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An unusual norcaradiene/tropylium rearrangement from a persistent amino-phosphonio-carbene

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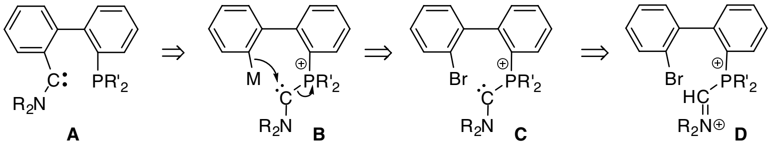
Abstract—An amino-phosphonio-carbene featuring a bromobiphenyl backbone was prepared and spectroscopically characterized at low temperature. This carbene was found to readily rearrange upon warm up, affording an original tricyclic phospholium derivative, presumably via a norcaradiene/tropylium isomerization.

Due to their strong σ-donor character, N-heterocyclic carbenes (NHCs) have found numerous applications as alternative ligands to phosphines for transition-metal catalysts.[1] Taking advantage of the substantial stabilization brought by a single heteroatom substituent (an amino or phosphino group),[2] the variety of available stable carbenes has been significantly increased over the last five years.[3] Accordingly, the steric and electronic properties of amino-carbenes could be varied in a broader range, as nicely illustrated by the cyclic amino-alkyl-carbenes (CAACs).[4]

The spectacular achievements reported with diphosphines featuring a diaryl backbone (especially BIPHEN and BINAP ligands)[5] prompted us to investigate related heteroditopic ligands combining amino-carbene and phosphine coordination sites. The synthesis of the representative biphenyl derivatives **A** (Scheme 1) was envisaged as a further application of the recently reported nucleophilic substitution at the carbene center of amino-phosphonio-carbenes.[6] Accordingly, dications **D** were considered as promising precursors for **A** via a deprotonation/metalation sequence involving intermediates **B** and **C**. Here we report the preparation and spectroscopic characterization at low temperature of an amino-phosphonio-carbene of type **C**. This compound was found to readily rearrange upon warm up, affording an original tricyclic derivative, presumably via a norcaradiene/tropylium isomerization.

The phosphonio-iminium salt **1** (dication of type **D**) was obtained by extrapolation of the procedure described for the tricyclohexyl and triphenylphosphines.[7] Accordingly, the readily available 2-bromo-2′-diphenylphosphinobiphenyl[8] was treated with the *C*-chloroiminium chloride in the presence of 2 equiv of trimethylsilyl triflate in CH_3CN (Scheme 2). Dication **1** was isolated in 82% yield as a pale yellow solid. The signals observed



Scheme 1. Proposed synthetic route to aminocarbene/phosphine derivatives **A**.

Keywords: Carbenes; Rearrangement; Norcaradiene; Tropylium.

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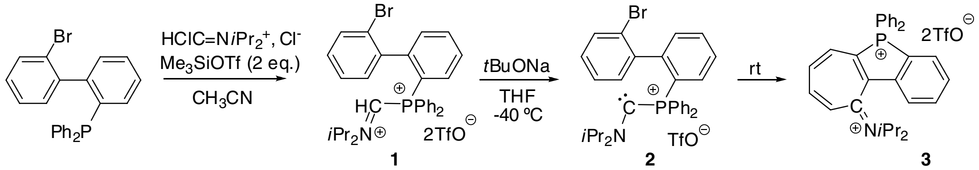

Scheme 2. Synthesis and rearrangement of the amino-phosphonio-carbene **2**.

at low-field in the ^{1}H (9.66 ppm, $^{2}J_{HP} = 23.7$ Hz) and ^{13}C NMR spectra (169.5 ppm, $^{1}J_{CP} = 63.5$ Hz) are diagnostic of the C–H iminium moiety of such dications.[9]

Deprotonation of dication **1** was achieved with sodium *t*-butoxide at −78 °C in THF.[10] Quite surprisingly, the ensuing carbene **2** could only be spectroscopically characterized at −40 °C. The shielding of the ^{31}P NMR signal by about 30 ppm upon deprotonation and the ^{13}C NMR chemical shift for the carbene center (δ 291.4 ppm, $^{1}J_{CP} = 112.2$ Hz) unambiguously establish the amino-phosphonio-carbene structure of **2**.[6] Upon warming to room temperature, carbene **2** cleanly rearranges within minutes into a new compound **3**, which was isolated as an orange solid.[11] The multi-nuclear data for **3** revealed interesting features: (i) the ^{31}P NMR chemical shift of **3** (23.0 ppm) is very similar to that of the dication **1**, (ii) the ^{1}H and ^{13}C NMR signals for the CH(*i*Pr) groups (^{1}H: 4.57 and 4.66 ppm; ^{13}C: 57.6 and 64.0 ppm) are in the typical range for an iminium, and (iii) the related ^{13}C NMR signal for the C=N^{+} moiety (166.8 ppm) is attributed to a quaternary center. Single crystals of **3** were grown from a CH_2Cl_2/Et_2O mixture at −30 °C and the X-ray diffraction study revealed a major reorganization of the carbene (Fig. 1). On the one hand, the amino-carbene, which is no longer bonded to the phosphorus atom, has apparently contributed to the conversion of one of the phenyl rings into a tropylium moiety. On the other hand, the phosphorus atom bridges the two aromatic rings, leading to a dicationic tricyclic structure.[12]

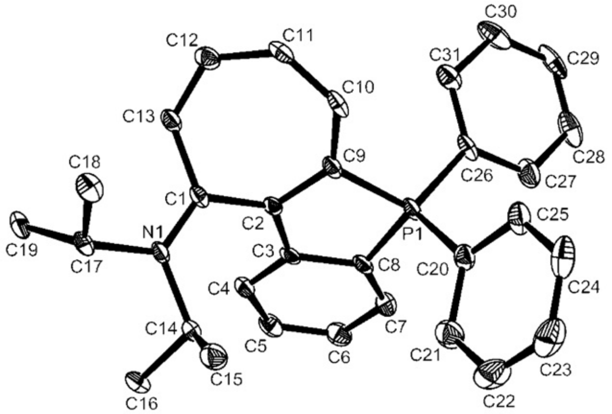

Figure 1. Thermal ellipsoid diagram (50% probability) of **3**, the hydrogen and counter-anions have been omitted for clarity.

Although the precise mechanism for the conversion of **2** into **3** remains rather obscure, the following hypothesis may be reasonably formulated (Scheme 3). First, nucleophilic attack of amino-carbene **2** on the biphenylbackbone would be favored by the electron-withdrawing phosphonio group. Second, the ensuing ylide **4** would attack back to the highly electron-deficient carbon center leading to the norcaradiene-type iminium **5**. Third, ring enlargement[13] would convert **5** into the corresponding amino-tropylium salt **6**. Last, the liberated phosphine would attack at the brominated *ortho* position to afford the tricyclic structure **3**.[14]

In conclusion, these results highlight the dramatic influence of the substitution pattern of amino-phosphonio-carbenes on their stability. The presence of a bromobiphenyl moiety induced an unusual rearrangement that presumably occurred via a norcaradiene/tropylium isomerization. Alternative routes to heteroditopic amino-carbene/phosphine ligands of type **A** are currently under investigation.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.11.099.

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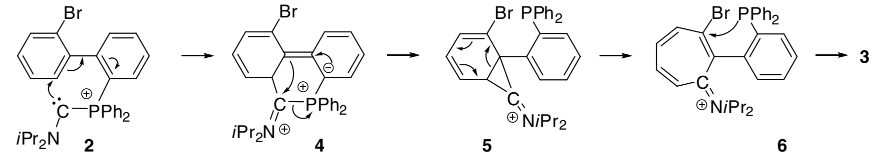

Scheme 3. Postulated mechanism for the rearrangement of **2** into **3**.

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9. A 1.2/1 mixture of 2-bromo-2′-diphenylphosphinobiphenyl (1.20 g, 2.88 mmol) and *C*-chloroiminium chloride (0.44 g, 2.40 mmol) was cooled to −30 °C and 20 mL of CH_3CN was added. After addition of Me_3SiOTf (0.87 mL, 4.80 mmol) at −30 °C, the mixture was warmed to room temperature and stirred for 2 h. All the volatiles were removed under vacuum and the resulting solid was washed with 3 × 20 mL of Et_2O yielding **1** as a pale yellow solid (1.6 g, 82%). Selected data: ^{31}P NMR (CD_3CN): δ 19.4; ^{1}H (CD$_3$CN): δ 0.82, 1.32, 1.63, 1.75 (d, $^3J_{HH} = 6.3$ Hz, 12H, CH_3), 4.21 (sept, $^3J_{HH} = 6.3$ Hz, 1H, CHCH$_3$), 4.79 (br, 1H, CHCH$_3$), 7.21–8.15 (m, 18H, CH_{aro}), 9.66 (d, $^2J_{HP} = 23.7$ Hz, 1H, CH=N); ^{13}C{^{1}H} NMR (CD_3CN): δ 18.8, 19.3, 24.0, 24.3 (s, CH_3), 65.2 (d, $^3J_{CP} = 5.2$ Hz, CHCH$_3$), 68.8 (d, $^3J_{CP} = 5.6$ Hz, CHCH$_3$), 169.5 (d, $^1J_{CP} = 63.5$ Hz, CH=N).
10. In a NMR tube, a 1/1 mixture of dication **1** (65 mg, 0.08 mmol) and *t*-BuONa (7.5 mg, 0.08 mmol) was cooled to −78 °C and 0.7 mL of THF was added. The tube was shaken until complete dissolution, warmed up to −40 °C, and analyzed directly by NMR. Selected data for **3**: ^{31}P NMR (THF): δ −13.8; ^{13}C{^{1}H} NMR (THF): δ 19.4 (s, CH_3), 58.6 (d, $^3J_{CP} = 27.6$ Hz, CHCH$_3$), 72.8 (d, $^3J_{CP} = 26.4$ Hz, CHCH$_3$), 291.4 (d, $^1J_{CP} = 112.2$ Hz, $C_{carbene}$).
11. A 1/1 mixture of dication **1** (500 mg, 0.60 mmol) and *t*-BuONa (58 mg, 0.60 mmol) was cooled to −78 °C and 10 mL of THF was added. The solution was warmed to room temperature and stirred for 2 h. All the volatiles were removed under vacuum and the resulting solid was washed with 20 mL of Et_2O. After extraction with CH_2Cl_2 and evaporation of the solvent, the solid was washed with 10 mL of THF. Recrystallization from CH_2Cl_2/Et_2O yielded **3** as orange crystals (43% yield). Selected data: ^{31}P NMR (CD_3CN): δ 23.0; ^{1}H NMR (CD_3CN): δ 1.11 and 1.48 (d, $^3J_{HH} = 6.3$ Hz, 6H, CH_3), 1.51 and 1.88 (d, $^3J_{HH} = 6.9$ Hz, 6H, CH_3), 4.57 (sept, $^3J_{HH} = 6.3$ Hz, 1H, CHCH$_3$), 4.66 (sept, $^3J_{HH} = 6.9$ Hz, 1H, CHCH$_3$), 7.46–8.29 (m, 18H, CH_{aro}); ^{13}C NMR{^{1}H} (CD_3CN): δ 17.5, 21.4, 21.7 and 22.3 (s, CH_3), 57.6 and 64.0 (s, CHCH$_3$), 166.8 (d, $J_{CP} = 25.4$ Hz, C=N). Crystallographic data (excluding structure factors) for **3** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Number CCDC-625764. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).
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