88. *Carbonyldi(tertiary arsine) Complexes of Rhenium.*

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The halogenocarbonyls of rhenium, Re(CO)$_5$X, react with *o*-phenylenebisdimethylarsine (Diars) in boiling ethanol to yield the complexes Re(CO)$_3$(Diars)X, which react with more ligand in sealed tubes at 270° to yield the bisdiarsine derivatives Re(CO)(Diars)$_2$X. Chlorine and bromine oxidise the monodiarsine compounds to produce the complexes of rhenium(IV) and rhenium(V), Re(Diars)Cl$_4$, Re(Diars)Br$_4$, and ReO(Diars)Cl$_3$. Seven-co-ordinate complexes of rhenium(III), [Re(CO)(Diars)$_2$X$_2$]X$_3$ (X = Br or I), may be derived also from the bisdiarsinehalogenocarbonyls. The perchlorate [Re(CO)(Diars)$_2$I$_2$]ClO$_4$ has been isolated from reaction of the tri-iodide complex with lithium perchlorate in ethanol.

PREVIOUS work[1] on the halogen oxidation of di(tertiaryarsine)-substituted Group VI carbonyls illustrated the tendency of the d^4 metal atoms chromium(II), molybdenum(II), and tungsten(II) to form complexes in which the metal atom has a co-ordination number of seven, *e.g.*, in [Cr(CO)$_2$(Diars)$_2$I]I, Mo(CO)$_3$(Diars)I$_2$, and [W(CO)$_4$(Diars)I]I (Diars = *o*-phenylenebisdimethylarsine). Isoelectronic with these d^4 metals are vanadium(I), niobium(I), tantalum(I), manganese(III), technetium(III), and rhenium(III), and this Paper reports the first stage in the exploration of the possibility of seven-co-ordination in these other systems.

From the halogenocarbonyls of rhenium, Re(CO)$_5$X, two carbonyl groups are known to be replaced readily,[2] and reaction with the diarsine in boiling ethanol produces the substituted derivatives Re(CO)$_3$(Diars)X, analogous to the manganese complexes.[3] Their physical properties (see Table) are consistent with their formulation as octahedral derivatives of rhenium(I), in that they are diamagnetic, non-conductors in nitrobenzene, and monomeric in benzene. Bisdiarsine derivatives, Re(CO)(Diars)$_2$X (see Table), are formed similarly by treatment of the complexes Re(CO)$_3$(Diars)X with more of the diarsine in sealed tubes at 270°. The replacement of four carbonyl groups in the Group VII halogenocarbonyls is unusual. It has been shown [4] that phenyl isocyanide can replace consecutively all five carbonyl groups of the bromocarbonyl, Mn(CO)$_5$Br; otherwise, only complexes containing a minimum of three carbonyl groups have been prepared. Indeed, reaction of

Halogenocarbonyldiarsine complexes.

Complex *	Colour	Λ_m §	concn. ($\times 10^3$M)	Mol. wt.¶ Found	Mol. wt.¶ Calc.	i.r. active C–O stretching vibrations in Nujol or CHCl$_3$
Re(CO)$_3$(Diars)I	White	0·02	1·26	698	683	2030, 1968, 1905
Re(CO)$_3$(Diars)Br	White	0·03	0·98	610	636	2040, 1960, 1912
Re(CO)$_3$(Diars)Cl	White	0·08	1·80	580	591	2037, 1950, 1910
Re(CO)(Diars)$_2$I	White		Insoluble			1800 (Nujol)
Re(CO)(Diars)$_2$Br	White		Insoluble			1792 (Nujol)
Re(CO)(Diars)$_2$Cl	White		Insoluble			1790 (Nujol)
Re(Diars)Br$_4$ †	Deep red	0·07	1·04	785	792	—
Re(Diars)Cl$_4$ ‡	Yellow	0·9	0·93	608	614	—
Re(Diars)OCl$_3$	Green	0·05	1·10	593	594	—
[Re(CO)(Diars)$_2$I$_2$]I$_3$	Black	26·7	0·77	Insoluble		1890 (Nujol)
[Re(CO)(Diars)$_2$I$_2$]ClO$_4$	Mauve	24·0	1·02	Insoluble		1892(Nujol)
[Re(CO)(Diars)$_2$Br$_2$]Br$_3$	Deep pink	26·9	1·29	Insoluble		1905 (Nujol)

* All diamagnetic in the solid state at 20°, except where marked † (μ_{eff} = 3·46 B.M.) and ‡ (μ_{eff} = 3·42 B.M.). § In nitrobenzene. ¶ Osmometrically in benzene or chloroform.

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[1] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1806; Lewis, Nyholm, Pande, and Stiddard, *J.*, 1963, 3600; Lewis, Nyholm, Pande, Sandhu, and Stiddard, *J.*, 1964, 3009.

[2] Hieber and Fuchs, *Z. anorg. Chem.*, 1941, **248**, 269; Abel and Wilkinson, *J.*, 1959, 1501.

[3] Osborne and Stiddard, *J.*, 1962, 4715.

[4] Joshi, Pauson, and Stubbs, *J. Organometallic Chem.*, 1963, **1**, 51.

the di(tertiary phosphine) 1,2-bisdiphenylphosphinoethane (Diphos) with the halogenocarbonyls of manganese yields the salt-like complex $[\mathrm{Mn(CO)_2(Diphos)_2}]\mathrm{X}$ rather than the monocarbonylbisdiphosphine derivative.[5]

Examination of the halogen oxidation of the monodiarsine complexes $\mathrm{Re(CO)_3(Diars)X}$ has led to the isolation of two types of product. Although iodine does not appear to react, chlorine and bromine oxidise their corresponding halogenocarbonyls in chloroform to yield the octahedral rhenium(IV) complexes $\mathrm{Re(Diars)Cl_4}$ and $\mathrm{Re(Diars)Br_4}$, which are monomeric in chloroform, non-conductors in nitrobenzene, and have magnetic moments, measured in the solid state at 20°, similar to those of the rhenium complex anions $\mathrm{ReX_6}^{2-}$.[6] Chlorine oxidises the complex $\mathrm{Re(CO)_3(Diars)Cl}$ in boiling ethanol to the rhenium(V) oxo-complex $\mathrm{ReO(Diars)Cl_3}$, similar to the complexes of the type $\mathrm{ReOL_2X_3}$.[7] In the infrared spectrum of the solid compound, two bands, at 991 and 970 cm.$^{-1}$, may be ascribed to Re=O stretching. The appearance of two bands may result from the existence of two isomers, or from the existence of oxygen atoms with different environments in the crystal. In dichloromethane, only one Re=O stretching vibration is observed, at 983 cm.$^{-1}$. The diamagnetism of the d^2-complex is explained readily using a simple model that assumes the Re–Cl and Re–As bonds to be equivalent (this is probably not a serious approximation, since π-bonding effects are likely to be axially directed). Under the influence of the C_{4v} ligand-field, a pair of d-orbitals (e symmetry) can overlap with filled p-orbitals (e symmetry) of the oxygen atom, thus destabilising the former orbitals. This leaves the non-bonding b_2-orbital of low energy to be filled by the two electrons, leading to a diamagnetic complex. In valence-bond terminology, the Re–O linkage is described as $\mathrm{Re}\underset{\longleftarrow}{=}\mathrm{O}$.

In contrast to the behaviour of the monodiarsine complexes, the compounds $\mathrm{Re(CO)(Diars)_2Br}$ and $\mathrm{Re(CO)(Diars)_2I}$ are oxidised smoothly with bromine and iodine, respectively, to seven-co-ordinate complexes of the type $[\mathrm{Re(CO)(Diars)_2X_2}]\mathrm{X_3}$, which are diamagnetic and behave as typical 1 : 1 electrolytes in nitrobenzene. The presence of the large anion may be necessary to stabilise the seven-co-ordinate species, and the non-existence of the $\mathrm{Cl_3}^-$ anion may be the reason for our failure to synthesise the corresponding chloro-complex. The tri-iodide has been replaced by perchlorate, however, by shaking a suspension of the complex $[\mathrm{Re(CO)(Diars)_2I_2}]\mathrm{I_3}$ in a saturated solution of lithium perchlorate in ethanol. Anion-exchange takes place quantitatively as shown by titration of the $\mathrm{I_3}^-$ ion with sodium thiosulphate.

EXPERIMENTAL

Halogenocarbonylrheniums.—The previously described preparation [8] involved high-pressure carbonylation of the complexes $\mathrm{K_2ReX_6}$. We have used different conditions, and typical experiments are as follows:

$$\mathrm{K_2ReI_6}\ (4\ \text{g.}) + \mathrm{CO}\ (45\ \text{atm.}) + \mathrm{Cu}\ (2\ \text{g.}) \xrightarrow[150^\circ]{6\ \text{hr.}} \mathrm{Re(CO)_5I}\quad (1{\cdot}5\ \text{g.})$$

$$\mathrm{K_2ReBr_6}\ (5\ \text{g.}) + \mathrm{CO}\ (60\ \text{atm.}) + \mathrm{Cu}\ (5\ \text{g.}) \xrightarrow[150^\circ]{8\ \text{hr.}} \mathrm{Re(CO)_5Br}\quad (1{\cdot}7\ \text{g.})$$

$$\mathrm{K_2ReCl_6}\ (4\ \text{g.}) + \mathrm{CO}\ (80\ \text{atm.}) + \mathrm{Cu}\ (6\ \text{g.}) \xrightarrow[200^\circ]{7\ \text{hr.}} \mathrm{Re(CO)_5Cl}\quad (2{\cdot}7\ \text{g.})$$

*Iodotricarbonyl-*o*-phenylenebisdimethylarsinerhenium*(I).—The iodocarbonyl (0·31 g.) and the diarsine (0·7 g.) were heated in boiling ethanol (10 ml.) for 1 hr. The white crystals which separated on cooling were recrystallised from ethanol, to give the *product* (0·4 g.) which was dried *in vacuo* (Found: C, 23·2; H, 2·4; As, 22·4; I, 18·5; Re, 27·0. $\mathrm{C_{13}H_{16}As_2IO_3Re}$ requires C, 22·9; H, 2·3; As, 22·0; I, 18·6; Re, 27·15%). The compound, together with the corresponding bromide and chloride, is stable in air and soluble in most polar and non-polar solvents.

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[5] Osborne and Stiddard, unpublished results.

[6] Figgis, Lewis, and Mabbs, *J.*, 1961, 3138.

[7] Chatt, Garforth, Johnson, and Rowe, *J.*, 1964, 1012; Johnson, Lock, and Wilkinson, *J.*, 1964, 1054.

[8] Hieber, Schuh, and Fuchs, *Z. anorg. Chem.*, 1941, **248**, 243.

Bromotricarbonyl-o-*phenylenebisdimethylarsinerhenium*(I).—The bromocarbonyl (0·3 g.) and the diarsine (0·3 g.) were heated in boiling ethanol (7 ml.) for 1 hr. The *product* (0·4 g.) was obtained as above (Found: C, 25·2; H, 2·75; As, 23·9; Br, 12·6; Re, 29·7. $C_{13}H_{16}As_2BrO_3Re$ requires C, 24·6; H, 2·5; As, 23·8; Br, 12·6; Re, 29·25%).

Chlorotricarbonyl-o-*phenylenebisdimethylarsinerhenium*(I).—The chlorocarbonyl (0·3 g.) and the diarsine (0·3 g.) were heated in boiling ethanol (5 ml.) for 1 hr. The *product* (0·35 g.) was obtained as above (Found: C, 26·4; H, 2·8; As, 25·1; Cl, 6·2; Re, 31·1. $C_{13}H_{16}As_2ClO_3Re$ requires C, 26·4; H, 2·7; As, 25·4; Cl, 6·2; Re, 31·5%).

Iodomonocarbonylbis-(o-*phenylenebisdimethylarsine*)*rhenium*(I).—The complex $Re(CO)_3(Diars)I$ (0·25 g.) and the diarsine (0·6 g.) were sealed in an evacuated tube and heated for 16 hr. at 270°. The white *product* (0·15 g.) was washed in hot ethanol and dried *in vacuo* (Found: C, 27·7; H, 3·8; As, 32·6; I, 13·85; Re, 20·0. $C_{21}H_{32}As_4IORe$ requires C, 27·6; H, 3·5; As, 32·8; I, 13·9; Re, 20·4%). The compound is stable in air and virtually insoluble in all organic solvents. The corresponding bromide and chloride show similar proproperties.

Bromomonocarbonylbis-(o-*phenylenebisdimethylarsine*)*rhenium*(I).—The complex $Re(CO)_3(Diars)Br$ (0·35 g.) and the diarsine (0·4 g.), treated as before, gave the *product* (0·3 g.) (Found: C, 29·2; H, 3·9; As, 34·5; Br, 9·2; Re, 21·7. $C_{21}H_{32}As_4BrORe$ requires C, 29·1; H, 3·7; As, 34·7; Br, 9·25; Re, 21·5%).

Chloromonocarbonylbis-(o-*phenylenebisdimethylarsine*)*rhenium*(I).—The complex $Re(CO)_3(Diars)Cl$ (0·35 g.) and the diarsine (0·5 g.) were heated as before at 270° for 14 hr. The *product* (0·35 g.) was washed with hot ethanol and dried *in vacuo* (Found: C, 30·7; H, 3·9; As, 36·3; Cl, 4·3; Re, 22·3. $C_{21}H_{32}As_4ClORe$ requires C, 30·7; H, 3·9; As, 36·5; Cl, 4·3; Re, 22·6%).

Tetrachloro-o-*phenylenebisdimethylarsinerhenium*(IV).—Through a hot solution of the complex $Re(CO)_3(Diars)Cl$ in chloroform (25 ml.), chlorine was passed slowly for 1 hr. The green solution was filtered hot, and, on cooling mustard-yellow crystals separated. Addition of light petroleum produced further crystals. Recrystallisation from chloroform–light petroleum yielded the *product* (0·26 g.) which was dried *in vacuo* (Found: C, 19·6; H, 2·9; As, 24·3; Cl, 23·1; Re, 30·1. $C_{10}H_{16}As_2Cl_4Re$ requires C, 19·6; H, 2·6; As, 24·4; Cl, 23·1; Re, 30·4%). The compound is soluble in benzene, chloroform, and nitrobenzene, but insoluble in light petroleum.

Tetrabromo-o-*phenylenedimethylarsinerhenium*(IV).—Excess of bromine was added to a solution of the complex $Re(CO)_3(Diars)Br$ (0·25 g.) in chloroform (10 ml.). The solution was heated to boiling and set aside overnight at 0°. The rich red *crystals* (0·22 g.) which formed were filtered off, washed with light petroleum, and dried *in vacuo* (Found: C, 15·1; H, 2·5; As, 18·5; Br, 40·2; Re, 23·2. $C_{10}H_{16}As_2Br_4Re$ requires C, 15·2; H, 2·0; As, 18·9; Br, 40·4; Re, 23·3%). The physical properties are similar to those of the analogous chloro-complex.

Oxotrichloro-o-*phenylenebisdimethylarsinerhenium*(V).—Through a hot solution of the complex $Re(CO)_3(Diars)Cl$ (0·3 g.) in ethanol (30 ml.), chlorine was passed slowly for 1 hr. The green crystals, which separated on cooling, were recrystallised from chloroform–light petroleum, to yield the *product* (0·25 g.) which was dried *in vacuo* (Found: C, 20·2; H, 2·7; As, 25·2; Cl, 18·25; Re, 31·0. $C_{10}H_{16}As_2Cl_3ORe$ requires C, 20·2; H, 2·7; As, 25·3; Cl, 18·0; Re, 31·3%). The complex is soluble in most organic solvents, but insoluble in light petroleum.

Di-iodomonocarbonylbis-(o-*phenylenebisdimethylarsine*)*rhenium*(III) *Tri-iodide*.—A mixture of the complex $Re(CO)(Diars)_2I$ (0·3 g.) and iodine (0·25 g.) in chloroform (35 ml.) was warmed gently. The black *crystals* (0·44 g.), which formed immediately, were filtered off, washed with chloroform, and dried *in vacuo* (Found: C, 17·6; H, 2·7; As, 20·6; I, 44·8; Re, 12·8. $C_{21}H_{32}As_4I_5ORe$ requires C, 17·6; H, 2·3; As, 21·1; I, 44·7; Re, 13·15%). The compound is stable in air, and insoluble in polar and non-polar solvents with the exception of nitrobenzene in which it has a low solubility.

Di-iodomonocarbonylbis-(o-*phenylenebisdimethylarsine*)*rhenium*(III) *Perchlorate*.—The complex $[Re(CO)(Diars)_2I_2]I_3$ (0·07 g.) was shaken in a saturated solution of lithium perchlorate in ethanol (20 ml.). The dark purple *product* (0·05 g.) was filtered off, washed with ether (10 ml.), and dried *in vacuo* (Found: C, 21·9; H, 2·5; I, 22·5. $C_{21}H_{32}As_4ClI_2O_5Re$ requires C, 22·1; H, 2·8; I, 22·3%). The compound is more soluble than the corresponding tri-iodide, but decomposes rapidly in solution.

Dibromomonocarbonylbis-(o-*phenylenebisdimethylarsine*)*rhenium*(III) *Tribromide*.—A suspension of the complex $Re(CO)(Diars)_2Br$ (0·17 g.) in chloroform (10 ml.) was treated with bromine (0·06 g.) in carbon tetrachloride (10 ml.). The deep pink *product* (0·25 g.) was filtered off, washed with chloroform (10 ml.), and dried *in vacuo* (Found: C, 21·3; H, 2·8; As, 24·6; Br, 33·5; Re, 15·2. $C_{21}H_{32}As_4Br_5ORe$ requires C, 21·3; H, 2·8; As, 24·6; Br, 33·7; Re, 15·7%). The physical properties are very similar to those of the tri-iodide complex.

Rhenium Analyses.—The compound to be analysed (0·05—0·1 g.) was fused in a nickel crucible with sodium carbonate (0·5 g.), sodium hydroxide (0·2 g.), and sodium peroxide (0·2 g.). The fused mixture was dissolved in water, and, after filtration, the per-rhenate content of the solution was measured colorimetrically.[9]

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[9] Martin, Meloche, and Webb, *Ind. Eng. Chem. Analyt. Edn.*, 1957, **29**, 527.