Generation and Spectroscopic Characterization of the First Chloro(2,4,6-tri-t-butylphenylimino)phosphine Complexes

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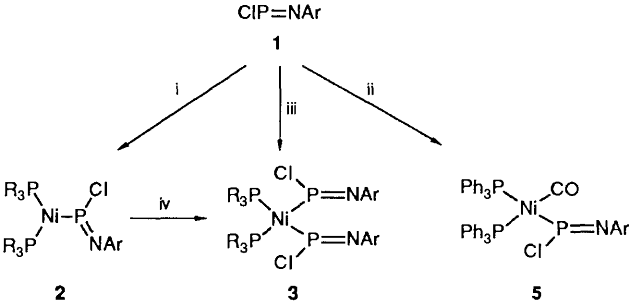
Reactions of X–P=NAr (Ar = 2,4,6-$Bu^t_3C_6H_2$; X = halogen), with a variety of nickel(0) and platinum(II) phosphine complexes afford the first examples of σ-complexes containing *P*-functionalized iminophosphines whose structures have been elucidated by NMR spectroscopy.

The coordination and organometallic chemistry of low-coordinate phosphorus compounds is still attracting a great deal of interest. The versatility of iminophosphines with respect to this field of chemistry has already been demonstrated,[1] with the great majority of coordination compounds, however, containing only amino-iminophosphine ligands. Here, we report on the first transition metal complexes containing the *P*-functionalized iminophosphine X–P=NAr (**I–III**).[2]

Thus, treatment of toluene solutions of the nickel alkene complexes $[(R_3P)_2Ni(C_2H_4)]$ (R = Ph, Bu^n, Et) with one



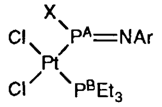
a; R=Ph
b; R=Bu^n
c; R=Et

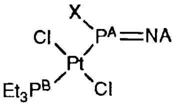
Scheme 1. *Reagents and conditions:* i, $[(R_3P)_2Ni(C_2H_4)]$ (1 mol. equiv.), toluene, −30 °C; ii, $[(Ph_3P)_2Ni(CO)_2]$ (1 mol. equiv.), heat or *hν*; iii, $[(R_3P)_2Ni(C_2H_4)]$ or $[(R_3P)_2Ni(cod)]$ (0.5 mol. equiv.), toluene; iv, **I** (1 mol. equiv.).

equivalent of **I** at −30 °C results in the evolution of ethylene and formation of the deeply coloured (dark red-brown) 16-electron species (**2a–c**).†

The presence of only one chloro-iminophosphine molecule in these nickel complexes is readily deduced from the AX_2 pattern in the ^{31}P ^1H NMR spectra of **2a–c**. The large coupling constants ($J_{PP} > 100$ Hz) and the rather deshielded resonances due to the iminophosphine moieties reveal their σ-coordination involving the phosphorus lone pair, thus indicating a trigonal planar environment on the nickel centre. This interpretation is supported by comparing the ^{31}P NMR data of **2a–c** with the chemical shifts found for η^2-bound iminophosphine ligands,[3] the phosphorus nuclei of which resonate at much higher field. Furthermore, the J_{PP} coupling constants are drastically reduced on going from coordinatively unsaturated to saturated nickel compounds. Strong support for this interpretation is provided by the marked dependence of the phosphorus chemical shifts of **2a–c** on the solvent. Thus, use of donor solvents like diethyl ether or tetrahydrofuran leads to increased shielding of the iminophosphine resonances with concomitant reduction of J_{PP}. This effect is also demonstrated by the following reactions.

Treatment of **2a–c** with a further equivalent of **I** furnishes the 18-electron species **3a–c**, the identity of which was again inferred from their ^{31}P NMR data.† The A_2X_2 type spectra together with the reduced phosphorus–phosphorus coupling constants are clearly indicative of a nickel centre surrounded tetrahedrally by two phosphine and two chloro-iminophosphine ligands. Alternatively, **3a–c** can be obtained by treating the appropriate $[(R_3P)_2Ni(cod)]$ complexes (cod = cycloocta-1,5-diene) with **I** in a 1 : 2 ratio. ^{13}C and ^1H NMR spectra were also recorded for **2** and **3** but were not particularly informative.





6 X = Cl
7 X = Br
8 X = I

9 X = Br
10 X = I

X-P=NAr
I, X=Cl
II, X=Br
III, X=I

Ar = 2,4,6-$Bu^t_3C_6H_2$

Surprisingly, a compound containing three σ-coordinated Cl-P=NAr molecules is formed by the reaction of the bis(alkene)complex $[(Ph_3P)Ni(C_2H_4)_2]$ generated *in situ* with two equivalents of **I**. $[(Ph_3P)Ni(ClP{=}NAr)_3]$ **4**, which is thermally quite labile, gives rise to an AX_3 spectrum with the observed data† fitting in well with those found for the above compounds. Complex **4** is formed together with an as yet unidentified phosphorus-containing product.

Only one carbonyl ligand can be substituted in $[(Ph_3P)_2Ni(CO)_2]$ by either thermal or photochemical activation, thus affording complex **5**, which was fully characterized by its spectroscopic data.† Again σ-coordination of the iminophosphine ligand to a tetrahedral nickel centre was observed. The ^{31}P NMR spectra of all the compounds mentioned so far remain unchanged in the presence of free ligand. In contrast to the findings of Scherer *et al.*,[4] who synthesized several amino-iminophosphine species starting from $[Ni(cod)_2]$, reaction of **1** with the latter did not produce isolable compounds but led to decomposition of the nickel complex with formation of nickel(0).

Treatment of $[(PtCl_2(PEt_3)_2]$ with **I** readily affords *cis*-$[(PtCl_2(PEt_3)(ClP{=}NAr)]$ **6**, which as expected exhibits a large $^1J_{PtP}$ coupling constant of 5778 Hz for σ-ligated chloroiminophosphines.† Analogous reactions with **II** and **III** in toluene lead to mixtures of *cis*-**7** and **8** and *trans*-isomers **9** and **10**, respectively.† Interestingly addition of light petroleum (b.p. 60–80 °C) converts the mixture of **7** and **9** into the *cis*-isomer **7** whereas the *trans*-isomer **10** is formed from a mixture of **8** and **10**. Spectroscopic evidence has also been obtained for halogen exchange reactions in the series of platinum(II) complexes.

The ligating properties of halogeno-iminophosphines towards zerovalent molybdenum and tungsten complexes are currently under study.

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† **2a**: $^{31}P\{^1H\}$ NMR: (32.2 MHz; ppm from ext. H_3PO_4; in C_6D_6; *J* values in Hz): 241.0 (t, *J* 107.8) and 28.9 (d, *J* 107.8); **2b**: $^{31}P\{^1H\}$ NMR: 266.9 (t, *J* 104.2) and 18.5 (d, *J* 104.2); **2c**: $^{31}P\{^1H\}$ NMR: 262.9 (t, *J* 100.3) and 25.8 (d, *J* 100.3).

3a: $^{31}P\{^1H\}$ NMR: 181.1 (t, *J* 37.3 and 29.2 (t, *J* 37.3); **3b**: $^{31}P\{^1H\}$ NMR: 169.9 (t, *J* 38.2) and 5.4 (t, *J* 38.2); **3c**: $^{31}P\{^1H\}$ NMR: 281.4 (t, *J* 31.7) and 17.4 (t, *J* 31.7 Hz). The shift value of 281.4 appears to be out of line, and efforts to confirm the structure suggested are in progress.

4: $^{31}P\{^1H\}$ NMR: 186.0 (d, *J* 14.5 and 27.7 (q, J 14.5).

5: $^{31}P\{^1H\}$ NMR: 172.4 (t, *J* 33.4 and 30.8 (d, *J* 33.4); $^{13}C\{^1H\}$ NMR: (50.0 MHz, in C_6D_6): δ 199.4 (m, CO); 149.8 (d, *J* 4.8), 149.2 (d, *J* 2.8), 143.5 (d, *J* 5.7), 137.7 (dd, *J* 3.9 and 30.5), 136.5 (ddd, *J* 1.9, 4.2 and 34.5): Ni–PN*C*, PNC*C*, PNCCC*C*, P*C*; 134.2–133.4 (m), 129.5–128.2 (m), 124.0 (d, *J* 2.2): Ni–PNCC*C*, PC*C*, PCC*C*, PCCC*C*; 36.7 (s, *o*-CMe_3); 34.8 (s, *p*-CMe_3); 33.1 (s, *o*-CMe_3); 31.7 (s, p-CMe_3); IR (pentane): ν 1993 cm^{-1}.

6: $^{31}P\{^1H\}$ NMR: δ(P^A) 70.6 [d, *J*(P^AP^B) 20]; δ(P^B) 15.9 [^1J(PtP^A) 5778, ^1J(PtP^B) 3227]: δ(Pt) −2588 ppm rel. to K_2PtCl_4.

7: $^{31}P\{^1H\}$ NMR: δ(P^A) 73.1 [d, *J* (P^AP^B) 16.7]; δ(P^B) 12.8 [^1J(PtP^A) 5662, ^1J(PtP^B) 3225].

8: $^{31}P\{^1H\}$ NMR: δ(P^A) 74.0 [d, *J*(P^AP^B) 19.5]; δ(P^B) 16.5 [^{1}J(PtP^A) 5693; ^1J(PtP^B 3228].

9: $^{31}P\{^1H\}$ NMR: δ(P^A) 121.7 [d, *J*(P^AP^B) 737.3]; δ(P^B) 8.5 [^1J(PtP^A) 3223; ^{1}J(PtP^B) 2622].

10: $^{31}P\{^1H\}$ NMR: δ(P^A 117.6 [d, *J*(P^AP^B) 740.5]; δ(P^B) 1.5 [^1J(PtP^A) 3238; ^1J(PtP^B) 2535].