Valence isomer of a β-diketiminate-supported phosphinidene: a case of C–H activation and ring contraction

Zheng Lu, Michael Findlater and Alan H. Cowley*

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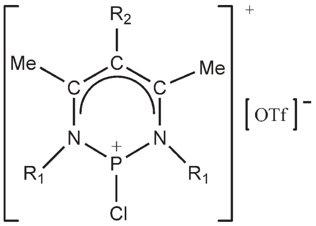
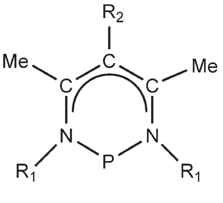
A valence isomer of a β-diketiminate-supported phosphinidene has been prepared by potassium metal reduction of the corresponding chlorophosphenium cation.

Despite the almost ubiquitous use of β-diketiminates as supporting ligands,[1] until recently the sole example of an N,N′-chelated compound of the electron-rich group 15, 16 and 17 elements was the tungsten complex, $[P\{N(H)C(C_5Me_5)C(H)C(H)NH\}\{W(CO)_5\}_2]$.[2] However, in 2006 we were able to isolate two chlorophosphenium cations as their trifluoromethylsulfonate (triflate) salts (**1**, **2**),[3] and more recently Lappert and co-workers disclosed a novel β-dialdiminatophosphenium triiodide[4] and Richards and co-workers reported further examples of halophosphenium cations.[5] In turn, the availability of **1** and **2** raised the prospect that they might prove useful as precursors to the corresponding phosphinidenes **3** and **4**, respectively. Phosphinidenes, the phosphorus analogues of carbenes, have attracted the attention of both the experimental and theoretical communities for several years. However, despite the presentation of convincing evidence for the intermediacy of such species[6] and the development of a fruitful phosphinidene coordination chemistry,[6,7] the only example of a non-ligated phosphinidene is (mesityl)P which was isolated in a glassy methylcyclohexane matrix at 77 K by UV irradiation of *trans*-2,3-dimethyl-1-mesitylphosphirane. This phosphinidene was shown to possess a triplet ground state.[8] No such compounds have been isolated at ambient temperature.



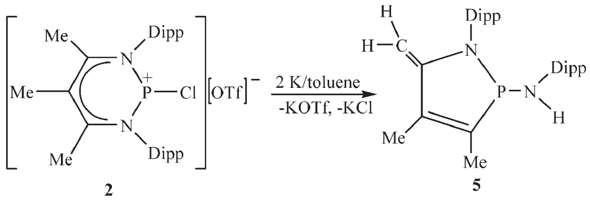
1 ($R_1 = C_6F_5$; $R_2 = H$)
2 ($R_1 = \text{Dipp}$; $R_2 = \text{Me}$)



3 ($R_1 = C_6F_5$; $R_2 = H$)
4 ($R_1 = \text{Dipp}$; $R_2 = \text{Me}$)

Dipp = 2,6-*i*-$Pr_2C_6H_3$

Treatment of **2**[3] with two equivalents of potassium metal in toluene solution at 25 °C for 8 h resulted, after workup of the reaction mixture and recrystallization from hexane, in ~30% yields of pale yellow crystalline **5** (Scheme 1). Although the low-resolution mass spectrum of **5** exhibits a peak at *m*/*z* 462 corresponding to the molecular ion of the targeted phosphinidene, examination of the ^{1}H NMR spectrum revealed the presence of a methylene group and an N–H moiety.[9] It was therefore necessary to appeal to X-ray crystallography to gain further insight into the molecular structure. Compound **5** crystallizes in the trigonal space group $R\bar{3}$ with $Z = 18$.[10] The crystalline state of **5** comprises an ensemble of individual molecules of a valence isomer of the desired phosphinidene (Fig. 1); there are no unusually short intermolecular contacts. The five-membered NCCCP ring is planar (sum of bond angles = 539.9(2)°) and the ring bond angles range from 88.61(11)° for N(1)–P(1)–C(3) to 115.94(17)° for C(1)–N(1)–P(1). Two carbon–carbon double bonds are evident in the structure, namely C(2)–C(3) (1.333(4) Å) and C(1)–C(4) (1.340(4) Å and the geometries at C(2), C(3) and N(1) are trigonal planar as evidenced by the sums of bond angles at these centers.



Scheme 1

There is considerable current interest in the reductive C–N bond cleavage of the NCCCN backbone of β-diketiminate complexes of

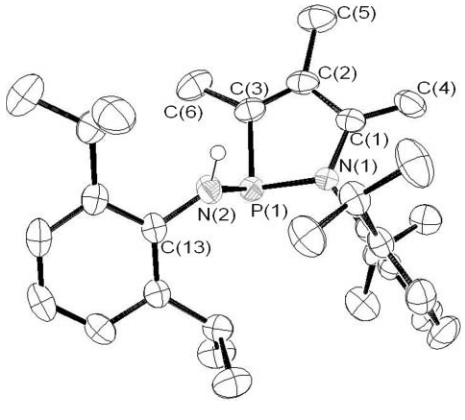
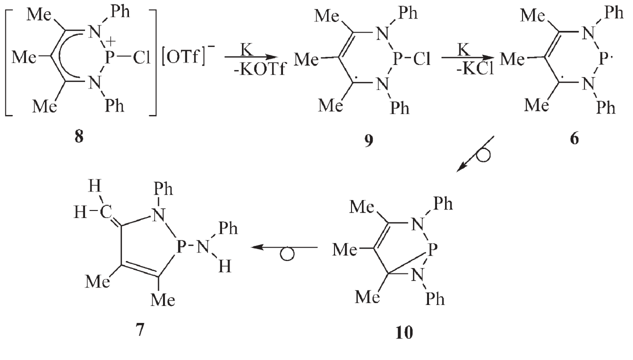


Fig. 1 View of **5** showing the atom numbering scheme and thermal ellipsoids at 40% probability with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): P(1)–N(1) 1.714(2), N(1)–C(1) 1.400(3), C(1)–C(4) 1.341(4), C(1)–C(2) 1.471(4), C(2)–C(3) 1.334(4), C(3)–P(1) 1.817(3), P(1)–N(2) 1.702(2), C(13)–N(2) 1.425(3); C(3)–P(1)–N(1) 88.69(11), P(1)–N(1)–C(1) 115.90(16), N(1)–C(1)–C(2) 109.1(2), C(1)–C(2)–C(3) 113.8(2), C(2)–C(3)–P(1) 115.2(2), P(1)–N(2)–C(13) 123.69(17).

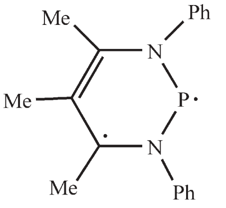
Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas, 78712, USA.
E-mail: cowley@mail.utexas.edu; Fax: (+1) 512-471-6822;
Tel: (+1) 512-471-7484

Ti, Zr and Hf since this transformation results in the formation of group 4 terminal imides supported by an azabutadienyl ligand system.[11] Although reductive C–N bond cleavage of the NCCCN backbone also takes place in the conversion of **2** to **5**, the outcome of this process is distinct from that reported for group 4 β-diketiminates[11] in the sense that an amido derivative of a 1,2-azaphospholine ring system is produced rather than an imido azabutadienyl derivative. A search of the literature revealed that there is only one reference to the 1,2-azaphospholine ring system, namely 2-(dimethylamino)-1,2-dimethyl-5-methylene-Δ^3-1,2-azaphospholine-2-oxide.[12] However, no X-ray crystal structure for this particular ring system was available previously. Moreover, we note that, although there are prior reports concerning the C–H activation of a β-methyl group of main group β-diketiminates,[13] we are not aware of the occurrence of *both* β-methyl activation and NCCCN ligand backbone cleavage.

In order to gain insight into the mechanism of formation of the phosphinidene valence isomer **5**, DFT calculations were carried out at the B3LYP level of theory[14] using the Gaussian 03 suite of programs[15] and the 6-31+G* basis set. In the interest of computational efficiency, the bulky Dipp substituents were replaced by Ph groups. Comparison of the energies of the idealized phosphinidene **6** with that of its valence isomer **7** reveals that the latter is more stable by 36.2 kcal mol^{-1}. Interestingly, **6** is computed to adopt a triplet ground state (note that only one canonical form is depicted; the other form is obtained by interchanging the unpaired electron and the double bond). The triplet–singlet gap is computed to be 13.8 kcal mol^{-1}. This result contrasts with a similar type of calculation on the all-hydrogen-substituted β-diketiminato phosphinidene, [HC(CH)$_2$(NH)$_2$]P, by Ellis and Macdonald[16] which revealed a singlet ground state. We have repeated this calculation and our results are in excellent agreement with those of these authors. Inferentially, the nature of the ground state of β-diketiminato phosphinidenes is dependent upon the nature of the ring substituents. A similar conclusion has been reached in the case of β-diketiminate-substituted boranediyls.[17] A plausible, albeit speculative, mechanism for the formation of the phosphinidene valence isomer is summarized in Scheme 2. Assuming that the two-electron reduction of the idealized chlorophosphenium ion **8** proceeds in two steps, addition of the first electron would generate the monoradical **9** (as in the case of **6**, only one canonical form is shown).[18] Addition of the second electron would then generate the triplet diradical phosphinidene **6**. The conversion of **6** to **10** takes place by intramolecular P–C bond formation to afford the bicylic diamagnetic derivative **10**, thereby liberating 24.5 kcal mol^{-1}. Finally, the phosphinidene valence isomer **7** is formed by N–C bond cleavage and hydrogen transfer from a β-methyl group to the nascent imido nitrogen center. The latter rearrangement is computed to be exothermic by 36.2 kcal mol^{-1}. In general, the computed metrical parameters for the model valence isomer **7** agree with the experimental values for **5** to within 2% or better. The sole exception is the P(1)–N(2)–C(13) bond angle (see Fig. 1 atom numbering). The fact that this angle is more obtuse for **5** (102.81°) than for the model phenyl-substituted compound **7** (98.03°) is attributable to the bulkier nature of the Dipp substituents.



Scheme 2



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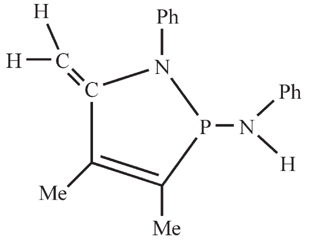

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In summary, we have prepared and structurally characterized the first example of a valence isomer of a phosphinidene supported by a β-diketiminate ligand. A mechanism for the conversion of the putative triplet β-diketiminato phosphinidene into the observed 1,2-azaphospholine derivative is proposed based upon DFT calculations.

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9 *Spectroscopic data* for **5**: ^{1}H NMR (299.89 MHz, C_6D_6): δ 0.99–1.34 (m, 24 H, CHMe_2), 1.78 (d, 3H, CH_3, $^3J_{PH}$ = 1.2 Hz), 1.82 (s, 3H, CH_3,), 3.01–3.77 (m, 4H, CHMe$_2$), 4.18 (d, 1H, NH, $^2J_{PH}$ = 3.3 Hz), 4.22 (s, 2H, CH_2), 6.98–7.29 (m, 6H, Ar); ^{13}C{^{1}H} NMR (74.97 MHz, C_6D_6): δ 15.82 (CH$_3$), 17.80 (CH$_3$), 23.67, 24.54, 24.98, 26.21 (CMe_2), 28.73, 29.35 (CMe_2), 85.34 (CC Hz), 109.78, 123.51, 123.80, 124.26, 142.78, 143.35, 147.82, 148.81, 149.56, 150.34 (Ar + C=C), 161.16 (CCH$_2$); ^{31}P{^{1}H} NMR (121.50 MHz, C_6D_6): δ 46.27 (s). HRMS (CI, CH$_4$): calc. for $C_{30}H_{44}N_2P$ [(M + H)]$^+$: 463.3242; found: 463.3238. IR (cm^{-1}): 1363 (=CH$_2$), 1635, 1647, 1653 (C=C), 3397 (NH).

10 *Crystal data* for **5**: $C_{30}H_{43}N_2P$ (462.23), trigonal, space group $R\bar{3}$, a = 38.7640(10), b = 38.764(2), c = 10.065(3) Å, V = 13098 Å^3, Z = 18, D_c = 1.056 g cm^{-3}, μ(Mo-Kα) = 0.113 mm^{-1}, T = 153(2) K, 6673 independent reflections (R_{int} = 0.0826), final R indices (310 parameters) for 6673 independent reflections [$I > 2\sigma(I)$] are R_1 = 0.0645, wR_2 = 0.1720, GOF = 1.025. CCDC number 640084. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704266c.

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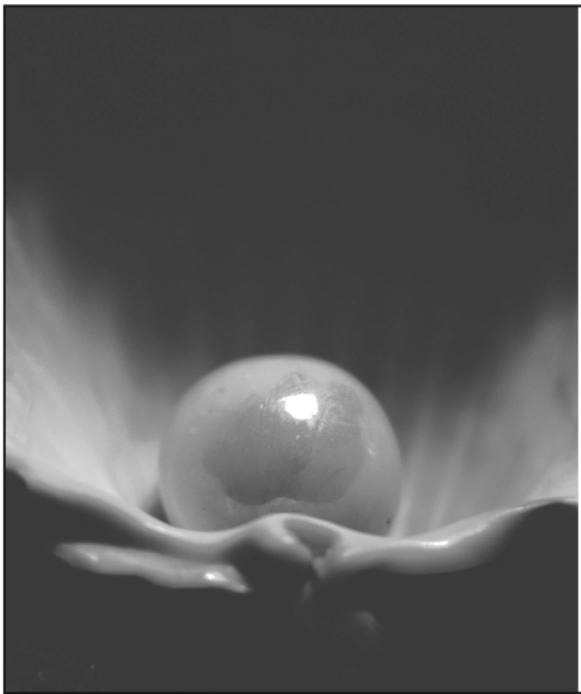

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