 mmol) of acetic anhydride was added to a solution of [$(Ph_3P)_2N$][$W(CO)_5$(SH)] (~0.03 mmol) in 0.6 mL of $CDCl_3$ in an NMR tube. An ^1H NMR spectrum of this mixture after 30 min demonstrated 68% conversion to [$(Ph_3P)_2N$]-[MeC(=O)SW$(CO)_5$]. After the solvent was evaporated and the residue dissolved in CH_2Cl_2, an IR spectrum of the solution confirmed the formation of this product. Similarly, an ^1H NMR spectrum taken 1 h after the preparation of a solution of 0.056 mmol of [$(Ph_3)_2N$]-[$W(CO)_5$(SH)] and 0.058 mmol of 2,4-dinitrophenyl acetate in 0.6 mL of $CDCl_3$ indicated the formation (48% conversion) of the thioacetate complex, which was also confirmed by IR.

Preparation of Thiobenzaldehyde Complexes, [(p-YC_6H_4)-CH=S]W$(CO)_5$, Y = NMe_2, OMe, or Me. A yellow solution of 0.448 g (0.500 mmol) of [$(Ph_3P)_2N$][$W(CO)_5$(SH)], 10 mL of THF, and 0.51 mmol of p-$Me_2NC_6H_4CHO$, p-$MeOC_6H_4CHO$, or p-Me-C_6H_4CHO was treated with 44 μL (0.50 mmol) of CF_3SO_3H. The reaction mixture immediately turned purple-black. After the volatile components were removed under vacuum, the residue was dissolved in 20:80 CH_2Cl_2/hexanes solvent and chromatographed in the same solvent on a 2 × 30 cm column of Florisil (60–100 mesh). The deep purple eluate was collected and evaporated under a stream of N_2 to give lustrous yellow plates of (p-$Me_2NC_6H_4CHS$)W$(CO)_5$, transparent purple needles of (p-$MeOC_6H_4CHS$)W$(CO)_5$, or a purple powder of (p-MeC_6H_4CHS)W$(CO)_5$. They were characterized as follows.

[(p-$Me_2NC_6H_4$)CH=S]W$(CO)_5$. IR (hexanes): 2068 cm^{-1} (m), 1947 (vs), 1938 (vs), 1925 (s). ^1H NMR ($CDCl_3$): τ −0.58 (s), CH; 6.82 (s), CH_3; 2.80 (m), Ph. Visible maxima (C_6H_6): 570 nm (47 800 M^{-1} cm^{-1}), 408 (20 600). Mp: 144–146 °C dec. Yield: 52%. Anal. ($C_{14}H_{11}NO_5SW$) C, H, N.

[(p-$MeOC_6H_4$)CH=S]W$(CO)_5$. IR (hexanes): 2070 cm^{-1} (m), 1956 (vs), 1946 (vs), 1937 (s). ^1H NMR ($CDCl_3$): τ −1.10 (s), CH; 2.60 (m), Ph; 6.07 (s), OMe. Visible maxima (C_6H_6): 544 nm (16 900 M^{-1} cm^{-1}), 359 (18 100). Mp: 108–110 °C dec. Yield: 32%. Anal. ($C_{13}H_8O_6SW$) C, H.

[(p-MeC_6H_4)CH=S]W$(CO)_5$. IR (hexanes): 2071 cm^{-1} (m), 1957 (s), 1948 (vs), 1940 (vs). ^1H NMR ($CDCl_3$): τ −1.11 (s), CH; 7.65 (s), Me; 2.52 (m), Ph. Visible maxima (C_6H_6): 543 nm (11 200 M^{-1} cm^{-1}), 368 (sh). Mp: 72–74 °C dec. Yield: 50%.

Preparation of [Et_4N][μ-RS[$W(CO)_5$]$_2$], R = $SnMe_3$, HgMe, C(=O)Me, CH_2Ph, Ph, or PPh_2. To a yellow solution of 0.406 g (0.500 mmol) of [Et_4N][μ-HS[$W(CO)_5$]$_2$] in 10 mL of THF was added 0.0243 g (0.577 mmol) of NaH (57% oil dispersion). The reaction mixture, which turned green immediately, evolved 0.49 mmol of H_2; it was stirred for 30 min. Then 0.58 mmol of Me_3SnCl, MeHgCl, MeCOCl, $PhCH_2Cl$, $PhSO_2Cl$, or Ph_2PCl was added and the solution was stirred for 2 h. The volatile components were evaporated under vacuum, and the residue was dissolved in acetone. This solution was added to an aqueous solution of [Et_4N]Br (0.27 M, 13.5 mmol) to give an immediate yellow-brown precipitate. After stirring for 1 h, the solution was filtered through Celite on a glass frit; the precipitate was washed through the frit with acetone, and the acetone solution was evaporated to leave a yellow powder. Repeated recrystallization of the powder from hot mixtures of $CHCl_3$ and hexanes gave transparent yellow needles of the products. They were characterized as follows.

[Et_4N][μ-Me_3SnS[$W(CO)_5$]$_2$]. IR (CH_2Cl_2): 2067 cm^{-1} (sh), 2055 (w), 1967 (sh), 1931 (vs), 1897 (sh), 1856 (m). ^1H NMR ($CDCl_3$): τ 6.74 (q), CH_2; 8.60 (t), CH_3; 9.51 (s), Me. Visible maxima (MeCN): 474 nm (776 M^{-1} cm^{-1}), 383 (sh), 356 (sh). Λ ($MeNO_2$) = 88 cm^2 Ω^{-1} M^{-1}. Mp: 103–105 °C dec. Yield: 51%. Anal. ($C_{21}H_{29}NO_{10}SSnW_2$) C, H.

[Et_4N][μ-MeHgS[$W(CO)_5$]$_2$]. IR (CH_2Cl_2): 2065 cm^{-1} (w), 2052 (sh), 1970 (sh), 1929 (vs), 1902 (sh), 1856 (m). ^1H NMR (acetone-d_6): τ 6.45 (q), CH_2; 8.58 (t), CH_3; 9.23 (s), Me. Visible maxima (MeCN): 450 nm (sh), 381 (sh). Λ ($MeNO_2$) = 97 cm^2 Ω^{-1} M^{-1}. Mp: 101–103 °C. Yield: 57%. Anal. ($C_{19}H_{23}HgNO_{10}SW_2$) C, H.

[Et_4N][μ-MeC(=O)S[$W(CO)_5$]$_2$]. IR (CH_2Cl_2): 2072 cm^{-1} (sh), 2062 (w), 1972 (sh), 1938 (vs), 1912 (sh), 1869 (m). IR (KBr): 1643 (w). ^1H NMR ($CDCl_3$): τ 6.77 (q), CH_2; 7.40 (s), Me; 8.62 (t), CH_3. Visible maxima (MeCN): 439 nm (1380 M^{-1} cm^{-1}), 369 (3260). Λ (MeCN) = 154 cm^2 Ω^{-1} M^{-1}. Mp: 94–96 °C. Yield: 45%.

[Et_4N][μ-$PhCH_2$S[$W(CO)_5$]$_2$]. IR (CH_2Cl_2): 2067 cm^{-1} (sh), 2055 (w), 1966 (sh), 1932 (vs), 1901 (sh), 1860 (m). ^1H NMR (acetone-d_6): τ 2.70 (m), Ph; 5.96 (s), CH_2; 6.48 (q), CH_2Me; 8.58 (t), CH_3. Visible maxima (MeCN): 449 nm (847 M^{-1} cm^{-1}), 374 (sh). Λ (MeCN) = 139 cm^2 Ω^{-1} M^{-1}. Mp: 96–98 °C. Yield: 34%. Anal. Calcd for $C_{25}H_{27}NO_{10}SW_2$: C, 33.32; H, 3.02. Found: C, 32.85; H, 2.61.

[Et_4N][μ-PhS[$W(CO)_5$]$_2$]. IR (CH_2Cl_2); 2068 cm^{-1} (sh), 2057 (w), 1970 (sh), 1935 (vs), 1908 (sh), 1861 (m). ^1H NMR (acetone-d_6): τ 2.67 (m), Ph; 6.50 (q), CH_2; 8.58 (t), CH_3. Visible maxima (MeCN): 455 nm (1620 M^{-1} cm^{-1}), 371 (sh). Λ (MeCN) = 147 cm^2 Ω^{-1} M^{-1}. Mp: 110–112 °C dec. Yield: 7%. Anal. ($C_{24}H_{25}NO_{10}SW_2$) C, H.

[Et_4N][μ-Ph_2PS[$W(CO)_5$]$_2$]. IR (CH_2Cl_2): 2067 cm^{-1} (sh), 2057 (w), 1976 (sh), 1930 (vs), 1910 (sh), 1860 (m). ^1H NMR (acetone-d_6): τ 2.38 (m), Ph; 6.50 (q), CH_2; 8.58 (t), CH_3. Visible maxima (MeCN): 428 nm (810 M^{-1} cm^{-1}), 372 (sh). Λ (MeCN) = 135 cm^2 Ω^{-1} M^{-1}. Mp: 130–132 °C. Yield: 37%. Anal. ($C_{30}H_{30}NO_{10}PSW_2$) C, H.

Preparation of [$(Ph_3P)_2N$][μ-MeC(=O)S[$W(CO)_5$]$_2$]. To a solution of [Et_4N][$W(CO)_5$I] (0.581 g, 0.500 mmol) in 10 mL of acetone at 0 °C was added 0.5 mL of a 1.0 M $AgBF_4$–acetone solution. Immediate precipitation of yellow AgI occurred, and the mixture was stirred for an additional 30 min at 0 °C. After 0.469 g (0.500 mmol) of [$(Ph_3P)_2N$][MeC(=O)SW$(CO)_5$] was added and the mixture stirred for 1 h, the suspension was diluted with 60 mL of Et_2O and filtered. The solution was treated with hexanes and cooled to −40 °C to yield transparent yellow plates of the product. ^1H NMR ($CDCl_3$): τ 2.50 (m), Ph; 7.39 (s), Me. ^{13}C NMR ($CDCl_3$): δ −203.3 (s), SC(=O); −203.1 (s), trans CO; −199.1 (s), cis CO ($J_{^{183}W-^{13}CO}$ = 128.0 Hz); −130.5 (m), Ph; −30.8 (s), Me. Λ (MeCN) = 142 cm^2 Ω^{-1} M^{-1}. Mp: 130–133 °C. Yield: 78%. Anal. ($C_{20}H_{23}NO_{11}SW_2$) H, S; C: calcd, 45.73; found, 45.02.

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Metal Ion Coordination to the Exocyclic Amine in a Pyrimidine Complex. Structure of (1-Methylcytosinato)pentaammineruthenium(III) Hexafluorophosphate, $[Ru(NH_3)_5(1\text{-}MeCyt^-)](PF_6)_2$

Bradford J. Graves and Derek J. Hodgson*

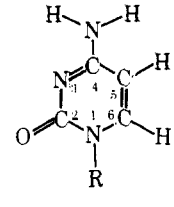
Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received March 7, 1979*

Abstract: The crystal and molecular structure of (1-methylcytosinato)pentaammineruthenium(III) hexafluorophosphate(V), $[Ru(NH_3)_5(C_5H_6N_3O)](PF_6)_2$, has been determined from three-dimensional X-ray data collected on an automatic diffractometer. The metal-pyrimidine complex crystallizes in the triclinic space group $P\bar{1}$ with two molecules in a cell of dimensions a = 14.760 (10) Å, b = 7.734 (4) Å, c = 8.779 (5) Å, α = 90.19 (3); β = 99.56 (3); and γ = 89.98 (4)°. Full-matrix, least-squares refinement of the structure using 3326 independent intensities has converged to a final, conventional R factor of 0.068. The crystals consist of isolated, monomeric units of $[Ru(NH_3)_5(1\text{-}MeCyt)]^{2+}$ cations which are surrounded by PF_6 anions. The molecular structure of the cation shows that the 1-methylcytosine anion is bound to ruthenium through the deprotonated exocyclic amine nitrogen atom. This is the first crystallographic example of metal coordination to an exocyclic amine of any purine or pyrimidine. The coordination around the ruthenium(III) center is roughly octahedral, the inner coordination sphere consisting of the five ammine nitrogen atoms with Ru-N bond lengths in the range 2.108 (7) to 2.136 (8) Å and the pyrimidine amine nitrogen atom with associated Ru-N distance of 1.983 (9) Å. This latter distance is short and is indicative of very strong σ bonding between the metal and the pyrimidine ligand.

Introduction

Crystallographic studies of transition-metal complexes of purines, pyrimidines, nucleosides, and nucleotides have been performed in recent years in order to gain an understanding of metal ion interactions with DNA.[1,2] Some metal ions stabilize double-helical DNA while others destabilize it,[3] and some metal ion complexes inhibit DNA replication[4] while others do not.

Crystallographic studies of metal complexes of derivatives of cytosine (Cyt) in which N(1) is blocked, I, including 1-methylcytosine (1-MeCyt), cytidine (Cyd), cytidine 5′-monophosphate (CMP), and cytidine 5′-triphosphate (CTP), nearly all demonstrate metal binding to N(3). The lone exception to this "rule" is the CMP complex of Mn(II), in which the only base atom to which the metal binds is O(2).[5] In several other complexes, varying degrees of metal-O(2) interaction in addition to the strong metal-N(3) binding have been noted, from a strong interaction in $[Ag(1\text{-}MeCyt)(NO_3)]$[6] to very weak contacts in complexes of mercury(II), copper(II), cadmium(II), and zinc(II).[1,7-10] Several other complexes, however, exhibit only the metal-N(3) bond noted above,[1,11-15] or that bond in conjunction with metal-phosphate interactions. Metal ion interactions with O(2) are not surprising, of course, since CNDO/2 molecular orbital calculations[16] based on the solid-state structure of cytidine[17] show that O(2) is more basic



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a, R = CH_3 (1-methylcytosine)
b, R = ribose (cytidine)
c, R = ribose 5′-monophosphate (CMP)
d, R = ribose 5′-triphosphate (CTP)

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