358. *Substituted Group VI Carbonyls. Part I. Ditertiary Arsine Carbonyls of Chromium, Molybdenum, and Tungsten.*

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Heating the hexacarbonyl of chromium, molybdenum, or tungsten and the ditertiary arsine, *o*-phenylenebisdimethylarsine, *in vacuo* gives first, the products $[\mathrm{MDiarsine(CO)_4}]^0$. Further heating at a higher temperature yields the bisdiarsine derivatives $[\mathrm{M(Diarsine)_2(CO)_2}]^0$. The physical properties of the products have been investigated: all these products are diamagnetic, monomeric, and non-electrolytes. Infrared spectra indicate that the two carbonyl groups in the compounds $[\mathrm{M(Diarsine)_2(CO)_2}]^0$ are *cis* to one another. The dipole moment of $[\mathrm{Mo(Diarsine)_2(CO)_2}]^0$ (6·5 D) supports the assignment of a *cis*-dicarbonyl octahedral configuration. These are the first tetrasubstituted Group VI carbonyls obtained by direct replacement of carbonyl groups from the hexacarbonyl.

This paper is the first of a series dealing with Group VI metal complexes containing as ligands carbonyl groups, ditertiary arsines, and their halogen oxidation products. We discuss the nature and structure of the products obtained when the ditertiary arsine reacts with the metal carbonyls. Part II deals with the action of halogens on the molybdenum carbonyl arsines, and Parts III and IV with the corresponding derivatives of tungsten and chromium.

It has been shown previously that one molecule of *o*-phenylenebisdimethylarsine readily replaces two carbon monoxide groups from nickel or iron carbonyls, products of the type NiDiarsine$(CO)_2$,[1] Ni$(Diarsine)_2$,[2,3] FeDiarsine$(CO)_3$,[2] and Fe$(Diarsine)_2$(CO) [2] having been isolated. A considerable number of monodentate ligands such as tertiary phosphines, tertiary arsines, and isonitriles displace carbon monoxide from nickel or iron carbonyl but replacement of several carbon monoxide groups from the Group VI carbonyls is much more difficult.* Indeed, before these investigations a maximum of three carbonyl groups per hexacarbonyl molecule had been directly replaced.

TABLE 1. *Previously reported substituted derivatives of Group VI carbonyls (obtained by direct replacement *).*

No. of CO replaced	Metal	Nature of ligand X
1, forming $M(CO)_5X$	Cr	–PPh_3, $AsPh_3$, $SbPh_3$, $P(CH_2{\cdot}CH_2{\cdot}CN)_3$,[a] CNR [b]
	Mo	–PPh_3,[a] CNR [b]
	W	–PPh_3,[a] CNR [b]
2, forming $M(CO)_4X_n$	Cr	–C_5H_5N, *o*-phen,[c] PPh_3 [h]
	Mo	–C_5H_5N, *o*-phen,[c] PPh_3 [h]
	W	–C_5H_5N, *o*-phen, 2,2′-bipy,[d] PPh_3 [h]
3, forming $M(CO)_3X_n$	Cr	–RNC, NH_3, H_2O,[e] dien [g]
	Mo	–C_5H_5N, *o*-phen–C_5H_5N,† [e] triarsine,[f] dien,[g] PPh_3, $AsPh_3$, $SbPh_3$, halides [g]
	W	–C_5H_5N, *o*-phen–C_5H_5N,† [e] triarsine,[f] dien [g]

* Compounds of the type $M(RNC)_6$ have been obtained indirectly. They represent examples of fully substituted carbonyls but have not been prepared by direct replacement. † Mixed ligands.

[a] Matthews, Magee, and Wotiz, *J. Amer. Chem. Soc.*, 1959, **81**, 2273. [b] Hieber and von Pigenot, *Chem. Ber.*, 1956, **89**, 193, 610. [c] Phenanthroline, Hieber and Muhlbauer, *Z. anorg. Chem.*, 1935, **221**, 349. [d] 2,2′-Bipyridyl, Hieber, and Romberg, *Z. anorg. Chem.*, 1935, **221**, 321. [e] Hieber, Abeck, and Platzer, *Z. anorg. Chem.*, 1955, **280**, 241. [f] $Me{\cdot}As(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}AsMe_2)_2$, Parish, Thesis, London, 1958. [g] Ethylenediamine, Abel, Bennett, and Wilkinson, *J.*, 959,1 2323. [h] Hieber and Peterhans, *Z. Naturforsch.*, 1959, **14**b, 462.

TABLE 2. *Properties of Complexes.*

Compound (D = Diarsine)	Colour and m. p.	Mol. condy. (10^{-3}M in nitrobenzene) (ohm^{-1})	C–O stretching frequency (cm.$^{-1}$) in $CHCl_3$	Molecular weight	
				cryoscop. in C_6H_6	calc.
$Cr(CO)_4D$	Very pale yellow, 170°	0·8	2012, 1922 1898	434 in 0·54% soln.	450
$Cr(CO)_2D_2$.........	Yellow, 226°	0·7	1845, 1771	654 in 0·77% soln.	680
$Mo(CO)_4D$	White, 158°	1·0	2026,* 1938 1923, 1914	478 in 0·52% soln.	494
$Mo(CO)_2D_2$	Pale yellow, 231°	0·9	1859, 1786	703 in 0·56% soln.	724
$W(CO)_4D$	Pale yellow, 168°	0·5	2016, 1923 1905, 1885	563 in 0·50% soln.	582
$W(CO)_2D_2$.........	Bright yellow, 237°	0·7	1850, 1774	823 in 0·69% soln.	812

* In cyclohexane. All bands quoted are strong. All of the above compounds are diamagnetic in the solid state at 20°.

The monodiarsine complexes are prepared by heating together the appropriate hexacarbonyl with excess of the diarsine in a sealed tube at 160—180° for about six hours. A pressure of carbon monoxide builds up in the reaction vessel (about 2 atm.) and this affects the amount of conversion. Unfortunately, it is not practicable to heat the reactants in such a manner as to drive off the carbon monoxide as it is formed (*e.g.*, under reflux with an inert gas) because the hexacarbonyl sublimes away as well. These monodiarsine derivatives have the properties shown in Table 2; they are clearly octahedral derivatives

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* We refer here to σ-bonded complexes only, not to the π-type such as the cyclopentadienyls.

[1] Nyholm, *J.*, 1951, 2906.

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

[3] Chatt and Hart, *Chem. and Ind.*, 1958, 1474.

of the zerovalent metal, being monomeric in benzene and non-electrolytes in nitrobenzene. The bisdiarsine derivatives require longer heating at a higher temperature with occasional removal of the accumulated carbon monoxide. This procedure is specially important to obtain the bisdiarsine chromium compound since the replacement of the second chelate group is much more difficult than with the corresponding molybdenum and tungsten compounds.

The infrared spectra of these complexes will be discussed later in greater detail by Mr. C. Barraclough and Dr. J. Lewis. However, the C–O stretching frequencies shown in Table 2 are in accord with predictions for a simple chelate octahedral structure in the case of the MDiarsine$(CO)_4$ complexes and with a *cis*-dicarbonyl arrangement in the case of the bisdiarsine compounds. The latter has been confirmed by measurement of the electric dipole moment, which gave a value of 6·5 D. It is of interest that, if carbonyl is assumed to have a greater capacity for double-bonding with the metal than the diarsine has, then one would expect a *cis*-arrangement of the two carbonyl groups for theoretical reasons based on the symmetry of the *dε*-orbitals involved in double bonding.[4]

EXPERIMENTAL

Mono-o-*phenylenebisdimethylarsinetetracarbonylchromium*(0).—Hexacarbonyl chromium (0·6 g.) and the diarsine (1·4 g.) were heated together in an evacuated tube (internal vol. ~100 ml.) for 6 hr. at 180°. Extraction with benzene and recrystallisation of the complex from ether yielded pale yellow *complex*, CrDiarsine$(CO)_4$ (0·8 g.) which, dried *in vacuo*, had m. p. (*in vacuo*) 170° (Found: C, 37·4; H, 3·7; As, 33·3; Cr, 11·6. $C_{14}H_{16}O_4As_2Cr$ requires C, 37·4; H, 3·6; As, 33·3; Cr, 11·6%). The compound decomposes slowly in air to a green residue; it is readily soluble in non-polar organic solvents and moderately soluble in alcohol and nitrobenzene.

Bis-o-*phenylenebisdimethylarsinedicarbonylchromium*(0).—The monodiarsine complex (0·5 g.) was heated with the diarsine (1·5 g.) for 6 hr. at 230°. The liberated carbon monoxide was pumped off, and heating continued for a further 3—6 hr. This procedure was repeated five times. The tube was then kept for 12 hr. at 20°, yellow crystals separating. The excess of diarsine was decanted and the crystals (0·1 g.) were washed several times with light petroleum and dried *in vacuo*, then having m. p. (*in vacuo*) 226° (Found: C, 38·7; H, 4·9; Cr, 7·7. $C_{22}H_{32}O_2As_4Cr$ requires C, 38·9; H, 4·8; Cr, 7·7%). The *compound*, which decomposes fairly rapidly in air, has solubilities similar to, but less than, those of the monodiarsine complex.

Mono-o-*phenylenebisdimethylarsinetetracarbonylmolybdenum*(0).—Hexacarbonyl molybdenum (0·5 g.) and diarsine (1·0 g.) were treated as above for 6 hr. at 150°. Extraction with benzene and recrystallisation of the *complex* from ether yielded white crystals (0·8 g.) which, dried *in vacuo*, had m. p. (*in vacuo*) 158° (Found: C, 34·0; H, 3·2; As, 29·8; Mo, 19·1. $C_{14}H_{16}O_4As_2Mo$ requires C, 34·0; H, 3·2; As, 30·3; Mo, 19·4%). The physical properties are very similar to those of the corresponding chromium compound.

Bis-o-*phenylenebisdimethylarsinedicarbonylmolybdenum*(0).—The preceding product (0·5 g.) and the diarsine (0·5 g.) were treated as above for 11 hr. at 200°. Extraction with, and recrystallisation from, benzene yielded yellow crystals (0·4 g.) of the *bisdiarsine complex* which, dried *in vacuo*, had m. p. (*in vacuo*) 231° (Found: C, 36·5; H, 4·4; Mo, 13·1. $C_{22}H_{32}O_2As_4Mo$ requires C, 36·5; H, 4·4; Mo, 13·2%). The physical properties of the compound are similar to those of the chromium analogue.

Mono-o-*phenylenebisdimethylarsinetetracarbonyltungsten*(0).—Hexacarbonyltungsten (0·7 g.) and the diarsine (1·0 g.) were caused to react as above for 6 hr. at 160°, and the product was extracted with benzene. Obtained from ether the pale yellow *complex* had m. p. (*in vacuo*) 186° (Found: C, 28·8; H, 2·8; As, 26·1; W, 31·3. $C_{14}H_{16}O_4As_4W$ requires C, 28·9; H, 2·8; As, 25·8; W, 31·7%). Its properties are very similar to those of the molybdenum analogue.

Bis-o-*phenylenebisdimethylarsinedicarbonyltungsten*(0).—The preceding complex (0·6 g.) and the diarsine (1·4 g.) were heated at 240° as above for 8 hr. After removal of the liberated carbon monoxide, heating was continued for a further 6 hr. and the procedure repeated twice more. Extraction with benzene yielded a mixture of mono- and bis-diarsine complex, the

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[4] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

latter being obtained pure by fractional crystallization from benzene–light petroleum. The yellow *bisdiarsine* complex melted (*in vacuo*) at 237° (Found: C, 32·6; H, 3·8; W, 22·3. $C_{22}H_{32}O_2As_4W$ requires C, 32·3; H, 4·0; W, 22·5%). The physical properties are very similar to those of molybdenum analogue.

Estimation of Chromium, Molybdenum, and Tungsten.—A known amount (0·1—0·2 g.) of the complex was carefully digested with a few drops of concentrated sulphuric acid in a weighed silica crucible over a low Bunsen flame. After removal of sulphur trioxide, the crucible was transferred to a muffle furnace. Complete conversion into the oxides Cr_2O_3, MoO_3, and WO_3 was ensured by ignition at 500°, 520°, and 750° respectively to constant weight.

Reproducibility was good (±0·2%) except when less than 0·1 g. of the complex was used. This ignition method gave very good agreement with a colorimetric determination of molybdenum.

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

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