

Short communication

The metallation of imino(triphenyl)phosphorane by ethylmagnesium chloride: The synthesis, isolation and X-ray structure of $[\text{Ph}_3\text{P}=\text{NMgCl} \cdot \text{O}=\text{P}(\text{NMe}_2)_3]_2$ ¹

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Received 2 April 1997; received in revised form 30 June 1997

Abstract

Imino(triphenyl)phosphorane, $\text{Ph}_3\text{P}=\text{NH}$ **1a**, is metallated by ethylmagnesium chloride to give the *N*-magnesiioiminophosphorane complex $[\text{Ph}_3\text{P}=\text{NMgCl} \cdot \text{O}=\text{P}(\text{NMe}_2)_3]_2$ **4**, whose X-ray structure has been determined. © 1998 Elsevier Science S.A.

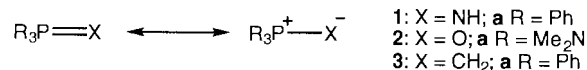
Keywords: X-ray diffraction; Iminophosphorane; Organomagnesium; Grignard reagent

1. Introduction

Iminophosphoranes **1** have attracted much interest as both neutral and anionic ligands to transition metals [1–3]. However, their main group metal chemistry is far less well developed. For example, no simple s-block metal-neutral iminophosphorane complexes are known and only one example of a s-block *N*-metallated (lithiated) iminophosphorane has so far been reported [4]. This is surprising on two counts. First, iminophosphorane anions are of considerable utility in both organic [1,2,5] and organometallic synthesis [2]. Secondly, iminophosphoranes are closely related to (i.e., are iso-electronic with) phosphine oxides **2**, which, particularly in the guise of hexamethylphosphoramide HMPA **2a**, have been used extensively as Lewis bases in s-block metal chemistry [6,7]. In this context, we herein report preliminary results of our investigations into the interaction of iminophosphoranes with organomagnesium compounds. In the presence of HMPA, imino(tri-

phenyl)phosphorane **1a** is metallated by EtMgCl , to give a *N*-magnesiioiminophosphorane complex.

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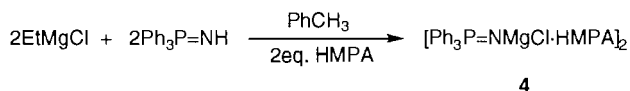
2. Results and discussion

Reaction of imino(triphenyl)phosphorane with EtMgCl in toluene solution yields a white precipitate that dissolves with the addition of HMPA. Refrigeration of this solution then affords a crop of colourless crystals. Characterisation of the isolated solid, ultimately by X-ray crystallography, identified it to be $[\text{Ph}_3\text{P}=\text{NMgCl} \cdot \text{O}=\text{P}(\text{NMe}_2)_3]_2$ **4** (Scheme 1).

In the solid state (Fig. 1), **4** dimerises through μ_2 -bridging nitrogen atoms of the deprotonated iminophosphorane group to give a square, planar Mg_2N_2 ring [$\text{Mg}-\text{N4}$ and $\text{Mg}-\text{N4a}$ distances, 2.038(1) and 2.039(1) Å, respectively; sum of four internal angles of Mg_2N_2 ring, 360°]. The terminal chlorine atoms bound to Mg adopt a *trans* configuration relative to this ring [$\text{Mg}-\text{Cl}$

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¹ Dedicated to Professor Ken Wade on the occasion of his 65th birthday in recognition of his outstanding contributions to inorganic and organometallic chemistry which continues to be an inspiration both in Durham and much further afield.



Scheme 1.

distance, 2.354(1) Å], and the distorted tetrahedral coordination of magnesium is completed by a terminal and neutral HMPA ligand bound to the metal centre [Mg–O distance, 1.960(1) Å]. The P–N bond length of the iminophosphorane anion in **4** [P2–N4, 1.555(1) Å] is shorter than found in the parent iminophosphorane [1.582(2) Å from neutron diffraction data measured at 20 K] [8]. This suggests the retention of a significant degree of P=N double bond character upon deprotonation and coordination, and is consistent with an essentially electrostatic interaction between the anion and the Mg cations. To our knowledge, complex **4** is the first example of an alkaline-earth metal-substituted iminophosphorane to be characterised in the solid state although Hall et al. [9] have previously reported the related X-ray structures of two imido-alkaline earth metal compounds, $[\text{Bu}^t\text{C}=\text{N}]_2\text{Be}_2$, and $[(\text{Ph}_2\text{C}=\text{N})\text{MgBr}]_2 \cdot 3\text{THF}$ [10], both of which contain

M_2N_2 rings with μ_2 -bridging $\text{R}_2\text{C}=\text{N}^-$ anions. In these two dimers, and in imidolithium compounds containing μ_2 -bridging $\text{R}_2\text{C}=\text{N}^-$ anions [11], the iminic nitrogen atoms possess a planar coordination geometry (i.e., the C=N bond vector is coplanar with the M_2N_2 ring). In contrast, N4 in **4** is pyramidalised and the P=N bond vector is at an angle to the Mg_2N_2 plane [P2–N4–X 166° (where X = midpoint between the two Mg atoms)]. While there is no obvious steric reason for this distortion, a striking similarity between the geometry of the $\text{Ph}_3\text{P}=\text{NMg}_2$ fragment in **4** and that of the ylide $\text{Ph}_3\text{P}=\text{CH}_2$ **3a** [12] (Fig. 2) hints at a possible electronic explanation. In **3a**, the Ph_3P group is distorted from C_{3v} symmetry such that the Ph–P bond perpendicular to the methylene plane (P1–C1, Fig. 2a) is unique and lengthened relative to the remaining two Ph–P bonds and the plane of the ylidic methylene group is tilted towards the unique Ph group. In **4** the same features are present (Fig. 2b): N4 is pyramidalized such that the NMg_2 plane is tilted towards P2–C21, which itself is longer than the other two Ph–P bonds. In **3a**, these structural features are attributed to the ylidic character of the P–CH₂ bond [12,13] and the compara-

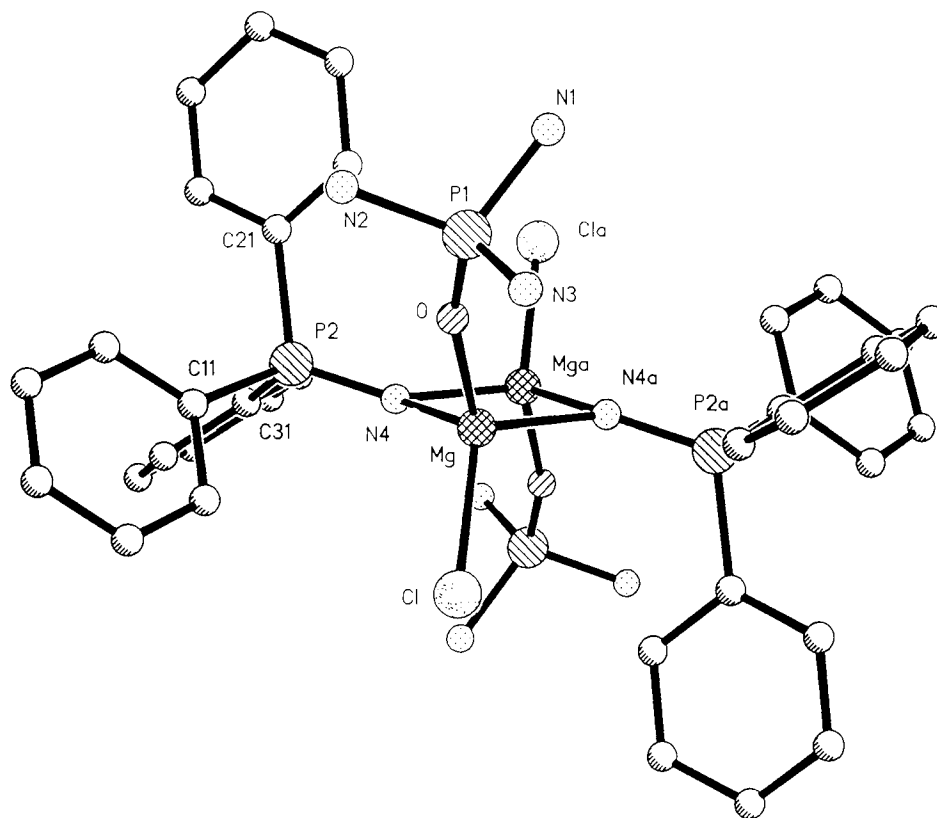


Fig. 1. Molecular structure of $[\text{Ph}_3\text{P}=\text{NMgCl} \cdot \text{O}=\text{P}(\text{NMe}_2)_3]_2$ **4**. All hydrogen atoms and HMPA methyl groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Mg–O, 1.960(1); Mg–N4, 2.038(1); Mg–Cl, 2.354(1); P2–N4, 1.555(1); P2–C11, 1.833(2); P2–C21, 1.845(2); P2–C31, 1.831(2); Mg–N4–Mga, 88.92(5); N4–Mg–N4a, 91.08(5).

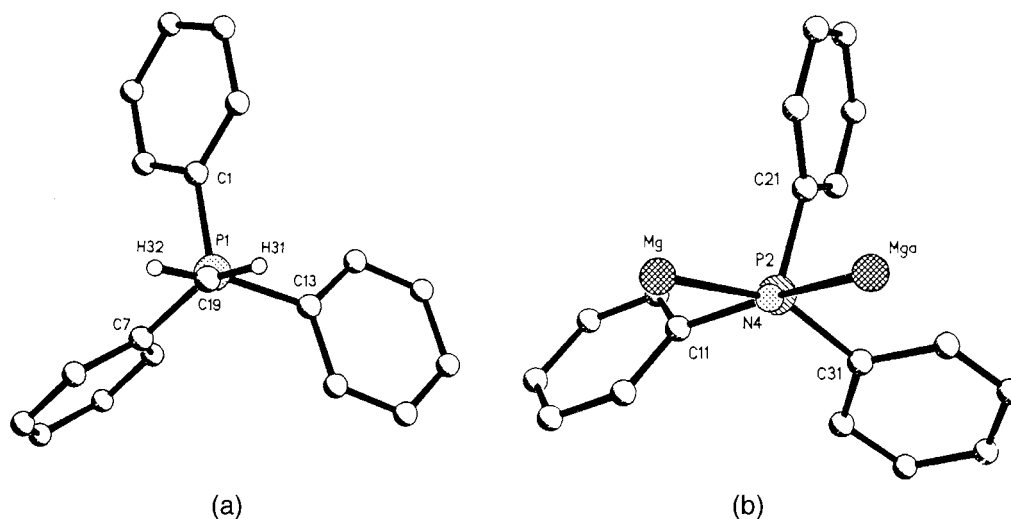


Fig. 2. View of (a) Ph_3PCH_2 [12] and (b) the Ph_3PNMg_2 fragment of **4** showing the pyramidalisation of (a) C19 and (b) N4.

ble geometry found in **4** may be traced to the isoelectronic relationship between R_3PCH_2 and R_3PN^- and the involvement of two lone pairs of electrons in **4** in (predominantly electrostatic) interactions with Lewis acidic Mg centres leaving one pair of electrons for π -bonding (or in a N p orbital).

Further evidence that the deviation from planarity at nitrogen may not be the result of either crystal packing or steric distortion comes from consideration of known structures containing the isoelectronic but neutral HMPA **2a**. A search of the Cambridge Structural Database (CSD) was performed, and nine crystal structures were found in which an HMPA oxygen atom μ_2 -bridges two Li atoms in a simple Li_2O_2 four-membered ring arrangement.² In all these cases, the oxygen atom of HMPA is pyramidalised. The angle P–O–X (where X = midpoint of the two oxygen-bound Li atoms) ranges from 158° to 176° (mean = 167°). Thus, the non planarity of an HMPA P–O unit complexed to two lithium atoms appears to be a general structural feature that may be traced to the ylidic character of the P–O bond in phosphine oxides. In more general terms, these observations on the geometries of R_3PXM_2 fragments (where X = N, O and M = Li, Mg) are consistent with the well-documented low-energy barrier to distortion from planarity of three-coordinate first row atoms bound to second row elements (e.g., NR_2 in silylamines [14] and aminophosphines [15,16] and, as already mentioned, CR_2 in phosphorus ylides [12,13]).

We are currently investigating the s-block metal chemistry of iminophosphoranes further. Preliminary results indicate that the reaction of iminophosphorane

with Grignard reagents does not always lead to metallation, and that magnesium species complexed by neutral N-unsubstituted iminophosphoranes may also be obtained.

3. Experimental details

All compounds were treated as air- and moisture-sensitive, accordingly all reactions and manipulations were carried out in an atmosphere of dry, pure N_2 or argon gas, using standard Schlenk procedures or a glove-box. Solvents were distilled over Na/K alloy. **1a** was prepared as described elsewhere [8] and stored in a glove-box, HMPA was obtained commercially and pre-dried over activated molecular sieve ($13\times$) prior to use. EtMgCl was obtained from Aldrich and used as received.

3.1. Preparation of $[\text{Ph}_3\text{P}=\text{NMgCl}\cdot\text{O}=(\text{NMe}_2)_3]_2$ **4**

A solution of **1a** (0.55 g, 2 mmol) in toluene (15 ml) was treated with EtMgCl (1 ml, 2 mmol of 2 M solution in Et_2O). After stirring at room temperature for 15 min, addition of HMPA (0.35 ml, 2 mmol) and gentle warming caused complete dissolution of a colourless precipitate into a pale yellow solution. Storage at 5°C for 24 h yielded a crop of X-ray quality crystals of **4** (0.73 g, 71%), m.p. $161\text{--}162^\circ\text{C}$. Elemental analysis calculated for $\text{C}_{24}\text{H}_{33}\text{ClMgN}_4\text{OP}_2$: C 56.03, H 6.70, N 10.60, P 11.66; found: C 55.95, H 6.46, N 10.87, P 12.02. ^1H NMR (200 MHz, C_6D_6 , TMS): $\delta = 2.0$ (18H, d, $^3J_{\text{PH}} = 9.7$ Hz, Me_2N); 7.2–8.3 (15H, m, ArH). ^{31}P NMR (101.2 MHz, C_6D_6 , 85% H_3PO_4): $\delta = 23.3$ (s, HMPA); 2.6 (s, $\text{Ph}_3\text{P}=\text{N}^-$).

² CSD refcodes: CIDZQA, CIPJOA, GIVBUI, JAKNAK, SEVDUS, VAHLUL, VASRUC, VUNGUG, ZEHMEE.

3.2. Crystal structure determination of $[Ph_3P = NMgC \cdot O = P(NMe_2)_3]_2 \cdot 4$

$C_{48}H_{66}Cl_2Mg_2N_8O_2P_4$, $M = 1030.49$, colourless crystal of $0.4 \times 0.3 \times 0.3$ mm size, $T = 150(2)$ K, triclinic, $a = 10.249(1)$, $b = 11.313(1)$, $c = 13.050(1)$ Å, $\alpha = 114.5(1)$, $\beta = 94.3(1)$, $\gamma = 96.3(1)^\circ$, $U = 1924.4(3)$ Å³ (from 483 reflections $12 < \theta < 28^\circ$), space group $P\bar{1}$, $Z = 1$, $D_c = 1.26$ g cm⁻³, graphite-monochromated Mo–K α radiation, $\lambda = 0.71073$ Å, $\mu = 0.31$ mm⁻¹; data collection on a Siemens 3-circle diffractometer with a CCD area detector ω scan mode, $2\theta \leq 60.7^\circ$, 11 101 total, 7148 unique, 6325 observed ($I > 2\sigma(I)$) data, $R_{int} = 0.0251$. The structure was solved by direct methods [15] and refined by full-matrix least squares [16] against F^2 (non-H atoms anisotropic, H atoms isotropic, 430 variables/7081 data) to $wR(F^2, \text{all data}) = 0.1168$, goodness-of-fit 1.14, $R(F, \text{obs. data}) = 0.0455$; $\Delta\rho_{max} = 0.55$ e Å⁻³.

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