1209. *Aliphatic Tri(tertiary arsine)carbonyls. Part II.** *Halogen Oxidation of Group VI Tricarbonyl Derivatives*

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The action of halogens on the compounds $M(CO)_3$(*l*-Triars) and $M(CO)_3$(*v*-Triars), M = Cr, Mo, and W [(*l*-Triars) = methylbis-(dimethylarsino-3-propyl)arsine and (*v*-Triars) = tris-1,1,1-(dimethylarsinomethyl)-ethane] has been investigated. The molybdenum and tungsten derivatives yield the seven-co-ordinate compounds $[M^{II}(CO)_3(\text{Triars})X]X$, X = Br and I, and the corresponding perchlorates and tetraphenylborates can be isolated from ethanolic solution. Neutral dicarbonyl compounds, $M^{II}(CO)_2(\text{Triars})X_2$ are formed by refluxing the above halides alone, or their tetraphenylborate salts with lithium halides in an appropriate alcohol. The conversion of the molybdenum tricarbonyl complex into the dicarbonyl complex is rapid at 60°, while the conversion of the corresponding tungsten complex is slow below 200°. The tricarbonyltriarsine complexes of chromium react at room temperature to give indefinite products; at −70°, however, an unstable compound $[Cr^{II}(CO)_3$(*l*-Triars)I]BPh_4 and a stable compound $[Cr^{II}(CO)_2$(*v*-Triars)I]BPh_4 can be isolated. The magnetic moment of the latter compound is 2·83 B.M., showing it to contain spin-paired chromium(II).

HALOGEN oxidation of substituted Group VI carbonyl complexes containing the bidentate ligands *o*-phenylenebisdimethylarsine-,[1-3] (diars)2,2′-bipyridyl,[4] and 2,5-dithiahexane[5] have yielded seven-co-ordinate derivatives containing metal atoms with d^4 and d^3 configuration. A detailed study of the tetracarbonyldiarsine and dicarbonylbisdiarsine derivatives of chromium, molybdenum, and tungsten has clearly illustrated that the type of oxidation product is dependent upon extent of carbonyl substitution and it is important to examine the reactions of tricarbonyl complexes. Thus, we studied concurrently the oxidation of Group VI derivatives $M(CO)_3$(Triars), where Triars is methylbis(dimethylarsino-3-propyl)-arsine (1-Triars), *tris*-1,1,1-(dimethylarsinomethyl)ethane (*v*-Triars), and *bis*(*o*-dimethylarsinophenyl)methylarsine (*o*-Triars). By use of these ligands, it was hoped that non-conducting seven co-ordinate complexes of chromium(II), $Cr(CO)_2(\text{Triars})I_2$, could be obtained. Preliminary results for *l*-Triars have been described;[6] results for *o*-Triars have been reported,[7] and we now set out investigations using the ligands *l*- and *v*-Triars.

Tungsten Compounds.—The compound $W(CO)_3$(*v*-Triars) reacts with two equivalents of bromine or iodine in benzene at room temperature to yield the crystalline, yellow products $[W(CO)_3$(*v*-Triars)X]X. The solubility of the products in ethanol (in contrast with the insolubility of similar diarsine derivatives) has allowed the preparation of perchlorate and tetraphenylborate salts $[W(CO)_3$(*v*-Triars)X]$[ClO_4,BPh_4]$. On refluxing the halogeno-halides in diethylene glycol monomethyl ether at 200°, carbon monoxide is released and the neutral complexes $W(CO)_2$(*v*-Triars)X_2 separate. The dichloro-complex $W(CO)_2$(*v*-Triars)Cl_2 is formed when the salt $[W(CO)_3$(*v*-Triars)Br]BPh_4 is refluxed with lithium chloride in n-propanol. All the compounds are stable to air and light for long periods.

Oxidation of the compound $W(CO)_3$(*l*-Triars) has not been re-examined: it has been reported earlier that derivatives of the type $[W(CO)_3$(*l*-Triars)X]X are formed.[6]

Molybdenum Compounds.—Halogen oxidation of the compound $Mo(CO)_3$(*v*-Triars)

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* Part I, preceding Paper.

[1] H. L. Nigam, R. S. Nyholm, M. H. B. Stiddard, *J.*, 1960, 1806.
[2] J. Lewis, R. S. Nyholm, C. S. Pande, and M. H. B. Stiddard, *J.*, 1963, 3600.
[3] J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *J.*, 1964, 3009.
[4] M. H. B. Stiddard, *J.*, 1962, 4712.
[5] H. C. E. Mannerskantz and G. Wilkinson, *J.*, 1962, 4454.
[6] J. Mašek, R. S. Nyholm, and M. H. B. Stiddard, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1714.
[7] C. D. Cook, R. S. Nyholm, and M. L. Tobe, *J.*, 1965, 4149.

parallels that of its tungsten analogue, but the conversion of the salt $[Mo(CO)_3(v\text{-Triars})X]X$ to the dicarbonyl-dihalide occurs more readily and is rapid in methanol at 60°. In fact the bromine oxidation is best carried out at low temperature, otherwise a mixture of the products $[Mo(CO)_3(v\text{-Triars})Br]Br$ and $Mo(CO)_2(v\text{-Triars})Br_2$ results. Oxidation of the compound $Mo(CO)_3(l\text{-Triars})$ with bromine produces a mixture even at −70°. The cation $[Mo(CO)_3(l\text{-Triars})Br]^+$ is stable in the absence of halide ion and may be isolated as the tetraphenylborate from methanol. The insoluble compound $Mo(CO)_2(l\text{-Triars})Br_2$ is obtained pure by washing the solid from the low temperature oxidation with ethanol after it has been warmed to room temperature.

Chromium Compounds.—Halogen oxidation of tricarbonyltriarsines in benzene at room temperature leads to complete decomposition; also carbon monoxide is lost leaving black tar. Preliminary spectrophotometric oxidation of the complex $Cr(CO)_3(l\text{-Triars})$ indicated the consumption of one equivalent of iodine.[6] On a preparative scale at −70° in toluene, the expected chromium(I) complex was not isolated. An unstable derivative of chromium(II), $[Cr(CO)_3(l\text{-Triars})I][BPh_4]$, however, was precipitated from a methanol extract of the low temperature oxidation products. The aerial decomposition of this compound can be followed magnetically, the magnetic moment rising to 3·0 B.M. after 24 hr. Under similar reaction conditions the compound $Cr(CO)_3(v\text{-Triars})$ yields an air-stable six-co-ordinate chromium(II) derivative, $[Cr(CO)_2(v\text{-Triars})I][BPh_4]$. In contrast with the reactions of the compound $Cr(CO)_3(o\text{-Triars})$,[7] chromium(III) complexes could not be isolated by further oxidation with bromine and iodine under a variety of conditions. Chlorine in chloroform, however, yields blue crystals which have the same properties as those of the compound $Cr(v\text{-Triars})Cl_3$, made by reaction of the complex $Cr(tetrahydrofuran)_3Cl_3$ with the ligand in tetrahydrofuran. The material obtained by chlorine oxidation has, however, a high chlorine content. Chlorine oxidation of other tricarbonyltriarsines has also indicated attack on the ligand.

DISCUSSION

Oxidation of the molybdenum and tungsten tricarbonyl compounds derived from all three triarsines yield air-stable oxidation products, $[M(CO)_3(Triars)X]X$. The tungsten complexes are pure, but the molybdenum complexes are increasingly contaminated with the products $[Mo(CO)_2(Triars)X^2]^0$ in the order $(o\text{-Triars}) \approx (v\text{-Triars}) < (l\text{-Triars})$. This contamination is reduced if the oxidation is carried out at low temperatures and is less with iodine than with bromine. The loss of carbon monoxide from the salts $[M(CO)_3(v\text{-Triars})X]X$ to give the product $M(CO)_2(v\text{-Triars})X_2$ is more readily effected with $M = Mo$ than when $M = W$. This order is consistent with previous observations of the lability of carbonyl groups in molybdenum and tungsten complexes.[2,3] The preparation of the complex $M(CO)_2(v\text{-Triars})Cl_2$ ($M = Mo$ or W) from the salts $[M(CO)_3(v\text{-Triars})Br][BPh_4]$ illustrates the lability of the halide ion attached to the cation. In addition to the chromium(II) compound here described, oxidation of the compound $Cr(CO)_3(o\text{-Triars})$ yields the seven-co-ordinate product $[Cr(CO)_3(o\text{-Triars})X]X$. Thus the products of oxidation of tricarbonyltriarsine complexes of chromium depend upon the triarsine. The complex $[Cr(CO)_2(v\text{-Triars})I][BPh_4]$ is paramagnetic with $\mu_{\text{eff}} = 2{\cdot}83$ B.M. This moment, equal to the spin-only value, may be compared with those of the only other well established examples of spin-paired chromium(II) complexes: for $[Cr(dipy)_3]Br_2,4H_2O$, $\mu_{\text{eff}} = 3{\cdot}27$ B.M.[8] and for $[Cr(dipy)_3][ClO_4]_2$, $\mu_{\text{eff}} = 2{\cdot}93 \pm 0{\cdot}03$ B.M.[9] The magnetic moment of the arsine- and dipyridyl-chromium(II) complexes should be close to the spin-only value, since deviations from O_h symmetry should be sufficient to largely quench any orbital contribution.

The most remarkable feature of the physical properties of the compounds listed in Tables 1 and 2 is the absence of any significant trend with respect to changing halogen and central metal. The carbonyl stretching frequencies of compounds of the same type are in

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[8] F. H. Burstall and R. S. Nyholm, *J.*, 1952, 3570.

[9] R. Perthel, *Z. Phys. Chem.* (*Leipzig*), 1959, **211**, 74.

TABLE 1

Compound	Colour	Conductance in $PnNO_2$ Λ_M (ohm^{-1} cm.^{2}) of 10^{-1}M solutions	$10^6\chi_M$[h] (μ_{eff})	Infrared spectrum in C–O stretching region (Nujol)		
$[W(CO)_3(v\text{-Triars})I]I$	Yellow	30·0	−265 (0·5 B.M.)	2030	1975	1940
$[W(CO)_3(v\text{-Triars})I][ClO_4]$	Yellow	72·0[a]	—	2035	1980	1940
$[W(CO)_3(v\text{-Triars})Br]Br$	Yellow	23·2	−156 (0·5 B.M.)	2050	1980	1940[f]
$[W(CO)_3(v\text{-Triars})Br][ClO_4]$	Yellow	86·0[a]	—	2045	1980	1920
$[W(CO)_3(v\text{-Triars})Br][BPh_4]$[b]	Yellow	21·5	—	2045	1995	1920
$[Mo(CO)_3(v\text{-Triars})I]I$	Yellow	28·3	−5 (0·9 B.M.)	2050	1990	1940[f]
$[Mo(CO)_3(v\text{-Triars})Br]Br$	Yellow	19·7	−26 (0·8 B.M.)	2050	1995	1940[f]
$[Mo(CO)_3(v\text{-Triars})Br][BPh_4]$[c]	Yellow	21·1	—	2055	2015	1930
$[Mo(CO)_3(l\text{-Triars})I]I$	Yellow	22·7	—	2050	1980	1940[f]
$[Mo(CO)_3(l\text{-Triars})Br][BPh_4]$[d]	Yellow	20·4	—	2045	1965	1935
$[Cr(CO)_2(v\text{-Triars})I][BPh_4]$[e]	Red	21·5	2780 (2·83 B.M.)	2035	1960	
$[Cr(CO)_3(l\text{-Triars})I][BPh_4]$	Brown	—	(1·3 B.M.)[g]	2030	1950	1895
$[W(CO)_2(v\text{-Triars})I_2]$	Red	0·7	—	1920	1845	
$[W(CO)_2(v\text{-Triars})Br_2]$	Yellow	1·3	100 (0·9 B.M.)	1920	1845	
$[W(CO)_2(v\text{-Triars})Cl_2$	Yellow	0·1	—	1920	1825	
$[Mo(CO)_2(v\text{-Triars})I_2]$	Orange	0·0	59 (1·0 B.M.)[i]	1920	1860	
$[Mo(CO)_2(v\text{-Triars})Br_2]$	Yellow	1·4	−246 (0·4 B.M.)	1935	1840	
$[Mo(CO)_2(v\text{-Triars})Cl_2]$	Yellow	0·6	+205 (1·1 B.M.)	1935	1845	
$[Mo(CO)_2(l\text{-Triars})I_2]$	Orange	0·1	—	1940	1855	
$[Mo(CO)_2(l\text{-Triars})Br_2]$	Yellow	2·0	—	1930	1840	

[a] Λ_M in methanol. Melting points: [b] 170—172°; [c] 148—149°; [d] 168°; [e] 100—106°, all decomp. [f] Spectra in chloroform. [g] Moment increases with time, see Experimental section. [h] Gouy method, 9·4 cm. tube calibrated with cobalt mercury thiocyanate. [i] No change in μ_{eff} at low temperature (92°K).

TABLE 2

Compound	Proton resonance spectra (p.p.m. in nitrobenzene)					Ultraviolet absorption maxima (molar extinction coefficients) in the range 250—450 mμ		
$[W(CO)_3(v\text{-Triars})I]I$	8·40	7·86		7·53		377 (1400)	290 (4500)[c]	
$[W(CO)_3(v\text{-Triars})Br]Br$	8·37	7·96		7·45		372 (830)	258 (14,600)[c]	
$W(CO)_2(v\text{-Triars})I_2$	—		7·81	—[b]		332 (620)	262 (2500)[d]	
$W(CO)_2(v\text{-Triars})Br_2$	—		7·81	—[b]		—	—	
$[Mo(CO)_3(v\text{-Triars})I][A]$	8·43	8·01	[7·81][a]	7·69	[A = BPh_4]	384 (850)	305 (3200)[c]	[A = I]
$[Mo(CO)_3(v\text{-Triars})Br][A]$	8·45	8·09	[7·83][a]	7·72	[A = BPh_4]	376 (640)	289 (1860)[c]	[A = Br]
$Mo(CO)_2(v\text{-Triars})I_2$			7·84	—[b]		375 (460)	260 (3300)[d]	
$Mo(CO)_2(v\text{-Triars})Br_2$			7·85	—[b]		367 (460)	262 (2200)[d]	
$[Cr(CO)_2(v\text{-Triars})I][BPh_4]$			7·83 (broad)			437 (25,000)[c]		
(v-Triars)	8·92	9·05		8·27				

[a] Impurity peak developing with time. [b] Compounds too insoluble to observe weaker resonances. Methanol. [d] Dimethyl sulphoxide.

many cases virtually identical, but the variations that do exist are apparently random. No significant difference in frequencies exist for compounds involving either the aromatic or aliphatic arsines. The average frequency shift from the charged tricarbonyls to the neutral dicarbonyls has the expected value of ~100 cm.$^{-1}$. [This shift was useful preparatively, since in some oxidations, notably of $Mo(CO)_3(l\text{-Triars})$ by bromine, both cationic and neutral species were formed.]

All the compounds exhibit residual paramagnetism (T.I.P.). The molar susceptibilities vary between −138 and +205 × 10^{-6} c.g.s.u., which taken with a diamagnetic correction of about 330 × 10^{-6} c.g.s.u. yield values of μ_{eff} in the range 0·4 to 1·1 B.M. Such values have not been noted before for similar seven-co-ordinate compounds. The susceptibility of the compound $Mo(v\text{-Triars})(CO)_2I_2$ was constant in the range 92—295°K. The effect is real since it exists through the whole range of compounds, and the temperature-independence shows that it is not due to chance impurities. The magnitude of the T.I.P. is not related apparently to the substituent halide or central metal. The ultraviolet absorption spectra (Table 2) do show an appropriate shift on changing the halide and a slight difference between complexes of molybdenum and tungsten.

The peak positions in the proton resonance spectra of some complexes containing the ligand *v*-Triars are recorded in Table 2, and compared with those of the free triarsine. The shift of 0·5 p.p.m. in the $C-CH_3$ resonance of the free arsine was shown to be diagnostic for a +1 charge in Part I.[10] The spectra of the $[Mo(CO)_3(v\text{-Triars})X]^+$ species are complicated by a growing peak at about 7·8 p.p.m. This peak is the only one observed in the spectra of $Mo(CO)_2(v\text{-Triars})X_2$ compounds, and must arise from slow loss of carbon monoxide at the sample temperature of 33°. The hope that splittings in the spectra of the oxidation products would develop owing to lowering of the molecular symmetry was not realised. Thus possible isomers could not be detected nor indications of the structural types obtained. We suggest, however, that the structure of the compounds $M(CO)_2(v\text{-Triars})X_2$ probably resembles either the 4 : 3 orientation established for $SeFe_3(CO)_9$ with a pair of donors from the 3- and 4-fold sets eclipsed,[11] or that established for NbF_7^{2-} where the 3- and 4-fold sets are staggered.[12]

EXPERIMENTAL

Iodotricarbonyltris-1,1,1-(dimethylarsinomethyl)ethanetungsten(II) *Iodide*.—The substance $W(CO)_3(v\text{-Triars})$ (1·06 g.) in benzene (150 ml.) was treated dropwise with iodine (0·4 g.) in the same solvent (8 ml.). The solution was stirred vigorously at room temperature. The precipitated yellow product (1·27 g.) was collected, washed with ether, and dried *in vacuo* (Found: C, 18·7; H, 3·1; As, 24·7; W, 20·2. $C_{14}H_{27}As_3I_2O_3W$ requires C, 18·6; H, 3·0; As, 24·8; W, 20·3%). The *compound* is stable in air, but decomposes slowly on exposure to light. It is very soluble in acetone and nitrobenzene, soluble in the lower alcohols and water, sparingly soluble in chloroform and insoluble in ether and light petroleum.

Bromotricarbonyltris-1,1,1-(dimethylarsinomethyl)ethanetungsten(II) *Bromide*.—The substance $W(CO)_3(v\text{-Triars})$ (0·7 g.) in benzene (120 ml.) was treated with bromine (0·16 g.) in the same solvent (25 ml.). The yellow *product* (0·81 g.) was obtained in a similar way to that described for the iodide (Found: C, 19·9; H, 3·5; As, 28·5; Br, 20·6. $C_{14}H_{27}As_3Br_2O_3W$ requires C, 20·7; H, 3·4; As, 27·7; Br, 19·7%). The physical properties resemble those of the iodo-iodide.

Iodotricarbonyltris-1,1,1-(dimethylarsinomethyl)ethanetungsten(II) *Perchlorate*.—The substance $[W(CO)_3(v\text{-Triars})I]I$ (0·08 g.) in a mixture of water (20 ml.) and acetone (5 ml.) was warmed and mixed with excess of aqueous, saturated magnesium perchlorate solution. The yellow crystals (0·06 g.), which slowly separated on cooling, were washed with a small volume of ethanol and dried *in vacuo* (Found: C, 19·4; H, 3·2; As, 25·7. $C_{14}H_{27}As_3ClIO_7W$ requires C, 19·1; H, 3·1; As, 25·6%). The physical properties resemble those of the iodo-iodide except that the compound is light-stable.

Bromotricarbonyltris-1,1,1-(dimethylarsinomethyl)ethanetungsten(II) *Perchlorate*.—The substance $[W(CO)_3(v\text{-Triars})Br]Br$ (0·09 g.) was treated similarly to the iodo-iodide to yield yellow crystals (0·08 g.) (Found: C, 19·9; H, 3·3; As, 26·6; Br, 9·3; Cl, 4·0. $C_{14}H_{27}As_3BrClO_7W$ requires C, 20·2; H, 3·3; As, 27·0; Br, 9·6; Cl, 4·3%).

Bromotricarbonyltris-1,1,1-(dimethylarsinomethyl)ethanetungsten(II) *Tetraphenylborate*.—The substance $[W(CO)_3(v\text{-Triars})Br]Br$ (0·2 g.) in methanol (8 ml.) was mixed with excess of solid sodium tetraphenylborate. The precipitated yellow product was recrystallised from acetone–ether yielding yellow plates (0·16 g.) which were collected, washed with methanol and ether, and dried *in vacuo* (Found: C, 43·4; H, 4·4; As, 21·4; Br, 7·7. $C_{38}H_{47}As_3BBrO_3W$ requires C, 43·4; H, 4·5; As, 21·4; Br, 7·6%). The *compound* is soluble in acetone and nitrobenzene, sparingly soluble in ethanol and chloroform, but insoluble in ether and non-polar solvents. It is stable to air and light.

Di-iododicarbonyltris-1,1,1-(dimethylarsinomethyl)ethanetungsten(II).—$[W(CO)_3(v\text{-Triars})I]I$ (0·35 g.) was refluxed in diethylene glycol monomethyl ether (4 ml.) at 200° for 20 min. From the brown solution, a brick-red crystalline product (0·21 g.) was slowly precipitated. It was

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[10] R. S. Nyholm, M. R. Snow, and M. H. B. Stiddard, preceding Paper.

[11] F. Dahl and P. W. Sutton, *Inorg. Chem.*, 1963, **2**, 1067.

[12] J. L. Hoard, *Acta Cryst.*, 1939, **61**, 1252.

collected, washed with methanol and ether, and dried *in vacuo* (Found: C, 18·1; H, 3·0; As, 26·0. $C_{13}H_{27}As_3I_2O_2W$ requires C, 17·8; H, 3·1; As, 25·6%). The *compound* is stable in air and light and insoluble in all common solvents unless highly polar, *e.g.*, nitrobenzene, dimethylformamide, and dimethyl sulphoxide.

Dibromodicarbonyltris-1,1,1-(*dimethylarsinomethyl*)*ethanetungsten*(II).— The substance [W(CO)$_3$(*v*-Triars)Br]Br (0·39 g.) was heated in n-propanol (5 ml.) at 100° for 15 min. The yellow product (0·29 g.) which separated from the brown solution was collected, washed with methanol and ether, and dried *in vacuo* (Found: C, 20·0; H, 3·9; As, 28·7; Br, 20·3; W, 22·9. $C_{13}H_{27}As_3Br_2O_2W$ requires C, 19·9; H, 3·5; As, 28·7; Br, 20·4; W, 22·7%).

Dichlorodicarbonyltris-1,1,1-(*dimethylarsinomethyl*)*ethanetungsten*(II).— The substance [W(CO)$_3$(*v*-Triars)Br]BPh$_4$ (0·39 g.) was heated in n-propanol (5 ml.) with excess of lithium chloride at 100° for 20 min. The yellow crystalline *product* (0·25 g.) which separated from the brown solution was collected, washed with methanol, acetone, and ether, and dried *in vacuo* (Found: C, 22·0; H, 3·9; As, 31·4; Br, 0·0; Cl, 9·9. $C_{13}H_{27}As_3Cl_2O_2W$ requires C, 22·5; H, 3·9; As, 32·3; Br, 0·0; Cl, 10·2%).

Iodotricarbonyltris-1,1,1-(*dimethylarsinomethyl*)*ethanemolybdenum*(II) *Iodide*.—The substance Mo(CO)$_3$(*v*-Triars) (1·1 g.) in benzene (120 ml.) was treated dropwise with iodine (0·48 g.) in benzene (9·5 ml.). The solution was vigorously stirred at room temperature. The precipitated yellow product (1·17 g.) was filtered off, washed with ether, and dried *in vacuo* (Found: C, 21·2; H, 3·5; As, 26·7. $C_{14}H_{27}As_3I_3MoO_3$ requires C, 20·5; H, 3·3; As, 27·5%). The physical properties resemble those of the corresponding tungsten iodo-iodide. The *complex* is less stable, however, especially when exposed to light.

Bromotricarbonyltris-1,1,1-(*dimethylarsinomethyl*)*ethanemolybdenum*(II) *Bromide*.—The substance Mo(CO)$_3$(*v*-Triars) (1·5 g.) in toluene (150 ml.) was cooled to −70°, and bromine (0·40 g.) in benzene (35 ml.) added dropwise to the vigorously stirred solution. The yellow precipitate (1·8 g.) was filtered off, washed with ether, and dried *in vacuo* (Found: C, 23·1; H, 3·9; As, 30·8; Br, 22·2. $C_{14}H_{27}As_3Br_2MoO_3$ requires C, 23·2; H, 3·8; As, 31·0; Br, 22·1%). The physical properties resemble those of the iodide. The *compound* gives a characteristic pink photodecomposition product on exposure to light.

Bromotricarbonyltris-1,1,1-(*dimethylarsinomethylethanemolybdenum*(II) *Tetraphenylborate*.—[Mo(CO)$_3$(*v*-Triars)Br]Br (0·36 g.) in methanol (10 ml.) was treated with excess of sodium tetraphenylborate. The precipitated yellow *product* was recrystallised from acetone–ether to yield yellow plates (0·27 g.) which were collected, washed with methanol and ether, and dried *in vacuo* (Found: C, 47·2; H, 4·75; As, 23·4; Br, 8·4. $C_{38}H_{47}As_3BBrMoO_3$ requires C, 47·4; H, 4·9; As, 23·3; Br, 8·3%). The physical properties resemble those of the corresponding tungsten analogue.

Di-iododicarbonyltris-1,1,1-(*dimethylarsinomethylethanemolybdenum*(II).—The substance [Mo(CO)$_3$(*v*-Triars)I]I (0·28 g.) was refluxed in methanol (5 ml.) for 5 min. The red crystals (0·15 g.) which were deposited were washed with methanol and ether and dried *in vacuo* (Found: C, 20·5; H, 3·3; As, 28·3; Mo, 12·0. $C_{13}H_{27}As_3I_2MoO_2$ requires C, 19·8; H, 3·4; As, 28·4; Mo, 11·7%). The compound is stable, very slightly soluble in acetone, but insoluble in common solvents other than the highly polar.

Dibromodicarbonyltris-1,1,1-(*dimethylarsinomethyl*)*ethanemolybdenum*(II).—The substance [Mo(CO)$_3$(*v*-Triars)Br]BPh$_4$ (0·21 g.) was refluxed for 10 min. in ethanol (4 ml.) with excess of lithium bromide. The precipitated yellow product (0·1 g.) was washed successively with acetone, methanol, and ether and dried *in vacuo* (Found: C, 22·5; H, 4·1; As, 31·9; Br, 22·9. $C_{13}H_{27}As_3Br_2MoO_2$ requires C, 22·4; H, 3·9; As, 32·3; Br, 23·0%). The *compound* turns pink on exposure to light; other physical properties resemble those of the tungsten analogue.

Dichlorodicarbonyltris-1,1,1-(*dimethylarsinomethyl*)*ethanemolybdenum*(II).—The substance [Mo(CO)$_3$(*v*-Triars)Br]BPh$_4$ (0·53 g.) was refluxed for 20 min. in ethanol (6 ml.) with excess of lithium chloride. The precipitated yellow *product* (0·16 g.) was treated similarly to the dibromide (Found: C, 25·9; H, 4·4; As, 37·0; Br, 0·0; Cl, 11·9. $C_{13}H_{27}As_3Cl_2MoO_2$ requires C, 25·7; H, 4·5; As, 37·0; Br, 0·0; Cl, 11·7%). The physical properties resemble those of the corresponding bromide.

Iodotricarbonylmethylbis(*dimethylarsino*-3-*propyl*)*arsinemolybdenum*(II) *Iodide*.—The substance Mo(CO)$_3$(*l*-Triars) (1·3 g.) in toluene (120 ml.) was cooled to −70° and treated with iodine (0·56 g.) in benzene (11·3 ml.). The yellow product (1·9 g.) was collected, washed with ether, and dried *in vacuo* (Found: C, 20·7; H, 3·3; As, 26·9. $C_{14}H_{27}As_3I_2MoO_3$ requires C, 20·5; H, 3·3;

As, 27·5%). The *compound* turns green when exposed to light; the physical properties otherwise resemble those of the corresponding *v*-Triars derivative.

Di-iododicarbonylmethylbis(dimethylarsino-3-propyl)arsinemolybdenum(II).—The substance [Mo(CO)$_3$(*l*-Triars)I]I (0·23 g.) was heated in n-propanol for 5 min. at 100°. The orange crystals (0·1 g.) which separated were washed with methanol and ether and dried *in vacuo* (Found: C, 20·3; H, 3·4; As, 28·2. $C_{13}H_{27}As_3I_2MoO_2$ requires C, 19·8; H, 3·4; As, 28·4%). The *compound* resembles the corresponding *v*-Triars compound in its physical properties; it is slightly more soluble in acetone and slowly turns yellow in air away from light.

Bromotricarbonylmethylbis(dimethylarsino-3-propyl)arsinemolybdenum(II) *Tetraphenylborate*.—Mo(CO)$_3$(*l*-Triars) (0·43 g.) in toluene (90 ml.) was cooled to −70° and bromine (0·12 g.) in benzene (10 ml.) added dropwise with vigorous stirring. The solution was decanted from the brown oil retained on the flask walls. The oil was dissolved in methanol (15 ml.) and excess of sodium tetraphenylborate was added to precipitate the yellow crystalline product (0·2 g.). It was recrystallised from acetone–ether (Found: C, 47·4; H, 4·8; As, 22·6; Br, 8·3. $C_{38}H_{47}As_3BBrMoO_3$ requires C, 47·7; H, 4·9; As, 23·3; Br, 8·3%). The physical properties resemble those of the other tetraphenylborate derivatives.

Dibromodicarbonylmethylbis(dimethylarsino-3-propyl)arsinemolybdenum(II).—The substance Mo(CO)$_3$(*l*-Triars) (0·23 g.) in toluene was cooled to −70° and bromine (0·06 g.) in benzene (5·2 ml.) was added. The precipitate separated as an oil and was decanted. On warming the oil to 40° carbon monoxide was evolved. The oil was pumped free from solvent, triturated with ethanol, and collected. The yellow powder (0·1 g.) was washed with acetone and dried *in vacuo* (Found: C, 22·5; H, 4·1; As, 32·4; Br, 22·9. $C_{13}H_{27}As_3Br_2MoO_2$ requires C, 22·4; H, 3·9; As, 32·3; Br, 23·0%). The *compound* turns slowly brown on exposure to light; the physical properties otherwise resemble those of the *v*-Triars analogue.

Iododicarbonyltris-1,1,1-(dimethylarsinomethyl)ethanechromium(II) *Tetraphenylborate*.—The substance Cr(CO)$_3$(*v*-Triars) (0·61 g.) in toluene (100 ml.) was cooled to −70° and iodine (0·29 g.) in benzene (29 ml.) added dropwise to the vigorously stirred solution. The mixture was filtered cold leaving a red powder (0·81 g.) which was triturated with light petroleum, dissolved in methanol, and mixed with a concentrated solution of sodium tetraphenylborate in methanol to crystallise lustrous red plates (0·41 g.). They were collected, washed with a small volume of methanol, then ether, and dried *in vacuo* (Found: C, 47·1; H, 5·1; As, 23·8. $C_{37}H_{47}As_3BCrIO_2$ requires C, 47·4; H, 5·1; As, 23·9%). The *compound* is soluble in methanol, very soluble in acetone, in which it rapidly decomposes, but insoluble in chloroform, ether, and water. It is stable in air for long periods, but slowly turns green, a change accelerated by light.

Iodotricarbonylmethylbis(dimethylarsine-3-propyl)arsinechromium(II) *Tetraphenylborate*.—The substance Cr(CO)$_3$(*l*-Triars) (0·39 g.) in toluene (80 ml.) was cooled to −70° and treated with iodine (0·19 g.) in benzene (19 ml.). Subsequent treatment, as given in the preceding preparation, gave brown plates (0·25 g.) (Found: C, 46·8; H, 5·5; As, 23·0. $C_{38}H_{47}As_3BCrIO_3$ requires C, 47·2; H, 4·9; As, 23·3%). The *compound* is very unstable as indicated by the increase of the magnetic moment with time. Seventy minutes after the preparation, $\mu_{eff} = 1·9$ B.M.; after 5½ hr., 2·6 B.M., and reached 3·0 B.M. after 25 hr. Extrapolation to zero time yields $\mu_{eff} = 1·3$ B.M. The brown compound darkens slowly with time, eventually turning black; the solubility properties resemble those of the previous compound.

Analyses and Physical Measurements.—These were performed as described previously.[10]

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