Cationic Complexes Containing Ruthenium–Mercury and Osmium–Mercury Bonds

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A RECENT paper[1] has described an impure compound containing an osmium–mercury bond, but otherwise no well-defined compounds of this type are known. We have previously mentioned that the ruthenium(0) complex, $Ru(CO)_3L_2$ [L = $P(Ph)_3$], reacts with mercuric halides.[2] Herein we report the products of this reaction between this ruthenium(0) complex (Ia) and the related osmium(0) complex (Ib)[3] with mercuric halides.

The sparingly-soluble crystalline solids have been identified as cationic derivatives of ruthenium(II) and osmium(II) in association with trihalogenomercury anions (II). The infrared spectra of (II) (Table) show a striking resemblance to those of other cationic tricarbonyl complexes of known stereochemistry such as (III),[3] but with a shift of carbonyl frequencies to lower wave-numbers. This shift is consistent with the difference in electronegativity of the mercury ligand compared to the halide ion.[4] The rather broad, strong peak centred near 2000 cm.$^{-1}$ probably represents the superposition of two peaks which are well resolved in the spectrum of the similar complexes (III).[3] Conductivity measurements made on nitrobenzene solutions (Table) support the formulation of compounds (II) as 1 : 1 electrolytes.

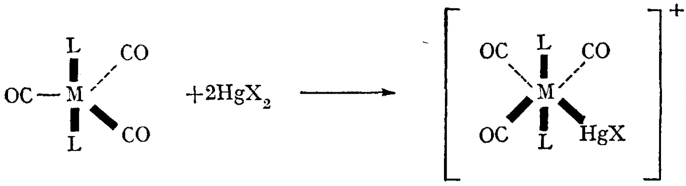
The crystalline solids (II) are quite light-sensitive but otherwise appear to be stable. The fact that ionic compounds are obtained in which

TABLE[a]

	Colour	Λ_m[b] ohm^{-1} cm.^{2} mole^{-1}	$c \times 10^3$ mole litre^{-1}	$\lambda_{C\equiv O}$ cm.$^{-1}$ (KBr pellets)	
$[RuHgCl(CO)_3(PPh_3)_2]HgCl_3$ ..	colourless	18·4	0·41	2075 (m)	2010 (s, broad)
$[RuHgBr(CO)_3(PPh_3)_2]HgBr_3$ ..	colourless	19·3	2·28	2070 (m)	2005 (s, broad)
$[RuHgI(CO)_3(PPh_3)_2]HgI_3$	yellow	19·2	2·36	2060 (m)	2000 (s, broad)
$[OsHgCl(CO)_3(PPh_3)_2]HgCl_3$ ..	colourless	19·3	0·93	2090 (m)	2020 (s, broad)
$[OsHgBr(CO)_3(PPh_3)_2]HgBr_3$ ..	colourless	21·2	0·70	2075 (m)	2010 (s, broad)
$[OsHgI(CO)_3(PPh_3)_2]HgI_3$ ..	pale yellow	20·6	1·00	2080 (m)	2015 (s, broad)
$[OsBr(CO)_3(PPh_3)_2]Br$	colourless	—	—	2140 (m)	2065 (s) 2040 (s)

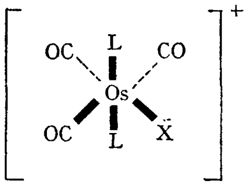
[a] Satisfactory elemental analyses have been obtained for all of the above complexes except the ruthenium–mercury chloride adduct. This substance appears to contain a mixture of both chloride and trichloromercury anions. For example, $[OsHgBr(CO)_3(PPh_3)_2HgBr_3$ requires: C, 30·8; H, 2·0; Hg, 26·4; Br, 21·0. Found: C, 31·1; H, 2·1; Hg, 26·55; Br, 20·9.

[b] Conductivities in nitrobenzene at 25°.



(I) M=Ru (a)
M=Os (b)

(II) X=Cl, Br, I



(III) X=Br, I

one of the mutually *trans*-carbonyl ligands is not displaced must be due in part to the low nucleophilicity of the accompanying trihalogenomercury anions.

The formation of complexes of this type is an excellent illustration of the general basic character of low-valent transition-metal complexes.[5]

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[1] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5331.

[2] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1965, **87**, 4008.

[3] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, to be published.

[4] R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 1965, 5337.

[5] During the typing of this manuscript the preparation of similar complexes involving iron–mercury bonds appeared: D. M. Adam, D. J. Cook, and R. D. W. Kemmitt, *Chem. Comm.*, 1966, 103.