

(Diphos)-molybdenum(I) and -tungsten(I) Dicarbonyl Complexes*

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THE occurrence of mononuclear complexes of molybdenum and tungsten in the oxidation state I is unusual, and hitherto only two classes of complex have been reported, $[\text{M}^{\text{I}}(\text{C}_6\text{H}_5)_2]^+$ ($\text{M} = \text{Mo}, \text{W}$)¹ and $[\text{Mo}(\text{C}_5\text{H}_5)(\text{C}_6\text{H}_5)]$.² Both of these series are very liable to oxidation. In contrast to these we now report air-stable complexes obtained by iodine oxidation of the corresponding bis(diphos)-molybdenum and -tungsten dicarbonyl complexes.

It has previously been shown that the halogen oxidation of di-(tertiary arsine)- and bipyridyl-substituted Group VI metal carbonyls provides a valuable method of preparation of compounds in which the metal has a low oxidation state and also an unusual stereochemistry.³⁻⁶ Thus, the compounds $\text{M}(\text{CO})_2(\text{diars})_2$,[†] where $\text{M} = \text{Cr}, \text{Mo}, \text{W}$, react with iodine and bromine to form seven-coordinate diamagnetic complexes of the bivalent metal, $[\text{M}^{\text{II}}(\text{CO})_2(\text{diars})_2\text{X}]_2$.

In the reaction of iodine with $\text{M}(\text{CO})_2(\text{diphos})_2$, three equivalents of iodine are absorbed without

evolution of carbon monoxide, to give red crystalline compounds $[\text{M}(\text{CO})_2(\text{diphos})_2]\text{I}_3$. The complexes are paramagnetic ($\mu_{\text{eff}} \sim 1.6-1.8$ B.M.), monomeric, and uni-univalent electrolytes in nitrobenzene. Only one strong carbonyl stretching frequency is observed, indicating a *trans* distribution of the carbonyl groups. The formulation of these complexes as derivatives of molybdenum and tungsten(I) has been confirmed by the isolation of the corresponding perchlorates, $[\text{M}(\text{CO})_2(\text{diphos})_2]\text{ClO}_4$ ($\text{M} = \text{Mo}, \text{W}$), from reaction of the tri-iodides with silver perchlorate in tetrahydrofuran.

There appears to be no tendency for the complexes to dimerise, as occurs with the $[\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]_2$ ($\text{M} = \text{Mo}, \text{W}$)^{7,8} and this may be related to the steric crowding that occurs due to the phosphine ligands. This steric effect may also account for the *trans*-distribution of the carbonyl groups rather than the expected *cis*-distribution.

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* Diphos = [bis(diphenyl)phosphinoethane].

† Diars = *o*-C₆H₄(AsMe₂)₂.

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