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ANIONIC CARBONYL COMPLEXES OF THE GROUP VI TRANSITION METALS WITH SULFUR CONTAINING LIGANDS

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Summary

Anionic complexes of the type $[M(CO)_4(dpet)]^-$ (where M is Cr, Mo or W and dpet is the anion of 2-(diphenylphosphino)ethanthiol) are readily prepared by the reaction of the Tl(dpet) and $[M(CO)_5X]^-$ anions (X = halogen). These complex anions appear to have the normal octahedral geometry with the dpet ligand coordinated through both the P and S atoms. When treated with methyl or allyl halides, neutral complexes of the type $M(CO)_4(dpet—R)$ are formed (where R is an allyl or methyl group now bound to the sulfur atom). By treating Tl^I salts of *o*-aminothiophenol (atp), *o*-methylmercaptophenol (mmp) and methylxanthic acid (mxt), with $[M(CO)_5]^-$ anions, the respective complexes $[M(CO)_4(atp)]^-$, $[M(CO)_4(mmp)]^-$ and $[M(CO)_5(mxt)]^-$ are formed.

Introduction

Our previous synthesis of anionic complexes of the type $[M(CO)_4(diket)]^-$ (where M is Cr, Mo or W and diket is a β-diketonate anion) proved to be very simple [1]. We wished to prepare similar derivatives with "softer" donor atoms and compare the properties of these materials with those of the tetracarbonyldiketonate complexes where the donor atoms on the chelating ligand are relatively "hard." We also hoped to prepare complexes with chelating groups containing both hard and soft donor atoms. Although neutral complexes of the Group VI metal carbonyls containing bidentate ligands with P,S,As (and even some combinations of these) as donor atoms are very well documented [2], very few complexes of these metals with uni-negative bidentate ligands are known in which S or P is the donor atom [3]. The 2-(diphenylphosphino)ethanethiolate (dept) anion is such a ligand; its chemistry has only been mentioned briefly in the literature [4]. The present work describes the preparation and properties of some Group VI metal carbonyl complexes of this ligand as well as some complexes formed from the anions of *o*-aminothiophenol, *o*-methylmercaptophenol and methylxanthic acid.

Results and discussion

The reaction of the Group VI metal pentacarbonylhalide anions with the thallium(I) salt of 2-(diphenylphosphino)ethanethiol proceeds readily in refluxing THF according to the equation:

$$[M(CO)_5X]^- + Tl[(C_6H_5)_2PCH_2CH_2S] \rightarrow TlX + \{M(CO)_4[(C_6H_5)_2PCH_2CH_2S]\}^-$$

The reaction gives good yields regardless of the cation, halide, or transition metal used. The yellow crystalline salts which are obtained are somewhat air sensitive, but otherwise are quite stable and in many respects resemble the $[M(CO)_4(\text{diket})]$ salts.

The infrared spectra in the CO stretching region for these salts are given in Table 1. Although four bands might be expected, only three are observed. Assuming C_{2v} symmetry for the complexes, the highest frequency band is almost certainly of A_1 species and the lowest frequency band of B_2 species. It appears that there is an overlap of the B_1 band and one of the A_1 bands, producing a broad, very intense band of intermediate frequency. The relatively low frequencies for these bands are as expected for anionic complexes. The NMR spectra of

TABLE 1

ANALYTICAL AND INFRARED DATA FOR SOME COMPLEXES OF (DIPHENYLPHOSPHINO)-ETHANETHIOL

Compound	Analysis: Found (calcd.)(%)				IR $\nu(c{=}O)$ (cm^{-1}) CH_2Cl_2 solution
	C	H	P	N	
$(C_6H_5)_4As\{Cr(CO)_4[(C_6H_5)_2PCH_2CH_2S]\}$	63.61	4.49	4.11		1976, 1860, 1793
	(63.63)	(4.32)	(3.90)		
$(C_6H_5)_4P\{Mo(CO)_4[(C_6H_5)_2PCH_2CH_2S]\}$	63.08	4.51	7.33		1990, 1850, 1790
	(63.65)	(4.32)	(7.82)		
$(C_2H_5)_4N\{W(CO)_4[(C_6H_5)_2P(CH_2CH_2S]\}$	46.18	5.40	4.57	2.36	1982, 1845, 1792
	(46.51)	(5.08)	(4.60)	(2.08)	
$Cr(CO)_4[CH_3SCH_2CH_3P(C_6H_5)_2]$	53.91	4.35	6.99		2014, 1910, 1879, 1847
	(53.80)	(4.08)	(7.30)		
$Mo(CO)_4[CH_3SCH_2CH_2P(C_6H_5)_2]$	48.77	3.66	6.20		2020, 1920, 1890, 1849
	(48.73)	(3.66)	(6.61)		
$W(CO)_4[CH_3SCH_2CH_2P(C_6H_5)_2]$	41.11	3.05	5.56		2012, 1910, 1890, 1859
	(40.95)	(3.08)	(5.58)		
$Cr(CO)_4[C_3H_5SCH_2CH_2P(C_6H_5)_2]$	56.55	4.61	6.84		2008, 1890, 1848
	(56.00)	(4.25)	(6.88)		
$Mo(CO)_4[C_3H_5SCH_2CH_2P(C_6H_5)_2]$	51.19	4.37	5.76		2008, 1890, 1848
	(51.02)	(3.87)	(6.26)		2020, 1890, 1834
$W(CO)_4[C_3H_5SCH_2CH_2P(C_6H_5)_2]$	43.84	3.23	5.45		2016, 1894, 1859
	(43.31)	(3.38)	(5.31)		
$W(CO)_4[CH_2{:}C(CH_3)CH_2SCH_2CH_2P(C_6H_5)_2]$	44.34	3.57	5.24		2012, 1887, 1855
	(44.31)	(3.55)	(5.19)		

the anions are all very similar and consist of broad complex multiplets for the aromatic protons and very broad, almost indiscernable signals for the methylenic protons.

The reaction of the $[M(CO)_4(dpet)]^-$ anions with allyl chloride was of some interest since anionic derivatives of the Group VI metal carbonyls undergo a variety of different reactions with the allyl halides. Thus $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ reacts by substitution to form a complex with the allyl group σ-bonded to the Mo [5], $Mo[(C_3H_3N_2)_3B](CO)_3^-$ gives π-allyl complexes with elimination of CO [6], $Mo(CO)_5Cl^-$ gives the dinuclear complex $[Mo_2(CO)_4(\pi\text{-}C_3H_5)_2Cl_3]^-$ [7], while the $[Mo(CO)_4(diket)]^-$ anions generally undergo an oxidative elimination reaction to give anions of the type $[Mo(CO)_2(\pi\text{-}C_3H_5)(diket)Cl]^-$ [1]. Since the $[M(CO)_4(dpet)]^-$ ions contain a ligand whose chemistry was relatively unknown, the mechanism and reaction products of the reaction with allyl chloride were not certain.

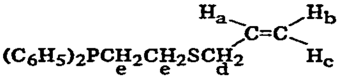
When $(C_6H_5)_4P[W(CO)_4(dpet)]$ was treated with an excess of allyl chloride at room temperature, an immediate precipitate of $[(C_6H_5)_4P]Cl$ was formed. No CO was evolved. Work-up of the solution gave a yellow solid compound with the composition $W(CO)_4(dpet)(C_3H_5)$. The reaction of allyl bromide and methallyl or crotyl chloride with $[W(CO)_4(dpet)]^-$ gave similar results. The analogous allyl complexes were obtained also from the Mo and Cr complex anions. The ease of reaction of the allyl halide with the $[M(CO)_4(dpet)]^-$ anions prompted us to investigate the reaction with CH_3I and $(CH_3)_3SnCl$. The reaction with CH_3I proceeded in a manner similar to that of the allyl halides, precipitating $[(C_6H_5)_4P]I$ and giving yellow complexes with the composition $M(CO)_4(dpet)(CH_3)$. Trimethyltin chloride did not react at all, even with heating to 65°C for several hours.

If the $[M(CO)_4(dpet)]^-$ anions reacted by a simple substitution process, then the most probable structure for both the allyl and methyl derivatives is a seven-coordinate complex with a metal—carbon σ bond. However, this is probably not the case. The infrared spectra in the CO stretching region of all these complexes are not very revealing (see Table 1). The CO stretching bands appear to be similar to those observed for the starting compounds except for the expected shift to higher frequencies on going from an anionic to a neutral complex.

The NMR data for the allyl derivatives, which are given in Table 2, proved to be quite interesting. The protons on the allyl group give a pattern quite typical of many organic allyl compounds but not what would be expected for a transition metal σ-allyl derivative. The chemical shift of the $=CH—CH_2—M$ protons in particular is observed at a fairly low field, much lower than would be expected if the allyl group were bound directly to the metal atom. In fact the chemical shift for these protons is even somewhat lower than, but similar to, the shifts observed in allyl sulfide [8]. The methylenic $P—CH_2—CH_2—S$ proton signal are a good deal sharper than observed in the parent compound, although the spectra were too complex to make assingments for $SCH_2—$ and $PCH_2—$ protons or to obtain P—H coupling constants. The spectra of the complexes of all three metals are quite similar. The NMR spectra of the methyl derivatives also suggest that there is no metal—carbon σ bond in these complexes. Again, the signal for the methyl protons is observed at fields similar to that observed for methyl sul-

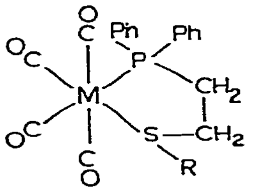
TABLE 2

NMR DATA FOR SOME (DIPHENYLPHOSPHINO)ETHANETHIOL AND RELATED COMPLEXES

Complex	Ligand	NMR τ (ppm)[a]
$[Cr(CO)_4(dpet)]^-$	$(C_6H_5)_2PCH_2CH_2S^-$	~2.5 C_6H_5; ~7.45 CH_2
$[Mo(CO)_4(dpet)]^-$		~2.5 C_6H_5; ~7.5 CH_2
$[W(CO)_4(dpet)]^-$		~2.6 C_6H_5; ~7.5 CH_2
$Cr(CO)_4(mdpet)$	$(C_6H_5)_2PCH_2CH_2SCH_3$	2.5 C_6H_5; ~7.47 CH_2; 7.74 CH_3
$Mo(CO)_4(mdpet)$		2.5 C_6H_5; ~7.32 CH_2; 7.60 CH_3
$W(CO)_4(mdpet)$		2.3 C_6H_5; ~7.12 CH_2; 7.32 CH_3
$Cr(CO)_4(adpet)$	 $(C_6H_5)_2P\underset{e}{CH_2}\underset{e}{CH_2}S\underset{d}{CH_2}(H_a)C{=}CH_bH_c$	~2.5 C_6H_5; ~4.2 H_a; 4.75 $H_b + H_c$ 6.79 H_d; 6.9-7.6 H_e
$Mo(CO)_4(adpet)$		~2.4 C_6H_5; 4.25 H_a; 4.71 $H_b + H_c$ 6.81 H_d; ~7.4 H_e
$W(CO)_4(adpet)$		~2.5 C_6H_5; ~4.3, H_a; 4.75 H_b + H_c 6.62 H_e; 6.9-7.6 H_e

[a] Taken in CD_3CN for the anionic complexes, CD_3COCD_3 for the neutral complexes.

fide [8] but much lower than expected for a methyltungsten (Mo or Cr) derivative. In addition, no coupling between the methyl protons and the ^{183}W nucleus is observed. It therefore seems quite unlikely that these complexes are seven-coordinate with a metal—carbon bond, but rather are six-coordinate complexes with the organic group bound to the sulfur as shown. The complexes, therefore, contain new ligands which are formed by the reaction of the methyl or allyl halide with the coordinated (dpet) group. The methyl complexes appear to be identical to those reported by Ross and Dobson which are formed directly from the metal carbonyl and $(C_6H_5)_2PCH_2CH_2SCH_3$ [9]. A mass spectrum of $W(CO)_4$-(dpet)(CH_3) (actually a mass spectrum of its thermal decomposition products since the sample decomposed leaving a large amount of tungsten containing residue) showed major fragments corresponding to $(C_6H_5)_2PCH_2CH_2SCH_3^+$ (mass found 260.07654; calcd. 260.07891) and CH_3S^+ (mass found 46.9956; calcd. 46.9956) which gives further support to the proposed structure. The possibility of large amounts of such fragments arising from a methyltungsten complex seems quite unlikely.

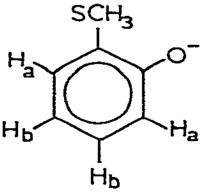
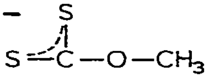
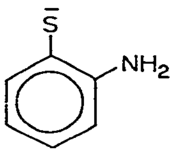


R = CH_3 or $CH_2CH{=}CH_2$

In addition to the 2-(diphenylphosphino)ethanethiolate complexes we have succeeded in preparing a few complexes of similar type with other sulfur-containing anionic ligands. Among the ligands of interest were the 2-(methylmercapto)phenoxide ion (mmp), the *o*-aminothiophenoxide ion (atp) and the methyl-

TABLE 3

ANALYTICAL, INFRARED AND NMR DATA FOR SOME Mo AND W CARBONYL COMPLEX ANIONS CONTAINING LIGANDS WITH SULFUR DONOR ATOMS

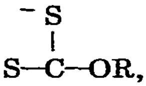
Compound	Ligand	Analysis: Found (calcd.)(%)				IR ν(C=O) (cm^{-1})	
		C	H	N(or P)	S	CH_2Cl_2 solution	NMR τ (ppm) in CD_3CN
$(C_2H_5)_4N$-[Mo(CO)$_4$(mmp)]		47.90 (47.80)	5.62 (5.71)	3.02 (2.93)	6.68 (6.71)	2001, 1870, 1795	H$_a$ 2.90, H$_b$ 3.60,
$(C_6H_5)_4P$-[W(CO)$_4$(mmp)]		54.57 (54.70)	3.72 (3.52)	3.87 (4.00)	4.22 (4.14)	1999, 1863, 1826, 1793	H$_a$ 2.90 H$_b$ 3.60 CH_3 7.43
$(C_6H_5)_4P$-[W(CO)$_5$(mxt)]		48.26 (48.19)	3.36 (3.01)	3.99 (4.00)	8.35 (8.32)	2070, 1929, 1855	CH_3 6.06
$(C_6H_5)_4P$-[W(CO)$_4$(atp)]		53.15 (53.55)	3.35 (3.44)	1.79 (1.84)	4.01[a] (4.06)[a]	2030, ~1895, 1839	Aromatic 3.50 NH_2 5.37

[a] Analysis P.

xanthate ion (mxt). In each case, the thallium(I) salt of the ligand was prepared, in the case of 2-(methylmercapto)phenoxide and *o*-amino-thiophenoxide by the reaction of the parent phenol with thallium(I) ethoxide, and for the methylxanthate by the reaction of sodium methylxanthate with thallous sulfate.

The [W(CO)$_4$Br]$^-$ ion reacts readily with Tl(mmp) in THF with the elimination of one mole of CO to form the [W(CO)$_4$(mmp)]$^-$ complex ion. A similar reaction takes place with the molybdenum analog. Although only three bands were observed for the CO stretching vibrations in the infrared spectrum for the molybdenum complex (see Table 3), the tungsten complex spectrum has four bands which is as expected for a tetracarbonyl complex with a bidentate chelating ligand. Presemably, the fact that only three bands are observed for the molybdenum complex is due to accidental overlap of the B_1 and one of the A_1 bands as also was observed for the M(CO)$_4$(dpet)$^-$ ions.

In a like manner, Tl(atp) reacts with [W(CO)$_5$Br]$^-$ to form the [W(CO)$_4$-(atp)]$^-$ complex. The infrared spectrum of this material also contains three CO stretching bands (one weak sharp band, one extremely intense, very broad band and another intense broad band). There is no reason to believe that the structure of this complex is different from those of the other tetracarbonyl complexes with bidentate ligands. It is of interest that on replacing the sulfur atom with oxygen, i.e., by using the *o*-aminophenoxide salt, no reaction with [W(CO)$_5$Br]$^-$ took place.



The xanthate ions, $S{-}\overset{{}^{-}S}{\overset{|}{C}}{-}OR$, of which the methyl derivative is one of the simplest and easily prepared, have the capability of forming either monodentate or bidentate complexes. It was of some interest, therefore, to determine what the nature of the Group VI metal carbonyl complexes would be if they could be formed. If one uses carefully dried Tl(mxt), the reaction with $[W(CO)_5Br]^-$ takes place smoothly in refluxing THF to yield the pentacarbonyl complex anion $[W(CO)_5(mxt]^-$. In this case, the methyl xanthate group is most likely functioning as a monodentate ligand forming complexes resembling the structurally similar carboxylate ions [10,11]. In certain other molybdenum complexes, such as $Mo_2O_3(S_2COC_2H_5)_4$ [12], the xanthate group acts as a bidentate ligand. The infrared spectrum of the $[W(CO)_5(mxt)]^-$ ions consists of three CO stretching bands as expected for a $M(CO)_5X$ type complex.

Experimental

Analyses. Elemental analyses were carried out by the Analytical and Information Division, Exxon Research and Engineering Co. The results are given in the appropriate tables.

Spectra. Infrared spectra were obtained either on a Perkin—Elmer Model 521 or a Beckman Model 20 Infrared Spectrometer. NMR spectral measurements were carried out on a Varian Model A-60 NMR spectrometer.

Synthesis

A. General. Because of the air-sensitive nature of the complexes and many of the starting materials, all work was carried out in a dry box under a nitrogen atmosphere and all solvents used were thoroughly dried by established procedures.

B. Reagents. The metal pentacarbonyl halide salts were prepared by the method of Abel, Butler and Reid [13]. 1-(Diphenylphosphino)ethanethiol was synthesized by the procedure given in the Geigy patent [4]. The thallium(I) salt of this material was prepared by combing exactly equivalent amounts of thallium(I) ethoxide and $(C_6H_5)_2PCH_2CH_2SH$ in benzene. All other starting reagents were obtained from commercial sources. *o*-Mercaptophenol was generously supplied by Hooker Chemical Inc.

Preparation of $[M(CO)_4(dpet)]^-$ salts. A solution of 0.01 mol of an appropriate metal pentacarbonyl halide salt in 100 ml THF was prepared and to it was added an exactly equivalent amount of the thallium(I) salt of (diphenylphosphino)ethanethiol. The mixture was refluxed for 15 min then was stirred at ambient temperature overnight. The solution was filtered and the clear filtrate was added to 200 ml of pentane. A yellow oil formed which crystallized slowly. The crystalline material was collected on a filter, ground to a fine powder and washed several times with additional pentane before drying. Yields are nearly quantitative.

Reactions of $[M(CO)_4(dpet)]^-$ salts

A. With Allyl Chloride. Ten ml of allyl chloride was added to 0.003 mol of the solid $[M(CO)_4\ dpet]^-$ salt in a small flask. A white solid formed immediately which was filtered leaving a yellow filtrate. The filtrate was evaporated to dryness and the residue was washed with small amounts of cold pentane. A yellow crystalline solid remained which was collected and dried. Yields of the $M(CO)_4$(allyl-dpet) complexes were approximately 75%.

B. Reaction with CH_3I. These reactions were carried out in a manner similar to that described for the allyl derivatives. Yields of the $M(CO)_4(CH_3dpet)$ complexes also were 75% or more.

Preparation of $[M(CO)_4mmp]^-$ salts. *o*-Methylmercaptophenol was prepared by the successive addition of *o*-mercaptophenol and methyl iodide to a solution of NaOH in methanol. The mixture was extracted with ether and the solvent evaporated, leaving crude *o*-methylmercaptophenol which was used without further purification. The thallium(I) salt of *o*-methylmercaptophenol was then prepared by the reaction of this product with thallium ethoxide in benzene. The Tl(mmp) (0.01 mol) was added to a solution of the $[M(CO)_5X]^-$ salt (0.01 mol) in 75 ml of THF. The solution was heated to boiling, then was stirred at room temperature overnight. The resulting solution was filtered and the filtrate added to 150 ml of pentane; this resulted in precipitation of the yellow $[M(CO)_4(mmp)]$ salt which was collected and dried. Yields were greater than 80%.

Preparation of $[M(CO)_4(oatp)]^-$ salts. These were prepared by the reaction of a $[M(CO)_5X]^-$ salt and Tl(oatp) (prepared from $TlOC_2H_5$ and *o*-aminothiophenol) in the same manner as described above for the $[M(CO)_4(mmp)]^-$ salts. Yields were similar.

Preparation of $(C_6H_5)_4P[W(CO)_5(mxt)]$. Thallium(I) methylxanthate was prepared by the reaction of thallous sulfate with sodium methylxanthate in water and was thoroughly dried by heating to 80°C for 3 h at 0.01 mmHg. This salt (3.31 g; 0.01 mol) was added to a solution of 7.45 g (0.01 mol) of $(C_6H_5)_4$-$P[W(CO)_5Br]$ in 70 ml of THF. This mixture was stirred at room temperature for 30 min then heated to boiling and filtered. The yellow filtrate was added to 150 ml of pentane which precipitated an oil which gradually crystallized. The crystalline material was collected, washed with additional pentane and dried. Yield was nearly quantitative.

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