

N,C-bonded β -diketiminato phosphonium cations

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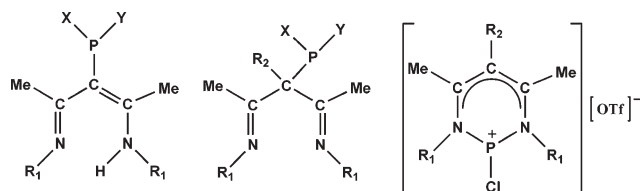
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The first examples of N,C-bonded β -diketiminato phosphonium cations have been isolated as their triflate or tetrachloroaluminate salts, both of which have been structurally characterized.

Despite the widespread use of β -diketiminates as supporting ligands, until recently there were no examples of such complexes of the group 15–17 elements¹ except for a β -bis(iminato)phosphorus complex of tungsten.² Initial attempts to prepare N,N'-chelated β -diketiminato derivatives of the group 15 elements resulted in the acyclic γ -carbon substituted compounds **1**³ and **2**.⁴ Subsequent work has revealed that changing some of the β -diketiminato substituents permits the isolation of the diimine isomers **3** and **4**, which can be converted into the chlorophosphonium salts **5** and **6**, respectively, by treatment with trimethylsilyl triflate (TMSOTf).^{5,6}



1: X = Y = Ph; R₁ = Dipp
2: X = Ph; Y = Cl; R₁ = Dipp
3: X = Y = Cl; R₁ = C₆F₅; R₂ = H
4: X = Y = Cl; R₁ = Dipp; R₂ = Me
5: R₁ = C₆F₅; R₂ = H
6: R₁ = Dipp; R₂ = Me

We now report the isolation of the first examples of N,C-bonded β -diketiminato-substituted phosphonium cations.⁷ Our initial effort focused on the use of the ligand [MeC(CMeNDipp)₂]H (L¹H, **7**; Dipp = 2,6-diisopropylphenyl)⁸ in the expectation that the presence of a γ -methyl group would disfavor substitution at this site. A toluene solution of [MeC(CMeNDipp)₂]Li (L¹Li) was treated with an equimolar quantity of PhPCl₂, following which the resulting yellow solution was added to one equivalent of AlCl₃. After work-up of the reaction mixture and recrystallization from hexane–CH₂Cl₂, a yellow crystalline product (**8**) was isolated in a 46% yield. Collectively, the NMR and MS data for **8**⁹ were consistent with the formula [L¹PPh][AlCl₄]. Unfortunately, the X-ray crystallographic data for this product were not of sufficient quality to allow a detailed discussion of metrical parameters.¹⁰ Nevertheless, the atom connectivities were clear (Fig. 1) and unequivocally establish that the structure of **8** corresponds to the one shown in Scheme 1. From the standpoint of the phosphorus center, **8** can be regarded as an imine donor-stabilized phosphonium ion.¹¹ Phosphonium ions with only two P–C bonds are not expected to

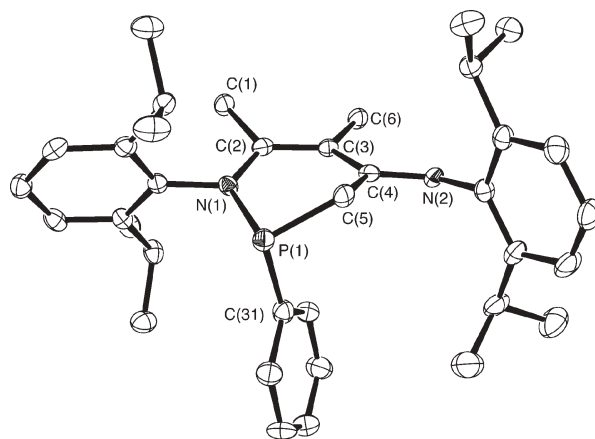
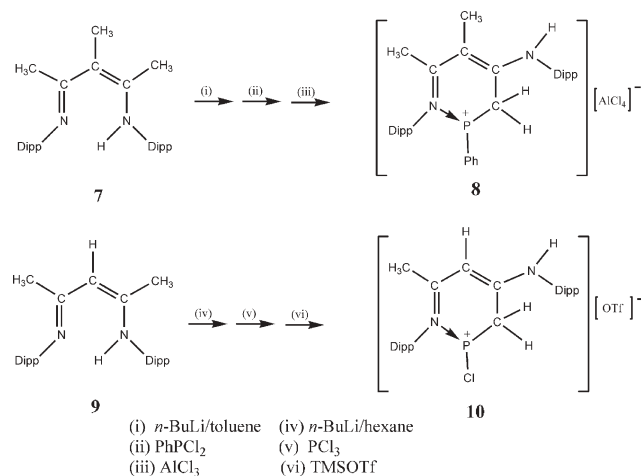


Fig. 1 View of the cation of **8** showing the atom connectivity with thermal ellipsoids at 30% probability and hydrogen atoms omitted for clarity.

be isolable because they lack sufficient π -donor stabilization. However, it is known that such cations can be isolated when coordinated to, for example, phosphorus donors.¹²

Attention was turned next to the use of the [HC(CMeNDipp)₂]H ligand (L²H, **9**) with a view to obtaining a phosphonium salt with improved crystallinity. It was thought that the use of this ligand might provide some insight into the necessity, or otherwise, of blocking the γ -position. As summarized in Scheme 1, the synthesis of **10** was carried out in a very similar fashion to that described for **8**, the main difference being the use of TMSOTf rather than AlCl₃ for chloride ion abstraction. Colorless,



Scheme 1 Preparation of N,C-chelated β -diketiminato phosphonium cations.

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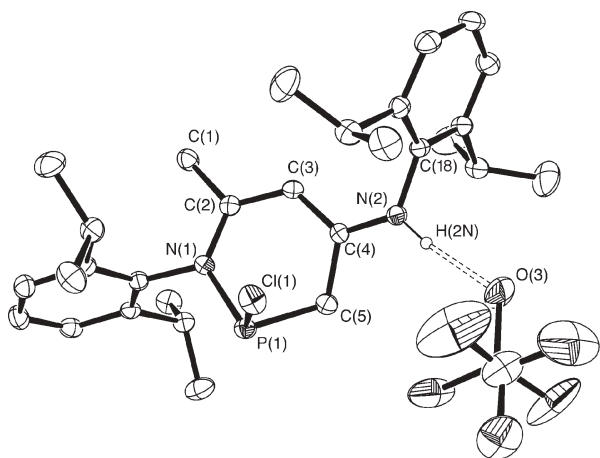


Fig. 2 View of **10** showing the hydrogen bond between the anion and cation with thermal ellipsoids at 30% probability. Selected bond distances (Å) and angles (°): P(1)–N(1) 1.718(3), P(1)–C(5) 1.821(4), P(1)–Cl(1) 2.0955(15), N(1)–C(2) 1.385(4), C(2)–C(3) 1.385(5), C(3)–C(4) 1.396(4), C(4)–C(5) 1.495(5), C(4)–N(2) 1.310(4), N(2)–C(18) 1.449(4), N(1)–P(1)–C(5) 97.90(15), N(1)–P(1)–Cl(1) 102.82(10), C(5)–P(1)–Cl(1) 96.74(12), P(1)–N(1)–C(2) 125.7(2), N(1)–C(2)–C(3) 121.9(3), C(2)–C(3)–C(4) 123.7(3), C(3)–C(4)–C(5) 119.3(3), C(4)–C(5)–P(1) 112.7(2), C(4)–N(2)–C(18) 126.0(3).

crystalline **10** was isolated in a 42% yield. The ^1H NMR spectral data for **10**⁹ are similar to those for **8**, suggesting an analogous mode of ligation for the β -diketiminato ligand. The presence of the triflate anion was evident from the ^{19}F NMR spectrum.⁹ The ^{31}P chemical shifts for **8** (δ 162.7) and **10** (δ 149.4) are similar and fall in the phosphonium ion region.

Confirmation of the structural assignment for **10** shown in Scheme 1 was provided by a single-crystal X-ray diffraction study.¹⁰ The crystalline state of **10** (Fig. 2) consists of an ensemble of phosphonium cations and triflate anions. For each ion pair, one of the triflate oxygen atoms [O(3)] is hydrogen bonded to the unligated nitrogen atom [N(2)] of the β -diketiminato ligand. The presence of this hydrogen bond is also evidenced by the detection of an IR-active vibration at 3215 cm^{-1} . The six-membered PNCCCC ring adopts an envelope conformation. The atoms P(1), N(1), C(2), C(3) and C(4) are planar within experimental error and the “flap” of the envelope forms an angle of 45.99° with respect to said plane. The P(1)–C(5) and C(4)–C(5) distances of 1.821(4) and 1.495(5) Å, respectively, correspond to single bonds and the N(1)–P(1) distance of 1.718(3) Å falls in the range observed for N→P donor–acceptor bonding. Although N(1)–C(2) and C(3)–C(4) are shown as double bonds in the canonical form depicted in Scheme 1 there is, in fact, considerable delocalization across the N(1)–C(2)–C(3)–C(4) fragment. Moreover, the C(4)–N(2) bond distance of 1.310(4) Å is indicative of partial double bond character. Finally, there is a wide scatter of bond angles within the PNCCCC ring, which range from $97.90(15)^\circ$ for N(1)–P(1)–C(5) to $125.7(2)^\circ$ for P(1)–N(1)–C(2).

In summary, the first examples of N,C-bonded β -diketiminato phosphonium ions have been prepared. These cations arise as a consequence of C–H activation of the β -diketiminato ligands employed. At what stage in the reaction sequence the C–H activations take place remains to be elucidated. However, as

pointed out in the context of alkaline earth^{13a} and Yb^{13b} β -diketiminato chemistry, a second deprotonation of a negatively charged β -diketiminato ligand would represent an unusual reaction pathway. Taken in conjunction with the work on group 15 β -diketiminates cited above, it is apparent that several reaction pathways of similar energy are available when metallated- β -diketiminates are treated with group 15 halide derivatives. The outcomes of such reactions depend, *inter alia*, on the nature of the β -diketiminato substituents, the particular group 15 reagent employed, the reaction stoichiometry and the reaction conditions.

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- Spectroscopic data for **8**: ^1H NMR (299.89 MHz, CD_2Cl_2): δ 0.88–1.36 (m, 24H, CHMe_2), 2.23 (s, 2H, CH_2), 2.29 (s, 3H, Me), 2.30 (s, 3H, Me), 2.68–2.75 (m, 4H, CHMe_2), 7.32–7.40 (m, 11H, Ar); ^{27}Al NMR (78.14 MHz, CD_2Cl_2): δ 103.33 (s, AlCl_4^-); ^{31}P NMR (121.50 MHz, CD_2Cl_2): δ 162.68 (s); HRMS (CI, CH_4): calcd for $\text{C}_{36}\text{H}_{47}\text{N}_2\text{P}$ 538.3677; found 538.3481. Spectroscopic data for **10**: ^1H NMR (299.89 MHz, CD_2Cl_2): δ 0.82–1.33 (m, 24H, CHMe_2), 2.58–2.63 (m, 7H, $\text{CHMe}_2 + \text{CH}_3 + \text{CH}_2$), 2.90 (sept, 2H, CHMe_2), 4.39 (s, 1H, CH), 7.00–7.30 (m, 6H, Ar), 9.05 (s, 1H, NH); ^{19}F NMR (282.41 MHz, CD_2Cl_2): δ –79.34 (s, 3F, OTf); ^{31}P NMR (121.50 MHz, CD_2Cl_2): δ 149.36; HRMS (CI, CH_4): calcd for $\text{C}_{29}\text{H}_{40}\text{N}_2\text{P}$ 447.2929; found 447.2931; IR (CH_2Cl_2): 3215 cm^{-1} (N–H stretch).
- Crystal data for 8*· CH_2Cl_2 : $\text{C}_{37}\text{H}_{49}\text{AlCl}_6\text{N}_2\text{P}$, $M_r = 792.43$, monoclinic, space group $P2_1/c$, $a = 13.640(5)$, $b = 13.086(5)$, $c = 23.778(5)$ Å, $\beta = 97.133(5)^\circ$, $V = 4211(2)$ Å³, $Z = 4$, $T = 153(2)$ K, $\mu = 0.494\text{ mm}^{-1}$, reflections collected/independent 30 020/9608 [$R_{\text{int}} = 0.1703$], $R_1 = 0.0727$ [$I > 2\sigma(I)$], and wR_2 [$I > 2\sigma(I)$] = 0.1434. *Crystal data for 10*: $\text{C}_{30}\text{H}_{41}\text{ClF}_3\text{N}_2\text{O}_3\text{PS}$, $M_r = 633.13$, triclinic, space group $P\bar{1}$, $a = 10.356(2)$, $b = 12.533(3)$, $c = 14.756(3)$ Å, $\alpha = 100.40(3)$, $\beta = 90.53(3)$, $\gamma = 110.49(3)^\circ$, $V = 1761.9(8)$ Å³, $Z = 2$, $T = 153(2)$ K, $\mu = 0.259\text{ mm}^{-1}$, reflections collected/independent 11 412/7893 [$R_{\text{int}} = 0.0431$], $R_1 = 0.0722$ [$I < 2\sigma(I)$] and $wR_2 = 0.1841$ [$I < 2\sigma(I)$]. Crystals of **8** and **10** were covered with a mineral oil prior to mounting on the goniometer of a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream liquid nitrogen cooling system. The data sets were corrected for absorption. CCDC 619044 and 617244. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611976j.
- A referee has suggested the name 5-azapenta-2,4-dienyl for this ligand.
- See, for example, N. Burford, D. E. Herbert, R. J. Ragogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.*, 2004, **126**, 17067.
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