

678. *Substituted Group VI Carbonyls. Part III.¹ The Action of Halogens on Carbonyldi(tertiary arsine)tungsten and Further Studies on Halogenocarbonylmolybdenum Complexes.*

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The action of halogens on the *o*-phenylenebisdimethylarsine (Diars) derivatives formed from hexacarbonyltungsten has been investigated. The complex $[\text{W}(\text{CO})_4(\text{Diars})]$ is oxidised at room temperature with two equivalents of iodine and bromine to produce, respectively, the seven-co-ordinate tungsten(II) derivatives, $[\text{W}(\text{CO})_4(\text{Diars})\text{I}]_3$ and $[\text{W}(\text{CO})_3(\text{Diars})\text{Br}_2]$. Use of an excess of bromine leads to a tungsten(III) complex $[\text{W}(\text{CO})_3(\text{Diars})\text{Br}_2]\text{Br}$. This is the first seven-co-ordinate tungsten(III) complex to have been described. Oxidation of the complex $[\text{W}(\text{CO})_2(\text{Diars})_2]$ with two equivalents of iodine and bromine yields also seven-co-ordinate tungsten(II) complexes $[\text{W}(\text{CO})_2(\text{Diars})_2\text{X}]\text{X}$. Reaction of an excess of these halogens results only in the formation of the corresponding trihalides $[\text{W}(\text{CO})_2(\text{Diars})_2\text{X}]\text{X}_3$, without further oxidation of the metal. As an extension of earlier work, oxidation of the complex $[\text{Mo}(\text{CO})_4(\text{Diars})]$ has been further investigated, and new paramagnetic complexes of molybdenum(II), $[\text{Mo}(\text{CO})_2(\text{Diars})\text{I}_2]$, and of molybdenum(III), $[\text{Mo}(\text{CO})_2(\text{Diars})\text{I}_3]$, are also described.

In Part II of this series,¹ oxidation of carbonyl(substituted diarsine)molybdenums was shown to yield complexes of seven-co-ordinate molybdenum(II). For example, bromine and iodine react with the compound $[\text{Mo}(\text{CO})_4(\text{Diars})]$ to produce the complexes $[\text{Mo}(\text{CO})_3(\text{Diars})\text{X}_2]$ [where Diars = *o*-C₆H₄(AsMe₂)₂]. In this paper, we describe the oxidation of similar tungsten complexes and the preparation of some new derivatives of molybdenum(II) and molybdenum(III).

Initially, halogen oxidations were studied spectrophotometrically¹ and measurements indicated that the complex $[\text{W}(\text{CO})_4(\text{Diars})]$ is oxidised by iodine and bromine to derivatives of tungsten(II). On a preparative scale, addition of iodine in any proportion to a chloroform or benzene solution of the carbonyldiarsine produced the tri-iodide $[\text{W}(\text{CO})_4(\text{Diars})\text{I}]_3$. Precipitation of this complex rather than of the monoiodide results presumably from the higher solubility of the latter. However, reduction of a suspension of the tri-iodide with sulphur dioxide readily furnishes the monoiodide $[\text{W}(\text{CO})_4(\text{Diars})\text{I}]\text{I}$. The formulation of these compounds implies that they should be diamagnetic 1 : 1 electrolytes, and the physical properties given in the Table are seen to be consistent with this suggestion.

Halogenocarbonylmetal complexes.

Complex	Colour	Mol. conductivity ($\Omega^{-1} \text{ cm}^2$) (10^{-3}M in PhNO_2)	Magnetism (μ_{eff} of solid at 20°)	C-O stretching frequencies (cm^{-1}) in Nujol
$[\text{W}(\text{CO})_3(\text{Diars})\text{Br}_2]$	Yellow	2.1	Diamag.	1905, 1942, 2030
$[\text{W}(\text{CO})_3(\text{Diars})\text{Br}_2]\text{Br}$...	Yellow-green	24.0	1.54	1915, 1950, 2041
$[\text{W}(\text{CO})_4(\text{Diars})\text{I}]\text{I}$	Orange	27.3	Diamag.	1960, 2005, 2040, 2082
$[\text{W}(\text{CO})_4(\text{Diars})\text{I}]_3$	Deep orange	25.0	Diamag.	1960, 2000, 2040, 2080
$[\text{W}(\text{CO})_2(\text{Diars})_2\text{Br}]\text{Br}$...	Yellow	24.3	Diamag.	1853, 1927
$[\text{W}(\text{CO})_2(\text{Diars})_2\text{Br}]\text{Br}_3$...	Deep yellow	28.1	Diamag.	1853, 1927
$[\text{W}(\text{CO})_2(\text{Diars})_2\text{I}]\text{I}$	Deep yellow	26.4	Diamag.	1852, 1925
$[\text{W}(\text{CO})_2(\text{Diars})_2\text{I}]_3$	Deep orange	27.2	Diamag.	1852, 1925
$[\text{Mo}(\text{CO})_2(\text{Diars})\text{I}_2]$	Deep orange	1.5	1.98	1887, 1942
$[\text{Mo}(\text{CO})_2(\text{Diars})\text{I}_3]$	Dark brown	1.6	1.40	1905, 1960

Further, gas-burette measurements indicated that no carbon monoxide was liberated from $[\text{W}(\text{CO})_4(\text{Diars})]$ on oxidation. Preparation of the perchlorate $[\text{W}(\text{CO})_4(\text{Diars})\text{I}]\text{ClO}_4$ or some other salt would be useful in characterising the complex, but this was precluded

¹ Part II, Nigam, Nyholm, and Stiddard, *J.*, 1960, 1806.

by unhelpful solubility relations. However, conductometric titration with mercuric perchlorate¹ certainly indicated that one halogen remains un-ionised in nitrobenzene. The solubilities of these halides and of most of the other complexes here described are unfortunately too small for molecular-weight determinations. It is noteworthy that oxidation of the complex $[\text{W}(\text{CO})_4(\text{Diars})]$ by iodine differs from those of complexes $[\text{Mo}(\text{CO})_4(\text{Diars})]$ and $[\text{W}(\text{CO})_4(\text{bipy})]$, for these give complexes of the type $[\text{M}(\text{CO})_3(\text{ligand})\text{I}_2]$.^{1,3} The reaction of $[\text{W}(\text{CO})_4(\text{Diars})]$ with an excess of iodine under a variety of conditions has also been investigated; although evidence for a tungsten(III) complex $[\text{W}(\text{CO})_3(\text{Diars})\text{I}_2]\text{I}$ was obtained, this could not be obtained pure.

Oxidation of the complex $[\text{W}(\text{CO})_4(\text{Diars})]$ by bromine yields several new compounds. At room temperature two equivalents of the halogen produces the seven-co-ordinate complex $[\text{W}(\text{CO})_3(\text{Diars})\text{Br}_2]$, analogous to the molybdenum complex $[\text{Mo}(\text{CO})_3(\text{Diars})\text{Br}_2]$ obtained under similar conditions. These two compounds have been shown to have similar physical characteristics, being diamagnetic, non-electrolytes, and monomeric in nitrobenzene, and having three characteristic C–O stretching modes in the infrared region. However, in contrast to the behaviour with the molybdenum compound $[\text{Mo}(\text{CO})_4(\text{Diars})]$, an excess of bromine does not displace all carbon monoxide from the tungsten complex, but a tungsten(III) complex $[\text{W}(\text{CO})_3(\text{Diars})\text{Br}_2]\text{Br}$ has been isolated after oxidation by an excess of the halogen in carbon tetrachloride. This seven-co-ordinate complex should have a spin-paired electron configuration d^3 and the observed magnetic moment, μ_{eff} 1.54 B.M., is in accord with this suggestion. The reduction of the magnetic moment below the spin-only value is not unusual for second- and third-row complexes. The theory is well-developed for regular octahedral complexes, but for seven-co-ordinate compounds other factors such as the marked deviation from cubic symmetry must be considered. The magnetic properties of d^4 and d^3 spin-paired seven-co-ordinate complexes will be discussed in detail when the corresponding complexes of chromium are presented later. Further, it is relevant that the three C–O stretching vibrations occur at higher frequencies than in the compound $[\text{W}(\text{CO})_3(\text{Diars})\text{Br}_2]$. This is consistent with the formulation of the tungsten(III) complex as containing a unipositive cation.

These halogen oxidations may be compared with recent further investigations of the reactions of iodine with the complex $[\text{Mo}(\text{CO})_4(\text{Diars})]$ under conditions more vigorous than those examined previously.¹ In boiling carbon tetrachloride, an octahedral molybdenum(II) complex $[\text{Mo}(\text{CO})_2(\text{Diars})\text{I}_2]$ (μ_{eff} 1.98 B.M.) is formed, and in boiling chloroform a seven-co-ordinate molybdenum(III) compound $[\text{Mo}(\text{CO})_2(\text{Diars})\text{I}_2]$ (μ_{eff} 1.40 B.M.). The influence of solvent on the nature of the products appears unusual and, perhaps, of potential importance.

Oxidation of the bisdiarsinetungsten complex, $[\text{W}(\text{CO})_2(\text{Diars})_2]$ follows the pattern established for the molybdenum analogue,¹ complexes of the type $[\text{W}(\text{CO})_2(\text{Diars})_2\text{X}]\text{X}$ being formed on reaction with two equivalents of iodine and bromine. It was again noted that an excess of halogen, at room or elevated temperature, neither displaced more carbon monoxide nor further oxidised the metal, but produced only the trihalides $[\text{W}(\text{CO})_2(\text{Diars})_2\text{X}]\text{X}_3$, which have properties almost identical with those of the monohalides. Recent work by Dr. S. S. Sandhu in this Department has shown that molybdenum and tungsten complexes of this type can also be prepared by high-pressure carbonylation of the complexes $[\text{M}(\text{Diars})_2\text{X}_2]$. These and similar reactions are under investigation.

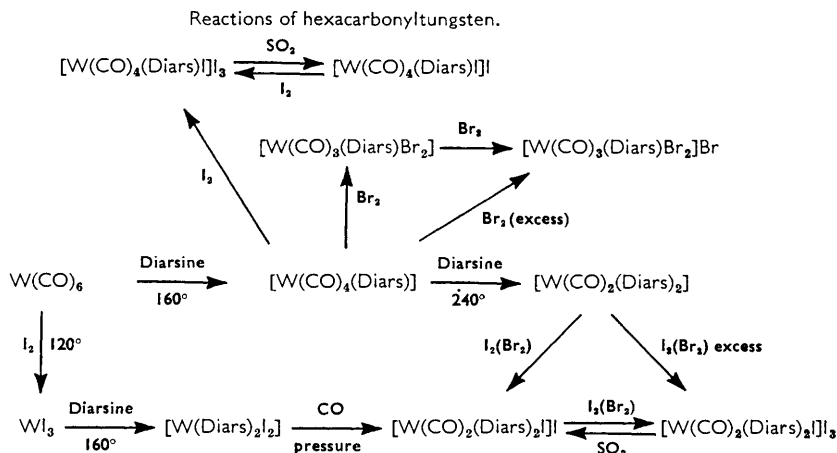
The annexed Scheme summarises the compounds formed in this study and their relations with those formed by carbonylation. Comparison with the behaviour of the molybdenum analogue shows that, on oxidation, the tungsten complex $[\text{W}(\text{CO})_4(\text{Diars})]$ releases carbon monoxide less readily. This order of behaviour appears to extend to chromium, for oxidation of the complex $[\text{Cr}(\text{CO})_4(\text{Diars})]$ results in complete loss of carbon

² Nigam, Nyholm, and Stiddard, *J.*, 1960, 1803.

³ Stiddard, *J.*, 1962, 4712.

monoxide; however, oxidation of the bisdiarsine compound results in the formation of the seven-co-ordinate chromium(II) complex $[\text{Cr}(\text{CO})_2(\text{Diars})_2\text{X}]\text{X}$.⁴

The existence of the complexes described above supports the suggestion that, in the second and third transition series at least, metals with d^4 or d^3 configuration give complexes of co-ordination number 7, the electrons being accommodated in low-lying d_{zz} and d_{yz} orbitals.¹ Further examples of this behaviour are being sought; the seven-co-ordinate d^4 complex $[\text{Re}(\text{CO})(\text{Diars})_2\text{I}_2]\text{I}$ has been prepared by Dr. G. J. Kirkham and will be reported later.



In addition to the seven-co-ordinate Diarsine complexes of bivalent molybdenum and tungsten described above and by us previously,¹ a series of similar complexes involving co-ordination of a chelating disulphide ligand has been described recently by Mannerskantz and Wilkinson.⁵

EXPERIMENTAL

Di-iododicarbonyl-o-phenylenebisdimethylarsinemolybdenum(II).—The complex $[\text{Mo}(\text{CO})_4(\text{Diars})]$ (0.5 g.) and iodine (0.54 g.) were refluxed in carbon tetrachloride (100 ml.) for about 3 hr. under dry nitrogen. After cooling, a red-brown precipitate (0.6 g.) was filtered off, washed with light petroleum, and dried *in vacuo* (Found: C, 20.9; H, 2.5; I, 36.0; Mo, 13.5. $\text{C}_{12}\text{H}_{16}\text{As}_2\text{I}_2\text{MoO}_2$ requires C, 20.8; H, 2.3; I, 36.7; Mo, 13.9%). The molecular weight (cryoscopy in 0.54% PhNO_2 solution) was 671 (calc., 692). The compound is reasonably stable towards air and moisture, is soluble in acetone or nitrobenzene, and sparingly soluble in chloroform, but practically insoluble in benzene, carbon tetrachloride, light petroleum, alcohol, or water.

Tri-iododicarbonyl-o-phenylenebisdimethylarsinemolybdenum(III).—The complex $[\text{Mo}(\text{CO})_4(\text{Diars})]$ (0.5 g.) and iodine (0.54 g.) were refluxed in chloroform (100 ml.) for ~4 hr. under dry nitrogen. After cooling, the dark brown crystals (0.45 g.) were filtered off, washed with light petroleum, and dried *in vacuo* (Found: C, 17.25; H, 2.1; I, 47.0; Mo, 11.3. $\text{C}_{12}\text{H}_{16}\text{As}_2\text{I}_3\text{MoO}_2$ requires C, 17.6; H, 2.0; I, 46.6; Mo, 11.7%). The compound is similar to, but markedly less soluble than, the above molybdenum(II) complex.

Dibromotricarbonyl-o-phenylenebisdimethylarsinetungsten(II).—The complex $[\text{W}(\text{CO})_4(\text{Diars})]$ (0.2 g.) in ice-cooled carbon tetrachloride (100 ml.) was treated with bromine (0.055 g.) in carbon tetrachloride (40 ml.) under nitrogen with stirring. The yellow product (0.21 g.) was filtered off under nitrogen, washed with light petroleum, and dried *in vacuo* (Found: C, 21.7; H, 2.3; As, 20.8; Br, 23.0; W, 25.0. $\text{C}_{13}\text{H}_{16}\text{As}_2\text{Br}_2\text{WO}_3$ requires C, 21.85; H, 2.2; As, 21.0; Br, 22.4; W, 25.7%). The molecular weight (cryoscopy in 0.48% PhNO_2 solution) was 732 (calc., 714). The compound decomposes slowly in air and is soluble in acetone or nitrobenzene, but only very slightly soluble in other common solvents.

⁴ Nyholm, Pande, and Stiddard, unpublished work.

⁵ Mannerskantz and Wilkinson, *J.*, 1962, 4454.

Dibromotricarbonyl-o-phenylenebisdimethylarsinetungsten(III) Bromide.—The complex $[\text{W}(\text{CO})_4(\text{Diars})]$ (0.2 g.) in carbon tetrachloride (100 ml.) was treated with bromine (0.11 g.) in the same solvent (40 ml.) under nitrogen with stirring. The yellow-green precipitate (0.22 g.) was washed with light petroleum and dried *in vacuo* (Found: C, 19.3; H, 2.4; As, 18.5; Br, 29.5; W, 23.0. $\text{C}_{13}\text{H}_{16}\text{As}_2\text{Br}_3\text{O}_3\text{W}$ requires C, 19.7; H, 2.0; As, 18.9; Br, 30.2; W, 23.2%). The compound is hygroscopic, decomposes readily in moist air, and is less soluble than the above tungsten(II) complex.

Iodotetracarbonyl-o-phenylenebisdimethylarsinetungsten(II) Tri-iodide.—The complex $[\text{W}(\text{CO})_4(\text{Diars})]$ (0.2 g.) in chloroform (25 ml.) was treated with iodine (0.18 g.) in chloroform (20 ml.), and the solution was boiled for several min. After cooling, the red-brown precipitate (0.30 g.) was filtered off, washed with light petroleum, and dried *in vacuo* (Found: C, 15.4; H, 1.5; I, 46.0; W, 17.2. $\text{C}_{14}\text{H}_{16}\text{As}_2\text{I}_4\text{O}_4\text{W}$ requires C, 15.4; H, 1.5; I, 46.5; W, 16.9%). The compound appears to be stable in air, is moderately soluble in acetone or nitrobenzene and sparingly soluble in chloroform, but insoluble in other solvents.

Iodotetracarbonyl-o-phenylenebisdimethylarsinetungsten(II) Iodide.—A suspension of the complex $[\text{W}(\text{CO})_4(\text{Diars})\text{I}]_3$ (0.2 g.) in ethanol (20 ml.) was treated with sulphur dioxide for about 30 min. The orange product (0.12 g.) was washed with ethanol and dried *in vacuo* (Found: C, 19.8; H, 2.0; I, 30.0; W, 22.4. $\text{C}_{14}\text{H}_{16}\text{As}_2\text{I}_2\text{O}_4\text{W}$ requires C, 20.1; H, 1.9; I, 30.4; W, 22.0%). Its properties are very similar to those of the tri-iodide.

Iododicarbonylbis-(o-phenylenebisdimethylarsine)tungsten(II) Iodide.—The complex $[\text{W}(\text{CO})_2(\text{Diars})_2]$ (0.2 g.) in chloroform (25 ml.) was treated with iodine (0.063 g.) in carbon tetrachloride (30 ml.) under nitrogen with stirring. The deep yellow compound (0.22 g.) which separated immediately was filtered off, washed with light petroleum, and dried *in vacuo* (Found: C, 25.1; H, 3.1; I, 24.2; W, 17.0. $\text{C}_{22}\text{H}_{32}\text{As}_4\text{I}_2\text{O}_2\text{W}$ requires C, 24.8; H, 3.0; I, 23.9; W, 17.3%). It is moderately soluble in acetone or nitrobenzene, but only very slightly soluble in other organic solvents.

Iododicarbonylbis-(o-phenylenebisdimethylarsine)tungsten(II) Tri-iodide.—Similar treatment of the complex $[\text{W}(\text{CO})_2(\text{Diars})_2]$ (0.2 g.) in chloroform (25 ml.) with iodine (0.13 g.) in carbon tetrachloride (40 ml.) produced the deep orange compound (0.27 g.) (Found: C, 19.9; H, 2.1; I, 38.8; W, 13.7. $\text{C}_{22}\text{H}_{32}\text{As}_4\text{I}_4\text{O}_2\text{W}$ requires C, 20.0; H, 2.5; I, 38.5; W, 14.0%). Its properties are very similar to those of the monoiodide.

Bromodicarbonylbis-(o-phenylenebisdimethylarsine)tungsten(II) Bromide.—The complex $[\text{W}(\text{CO})_2(\text{Diars})_2]$ (0.2 g.) in chloroform (25 ml.) was treated slowly with bromine (0.04 g.) in carbon tetrachloride (20 ml.) with stirring under nitrogen. The deep yellow product (0.25 g.) was treated as above (Found: C, 26.9; H, 3.3; Br, 16.3; W, 18.6. $\text{C}_{22}\text{H}_{32}\text{As}_4\text{Br}_2\text{O}_2\text{W}$ requires C, 27.2; H, 3.3; Br, 16.5; W, 18.9%). The properties are similar to those of the corresponding iodide.

Bromodicarbonylbis-(o-phenylenebisdimethylarsine)tungsten(II) Tribromide.—Treatment, as above of the complex $[\text{W}(\text{CO})_2(\text{Diars})_2]$ (0.2 g.) in chloroform (25 ml.) with bromine (0.1 g.) in carbon tetrachloride (25 ml.) yielded this compound (Found: C, 23.6; H, 3.0; Br, 29.2; W, 16.0. $\text{C}_{22}\text{H}_{32}\text{As}_4\text{Br}_4\text{O}_2\text{W}$ requires C, 23.3; H, 2.8; Br, 28.3; W, 16.2%). Its properties are similar to those described for the corresponding compounds above.

Physical Measurements and Analyses.—These were carried out as described previously.^{1,2}

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