Heterotopic Ligands: Synthesis and Complexation Properties of Phosphine-functionalized Dipodal Macrocycles

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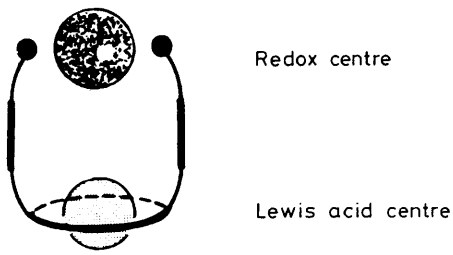
The synthesis of a series of phosphine-functionalized dipodal macrocycles is described; prior co-ordination of a cation within the macrocyclic cavity regulates the ligand structure aiding formation of heterodinuclear complexes.

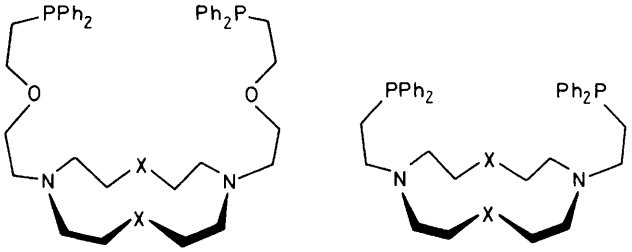
Attachment of two side chains to a macrocyclic framework yields dinucleating ligands capable of binding metals both within the macrocyclic cavity and between the functionalized side arms. This generates a heterotopic ligand which may exhibit haptoselectivity: the selective binding of a given cation at a given subunit in a polytopic ligand. There is considerable interest in such dinucleating systems in which two metals are bound in close proximity.[2] In particular, a ditopic ligand which combines a subunit containing 'soft' binding sites with one bearing 'hard' sites should form dinuclear complexes displaying respectively a redox and a Lewis acid metal ion centre[1] (see representation A).



(A)

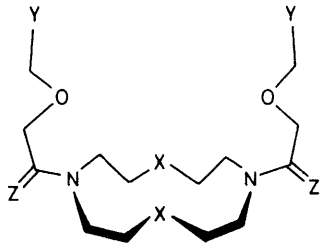
We now report the synthesis of four new dipodal macrocycles (**1**)—(**4**) and preliminary studies of their co-ordination chemistry. Functionalization of the secondary nitrogen sites in the parent monocycles permits the introduction of diphenylphosphino groups.

Reaction of 1,7-diaza-4,10-dioxacyclododecane with 3-oxaglutaric anhydride yields (**5**) (CH_2Cl_2; 90% yield) which may be reduced to (**6**) (borane–tetrahydrofuran, THF; 92% yield) and converted into (**7**) ($SOCl_2$; 0 °C; 90% yield). The free amine reacts with potassium diphenylphosphide in dioxane[3] to give (**1**) which may be recrystallised from methanol [45%; m.p. 89—90 °C; δ (^{31}P) −19.8 p.p.m.]. Similarly (**2**) may be prepared from 1,7-diaza-4,10-dithiacyclododecane in 54% overall yield [m.p. 94—95 °C; δ(^{31}P) −20.3 p.p.m.]. Treatment of 1,7-diaza-4,10-dithiacyclododecane with chloroacetyl chloride (Et_3N; CH_2Cl_2) yields (**10**) (90% yield) which may be selectively reduced to (**11**) (borane–THF; 0 °C; 63% yield) and converted into (**4**) by reaction with diphenylphosphide [82% yield; m.p. 131—133 °C; δ(^{31}P) −18.3 p.p.m.]. Condensation of 1,7-diaza-4,10-dioxacyclododecane with ethylene oxide gives (**8**) (94% yield) which may be converted successively into (**9**)

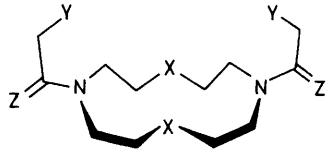


(1) X = O
(2) X = S

(3) X = O
(4) X = S



(5), Z = O, Y = CO_2H
(6), Z = H_2, Y = CH_2OH
(7), Z = H_2, Y = CH_2Cl

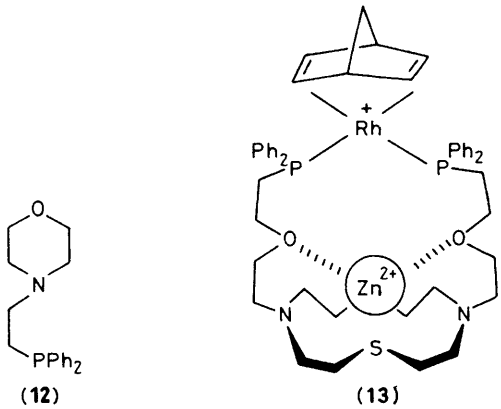


(8), X = O, Y = OH, Z = H_2
(9), X = O, Y = Cl, Z = H_2
(10), X = S, Y = Cl, Z = O
(11), X = S, Y = Cl, Z = H_2

($SOCl_2$; 0 °C; 91% yield) and (**3**) [$KPPh_2$, dioxane; 45%; m.p. 108—109 °C; δ (^{31}P) −18.9 p.p.m.].†

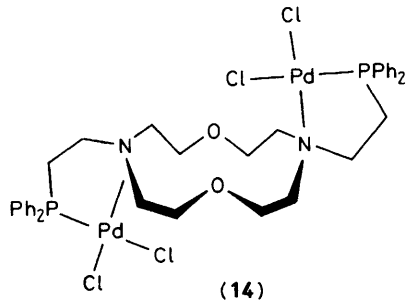
Compounds (**1**) and (**2**) behave quite distinctly in their reactions with d^8 metal ions and complexes. Reaction of (**1**) with K_2PtCl_4 in aqueous acetone gives the colourless *cis*-[(**1**)–$PtCl_2$] complex selectively [δ (^{31}P) +4.5 p.p.m., J_{PtP} 3633 Hz; ν(Pt–Cl) 318 and 281 cm^{-1}], while reaction with $PdCl_2(PhCN)_2$ (1 equiv.) in dichloromethane yields the more stable *trans*-isomer as the major species in solution [>95%; δ (^{31}P) +13.0 p.p.m.; ν (Pd–Cl) 348 cm^{-1}] together with small amounts of the *cis*-isomer [<5%; δ(^{31}P) +24.1 p.p.m.].‡ The large-ring chelating diphosphine may be expected preferentially to form a *trans*-diphosphine palladium complex.[4] With (**2**), on the other hand, non-selective co-ordination to both soft S_2 and P_2 binding sites occurs, giving for example a dipalladium dichloride complex with $PdCl_2(PhCN)_2$.

Compound (**1**) binds Ca^{2+} ($CaCl_2$) in methanol to form a 1:1 complex (for an analogy see ref. 5) which reacts with $PdCl_2(PhCN)_2$ to form a heterodinuclear complex [δ(^{31}P) +18.3 p.p.m., ν(PdCl) 314 and 281 cm^{-1}]. Ligands (**1**) and (**2**)



(12)

(13)



(14)

permit the formation of such heterodinuclear complexes *via* stepwise complexation in either manner. Thus (**1**) reacts with $PdCl_2(PhCN)_2$ in dichloromethane to generate the yellow *trans*-[(**1**)–$PdCl_2$] which upon reaction with excess of copper(II) perchlorate in methanol precipitates the mixed complex in which there is probably a *cis*-phosphine binding unit [ν(PdCl) 313 and 278 cm^{-1}]. In the opposite sense, compound (**2**) reacts with zinc perchlorate in acetone to give [(**2**)–$Zn(ClO_4)_2$] [δ(^{31}P) −22.7 p.p.m.], and this forms the mixed complex [(**2**)–Rh(nbd)$^+$·Zn]$^{3+}$3ClO_4^- (nbd = bicyclo-[2.2.1]hepta-2,5-diene) upon treatment with $Rh(nbd)_2^+$·ClO_4^- [J_{RhP} 155 Hz, δ(^{31}P) +17.8 p.p.m.].[11] In this case the zinc ion, which may be expected to bind on top of the small macrocycle,[1b,6,7] serves to *regulate* the ligand structure by additional binding to the oxygens in the lateral 'arms' facilitating formation of the *cis*-diene diphosphine–rhodium complex (**13**).§ Indeed in the absence of zinc ions reaction with 1 equiv. of $[Rh(nbd)_2]^+$ failed to give a definable complex and addition of excess $[Rh(nbd)_2]^+$ appears to give a dirhodium complex whose structure is not yet defined in which the rhodium diene units are probably bound to *cis* P_2 and S_2 donors.[7]

Ligands (**3**) and (**4**) in principle may function either with P_2 or PN binding sites. Ligand (**3**) reacts with $PdCl_2(PhCN)_2$ in dichloromethane to give the NP bound dipalladium complex [δ(^{31}P) +49.2 p.p.m.] with the two palladium atoms probably bound *trans* on opposite sides of the monocycle, structure (**14**), while reaction with $Rh_2Cl_2(CO)_4$ in methanol gives a bright yellow complex [δ(^{31}P) +59.7 p.p.m., J_{RhP} 172 Hz; ν(CO) 1977 cm^{-1}] with a similar geometry. The model morpholinophosphine (**12**) under similar conditions also forms a monomeric NP-bound RhClCO complex [δ(^{31}P) +81.5 p.p.m., J_{RhP} 170 Hz; ν(CO) 1965 cm^{-1}] with the nitrogen *trans* to the bound CO.[8,9] Reaction of (**4**) with $Rh_2Cl_2(CO)_4$ gave no well defined products whereas with

† All new compounds gave spectroscopic and analytical data consistent with their structures. ^{31}P N.m.r. chemical shifts are relative to 85% H_3PO_4 with upfield shifts negative.

‡ Spectroscopic properties of complexes are in agreement with the proposed structures taking into account the relevant literature data (refs. 8, 10, and 11).

§ Similar routes permit the isolation of mixed $[ZnPdCl_2]^{2+}$, $[CuRh(CO)Cl]^{2+}$ and $[Cu–PtCl_2]^{2+}$ complexes of (**1**) and (**2**).

$Rh_2(nbd)_2Cl_2$ followed by reaction with fluoroborate anion a dirhodium complex was formed [$\delta(^{31}P)$ +24.1 p.p.m., J_{RhP} 170 Hz] in which again there is presumably *cis*-co-ordination of the metal to S_2 and P_2 binding sites on opposite sides of the macrocycle.

In conclusion, the diphosphines (**1**)—(**4**) are versatile heterotopic ligands with which well defined homo- or hetero-dinuclear complexes may be formed by stepwise complexation. With (**1**) and (**2**) prior co-ordination of a hard cation regulates the ligand structure facilitating complexation of a soft metal ion to the generated *cis* diphosphine site and modifying its properties. In particular one can envisage that both centres could co-operate for the activation of a substrate bound between them.[1]

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