770. *Substituted Group VI Carbonyls. Part V.* Tritertiary Arsine Tricarbonyl Complexes and their Reaction with Halogens*

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The hexacarbonyls of chromium, molybdenum, and tungsten react with the tritertiary arsine, bis-(*o*-dimethylarsinophenyl)methylarsine (TTAS) to form stable tricarbonyl–metal (M) complexes of the type $[M(CO)_3(TTAS)]$. The action of halogens on these complexes has been investigated. Two g.-atoms of bromine or iodine are consumed per mole of complex, yielding salts of the type $[M(CO)_3(TTAS)X]X$, in which the metal atom is presumably seven co-ordinate. The stability of these salts in solution decreases in the order, $M = W > Mo > Cr$; the tungsten(II) complex is fairly inert, losing carbon monoxide only very slowly, whereas the molybdenum(II) compound loses one mole of carbon monoxide when warmed in methanol to form the non-electrolyte species $[Mo(CO)_2(TTAS)X_2]^0$. The chromium(II) complex readily undergoes further oxidation with complete loss of carbon monoxide to form complexes of the type $[Cr(TTAS)X_3]$, where X = Br and I; the trichlorocomplex has been made by a different procedure.

IN previous Parts of this Series,[1] which dealt with the action of bromine and iodine upon various arsine-substituted carbonyls of the elements, Cr, Mo, and W, it was shown that, whereas the hexacarbonyls react with halogen to form MX_3, stable complexes of oxidation states (II) and (III) are formed when some of the carbonyl groups are replaced by arsine donors. The ditertiary arsine, *o*-phenylenebis(dimethylarsine) (Diars), forms two series of complexes, $[M(Diars)(CO)_4]$ and $[M(Diars)_2(CO)_2]$, which differ in their reactions with halogens. On oxidation, the complex $[Cr(Diars)(CO)_4]$ loses all carbon monoxide with the formation of a Cr(III) derivative, whereas, with molybdenum, the seven-co-ordinate species $[Mo(Diars)(CO)_3X_2]$ can be obtained, even though further oxidation with expulsion of all the carbon monoxide can occur under more vigorous conditions. Tungsten forms the ionic $[W(Diars)(CO)_4I]I$ and the analogous bromo-complex. The latter can lose carbon monoxide to form the non-electrolyte, $[W(Diars)(CO)_3Br_2]$, and can also be oxidised to a complex of tungsten(III) that still contains carbon monoxide, *viz.* $[W(Diars)(CO)_3Br_2]Br$. The bis-diarsine carbonyls retain the remaining carbon monoxide more strongly and the complexes of all three metals can be oxidised to the seven-co-ordinate $[M(Diars)_2(CO)_2X]X$ without loss of carbon monoxide. It was therefore important to examine the action of

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* Part IV, J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *J.*, 1964, 3009.

[1] (*a*) H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J.*, 1960, 1803; 1806; (*b*) J. Lewis, R. S. Nyholm, C. S. Pande, and M. H. B. Stiddard, *J.*, 1963, 3600.

bromine and iodine upon complexes containing three donor arsenic atoms and three carbonyl groups, in order to see whether the reaction product would be: (*a*) a seven-co-ordinate non-electrolyte, *viz.* $[M(TTAS)(CO)_2X_2]^0$; (*b*) a seven-co-ordinate salt retaining all the original carbon monoxide, *viz.* $[M(TTAS)(CO)_3X]X$; or, (*c*) a species, formally of oxidation state (I), which was either a dimer with a metal–metal bond or else a monomer with an unpaired spin, *i.e.*, $[M(TTAS)(CO)_2I]_n$. We describe the use here of the recently prepared tridentate ligand,[2] bis-(*o*-dimethylarsinophenyl)methylarsine (TTAS) $MeAs(C_6H_4{\cdot}AsMe_2\text{-}o)_2$ to obtain complexes of the type $[M(TTAS)(CO)_3]$; these complexes and their halogen oxidation products are described in this Paper. It should be mentioned that, with other triarsines, different products, which will be reported later, can be obtained.

Complexes of the Type $[M(TTAS)(CO)_3]$.—The hexacarbonyls of the Group VI metals react with the tritertiary arsine in boiling mesitylene to give the tricarbonyl triarsine derivatives $[M(TTAS)(CO)_3]$. These are stable crystalline solids, which are monomeric and non-conducting in acetone solution and diamagnetic in the solid. All three are very soluble in chloroform and acetone, but are insoluble, or only slightly soluble, in the other common organic solvents. The properties of these compounds are given in Table 1.

TABLE 1

Properties of the complexes

Compound	Colour	*M* Calc.	*M* Found *	χ (c.g.s. units; 20°)	C–O † stretching frequencies (cm.$^{-1}$)
$[Cr(TTAS)(CO)_3]$	Yellow	588	583 600	−253	1923s 1830b
$[Mo(TTAS)(CO)_3]$	White	632	665 637	−279	1932s 1832b
$[W(TTAS)(CO)_3]$	Pale yellow	720	726 719	−203	1930s 1830b

* Measured in acetone. The two entries refer to 2×10^{-2} and 4×10^{-2}M-solutions, respectively.
† Nujol mulls. s = sharp, b = broad. All bands reported are strong.

The infrared spectra have two strong bands assigned to the C–O stretch and the broadness of the band at the higher frequency suggests that two of the three expected bands occur here and are unresolved. Like the diarsine derivatives of the hexacarbonyls, these new triarsine compounds are very stable to air and moisture.

Oxidation with Halogens.—Preliminary spectrophotometric studies in dilute solution indicated that the molybdenum and tungsten complexes of the type $[M(TTAS)(CO)_3]$ reacted with exactly 2 g.-atoms of iodine per mole of complex and more iodine could then be added without further chemical change. A similar experiment with the chromium complex was inconclusive, because a rapid increase of absorption in the early part of the titration obscured the end-point; the reason for this behaviour is not known.

On a preparative scale, it was found that all three complexes reacted smoothly and rapidly with two equivalents of bromine or iodine to give cations of the type $[M(TTAS)(CO)_3X]^+$. When treated with the halogens in chloroform or benzene solution, the molybdenum and tungsten complexes yielded the derivatives $[M(TTAS)(CO)_3Br]Br$ and $[M(TTAS)(CO)_3I]I$; however, the chromium complex $[Cr(TTAS)(CO)_3I]I_3$, was formed in benzene solution only. In chloroform solution, all the carbon monoxide was lost and the metal oxidised to chromium(III). These derivatives of chromium(II), molybdenum(II), and tungsten(II) are moderately stable in moist air, the order of stability being W > Mo > Cr; sunlight causes their rapid decomposition and the chromium compound is best kept in a sealed tube in the dark. The complexes behave as 1 : 1 electrolytes in nitromethane and are diamagnetic in the solid state. Conductometric titration showed clearly that only one of the two atoms was ionic and, incidentally, demonstrated that the complex was substitutionally inert. The titration of $[W(TTAS)(CO)_3I]I$ with silver perchlorate in nitromethane solution is shown in Figure 1. The end-point is sharp at the

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[2] R. G. Cunninghame, R. S. Nyholm, and M. L. Tobe, *J.*, 1964, 5800.

addition of one equivalent of silver perchlorate. It was not possible, however, to isolate the perchlorate of the complex from this solution, probably because it is too soluble. The properties of these complexes are collected in Table 2. The infrared spectra of all these compounds contain three peaks that can be assigned to the carbon–oxygen stretch; it is noteworthy that there is a shift to higher frequencies compared with the carbonyl-arsine complexes in the zero oxidation state. This is in agreement with the observations made on the ditertiary arsine system and reflects the increase in the positive charge on the metal.[1b] The appearance of a fourth peak in the bromo-derivatives is probably due to the presence of impurity, since there was a tendency for these complexes to decompose slightly during their preparation and recrystallisation. This is also reflected in their analyses.

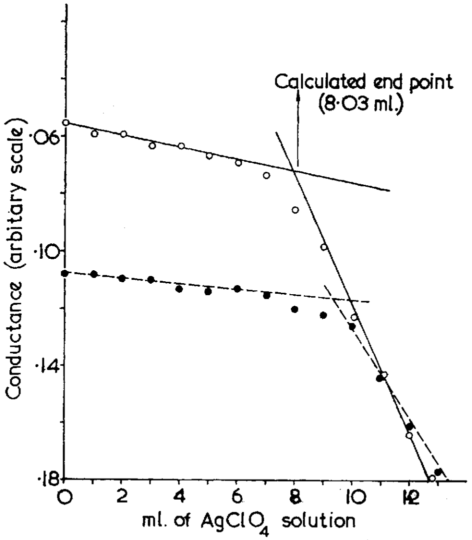

FIGURE 1. Conductometric titrations in nitromethane of silver perchlorate with – – –●– – – tetra-n-butylammonium iodide (1·279 × 10^{-3}M) and —O—O— [W(TTAS)(CO)$_3$I]I (1·105 × 10^{-3}M) (corrected for dilution)

TABLE 2

Properties of the halogeno-complexes

Compound	Colour	Molecular conductivity in CH$_3$·NO$_2$ (Ω^{-1} cm.^{2}) (10^{-3}M)	C–O stretching frequencies (cm.$^{-1}$)
[Cr(CO)$_3$(TTAS)I]I$_3$	Brown	74·2 87·7	2022 1966 1930
[Mo(CO)$_3$(TTAS)I]I	Orange	66·5 71·3	2046 1990 1965
[Mo(CO)$_3$(TTAS)Br]Br	Yellow	70·2 73·8	2045 1987 1968 (1940)
[W(CO)$_3$(TTAS)I]I	Orange	81·2 83·1	2046 1980 1952
[W(CO)$_3$(TTAS)Br]Br	Yellow	70·3 75·0	2048 1992 1975 (1948)
[Mo(CO)$_2$(TTAS)I$_2$]	Orange	7·5	1960 1880
[Mo(CO)$_2$(TTAS)Br$_2$]	Orange	6·3	1975 1880

Complexes of the Type [Mo(TTAS)(CO)$_2$X$_2$]^0.—The [Mo(TTAS)(CO)$_3$X]X complexes dissolved in hot methanol with immediate evolution of carbon monoxide. The non-electrolyte [Mo(TTAS)(CO)$_2$X$_2$] then crystallised from solution. A similar reaction was not observed for the tungsten compound although prolonged refluxing in propanol caused the colour to change from yellow to red. A brown solid, which was difficult to purify, was obtained when this solution was cooled. The bromo- and iodo-molybdenum complexes dissolve in nitromethane to give virtually non-conducting solutions. The solids are diamagnetic and the infrared spectra have the expected two bands that can be assigned to a C–O stretch.

Compounds of the Type [Cr(TTAS)X_3].—Unless the reaction is carried out carefully in benzene solution, the chromium(0) complex [Cr(TTAS)$(CO)_3$] loses all its carbon monoxide on oxidation with bromine or iodine. When a chloroform solution of the tricarbonyl triarsine complex is treated with bromine or iodine, deep blue, or green, solutions, respectively, are formed and crystals of the triarsine trihalide slowly separate. The complexity of the colour changes indicates that the reaction goes through a coloured intermediate, but this could not be isolated. The trichloro-complex, which could not be prepared in this fashion, was obtained by heating the chromic chloride–tetrahydrofuran complex [Cr$(THF)_3Cl_3$] with the triarsine in tetrahydrofuran. These complexes are very stable and behave as non-electrolytes in acetone solution. They are paramagnetic with a magnetic moment corresponding to three unpaired spins; all three are isomorphous with the corresponding cobalt(III) complexes.[2] The physical properties are summarised in Table 3 and the absorption spectra are shown in Figure 2.

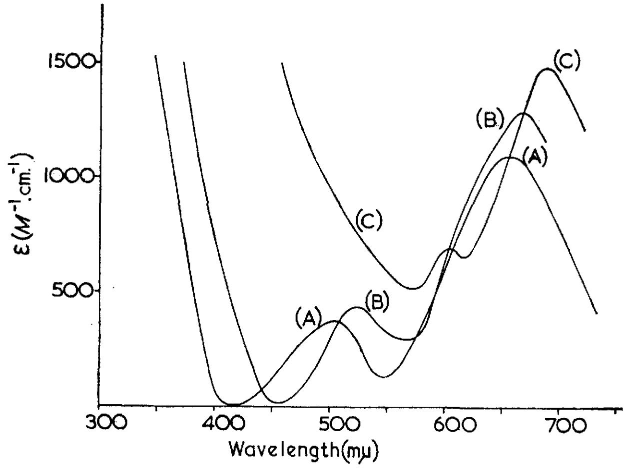

FIGURE 2. Ultraviolet and visible absorption spectra of
(A) [Cr(TTAS)Cl_3];
(B) [Cr(TTAS) Br_3];
(C) [Cr(TTAS)I_3]

TABLE 3

Properties of trihalogenotriarsinechromium(III)

Compound	Colour	Molecular conductivity in (Ω^{-1} cm.^{2}) acetone (10^{-3}M)	μ_{eff} (B.M.)
[Cr(TTAS)Cl_3]	Blue	2·3	3·7
[Cr(TTAS)Br_3]	Deep blue	3·8	3·7
[Cr(TTAS)I_3]	Deep green	3·0	3·8

EXPERIMENTAL

Bis-(*o*-dimethylarsinophenyl)methylarsine was prepared in 60% yield by the reaction of *o*-lithiophenyldimethylarsine with methyldichloroarsine.[2]

Bis-(o-*dimethylarsinophenyl*)*methylarsinetricarbonylchromium*(0).—Chromium hexacarbonyl (2·96 g.), the triarsine (5·92 g.), and mesitylene (20 ml.) were heated in an oil-bath for 4 hr. at 190—200°. The reaction was performed in an atmosphere of nitrogen and the sublimed hexacarbonyl was returned mechanically to the reaction mixture from time to time. The flask was cooled and the contents washed into cold petroleum (b. p. 40—60°; 100 ml.), the precipitate dissolved in boiling benzene (150 ml.), and the solution treated with activated charcoal and filtered. Hot petroleum (b. p. 40—60°; 110 ml.) was then added and the mixture set aside in the refrigerator. Yellow needles of the complex were obtained (5·1 g.) and dried *in vacuo* (0·01 mm.) at 78°. This also served to remove the last traces of the unchanged hexacarbonyl (Found: C, 41·2; H, 3·95; As, 37·7. $C_{20}H_{23}As_3CrO_3$ requires C, 40·8; H, 3·9; As, 38·3%).

Bis-(o*-dimethylarsinophenyl)methylarsinetricarbonylmolybdenum*(0).—Molybdenum hexacarbonyl (2·84 g.), the triarsine (4·89 g.), and mesitylene (17 ml.) were heated for 3 hr. in an oil-bath at 160—170°. The same procedure as was used for the chromium complex gave white needles (4·9 g.) (Found: C, 38·0; H, 3·7; As, 35·4. $C_{20}H_{23}As_3MoO_3$ requires C, 38·0; H, 3·65; As, 35·6%).

Bis-(o*-dimethylarsinophenyl)methylarsinetricarbonyltungsten*(0).—Tungsten hexacarbonyl (3·9 g.), the triarsine (5·17 g.), and mesitylene (20 ml.) were heated at 200°. The procedure outlined above gave pale yellow needles (6·3 g.) (Found C, 32·7; H, 3·5; As, 33·5. $C_{20}H_{23}As_3O_3W$ requires C, 33·3; H, 3·2; As, 31·3%).

Iodotricarbonylbis-(o*-dimethylarsinophenyl)methylarsinechromium*(II) *Triodide.*—[Cr(TTAS)(CO)$_3$] (1·18 g.) was dissolved in hot benzene (100 ml.), and the solution cooled to room temperature with vigorous stirring. Iodide (0·254 g.) dissolved in benzene (20 ml.) was added drop by drop during ½ hr., and the precipitate was filtered off under a stream of nitrogen and washed with a little benzene. More iodine (0·254 g.) dissolved in benzene was added to the filtrate and the precipitate removed as before. This procedure was repeated a further four times, and a total yield of brown crystalline material of 2·06 g. was obtained. A gas burette incorporated in the reaction vessel showed that no carbon monoxide was evolved during the reaction. Further recrystallisation was not possible without decomposition (Found: C, 22·9; H, 2·5; As, 19·0; I, 46·0. $C_{20}H_{23}As_3CrI_4O_3$ requires C, 21·9; H, 2·1; As, 20·5; I, 46·3%).

Bromotricarbonylbis-(o*-dimethylarsinophenyl)methylarsinemolybdenum*(II) *Bromide.*—[Mo(TTAS)(CO)$_3$] (0·59 g.) dissolved in chloroform (30 ml.), and a solution of bromine (0·1 g.) in chloroform (10 ml.) was added drop by drop to the rapidly stirred solution. The yellow crystalline material (0·52 g.) obtained after removal of the solvent, was washed with benzene and dried *in vacuo*. The *complex* darkens to a deep maroon colour on prolonged exposure to air and to light (Found: C, 31·5; H, 3·4; Br, 20·5. $C_{20}H_{23}As_3Br_2MoO_3$ requires C, 30·3; H, 2·9; Br, 20·2%).

Iodotricarbonylbis-(o*-dimethylarsinophenyl)methylarsinemolybdenum*(II) *Iodide.*—[Mo(TTAS)(CO)$_3$] (0·63 g.) in chloroform (20 ml.) was treated with a solution of iodine (0·254 g.) in chloroform (20 ml.). No gas was evolved, and the yellow *complex* obtained by evaporating the solvent was washed with benzene and dried *in vacuo* (Found: C, 26·0; H, 2·8; As, 25·5; I, 28·0. $C_{20}H_{23}As_3I_2MoO_3$ requires C, 27·1; H, 2·6; As, 25·4; I, 28·7%).

Bromotricarbonylbis-(o*-dimethylarsinophenyl)methylarsinetungsten*(II) *Bromide.*—[W(TTAS)(CO)$_3$] (0·36 g.) was dissolved in chloroform and treated with bromine (0·08 g.) in the way outlined above. No gas was evolved, and the yellow crystalline residue obtained after the removal of solvent was washed with benzene and dried *in vacuo*. The *compound* is soluble in acetone, chloroform, and nitromethane but insoluble in benzene and petroleum (b. p. 90—105°). The colour darkens on prolonged exposure to air and light (Found: C, 26·7; H, 2·7; As, 26·35; Br, 18·3. $C_{20}H_{23}As_3Br_2O_3W$ requires C, 27·3; H, 2·6; As, 25·6; Br, 18·2%).

Iodotricarbonylbis-(o*-dimethylarsinophenyl)methylarsinetungsten*(II) *Iodide.*—[W(TTAS)(CO)$_3$] (0·72 g.) was dissolved in chloroform (20 ml.) and treated with a solution of iodine (0·254 g.) in chloroform (25 ml.). No gas was evolved and, after removal of the chloroform, the glistening orange plates (0·94 g.) were washed with a little benzene and dried *in vacuo*. The solubility properties are similar to those of the bromobromide (Found: C, 24·0; H, 2·6; As, 23·0; I, 26·0. $C_{20}H_{23}As_3I_2O_3W$ requires, C, 24·6; H, 2·4; As, 23·1; I, 26·1%).

Dibromodicarbonylbis-(o*-dimethylarsinophenyl)methylarsinemolybdenum*(II).—[Mo(TTAS)(CO)$_3$Br]Br (0·58 g.) was treated with boiling methanol (50 ml.). The immediate dissolution of the complex was accompanied by effervescence, and the resulting orange solution was boiled for 1 min. and the cooled. The crystalline *complex*, which had started to separate from the hot solution, was filtered off, washed with a little methanol, and dried *in vacuo* (0·36 g.) (Found: C, 30·3; H, 3·4; As, 29·1; Br, 20·5. $C_{19}H_{23}As_3Br_2MoO_2$ requires C, 29·8; H, 3·0; As, 29·45; Br, 29·9%).

Di-iododicarbonylbis-(o*-dimethylarsinophenyl)methylarsinemolybdenum*(II).—This compound was prepared from [Mo(TTAS)(CO)$_3$I]I (0·58 g.) by the method described above (Found: I, 29·6. $C_{19}H_{23}As_3I_2MoO_2$ requires I, 29·6%).

Trichlorobis-(o*-dimethylarsinophenyl)methylarsinechromium*(III).—Trichlorotris(tetrahydrofuran)chromium(III) (0·4 g.) was dissolved in boiling tetrahydrofuran (50 ml.) and the solution filtered under nitrogen. The triarsine (1·1 g.) dissolved in tetrahydrofuran (30 ml.) was added to the hot solution and the mixture left overnight at 0°. The precipitated *complex* was crystallised from hot ethanol containing 10% hydrochloric acid and obtained as shining blue platelets (0·2 g.) (Found: C, 33·9; H, 3·9; Cl, 17·3. $C_{17}H_{23}As_3Cl_3Cr$ requires C, 33·4; H, 3·8; Cl, 17·5%).

Tribromobis-(o-*dimethylarsinophenyl*)*methylarsinechromium*(III).—[Cr(TTAS)(CO)$_3$] (0·59 g.) was dissolved in chloroform (50 ml.) and treated with a solution of bromine (0·24 g.) in chloroform (20 ml.). The mixture was boiled for 1 min., and the resultant deep blue solution cooled. A deep blue precipitate started to separate while the solution was still hot, and increased in quantity when the mixture was left overnight in the refrigerator. The *complex* was filtered off (0·4 g.) and crystallised from the smallest amount of hot dichloromethane–methanol (1 : 4) (Found: C, 27·3; H, 3·4. $C_{17}H_{23}As_3Br_3Cr$ requires C, 27·4; H, 3·1%).

Tri-iodobis-(o-*dimethylarsinophenyl*)*methylarsinechromium*(III).—[Cr(TTAS)(CO)$_3$] (0·59 g.) was dissolved in chloroform (30 ml.) and oxidised with a solution of iodine (0·38 g.) in chloroform (30 ml.). The solution was stirred and warmed, whereupon it began to effervesce, the colour changed to dark green and a green solid separated; the mixture was cooled overnight and the *complex* was filtered off, washed with a little chloroform, and dried *in vacuo* (0·5 g.) (Found: C, 22·0; H, 2·3; As, 24·75. $C_{17}H_{23}As_3CrI_3$ requires C, 23·05; H, 2·6; As, 25·4%).

Infrared Spectra.—Infrared spectra were measured on a Grubb–Parsons double-beam grating instrument, type GS2A.

Visible and Ultraviolet Spectra.—A Unicam S.P. 500 spectrophotometer was used.

Molecular Weights.—A Mechrolab Vapour Pressure Osmometer type 301A was used.

Conductivity Measurements.—A Phillips conductivity meter type PR 9506 was used.

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