An N,N′-chelated phosphenium cation supported by a β-diketiminate ligand

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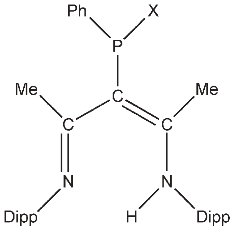
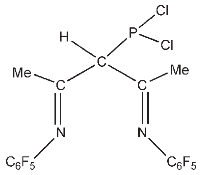
The first example of a phosphenium cation supported by N,N′-chelation of a β-diketiminate ligand has been prepared and structurally characterized.

N,N′-chelated β-diketiminate complexes are known for an increasingly large number of transition metal, lanthanide and main group elements.[1] Several of these complexes have found useful applications, particularly in the field of catalysis. In terms of main group chemistry, β-diketiminate ligands have been used advantageously for the stabilization of unusual oxidation states and novel bonding arrangements.[2] However, there is a gap in our knowledge in this area of chemistry in the sense that there are no examples of uncoordinated N,N′-chelated β-diketiminate complexes[3] of the electron-rich elements from groups 15, 16 and 17. Previous attempts to prepare β-diketiminates that incorporate chelated phosphorus-containing moieties resulted in the γ-carbon-substituted acyclic derivatives, **1**[4] and **2**.[5]

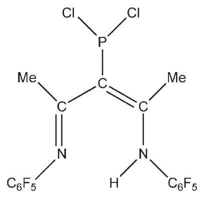


1 (X = Ph)
2 (X = Cl)

It has been suggested that this outcome is due to steric encumbrance by the bulky 2,6-diisopropylphenyl (Dipp) ligands and the unfavorable bite angle of the six-membered β-diketiminate ring with respect to phosphorus chelation.[4a] A further factor disfavoring the chelation of electron-rich phosphorus-containing fragments is the donor character of the flanking nitrogen atoms of the β-diketiminate ligand. Taking the foregoing issues into consideration, it occurred to us that the N,N′-chelated phosphorus-containing fragment needed to be as small and electronegative as possible. Cationic halophosphorus moieties, $[PX]^+$, seemed like excellent potential candidates. Two further choices were made in an effort to optimize the conditions required for N,N′-chelation, namely (i) reduction of the electron density on the nitrogen atoms of the β-diketiminate ligand by the use of electronegative substituents, and (ii) changing the γ-carbon substituent from H to alkyl in order to disfavor phosphorus substitution at this site. Accordingly, the β-diketiminate ligands $[HC(CMe)_2(NC_6F_5)_2]^-$ (L_1^-)[6] and $[MeC(CMe)_2(NDipp)_2]^-$ (L_2^-)[7] were employed for the syntheses described herein. Treatment of L_1H with $NaNH_2$ in Et_2O/hexane solution resulted in the *in situ* formation of L_1Na which, in turn, was allowed to react with a hexane solution of PCl_3. The initially formed product of the latter reaction is the bis-imine derivative **3a**. However, when crystals of **3a** are dissolved in *e.g.* C_6D_6 or CD_2Cl_2, the conversion of **3a** to the iminoamine isomer, **3b**, is detectable within minutes by NMR spectroscopy.[8]



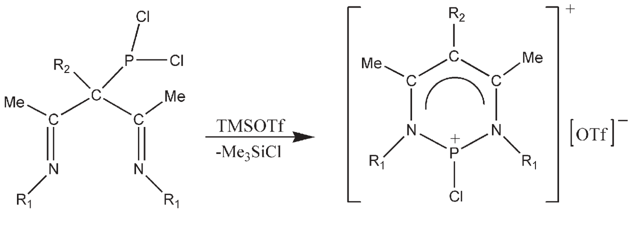
3a



3b

At equilibrium, which is achieved in ∼1 day, the molar composition of the **3a**/**3b** mixture is approximately 2 : 3. The structure of **3a** was determined by single-crystal X-ray diffraction (Fig. 1).[9] That **3a** exists in the diimine form is clear from the presence of two short carbon–nitrogen bonds, C(2)–N(1) and C(4)–N(2), two single carbon–carbon bonds, C(2)–C(3) and C(3)–C(4), the tetrahedral geometry at C(3), and the trigonal planar geometries at C(4) and C(5).[10] X-Ray crystallographic data for compounds **1**[4] and **2**,[5] which are closely related to **3b**, have been published already.

Treatment of freshly crystallized **3a** with trimethylsilyl triflate (TMSOTf) in CH_2Cl_2 solution results in Me_3SiCl elimination and formation of the chlorophosphenium salt **4**. The elemental composition of the cation was established as $C_{17}H_7ClF_{10}N_2P$ on the basis of HRMS (CH_4, CI, positive mode) and the presence of the H, CH_3 and C_6F_5 ring substituents and the triflate anion was clear from ^1H and ^{19}F NMR spectroscopic data.[8] The ^{31}P chemical shift of δ 106.81 is close to that of structurally authenticated **6** (δ 97.23).[8]



3a ($R_1 = C_6F_5$; R_2 = H)
5 (R_1 = Dipp; R_2 = Me)

4 ($R_1 = C_6F_5$; R_2 = H)
6 (R_1 = Dipp; R_2 = Me)

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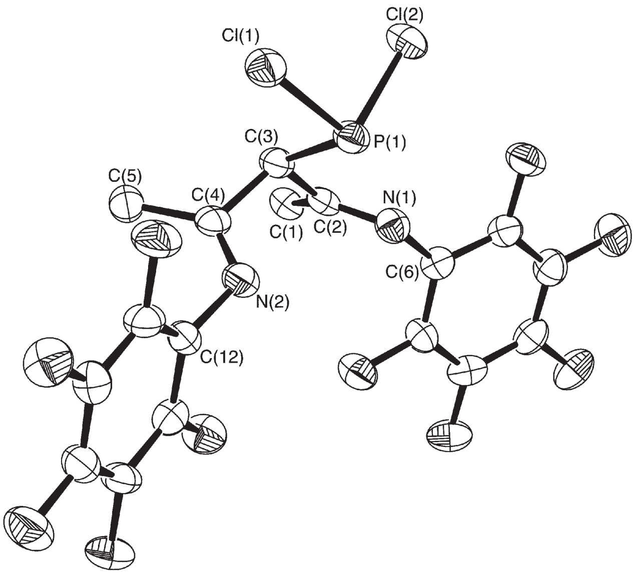

Fig. 1 View of **3a** showing the atom numbering scheme and thermal ellipsoids at 40% probability with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): P(1)–C(3) 1.864(5), P(1)–Cl(1) 2.0747(15), P(1)–Cl(2) 2.0675(15), C(2)–C(3) 1.514(5), C(3)–C(4) 1.532(5), C(2)–N(1) 1.284(5), C(4)–N(2) 1.281(5); P(1)–C(3)–C(2) 107.3(2), P(1)–C(3)–C(4) 107.0(3), C(2)–C(3)–C(4) 111.5(3), C(1)–C(2)–C(3) 117.4(4), C(1)–C(2)–N(1) 128.5(4), C(3)–C(2)–N(1) 114.0(4), C(3)–C(4)–C(5) 117.2(4), C(3)–C(4)–N(2) 115.0(4), C(5)–C(4)–N(2) 127.8(4).

Compound **5**, which is formed *via* the reaction of L_2H with *n*-BuLi in hexanes, followed by treatment with PCl_3, has not been obtained in a pure state due to the concomitant formation of as yet unidentified products, the quantities of which increase with time (as monitored by $^{31}P\{^1H\}$ NMR spectroscopy). In order to maximize the yield of the desired chlorophosphenium salt **6**, it is best to treat **5** with TMSOTf in CH_2Cl_2 solution as soon as the reaction of L_2Li with PCl_3 is complete. After work-up of the reaction mixture and recrystallization from pentane/CH_2Cl_2, colorless, crystalline **6** was isolated in an overall yield of 54% based on the consumption of L_2H.

The X-ray crystal structure of **6**[9] reveals an ensemble of chlorophosphenium cations and triflate anions and the closest cation–anion contact is 3.312(7) Å between Cl(1) and a triflate fluorine atom. The cyclic cation (Fig. 2) consists of a PCl^+ moiety which is N,N′-chelated by the β-diketiminate ligand, L_2. The metrical parameters for the six-membered PN_2C_3 ring indicate that the geometry tends towards an alternating, somewhat localized distribution of electron density as reflected by the 0.2–0.3 Å differences in the C–C, C–N and N–P distances. The geometry of the PN_2C_3 ring is non-planar (sum of bond angles = 708.6(2)°). However, the atoms N(1), C(1), C(2), C(3) and N(2) are approximately coplanar and P(1) deviates from the said plane by 0.549(3) Å. The average N–P bond distance is 1.716(2) Å. Due to the presence of a stereochemically active lone pair at P(1), the chloride ligand is approximately orthogonal to the PN_2C_3 ring. (The Cl(1)–P(1)–N(1) and Cl(1)–P(1)–N(2) angles are 97.41(9) and 102.65(9)°, respectively). Overall, the structure of the cation of **6** bears a close resemblance to that of the neutral germanium(II) β-diketiminate $[HC(CMe)_2(NDipp)_2]GeCl$ with which it is isovalent.[11]

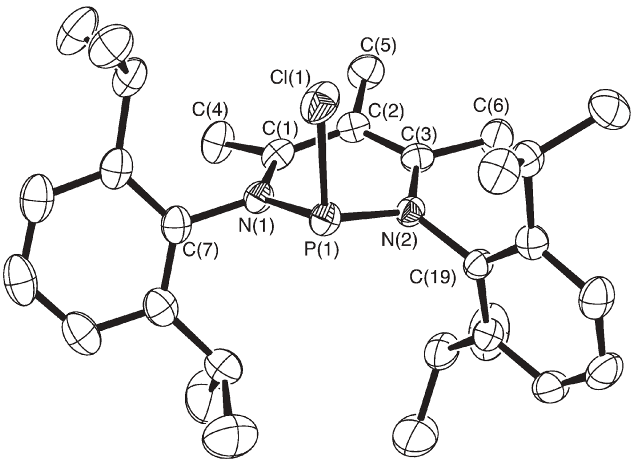

Fig. 2 View of the cation of **6** showing the atom numbering scheme and thermal ellipsoids at 40% probability and hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): P(1)–Cl(1) 2.0923(11), P(1)–N(1) 1.731(2), P(1)–N(2) 1.701(2), N(1)–C(1) 1.359(4), N(2)–C(3) 1.381(4), C(1)–C(2) 1.405(4), C(2)–C(3) 1.377(4); N(1)–P(1)–N(2) 97.51(12), N(1)–P(1)–Cl(1) 97.41(9), N(2)–P(1)–Cl(1) 102.65(9), P(1)–N(1)–C(1) 123.96(19), P(1)–N(2)–C(3) 122.80(18), N(1)–C(1)–C(2) 121.4(2), N(2)–C(3)–C(2) 121.2(3), C(1)–C(2)–C(3) 121.7(3), C(1)–C(2)–C(5) 119.0(2), C(3)–C(2)–C(5) 118.6(3).

As illustrated in Fig. 3, one of the salient aspects of the structure of **3a** relates to the short P(1)···N(1) and P(1)···N(2) contacts of 2.690(4) and 2.894(4) Å, respectively. Both of these distances are appreciably shorter than the sum of van der Waals radii for P and N (3.40 Å).[12] We believe that this structural feature may provide an important clue regarding the mechanism by which **3a** and **5** are converted into **4** and **6**, respectively. Phosphenium ion formation can be envisaged as occurring by a concerted process in which P(1)–N(1) and P(1)–N(2) bond formation is accompanied by concomitant rupture of the P(1)–C(3) bond as a chloride anion is abstracted from P(1). Alternatively, P(1)–N(1) formation and P(1)–C(3) cleavage could occur in a first step, followed by rotation of the C(4)–N(2) imine group around the C(3)–C(4) bond to effect ring closure.

Density Functional Theory (DFT) calculations have been performed on phosphenium ion **6** at the B3LYP level of theory using the 6-31+G(d) basis set. The input parameters for the geometry optimization were generated from the X-ray crystallographic data set for **6**. In general, the computed metrical parameters lie within 2% of the experimental values. The HOMO and LUMO for **6** are aryl ring bonding and β-diketiminate π* in character, respectively, and the HOMO–LUMO gap is

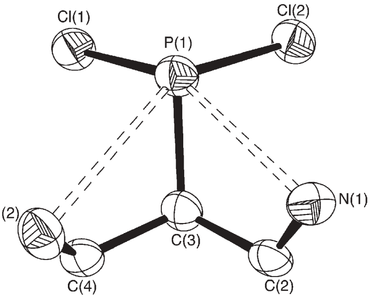

Fig. 3 View of the skeleton of **3a** showing the short N···P contacts.

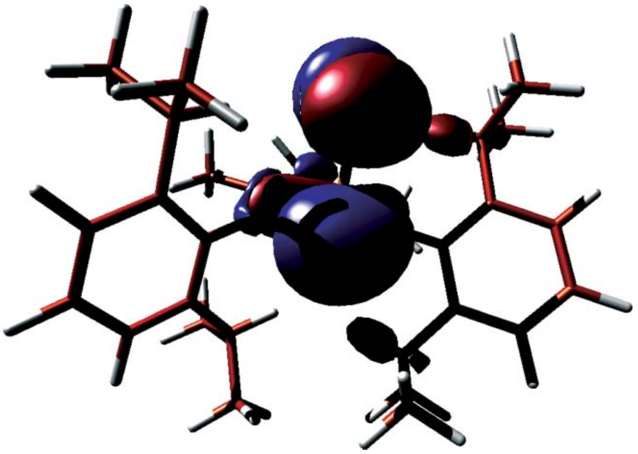

Fig. 4 The HOMO−5 orbital of the cation of **6** showing the phosphorus lone pair.

86.55 kcal mol^{-1}. As shown in Fig. 4, the orbital that features the most phosphorus lone pair character is the HOMO−5.

In summary, we have prepared, structurally characterized and theoretically modeled the first example of a phosphenium ion supported by N,N′-chelation of a β-diketiminate ligand. Diimine isomers of acyclic, phosphorus–carbon bonded β-diketiminates have also been isolated and structurally authenticated. These diimine isomers play an important role as precursors to the cyclic N,N′-chelated phosphenium ions.

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Notes and references

1 For an excellent review, see: L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031.

2 See, for example: (*a*) H. W. Roesky and S. S. Kumar, *Chem. Commun.*, 2005, 4027; (*b*) N. J. Hardman and P. P. Power, *Chem. Commun.*, 2001, 1184.

3 The sole example of a coordinated phosphorus-containing N,N′-chelated β-diketiminate is [P{N(H)C(C_5Me_5(C(H)C(H)NH}{W$(CO)_5$}$_2$]. See: M. Schiffer and M. Scheer, *Angew. Chem., Int. Ed.*, 2001, **40**, 3413.

4 (*a*) P. J. Ragogna, N. Burford, M. D'eon and R. McDonald, *Chem. Commun.*, 2003, 1052; (*b*) N. Burford, M. D'eon, P. J. Ragogna, R. McDonald and M. J. Ferguson, *Inorg. Chem.*, 2004, **43**, 734.

5 P. B. Hitchcock, M. F. Lappert and J. E. Nycz, *Chem. Commun.*, 2003, 1142.

6 A. Panda, M. Stender, R. J. Wright, M. M. Olmstead, P. Klavins and P. P. Power, *Inorg. Chem.*, 2002, **41**, 3909.

7 The new ligand L_2H was prepared *via* the reaction of 3-methyl-2,4-pentanedione, $DippNH_2$ and *p*-toluenesulfonic acid following the protocol described in ref. 6.

8 *Spectroscopic data*: for **3a**: ^{1}H NMR (299.89 MHz, C_6H_6): δ 1.44 (d, 6H, $^4J_{PH}$ = 0.9 Hz, Me), 4.04 (d, 1H, $^2J_{PH}$ = 4.5 Hz, CH); ^{19}F NMR (282.41 MHz, C_6D_6): δ −151.94 (m, 4F, *o*-F), −161.62 (t, 2F, $^3J_{FF}$ = 20.9 Hz, *p*-F), −163.25 (m, 4F, *m*-F); ^{31}P{^{1}H} NMR (121.50 MHz, C_6D_6): δ 160.36 (s). HRMS (CI, CH_4): calc. for $C_{17}H_7Cl_2F_{10}N_2P$ [(M + H)$^+$] 530.9642; found 530.9642. For **3b**: ^{1}H NMR (299.89 MHz, C_6D_6): δ 2.11 (d, 6H, $^4J_{PH}$ = 3.9 Hz, Me), 14.17 (s, 1H, NH); ^{19}F NMR (282.41 MHz, C_6D_6): δ −149.16 (m, 4F, *o*-F), −158.04 (t, 2F, ^3J = 20.9 Hz, *p*-F), −162.26 (m, 4F, *m*-F); ^{31}P{^{1}H} NMR (121.50 MHz, C_6D_6): δ 160.93 (s). HRMS (CI, CH_4): calc. for $C_{17}H_7Cl_2F_{10}N_2P$ [(M + H)$^+$] 530.9642; found 530.9642. For **4**: ^{1}H NMR (300.14 MHz, CH_2Cl_2): δ 2.64 (s, 6H, Me), 7.36 (s, 1H, CH); ^{19}F NMR (282.41 MHz, CH_2Cl_2): δ −79.92 (s, 3F, OTf$^-$), −146.43 (m, 4F, *o*-F), −158.08 (m, 2F, *p*-F), −161.51 (m, 4F, *m*-F); ^{31}P{^{1}H} NMR (121.50 MHz, CH_2Cl_2): δ 106.81 (s) HRMS (CI, CH_4): calc. for $C_{17}H_7ClF_{10}P$ [(M + H)$^+$] 494.9876; found 494.9845. For **6**: ^{1}H NMR (300.14 MHz, CD_2Cl_2): δ 1.10 (d, 6H, J = 6.6 Hz, CH*Me*$_2$), 1.29 (d, 6H, J = 6.6 Hz, CH*Me*$_2$), 1.32 (d, 6H, J = 6.6 Hz, CH*Me*$_2$), 1.34 (d, 6H, J = 6.6 Hz, CHMe$_2$), 2.43 (s, 6H, Me), 2.44 (s, 3H, Me), 2.71 (sept, 2H, J = 6.6 Hz, C*H*Me$_2$), 2.90 (sept, 2H, J = 6.6 Hz, C*H*Me$_2$), 7.41–7.54 (m, 6H, Ar); ^{19}F NMR (282.41 MHz, CD_2Cl_2): δ −79.26 (s, 3F, OTf$^-$); ^{31}P{^{1}H} NMR, 121.50 MHz): δ 97.23 (s).

9 *Crystal data*: for **3a**; $C_{17}H_7Cl_2F_{10}N_2P$, M_r = 531.12, orthorhombic, space group $Pna2_1$, a = 23.649(5), b = 6.050(5), c = 13.385(5) Å, V = 1.914.8(18) Å^3, Z = 4, T = 153(2) K, μ = 0.526 mm^{-1}, reflections collected/independent = 6534/3808 (R_{int} = 0.0423), R_1 ($I > 2\sigma(I)$) = 0.0457 and wR_2 ($I > 2\sigma(I)$) = 0.0865. For **6**: $C_{31}H_{43}ClF_3N_2O_3PS$, M_r = 647.16, monoclinic, space group $P2_1/c$, a = 14.742(3), b = 12.911(3), c = 18.370(4) Å, β = 110.87(3)°, V = 3267.0(14) Å^3, Z = 4, T = 153(2) K, μ = 0.281 mm^{-1}, reflections collected/independent = 13840/7433 (R_{int} = 0.0474), R_1 ($I > 2\sigma(I)$) = 0.0633 and wR_2 ($I > 2\sigma(I)$) = 0.1554. Crystals of **3a** and **6** 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. Both data sets were corrected for adsorption. CCDC 603059 (**3a**) and 603060 (**6**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607549e.

10 We have also prepared the PhPCl analogue of **3a** by substituting $PhPCl_2$ for PCl_3 in the synthetic procedure. The X-ray crystal structure is very similar to that of **3a** and also features short P···N contacts (2.633(9) and 3.054(10) Å). Akin to **3a**, the PhPCl analogue also undergoes conversion to the corresponding iminoamine isomer.

11 Y. Ding, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Organometallics*, 2001, **20**, 1190.

12 Values taken from: A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.