Unique ligand imposed distortions in a nickel(II) 1,5,9-triphospha-cyclododecane complex

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1,5,9-Triethyl-1,5,9-triphosphacyclododecane ([12]ane-P$_3$Et$_3$, L) reacts with NiBr$_2$ to afford the salt [NiLBr]Br which is shown by X-ray crystallography to have an unusually distorted structure as a result of constraints imposed by the ligand L.

Triaza and trithia cycloalkanes are well known to form stable nickel compounds in a variety of oxidation states and with properties that are unique to complexes of these ligand sets.[1] There are few examples of Ni complexes of macrocyclic polyphosphines and none with macrocyclic triphosphines. In view of the coordination control as well as the relative kinetic stability that may arise in complexes of phosphorus macrocycles, we have studied reactions of 1,5,9-triethyl-1,5,9-triphosphacyclododecane ([12]aneP$_3$Et$_3$, L) and report preliminary results of this study here.

Reactions of L with NiBr$_2$ in ethanol give rise to deep red solutions from which red crystals of **1** may be isolated and for which analytical data indicate the formula NiLBr$_2$.† The crystals are only slightly air-sensitive but solutions are readily oxidised by air giving rise to oxides of L. **1** is readily soluble in Me$_2$SO but is insoluble in hydrocarbons and aliphatic ethers and only poorly soluble in relatively polar organic solvents such as THF, CH$_2$Cl$_2$ and MeNO$_2$. **1** has only been isolated in reasonable yield when prepared in alcohols, black oils are formed in THF or CH$_2$Cl$_2$. **1** is a conductor in Me$_2$SO ($\Lambda_M = 21$ cm^2 ohm^{-1} mol^{-1}), a value close to other monocationic Ni^{II} complexes such as [Ni(NP$_3$)I]BF$_4$ [$\Lambda_M = 14$ cm^2 ohm^{-1} mol^{-1}, NP$_3$ = N(CH$_2$PPh$_2$)$_3$][2a] and is thus better formulated as the salt [NiLBr]$^+$Br$^-$. **1** is also diamagnetic, giving rise to sharp NMR spectra and so presumably does not have a tetrahedral Ni^{II} atom. The ^{31}P{^{1}H} NMR spectrum consists of a singlet (δ -3.0) indicating fluxionality in solution since a static distorted four-coordinate geometry would not have magnetically equivalent phosphorus atoms. The spectrum is temperature invariant (25 to -70 °C). This fluxionality may in part be due to halide lability since warming solutions of **1** in Me$_2$SO gives rise to solutions for which conductivity measurements indicate the solute to be dicationic ($\Lambda_M = 229$ cm^2 ohm^{-1} mol^{-1}) by comparison to related dicationic Ni complexes {*e.g.* for [Ni{η^2-1,2-C$_6$H$_4$(PEt$_2$)$_2$}$_2$], $\Lambda_M = 182$ cm^2 ohm^{-1} mol^{-1}}.[3]

The structure of the cation of **1** is presented in Fig. 1.‡ The geometry around the four-coordinate d^8 Ni atom is heavily distorted from either of the common, regular four-coordinate geometries.

Whereas the Ni–P distances are all similar [av. 2.151(1) Å] [Ni(NP$_3$)I]$^+$ [av. 2.22(1) Å],[8] the distortion is manifested in the bond angles around Ni where one of the P–Ni–P angles is considerably larger than the other two [126.43(4)° *vs.* 94.80(4) and 96.29(4)°]; similarly one of the Br–Ni–P angles is much larger than the other two [155.60(4)° *vs.* 94.52(3) and 96.19(3)°]. Distortions from square planar towards tetrahedral structures arising from steric encumbrance of the ligands are well known for Ni^{II} phosphine complexes. Examples are [Ni(CH$_2$SiMe$_3$)Cl(PMe$_3$)$_2$]$^+$ and [Ni(CH$_2$SiMe$_3$)(PMe$_3$)$_3$]$^+$ where the substitution of Cl, in the former, by PMe$_3$ increases the distortion around Ni, albeit less severe, approaches that in **1**.[4] Other than the direct bonding contacts between Ni and the
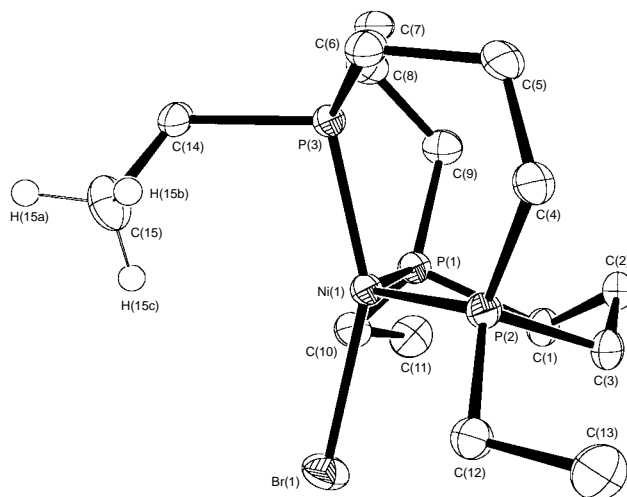

Fig. 1 The molecular structure and atom labelling scheme of [NiLBr]Br **1**. Isotropically refined hydrogen atoms closest to Ni [on C(15)] are included, all others are excluded for clarity. Selected bond lengths (Å) and angles (°): Br(1)–Ni(1) 2.329(1), Ni(1)–P(3) 2.124(1), Ni(1)–P(1) 2.163(1), Ni(1)–P(2) 2.167(1), P(3)–Ni(1)–P(1) 94.80(4), P(3)–Ni(1)–P(2) 96.29(4), P(1)–Ni(1)–P(2), 126.43(4), P(3)–Ni(1)–Br(1) 155.60(4), P(1)–Ni(1)–Br(1) 94.52(3), P(2)–Ni(1)–Br(1) 96.19(3).

three phosphorus and one bromine atoms in **1**, the closest intramolecular interaction with the nickel is to a P–Et hydrogen atom on C(15) at 2.85 Å and is thus considered to be non-bonding. There are no other interactions that could explain the distortion. A striking comparison is with the related ligands [12]aneN$_3$ and [12]aneS$_3$ which both form high-spin octahedral complexes with Ni^{II}, the latter forms a bis-macrocycle sandwich with six coordinated S atoms.[1,5] The related 9-membered nitrogen macrocycles, [9]aneN$_3$ and [9]aneN$_3$Me$_3$, also favour octahedral geometries, although the latter is reported not to form a bis-ligand complex of Ni^{II} owing to steric interactions between the methyl substituents.[1] It appears then that steric crowding is not responsible for forcing the distortion observed in **1** unlike in the PMe$_3$ complexes above, however space filling models[6] give a better view of its coordination sphere (Fig. 2) showing the apparent coordination vacancy arising from the distortion. This vacancy is highlighted by rotation of the P–Et[C(14)] bond [Fig. 2(*b*)], which might be expected to be facile in solution, such that the methyl group [C(15)] is removed from the proximity of the nickel atom. These views indicate that the structure might best be described as a distorted trigonal bipyramid with a vacant vertex. Although this behaviour is unexpected and unique for d^8 Ni^{II} phosphine complexes, there are other examples of four-coordinate d^8 complexes that show distortions from either square-planar or tetrahedral geometries as a result of electronic influences.[7] A relevant comparison with **1** in this context is the structure of [Ru(CO)$_2$(PBu$^t_2$Me)$_2$] **2** which exhibits a similar distortion from a square-planar geometry and whose structure was also described as trigonal bipyramidal in which one equatorial ligand is absent; the '*transoid*' (P–Ru–P) and '*cisoid*' (C–Ru–C) angles are
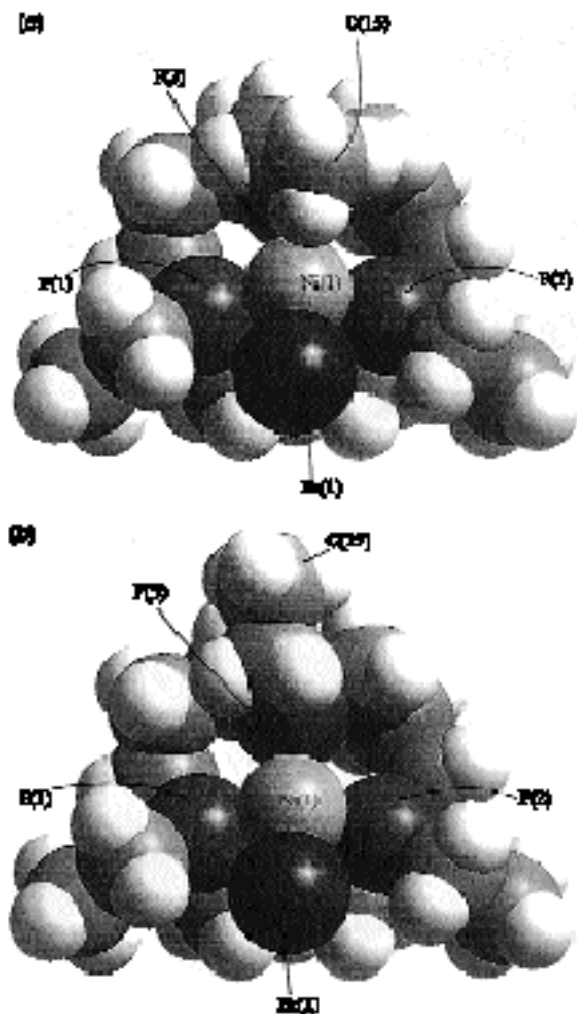
Fig. 2 Space filling models of [Ni([12]aneP$_3$Et$_3$)Br]$^+$; (*a*) crystallographically determined configuration, (*b*) ethyl group rotated away from Ni [around P(3)–C(14)]

165.56(8) and 133.3(4), respectively.[8] In this case, *ab initio* calculations (on the PH$_3$ analogue) at the RHF/MP2 level indicated that the observed structure was very close to the most stable ground state configuration and a more regular square-planar geometry was disfavoured. This is in contrast to analogous Rh^{I} complexes where the reverse is true; this difference was said to arise from a π-bonding stabilisation in the Ru carbonyl that is not as significant in Rh^{I} owing to differences in d-orbital energies. This explanation also implies that related Ni^{II} compounds would favour regular square-planar geometries in the ground state and especially in **1** where the tertiary alkyl phosphine donors are expected to be less efficient π acceptors than CO in **2**. The electronic preference for a square-planar ground state configuration in **1** is further supported by EHMO calculations[9] on the idealised system, [Ni(PH$_3$)$_3$Br]$^+$. Three geometries were studied: square planar, trigonal bipyramidal having a vacant equatorial site, and tetrahedral. The square-planar geometry is found to be the most stable owing to minimisation of antibonding Ni–Br interactions; the bipyramid and tetrahedron are destabilised by 133 and 204 kJ mol^{-1} respectivley.

The structure of **1** also contrasts with Ni^{II} complexes of tripodal ligands such as N(CH$_2$L′)$_3$ (L′ = PPh$_2$, SH) for which trigonal-bipyramidal geometries predominate.[2] A related tripodal tris-amidate ligand {N[CH$_2$C(O)NBu^t]$_3$$^{3-}$} has been shown to support a high-spin trigonal monopyramidal structure in its Ni^{II} complex although the absence of one axial ligand (*trans* to tertiary N) was explained as due to the steric bulk of the tertiary butyl groups precluding coordination of the fifth ligand.[10]

It appears then that the distortion observed in **1** is not due to either electronic influences or steric factors arising from ligand substituents but rather to the unique feature of the macrocycle in restricting the freedom of the phosphorus donors, forcing them to adopt the coordination configuration observed. The strong preference of the nickel for a low-spin configuration in the presence of the three high-field phosphorus ligands also clearly dominates, destabilising tetrahedral or octahedral coordination geometries. This demonstrates a marked difference in the coordination behaviour of this [12]aneP$_3$ macrocycle in comparison to directly analogous N$_3$ and S$_3$ macrocycles as well as related tripodal ligands; it also indicates that the properties of its complexes will differ markedly from those of other ligands.

The synthesis of other Ni complexes and their reactions with small molecules and unsaturated substrates are currently being studied; preliminary results indicate that tetrahedral Ni^0 carbonyl complexes of L {[NiL(CO)$_3$]$_3$, [NiL(CO)] and [NiL(CO)]$^+$} are readily formed.

Notes and References

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