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Reactions of *cis*-$[MCl_2(PPh_2Cl)_2]$ (M = Pd or Pt), or $[PdCl_2(PPhCl_2)_2]$ with α-amino-acid Esters, Monosaccharides, Thiomonosaccharides, or Nucleosides

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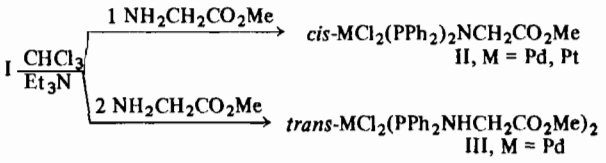
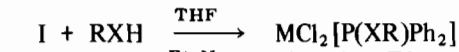
There is considerable current interest in transition metal complexes containing biologically important ligands. We are interested in functionalizing optically active natural products (*e.g.* with organo-phosphorus groups) with the aims of 1) improving their coordinating ability and 2) providing a simple route to optically active ligands which are potentially useful in transition metal catalysed asymmetric induction. Metal complexes containing optically active phosphines derived from tartaric acid [1] or menthol [2] have been successfully used as catalysts for asymmetric induction. We have previously reported [3] the preparation of bidentate phosphines, $(Ph_2P)_2NCHRCO_2Me$, derived from α-amino-acid esters, and metal complexes thereof. We now describe Pt and Pd complexes of monodentate phosphines comtaining α-amino-acid ester, monosaccharide, thiomonosaccharide, or nucleoside groups. These phosphines have been synthesised at the metal by an HCl elimination reaction between chlorophosphine metal complexes and RNH_2, ROH or RSH compounds. Reactions of coordinated halophosphines have recently been reviewed [4].

The chlorophosphine complexes *cis*-$MCl_2(PPh_2Cl)_2$, I (M = Pd or Pt) or $PdCl_2(PPhCl_2)_2$ are easily obtained from the reaction of $MCl_2(NCPh)_2$ with Ph_2PCl or $PhPCl_2$ in alcohol-free chloroform. The preparation of these complexes from MCl_2 and Ph_2PCl or $PhPCl_2$ has been described in a thesis [5]; we find this to be a less satisfactory route. Reactions with alcohols were also carried out, and some of the results have been quoted in a review [4].

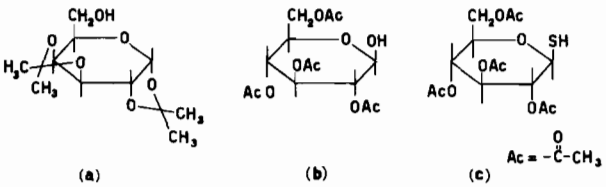
Reaction of I with one equivalent of glycine methyl ester affords, in low yield, the previously reported complexes II. With two equivalents of ester, II is obtained when M = Pt, but for M = Pd a *trans* compound III, [ν(NH), KBr, 3320 cm^{-1}; τNH, $CDCl_3$, 5.42], containing two monodentate aminophosphines is formed.



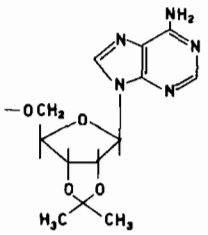
We have found synthesis at the metal to be especially useful for sugar-containing phosphines, where isolation of the pure ligand is more difficult (some sugar-containing phosphines have recently been described [6]). Thus, 1,2,3,4-di-O-isopropylidene-α-D-galactopyranose (a), 2,3,4,6-tetra-O-acetyl-β-D-glucopyranose (b), or 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranose (c) react with I to give the corresponding ester complexes IV in high yield:



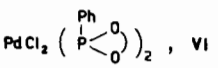
RXH =

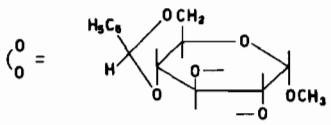


Similarly, 2′,3′-O-isopropylidine-adenosine reacts with I, M = Pd, to give the complex V, $MCl_2(PPh_2OR)_2$, where RO =



The phenyldichlorophosphine complex $PdCl_2(PPhCl_2)_2$ reacts with methyl-4,6-O-benzylidene-α-D-glucopyranoside to give a complex containing a λ^3-dioxaphospholane ligand,





We have also obtained complexes $PdCl_2[P(XR)_2Ph]_2$, VIIa, VIIc, containing two sugar groups attached to each phosphorus atom, from the reaction of $PdCl_2(PPhCl_2)_2$ with the pyranoses (a) or (c). Physical and spectral data are in the Table.

We are currently studying the use of these complexes as catalysts, and their physiological proper-

TABLE. Physical and Spectral Data.[a]

Compound		Colour	M.Pt. (°C)	(M–Cl)[b] (cm^{-1})	$[\alpha]^{25}_{546}$[c]
I,	M=Pd	Yellow	230–2 dec.	301, 326	–
I,	M=Pt	White	266–8 dec.	302, 327	–
III,	M=Pd	Yellow	188 dec.	355	–
IVa,	M=Pd	Pale yellow	130 dec.	315, 292	–72
IVa,	M=Pt	White	135 dec.	316, 291	–47
IVb,	M=Pd	Beige	116 dec.	315, 291	–60
IVc,	M=Pd	Orange	114 dec.	310(broad)	–74
IVc,	M=Pt	Pale yellow	109 dec.	299(broad)	–78
V,	M=Pd	Beige	156 dec.	d	not measured
VI,	M=Pd	Yellow	120 dec.	323, 298	+24
VIIa,	M=Pd	Cream	113 dec.	318, 300	–60
VIIc,	M=Pd	Yellow	122 dec.	309(broad)	–35

[a] Satisfactory analytical and spectroscopic data were obtained for all complexes. [b] In KBr for I, II and III; nujol in all other cases. [c] 2–10 mgs ml^{-1} in acetone. [d] not positively identified.

ties. *cis*-Dichlorodipeptide ester complexes of Pt have recently been found to have anti-tumor activity [7].

Acknowledgment

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