

359. *Substituted Group VI Carbonyls. Part II.* The Action of Halogens on Di(tertiary arsine)molybdenum Carbonyls.*

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The action of halogens on $\text{Mo}(\text{Diarsine})(\text{CO})_4$ and $\text{Mo}(\text{Diarsine})_2(\text{CO})_2$ has been investigated. Treatment of one mole of the former with two equivalents of iodine or bromine yields a compound $\text{Mo}(\text{Diarsine})(\text{CO})_3\text{I}_2$ (or Br_2), one mole of carbon monoxide being liberated. These compounds are diamagnetic and the molecular weight and molecular conductivity in nitrobenzene show that they are seven-covalent derivatives of bivalent molybdenum. The bisdiarsine compound, $\text{Mo}(\text{Diarsine})_2(\text{CO})_2$, on treatment with two equivalents of iodine also yields a seven-covalent bivalent molybdenum complex. This is a uni-univalent electrolyte having the formula $[\text{Mo}(\text{Diarsine})_2(\text{CO})_2\text{I}]$, no carbon monoxide being evolved in the reaction. The use of bromine gives rise to the corresponding monobromide. Excess of bromine reacts with $\text{Mo}(\text{Diarsine})_2(\text{CO})_2$ to yield the tribromide $[\text{Mo}(\text{Diarsine})_2(\text{CO})_2\text{Br}]_3$. With $\text{Mo}(\text{Diarsine})(\text{CO})_4$, however, excess of bromine gives the quadrivalent molybdenum compound $\text{Mo}(\text{Diarsine})\text{Br}_4$. The existence of the seven-covalent molybdenum(II) compounds, and of many other complexes of the transition metals such as $\text{K}_4\text{Mo}(\text{CN})_7$ and $[\text{Re}(\text{Diarsine})_2\text{Cl}_4]\text{ClO}_4$, in which the metal atom is seven- or eight-covalent, with ligands like carbon monoxide is explained in terms of a nine-orbital rule.

It has been shown previously that treatment of di(tertiary arsine)-substituted metal carbonyls with halogens provides a valuable method for preparing compounds in which the metal atom has an unusual stereochemistry, *e.g.*, *cis*-di-iodonickel in $\text{NiI}_2\text{Diarsine}$,¹ or unusual oxidation states, *e.g.*, univalent iron in $\text{Fe}(\text{Diarsine})(\text{CO})_2\text{I}$.² The reaction of halogens upon $\text{Mo}(\text{Diarsine})(\text{CO})_4$ and $\text{Mo}(\text{Diarsine})_2(\text{CO})_2$ also yields unusual new types of compound. The reactions were carried out in non-aqueous solvents such as chloroform and benzene and it was convenient to study these reactions in the first instance by spectrophotometric titration since the more usual conductometric or potentiometric methods of titration are not easily applicable in these solvents. Fig. 1 shows the result obtained when

* Part I, preceding paper.

¹ Nyholm, *J.*, 1951, 2906.

² Nigam, Nyholm, and Rao, *J.*, 1959, 1397.

Mo(Diarsine)(CO)₄ is titrated with iodine, the optical density being measured at 500 m μ where there occurs a strong absorption peak for molecular iodine in chloroform. It may be seen that 2 equiv. of iodine are absorbed during the reaction, excess of iodine accumulating thereafter. The product of this reaction has an analysis corresponding with the formula Mo(Diarsine)(CO)₃I₂, indicating the loss of one mole of carbon monoxide; this has been confirmed by using a gas burette to collect the evolved carbon monoxide. A

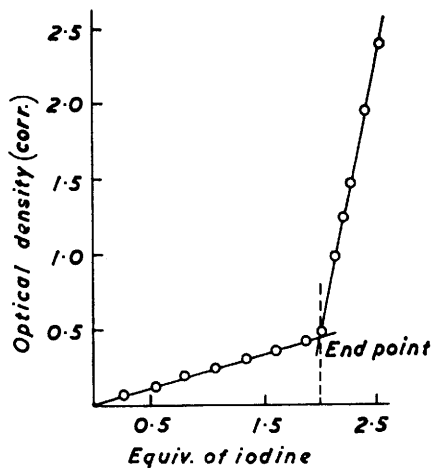


FIG. 1. Spectrophotometric titration of Mo(Diars)(CO)₄ with iodine in CCl₄ ($\lambda = 500 \text{ m}\mu$; 1 cm. cell).

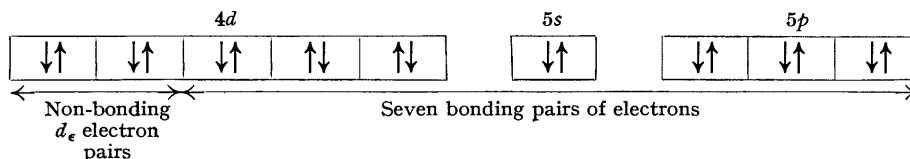
similar reaction occurs with bromine. As may be seen from Table 1, both the iodo- and the bromo-compound are non-electrolytes in nitrobenzene, in which solvent they have also been found to be monomeric as shown by cryoscopic molecular-weight measurements.

TABLE 1. Properties of molybdenum ditertiaryarsine carbonyl halide complexes.

Derivative of	Compound ¹	Colour	Mol. condy. (ohm ⁻¹) (10 ⁻³ M in Ph·NO ₂ soln.)	C-O stretching frequency (cm. ⁻¹) in Nujol, infra- red	Mol. weight:	
					Cryoscop. in Ph·NO ₂	Calc.
Mo(Diars)(CO) ₄	Mo ^{II} (Diars)(CO) ₃ I ₂	Golden-yellow	1.2	2053, 1982, 1925	698 in 0.53% soln.	720
	Mo ^{II} (Diars)(CO) ₃ Br ₂	Deep orange	2.2	2023, 1971, 1921	634 in 0.45% soln.	626
	Mo ^{IV} (Diars)Br ₄	Orange-brown	11.6	Nil	682 in 0.24% soln.	702
Mo(Diars) ₂ (CO) ₂	[Mo ^{II} (Diars) ₂ (CO) ₂ I]I	Pale yellow	27.4	1960, 1888	— ²	978
	[Mo ^{II} (Diars) ₂ (CO) ₂ Br]Br	Pale yellow	23.5	1959, 1888	— ²	884
	[Mo ^{II} (Diars) ₂ (CO) ₂ Br]Br ₃	Deep yellow	20.5	1959, 1890	— ²	1044

¹ All compounds are diamagnetic except Mo(Diars)Br₄ for which $\mu_{\text{eff}} = 1.96 \text{ B.M.}$ at 20° c. ² Solubility too small.

The complexes thus appear to be seven-covalent derivatives of bivalent molybdenum, the electron configuration being as follows:



Such a formulation implies the absence of any unpaired electrons, which is in agreement with the observed diamagnetism. If it be assumed that the σ -bonding orbitals involve the use of $4d_{xy}, 2s5p^3$ orbitals, then a pentagonal bipyramidal arrangement of the attached groups is expected; ³ one possibility is shown in Fig. 2. It must be stressed that such an arrangement is purely hypothetical at present. There is no certainty that the two halogen atoms would occupy the two axial positions; this seems most probable, however, since the two axial bonds are longer than the other five and are expected to be the positions where the most electronegative ligands would be attached. However, in any case, the pentagonal bipyramidal arrangement would at best be an approximation since several factors would tend to cause deviations from this ideal shape. These are: (i) all seven atoms are not the same; (ii) double bonding between the molybdenum atoms and the carbon monoxide and arsine ligands would undoubtedly lead to electron distributions

FIG. 2. Proposed pentagonal bipyramidal structure for $\text{Mo}(\text{Diars})_2(\text{CO})_2\text{I}_2$.

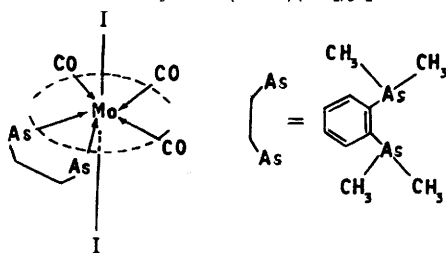
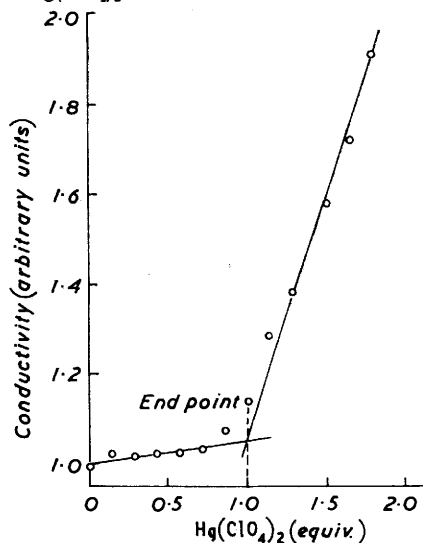


FIG. 3. Conductometric titration of $1.0 \times 10^{-3} \text{M} [\text{Mo}(\text{Diars})_2(\text{CO})_2\text{Br}]\text{Br}$ against $\text{Hg}(\text{ClO}_4)_2$ in nitrobenzene.



which would affect any simple conclusions as to the stereochemistry based upon σ -bonding alone; (iii) steric effects may well be important, especially in the pentagonal plane.

On treatment with iodine in chloroform under the same conditions the bisdiarsine dicarbonyl also absorbs two equivalents of iodine and again yields a seven-covalent derivative, $[\text{Mo}(\text{Diarsine})_2(\text{CO})_2\text{I}]\text{I}$. In this instance gas-burette measurements confirm that no carbon monoxide is evolved and, as shown in Table 1, the product has a molecular conductivity consistent with its formulation as a uni-univalent electrolyte. Unfortunately, its low solubility in nitrobenzene precludes measurement of the molecular weight in this solvent. The complex is diamagnetic as in the case of $\text{Mo}(\text{Diarsine})(\text{CO})_3\text{I}_2$. The corresponding bromo-bromide $[\text{Mo}(\text{Diarsine})_2(\text{CO})_2\text{Br}]\text{Br}$ has also been prepared and treatment of this compound with excess of bromine yields a tribromide of the $\text{Mo}(\text{II})$ complex and not a derivative of molybdenum of a higher oxidation state. Attempts to prove that one of the bromine atoms in the compound $[\text{Mo}(\text{Diarsine})_2(\text{CO})_2\text{Br}]\text{Br}$ is ionised by isolating a perchlorate have not been successful owing to unsuitable solubility relations, the perchlorate being apparently more soluble than the bromide in the solvents employed. However, a novel technique has been used to show that one of the two bromine atoms is ionised, as shown in Fig. 3; the compound $[\text{Mo}(\text{Diarsine})_2(\text{CO})_2\text{Br}]\text{Br}$ has been titrated conductometrically in nitrobenzene solution with a solution of mercuric perchlorate.

³ See Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 339, for references.

The latter, like the molybdenum compound, is a strong electrolyte in this solvent and the reaction which occurs is simply $\text{Br}^- + \frac{1}{2}\text{Hg}^{++} \longrightarrow \frac{1}{2}\text{HgBr}_2$, there being practically no change in conductivity until all the free Br^- ions are converted into un-ionised mercuric bromide. A sudden increase in conductivity is to be expected after one equivalent of mercuric perchlorate has been added—as is observed. It has been found that the use of this reagent in conductometric titrations in nitrobenzene is very useful for establishing the nature of the free anion when the isolation of a salt to confirm its presence is difficult.

These derivatives appear to be the first seven-co-ordinate σ -bonded compounds of bivalent molybdenum to be described. The occurrence of a considerable number of seven- and eight-co-ordinate derivatives of the metals of the first half of the transition series (see Table 2) can be understood in terms of a tendency of the transition metal atom to make use of all nine orbitals [five $(n-1)d$, one ns , and three np] for σ -bonding pairs, for non-bonding pairs, or for single electrons. The co-ordination number of a metal atom is limited in the first instance by the number of bonding orbitals available. If it is assumed that no "outer" d orbitals are employed, then clearly the best chance of obtaining a co-ordination number of seven or eight occurs when the number of non-bonding d electrons is four or less.

The "inert-gas rule" for metal carbonyls is the ideal case of the above principle; the metal atoms combine with carbon monoxide, or with one another, so as to place a pair of electrons (σ -bonding or lone pairs) in each of the nine orbitals, the complexes being diamagnetic. Now carbon monoxide is generally regarded as the most "covalent" bonding ligand of all, and as we replace some or all of these by other ligands which are fairly similar (*e.g.*, CN^- , RNC , tertiary phosphines, tertiary arsines, NO , etc.) all nine orbitals are still used but paramagnetism may arise. Thus in $[\text{Mn}(\text{CO})_4(\text{Ph}_3\text{P})]^0$ one of the nine orbitals contains a single unpaired electron. In such compounds the co-ordination number of the metal atom depends upon the number of orbitals used by the non-bonding electrons, indicated in turn by the number of unpaired electrons. Hund's rules favour the maximum number of singly occupied orbitals, *e.g.*, $\text{K}_3\text{Cr}(\text{CN})_6$ has three unpaired electrons, but pairing can occur when there is a decrease in the inter-electronic repulsion between electrons of opposite spin in the same orbital. As expected, this pairing occurs

TABLE 2. Co-ordination number and unpaired electrons.

Number of non-bonding d -electrons	Number of unpaired d -electrons	Co-ordination number	Examples
0	0	9	—
1	1	8	$\text{K}_9\text{Mo}(\text{CN})_8$
2	2	7	$\text{K}_4\text{V}(\text{CN})_7(?)$
	0	8	$\text{K}_3\text{Re}(\text{CN})_8$, $\text{K}_4\text{Mo}(\text{CN})_8$ $[\text{Re}(\text{Diarsine})_2\text{Cl}_4]\text{ClO}_4$
3	3	6	$\text{K}_3\text{Cr}(\text{CN})_6$, K_2ReCl_6
	1	7	$\text{K}_4\text{Mo}(\text{CN})_7$
4	4	5	$[\text{Mn}(\text{Diarsine})\text{Br}_2\text{H}_2\text{O}]\text{Br}$
	2	6	$[\text{Cr}(\text{Bipyridyl})_3]^{2+}$ $[\text{Re}(\text{Diarsine})_2\text{Cl}_2]^+$
	0*	7	$\text{Mo}(\text{Diarsine})(\text{CO})_3\text{I}_2$ $\text{C}_5\text{H}_5\text{V}(\text{CO})_4 \uparrow$

* Diamagnetism occurs also in $[\text{ReCl}_4]^-$ but here the "nine-orbital rule" is not obeyed as ligands of high electronegativity are present. $\uparrow \text{C}_5\text{H}_5 =$ cyclopentadienyl.

more readily as we pass down a vertical column in the transition series, *e.g.*, from $\text{Cr}(\text{III})$ to $\text{Mo}(\text{III})$. Thus, whereas $\text{K}_3\text{Cr}(\text{CN})_6$ has three spins, the $\text{Mo}(\text{III})$ complex, $\text{K}_4\text{Mo}(\text{CN})_7$ has only one, the metal atom being seven-covalent.⁴ In this case the inter-electronic repulsions in the d_e orbitals are now less than the effect due to the ligand field. Table 2

⁴ Steele, *Austral. J. Chem.*, 1957, **10**, 404 and references therein; Smith (personal communication, 1959) has shown that $\mu_{\text{eff}} = 1.7$ B.M.

summarises the cases where seven and eight co-ordination are expected in terms of the number of unpaired electrons.

It must be stressed that the above principles refer to compounds containing mainly ligands of the CO type, *i.e.*, those for which some d_{π} -bonding by the metal is believed to occur; no attempt is made to discuss complexes with the more electronegative ligands such as $R\cdot CO\cdot O^-$ or Cl^- , where the bonds are more ionic and in which the nine-orbital rule is not necessarily obeyed (*e.g.*, $TiCl_4$). To sum up, it is suggested that the occurrence of co-ordination numbers seven and eight with transition-metal complexes using ligands like carbon monoxide can be understood in terms of an extension of the "inert-gas rule" for metal carbonyls. Since paramagnetism can occur in many of these compounds the more general term "nine-orbital rule" is proposed, the "inert-gas rule" being a special case thereof.

One can include the π -type complexes in the scheme if one adopts the Fischer⁵ picture of the bond formed in these compounds. Thus in cyclopentadienylvanadium tetracarbonyl, in which the metal is univalent, one assumes that the cyclopentadienyl radical supplies three σ -bonding pairs of electrons, so far as the metal is concerned, making with the four carbon monoxide groups, seven pairs of bonding electrons in all (see Table 2).

Treatment of $Mo(Diarsine)(CO)_4$ with a large excess of bromine has yielded the only compound of molybdenum with an oxidation state higher than two in this investigation. The product has the empirical formula $Mo(Diarsine)Br_4$. Its molecular weight is close to that of the formula weight, which is consistent with both a monomeric $[Mo(Diarsine)Br_4]^0$ or a salt-like $[Mo(Diarsine)_2Br_2][MoBr_6]$ structure. The molecular conductivity in nitrobenzene is only about one-fifth of that required for the salt-like structure if completely dissociated. It is suggested, therefore, that the complex is a non-electrolyte which undergoes some dissociation in nitrobenzene. The absence of appreciable free bromide ion is established by the fact that there is no inflexion on titration with mercuric perchlorate in nitrobenzene solution. The magnetic moment of the compound (1.96 B.M.) is less than that expected for two unpaired electrons, but this can be understood readily in terms of Kotani's theory.⁶ For a d_e^2 octahedral complex the moment varies according as the ratio of kT to λ changes, where λ is the spin-orbit coupling constant. As the temperature decreases and/or λ increases (*i.e.*, with the second- and third-row transition elements) so μ decreases and may be as low as 1.22 B.M. The value of 1.96 B.M. at 20° C is of the order expected for quadrivalent molybdenum.

The infrared spectra are given in Table 1 and these support the structures assigned. Apart from their diagnostic value in establishing the absence of CO in $Mo(Diarsine)Br_4$, it is possible to draw the following conclusions: (i) the similarity of the bands in $Mo(Diarsine)(CO)_3I_2$ and $Mo(Diarsine)(CO)_3Br_2$ indicates that the structures are very similar; (ii) the suggestion that $[Mo(Diarsine)_2(CO)_2Br]Br_3$ is a tribromide of an Mo^{II} complex and does not involve further oxidation is strongly supported by the fact that its infrared spectrum is almost exactly identical with that of $[Mo(Diarsine)_2(CO)_2Br]Br$; (iii) the presence of two bands due to C-O stretching in the complex $[Mo(Diarsine)_2(CO)_2Br]Br$ strongly supports the view that the two CO groups are *cis* and not in the *trans*-apical positions in which we have arbitrarily placed the halogen atoms in Fig. 2.

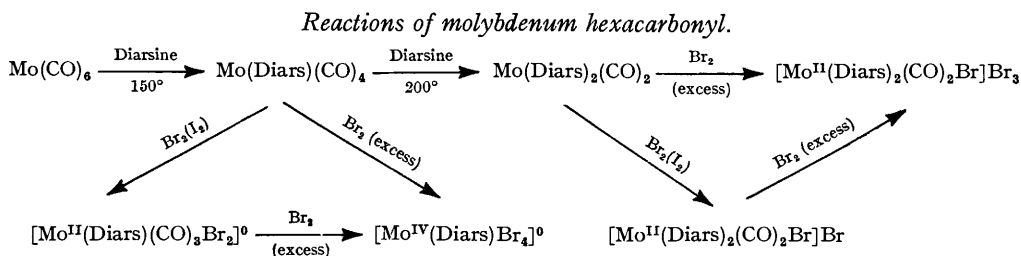
Reference should be made to the fact that the triarsine, $AsMe_2\cdot[CH_2]_3\cdot AsMe\cdot[CH_2]_3\cdot AsMe_2$, also gives rise to seven-co-ordinate bivalent molybdenum complexes.⁷ On treatment with bromine the compound $Mo(Triarsine)(CO)_3$, referred to in Table 1, Part I, p. 1804, forms $[Mo(Triarsine)(CO)_2Br_2]^0$ with the loss of one mol. of carbon monoxide. This is undoubtedly very similar to $Mo(Diarsine)(CO)_3Br_2$, since it is monomeric and a non-electrolyte. These triarsine complexes will be described later in detail.

⁵ Fischer, "International Conference on Co-ordination Chemistry," London, 1959 (*Chem. Soc. Special Publ.*, 1959, No. 13, p. 73).

⁶ Kotani, *J. Phys. Soc. Japan*, 1949, 4, 293.

⁷ Parish Thesis, London, 1958.

The reactions which occur and the new compounds formed in this investigation are summarised in the annexed diagram.



EXPERIMENTAL

Di-iodomono-o-phenylenebisdimethylarsinetricarbonylmolybdenum(II).—Mo(Diars)(CO)₄ (0.5 g.) in chloroform (50 ml.) was treated with iodine (0.25 g.) (*i.e.*, Mo: I = 1.2:1) in chloroform (10 ml.) under nitrogen with vigorous stirring. One mole of carbon monoxide per mole of Mo(Diars)(CO)₄ was liberated, the compound Mo(Diars)(CO)₃I₂ (0.5 g.) crystallised slowly at 0° as golden-yellow crystals after addition of light petroleum (10 ml.); it was washed with light petroleum and dried *in vacuo* (Found: C, 21.8; H, 2.6; I, 35.6; Mo, 13.2. C₁₃H₁₆O₃As₂I₂Mo requires C, 21.7; H, 2.2; I, 35.3; Mo, 13.3%). When heated *in vacuo* it chars at about 200°. The compound is moderately soluble in non-polar organic solvents and in nitrobenzene but is insoluble in light petroleum. It decomposes fairly rapidly in moist air.

Dibromomono-o-phenylenebisdimethylarsinetricarbonylmolybdenum(II).—Mo(Diars)(CO)₄ (0.5 g.) in cyclohexane (150 ml.) was treated slowly with bromine (0.16 g.) in carbon tetrachloride (25 ml.) under nitrogen, as above, with efficient stirring to avoid local concentrations of the halogen. One mol. of carbon monoxide was liberated. The orange precipitate (0.5 g.) was filtered off, washed with light petroleum, and dried *in vacuo* (Found: C, 25.0; H, 2.7; Br, 25.7; Mo, 15.1. C₁₃H₁₆O₃As₂Br₂Mo requires C, 24.9; H, 2.6; Br, 25.5; Mo, 15.3%). When heated, this compound charred at about 200°; its physical properties are very similar to those of the di-iodide.

Tetrabromo-o-phenylenebisdimethylarsinemolybdenum(IV).—Mo(Diars)(CO)₄ (0.5 g.) in chloroform (30 ml.) was shaken vigorously with bromine (2 g.; *i.e.*, a large excess) in chloroform (20 ml.). Four mols. of carbon monoxide were evolved and the orange-brown crystals (0.2 g.) of MoBr₄(Diars) which separated were washed with light petroleum and dried *in vacuo*; they had m. p. (vac.) 210° (decomp.) (Found: C, 17.0; H, 2.7; Br, 45.4; Mo, 13.4. C₁₀H₁₆As₂Br₄Mo requires C, 17.1; H, 2.3; Br, 45.6; Mo, 13.7%). The compound is very sparingly soluble in non-polar organic solvents and only moderately soluble in alcohol and nitrobenzene.

Monoiodobis-o-phenylenebisdimethylarsinedicarbonylmolybdenum(II) *Monoiodide*.—Mo(Diars)₂(CO)₂ (0.25 g.) in chloroform (25 ml.) was treated with iodine (0.09 g.) in chloroform (30 ml.) as above. Pale yellow crystals (0.2 g.), which separated at once without evolution of carbon monoxide, were washed with light petroleum and dried *in vacuo*, then having m. p. (vac.) 195° (decomp.) (Found: C, 27.0; H, 3.4; I, 25.2; Mo, 9.7. C₂₂H₃₂O₂As₄IMo requires C, 27.0; H, 3.3; I, 26.0; Mo, 9.8%). The compound is sparingly soluble in the usual organic solvents and only moderately soluble in nitrobenzene. Other properties are similar to those of preceding derivatives.

Monobromobis-o-phenylenebisdimethylarsinedicarbonylmolybdenum(II) *Monobromide*.—Mo(Diars)(CO)₂ (0.4 g.) in chloroform (25 ml.) was treated slowly with bromine (0.1 g.) in carbon tetrachloride (20 ml.) as above. A pale yellow crystalline compound (0.3 g.) appeared immediately without evolution of carbon monoxide. It was well washed with light petroleum and dried *in vacuo*; its m. p. (vac.) was 200° (decomp.) (Found: C, 30.2; H, 3.7; Br, 18.5; Mo, 10.6. C₂₂H₃₂O₂As₄Br₂Mo requires C, 29.9; H, 3.6; Br, 18.2; Mo, 10.9%). Its physical properties are similar to those of the corresponding iodo-molybdenum(II) iodide.

Monobromobis-o-phenylenebisdimethylarsinedicarbonylmolybdenum(II) *Tribromide*.—Mo(Diars)₂(CO)₂ (0.2 g.) in chloroform (20 ml.) was treated with excess of bromine (0.1 g.) in carbon tetrachloride (20 ml.) as above. An orange complex (0.2 g.) was precipitated at once, without evolution of carbon monoxide. This was washed with light petroleum and dried

