

Reactions of Halogen(2,4,6-tri-*tert*-butylphenylimino)phosphine Complexes with Electrophiles and Nucleophiles: Abstraction or Substitution of the Halogen

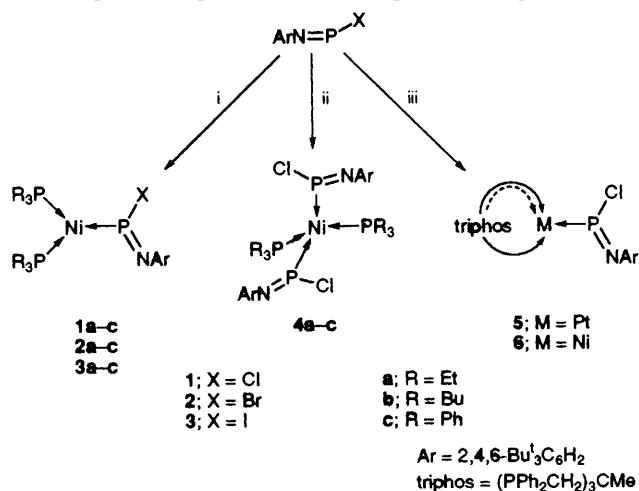
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The structure of the first nickel halogeniminophosphine complex, *i.e.* (PEt₃)₂Ni(X-P=NAr)₂ (Ar = 2,4,6-tri-*tert*-butylphenyl); X = Cl is reported; reactions of this and related compounds with AlCl₃ afford the cationic complexes **7–10**; the alkyliminophosphine complexes **12** and **13** are obtained by treatment of the chloroiminophosphine complexes **1a** and **4a** with Grignard reagent.

Recently, we described the first complexes of the 16-electron chloroiminophosphine complexes **1a–c** and the 18-electron species **4a–c**.¹ Owing to the functionality at the low coordinated phosphorus atom these compounds are expected to show versatile reactivity. Here we report the first structure of these complexes and describe their reactions with Lewis acids and Grignard reagent. In order to gain an insight into the



Scheme 1 Reagents and conditions: i, [Ni(R₃P)₂(cod)] (1 equiv.), toluene, 0 °C; ii, [Ni(R₃P)₂(cod)] (0.5 equiv.), toluene, 0 °C, iii, [Ni(triphos)] or [Pt(Me₂PhP)(triphos)] (1 equiv.), toluene, 0 °C

reaction behaviour we also report the synthesis of the bromo- and iodo-analogues of compounds **1a–c**.

The single crystal X-ray analysis of complex **4a**[†] confirms the structure which was deduced from ³¹P NMR data[‡] in which the nickel centre is surrounded by four phosphorus atoms in a nearly ideal tetrahedral arrangement. The molecular structure possesses crystallographic C₂ symmetry with

[†] *Crystal data* for **4a**: Red single crystals of **4a** were grown from benzene at room temp. C₄₈H₈₈Cl₂N₂NiP₄, *M* = 946.7, monoclinic, space group *P2₁/n*, *a* = 11.221(3), *b* = 15.953(4), *c* = 15.451(4) Å, β = 92.33(2)°, *V* = 2763.6(11) Å³; *Z* = 2; *D_c* = 1.14 mg mm⁻³; μ(Mo-Kα) = 0.59 mm⁻¹ *F*(000) = 1024; λ(Mo-Kα) = 0.71073 Å; *R* = 0.088 [*R_w* = 0.069, w⁻¹ = σ²(*F*)] [4904 unique reflections, 3363 data with *F* > 4.0σ(*F*)]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[‡] *Selected NMR data* for **4a**: ³¹P (C₆D₆), δ 162.7 (t, 37.1 Hz), 13.3 (t, 37.1 Hz); ¹H (C₆D₆), δ 7.36 (b, 12H) PCH₂CH₃, 1.4 (s, 54H) Bu^t, 1.2 (b, 18H) PCH₂CH₃, **2a**: ³¹P (C₆D₆), δ 250.2 (t, 103.1 Hz), 22.4 (d, 103.1 Hz); **2b**: ³¹P (C₆D₆), δ 251.6 (t, 107.3 Hz), 15.0 (d, 107.3 Hz); ¹H (C₆D₆), δ 7.33 (s, 2H) Ar, 2.0 (b, 12H) PCH₂CCC, 1.5 (b, 27H) Bu^t, 1.3 (b, 24H) PCCCH₂CH₂C, 1.0 (b, 18H) PCCCCH₃; **2c**: ³¹P (C₆D₆), δ 229.0 (t, 109.7 Hz), 26.9 (d, 109.7 Hz); ¹H (C₆D₆), δ 7.0–7.8 (b, 32H) H_{arom}, 1.36 (s, 9H) *p*-Bu^t, 1.28 (m, 18H) *o*-Bu^t; **5** two isoimers: ³¹P (C₆D₆) (*a*) δ 230.9 (t, 73.2 Hz; ¹J_{PtP} 5581 Hz), -5.5 (d, 73.2 Hz; ¹J_{PtP} 3505 Hz); -27.2; (*b*) δ 227.9 (t, 73.2 Hz; ¹J_{PtP} 5581 Hz), -4.0 (d, 73.2 Hz; ¹J_{PtP} 3505 Hz); -27.2; **6**: ³¹P (C₆D₆), δ 174.6 (q, 25.7 Hz), 13.9 (d, 25.7 Hz).

the Ni atom lying on a twofold axis. As predicted by theoretical investigations² the chloroiminophosphine is η^1 -bonded as a consequence of the carbene-like frontier orbital sequence. The bond length Ni–P(=N) (207 pm) is about 7% shorter than the Ni–PR₃ distance (222 pm) which can be attributed not only to the different hybridisation state of the phosphorus atoms but also to a back donation from the metal

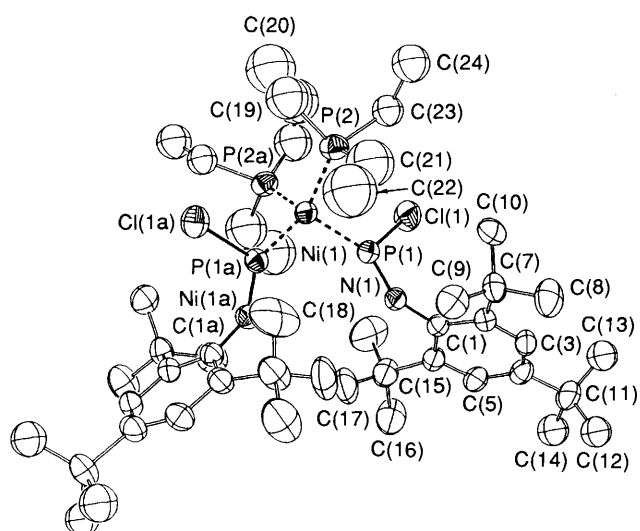
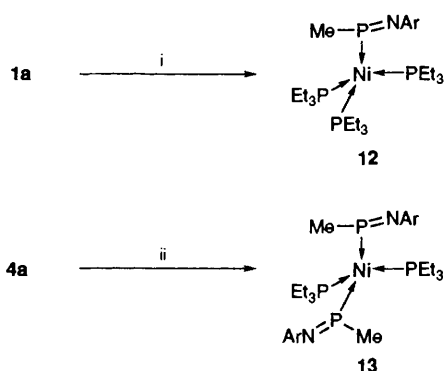
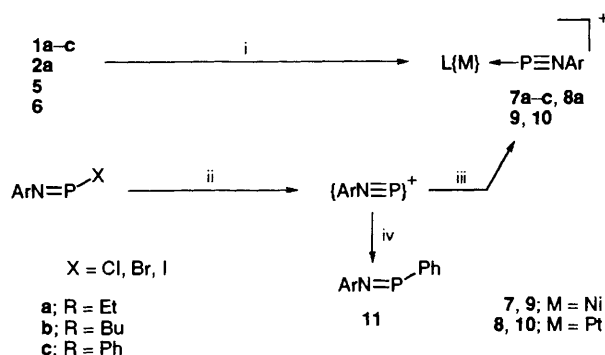


Fig. 1 ORTEP view of the structure **4a**, with ellipsoids drawn at the 30% probability level. Selected distances (Å) and angles (°) are: Ni–P(1) 2.069(2), Ni–P(2) 2.221(2), P(1)–Cl(1) 2.145(3), P(1)–N(1) 1.498(5), P(1)–Ni–P(2) 107.8(1), P(1)–Ni–P(1a) 109.4(1), P(2)–Ni–P(1a) 110.9(1), P(2)–Ni–P(2a) 110.3(1), Cl(1)–P(1)–N(1) 108.1(2), P(1)–N(1)–C(1) 142.1(5)

atom to the ligated P=N fragment. Compared with the free ligand the P–N–C(1) angle (142.1°) is reduced by 12.7° which correlates with a reduced s-character of the P=N double bond.

The 16-electron bromo- and iodo-iminophosphine complexes **2a–c** and **3a–c** can be obtained in good yields by treatment of Ni(R₃P)₂(cod) (cod = cycloocta-1,5-diene) with the halogenated iminophosphine (1 equiv.). Comparison of the chemical shift of the low-coordinated phosphorus atoms with the electronegativity of the attached halogen reveals that the nucleus becomes more shielded ($\Delta\delta \sim 20$ ppm) the lower the electronegativity of the halogen. This is opposite to the free ligands, reflecting that the chemical shift of the coordinated phosphorus is strongly influenced by back donation of the metal.

Compounds **5** and **6**, which are with respect to the latter more sensitive towards thermal decomposition, were generated by reaction of the iminophosphine with Pt(Me₂PhP)(triphos) or Ni(triphos) [triphos = (PPh₂CH₂)₃CMe]. In solution two isomers of the platinum complex **5** exists.

Treatment of **1a–c** with AlCl₃ at 0 °C in the presence of the corresponding phosphine yields the cationic complexes **7a–c**. The presence of one [P≡N]⁺ moiety and three phosphine groups is indicated by the AX₃ coupling pattern in the ³¹P{¹H}-NMR spectra. Both, the large ²J_{PP} (65–93 Hz) and the relatively large ¹J_{PtP}-coupling constants (2817 Hz)³ in **8a** give evidence for an η^1 -coordination of the cationic iminophosphine ligands, which is further confirmed by use of triphos as a ligand. The complexes **9** and **10**, made in the same way as compounds **7**, also show the AX₃ coupling pattern, while a side-on coordination would lead to an AX₂ pattern as a consequence of the loss of one ligand.^{3b} Furthermore, solid-state NMR spectra of the nickel compounds **7a** and **9** have been carried out and confirm that the structure in solution is the same as those in the solid state.

The much larger ¹J_{PtP=N} value in **10** with respect to **8a** is in agreement with earlier investigations^{4,5} and results from the division of s-character in the Pt hybrids used to bind to the ligands. Thus, the geometry of triphos leads to an increased p-character of the Pt triphos bond (angle P–Pt–P ~ 95°); as a consequence the Pt P≡N bond has more s-character and therefore shows an increased coupling constant.⁵ However, the ¹J_{PtP=N} values in both complexes are smaller than expected. This is due to the positive charge of the iminophosphine ligand which results in a decreased electron density at the phosphorus atom and finally in a reduced coupling constant.⁶

Treatment of the compounds **1a–3a** with NaBPh₄ yields the expected cation **7a** only with the bromo- or iodo-complexes while the chloroiminophosphine complex **1a** remains unaffected. A more direct synthetic route is to prepare the free iminophosphine-cation first followed by complexation. However, this reaction has to be carried out below –70 °C, otherwise a substitution reaction of the halogen by a phenyl group from the BPh₄[–] results in the formation of the phenyliminophosphine **11**.⁷ Treatment of the compounds **1a** or **4a** with MeMgI leads to a substitution reaction yielding the

§ Selected spectroscopic data for **7a**: ³¹P (C₆D₆), δ 209.9 (q, 64.7 Hz), 18.6 (d, 64.7 Hz); ¹H (C₆D₆), δ 7.4 (s, 2H) Ar, 1.44 (m, 18H) PCH₂C, 1.4 (s, 18H) *o*-Bu^t, 1.38 (s, 9H) *p*-Bu^t, 1.24 (s, 27H) PCCCH₃; ²⁷Al (C₆D₆), δ 102.9 (s); MS [FAB/*meta*-nitrobenzyl alcohol (*m*NBA)]: *m/z* (%) = 702.2 (3.4) [M⁺], 584.2 (68.2) [M⁺–PEt₃], 466.2 (76.4) [M⁺–2PEt₃], 290.0 (56.4) [M⁺–Ni(PEt₃)₃]; **7b**: ³¹P (C₆D₆), δ 211.1 (q, 67.6 Hz), 11.5 (d, 67.6 Hz); ¹H (C₆D₆), δ 7.38 (s, 2H) Ar, 1.55 (b, 18H) PCH₂CCC, 1.48 (b, 36H) PCCH₂CH₂C, 1.34 (b, 36H) Bu^t, 0.94 (s, 27) PCCCH₃; ²⁷Al (C₆D₆), δ 102.6 (s); MS (FAB/*m*NBA): *m/z*(%) = 752.5 (50.9) [M⁺ – PBu₃], 550.3 (49.1) [M⁺ – 2PBu₃], 462.3(45.5) [M⁺ – P=N–Ar], 290.2 (56.4) [M⁺ – Ni(PBu₃)₃]; **7c**: ³¹P (C₆D₆), δ 210.6 [m(b)]; 27.7 [d(b) 69.2 Hz]; **8a**: ³¹P (C₆D₆), δ 128.0 (q, 92.3 Hz; ¹J_{PtP} 2817 Hz), 4.4 (d, 92.3 Hz; ¹J_{PtP} 3651 Hz); **9**: ³¹P (C₆D₆), δ 192.7 (q, 34.2 Hz), 22.9 (d, 34.2 Hz); **10**: ³¹P (C₆D₆), δ 138.1 (q, 97.7 Hz, ¹J_{PtP} 6250 Hz), –3.9 (d, 97.7 Hz; ¹J_{PtP} 3123 Hz).

complexes **12**¶ and **13**. These complexes are of particular interest, because the free methyl-iminophosphine is unstable towards dimerisation.⁸

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¶ Selected NMR data of **12**: ³¹P (C₆D₆), δ 289.1 (q, 41.2 Hz), 9.5 (d, 41.5 Hz); **13**: ³¹P (C₆D₆), δ 313.7 (t, 15.3 Hz), 16.5 (t, 15.3 Hz); ¹³C (C₆D₆), δ 14.1 (d, 103.1 Hz) Me-P=N.

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