A β-diketiminato hydroxyphosphenium cation: phosphinous acid–secondary phosphine oxide tautomerism revisited

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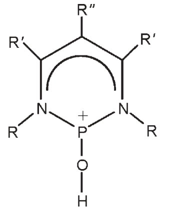
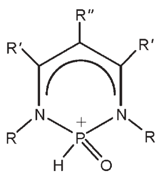
Received (in Austin, TX, USA) 26th October 2007, Accepted 13th November 2007
First published as an Advance Article on the web 28th November 2007
DOI: 10.1039/b716389d

The first example of a β-diketiminato-supported hydroxyphosphenium cation has been prepared, structurally characterized, and modeled by DFT calculations.

β-Diketiminates have now emerged as one of the most important classes of ligand.[1] Notwithstanding their widespread use, until recently there were no examples of uncoordinated N,N′-chelated β-diketiminate complexes of the group 15 elements.[2] Chlorophosphenium salts, the first such examples, were accessed synthetically by treatment of precursor diimines with trimethylsilyl triflate.[3] More recently, it has been shown that other halophosphenium salts can be prepared by metathetical routes.[4,5] Given that the phosphorus center in halophosphenium cations features a coordination number of three, a lone pair of electrons, and a formal positive charge, it was of interest to determine whether such cations would undergo nucleophilic substitution reactions. The hydroxide anion was chosen as the attacking nucleophile because it was not clear *a priori* whether the resulting product would be a hydroxyphosphenium cation (**A**), a hydrophosphoryl tautomer (**B**), or an equilibrium mixture of the two. This type of tautomerism is well known in the context of the phosphinous acid–secondary phosphine oxide dichotomy (eqn (1)).[6] Generally speaking, this equilibrium is shifted to the far right in the case of neutral compounds. The sole exception to this generalization is the CF_3-substituted derivative, $(CF_3)_2POH$, which was reported by Griffiths and Burg over four decades ago.[7,8] The preference for the phosphinous acid tautomer in this case has been attributed to the reduced electron density at the phosphorus center due to the powerful electron-withdrawing character of the CF_3 substituents.[6] Given the formal +1 charge on the phosphorus atom of the tautomeric pair **A** and **B**, it was of interest to establish which structure is preferred in β-diketiminatophosphorus cations of this type.



A



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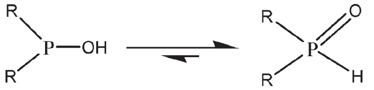

(1)

The new bromophosphenium salt $[\{MeC(CMe)_2(Ndpp)_2\}PBr][OTf]$ (**1**: dpp = 2,6-i-$Pr_2C_6H_3$) was prepared in 62% yield in a similar fashion to the analogous chlorophosphenium salt $[\{MeC(CMe)_2(Ndpp)_2\}PCl][OTf]$ (**2**).[3] The spectroscopic characteristics of **1** are similar to those of **2**.[9] A single-crystal X-ray diffraction study of **1** revealed that it is isomorphous with **2** and that the ring conformation and metrical parameters for the two cations are comparable.[10] Treatment of **1** with an equimolar quantity of NaOH in toluene solution at ambient temperature gave, after workup of the reaction mixture, a small yield (~20%) of a pale yellow crystalline compound corresponding to the composition $[\{MeC(CMe)_2(Ndpp)_2\}POH][OTf]$ (**3**).[9,11] The absence of ^{31}P–^{1}H coupling in the ^{31}P and ^{1}H NMR spectra[9] and the presence of an IR peak in the O–H stretching region (3364 cm^{-1}) suggested that the cation of **3** adopts the hydroxyphosphenium structure **A** (R = dpp; R′ = R″ = Me). This structure assignment was confirmed by X-ray crystallography.[10] The solid state structure of **3** (Fig. 1) comprises an array of hydroxyphosphenium cations and triflate anions. The O–H group of the cation is hydrogen-bonded to an oxygen atom of the triflate anion with distances of 1.82 and 0.82 Å for the (S)O···H and (P)O···H interactions, respectively, and an O···H···O angle of 162.3°. The

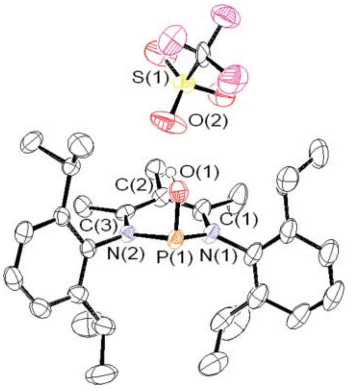

Fig. 1 View of the hydroxyphosphenium salt **3** showing the cation–anion hydrogen bonding. The thermal ellipsoids are drawn at 30% probability. Selected bond distances (Å) and angles (°): P(1)–O(1) 1.584(2), P(1)–N(1) 1.741(1), P(1)–N(2) 1.755(2), N(1)–C(1) 1.360(4), N(2)–C(3) 1.344(3), C(1)–C(2) 1.391(4), C(2)–C(3) 1.410(4), N(1)–P(1)–N(2) 95.68(11), N(1)–P(1)–O(1) 104.02(11), N(2)–P(1)–O(1) 102.51(11), P(1)–N(1)–C(1) 124.2(2), P(1)–N(2)–C(3) 125.3(2), N(1)–C(1)–C(2) 121.4(2), N(2)–C(3)–C(2) 121.9(3), C(1)–C(2)–C(3) 121.2(3).

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atoms N(1), C(1), C(2), C(3) and N(2) are approximately coplanar and the fold angle between this plane and the N(1)–P(1)–N(2) plane is 26.3(2)°. As in the case of the analogous chlorophosphenium cation,[3] there is an alternation of bond distances within the β-diketiminate ring; however, this effect is less pronounced in **3** than in **1**. The average N–P bond distance of 1.748(2) Å in **3** is slightly longer than that in the bromophosphenium cation (1.723(2) Å). The P–O bond distance of 1.584(2) Å in **3** may be compared with the electron diffraction value of 1.661(4) Å reported for $(CF_3)_2POH$.[6b]

Given the existence of the anion–cation hydrogen bond in **3**, it was conceivable that the presence of such a bond could have biased the equilibrium (eqn (1)) in favor of the P–OH tautomer **A** (R = dpp; R′ = R″ = Me). Moreover, it has been reported that the phosphinous acid tautomer can be stabilized by coordination to transition metals.[12] Accordingly, it was of interest to examine the X-ray crystal structure of a phosphenium salt that does not feature hydrogen bonding or other types of interaction. Fortuitously, on one occasion it was possible to isolate a small number of morphologically distinct crystals of a second product from the reaction of **1** with NaOH. Examination of one of these crystals by X-ray diffraction[10] showed it to be $[\{MeC(CMe)_2(Ndpp)_2\}POH]Br$ (**4**). The salt **4** crystallizes in the orthorhombic space group *Pbca* with *Z* = 8. Although the structure is not of high quality, it is clear that the conformation and metrical parameters of the C_3N_2P ring of **4** (Fig. 2) bear a close resemblance to those of **3**. The closest contact occurs between a bromide anion and a β-methyl group hydrogen of the β-diketiminate ligand of the cation. However, the contact distance of 3.377 Å exceeds the sum of van der Waals radii for H and Br (3.05 Å). Taken collectively, the X-ray crystallographic results for **3** and **4** imply that the adoption of the P(III) hydroxyphosphenium tautomeric form **A** is not a consequence of triflate oxygen–hydroxide hydrogen bonding in the case of **3**.

Despite the fact that the X-ray crystallographic studies indicate that the hydroxyphosphenium structure is preferred in the solid state, it was of interest to probe the tautomeric preference in the absence of any solid state constraints. Accordingly, DFT calculations were performed on the model cations **5** and **6** using the B3LYP method and the 6-31+G(d) basis set. These calculations revealed that **5** is more stable than **6** by 38.95 kJ mol^{-1}. Analogous calculations on $(CF_3)_2POH$ and $(CF_3)_2P(O)H$ showed the former to be more stable by 30.89 kJ mol^{-1}. A DFT calculation was also carried out on the actual cation $[\{MeC(CMe)_2(Ndpp)_2\}POH]^+$ ($\mathbf{3^+}$) with the 3-21+G basis set. The input parameters for the geometry optimization were generated from the X-ray crystallographic data set for **3**. In general, the computed metrical parameters lie within 3% of the experimental values. The HOMO and LUMO of $\mathbf{3^+}$ are aryl ring bonding and β-diketiminate π* in character, respectively, and the HOMO–LUMO gap is computed to be 189 kJ mol^{-1}. As illustrated in Fig. 3, the orbital that exhibits the most phosphorus lone pair character is the HOMO-5. The computed charge at the phosphorus atom is +1.03.

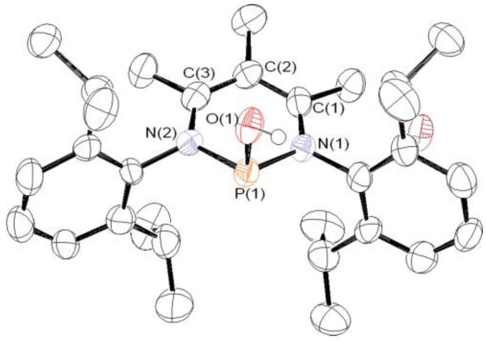


Fig. 2 View of the hydroxyphosphenium salt **4** with thermal ellipsoids drawn at 30% probability. Selected bond distances (Å) and angles (°): P(1)–O(1) 1.583(6), P(1)–N(1) 1.749(6), P(1)–N(2) 1.750(7), N(1)–C(1) 1.361(10), N(2)–C(3) 1.345(10), C(1)–C(2) 1.397(11), C(2)–C(3) 1.379(11), N(1)–P(1)–N(2) 95.6(3), N(1)–P(1)–O(1) 103.9(3), N(2)–P(1)–O(1) 102.6(3), P(1)–N(1)–C(1) 125.5(5), P(1)–N(2)–C(3) 124.6(6), N(1)–C(1)–C(2) 121.6(7), N(2)–C(3)–C(2) 123.3(8), C(1)–C(2)–C(3) 121.4(8).

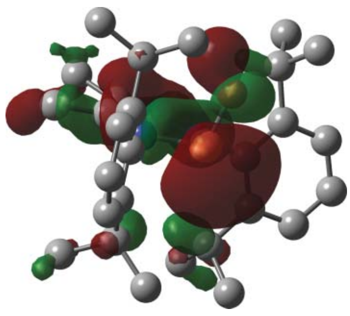
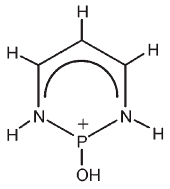


Fig. 3 Phosphorus lone pair character of the HOMO-5 orbital of the cation $\mathbf{3^+}$.



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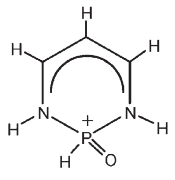

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We are grateful to the Robert A. Welch Foundation (F-0003) for financial support of this work.

Notes and references

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8 The compound $(C_6F_5)_2POH$, originally claimed as a phosphinous acid, subsequently was shown to exist in the tautomeric secondary phosphine oxide form in the solid state at ambient temperature. See ref. 6*a* and references therein.

9 Spectroscopic data for **1**: ^1H NMR (300 MHz, CD_2Cl_2): δ 7.64–7.40 (m, 6H, Ar), 2.96 (sept, 2H, J = 6.6 Hz, C*H*Me_2), 2.65 (sept, 2H, J = 6.6 Hz,

C*H*Me$_2$), 2.46 (s, 3H, C*H*$_3$), 2.44 (s, 6H, C*H*$_3$), 1.32 (d, 6H, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.26 (d, 6H, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.24 (d, 6H, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$), 1.09 (d, 6H, *J* = 6.6 Hz, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, CD$_2$Cl$_2$): δ 170.13 (*C*N), 147.58, 145.56, 127.35, 126.51 (Ar), 132.45 (*C*F$_3$), 117.89 (*C*CH$_3$), 30.37, 29.80 (*C*Me$_2$), 26.66, 25.31, 24.27, 23.74 (C*Me$_2$*), 22.98, 22.51 (*C*H$_3$), 17.18 (*C*H$_3$). ^{19}F NMR (282.41 MHz, CD$_2$Cl$_2$): δ −79.27. ^{31}P{^{1}H} NMR (121.50 MHz, CD$_2$Cl$_2$): δ 102.16. HRMS (CI$^+$, CH$_4$): calcd for C$_{30}$H$_{43}$N$_2$PBr 541.2347; found 541.2343. Spectroscopic data for **3**: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 7.62–7.31 (m, 6H, Ar), 4.38 (s, 1H, O*H*), 3.07 (sept, 2H, *J* = 6.6 Hz, C*H*Me$_2$), 2.82 (sept, 2H, *J* = 6.6 Hz, C*H*Me$_2$), 2.23 (s, 6H, C*H*$_3$), 2.21 (s, 3H, C*H*$_3$), 1.34–1.05 (m, 24H, CH(C*H*$_3$)$_2$). ^{31}P NMR (121.50 MHz, C$_6$D$_6$): δ 71.11 (s). ^{19}F NMR (282.41 MHz, CD$_2$Cl$_2$) δ −79.25. FTIR (CH$_2$Cl$_2$): 3364 cm^{-1} (O–H stretch). HRMS (CI, CH$_4$): calcd for C$_{30}$H$_{44}$N$_2$OP 479.3191; found 479.3187.

10 *Crystal data* for **1**: C$_{31}$H$_{43}$BrF$_3$N$_2$O$_3$PS, M_r = 691.61, monoclinic, space group *P*2$_1$/*c*, *a* = 14.568(5), *b* = 12.712(5), *c* = 18.815(5) Å, β = 110.769(5)°, *V* = 3257.9(19) Å^3, *Z* = 4, *T* = 153(2) K, μ = 1.426 mm^{-1}, reflections collected/independent 13 329/7428 [$R_{\rm int}$ = 0.0380], *R*1 = 0.0427 [$I > 2\sigma(I)$] and w*R*2 [$I > 2\sigma(I)$] = 0.1003. *Crystal data* for **3**: C$_{31}$H$_{44}$F$_3$N$_2$O$_4$PS, M_r = 628.71, orthorhombic, space group *P*2$_1$2$_1$2$_1$, *a* = 8.9393(18), *b* = 12.215(2), *c* = 30.199(6) Å, *V* = 3297.5(11) Å^3, *Z* = 4, *T* = 153(2) K, μ = 0.200 mm^{-1}, reflections collected/independent 5512/5512 [$R_{\rm int}$ = 0.0000], *R*1 = 0.0531 [$I > 2\sigma(I)$] and w*R*2 = 0.1294 [$I > 2\sigma(I)$]. *Crystal data* for **4**: C$_{30}$H$_{44}$BrN$_2$OP, M_r = 559.55, orthorhombic, space group *Pbca*, *a* = 16.119(3), *b* = 14.615(3), *c* = 25.530(5) Å, *V* = 6014(2) Å^3, *Z* = 8, *T* = 153(2) K, μ = 1.444 mm^{-1}, reflections collected/independent 21 481/6888 [$R_{\rm int}$ = 0.3074], *R*1 = 0.0915 [$I > 2\sigma(I)$] and w*R*2 [$I > 2\sigma(I)$] = 0.1908. Crystals of **1**, **3** and **4** were covered with mineral oil prior to mounting on the goniometer of a Nonius Kappa diffractometer equipped with an Oxford Cryostream liquid nitrogen cooling system. The data sets were corrected for absorption. CCDC 664930, 664931 and 664932, respectively. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b716389d.

11 Treatment of **1** with an equimolar quantity of water at 25 °C resulted in the formation of [MeC(H){C(Me)N(H)(dpp)}$_2$](OTf)$_2$, the bis-triflate salt of the diprotonated ligand.

12 See *e.g.*: J. Chatt and B. T. Heaton, *J. Chem. Soc. A*, 1968, 2745; C. S. Kraihanzel and C. M. Bartish, *J. Am. Chem. Soc.*, 1972, **94**, 3572; E. Lindner and B. Schilling, *Chem. Ber.*, 1977, **110**, 3266. Several transition metal complexes of phosphinous acids are active catalysts. See: N. V. Dubrovina and A. Börner, *Angew. Chem., Int. Ed.*, 2004, **43**, 5883.