

578. Substituted Group VI Carbonyls. Part IV.¹ The Actions of Halogens on Carbonyldi(tertiary arsine) Complexes of Chromium.

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The actions of halogens on the compounds $\text{Cr}(\text{CO})_4(\text{Diars})$ and $\text{Cr}(\text{CO})_2(\text{Diars})_2$ [$\text{Diars} = o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$] have been investigated. From the former, complexes of chromium(III) only, of the composition $\text{Cr}(\text{Diars})\text{X}_3$ ($\text{X} = \text{Br}, \text{I}$), were isolated. These are believed to be halogen-bridged, octahedrally co-ordinated dimers: the bromide, which is very unstable towards water vapour, readily hydrates to give the known six-co-ordinate compound $[\text{Cr}(\text{Diars})(\text{H}_2\text{O})\text{Br}_2]_0$. Oxidation of the bisdiarsine compound at room temperature produces seven-co-ordinate complexes of chromium(II), $[\text{Cr}(\text{CO})_2(\text{Diars})_2\text{X}]_2\text{X}$, isomorphous with the corresponding molybdenum(II) and tungsten(II) compounds. Excess of halogen produces the trihalide complex without further oxidation of the metal. However, reaction of iodine in boiling carbon tetrachloride yields the chromium(III) complex $[\text{Cr}(\text{Diars})_2\text{I}_2]_3$. The difference in behaviour between the tetracarbonylmonodiarsine complexes of chromium, molybdenum, and tungsten towards halogens is discussed. It is suggested that the instability of seven-co-ordinate monodiarsine complexes of chromium(II), as compared with molybdenum(II) or tungsten(II), is due to the much larger $(n-1)d \rightarrow np$ separation. With dicarbonylbisdiarsinechromium complexes, the carbonyl groups are more strongly bound and the difference between chromium, molybdenum, and tungsten is less obvious.

In Parts I, II, and III of this series^{2,1} it was shown that the oxidation of carbonyldiarsine complexes of molybdenum(0) and tungsten(0) provides a valuable method for producing bivalent compounds of these elements, these being usually seven-co-ordinate. Thus, the compound $\text{Mo}(\text{CO})_4(\text{Diars})$ reacts with iodine to form the seven-co-ordinate non-electrolyte $[\text{Mo}(\text{CO})_3(\text{Diars})\text{I}_2]_0$. We now report the halogen oxidation of the analogous chromium complexes (see Table). Such reactions are of considerable interest for two reasons:

Properties of halogenodiarsinechromium complexes.

Compound	Colour	μ_{eff} (B.M.) *	Λ_m of 10^{-3}M solutions in PhNO_2 ($\text{ohm}^{-1}\text{cm.}^2$)	Infrared spectrum in C—O stretching region (Nujol) †
$[\text{Cr}(\text{Diars})\text{Br}_3]_2$	Green	3.87	2.4	—
$\text{Cr}(\text{Diars})(\text{H}_2\text{O})\text{Br}_3$	Blue	3.85	1.5	—
$[\text{Cr}(\text{Diars})\text{I}_3]_2$	Brown	3.82	1.7	—
$[\text{Cr}(\text{CO})_2(\text{Diars})_2\text{Br}]\text{Br}$	Pale yellow	Diamag.	22.7	1925, 1865
$[\text{Cr}(\text{CO})_2(\text{Diars})_2\text{Br}]\text{Br}_3$	Yellow	Diamag.	26.2	1925, 1865
$[\text{Cr}(\text{CO})_2(\text{Diars})_2\text{I}]\text{I}$	Deep orange	Diamag.	25.8	1923, 1863
$[\text{Cr}(\text{CO})_2(\text{Diars})_2\text{I}]\text{I}_3$	Brown	Diamag.	29.5	1923, 1863
$[\text{Cr}(\text{Diars})_2\text{I}_2]_3$	Dark green	3.83	26.1	—

* In solid state at 20°. † All bands are very strong.

(i) previously no diarsine complex of chromium(II) has been isolated,⁴ and (ii) we wished to see whether it was possible to prepare seven-co-ordinate compounds of chromium(II).

At room temperature, bromine reacts readily with the compound $\text{Cr}(\text{CO})_4(\text{Diars})$ in carbon tetrachloride yielding a green amorphous derivative of chromium(II); there is no evidence for the formation of complexes of intermediate oxidation states. The compound, of composition $\text{Cr}(\text{Diars})\text{Br}_3$, is very unstable towards water vapour, producing,

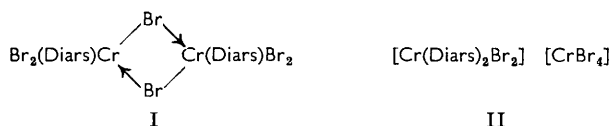
¹ Part III, Lewis, Nyholm, Pande, and Stiddard, *J.*, 1963, 3600.

² Part I, Nigam, Nyholm, Stiddard, *J.*, 1960, 1803.

³ Part II, Nigam, Nyholm, and Stiddard, *J.*, 1960, 1806.

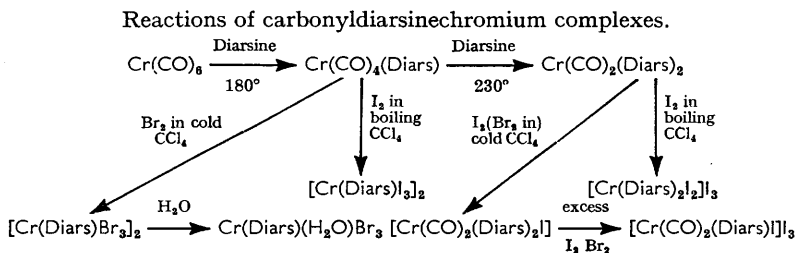
⁴ Nyholm and Sutton, *J.*, 1958, 560.

almost immediately on exposure to air, the known blue compound $[\text{Cr}(\text{Diars})(\text{H}_2\text{O})\text{Br}_3]^{0.4}$. The increase in weight during this hydration corresponds exactly with one molecule of water per molecule of $\text{Cr}(\text{Diars})\text{Br}_3$; the presence of water in the aquo-complex has been confirmed by infrared measurements ($\text{H}-\text{O}-\text{H}$ bending mode at 1613 cm^{-1}). Although the physical properties of the green compound in solution were difficult to determine, it is of interest to consider possible structures. Since one expects five-co-ordinate complexes of chromium(III) to be very unstable because of the d^3 configuration of the metal atom, a structure (I), in which the expected octahedral arrangement of ligands is achieved by dimerisation, seems reasonable, although a structure such as (II) cannot be ignored. We favour structure (I) because: (a) nitrobenzene solutions of the compounds are virtually



non-conducting, and (b) the reflectance spectra of the green and the blue compound in the visible region are very similar, indicating presumably similar environments of the chromium atoms. Unfortunately, solutions of the green compound were too unstable for molecular weights to be determined. No reaction of the compound $\text{Cr}(\text{CO})_4(\text{Diars})$ with iodine at room temperature could be detected, but in boiling carbon tetrachloride all carbon monoxide is expelled to give a brown product of composition $\text{Cr}(\text{Diars})\text{I}_3$, analogous with the bromide discussed above. In contrast to the bromide, however, the complex shows no tendency to react with water vapour.

Oxidation of dicarbonylbisdiarsinechromium follows the pattern established previously for the molybdenum and tungsten analogues.^{1,3} At room temperature, reaction with two equivalents of iodine or bromine yields products which are diamagnetic, 1:1 electrolytes, and strictly isomorphous with the molybdenum(II) and tungsten(II) compounds $[\text{M}(\text{CO})_2(\text{Diars})_2\text{X}]_2\text{X}$. Clearly they must be formulated similarly, *viz.*, $[\text{Cr}(\text{CO})_2(\text{Diars})_2\text{X}]_2\text{X}$, and are the first known examples of chromium(II) (d^4) complexes in which the metal has a co-ordination number of seven. Also it is surprising that the treatment with excess of these halogens at room temperature does not effect oxidation to chromium(III) species, but simply forms the trihalide complexes $[\text{Cr}(\text{CO})_2(\text{Diars})_2\text{X}]_2\text{X}_3$. It is only after prolonged heating with iodine in carbon tetrachloride that carbon monoxide is expelled to yield the chromium(III) derivative $[\text{Cr}(\text{Diars})_2\text{I}_2]_2\text{I}_3$. No well-defined product could be isolated after similar treatment with bromine. A summary of these reactions is given in the annexed scheme.



The behaviour of the carbonyldiarsine complexes of all three metals, chromium, molybdenum, and tungsten, towards bromine and iodine having been studied, it is of interest to compare their behaviour and attempt to understand their similarities and differences. Each dicarbonylbisdiarsine complex gives rise to a seven-co-ordinate $[\text{M}^{\text{II}}(\text{CO})_2(\text{Diars})_2\text{X}]^+$ cation on halogen oxidation. It is noteworthy that under these conditions no carbonyl groups are displaced. This is in keeping with the observation

that, with increasing substitution, the remaining carbonyl groups are more strongly held. Thus the trend of the C–O stretching frequencies in the compounds $\text{Cr}(\text{CO})_6$, $\text{Cr}(\text{CO})_4(\text{Diars})$, and $\text{Cr}(\text{CO})_2(\text{Diars})_2$ support the idea that metal–carbon double bonding increases as the number of carbonyl groups decreases. Although we have no *X*-ray proof that the metal atom is seven-co-ordinate, the physical properties are entirely consistent with this view, especially since so many seven-co-ordinate complexes of metals with the d^4 configuration are now known.⁴

In contrast, considerable variation in behaviour is shown by the monodiarsine complexes towards halogens and, as noted previously,³ there is an increasing tendency for carbon monoxide to be lost on oxidation in the order chromium > molybdenum > tungsten. If one assumes that d_π bonding to carbonyl groups increases as the energy required to remove non-bonding electrons from the metal atoms decreases, then the above order can be understood.⁵ In addition to the high interelection repulsion energy, a further factor tending to inhibit seven-co-ordination by chromium, is the relatively large $(n-1)d \rightarrow np$ separation in the chromium(II) atom as compared with the molybdenum(II) and tungsten(II) atoms. As an indication of this, the $(n-1)d^1 \rightarrow np^1$ promotion energies⁶ for the ions Sc^{2+} , Y^{2+} , and La^{2+} are, respectively, 61,102, 41,401, and 42,015 cm^{-1} (these ions are chosen to obtain d^1 atoms with two positive charges). Whilst we do not suggest that the atoms in the complexes bear a positive charge of two units and recognise that promotion energies are sensitive to formal charge, nevertheless, for comparison, the above figures appear to be significant and the fact that the $(n-1)d \rightarrow np$ spread is probably about 50% greater for chromium(II) than for molybdenum(II) and tungsten(II) suggests very strongly that d orbitals are less accessible in chromium and that seven-co-ordination using three of them is more difficult.

Similar observations have been made by Dr. J. Mašek⁷ from a study of the behaviour towards halogens of complexes of the type $\text{M}(\text{CO})_3(\text{Triarsine})$ (where Triarsine is $\text{Me}_2\text{As}(\text{CH}_2)_3\text{AsMe}(\text{CH}_2)_3\text{AsMe}_2$). When treated with iodine, the tungsten complex yields $[\text{W}(\text{CO})_3(\text{Triarsine})\text{I}]\text{I}$, the molybdenum derivative loses one molecule of carbon monoxide to give $[\text{Mo}(\text{CO})_2(\text{Triarsine})\text{I}_2]^0$ whereas the chromium complex loses *all* carbon monoxide, after forming an unstable univalent intermediate, possibly $[\text{Cr}(\text{CO})_2(\text{Triarsine})\text{I}]^0$.

EXPERIMENTAL

$\mu\mu'$ -Dibromobis-*o*-phenylenebisdimethylarsinetetrabromodichromium(III).—The complex $\text{Cr}(\text{CO})_4(\text{Diars})$ (0.32 g.) in carbon tetrachloride (50 ml.) was treated with bromine (0.35 g.) in the same solvent (25 ml.) under nitrogen with vigorous stirring. The solvent was removed under reduced pressure, leaving the green product (0.3 g.), which was dried *in vacuo* (Found: Cr, 8.8; Br, 41.6. $\text{C}_{20}\text{H}_{32}\text{As}_4\text{Br}_6\text{Cr}_2$ requires Cr, 9.0; Br, 41.5%). The compound is very rapidly hydrated in moist air, so that carbon and hydrogen analyses were not possible. It is only slightly soluble in common solvents, in which it quickly decomposes.

Tribromoquo-*o*-phenylenebisdimethylarsinechromium(III).—The green compound described above, prepared from 0.2 g. of $\text{Cr}(\text{CO})_4(\text{Diars})$, readily absorbed water vapour to produce the blue *quo-compound* (Found: C, 19.7; H, 3.5; As, 25.0; Br, 41.0; Cr, 8.4. $\text{C}_{10}\text{H}_{18}\text{As}_2\text{Br}_3\text{CrO}$ requires C, 20.1; H, 3.0; As, 25.2; Br, 40.3; Cr, 8.7%). It is soluble in acetone, nitrobenzene, and nitromethane, but only very slightly soluble in other common solvents.

$\mu\mu'$ -Di-iodobis-*o*-phenylenebisdimethylarsinetetraiododichromium(III).—A mixture of the complex $\text{Cr}(\text{CO})_4(\text{Diars})$ (0.2 g.) and iodine (0.32 g.) in carbon tetrachloride (40 ml.) was refluxed under nitrogen for 20 hr. The dark brown product (0.21 g.), which separated during reaction, was filtered off, washed with carbon tetrachloride and light petroleum, and dried *in vacuo* (Found: C, 16.6; H, 2.0; I, 52.9; Cr, 7.4. $\text{C}_{20}\text{H}_{32}\text{As}_4\text{CrI}_4$ requires C, 16.7; H, 2.2; I, 53.0; Cr, 7.2%). The solubilities of the compound are similar to those of the corresponding bromide and solutions are similarly unstable.

Monoiododicarbonylbis-*o*-phenylenebisdimethylarsinechromium(II) Iodide.—The compound

⁵ Nyholm, Tilden Lecture, *Proc. Chem. Soc.*, 1961, 273.

⁶ Moore, "Atomic Energy Levels," U.S. Nat. Bur. Standards.

⁷ See Nyholm, Mašek, and Stiddard, *Coll. Czech. Chem. Comm.*, in the press.

$\text{Cr}(\text{CO})_2(\text{Diars})_2$ (0.2 g.) in dichloromethane (30 ml.) was treated with iodine (0.075 g.) in carbon tetrachloride (25 ml.) under nitrogen with constant stirring. The product (0.22 g.), which separated immediately, was washed with light petroleum and dried *in vacuo* (Found: C, 28.4; H, 3.6; I, 27.1; Cr, 6.0. $\text{C}_{22}\text{H}_{32}\text{As}_4\text{CrI}_2\text{O}_2$ requires C, 28.3; H, 3.4; I, 27.2; Cr, 5.6%). The compound which is isomorphous with the corresponding molybdenum and tungsten compounds, is sparingly soluble in acetone and nitrobenzene, but is insoluble in all other common solvents.

Monoiododicarbonylbis-o-phenylenebisdimethylarsinechromium(II) Tri-iodide.—Similar treatment of the complex $\text{Cr}(\text{CO})_2(\text{Diars})_2$ (0.2 g.) in dichloromethane (30 ml.) with iodine (0.15 g.) in carbon tetrachloride (40 ml.) produced the compound (0.28 g.) (Found: C, 22.2; H, 2.6; I, 42.2; Cr, 4.6. $\text{C}_{22}\text{H}_{32}\text{As}_4\text{CrI}_4\text{O}_2$ requires C, 22.2; H, 2.7; I, 42.7; Cr, 4.4%). The physical properties are similar to those of the monoiodide.

Monobromodicarbonylbis-o-phenylenebisdimethylarsinechromium(II) Bromide.—The compound $\text{Cr}(\text{CO})_2(\text{Diars})_2$ (0.2 g.) in dichloromethane (250 ml.) was treated with bromine (0.047 g.) in carbon tetrachloride (25 ml.) under nitrogen with constant stirring. Very efficient stirring was required to avoid local concentrations of bromine. The precipitated product (0.21 g.) was filtered off under nitrogen, washed with light petroleum, and dried *in vacuo* (Found: C, 31.2; H, 4.3; Br, 18.9; Cr, 6.5. $\text{C}_{22}\text{H}_{32}\text{As}_4\text{Br}_2\text{CrO}_2$ requires C, 31.4; H, 3.8; Br, 19.0; Cr, 6.2%). The physical properties are similar to those of the corresponding iodide.

Monobromodicarbonylbis-o-phenylenebisdimethylarsinechromium(II) Tribromide.—Similar treatment of the complex $\text{Cr}(\text{CO})_2(\text{Diars})_2$ (0.2 g.) in dichloromethane (25 ml.) with bromine (0.1 g.) in carbon tetrachloride (40 ml.) produced the compound (0.25 g.) (Found: C, 26.7; H, 3.7; Br, 31.6; Cr, 5.5. $\text{C}_{22}\text{H}_{32}\text{As}_4\text{Br}_4\text{CrO}_2$ requires C, 26.4; H, 3.2; Br, 32.0; Cr, 5.2%). The properties are very similar to the other chromium(II) complexes.

Di-iodobis-o-phenylenebisdimethylarsinechromium(III) Tri-iodide.—A mixture of the compound $\text{Cr}(\text{CO})_2(\text{Diars})_2$ (0.25 g.) and iodine (0.83 g.) in carbon tetrachloride (160 ml.) was refluxed for 18 hr. under nitrogen. The green solid (0.35 g.), which separated during reaction, was filtered off, washed with carbon tetrachloride, and dried *in vacuo* (Found: C, 18.8; H, 2.3; I, 51.05; Cr, 4.1. $\text{C}_{20}\text{H}_{32}\text{As}_4\text{CrI}_3$ requires C, 19.1; H, 2.5; I, 50.4; Cr, 4.1%). The compound is sparingly soluble in nitrobenzene and nitromethane, but insoluble in other solvents.

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

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