Tertiary Phosphine and Arsine Chalcogenide Derivatives of the Group VI Metal Carbonyls

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Summary The addition of the title ligands to u.v.-irradiated tetrahydrofuran solutions of $Cr(CO)_6$ or $W(CO)_6$ have produced new derivatives of the type $M(CO)_5L$; ^1H n.m.r. studies in benzene show these compounds to be associated with the solvent molecule.

FEW compounds of the type $M(CO)_{6-x}L_x$ are known, where L is a ligand containing a chalcogen atom (S,Se) functioning as a two-electron donor.[1] More often such ligands occur as bridging groups. In view of the lack of knowledge on these simple substituted carbonyl compounds, especially the selenides, we have undertaken a study of the synthesis and reactivity of some tertiary phosphine and arsine chalcogenide complexes of the Group VI metal carbonyls. Thermal reactions between the carbonyls and chalcogenide ligands produced decomposition products; however, an extensive series of compounds of the type $M(CO)_5L$ (M=Cr, W; L=Me_3PS, Me_2PhPS, Ph_3PS, Me_3AsS, and Me_2PhPSe) was obtained, as moderately air-stable yellow crystalline solids, upon the addition of L to u.v.-irradiated tetrahydrofuran solutions of the appropriate metal carbonyl. Yields rarely exceeded 50%. Good elemental analyses were obtained and for $Cr(CO)_5Me_3PS$ the mass spectrum showed the parent molecular ion (*m/e* 300). The molybdenum analogues could be isolated with difficulty and in lower yields.

The i.r. spectra (cyclohexane) of the complexes in the CO stretching region is of interest. A typical spectrum [*e.g.* $Cr(CO)_5Me_3PS$] shows five well spaced bands at 2062m, 1984m, 1944s, 1927s, and 1909s cm^{-1}, suggesting, that as a consequence of the nonlinearity of the M–S(Se)–P bond,[2] the interaction between the co-ordinated ligand and the equatorial CO groups is considerable. The relative values of the CO frequencies for analogous sulphide and selenide complexes indicate that the contribution by these ligands to the total charge accumulation on the central metal atom is similar. The P=S and P=Se stretching frequencies decrease by about 10 to 25 cm^{-1} on co-ordination, consistent with the bonding of the chalcogen atoms to the metal.[3] ^1H n.m.r. studies of the methylated derivatives in benzene show an upfield shift (0·2—0·3 τ) of the methyl protons, with respect to the free ligand, indicating association of the solvent with the complexes to produce a shielding effect. Evidence has been presented previously for similar interactions in benzene solutions of unco-ordinated trimethyl-phosphine and -arsine sulphides.[4] In $CDCl_3$ the protons move slightly to lower field ($<$0·2 τ) on co-ordination.

Initial experiments show that the chalcogenides are readily displaced by carbon monoxide or tertiary phosphines, but studies on the reactivity of these sulphur and selenium donor complexes are continuing.

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