910. *2,2′-Bipyridyl Derivatives of Group VI Carbonyls.*

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Reaction of 2,2′-bipyridyl with hexacarbonyl-chromium, -molybdenum, and -tungsten in an inert solvent at 120—130° produces compounds of the type $M(CO)_4(bipy)$. Further replacement of carbonyl groups seems impossible. The physical properties of these compounds have been investigated, and their reactions with halogens. Spectrophotometric titrations indicate that $Cr(CO)_4(bipy)$ reacts with three equivalents of iodine and one equivalent of bromine; $Mo(CO)_4(bipy)$ and $W(CO)_4(bipy)$ react with two equivalents of these halogens. Pure compounds $Mo(CO)_3(bipy)Br_2$, $W(CO)_3(bipy)I_2$, and $W(CO)_3(bipy)Br_2$ have been isolated, also a complex which is tentatively formulated $[Mo(CO)_3(bipy)I_2]_2$. All these oxidation products are considered to be seven-covalent derivatives of molybdenum(II) and tungsten(II).

ALTHOUGH 2,2′-bipyridyl (bipy) derivatives of carbonyl compounds of Group VI metals have been known for some time,[1] their physical properties do not appear to have been examined fully. Since several other supposed carbonyl-2,2′-bipyridyl complexes have been shown to be salt-like it seemed worthwhile to re-examine the Group VI compounds. Further, oxidation of these compounds has not been examined previously.

Complexes $M(CO)_4(bipy)$ are formed readily, with evolution of two mol. of carbon monoxide, when the metal carbonyl is refluxed with one equivalent of the ligand in toluene or xylene. These products are given in Table 1. They are obviously octahedral derivatives of the metals in their zerovalent states, being diamagnetic (d_ϵ^6) in the solid, and non-electrolytes in nitrobenzene and nitromethane. Their rather limited solubility prevented accurate determination of the molecular weights, but they are certainly monomeric in boiling benzene.

TABLE 1.

Carbonylbipyridyl complexes.*

Compound	Colour	Molar conductance (ohm^{-1} cm.^{2}) of 10^{-3}M-solutions in		C–O stretching frequencies (cm.$^{-1}$) in $CHCl_3$
		$PhNO_2$	$MeNO_2$	
$Cr(CO)_4(bipy)$ ...	Deep orange	0·030	0·62	2010m, 1908vs, 1888sh, 1833s
$Mo(CO)_4(bipy)$	Red	0·047	0·82	2014m, 1911vs, 1882sh, 1830s
$W(CO)_4(bipy)$ ...	Maroon	0·043	0·63	2008m, 1900vs, 1880sh, 1929s

* All are diamagnetic in the solid state at 20°.

Abel, Bennett, and Wilkinson [2] have recorded the spectrum of $Mo(CO)_4(bipy)$ without

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[1] Hieber and Muhlbaur, *Z. anorg. chem.*, 1935, **221**, 337; Hieber and Romberg, *ibid.*, p. 349.

[2] Abel, Bennett, and Wilkinson, *J.*, 1959, 2323.

comment and their values agree reaonably with ours. With C_{2v} symmetry, these compounds are expected to show four C–O stretching modes active in the infrared region.[3,4] Orgel[4] suggests that a pair of bands, one very strong and the other weak, separated by about 100—120 cm.$^{-1}$, and two bands of intermediate strength, would be expected. This simple analysis is in excellent agreement with experiment. For comparison with similar carbonyls, Orgel[5] suggests that the average frequency of the bands should be used rather than any individual member. Comparison of the analogous diphosphine,[3] diarsine,[6] and bipyridyl compounds shows the average C–O stretching frequencies to decrease in this order, *e.g.*, $Mo(CO)_4$(diphosphine), $Mo(CO)_4$(diarsine), and $Mo(CO)_4$(bipy) have average values of 1926, 1913, and 1908 cm.$^{-1}$, respectively, measured in 1,2-dichloroethane (diphosphine = 1,2-bisdiphenylphosphinoethane). This means, probably, that the π-character of the metal–carbon bond is greatest in the bipyridyl compounds, and possibly that this apparent increase in the availability of d_π-electrons indicates 2,2′-bipyridyl as having a lower capacity for π-bonding than ditertiary phosphines and arsines (the latter suggestion, however, neglects the effect of superior donor properties of nitrogen which should also enhance d_π-electron donation to CO).

It might be expected that further reaction of the bipyridyl with $M(CO)_4$(bipy) would lead to complexes $M(CO)_2(bipy)_2$. Attempts to prepare such compounds under reflux and in sealed tubes were unsuccessful. Also reaction of $Mo(CO)_3$(mesitylene) with an excess of bipyridyl led only to decomposition. It is presumed that the greater strength of the metal–carbon bonds in the mono-organic compounds than in the carbonyl-only complexes explains the reluctance of the former to undergo further reaction. On the other hand, a carbonyl group *cis* to the bipyridyl in the product $Mo(CO)_4$(bipy) is readily replaced by various ligands, to give compounds of the type $Mo(CO)_3$(bipy)(ligand); this behaviour is readily understood in terms of the differing strengths of M–C bonds in positions *cis* and *trans* to the bipyridyl and will be discussed in a later publication.

Initially, oxidation of the bipyridyl complexes was studied spectrophotometrically,[7] and results indicated that $Mo(CO)_4$(bipy) and $W(CO)_4$(bipy) react with two equivalents of iodine and bromine. The chromium compound, $Cr(CO)_4$(bipy), however, reacts with one equivalent of bromine and three equivalents of iodine. Oxidation to chromium(III) is not unexpected and, indeed, oxidation of the complex $Cr(CO)_4$(diarsine) produces only a tervalent complex.[8] The oxidation by bromine is not readily explained, but attack on the ligand is possible. Unfortunately, in neither case could a product be isolated when reactions were carried out on a preparative scale.

The complex $W(CO)_4$(bipy) reacted with iodine and bromine with release of one molecule of carbon monoxide, to give the tungsten(II) derivatives, $W(CO)_3(bipy)X_2$, whose properties are listed in Table 2. They are diamagnetic (d^4) non-electrolytes, unstable to light and air, and certainly similar to the seven-covalent diarsine complexes described previously.[7] Although the complexes $W(CO)_3(bipy)I_2$ and $W(CO)_3(bipy)Br_2$ show initial conductances in nitrobenzene and nitromethane expected of non-electrolytes, the values increase rapidly (especially in nitromethane), perhaps owing to establishment of the equilibrium

$$\mathrm{W(CO)_3(bipy)X_2} + \text{solvent} \rightleftharpoons \mathrm{W(CO)_3(bipy)(solvent)X^+} + \mathrm{X^-}$$

which is supported by the infrared spectrum of $W(CO)_3(bipy)Br_2$ in nitromethane where the solvent causes no significant shifts of the carbonyl frequencies (some shift might have been expected but, at least, disproportionation of the complex is excluded). Unfortunately, the compounds were too unstable in solution for molecular weights to be determined.

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[3] Chatt and Watson, *J.*, 1961, 4980.
[4] Orgel, *Inorg. Chem.*, 1962, **1**, 25.
[5] Orgel, personal communication.
[6] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1803.
[7] Nigam, Nyholm, and Stiddard, *J.*, 1960, 1806.
[8] Nigam, Nyholm, and Stiddard, unpublished work.

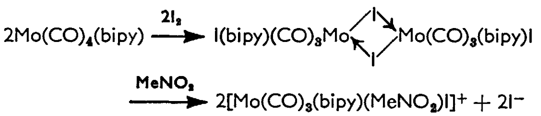
TABLE 2.

Halogenocarbonylbipyridyl complexes.*

Compound	Colour	Mole. conductance (ohm^{-1} cm.^{2}) of 10^{-3}M-solutions in		C–O stretching frequencies ‡ (cm.$^{-1}$) in	
		$PhNO_2$	$MeNO_2$	$CHCl_3$	$MeNO_2$
$[Mo(CO)_3(bipy)I_2]_2$	Orange-brown	0·36	2·5	2040s, 2018s, 1976, 1935, 1888w	2038, 1970, 1931
$Mo(CO)_3(bipy)Br_2$	Deep yellow	0·25	2·4	2056, 1987, 1930	
$W(CO)_3(bipy)I_2$	Orange	0·28	2·3	2023, 1952, 1910	
$W(CO)_3(bipy)Br_2$	Deep yellow	0·27	2·9	2037, 1959, 1908	2038, 1956, 1910

* All are diamagnetic in the solid state at 20°. † Extrapolated to zero time. ‡ CO bands are very strong unless indicated otherwise.

The complex $Mo(CO)_4$(bipy) reacts with bromine, to give a compound analogous to those just discussed and with very similar properties. However, oxidation by iodine results in a unique product which, although diamagnetic and a non-electrolyte, with empirical formula $Mo(CO)_3(bipy)I_2$, has infrared absorption in chloroform clearly indicating that it is not the simple seven-covalent type for which only three C–O stretching modes are to be expected. In nitromethane, on the other hand, a simple spectrum, very similar to those of the other halogen derivatives, is found. As a tentative explanation of these facts, it is suggested that the following reactions occur:



Acceptance of the bridged structure would require seven-covalency of the metal atom to occur by replacement of one of the nitrogen atoms in $Mo(CO)_4$(bipy) by iodine. In other words, in this complex, 2,2′-bipyridyl acts as a monodentate ligand. Attempts at verification of this suggestion by cleaving the bridging halogens and quarternising the free tertiary nitrogen atoms were unsuccessful. Attempts at molecular-weight determination were frustrated by instability of the solutions.

EXPERIMENTAL

*Tetracarbonylmono-*2,2′*-bipyridylchromium*(0).—Hexacarbonylchromium (1·1 g.) and the bipyridyl (0·8 g.) were refluxed in toluene (50 ml.) for 2 hr. under nitrogen. The deep orange crystals (1·5 g.) which were formed on cooling were washed with light petroleum (60 ml.) and dried *in vacuo* (Found: C, 51·6; H, 3·1; N, 8·2; Cr, 16·1. $C_{14}H_8CrN_2O_4$ requires C, 52·5; H, 2·5; N, 8·8; Cr, 16·3%). The *complex* was stable to air and moisture, moderately soluble in non-polar solvents, alcohol, nitromethane, and nitrobenzene, but insoluble in petroleum and water.

*Tetracarbonylmono-*2,2′*-bipyridylmolybdenum*(0).—Hexacarbonylmolybdenum (1·4 g.) and bipyridyl (0·8 g.) were refluxed in toluene (50 ml.) for 1½ hr. under nitrogen. After cooling, the maroon crystalline *complex* (1·8 g.) was washed with toluene (15 ml.) and light petroleum (30 ml.) and dried *in vacuo* (Found: C, 46·6; H, 2·6; N, 7·6; Mo, 26·0. $C_{14}H_8MoN_2O_4$ requires C, 46·1; H, 2·2; N, 7·7; Mo, 26·4%). The physical properties are similar to those of the corresponding chromium compound.

*Tetracarbonylmono-*2,2′*-bipyridyltungsten*(0).—Hexacarbonyltungsten (1·7 g.) and bipyridyl (0·8 g.) were refluxed in xylene (80 ml.) for 2 hr. under nitrogen. The deep red *complex* (2·2 g.), which crystallised as needles on cooling, was washed with light petroleum (50 ml.) and dried *in vacuo* (Found: C, 37·0; H, 2·2; N, 6·8; W, 40·3. $C_{14}H_8N_2O_4W$ requires C, 37·2; H, 1·8; N, 6·2; W, 40·7%). The physical properties are very similar to those of the chromium analogue.

*Di-iodotricarbonylmono-*2,2′*-bipyridyltungsten*(II).—The complex $W(CO)_4$(bipy) (0·1 g.) in chloroform (150 ml.) was treated with iodine (0·056 g.) in chloroform (20 ml.) with stirring. The *compound* (0·09 g.) which crystallised slowly at 0° as bright orange crystals after addition of light petroleum (30 ml.) was dried *in vacuo* (Found: C, 23·3; H, 1·8; I, 37·7; N, 4·4; W, 27·2. $C_{13}H_8I_2N_2O_3W$ requires C, 23·1; H, 1·2; I, 37·5; N, 4·1; W, 27·1%). It is unstable in air and to light and is readily soluble in polar and non-polar solvents in which it quickly decomposes. It is insoluble in light petroleum.

*Dibromotricarbonylmono-*2,2′*-bipyridyltungsten*(II).—The complex $W(CO)_4$(bipy) (0·1 g.) in chloroform (100 ml.) was treated with bromine (0·035 g.) in carbon tetrachloride (15 ml.) with stirring. The *product* (0·1 g.), which crystallised slowly at 0° as bright orange needles after addition of light petroleum (50 ml.), was dried *in vacuo* (Found: C, 26·9; H, 1·8; Br, 27·6; N, 4·7; W, 31·2. $C_{13}H_8Br_2N_2O_3W$ requires C, 26·8; H, 1·4; Br, 27·4; N, 4·8; W, 31·5%) and had properties similar to those of the corresponding di-iodo-compound.

*Dibromotricarbonylmono-*2,2′*-bipyridylmolybdenum*(II).—The complex $Mo(CO)_4$(bipy) (0·2 g.) in chloroform (150 ml.) was treated with bromine (0·09 g.) in carbon tetrachloride (70 ml.). The *compound* (0·1 g.), which crystallised slowly as bright orange needles at 20°, was dried *in vacuo* (Found: C, 31·2; H, 1·6; Br, 32·6; N, 5·8; Mo, 19·0. $C_{13}H_8I_2N_2O_3Mo$ requires C, 31·5; H, 1·6; Br, 32·2; N, 5·6; Mo, 19·4%) and was similar to, but less stable than, the tungsten analogues.

*Iodination of Tetracarbonylmono-*2,2′*-bipyridylmolybdenum*(0).—The compound $Mo(CO)_4$(bipy) (0·1 g.) in chloroform (150 ml.) was treated with iodine (0·07 g.) in chloroform (10 ml.) with stirring. On addition of light petroleum (50 ml.), the complex suspected of being *di-μ-iododi-iodohexacarbonylbis-*2,2′*-bipyridylmolybdenum*(II) (0·04 g.) was precipitated slowly at 0° as orange-brown crystals, which were dried *in vacuo* (Found: C, 26·9; H, 1·6; I, 42·7; N, 4·6; Mo, 16·0. $C_{26}H_{16}I_4N_4O_6Mo_2$ requires C, 26·5; H, 1·4; I, 43·1; N, 4·8; Mo, 16·3%). It has properties similar to those of the molybdenum(II) compound described above.

Determination of Metals and Halogens.—Metals were determined by a method similar to that already described,[6] except that nitric acid rather than sulphuric acid was used for initial digestion. Halogens were determined gravimetrically as silver salts.

Measurement of Carbon Monoxide Evolved.—This was done by a method similar to that described previously.[7] Some average values are: $Mo(CO)_6$ with bipy 1·98; $Mo(CO)_4$(bipy) with I_2 0·99, and with Br_2 1·20; $W(CO)_4$(bipy) with I_2 0·96, and with Br_2 0·98 mol.

Infrared Spectra.—These were kindly measured by Dr. G. W. Gray of this Department using a Unicam S.P. 100 spectrometer.

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