Nature of the bonding in a carbene–phosphinidene: a main group analogue of a Fischer carbene complex? Isolation and characterisation of a bis(borane) adduct

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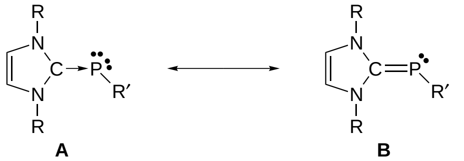
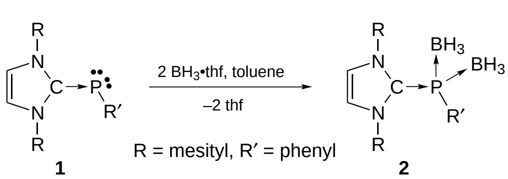
The reaction of the carbene–phosphinidene (1,3-dimesitylimidazolin-2-ylidene)PPh 1 with BH$_3$·thf affords the corresponding P-bonded bis(borane) adduct, thus demonstrating the availability of two lone pairs on the phosphorus centre; base competition studies reveal that 1 is a strong phosphorus base and, by means of cyclic voltammetry, it is established that 1 undergoes facile oxidation.

It has been demonstrated recently[1,2] that stabilised carbenes are sufficiently nucleophilic to depolymerise cyclopolyphosphines such as (PPh)$_5$ and (PCF$_3$)$_4$ and produce compounds of the type (carbene)PR. Two extreme canonical forms, **A** and **B**, can be written for such species. Form **A** represents a phosphinidene adduct of a carbene and involves a carbon–phosphorus dative bond of order one whilst **B** corresponds to a conventional phosphaalkene and features a double bond between carbon and phosphorus. There is, in fact, an interesting parallel with transition metal carbene complexes, albeit with the roles of metal and carbene being played by carbene and phosphinidene respectively in the cases of forms **A** and **B**. Thus the low-valent form **A** resembles a Fischer-type complex and the high-valent form **B** is akin to a Schrock-type alkylidene complex. In terms of metrical parameters, it has been found[1,2] that the P–C(carbene) bond is only *ca*. 4% longer than the P–C(R) single bond and that the P–C(R) moiety is twisted out of the carbene plane by 18–20°. Taken in concert with the high-field ^{31}P chemical shifts, these data imply that the pπ–pπ bond between carbon and phosphorus is not well developed. It occurred to us that further important information regarding the electronic structures of these compounds might stem from Lewis-basicity and electrochemical studies. The Lewis-base behaviour was expected to be particularly revealing since a conspicuous difference between **A** and **B** concerns the fact that these forms feature two and one phosphorus lone pairs, respectively. Treatment of **1**[2] with BH$_3$·thf in toluene solution resulted in the exclusive formation of the bis(borane) adduct **2** (Scheme 1).†



A **B**



1 **2**

Scheme 1

Interestingly, no evidence for a 1 : 1 BH$_3$ adduct could be found by NMR titration.‡ The X-ray crystal structure of **2** (Fig. 1)§ confirmed the attachment of two BH$_3$ groups to the phosphorus centre and, in addition, showed that the P–C(carbene) bond lengthened by 0.093 Å and the C–P–C angle increased by 4.9° in the conversion of **1** to **2**. An increase in bond length is anticipated if it is assumed that **1** features a modicum of back π-bonding from phosphorus to the carbene carbon atom which is lost upon borane attachment. Such a view finds a parallel in the molecular orbital theory of Fischer-type carbene complexes.[3] It should be noted, however, that some of the increase in the P–C(carbene) bond length could be accounted for by increased steric interactions. The increase in bond angle is consistent with the valence shell electron pair repulsion (VSEPR) model[4] in the sense that two lone pairs in **1** are replaced by two bond pairs in **2**. The P–B bond lengths [av. 1.946(2) Å] are normal and the geometry at phosphorus is approximately tetrahedral. The following additional points are also noteworthy: (*i*) the formation of **2** can be regarded as an example of base-induced coordination[5] of an electrophilic fragment (a phosphinidene in this case), and (*ii*) given that BH$_3$ and M(CO)$_5$ moieties (M = Cr, Mo, W) are isolobal, there is an interesting parallel between **2** and base·E(R)[M(CO)$_5$]$_2$ (E = P, As) complexes.[6]

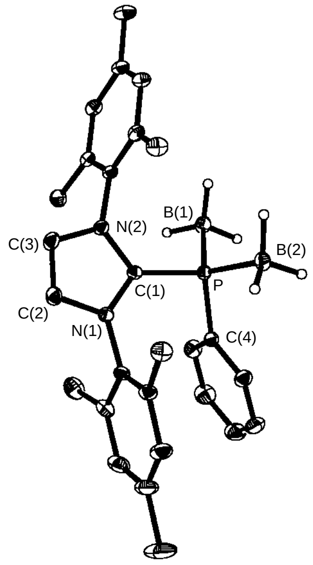


Fig. 1 Molecular structure of **2** showing the atom numbering scheme. Selected distances (Å) and angles (°): P–C(1) 1.856(2), P–C(4) 1.828(2), P–B(1) 1.945(2), P–B(2) 1.948(2), C(1)–N(1) 1.355(2), N(1)–C(2) 1.377(2), C(2)–C(3) 1.337(2), N(2)–C(3) 1.374(2), C(1)–N(2) 1.358(2); C(1)-P–C(4) 104.78(7), C(1)–P–B(1) 109.33(8), C(1)–P–B(2) 109.20(8), B(1)–P–B(2) 117.46(10), C(4)–P–B(1) 106.60(9), C(4)–P–B(2) 108.71(9), N(1)–C(1)–N(2) 105.14(13), C(1)–N(1)–C(2) 110.33(14), N(1)–C(2)–C(3) 106.9(2), C(2)–C(3)–N(2) 107.6(2), C(3)–N(2)–C(1) 109.96(13).

An attempt at qualitative basicity assessment of **1** was made by treatment of **2** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), and PAr_3 **3** [Ar = $C_6H_2(OMe)_3$-2,4,6]. It was found that both DBU and DBN removed the BH_3 moieties from **2** quantitatively whilst **3**, the most basic tertiary phosphine known so far (pK_a 11.2),[7] failed to react. The pK_a of **1** is therefore likely to exceed 11.2.

Further support for the carbene–phosphinidene bonding description (form **A**) stemmed from cyclic voltammetry experiments.¶ Thus, acetonitrile solutions of **1** exhibit an irreversible one-electron oxidation at −0.08 V (*vs*. SCE). Such a low oxidation potential is consistent with an electron-rich phosphorus centre since the one-electron oxidation potentials of typical phosphaalkenes fall in the range 1.07–2.94 V (*vs*. SCE).[8]

Finally, an effort was made to prepare a 1 : 1 adduct of **1** by treatment with an equimolar quantity of the more sterically demanding Lewis acid, BPh_3. Interestingly, this reaction resulted in phenylphosphinidene extrusion and formation of the cyclopolyphosphines $(PPh)_3$, $(PPh)_4$, and $(PPh)_5$.[9] The facile oxidation of carbene–phosphinidenes, coupled with the high basicity at phosphorus, portends an interesting reaction chemistry for these species.

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Footnotes

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† *Experimental procedure*: $BH_3 \cdot thf$ (3.3 cm^3, 1 m solution in thf) was added dropwise over a 5 min period to a stirred solution of the 1,3-dimesitylimidazolin-2-ylidenephenylphosphinidene complex (0.68 g, 1.65 mmol)[2] in 50 cm^3 of toluene. During the course of the addition, the solution turned from yellow to colourless. A large amount of white precipitate formed, and an NMR assay of the supernatant liquid indicated complete precipitation of all phosphorus-containing species. The supernatant liquid was removed, and the residual solid was pumped dry and recrystallised from CH_2Cl_2 (1 day, −20 °C) (yield 0.53 g, 1.2 mmol, 73%), mp 200–203 °C. Anal. Calc. for $C_{27}H_{35}B_2N_2P$; C, 73.67; H, 8.01; N, 6.36. Found: C, 73.60; H, 7.98; N, 6.21%.

‡ *Selected spectroscopic data* for **2**: ^1H NMR (CD_2Cl_2, 300.10 MHz, 298 K) δ 7.59–7.52 (m, aryl, 2 H), 7.30–7.25 (m, aryl, 1 H), 7.12 (s, NCH, 2 H), 7.10–7.05 (m, aryl, 2 H), 6.92 (s, mes CH, 4 H), 2.34 (s, mes *p*-CH_3, 6 H), 2.05 (s, mes *o*-CH_3, 12 H), 0.25–1.0 (br, BH_3, 6 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.48 MHz, 298 K) δ 152.3 (d, $^1J_{PC}$ 32 Hz, NCP), 141.2 (s, *ipso* C_{mes}), 135.9 (s, *o*-C_{mes}), 135.0 (d, $^2J_{PC}$ 8 Hz, *o*-C_{aryl}), 132.9 (s, *p*-C_{mes}), 130.1 (d, $^1J_{PC}$ 39 Hz, *ipso*-C_{aryl}), 130.0 (s, *p*-C_{aryl}), 129.5 (s, *m*-C_{mes}), 127.7 (d, $^3J_{PC}$ 8 Hz, *m*-C_{aryl}), 126.4 (s, CN*C*), 21.2 (s, *p*-CH_3), 18.4 (s, *o*-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.50 MHz, 298 K) δ 4 (br).

§ *Crystal data* for **2**: $C_{27}H_{35}B_2N_2P$, $M = 440.16$, monoclinic, space group $P2_1/c$, $a = 19.957(1)$, $b = 8.462(1)$, $c = 15.163(1)$ Å, $\beta = 94.551(4)°$, $U = 2552.9(4)$ Å^3, $Z = 4$, $D_c = 1.145$ g cm^{-3}, $F(000) = 944$, $T = 153(2)$ K. 5851 independent reflections were collected on a Siemens P4 diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), $2.05 < \theta < 27.50°$, $\mu = 1.25$ cm^{-1}, an absorption correction was applied (face indexed): $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}} = 0.10$ and $R = \Sigma|F_o - F_c|/\Sigma F = 0.045$ for reflections with $I/2\sigma(I) > 2.0$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/434.

¶ Cyclic voltammetry experiments were performed in a helium-filled drybox using a BAS100 electrochemical analyser and a platinum disk working electrode (area = 0.031 cm^2). The reference electrode, a silver wire immersed in 0.01 m $AgSO_3CF_3$–MeCN within a frit, was referenced to an SCE after experiments.

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