DALTON
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Preparation of a cyclic trimer with a Ni_3P_3 core: aggregation and conformation driven by steric demand†

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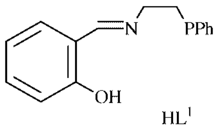
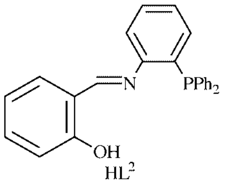
Reaction of the secondary phosphine tridentate Schiff's base ligand *o*-$C_6H_4(OH)(CH{=}N\{CH_2\}_2PHPh)$ with nickel chloride results in double deprotonation of the ligand and formation of a highly unusual trimeric structure; the cyclic Ni_3P_3 core adopts a distorted boat conformation in which phosphide donors bridge between the metal centres in preference to phenolate.

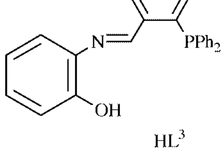
There has been significant interest over many years in ligands containing a mixture of hard (O or N) and soft (P or S) donor atoms. Most widely studied have been bidentate ligands with one phosphorus together with either oxygen or nitrogen donor atoms.[1] These are of particular interest in that they are able to form hemi-labile complexes in which the ligand coordination mode can switch from bidentate to monodentate and back again. This is a valuable property in the context of catalysis allowing facile, reversible generation of coordinatively unsaturated metal centres.[2] We were interested in reports on tridentate Schiff base ligands (*e.g.* HL^1–HL^3) having a P,N,O donor set.[3–5] Two types of mononuclear complex with nickel have been reported: octahedral 2:1 complexes[4] of general formula $[Ni(L)_2]$ (HL = HL^1–HL^3) and square planar 1:1 complexes,[5] either [Ni(L)Cl] or [Ni(HL)Cl]Cl depending on the ligand used. Related palladium(II) complexes with PNO donor phosphinohydrazones have been shown to be active catalysts in the hydrogenation of styrene and phenylacetylene.[6]



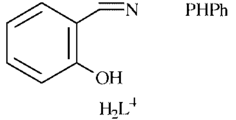
HL^1



HL^2



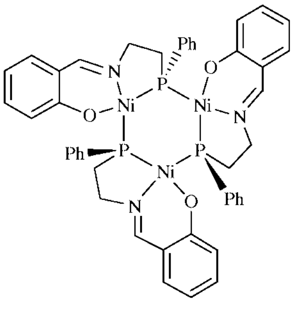
HL^3



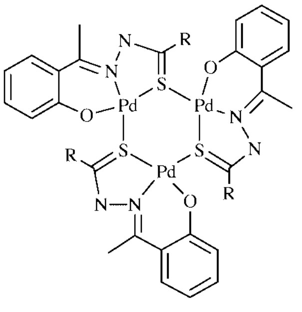
H_2L^4

In the above nickel complexes the ligands are monoanionic through deprotonation of the phenolic OH group. In the course of our studies on similar systems we decided to investigate the novel, analogous secondary phosphine ligand H_2L^4, prepared by condensation of salicylaldehyde and 2-(phenylphosphino)ethylamine.‡ This ligand was chosen since it offered potential as a dianionic ligand and the possibility of further functionalisation at phosphorus.

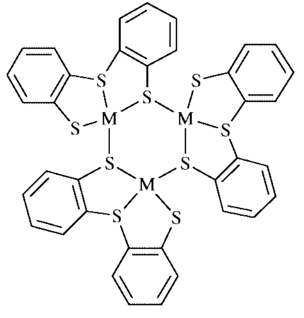
Reaction of H_2L^4 with anhydrous $NiCl_2$ in refluxing ethanol resulted in a dark brown solution, which after work up yielded an orange-brown solid, $[Ni(L^4)]_3$ **1**. From the IR spectrum it was immediately clear that the ligand had indeed been doubly deprotonated, since the characteristic absorbances arising from the phenolic O–H and the P–H stretches were absent, although the spectrum was otherwise as expected for the complexed Schiff's base ligand.§ The ^1H NMR spectrum, despite being somewhat broadened (suggesting some conformational mobility since the complex is diamagnetic) was also consistent with "$Ni(L^4)$". While the pattern of peaks observed for the CH_2 and the phenyl protons was particularly complex, the *o*-C_6H_4 protons between δ 6.5 and 7.1 and the imine proton at high field (δ 8.95) were characteristic of these systems. Attempts at VT NMR were thwarted by the low solubility of the complex below room temperature in all solvents. The EI MS showed only the presence of $[Ni(L^4)]^+$ and its dimer.



1



2 R = NHEt



3 M = Ni, Pd

Crystals of the complex were obtained by slow evaporation of an NMR sample ($CDCl_3$) and X-ray diffraction¶ revealed the structure to be a highly unusual cyclic trimer, $[Ni(L^4)]_3$ (Fig. 1) in which the nickel atoms have almost square planar geometry. The coordination sphere comprises the three ligand donor atoms, with a fourth bond to a bridging phosphide group from a neighbouring $Ni(L^4)$ unit. This surprised us initially, given that the phosphide group would appear to be more sterically demanding and that many phenoxide bridged bimetallic Schiff base complexes are known.[7] However, both phosphides[8] and sulfides[9] are also known to have a strong tendency to bridge metal centres, indeed this case shows that the need for

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† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/b0/b001098g/

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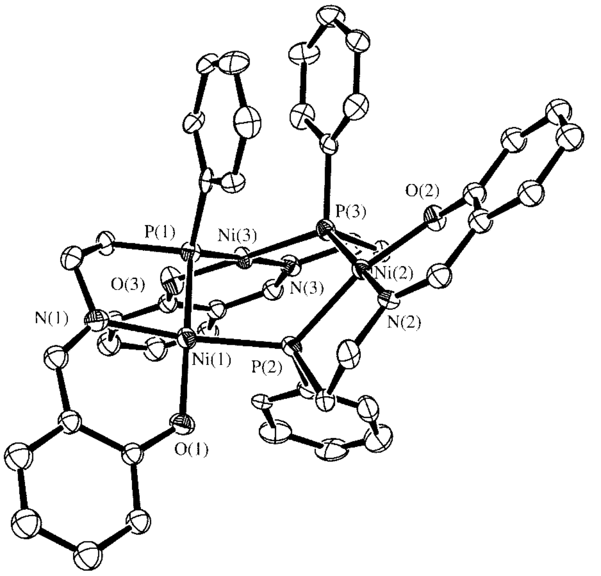

Fig. 1 The X-ray Crystal Structure of **1** showing a partial atom labelling scheme and with thermal ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Ni(1)–P(1) = 2.162(2), Ni(1)–P(2) = 2.202(2), Ni(1)–O(1) = 1.882(4), Ni(1)–N(1) = 1.919(5), Ni(2)–P(2) = 2.176(2), Ni(2)–P(3) = 2.193(2), Ni(2)–O(2) = 1.873(4), Ni(2)–N(2) = 1.919(5), Ni(3)–P(3) = 2.182(2), Ni(3)–P(1) = 2.185(2), Ni(3)–O(3) = 1.891(4), Ni(3)–N(3) = 1.901(5), P(1)–Ni(1)–P(2) = 89.35(7), P(1)–Ni(1)–O(1) = 169.02(14), P(1)-Ni(1)–N(1) = 88.6(2), P(2)–Ni(1)–O(1) = 90.11(14), P(2)–Ni(1)–N(1) = 171.3(2), O(1)–Ni(1)–N(1) = 93.5(2), P(2)–Ni(2)–P(3) = 91.46(7), P(2)–Ni(2)–O(2) = 165.22(14), P(2)–Ni(2)–N(2) = 88.9(2), P(3)–Ni(2)–O(2) = 88.28(13), P(3)–Ni(2)–N(2) = 173.1(2), O(2)–Ni(2)–N(2) = 93.1(2), P(3)–Ni(3)–P(1) = 88.47(7), P(3)–Ni(3)–O(3) = 177.20(14), P(3)–Ni(3)–N(3) = 88.6(2), P(1)–Ni(3)–O(3) = 88.73(13), P(1)–Ni(3)–N(3) = 175.8(2), O(3)–Ni(3)–N(3) = 94.2(2).

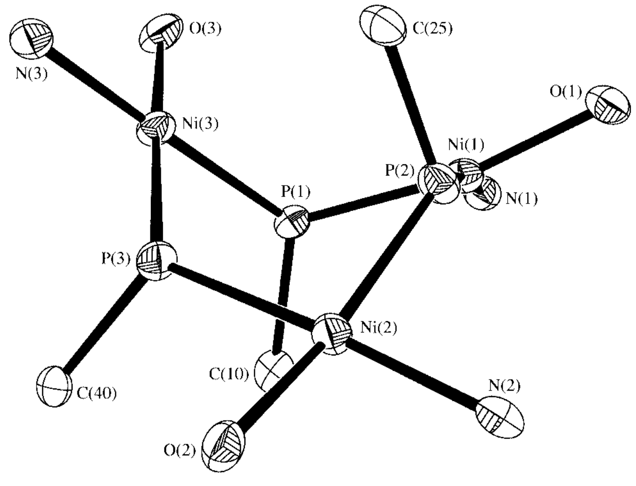

Fig. 2 The distorted Ni_3P_3 core of **1**, showing the orientations of the nickel coordination spheres and the phenyl substituents on phosphorus.

phosphide to bridge is sufficiently great to overcome the unfavourable steric factors. The resultant alternating Ni_3P_3 ring has a highly distorted boat structure (Fig. 2). This is driven by steric effects, which dictate a "*syn*, *syn*, *anti*" disposition of the phosphorus phenyl substituents, whereas the generally more favoured chair conformation requires a sterically congested "*syn*, *syn*, *syn*" arrangement of the phenyl groups. This assertion is supported by the fact that the only other crystallographically characterised, directly analogous ring system, that found in $[CpNi(PH_2)]_3$, in the absence of such marked steric influence at the bridging atom adopts the intuitively expected chair conformation.[10] Furthermore, the structurally related thiosemicarbazone complex, **2**,[11] and the thiolate system, **3**,[12] both give trimeric complexes in which the central M_3S_3 rings (**2**, M = Pd; **3**, M = Ni, Pd) also adopt a chair conformation in which the planar ligands adopt a propellor-like conformation. These ligands have no substituents on the bridging sulfur atoms and the steric effect of the remainder of the ligand is not sufficient to alter the ring conformation. It is notable that the more sterically demanding phosphide, PPh_2^- forms a nickel complex, $[CpNi(\mu\text{-}PPh_2)]_2$, which is dimeric in nature.[8] This is more typical behaviour among known bridging phosphide species. Studies are ongoing to ascertain whether by further steric manipulation other aggregation states can be obtained.

Acknowledgements

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Notes and references

‡ Preparation of H_2L^4: 2-(phenylphosphino)ethylamine (0.50 g, 3.3 mmol) and salicylaldehyde (0.42 g, 3.3 mmol) were stirred together for 10 min under an N_2 atmosphere and placed in the freezer overnight. The resulting air-sensitive yellow solid was used without further purification. Its identity was confirmed by EI MS (M^+ = 257 (85%); calcd. for $C_{15}H_{16}NOP$ = 257 u).

§ Preparation of $[Ni(L^4)]_3$: anhydrous $NiCl_2$ (0.43 g, 3.3 mmol) was dissolved in absolute ethanol (15 ml) under a flow of dry dinitrogen and ligand H_2L^4 (0.77 g, 3.0 mmol) was added. The mixture was refluxed for 2 h and placed in the freezer. The crop of orange-brown solid obtained (0.14 g, 12%) was filtered off, washed with diethyl ether and dried *in vacuo*. A further crop was obtained by reducing the volume and replacing in the freezer (0.45 g, 38%); mp 238–240 °C (decomp.). An analytical sample was recrystallised from chloroform (Found: C, 48.15; H, 4.21; N, 3.99; P, 8.21. $C_{45}H_{42}N_3Ni_3O_3P_3\cdot 2CHCl_3$ requires C, 47.82; H, 3.76; N, 3.56; P, 7.87%). ν_{max}/cm^{-1} 1605 (ν(C=N), Nujol mull). δ_H (400 MHz; solvent: $CDCl_3$) 1.59 (br, m, 6H), 3.14 (br, s, 2H), 3.48 (br, s, 2H), 3.72 (br, s, 1H), 4.17 (br, s, 1H), 6.51 (br, s, 3H), 6.81 (br, s, 3H), 6.90 (br, s, 3H), 7.06 (br, s, 3H), 7.24–8.39 (br, m, 15H), 8.95 (br, s, 3H).

¶ Crystal data for complex **1**: $C_{45}H_{42}N_3Ni_3O_3P_3\cdot CHCl_3$, M = 1061.24, monoclinic, space group $P2_1/c$ (no. 14), a = 12.698(3), b = 18.833(3), c = 19.677(3) Å, β = 107.16(1)°, U = 4496(1) Å^3, Z = 4, μ = 1.573 mm^{-1}, T = 123 K, R_1 = 0.043, wR = 0.089, GOF = 1.013 for 3474 reflections with $I > 2\sigma(I)$, 550 parameters. CCDC reference number 186/1900. See http://www.rsc.org/suppdata/dt/b0/b001098g/ for crystallographic files in .cif format.

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