Tertiary Phosphine and Arsine Chalcogenide Derivatives of Group VI Metal Carbonyl Complexes

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The preparation of a series of complexes $[M(CO)_5L]$ [M = Cr or W; L = Me_3PS, Me_2PhPS, $MePh_2PS$, Ph_3PS, Me_2PhPSe, Me_3AsS, or $Ph_2P(S)CH_2P(S)Ph_2$; M = Mo, L = Me_2PhPS; M = W, L = Ph_3AsO] is reported. I.r. and ^1H n.m.r. spectra are discussed. The chalcogenide ligands are readily displaced by CO and Ph_3P, and with MeI ionic species, *e.g.* $[Me_2PhPSMe][M(CO)_5I]$, are formed. For L = $Ph_2P(S)CH_2P(S)Ph_2$ spectroscopic evidence indicates the ligand is acting in a monodentate fashion.

STABLE complexes of the type $[M(CO)_{6-x}L_x]$, where L is a chalcogen (S,Se) donor ligand functioning as a formal two-electron donor, are few in number, especially when compared with the analogous phosphine and arsine complexes.[1] More often such ligands occur as bridging groups. In this paper, we therefore report the results of a study of the synthesis and reactivity of a series of simple substituted Group VI metal carbonyl derivatives $[M(CO)_5L]$ (L = tertiary phosphine or arsine chalcogenide). It is of interest that a single-crystal *X*-ray study[2] on one of the complexes, $[Cr(CO)_5(Me_3PS)]$, shows the chalcogen ligand to be essentially a σ-donor whereas other bivalent chalcogen ligands (*e.g.* R_2S) are recognised to act as π-acceptors.[3] A preliminary account of some of this work has already been published.[4]

RESULTS AND DISCUSSION

Preparations.—The complexes $[M(CO)_5L]$ (L = Me_3PS, Me_2PhPS, $MePh_2PS$, Ph_3PS, Me_2PhPSe, *or* Me_3AsS). Thermal reactions between the carbonyl complexes and the chalcogenide ligands produced decomposition products; however the chromium and tungsten complexes could be obtained as moderately air-stable, yellow, crystalline solids on addition of L to u.v.-irradiated tetrahydrofuran solutions of the appropriate metal carbonyl complex. The triphenylphosphine sulphide complexes could not be obtained analytically pure. Difficulty in preparation of Ph_3PS complexes has been noted previously,[5] and is presumably a reflection of the lower basicity of the ligand. During the course of this work the preparation of one of the complexes, $[Cr(CO)_5(MePh_2PS)]$, was reported elsewhere.[6] The monomeric nature of the complexes is confirmed in the case of $[Cr(CO)_5(Me_3PS)]$ from its mass spectrum (parent molecular ion *m/e* 300) and the single-crystal study.[3] The molybdenum analogues, which could be isolated only with difficulty, rapidly dissociate in solution to the parent hexacarbonyl complex.

The complexes $[W(CO)_5L]$ (L = Ph_3AsO or Me_3AsO). A cursory study on some of the corresponding arsine oxide complexes resulted only in isolation of one complex *viz.* $[W(CO)_5(Ph_3AsO)]$. From the same reaction $[W(CO)_5(Ph_3As)]$ was identified, and this complex was also produced on heating the arsine oxide complex for 10 min in benzene. In the analogous reaction with Me_3AsO only $[W(CO)_5(Me_3As)]$ was found along with unidentifiable products. Although bis- and tris-phosphine oxide and -arsine oxide Group VI carbonyl derivatives are known,[7] we have not yet succeeded in obtaining the related sulphide and selenide complexes.

I.r. and ^1H *N.m.r. Spectra.*—I.r. spectral data for the complexes are given in Table 1 and show the P=S and P=Se stretching frequencies to have decreased on coordination, consistent with bonding of the chalcogen atoms to the metal.[8] In the CO stretching region five well spaced bands were observed implying that the overall symmetry is not as high as C_{4v}, generally assumed for $[M(CO)_5L]$ molecules.[9] All the fundamental CO stretching frequencies became i.r.-active and the *E* mode was no longer doubly degenerate. Such a divergence from the C_{4v} selection rules must be a result of the unsymmetrical relation of the tertiary phosphine or arsine chalcogenide ligand with the equatorial metal carbonyl groups, since the *X*-ray study on $[Cr(CO)_5(Me_3PS)]$ indicates there are no significant steric indications.[3] Moreover, although the splitting of the *E* mode was somewhat ligand dependent, it was not sensitive to the size of the metal; analogous chromium and tungsten complexes showed virtually identical spectra. In contrast, in certain alkyl and acyl derivatives $[RM(CO)_5]$ (M = Mn or Re) the splitting of the *E* mode can be related to the relative sizes of the manganese and rhenium atoms and implies a greater steric interaction in the former case.[10]

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In view of the lower symmetry of the chalcogenide complexes, CO stretching-frequency comparisons should be made with caution. However the considerably lower frequencies observed for the $[M(CO)_5(R_3PS)]$ complexes, especially for A_1', when compared with the analogous phosphine derivatives $[M(CO)_5(R_3P)]$,[11,12] are consistent with the insignificant π-acceptor properties of the sulphide ligands. Few data are available for substituted carbonyl complexes containing similar *O*-, *S*-, and *Se*-donor ligands.[9] Therefore it is of interest to find that the CO stretching frequencies for the analogous sulphide and selenide complexes indicate that the contribution by these ligands to the total charge contribution on the central metal atom is not markedly different. The lower frequencies observed for the Ph_3AsO complex and for the previously reported $[M(CO)_5\{(Me_2N)_3PO\}]$ derivatives[13] may not be interpreted in terms of metal–chalcogenide π-bonding differences, but in part can be related to the greater basicity of the oxide ligands.[14]

TABLE 1

Spectral data for the complexes

Compound	CO Stretching wavenumbers (cm^{-1})[a]				ν(P=S)[b] /cm^{-1}	Methyl proton n.m.r. measurements		
	A_1''(m)	B_1(m)	E(vs)	A_1'(s)		τ (PCH$_3$)[c]	Δτ[d]	$J(^{31}P^1H)$
Me_3PS					565	8·21	0·71	13·2
$[Cr(CO)_5(Me_3PS)]$	2 062	1 984	1 927, 1 944	1 909	545	8·10	1·00	13·2
$[W(CO)_5(Me_3PS)]$	2 068	1 983	1 922, 1 938	1 907	541	8·08	1·11	12·6
Me_2PhPS					590	8·03	0·57	13·2
$[Cr(CO)_5(Me_2PhPS)]$	2 061	1 984	1 929, 1 940	1 912	568	7·89	0·89	13·2
$[W(CO)_5(Me_2PhPS)]$	2 068	1 977	1 925, 1 935	1 908	564	7·86	0·93	13·2
$[Mo(CO)_5(Me_2PhPS)]$	2 071	*e*	1 933, 1 945	1 913	572	8·76[f]	*g*	12·8
$MePh_2PS$					619, 608	7·82	0·37	12·0
$[Cr(CO)_5(MePh_2PS)]$	2 066	1 981	1 932, 1 942	1 911	587	7·61	0·70	12·6
$[W(CO)_5(MePh_2PS)]$	2 061	1 975	1 925, 1 932	1 907	*h*	7·60	0·70	12·7
Ph_3PS					637			
$[Cr(CO)_5(Ph_3PS)]$	2 062	1 981	1 932, 1 942	1 910	628			
$[W(CO)_5(Ph_3PS)]$	2 067	1 976	1 931, 1 938	1 906	622			
Me_2PhPSe					495[i]	7·82	0·62	13·2
$[Cr(CO)_5(Me_2PhPSe)]$	2 058	1 980	1 927, 1 941	1 912	483[i]	7·81	0·92	13·2
$[W(CO)_5(Me_2PhPSe)]$	2 064	1 975	1 924, 1 935	1 907	482[i]	7·77	0·99	12·6
Me_3AsS					473[j]	8·17	0·80	
$[Cr(CO)_5(Me_3AsS)]$	2 060	1 985	1 924, 1 942	1 905	*k*	8·05	1·08	
$[W(CO)_5(Me_3AsS)]$	2 066	1 980	1 919, 1 936	1 904	450[j]	8·10	1·10	
Ph_3AsO					876[l]			
$[W(CO)_5(Ph_3AsO)]$	2·065	1 963	1 918	1 888	863[l]			
$[Me_2PhPSMe]I$					535	7·06, 7·42[m]		13·5, 15·0[m]
$[Me_2PhPSMe][Cr(CO)_5I]$	2 068	1 982	1 928	1 873[n]	533	7·33, 7·50[m]		13·5, 15·0[m]
$[Me_2PhPSMe][W(CO)_5I]$	2 060	1 981	1 926	1 866[n]	534	7·38, 7·59[m]		13·5, 15·0[m]
bdm[o]					628s, 616m, 596m	6·02[p]		13·4
$[Cr(CO)_5(bdm)]$	2 066	1 982	1 926, 1 936	1 909	616s, 602s, 595sh	5·90[q]		
$[W(CO)_5(bdm)]$	2 068	1 983	1 925, 1 933	1 910	*h*	5·92[r]		

[a] In cyclohexane. [b] As Nujol mulls. [c] In $CDCl_3$. [d] $\Delta\tau = \tau C_6H_6 - \tau CDCl_3$. [e] Obscured by $[Mo(CO)_6]$ absorption. [f] In C_6H_6. [g] Not recorded. [h] Obscured by δ(WCO). [i] ν(P=Se). [j] ν(As=S). [k] Obscured by ν(Cr–CO). [l] ν(As=O). [m] S–Me. [n] In $CHCl_3$. [o] bdm = Bis(diphenylphosphinothioyl)methane. [p] P–CH$_2$–P, triplet due to coupling with equivalent ^{31}P nuclei. [q] Not resolved due to sample decomposition. [r] P–CH$_2$–P, Doublet of doublets due to coupling with non-equivalent ^{31}P nuclei.

^1H N.m.r. spectral data for the complexes are listed in Table 1. Comparison of the spectra in $CDCl_3$ of the methylated ligands and their complexes showed that the methyl protons experienced a slight deshielding effect on co-ordination. In benzene solution however the protons moved upfield, indicating an association of the aromatic solvent molecules with the solute to produce a shielding effect. Evidence has been presented for similar interactions in benzene solution of unco-ordinated trimethyl-phosphine and -arsine sulphides.[15] This increase in the aromatic-solvent induced shift,[16] termed Δτ, on co-ordination has also been observed for alkyl isocyano-derivatives of chromium carbonyl,[17] and may be related to an increased positive charge on the phosphorus atom as a result of donation of electrons from the chalcogenide donor atom to the metal. This correlates with the fact that the phosphorus atom in the related $(RO)_3PS$ ligands becomes more susceptible to nucleophilic attack on co-ordination.[18] The Δτ values decrease with increasing phenyl substitution on the ligand.

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Reactivity of the Complexes.—Consistent with the fact that the metal–chalcogenide bond is essentially of unit bond order, we found that the co-ordinated chalcogenide ligand was readily displaced under mild conditions. Thus carbon monoxide when bubbled through benzene solutions of complexes $[M(CO)_5L]$ ($M = Cr$ or W; $L = Me_2PhPS$ or Me_2PhPSe) warmed under reflux for 30 min yielded the parent hexacarbonyl complex. Under similar conditions reaction of the complexes with triphenylphosphine yielded mainly $[M(CO)_5(Ph_3P)]$ as well as *trans*-$[M(CO)_4(Ph_3P)_2]$, $[M(CO)_6]$, and the free phosphine chalcogenide. Separate experiments indicated that the hexacarbonyl complex arises from thermal decomposition of the sulphide complex.

TABLE 2

Analytical data and m.p.s for the complexes

Complex	Analytical data (%) [a] C	H	S	M.p. (t/°C) [b]
$[Cr(CO)_5(Me_3PS)]$	32·5(32·0)	3·3(3·0)	10·7(10·7)	87
$[W(CO)_5(Me_3PS)]$	22·8(22·25)	2·3(2·1)	8·25(7·4)	105
$[Cr(CO)_5(Me_2PhPS)]$	43·1(43·1)	3·0(3·0)	9·1(8·8)	74
$[W(CO)_5(Me_2PhPS)]$	31·9(31·6)	2·3(2·2)	6·6(6·5)	91
$[Mo(CO)_5(Me_2PhPS)]$	37·15(38·4)	2·7(2·7)		70 (decomp.)
$[Cr(CO)_5(MePh_2PS)]$	51·0(51·0)	3·2(3·1)	7·6(7·6)	86
$[W(CO)_5(MePh_2PS)]$	39·1(38·9)	2·4(2·3)	6·2(5·8)	106
$[Cr(CO)_5(Ph_3PS)]$	58·3(56·8)	3·6(3·1)		*c*
$[W(CO)_5(Ph_3PS)]$	45·4(44·7)	2·7(2·4)	6·7(5·2)	123
$[Cr(CO)_5(Me_2PhPSe)]$	38·3(38·2)	2·7(2·7)		95
$[W(CO)_5(Me_2PhPSe)]$	29·2(28·7)	2·0(2·0)		121
$[Cr(CO)_5(Me_3AsS)]$	27·8(27·9)	2·7(2·6)	9·9(9·3)	109
$[W(CO)_5(Me_3AsS)]$	20·2(20·2)	1·9(1·9)	6·4(6·7)	123
$[W(CO)_5(Ph_3AsO)]$	42·9(42·7)	2·6(2·3)		90 (decomp.)
$[Me_2PhPSMe][Cr(CO)_5I]$	32·9(33·3)	2·9(2·8)	24·7(25·2) [d]	68
$[Me_2PhPSMe][W(CO)_5I]$	26·6(26·4)	2·3(2·2)	19·7(20·0) [d]	72
$[Cr(CO)_5(bdm)]$ [e]	57·0(56·3)	3·9(3·5)	10·4(10·0)	135 (decomp.)
$[W(CO)_5(bdm)]$ [e]	47·7(46·6)	3·2(2·8)	8·9(8·3)	130

[a] Calculated values in parentheses. [b] decomp. = Decomposed. [c] Not recorded. [d] I. [e] bdm = Bis(diphenylphosphinothioyl)methane.

Treatment of the complexes with excess of methyl iodide at room temperature afforded the anionic carbonyl derivatives $[M(CO)_5I]^-$ ($M = Cr$ or W), the counter cation being the methylated phosphine sulphide, $[Me_2PhPSMe]^+$ [equation (1)]. The formulation was confirmed by treating u.v.-irradiated solutions of the

$$[M(CO)_5(Me_2PhPS)] \xrightarrow{MeI} [Me_2PhPSMe][M(CO)_5I] \quad (1)$$

hexacarbonyl complex in tetrahydrofuran with $[Me_2PhPSMe]^+I^-$, thereby isolating identical products. This result may be contrasted with the oxidative addition of methyl iodide to *trans*-$[Fe(CO)_3(Me_3P)_2]$ to give the acetyliodo-derivative *trans*-$[FeI(COMe)(CO)_2(Me_3P)_2]$.[19]

The Complexes $[M(CO)_5L][L = Ph_2P(S)CH_2P(S)Ph_2]$.—Although chelating phosphines,[20] arsines,[21] and stibines [22] have been reported to function as monodentate ligands, no such complexes have been reported for the analogous phosphine sulphides. Isolation of the $[M(CO)_5L]$ chromium and tungsten derivatives of bis(diphenylphosphinothioyl)methane was achieved in a manner similar to that described for the monodentate phosphine sulphide complexes. Evidence for the monodentate nature of the ligand is as follows. The i.r. spectra (Table 1) in the CO stretching region are virtually identical to those observed for the corresponding R_2R^1PS complexes, and for the chromium complex one strong band at 616 cm^{-1} and two at 602 and 595 cm^{-1} can be assigned to the P=S stretching frequency of the free and co-ordinated P=S groups respectively. Chelated complexes show P=S bands at lower frequencies (580—560 cm^{-1}).[23] In the n.m.r. spectra, the observation of a doublet of doublets centred at τ 5·92, assignable to the methylene protons, signifies the non-equivalence of the phosphorus atoms. A triplet would be expected for a chelated [23] or bridging ligand. Attempts to convert these complexes to $[M(CO)_4L][L = Ph_2P(S)CH_2P(S)Ph_2]$ or $[M(CO)_5]_2L$, L now acting as a bidentate or bridging ligand respectively, have so far been unsuccessful, although similar reactions have been observed for phosphines,[20] arsines,[21] and stibines.[22]

EXPERIMENTAL

I.r. spectra (4 000—250 cm^{-1}) were recorded using a Beckman IR 20 spectrophotometer. N.m.r. spectra were measured using a JEOL JNM–C–60 HL spectrometer. Microanalyses were carried out by Dr. A. Campbell, University of Otago. Analytical data are summarised in Table 2.

All reactions were performed under an atmosphere of

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oxygen-free nitrogen; all complexes isolated were washed with pentane, and dried *in vacuo* at 25 °C. Tetrahydrofuran was sodium-dried; other laboratory-grade solvents were used as purchased. Trimethyl- and triphenyl-phosphine sulphide were used as obtained from Maybridge Chemical Co., triphenylarsine oxide from Koch–Light Laboratories Ltd., while dimethylphenylphosphine sulphide [14] and selenide,[24] methyldiphenylphosphine sulphide,[14] and trimethylarsine sulphide [25] were prepared by literature methods.

The Complexes $[M(CO)_5L]$ [M = Cr or W; L = Me_3PS, Me_2PhPS, $MePh_2PS$, Ph_3PS, Me_2PhPSe, Me_3AsS, and $Ph_2P(S)CH_2P(S)Ph_2$].—These were obtained in 40—70% yield by similar methods of which the following is typical.

The complex $[Cr(CO)_6]$ (0·66 g, 3 mmol) was dissolved in tetrahydrofuran (60 cm^3) and the solution irradiated in an u.v. cell for 1 h. Me_3PS (0·3 g, 3 mmol) dissolved in tetrahydrofuran (20 cm^3), was added to the orange solution and the mixture stirred for 1 h. The solvent was completely removed under vacuum and the excess of $[Cr(CO)_6]$ sublimed from the residue *in vacuo* at room temperature. The resultant solid was dissolved in benzene (50 cm^3) and filtered through Kieselguhr to give a yellow solution, which was reduced in volume to 10 cm^3. On addition of n-hexane, bright yellow *crystals* (0·55 g, 61%) were formed.

For L = Ph_3PS it was found necessary to continue the irradiation for 10 min after the addition of the ligand to the appropriate solution. The complex $[W(CO)_5(Ph_3AsO)]$ was isolated in 10% yield by a procedure similar to that outlined above except that the residue was extracted with warm n-hexane; $[W(CO)_5(Ph_3As)]$ was also found, together with unidentifiable products, in the residue. Where M = W and L = Me_3AsO it was found that, when the residue was extracted with warm n-hexane, only the complex $[W(CO)_5(Me_3As)]$ could be isolated and characterised. The complex $[Mo(CO)_5(Me_2PhPS)]$ was prepared by direct irradiation of $[Mo(CO)_6]$ and the ligand in benzene solution.[26] Due to rapid decomposition in solution, samples were always contaminated with the parent hexacarbonyl complex. Yield 10%.

Reaction of $[M(CO)_5(Me_2PhPS)]$ (M = Cr or W) *with* L (L = CO or Ph_3P).—These reactions were all carried out in a similar manner of which the following is typical.

Triphenylphosphine (0·32 g, 1·15 mmol) was added to a solution of the complex $[Cr(CO)_5(Me_2PhPS)]$ (0·42 g, 1·15 mmol) in benzene (10 cm^3) and the mixture heated under gentle reflux for 1 h. The i.r. spectrum of the reaction mixture indicated the presence of $[Cr(CO)_6]$ as well as the phosphine derivatives. The solvent was removed under reduced pressure and $[Cr(CO)_6]$ sublimed from the residue *in vacuo*. Fractional crystallisation from benzene–hexane (or chromatography on alumina) yielded two products, identified as *trans*-$[Cr(CO)_4(Ph_3P)_2]$ (0·04 g, 0·06 mmol) and $[Cr(CO)_5(Ph_3P)]$ (0·37 g, 0·8 mmol) from their i.r. spectra.

Preparation of $[Me_2PhPSMe][M(CO)_5I]$ (M = Cr or W).—*Method* (A). The complexes $[M(CO)_5(Me_2PhPS)]$ (0·3 mmol) were dissolved in methyl iodide (5 cm^3) and the resulting solution stirred for 20 h. After removal of methyl iodide under reduced pressure, the residue was dissolved in acetone (20 cm^3) and filtered through kieselguhr. Reduction of the volume, followed by addition of diethyl ether and cooling to 0 °C, allowed isolation of the *product* as yellow crystals. Yields were 50—60%.

Method (B). The complex $[M(CO)_6]$ (0·73 mmol) was dissolved in tetrahydrofuran (60 cm^3) and irradiated for 1 h. $[Me_2PhPSMe]I$ (0·74 mmol) was added and after stirring for a further 4 h the unreacted starting material was filtered off. The solvent was removed under vacuum and the residue treated as described in method (A).

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