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C-Phosphanyl-*C*-chloroiminium salts as electrophilic carbene synthetic equivalents

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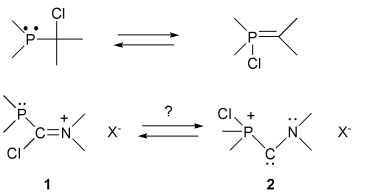
_C_-Phosphanyl-_C_-chloroiminium salts formally react as phosphonio(amino)carbenes with *tert*-butyl isocyanide and trimethylphosphine, and as R_2NC^+ with vinyl ether and diisopropylamine.

In the last fifteen years, several types of stable singlet carbenes have been isolated.[1] However, although both transient nucleophilic and electrophilic singlet carbenes are known,[2] all the stable carbenes prepared so far feature a strong nucleophilic character. We have recently shown that a single amino group was sufficient to stabilise a carbene moiety,[3] and therefore we attempted the preparation of stable phosphonio-substituted aminocarbenes **2**, hoping that the electron withdrawing R_3P^+ group would confer electrophilic properties to the carbene centre.

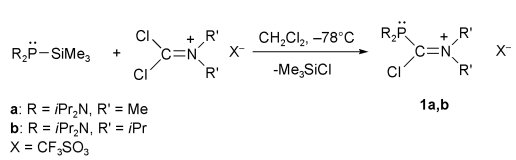
Since α-haloalkylphosphines readily undergo spontaneous 1,2-(C→P)-halotropic shifts,[4] we chose to prepare *C*-phosphanyl-*C*-chloroiminium salts **1** as transient precursors to carbenes **2** (Scheme 1). It is known that *N*,*N*-disubstituted(chloromethylene)iminium salts react with the bis(diisopropylamino)-(trimethylstannyl)phosphine to afford *C*-phosphanyliminium salts.[5] Similarly, the corresponding dichloromethyleneiminium salt[6] cleanly reacts with the corresponding bis(diisopropylamino)(trimethylsilyl)phosphine affording derivatives **1a**,**b**,† which were isolated as yellow crystals in 87 and 91% yield, respectively (Scheme 2).

The ^{31}P NMR spectra of **1a** and **1b** (+70 ppm) did not differentiate between structures **1** and **2**, but the appearance in the ^{13}C NMR spectra of a signal at 193 ppm (**1a**: J_{PC} 92 Hz, **1b**: J_{PC} 108 Hz), was strongly suggestive of the *C*-phosphanyl-*C*-chloroiminium form **1**.[7] The structure of **1a** was established by an X-ray diffraction study (Fig. 1).‡ In agreement with the lower inversion barrier of nitrogen compared to phosphorus,[8] the nitrogen atom is in a planar environment, while the phosphorus atom is strongly pyramidalized (sum of the angles: 311.97°), and the P(1)–C(1) (1.891 Å) and the C(1)–N(1) (1.287 Å) bond lengths are in the range expected for a single and a double bond, respectively.

The desired carbenes **2** were however not formed, but taking into account that the halogenotropy is a reversible process,[9] the



Scheme 1



Scheme 2

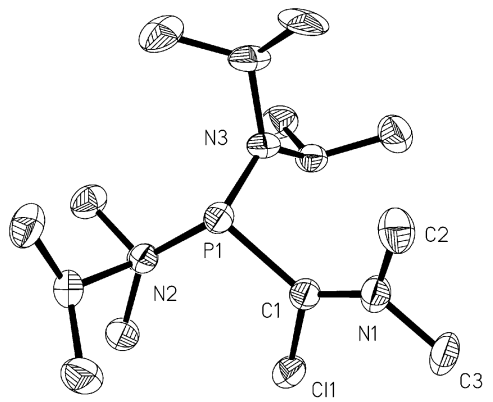


Fig. 1 Solid state structure of compound **1a**. Selected bond lengths [Å] and angles [°]: C(1)–N(1) 1.287(3), C(1)–Cl(1) 1.718(3), C(1)–P(1) 1.891(2), P(1)–N(2) 1.6745(19), P(1)–N(3) 1.680(2); N(1)–C(1)–Cl(1) 116.28(19), N(1)–C(1)–P(1) 123.8(2), Cl(1)–C(1)–P(1) 119.52(13), N(2)–P(1)–N(3) 111.89(11), N(2)–P(1)–C(1) 104.30(10), N(3)–P(1)–C(1) 95.78(10). The solvent (CH_2Cl_2) and the triflate anion are omitted for clarity.

reactivity of **1a** was investigated (Scheme 3).† Interestingly, iminium salt **1a** reacted slowly with *tert*-butyl isocyanide at room temperature giving the corresponding phosphonio-(amino)keteneimine **3**, which was isolated as a red oily material in 75% yield (Scheme 3). The structure of **3** was unambiguously established by the two characteristic ^{13}C NMR signals [> C=*C*=N–, δ 158.0, J_{PC} = 56.7 Hz), > *C*=C=N δ 76.4, J_{PC} = 249.7 Hz], and the infra-red absorption ν(CCN) located at 2049 cm^{-1}. Similarly, a quantitative reaction was observed when one equivalent of trimethylphosphine was added at −78 °C to a solution of **1a** in CH_2Cl_2. After 3 h at room temperature the formation of ylide **4** was indicated by an AX system in the ^{31}P NMR spectra [δ 83.1 (NP), 20.2 (CP), J_{PP} = 216.6 Hz]. Compound **4** was isolated as orange crystals in 56% yield and its structure was established by an X-ray diffraction analysis.[10]

The formation of keteneimine **3** and ylide **4** highlighted the electrophilic character of the central carbon center of **1a**, which formally reacts as a carbene. Interestingly, no reaction was observed on reacting **1a** with electron poor alkenes such as methyl acrylate or styrene. In contrast, when one equivalent of ethyl vinyl ether was added to **1a** a clean reaction occurred leading to the α,β-unsaturated iminium salt **5**[11] with concomitant elimination of bis(diisopropylamino)chlorophosphine. A similar nucleophilic displacement was observed on reacting **1a** with one equivalent of diisopropylamine. Here again, the quantitative formation of the chlorophosphine occurred, and the formamidinium salt **6**[12] was isolated (Scheme 3).

Most probably, the reactions leading to **5** and **6** involve a nucleophilic addition of the reagent followed by 1,2-(C→P)-chlorotropic shift, as observed in the reactions of **1a** with isonitrile and phosphine. Then, due to the presence of an acidic hydrogen, the phosphonium salts **7** are formed, which undergo phosphine elimination aided by the two electron-donating substituents at carbon, as shown in Scheme 4 for derivative **5**.

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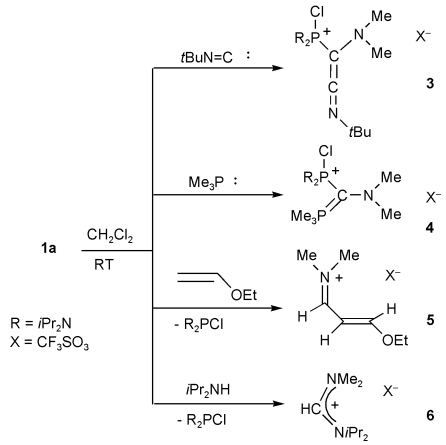
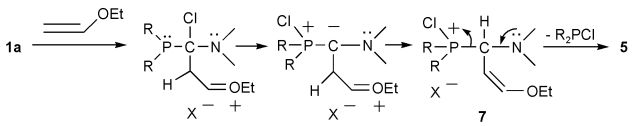


Scheme 3



Scheme 4

Work is in progress to synthesise a stable (amino)(phosphonio)carbene which might be a synthetic equivalent of the hitherto unknown monocoordinate cation R_2NC^+.[13]

Notes and references

† Synthesis of *C*-phosphanyliminium salts **1a,b**: To a CH_2Cl_2 solution (3 mL) of dichloroiminium salt (0.3 mmol) was added at −78 °C one equivalent of bis(diisopropylamino)trimethylsilylphosphine (0.3 mmol). When the temperature reached 0 °C, the solvent was removed under vacuum, and the yellow solid was washed with ether. Iminium salts **1a** and **1b** were obtained as yellow crystals by recrystallisation from a CH_2Cl_2/Et_2O solution at −20 °C. **1a**: 0.12 g (87%); m.p. 80 °C (decomp.); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 68.9. ^1H NMR ($CDCl_3$): δ = 1.18 (d, $^3J_{HH}$ = 6.6 Hz, 12 H; CH_3C), 1.25 (d, $^3J_{HH}$ = 6.6 Hz, 12 H; CH_3C), 3.49 (sept d, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 13.2 Hz, 4 H; NC*H*CH_3), 4.21 (d, $^4J_{PH}$ = 5.1 Hz, 3 H; NCH_3), 4.28 (s, 3 H, NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.0 (m; $CHCH_3$), 47.1 (m; *C*HN), 49.3 (d, $^3J_{PC}$ = 26.8 Hz; CH_3N), 49.8 (d, $^3J_{PC}$ = 4.0 Hz; CH_3N), 121.1 (q, $^1J_{CF}$ = 320.0 Hz; CF_3), 193.2 (d, $^1J_{PC}$ = 92.0 Hz; PC). **1b**: 0.14 g (91 %); m.p. 70 °C (decomp.); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 70.0. ^1H NMR ($CDCl_3$): δ = 1.18 (d, $^3J_{HH}$ = 6.6 Hz, 12 H; CH_3CHNP), 1.28 (d, $^3J_{HH}$ = 6.6 Hz, 12 H; CH_3CHNP), 1.54 (d, $^3J_{HH}$ = 6.4 Hz, 6 H; CH_3CHNC), 1.66 (d, $^3J_{HH}$ = 6.7 Hz, 6 H; CH_3CHNC), 3.62 (sept d, $^3J_{HH}$ = 6.6 Hz, $^3J_{PH}$ = 2.5 Hz, 4 H; PNC*H*), 4.77 (sept, $^3J_{HH}$ = 6.7 Hz, 1 H; CNC*H*), 5.23 (sept d, $^3J_{HH}$ = 6.4 Hz, $^4J_{PH}$ = 13.7 Hz, 1 H; CNC*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.0 (s; PNCH*C*H_3), 20.2 (d, $^3J_{PC}$ = 1.4 Hz; PNCH*C*H_3), 23.9 (d, $^4J_{PC}$ = 6.8 Hz; CNCH*C*H_3), 24.4 (d, $^4J_{PC}$ = 6.2 Hz; CNCH*C*H_3), 49.8 (s; *C*HNP), 59.5 (s; *C*HNC), 63.8 (d, $^3J_{PC}$ = 37.7 Hz; *C*HNC), 121.1 (q, $^1J_{CF}$ = 320.0 Hz; CF_3), 193.5 (d, $^1J_{PC}$ = 108.5 Hz; PC).

General procedure for the reactions leading to **3**–**6**. To a CH_2Cl_2 solution (3 mL) of *C*-phosphanyliminium salt **1a** (0.15 g, 0.3 mmol) was added at −78 °C two equivalents of reagent (see Scheme 3) in toluene or CH_2Cl_2 solution. The solution was allowed to warm and stirred for one night at room temperature. The solvent was removed under vacuum, and the residue was washed with ether. **3**: Red-brown oil after evaporation of solvent (0.13 g, 75%). **4**: Orange crystals by recrystallisation from a CH_2Cl_2/Et_2O solution at −20 °C (97 mg, 56 %). **5**: Dark oil after evaporation of solvent (0.06 g, 72%). **6**: Pale yellow crystals by recrystallisation from a THF solution at −20 °C (0.06 g, 60%).

‡ *Crystal data* for **1a**: $C_{17}H_{36}N_3Cl_3F_3O_3PS$, M = 556.87, orthorhombic, *Fdd*2, a = 22.835(1), b = 58.461(3), c = 8.089(1) Å, V = 10798.3(11) Å^3, Z = 16, ρ_c = 1.370 Mg m^{-3}, μ(Mo Kα) = 0.519 mm^{-1}, 32802 reflections (5505 independent, R_{int} = 0.0512), 307 parameters, $R1$ [$I > 2\sigma(I)$] = 0.0399, *wR*2 [all data] = 0.0960, largest electron density residue: 0.547 e Å^{-3}. Data were collected at low temperature (T = 193(2) K) using oil-coated shock-cooled crystals on a Bruker-AXS CCD 1000 diffractometer with MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[14] and refined using the least-squares method on F^2.[15] Two positions for a disordered isopropyl were refined anisotropically by using 43 ADP- and distances-restraints. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = (\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2)^{0.5}$. CCDC 190033. See http://www.rsc.org/suppdata/cc/b2/b206641f/ for crystallographic data in CIF or other electronic format.

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