Cationic Trialkyl Phosphite Complexes of Gold, Silver, and the Platinum Metals

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Summary Ligand displacement reactions performed in polar solvents afford a convenient route to an extensive series of cationic trialkyl phosphite complexes of gold, silver, and all six platinum metals, which may be isolated in the form of their tetraphenylborate salts

ALTHOUGH trialkylphosphine complexes of the "b" class transition metals have been extensively studied, little is known concerning derivatives of the related trialkyl phosphite ligands This paucity of data may be ascribed, in part, to the ease of solvolysis of trialkyl phosphites and to the emphasis placed on the highly soluble neutral complexes in previous work

We now report a general synthesis whereby trialkyl phosphite derivatives of class ' b" transition metals may be obtained in the form of complex cations, and isolated as their tetraphenylborate salts Labile olefin, triphenyl-

TABLE

Cationic trialkyl phosphite complexes

$[RuL_6]^{2+}$	$[RhL_5]^+$	$[PdL_4]^{2+}$	$[AgL_4]^+$
$[RuXL_5]^+$		$[PdL_5]^{2+}$	
$[RuHL_5]^+$		$[PdXL_3]^+$	
	$[IrL_5]^+$	$[PtL_4]^{2+}$	$[AuL_4]^+$
$[OsXL_5]^+$		$[PtXL_3]^+$	

L = $P(OMe)_3$ and/or $P(OEt)_3$ X = Cl and/or Br Precursors used to prepare the complex cations were — $[RuX_2$-(bicycloheptadiene)$]_n$ $RuHCl(PPh_3)_3$ $OsX_2(PPh_3)_3$ [RhCl-(cyclo octa 1,5 diene)$]_2$ $[IrHCl_2$(cyclo octa 1 5 diene)$]_2$ PdX_2L_2, PtX_2L_2 AgCl and AuCl(cyclo octene) $[IrHCl_2$(cyclo octa-1 5-diene)$]_2$ reacts with trialkyl phosphite (L) in the corresponding alcohol to afford $[Ir(C_8H_{12})L_3]^+$ [1] which may be subsequently treated with more phosphite in benzene solution to afford $[IrL_5]^+$ Examples of the cationic trialkyl phosphite species $[RhL_5]^+$ [2] $[AgL_4]^+$ [3] $[PtL_4]^{2+}$ [4] and $[PdL_4]^{2+}$ [5] have previously been isolated[2 3] or studied in solution[4 5] by other workers phosphine, or trialkyl phosphite derivatives of the appropriate transition-metal halides react with trialkyl phosphites, $P(OR)_3$, in alcohol (ROH) or MeCN to afford clear solutions from which the required salts may be isolated on addition of sodium tetraphenylborate. By this simple expedient cationic trialkyl phosphite complexes of gold, silver and all six platinum metals have been readily isolated (see Table).

The new complex salts have been characterised by analysis, conductivity measurements (MeCN), and proton n.m.r. spectroscopy (the latter technique gave the ratio of trialkyl phosphite ligands to tetraphenylborate anions present in each salt). The ruthenium, osmium, iridium, and platinum complexes are stable while those of rhodium, palladium, silver, and gold decompose or dissociate readily. With the exception of the palladium derivatives $[PdL_5][BPh_4]_2$, which are yellow, all the new cationic complexes are colourless crystals. Those containing monocations crystallise slowly from their reaction solutions and are readily soluble in chloroform, dichloromethane, and methyl cyanide; those containing dications are deposited very rapidly and are sparingly soluble only in dichloromethane and methyl cyanide. The proton n.m.r. spectra arising from the cationic trialkyl phosphite complexes are complicated by virtual coupling and ligand exchange processes, and exhibit a remarkable variety of inter- and intra-ligand coupling patterns. A detailed investigation of these spectra is in progress.

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[1] L. M. Haines and E. Singleton, *J. Organometallic Chem.*, 1970, **25**, C83.

[2] M. J. Nolte, G. Gafner, and L. M. Haines, *Chem. Comm.*, 1969, 1406.

[3] K. J. Coskran, T. J. Huttemann, and J. G. Verkade, *Advan. Chem. Ser.*, 1967, **62**, 590.

[4] W. McFarlane, *Chem. Comm.*, 1968, 393.

[5] G. A. Levshina, A. D. Troitskaya, and R. R. Shagidullin, *Russ. J. Inorg. Chem.*, 1966, **11**, 985.