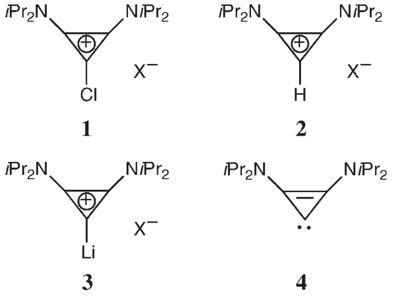

Scheme 1. Schematic representation of bis(diisopropylamino) derivatives of chlorocyclopropenium **1**, cyclopropenium **2**, cyclopropenylidene–lithium adduct **3**, and cyclopropenylidene **4**.

Carbenes

DOI: 10.1002/ange.200602701

Isolation of Cyclopropenylidene–Lithium Adducts: The Weiss–Yoshida Reagent**

*Vincent Lavallo, Yutaka Ishida, Bruno Donnadieu, and Guy Bertrand**

In the 1950s, Breslow[1] and Wanzlick[2] realized that the stability of a carbene could be dramatically enhanced by the presence of amino substituents, but they were unable to isolate a "monomeric" carbene.[3] It was only in 1991, three years after the isolation of a (phosphino)(silyl)carbene,[4] that a bottleable diamino carbene, namely an imidazol-2-ylidene, was prepared.[5] Even more strikingly, in a paper entitled "1,2,3,4-Tetraphenylimidazol-2-ylidene: The Realization of Wanzlick's Dream", Arduengo et al.[6] reported that a modification of the experimental procedure published by Wanzlick's group makes it possible to isolate one of the exact same carbenes that was postulated in 1970.[7]

Wanzlick was not the only one to nearly isolate the first stable carbene. Indeed, in the 1970s, Yoshida[8] and Weiss[9] attempted independently the preparation of the bis(diisopropylamino)cyclopropenylidene **4** (Scheme 1). Recently, we isolated exactly the same carbene after deprotonation of cyclopropenium salt **2** ($X = BPh_4$) with potassium bis(trimethylsilyl)amide.[10] Among the routes used by Yoshida and Weiss were lithium/halogen exchange from **1** ($X = ClO_4$)[9a] and the deprotonation of **2** ($X = ClO_4$),[8a,b] both with *n*BuLi. However, they were not able to isolate the resulting product. Initially, Yoshida claimed the successful synthesis of the free cyclopropenylidene **4**,[8a] but several years later he[8b–e] and Weiss[9a] concluded concurrently that the compound in question was more likely the carbene–lithium adduct **3** ($X = ClO_4$). More recently, Tamm, Hahn, et al.[11] repeated the lithium/halogen exchange reaction of **1** ($X = ClO_4$ and CF_3SO_3) with *n*BuLi and described the product as stable only at low temperatures. It has also been shown that this compound, generated in situ, effectively transfers the cyclopropenylidene moiety **4** to a number of substrates, including transition metals and main-group fragments.[8,9,11,12]

Weiss proposed the formation of the carbene–lithium adduct **3** ($X = ClO_4$), rather than that of the free carbene **4**, based primarily on the observation that no $LiClO_4$ precipitated from the reaction mixture.[9a] The only spectroscopic data that exist for the Weiss–Yoshida (W–Y) reagent is a single report of a lithium NMR chemical shift.[8d] All these experimental observations, including the transfer reactions, do not rule out the possibility that the W–Y reagent could actually be the free carbene **4**. Indeed, carbenes that can be isolated as free species do not generally form stable complexes with simple lithium salts (LiX, X = halogen or more weakly coordinating anion),[13,14] although there are two exceptions.[15]

This analysis prompted us to reinvestigate the exact nature of the W–Y reagent. First, we reproduced the lithium/halogen exchange reaction with *n*BuLi, but to avoid any potential explosive hazards resulting from the perchlorate anion, the chlorocyclopropenium tetrafluoroborate salt **1** ($X = BF_4$) was used as a precursor. After the reaction mixture had been stirred for ten minutes at −78 °C, a very clean reaction occurred and crucially, a ^{13}C NMR signal at $\delta = 167$ ppm was observed. This signal is shifted to high field compared to that of the carbene carbon nucleus of the free cyclopropenylidene **4** ($\delta = 185$ ppm),[10] exactly as expected for a lithium complex. Indeed, it has been shown for the exceptions mentioned above[15] that such a complexation induces an upfield shift of about 20 ppm. Surprisingly, the ^{13}C NMR spectrum remained unchanged when the solution was warmed to room temperature. After evaporation of the solvent under high vacuum, the residue was washed with hexane to afford a highly air-sensitive white powder, which was recrystallized in diethyl ether at −25 °C. The resulting colorless crystals (m.p. 88–90 °C (decomp), 45 % yield) were subjected to a single-crystal X-ray diffraction study.[16] In the solid state, **3** is a polymeric chain with an overall stoichiom-

---

[*] V. Lavallo, Dr. Y. Ishida, B. Donnadieu, Prof. G. Bertrand
UCR–CNRS Joint Research Chemistry Laboratory (UMI 2957)
Department of Chemistry
University of California
Riverside, CA 92521-0403 (USA)
Fax: (+1) 951-827-2725
E-mail: gbertran@mail.ucr.edu

[**] We are grateful to the NIH (R01 GM 68825) and Rhodia for financial support of this work, and to the JSPS for a Fellowship to Y.I.

etry of five $LiBF_4$ units per four carbene ligands (Figures 1 and 2). Each cyclopropenylidene moiety is bonded to a lithium cation, which is coordinated by three fluorine atoms from three different tetrafluoroborate anions. The lithium cations that are not complexed by a cyclopropenylidene moiety are tetrahedrally coordinated by fluorine atoms from four different BF_4 anions. The carbene–lithium bond length (C1–Li1 2.093 Å) is significantly shorter than those observed in the few other reported carbene–lithium adducts (2.135–2.155 Å).[17]

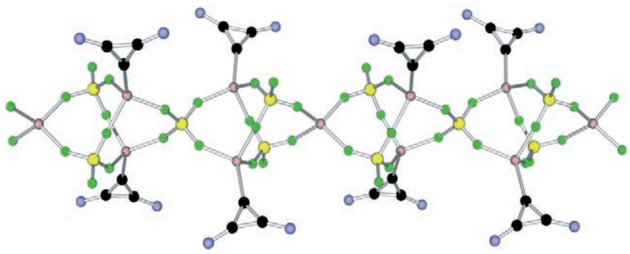

Figure 1. Molecular view of the structure of polymeric **3** in the crystal (C black, N blue, Li pink, B yellow, F green). The isopropyl groups on the nitrogen atoms have been omitted for clarity.

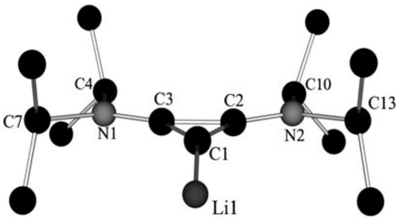

Figure 2. Molecular view of the structure of **3**. Selected bond lengths [Å] and angles [°]: Li1-C1 2.139(7), C1-C2 1.399(5), C1-C3 1.418(5), C2-C3 1.389(5), C2-N2 1.334(4), C3-N1 1.320(5); Li1-C1-C2 150.3(3), Li1-C1-C3 148.9(3), C2-C1-C3 59.1(3), C1-C2-N2 146.8(3), C3-C2-N2 152.0(4), C1-C2-C3 61.2(3), C1-C3-N1 147.5(4), C2-C3-N1 152.8(4), C1-C3-C2 59.8(3), C3-N1-C7 117.1(3), C3-N1-C4 121.0(3), C4-N1-C7 121.4(3), C2-N2-C13 116.9(3), C2-N2-C10 122.3(3), C10-N2-C13 120.7(3).

If we view the conjugate acid (**2**) of the cyclopropenylidene **4** as a proton/carbene complex, there are clearly several structural and spectroscopic trends (Table 1). An elongation of the exocyclic C–N bonds is observed through the series **2** < **3** < **4**, which corresponds to decreased π donation from the amino groups. This trend is confirmed by the observed rotational barriers about the C–N bond, as deduced from variable-temperature NMR experiments. The bond angle about the carbene center contracts along the series **2** > **3** > **4**, which suggests an increase in s character for the exocyclic sp hybrid-type orbital. All of the relevant geometric parameters for **3** are closer to those for the free cyclopropenylidene **4** than its proton complex **2**, thus indicating a certain amount of ionic character in the carbene–lithium bond.

Table 1: Comparison of the geometric parameters, rotational barrier (E_{rot}) about the C_{ring}–N bonds, and spectroscopic data for compounds **2**, **3**, and **4**.

Compound	C_{ring}–N[a] [Å]	Carbene angle [°]	E_{rot}[b] [kJ mol^{-1}]	δ (^{13}C)[c] [ppm]
2[10]	1.306	62.3	75	99
3	1.328	59.1	56	167
4[10]	1.334	57.2	53	185

[a] Average value of the C_{ring}–N bond lengths. [b] Calculated based on variable-temperature NMR experiments. [c] Chemical shift for the carbene carbon atom in **4** and the corresponding carbon atoms in **2** and **3**.

To test the lability of cyclopropenylidene **4** from the Li^+ ion we attempted, unsuccessfully, solvent extraction of the free carbene with several nonpolar solvents. We then tried to sequester the metal ion into a strong complexing agent. Upon addition of an excess of [12]crown-4 to a solution of **3** in diethyl ether, a yellow solid precipitated immediately. After recrystallization from THF/Et_2O, the compound was isolated as yellow crystals (m.p. 105–107 °C (decomp)) in 60 % yield. The ^{13}C NMR spectrum showed signals characteristic of the crown ether. Compared to **3**, the chemical shifts for the carbene carbon atom and the other two ring carbon atoms remained essentially the same ($\Delta\delta = 3$ and $\Delta\delta < 1$ ppm, respectively). These results clearly rule out the presence of the free cyclopropenylidene **4**. A single-crystal X-ray diffraction study showed the formation of tertiary complex **5** (Figure 3). Although the structure's disorder precludes detailed discussion of the geometric parameters, it can be seen that it is a monomeric carbene–lithium complex, a type of compound which has eluded isolation thus far.[17,18] These results are in contrast with Alder's observation[15a] that addition of [12]crown-4 to the *N*,*N*-diisopropyltetrahydropyrimid-2-ylidene $LiBF_4$ complex induces the liberation of the free carbene. This finding suggests that cyclopropenylidene **4** coordinates lithium cations much more strongly than N-heterocyclic carbenes.

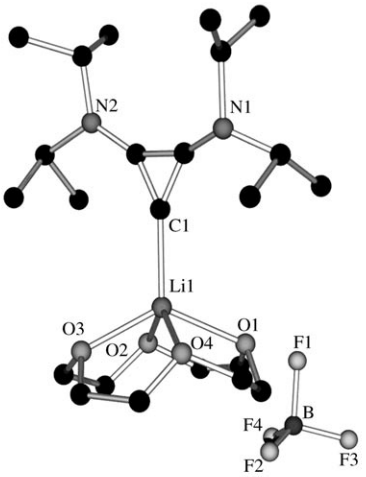

Figure 3. Molecular view of the structure of **5** in the crystal. Owing to thermal disorder, geometric parameters cannot be accurately discussed.

We then turned our attention to the deprotonation route. When *n*BuLi was used as a base, as Yoshida et al. did with **2**

($X = ClO_4$),[8a,b] the reaction with **2** ($X = BF_4$) appeared to be very clean. The ^1H and ^{13}C NMR data of the resulting product are identical to those of the lithium complex **3** that was obtained by the lithium/halogen exchange reaction. Interestingly, when *n*BuLi is replaced by potassium bis(trimethylsilyl)amide, under identical experimental conditions, multinuclear NMR spectroscopy shows the clean formation of the free cyclopropenylidene **4**. After work up, carbene **4** was isolated in 53 % yield, which compares advantageously with the 20 % yield observed when the cyclopropenium salt **2**, with BPh_4 as a counteranion, was used for the deprotonation reaction.[10]

From these results as a whole, it appears that free cyclopropenylidene **4** cannot be generated by using *n*BuLi or any other lithium-containing bases. In contrast to Li^+, the presence of K^+ ions does not prevent the isolation of the free carbene **4**. Moreover, comparing our results with the previous reports, it seems that the counteranion of the cyclopropenium precursors **1** and **2** has a considerable importance with respect to the stability of the lithium cyclopropenylidene complexes. In fact, in our hands, all attempts to isolate the lithium cyclopropenylidene complex with the BPh_4^- counterion instead of BF_4^- failed.

It can be concluded that Weiss and Yoshida were not lucky. They had the right cyclopropenium cation, but they did not choose the right counteranion to isolate the first carbene–lithium complex. Moreover, had they chosen the right base and counteranion combination, they would have isolated the first stable carbene. The isolation of both the free carbene and its lithium adduct should allow for the proliferation of cyclopropenylidene chemistry.

Experimental Section

1 and **2** ($X = BF_4$) were obtained from **1** and **2** ($X = Cl$) by the reported procedure,[19,10] with the exception that $NaBF_4$ was used for the anion exchange. **1** ($X = BF_4$): 30.0 g, 90 %, m.p. 120–121 °C; **2** ($X = BF_4$): 33.5 g, 90 %, m.p. 121–122 °C.

3 ($X = BF_4$): *n*BuLi (1 equiv) was added to a suspension of **1** ($X = BF_4$; 3.00 g, 8.36 mmol) or **2** ($X = BF_4$; 3.00 g, 9.25 mmol) in diethyl ether (80 mL) at −78 °C. The reaction was stirred for 15 minutes and then warmed to room temperature. After concentration in a vacuum and washing with hexane (40 mL), a white powder was obtained. The residue was recrystallized from a solution of diethyl ether at −25 °C, and colorless crystals were obtained (yield: 1.59 g (45 %) from **1**, 1.88 g (48 %) from **2**). M.p. 88–90 °C (decomp); ^1H NMR (C_6D_6, 25 °C, 300 MHz): $\delta = 3.62$ (br m, 4H, CH), 1.21 ppm (br m, 24H, CH_3); ^{13}C NMR ([D_8]THF, 25 °C, 75 MHz): $\delta = 166.8$ (CLi), 154.9 (C_{ring}), 50.4 (br, CH), 21.1 ppm (CH_3); ^7Li NMR ([D_8]THF, 25 °C, 233 MHz): $\delta = 0.27$ ppm (rel. to LiCl in D_2O as external standard).

5: At room temperature, [12]crown-4 (2 equiv) was added to a solution of **3** (2.00 g, 4.72 mmol) in diethyl ether (60 mL), and a precipitate immediately formed. The yellow solid was washed with hexane (40 mL) and dried in a vacuum. The residue was recrystallized from THF/Et_2O (50/50) at −25 °C, and yellow crystals were obtained (yield: 1.43 g, 60 %). M.p. 105–107 °C (decomp); ^1H NMR ([D_8]THF, 25 °C, 300 MHz): $\delta = 4.00$ (sept, 4H, CH, $J = 6.7$), 3.57 (s, 16H, CH_2), 1.41 ppm (d, 24H, CH_3, $J = 6.7$); ^{13}C NMR ([D_8]THF, 25 °C, 75 MHz): $\delta = 164.6$ (CLi), 154.6 (C_{ring}), 52.1 (br, CH), 48.8 (br, CH), 20.9 ppm (CH_3); ^7Li NMR ([D_8]THF, 25 °C, 233 MHz): $\delta = -0.10$ ppm (rel. to LiCl in D_2O as external standard).

Received: July 7, 2006

Keywords: carbenes · complexation · cyclopropenylidenes · lithium · structure elucidation

---

[1] R. Breslow, *J. Am. Chem. Soc.* **1958**, *80*, 3719.
[2] H.-W. Wanzlick, *Angew. Chem.* **1962**, *74*, 129; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 75.
[3] a) R. W. Hoffmann, *Angew. Chem.* **1968**, *80*, 823; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 754; b) A. J. Arduengo III, R. Krafczyk, *Chem. Unserer Zeit* **1998**, *32*, 6; c) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913.
[4] a) A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463; b) A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand, *Angew. Chem.* **1989**, *101*, 617; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 621.
[5] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.
[6] A. J. Arduengo III, J. R. Goerlich, R. Krafczyk, W. J. Marshall, *Angew. Chem.* **1998**, *110*, 2062; *Angew. Chem. Int. Ed.* **1998**, *37*, 1963.
[7] H.-J. Schönher, H.-W. Wanzlick, *Justus Liebigs Ann. Chem.* **1970**, *731*, 176.
[8] a) Z. Yoshida, *Abstr. 2nd Int. Symp. Chemistry of Nonbenzenoid Aromatic Compounds*, Lindau **1974**, p. 23; b) Z. Yoshida, H. Konishi, S. Sawada, H. Ogoshi, *J. Chem. Soc. Chem. Commun.* **1977**, 850; c) H. Konishi, S. Matsumoto, Y. Kamitori, H. Ogoshi, Z. Yoshida, *Chem. Lett.* **1978**, 241; d) Z. Yoshida, *Pure Appl. Chem.* **1982**, *54*, 1059; e) S. Miki, T. Ohno, H. Iwasaki, Z. Yoshida, *J. Phys. Org. Chem.* **1988**, *1*, 333.
[9] a) R. Weiss, C. Priesner, H. Wolf, *Angew. Chem.* **1978**, *90*, 486; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 446; b) R. Weiss, C. Priesner, H. Wolf, *Angew. Chem.* **1979**, *91*, 505; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 472; c) R. Weiss, M. Hertel, H. Wolf, *Angew. Chem.* **1979**, *91*, 506; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 473; d) R. Weiss, H. Wolf, *Chem. Ber.* **1980**, *113*, 1746.
[10] V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller, G. Bertrand, *Science* **2006**, *312*, 722.
[11] a) M. Tamm, A. Grzegorzewski, F. E. Hahn, *J. Organomet. Chem.* **1995**, *501*, 309; b) H. Schumann, M. Glanz, F. Girgsdies, F. E. Hahn, M. Tamm, A. Grzegorzewski, *Angew. Chem.* **1997**, *109*, 2328; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2232.
[12] a) R. Gompper, E. Bartmann, *Angew. Chem.* **1978**, *90*, 490; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 456; b) R. Gompper, U. Wolf, *Liebigs Ann. Chem.* **1979**, 1406.
[13] One of the most classical methods for the preparation of stable free carbenes is the deprotonation of the conjugate acid; very often lithium salts are present and no complexation occurs.
[14] a) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; b) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39; c) N. Kuhn, A. Al-Sheikh, *Coord. Chem. Rev.* **2005**, *249*, 829.
[15] a) R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufali, C. P. Butts, E. Linehan, J. M. Oliva, A. G. Orpen, M. J. Quayle, *Chem. Commun.* **1999**, 241; b) M. Otto, S. Conejero, Y. Canac, V. D. Romanenko, V. Rudzevitch, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 1016.
[16] CCDC-613889 (**3**) and CCDC-613890 (**5**) 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.

[17] a) G. Boche, C. Hilfe, K. Harms, M. Marsch, J. C. W. Lohrenz, *Angew. Chem.* **1995**, *107*, 509; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 487; b) C. Hilf, F. Bosold, K. Harms, J. C. W. Lohrenz, M. Marsch, M. Schimeczek, G. Boche, *Chem. Ber. Recl.* **1997**, *130*, 1202; c) C. Hilf, F. Bosold, K. Harms, M. Marsch, G. Boche, *Chem. Ber. Recl.* **1997**, *130*, 1213; d) A. J. Arduengo III, M. Tamm, J. C. Calabrese, F. Davidson, W. J. Marshall, *Chem. Lett.* **1999**, 1021; e) R. Fränkel, C. Birg, U. Kernbach, T. Habereder, H. Nöth, W. P. Fehlhammer, *Angew. Chem.* **2001**, *113*, 1961; *Angew. Chem. Int. Ed.* **2001**, *40*, 1907; f) P. L. Arnold, S. A. Mungur, A. J. Blake, C. Wilson, *Angew. Chem.* **2003**, *115*, 6163; *Angew. Chem. Int. Ed.* **2003**, *42*, 5981; g) P. L. Arnold, M. Rodden, K. M. Davis, A. C. Scarisbrick, A. J. Blake, C. Wilson, *Chem. Commun.* **2004**, 1612.

[18] All carbene–lithium complexes isolated so far[17] are dimers or higher-order aggregates.

[19] Z. Yoshida, Y. Tawara, *J. Am. Chem. Soc.* **1971**, *93*, 2574.