# 1208. *Aliphatic Tri(tertiary arsine)carbonyls. Part I. Derivatives of Group VI and Group VII Metals*

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Reaction of tris-1,1,1-(dimethylarsinomethyl)ethane (*v*-Triars)* with the hexacarbonyls of chromium, molybdenum, and tungsten yield the derivative $M(CO)_3$(*v*-Triars); with hexacarbonyltungsten, a tetracarbonyl, $W(CO)_4)$(*v*-Triars), in which the triarsine is behaving as a bidentate ligand, is also formed. A similar compound, $Re(CO)_3$(*v*-Triars)Cl, containing one unco-ordinated arsenic atom is formed from the halogenocarbonyl $Re(CO)_5Cl$. This compound is shown to exist in two isomeric forms. The cationic complexes, $[M(CO)_3$(*v*-Triars)$]ClO_4$ (M = Mn or Re) are formed when the triarsine is heated with tricarbonylmesitylenemanganese perchlorate and hexacarbonylrhenium perchlorate respectively. The differential shifts of the proton resonance spectra of the complexes, relative to that of the free triarsine are discussed.

TERDENTATE substitution in Group VI hexacarbonyls has been effected by diethylenetriamine,[1] diethylene glycol dimethyl ether,[2] 3,6,9-trithiaundecane,[3] several tri(tertiary phosphines),[4] and two tri(tertiary arsines), namely methylbis(dimethyl-3-propyl)arsine[5] (*l*-Triars) and bis(*o*-dimethylarsinophenyl)methylarsine[6] (*o*-Triars). In Group VII,

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* The nomenclature arises because this terdentate group co-ordinates in three vicinal positions.

[1] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J.*, 1959, 2323.
[2] R. P. M. Werner and T. H. Coffield, *Chem. and Ind.*, 1960, 936.
[3] H. C. E. Mannerskantz and G. Wilkinson, *J.*, 1962, 4454.
[4] J. Chatt and H. R. Watson, *J.*, 1961, 4980.
[5] J. Mašek, R. S. Nyholm, and M. H. B. Stiddard, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1714.
[6] C. D. Cook, R. S. Nyholm, and M. L. Tobe, *J.*, 1965, 4194.

although a number of derivatives of manganese(I) and rhenium(I) of the type $[M(CO)_3L_2X]^0$, $[M(CO)_4L_2]^+$, and $[M(CO)_2(L_2)_2]^+$, where $L_2$ represents two unidentate or one bidentate ligand,[3,7-10] have been prepared, little information is available concerning the reaction of terdentate ligands. Diethylenetriamine (dien) reacts with the salt $[Mn(CO)_3(mesitylene)]I$ to yield the product $[Mn(CO)_3(dien)]I$;[11] 3,6,9-trithiaundecane displaces only two carbonyl groups from bromopentacarbonylmanganese to yield the tricarbonyl complex containing one unco-ordinated sulphur atom.

We now report cationic tricarbonyl derivatives of manganese and rhenium containing tris-1,1,1-(dimethylarsinomethyl)ethane (*v*-Triars) and compare their properties with the corresponding Group VI compounds. The complexes $W(CO)_4$(*v*-Triars) and $Re(CO)_3$(*v*-Triars)Cl, in which the triarsine is behaving as a bidentate ligand, are described also.

*Group VI Compounds.*—The Group VI tricarbonyl complexes $M(CO)_3$(*v*-Triars) were prepared by established methods.[5] The ligand *v*-Triars is capable of vicinal co-ordination only, so that the three carbonyl groups must also be in *cis* positions. This is confirmed by the infrared spectra in the C–O stretching region (see Table) which are typical for such *cis* tricarbonyl complexes. Reaction of hexacarbonyltungsten yielded two products in roughly equal yield: the expected tricarbonyl and a tetracarbonyl in which the triarsine acts as a bidentate ligand. The latter may be converted into the former on heating at 180° under nitrogen. The tetracarbonyl has a low melting point (93·5—94·5°) compared with that of the tricarbonyl (>330°); the infrared spectrum of this tetracarbonyl in the C–O stretching region is consistent with *cis* disubstitution and, as expected, the compound reacts readily with methyl iodide in boiling ethanol to form a methiodide. The formation of the tetracarbonyl complex reflects the established increasing difficulty of substitution in Group VI carbonyls in the order $Mo \leqslant Cr < W$.

*Group VII Compounds.*—A compound analogous to bromotricarbonyl-3,6,9-trithiaundecanemanganese[3] could not be prepared by reaction of the triarsine with bromopentacarbonylmanganese under a variety of conditions. However, reaction of chloropentacarbonylrhenium with the triarsine in xylene at 140° yielded the compound $Re(CO)_3$(*v*-Triars)Cl, the spectrum of which is typical of a *cis* disubstituted halogenocarbonyl. The compound, after melting at 121—122°, gives a white crystalline solid at 200°, the spectrum of which is almost identical with that of the complex $[Re(CO)_3$(*v*-Triars)$]ClO_4$. The formation of the cation $[Re(CO)_3$(*v*-Triars)$]^+$ has been confirmed by subsequent extraction of the tetraphenylborate. If, (*a*) heating is continued to 270°, or (*b*) a mixture of the tetraphenylborate and tetraethylammonium chloride is heated to 270°, or (*c*) iodotricarbonyltriarsinerhenium is heated to 290°, gas is evolved from the melts and the appearance of two low-frequency bands in the infrared spectra of the products may indicate formation of the compound $Re(CO)_2$(*v*-Triars)X, but separation could not be effected. The halide ion substitution of the $[Re(CO)_3$(*v*-Triars)$]^+$ cation is analogous with the reaction of tetraethylammonium halides with Group VI carbonyls.[11] The cation was also produced by direct reaction: the complex $[Re(CO)_3$(*v*-Triars)$]ClO_4$ resulted from heating the triarsine with hexacarbonylrhenium perchlorate in boiling cyclohexane. The corresponding manganese complex was obtained similarly from the manganese salt $[Mn(CO)_3(mesitylene)]ClO_4$.[12]

In attempting to prepare tricarbonylmesitylenerhenium perchlorate by a method analogous with that described for the corresponding manganese complex,[12] a low yield of hexacarbonylrhenium perchlorate was obtained. Under the conditions described, a carbon

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[7] E. W. Abel and G. Wilkinson, *J.*, 1959, 1501.

[8] E. J. Kirkham, A. G. Osborne, R. S. Nyholm, and M. H. B. Stiddard, *J.*, 1965, 550.

[9] Th. Kruck and M. Noack, *Chem. Ber.*, 1963, **96**, 3028.

[10] A. G. Osborne and M. H. B. Stiddard, *J.*, 1962, 4715; 1965, 700.

[11] E. W. Abel, I. S. Butler, and J. G. Reid, *J.*, 1963, 2068.

[12] G. Winkhaus, L. Pratt, and G. Wilkinson, *J.*, 1961, 3807.

monoxide transfer reaction must occur to produce this compound, which has been prepared previously by high-pressure carbonylation.[13]

*Physical Properties of the Compounds.*—The infrared spectra of the substituted Group VI carbonyl complexes in the C–O stretching closely resemble those of similar compounds containing the ligands *l*- and *o*-Triars. The spectra, which are virtually identical whether measured using mulls or solutions, are entirely consistent with the suggested structures. The spectra of the cationic species are very similar in profile to the isoelectronic and isostructural neutral species and the expected shift to higher frequencies is observed.

Physical properties of carbonyltriarsines

| No. | Compound | Cond.* in $PhNO_2$ | Infrared spectrum (Nujol) C–O stretching region | Infrared spectrum (Nujol) 850—950 cm.$^{-1}$ region |
|---|---|---|---|---|
| 1 | $Cr(CO)_3$(*v*-Triars) | 0·0 | 1923 (s) 1825 (s, b) [a] | 890 (m) 874 (m) |
| 2 | $Mo(CO)_3$(*v*-Triars) | 0·0 | 1935 (s) 1835 (s, b) [a] | 892 (m) 872 (m) |
| 3 | $W(CO)_3$(*v*-Triars) | 0·0 | 1930 (s) 1835 (s, b) [a] | 895 (m) 873 (m) |
| 4 | $W(CO)_4$(*v*-Triars) | 0·0 | 2010 (s) 1900 (sh) | 900 (m) 882 (s) |
| | | | 1890 (s) 1870 (sh) | 868 (w) 853 (w) |
| 5 | $[W(CO)_4(CH_3$.*v*-Triars)]I | 27·1 | 2030 (s) 1935 (s) | 963 (s) 908 (m) |
| | | | 1910 (s) 1890 (s) 1850 (s) | 881 (s) 862 (m) |
| 6 | $[Mn(CO)_3$(*v*-Triars)]$ClO_4$ | 22·5 | 2005 (s) 1915 (s, b) | 903 (m) 892 (m) |
| 7 | $[Re(CO)_3$(*v*-Triars)]$ClO_4$ | 24·6 | 2025 (s) 1925 (s, b) | 910 (m) 899 (s) |
| 8 | $[Re(CO)_3$(*v*-Triars)Cl][e] | 0·6 | 2025 (s) 1935 (s) | 905 (s) 885 (s) |
| | | | 1895 (s) | 867 (m) 859 (w) |
| 9 | (*v*-Triars) | — | — | 890 (s) 860 (s, b) 840 (sh) |

| | | Proton resonance spectra (p.p.m.) | | |
|---|---|---|---|---|
| No. | $10^6 \chi^1_M$ [c] $\mu_{eff}$ B.M. | $CH_2$–As | $CH_3$–As | $CH_3$–C |
| 1 | +238 [0·7] | 8·62 [d] | | 8·87 [b] |
| 2 | +148 [0·6] | 8·52 | 8·61 | 8·83 [b] |
| 3 | +127 [0·5] | 8·39 | 8·44 | 8·87 [b] |
| 4 | — | 8·88 | 9·02 | |
| | | 8·14 8·10 | 8·43 8·39 | |
| 5 | — | — | — | — |
| 6 | +134 [0·5] | 8·00 | 8·19 | 8·53 [b] |
| 7 | +126 [0·5] | 7·87 | 8·02 | 8·57 [b] |
| 8 | — | 8·78 8·82 | 8·99 9·01 | [f] |
| | | 7·99 | 8·27 8·31 | |
| 9 | — | 8·27 | 9·05 | 8·92 [a] |

* $\Lambda_M(\Omega^{-1}$ cm.$^2$) of $10^{-3}$M solution.

[a] Chloroform solution. [b] Nitrobenzene solution. [c] Gouy method, 9·4 cm. tube calibrated with cobalt mercury thiocyanate. $\chi_g$ (20°) = 16·44 × $10^{-6}$ c.g.s. Pascal constants used in calculating $\chi^1_M$. [d] Proton resonance fortuitously overlapped. [e] Proton resonances of equal intensity. [f] Resonances overlapped by peaks due to As–$CH_2$.

Bands at 885 and 846 cm.$^{-1}$ in the infrared spectrum of *o*-phenylenebisdimethylarsine have been assigned [14] to methyl–arsenic rocking modes. It was observed that these vibrations were apparently sensitive to steric interactions and were shifted to higher frequencies on co-ordination of the arsine to metal ions. The shifts on co-ordination to zerovalent metal atoms (Table) are quite small and additional bands are observed when more than one type of arsenic atom is present in the complex.

The compounds listed in the Table all have the *d* electron configuration $(t_{2g})^6$ and exhibit residual paramagnetism of about 200 × $10^{-6}$ c.g.s.u. Griffith and Orgel [15] predict the residual paramagnetism (T.I.P.) for cobalt(III), $(t_{2g})^6$ to be of the order 195 × $10^{-6}$ c.g.s.u., consistent with experiment. Their suggestion, that the effect is general for this electronic configuration, is confirmed by our observations (see Table).

In Figure 1, the proton resonance spectra of the tricarbonyltriarsine complexes are schematically compared. No spin–spin splittings were observed. In the neutral complexes, the C–$CH_3$ resonance is virtually unshifted, while that of the As–$(CH_3)_2$ and

[13] W. Hieber and Th. Kruck, *Angew. Chem.*, 1961, **73**, 580; *Z. Naturforsch.*, 1961, **16***b*, 709.
[14] G. A. Rodley, Ph.D. Thesis, University of London, 1963.
[15] J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, 1957, **53**, 601.

As–$CH_2$– groups are shifted in opposing directions relative to the free triarsine. In the chromium compound, this effect has led to fortuitous overlapping of the As–$(CH_3)_2$ and As–$CH_2$– resonances. The cationic complexes show a similar trend with a superimposed deshielding of up to 0·5 p.p.m. Similar opposing shifts were observed in the proton resonance spectra of the tetracarbonyl-2,5-dithiahexane complexes of chromium and

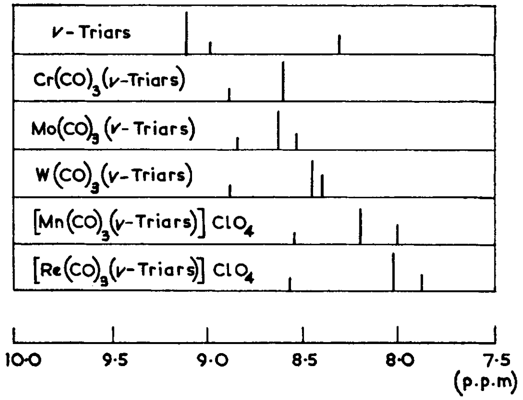

FIGURE 1. Comparison of the proton resonance spectra of *v*-Triars complexes

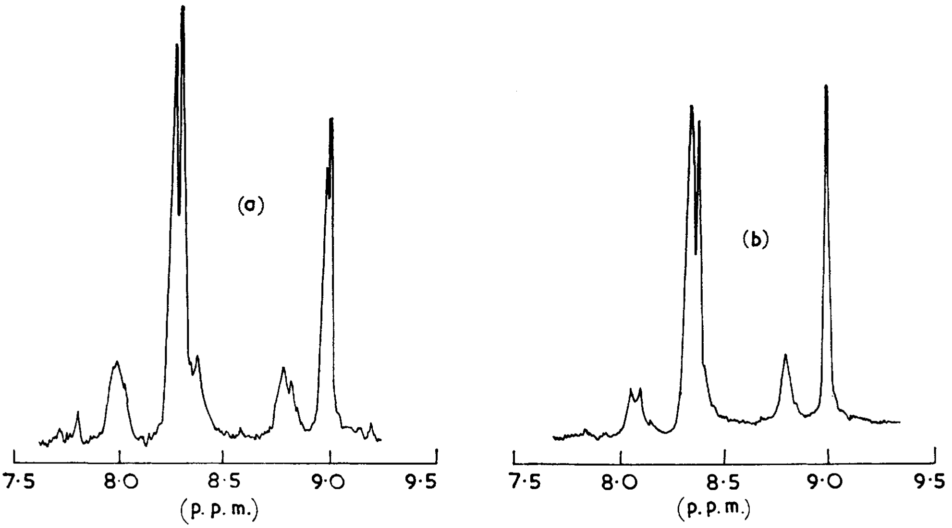

FIGURE 2. Proton resonance spectra of (*a*) [Re(CO)$_3$(*v*-Triars)Cl] and (*b*) W(CO)$_4$(*v*-Triars)

molybdenum.[3] These effects may be explained by considering the magnetic anisotropies of the central metal and the carbonyl groups. McConnell[16] has derived an approximate relationship between the chemical shift averaged over all orientations, $\sigma_{av}$, and the difference between the molecular susceptibilities parallel ($\chi_{\parallel}$) and perpendicular ($\chi_{\perp}$) to an axially symmetrical group of electrons. Thus for a proton at a distance $r$ from an electrical centre and at an acute angle $\theta$ to the principal axis

$$\sigma_{av} = \frac{(\chi_{\parallel} - \chi_{\perp})(1 - 3\cos^2\theta)}{3r^3}$$

A reasonable molecular geometry being assumed for the compound Cr(CO)$_3$(*v*-Triars), the difference between the molar susceptibilities is calculated to be $-48 \times 10^{-6}$ and

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[16] H. M. McConnell, *J. Chem. Phys.*, 1957, **27**, 226.

$-170 \times 10^{-6}$ c.g.s.u. from the shifts of the As–$CH_2$– and As–$(CH_3)_2$ resonances, respectively. These and the corresponding values for molybdenum ($-37 \times 10^{-6}$ and $-188 \times 10^{-6}$ c.g.s.u.) and for tungsten ($-40 \times 10^{-6}$ and $-270 \times 10^{-6}$ c.g.s.u.) may be rationalised in terms of the differential effects of the carbonyl groups. The diamagnetic anisotropy of carbon monoxide is unknown. Qualitatively, however, the carbonyl groups will deshield protons in a cone of revolution perpendicular to their axes and models show that the As–$(CH_3)_2$ protons lie 4·4 Å from the centre of a carbonyl group and are an angle of 18° from the normal to its axis. For the As–$CH_2$– protons, the corresponding values at 6·2 Å and 44°. Hence the predicted ratio of the shifts due to the carbonyl group $\sigma_{av}(As(CH_3)_2)/\sigma_{av}(As{-}CH_2{-}) =$ 9·3. It seems, therefore, that this is the reason for the large values of $(\chi_{\parallel} - \chi_{\perp})$ obtained above for the As–$(CH_3)_2$ protons.

The proton resonance spectra of $W(CO)_4$(*v*-Triars) and $Re(CO)_3$(*v*-Triars)Cl, in which the ligand is behaving as a bidentate, are shown in Figure 2, and clearly illustrate the unco-ordinated –$As(CH_3)_2$ group. Further, the existence of two isomeric forms of the rhenium(I) compound are indicated.

## EXPERIMENTAL

*Tricarbonyltris*-1,1,1-(*dimethylarsinomethyl*)*ethanechromium*(0).— Hexacarbonylchromium (1·5 g.) and the triarsine (2·6 g.) were refluxed in mesitylene (8 ml.) under nitrogen for 4 hr. On cooling, mesitylene and excess of hexacarbonyl were removed by warming to 70° *in vacuo*. The crude product in acetone (150 ml.) was filtered through alumina. After partial removal of the solvent under reduced pressure, the yellow product (2·7 g.) was completely crystallised by addition of light petroleum, collected, and dried *in vacuo* (Found: C, 33·3; H, 5·2; As, 43·5. $C_{14}H_{27}As_3CrO_3$ requires C, 32·3; H, 5·2; As, 43·2%). The *compound* is soluble in acetone, chloroform, and benzene, but only slightly soluble in alcohol, ether, and light petroleum. The molybdenum and tungsten compounds are progressively less soluble. All the compounds are stable in the solid state and moderately stable in solution. The molybdenum compound decomposes rapidly in chloroform.

*Tricarbonyltris*-1,1,1-(*dimethylarsinomethyl*)*ethanemolybdenum*(0).— Hexacarbonylmolybdenum (5·4 g.) and the triarsine (7·8 g.) were refluxed in *o*-xylene (10 ml.) under nitrogen for 3 hr. Subsequent treatment similar to that outlined above gave the colourless product (6·9 g.) (Found: C, 29·8; H, 5·1; As, 38·9; $C_{14}H_{27}As_3MoO_3$ requires C, 29·8; H, 4·8; As, 39·8%).

*Tricarbonyltris*-1,1,1-(*dimethylarsinomethyl*)*ethanetungsten*(0).—Hexacarbonyltungsten (12 g.) and the triarsine (13 g.) were refluxed in mesitylene (20 ml.) under nitrogen for 6 hr. Removal of mesitylene and excess of hexacarbonyl as above leaves a residue of the compound and $W(CO)_4$(*v*-Triars). Extraction with hot methanol (2 × 50 ml.) removed the tetracarbonyl and the *compound* (6·6 g.) was recrystallised from acetone–light petroleum, and dried *in vacuo* (Found: C, 25·9; H, 4·5; As, 34·3. $C_{14}H_{27}As_3O_3W$ requires C, 25·8; H, 4·2; As, 34·5%).

*Tetracarbonyltris*-1,1,1-(*dimethylarsinomethyl*)*ethanetungsten*(0).—Evaporation of the methanol extract from the preceding preparation at reduced pressure yielded the product (7·9 g.) which was recrystallised from methanol, and dried *in vacuo* (Found: C, 27·0; H, 4·0; As, 32·6. $C_{15}H_{27}As_3O_4W$ requires C, 26·5; H, 4·0; As, 33·0%). The *compound* is readily soluble in all organic solvents. It was converted into the tricarbonyl complex as follows: $W(CO)_4$(*v*-Triars) (5·5 g.) was heated at 200° for 40 min. under nitrogen. Gas evolution commenced at 180° and after 15 min. the mixture had set solid. On cooling, the crude crystals were titurated with methanol (20 ml.) and recrystallised from acetone–light petroleum. The white crystals (4·1 g.) were collected, washed with light petroleum, and dried *in vacuo*.

*Tetracarbonyl*-1-*trimethylarsinomethylbis*-1,1-(*dimethylarsinomethyl*)*ethanetungsten*(0) *Iodide*.— $W(CO)_4$(*v*-Triars) (0·1 g.) was refluxed in methanol (3 ml.) with excess of methyl iodide for 1 hr. Addition of ether yielded white crystals (0·1 g.) which were washed with ethanol–ether and dried *in vacuo* (Found: C, 23·5; H, 3·9; As, 27·2. $C_{16}H_{30}As_3O_4W$ requires C, 23·4; H, 3·7; As, 27·3%). The stable *compound* is water-soluble.

*Tricarbonyltris*-1,1,1-(*dimethylarsinomethyl*)*ethanemanganese*(I) *Perchlorate*.—Tricarbonylmesitylenemanganese(I) perchlorate (3·45 g.) and the triarsine (3·9 g.) were refluxed in cyclohexanone (35 ml.) under nitrogen for 90 min. The product crystallised on cooling by the addition of ether (40 ml.). Recrystallisation from acetone–ether gave pale cream crystals (3·7 g.), which were collected, washed with chloroform, and dried *in vacuo* (Found: C, 26·7; H, 4·3; As, 35·8; Cl, 5·3. $C_{14}H_{27}As_3ClMnO_7$ requires C, 27·0; H, 4·4; As, 36·1; Cl, 5·7%). The stable *compound* is soluble in acetone and alcohol, but insoluble in ether and chloroform.

*Hexacarbonylrhenium*(I) *Perchlorate.—Method* 1. Chloropentacarbonylrhenium (3·6 g.) was ground with anhydrous aluminium chloride (3·0 g.) and carbonylated at 90 atm. in a small (150 ml.) bomb. After heating for 50 hr. at 90°, the product was hydrolysed with ice–water (20 ml.) and filtered. An excess of 60% perchloric acid was added to crystallise the *product* (3·6 g.) which was collected, washed with water–methanol and ether, and dried *in vacuo* (Found: C, 15·8; Cl, 7·8. $C_6ClO_{10}Re$ requires C, 15·9; Cl, 7·8%).

*Method* 2.—Chloropentacarbonylrhenium (2·7 g.), mesitylene (10 ml.), and anhydrous aluminium chloride (1·0 g.) were heated in ligroin at 95° for 1 hr. The mixture was cooled, treated with ice–water (50 ml.), and filtered. The dimer $[Re(CO)_4Cl]_2$ is the chief product collected. To the aqueous phase of the filtrate was added excess of perchloric acid (60%) and the white crystals (0·43 g.) which precipitated were collected, recrystallised from ethanol, and dried *in vacuo* (Found: C, 16·3; Cl, 8·3%).

*Tricarbonyltris*-1,1,1-(*dimethylarsinomethyl*)*ethanerhenium*(I) *Perchlorate.*—Hexacarbonylrhenium perchlorate (2·1 g.) and the triarsine (1·9 g.) were heated in boiling cyclohexanone (20 ml.) under nitrogen for 60 min. Gas evolution commences at about 115° and ceases after 20 min. The product was crystallised on cooling by the addition of ether (60 ml.). Recrystallisation from acetone–ether gave colourless *crystals* (1·5 g.), which were collected, washed with chloroform, and dried *in vacuo* (Found: C, 22·2; H, 3·6; As, 29·7; Cl, 4·9. $C_{14}H_{27}As_3ClO_7Re$ requires C, 22·3; H, 3·6; As, 29·8; Cl, 4·7%). The physical properties resemble those of the analogous manganese compound.

*Tricarbonyltris*-1,1,1-(*dimethylarsinomethyl*)*ethanerhenium*(I) *Tetraphenylborate.*—Excess of solid sodium tetraphenylborate was added to a saturated solution of $[Re(CO)_3(v\text{-Triars})]ClO_4$ in ethanol. Water was added to precipitate completely the product and to remove sodium salts on filtration. After drying (0·1 mm./$P_2O_5$) thd pure *product* was obtained as white plates on recrystallisation from acetone–ether (Found: C, 46·8; H, 4·9; As, 23·7. $C_{38}H_{14}BAs_3O_3Re$ requires C, 46·9; H, 4·9; As, 23·1%).

*Chlorotricarbonyltris*-1,1,1-(*dimethylarsinomethyl*)*ethanerhenium*(I).— Chloropentacarbonylrhenium (1·05 g.) and the triarsine (1·3 g.) were heated in boiling xylene (10 ml.) under nitrogen for 1 hr. Removal of xylene (80°/20 mm.) left an oil which was allowed to stand overnight at 0°. The paste that developed was triturated with light petroleum, recrystallised from ethanol, washed with ether, and dried *in vacuo* (Found: C, 24·3; H, 4·1; As, 32·4; Cl, 4·9. $C_{14}H_{27}AsClO_3Re$ requires C, 24·4; H, 4·0; As, 32·6; Cl, 5·1%). The *compound* is soluble in all organic solvents, but insoluble in water.

*Infrared Spectra.*—These were recorded on a Grubb–Parsons double-beam grating instrument type GS2A, and on a Perkin-Elmer 337 spectrometer.

*Nuclear Magnetic Resonance Spectra.*—Spectra of 0·1—0·2M solutions were recorded using a Perkin-Elmer 60 megacycle/sec. instrument.

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