DOI: 10.1002/anie.200701588

Carbenoid Compounds

From a Stable Dianion to a Stable Carbenoid**

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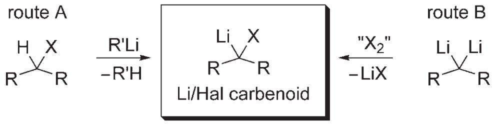
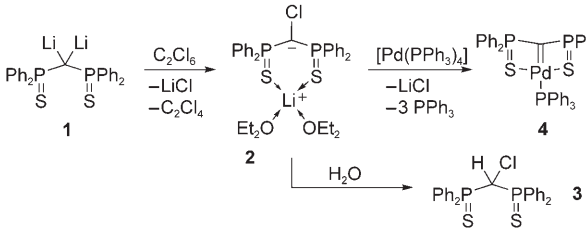
Organometallic compounds have demonstrated major utility in organic synthesis for the formation of C–C and C–heteroelement bonds.[1] Among these, α-halogenated derivatives (typically R_2CLiX) have attracted much attention for their unusual electrophilic character. These molecules have been named "carbenoids" since they can formally release the carbene fragment when trapped with an electron-rich center (alkenes, carbanions, etc.).[2,3] In the absence of any trapping reagent, Li/halogen (Li/Hal) carbenoids decompose at low temperature by α-elimination of LiX.[2,4] For instance, the carbenoid $LiCHCl_2$ decomposes around −100 °C.[5] Nevertheless, extensive work has been devoted to the synthesis and characterization of carbenoid derivatives. The general synthetic method relies on the α-metalation of halogenoalkanes (Scheme 1, route A). Owing to their instability, these molecules have mostly been studied by NMR spectroscopy and theoretical calculations.[2] To date, only a few X-ray structures have been recorded: Boche and co-workers succeeded in determining the X-ray structure of the unstable $LiCHCl_2\cdot$(pyridine)$_3$ carbenoid,[6] and so far the most stable carbenoid was characterized by Niecke and co-workers as an ylene(phosphoranylidene)carbenoid that decomposes at −10 °C.[7]



Scheme 1.

We have recently illustrated the use of thiophosphinoyl groups in the stabilization of highly reduced carbon centers and isolated stable geminal dianion **1**.[8] We postulated that a similar strategy could also be applied to stabilize a carbenoid. Herein we report on a new synthetic path to Li/Hal carbenoids by mild oxidation of geminal dianions (Scheme 1, route B)[9] and validate this hypothesis by isolating the first Li/Hal carbenoid that is stable at room temperature.

The oxidation of the geminal dianion **1** was undertaken by using hexachloroethane in diethyl ether (Scheme 2). The reaction was monitored by ^{31}P NMR spectroscopy and showed the complete formation of a sole compound (**2**), characterized by a singlet at $\delta = 45.5$ ppm (vs. $\delta = 20.6$ ppm for **1**), within a few minutes.[10] Compound **2** was isolated in quantitative yield after removal of LiCl by centrifugation and fully characterized by NMR spectroscopy (^{1}H and ^{13}C). This reaction validates the relevance of route B for the synthesis of carbenoids. Surprisingly, **2** proved to be stable in the solid state and in solution up to 60 °C. Above this temperature, decomposition of **2** to a mixture of intractable products was observed. The electronic reasons behind this exceptional stability were sought after. Carbenoids are usually highly unstable species, and their electronic structure has been investigated mainly by low-temperature NMR spectroscopy, which was corroborated by theoretical calculations.[2a,11] The most striking point for these species concerns the ^{13}C NMR chemical shift of the Li/Hal carbenoid (R_2CLiX) center, which is deshielded compared to that of the hydrogenated species (R_2CHX). This deshielding has been attributed to a weakening of the carbon–halogen bond upon metalation (paramagnetic contribution of the σ^*_{C-X} orbital to the ^{13}C NMR chemical shift). For example, a deshielding of 50.0 ppm has been measured by Seebach et al. for $LiCHCl_2$ in THF.[12] Further insights into the electronic structure of **2** were provided by its ^{13}C NMR spectrum. In **2**, the central carbon atom resonates at $\delta = 38.5$ ppm as a triplet ($^1J_{CP} = 80.0$ Hz). For the purpose of comparison, the hydrogenated species (**3**) was synthesized by trapping **2** with water. Compound **3** was fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and X-ray diffraction analysis.[13] A shielding of $\delta = 15.2$ ppm was clearly measured for the central ^{13}C atom on going from **3** ($\delta = 53.7$ ppm) to **2**. This observation reveals that in carbenoid



Scheme 2.

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[**] The authors thank the CNRS and the Ecole Polytechnique for the financial support and IDRIS for the allowance of computer time (project no. 71616).

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2 the paramagnetic contribution is lowered and the C–Cl bond remains strong.

This feature was confirmed by a study of the metric parameters of **2** (Figure 1).[13] Indeed the C–Cl bond length in **2** (1.781(2) Å) is as short as in **3** (1.796(4) Å).[14] The carbon atom is planar (Σangles = 359.9°) and strongly stabilized by the two phosphorus atoms (P–C 1.726 Å (av) in **2** vs. 1.860 Å (av) in **3**). Moreover, the X-ray structure reveals the stabilization of the lithium cation by the two sulfur atoms and two molecules of diethyl ether. This coordination most likely prevents LiCl elimination and therefore accounts for the increased thermal stability of **2**. Such an effect is consistent with the higher stability of carbenoids observed in coordinating solvents.[2a]

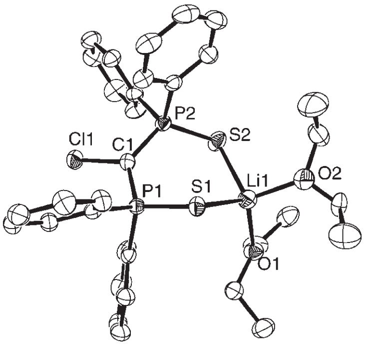

Figure 1. ORTEP plot of **2** (ellipsoids set as 50% probability). Selected bond lengths [Å] and angle [°]: P1-C1 1.722(2), P2-C1 1.730(2), C1-Cl1 1.781(2), P1-S1 1.987(1), P2-S2 1.995(1); P1-C1-P2 127.7(1).

Theoretical calculations have been performed to rationalize these findings in detail. The geometry optimized on the complete system is in excellent agreement with the experimental structure.[15] Analysis of the carbon hybridization state indicates that the carbon atom possesses a lone pair in a pure p orbital, stabilized by negative hyperconjugation into the phosphorus antibonding orbitals. This observation is in agreement with previous results obtained for dianion **1**, which showed that in this system a pure p lone pair is more efficiently stabilized by negative hyperconjugation than a sp^2-hybridized lone pair. As a consequence, the carbon s character in the C–Cl bond remains high, and the carbon atom directs a hybrid orbital with 21.9% s character towards the chloride atom (18.6% in **3**). For comparison, in the carbenoid $LiCH_2Cl{\cdot}(OMe_2)_3$ most of the 2s character is concentrated in the C–Li bond (34.3%) so that only 11.0% is left for the C–Cl bond (vs. 19.0% in CH_3Cl), thus accounting for the weakness of the C–Cl bond. Accordingly, the C–Cl Wiberg bond index remains constant between **3** (0.88) and **2** (0.84), and it significantly increases for the C–P bonds (from 0.81 in **3** to 1.09 in **2**). These findings are in agreement with the experimental data (shielding of the carbon atom and short C–Cl bond). To conclude, the stability of carbenoid **2** comes from 1) the coordination of the lithium cation by the thiophosphinoyl arms and 2) the stabilization of the carbon lone pair in a pure p orbital, which leads to a rather strong C–Cl bond.

To determine whether carbenoid **2** may be used as a carbene precursor (i.e., whether the C–Cl bond may be cleaved), we investigated its reactivity towards several transition-metal complexes. Results from our studies with palladium complexes are presented here. Compound **2** reacts slowly with $[Pd^0(PPh_3)_4]$ in THF at room temperature to form complex **4**, LiCl, and triphenylphosphine, thus showing that indeed carbenoid **2** is a convenient source of a carbene ligand (Scheme 2). Interestingly, complex **4** can also be prepared by using dianion **1** as the carbene precursor and $[PdCl_2(PPh_3)_2]$.[16,17] To the best of our knowledge, this reactivity is the first example of the use of a Li/Hal carbenoid as a precursor for the synthesis of a carbene complex. The mechanism of this unprecedented transformation was investigated by DFT calculations. Two mechanisms (A and B, Figure 2) can be proposed, depending on the nature of the C–Cl bond cleavage. Indeed, the metal center may act as a nucleophile through displacement of the chloride anion (nucleophilic substitution, mechanism A) or insert into the

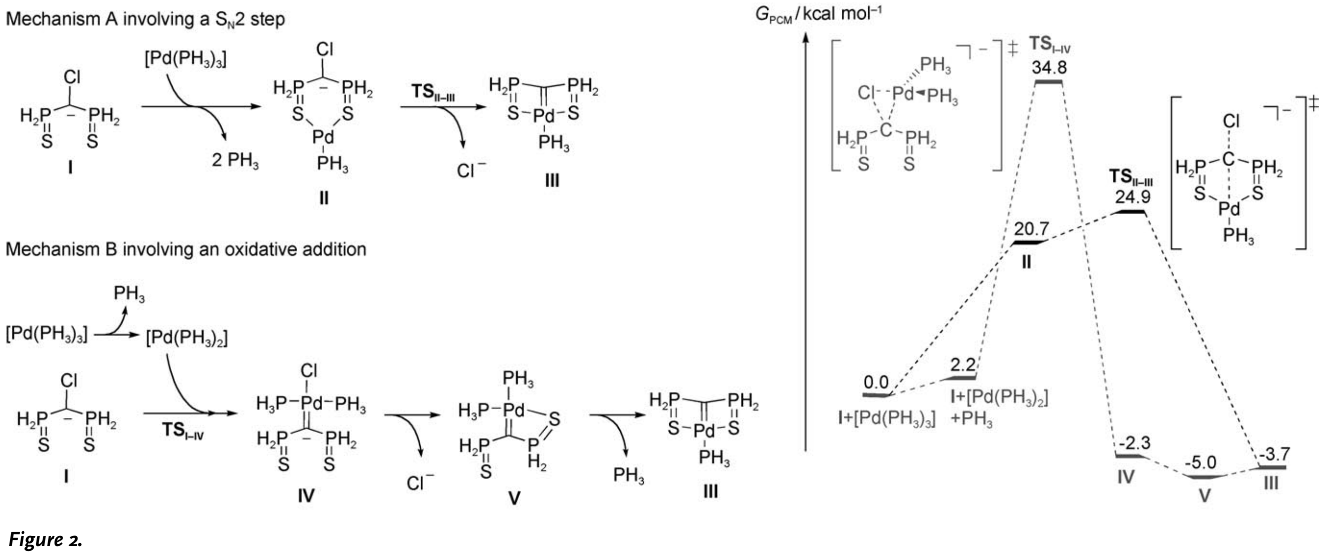

Figure 2.

C−Cl bond (oxidative addition, mechanism B). The results of calculations that were carried out on a model system are presented in Figure 2.[15]

As the coordination of the lithium cation may play an important role in the reactivity of the carbenoid,[18] both mechanisms have been computed in the presence and in the absence of a $[Li(OMe_2)_2]^+$ counterion. We have found that the presence of $[Li(OMe_2)_2]^+$ does not have much influence on both energetic profiles and, for the sake of simplicity, only the mechanisms in the absence of the counterion are presented (see the Supporting Information for the mechanism in the presence of the cation).[19] Formation of complex **III** is a slightly exergonic process ($\Delta G_{\mathrm{PCM,I-III}} = -3.7\ \mathrm{kcal\,mol^{-1}}$; PCM = polarizable continuum model). Pathway A proceeds in two steps, namely coordination of the thiophosphinoyl arms of **I** to the palladium(0) fragment yielding complex **II** and a subsequent S_N2 step yielding **III** (via $\mathbf{TS_{II-III}}$). This pathway requires an overall energy of $24.9\ \mathrm{kcal\,mol^{-1}}$. The alternative mechanism B relies on an oxidative addition step: The active $[Pd^0(PH_3)_2]$ species[20] inserts into the C−Cl bond to form complex **IV** (via $\mathbf{TS_{I-IV}}$). Complex **III** is then formed after elimination of the chloride ion, and PH_3 is formed upon coordination of the thiophosphinoyl arms (via **V**). The oxidative addition is the rate-determining step of this pathway and requires an activation energy of $34.8\ \mathrm{kcal\,mol^{-1}}$. Therefore, comparison of the two energetic profiles clearly shows that formation of the carbene complex results from an S_N2 attack of the palladium(0) center, which displaces the chloride anion (LiCl in the presence of lithium ions). This mechanism definitely demonstrates the electrophilic nature of **2**, a characteristic property of carbenoids. According to this mechanism, further developments of this reactivity to form carbene complexes should focus on electron-rich metal centers to promote the S_N2 step.

In conclusion, we have developed a new synthetic approach towards carbenoids on the basis of the oxidation of a geminal dianion. The use of electron-withdrawing substituents proved to be efficient for the stabilization of the carbenoid center and therefore allowed us to synthesize the first Li/Hal carbenoid that is stable at room temperature. Reactivity investigations showed that Li/Hal carbenoids can be used to form carbene complexes with electron-rich metal centers.

Experimental Section

All experiments were carried out in a dry argon or nitrogen atmosphere using distilled and degassed solvents.

2: Hexachloroethane (94.8 mg, 0.40 mmol) was added to a solution of **1** (0.40 mmol) in diethyl ether (3 mL) at −40 °C and stirred for 5 minutes while being allowed to room temperature. LiCl was removed by centrifugation, and the solvents were then evaporated to afford **2** as a yellow solid in 100 % yield (260 mg, 0.40 mmol). ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): $\delta = 7.11$–7.35 (m, 12H; H_{meta} and H_{para}), 7.98 ppm (brs, 8H; H_{ortho}); ^{31}P{^{1}H} NMR (121.5 MHz, [D$_8$]THF, 25 °C, 85 % H_3PO_4 as external standard): $\delta = 45.5$ ppm (s); ^{13}C{^{1}H} NMR (75.465 MHz, $CDCl_3$, 25 °C, [D$_8$]THF ($\delta = 68.6$ ppm) as internal reference): $\delta = 38.5$ (t, ^1J(C,P) = 80.0 Hz; PCP), 127.7 (t, ^3J(C,P) = 6.1 Hz; C_{meta}), 130.1 (s; C_{para}), 133.6 (t, ^2J(C,P) = 5.1 Hz; C_{ortho}), 139.1 ppm (AXX′, ΣJ(C,P) = 129.0 Hz; C_{ipso}). Elemental analysis (%) calcd for $C_{33}H_{40}ClLiO_2P_2S_2$: C 62.21, H 6.33; found: C 62.24, H 6.41.

For syntheses of **3** and **4**, see the Supporting Information.

Received: April 11, 2007
Published online: July 2, 2007

Keywords: carbenes · carbenoids · density functional calculations · lithium · phosphorus

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[13] X-ray structure data : Nonius KappaCCD diffractometer, φ and ω scans, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator, $T = 150$ K, structure solution with SIR97,[21a] refinement against F^2 with SHELXL-97[21b] with anisotropic thermal parameters for all non-hydrogen atoms, calculated hydrogen positions with riding isotropic thermal parameters. Data collection for **2**: $C_{33}H_{40}ClLiO_2P_2S_2$, $M_r = 637.10$, crystal dimensions $0.20 \times 0.20 \times 0.10$ mm, triclinic, space group $P\bar{1}$, $a = 10.539(1)$, $b = 10.672(1)$, $c = 16.889(1)$ Å, $\alpha = 82.135(1)$, $\beta = 72.243(1)$, $\gamma = 68.526(1)°$, $V = 1682.8(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.257\ \mathrm{g\,cm^{-3}}$, $\mu = 0.361\ \mathrm{cm^{-1}}$, F-

$F(000) = 672$, $\theta_{max} = 27.48°$, *hkl* ranges: −13 to 13, −13 to 13, −15 to 21, 10774 reflections collected, 7683 unique reflections ($R_{int} = 0.0156$), 6072 reflections with $I > 2\sigma(I)$, 401 parameters refined, $GOF(F^2) = 1.042$, final *R* indices ($R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $R1 = 0.0376$, $wR2 = 0.1030$, max/min residual electron density 0.778(0.048)/−0.340(0.048) e Å^{-3}. For the data collection for **3**, see the Supporting Information. CCDC-643274 and -643275 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[20] It has been shown that, in solution, $[Pd(PPh_3)_4]$ dissociates to form $[Pd(PPh_3)_3]$ and PPh_3. The oxidative addition step proceeds via the coordinatively unsaturated $[Pd(PPh_3)_2]$ complex; see: C. Amatore, A. Jutand, *J. Organomet. Chem.* **1999**, *576*, 254–278; A. Jutand, A. Mosleh, *Organometallics* **1995**, *14*, 1810–1817; C. Amatore, A. Jutand, F. Khalil, M. A. Mbarki, L. Mottier, *Organometallics* **1993**, *12*, 3168–3178.

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