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

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Abstract

A lithium-halogen exchange reaction occurs when the chloro[bis(diisopropylamino)] cyclopropenium tetrafluoroborate salt **1** (X = BF_4) is treated with *n*-butyllithium. The resulting cyclopropenylidene-lithium adduct **3** has been isolated in 45% yield. In the solid state, this compound exists as a polymeric chain with an overall stoichiometry of two $LiBF_4$ per carbene ligand. Addition of 12-crown-4-ether does not liberate the carbene from the lithium cation, but affords a monomeric tertiary complex (60% yield) that includes the crown ether. Moreover, complex **3** can also be synthesized by depro tonation of the bis(diisopropylamino)cyclopropenium tetrafluoroborate salt **2** (X = BF_4) with *n*-butyllithium, whereas using potassium bis(trimethylsilyl)amide the free cyclopropenylidene was isolated in 53% yield. These results as whole seem to demonstrate that only certain counteranions allow for the isolation of cyclopropenylidene-lithium adducts, and only bases not containing lithium allow for the isolation of the free cyclopropenylidene. The former and the latter presumably prevented Weiss and Yoshida from isolating what would have been the first example of a stable carbene-lithium adduct and a free carbene, respectively.

Keywords

Carbenes; cyclopropenylidene; Li; Complex

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 bottle-able 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[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 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** (Fig. 1). Recently, we isolated the exact same carbene (**4**) 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

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[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 with X = halogen or weaker coordinating anion),[13,14] although there are two exceptions.[15]

This analysis prompted us to re-investigate 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 due to the perchlorate anion, the chlorocyclopropenium tetrafluoroborate salt **1** (X = BF_4) was used as a precursor. After stirring for ten minutes at −78 °C, a very clean reaction occurred and crucially, a ^{13}C NMR signal at 167 ppm was observed. This signal is shifted to high field compared to that of the carbene carbon nucleus of the free cyclopropenylidene **4** (185 ppm),[10] exactly what is 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 dec., 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 stoichiometry of two $LiBF_4$ per carbene ligand (Figs. 2 and 3). 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 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 ion adducts (2.135−2.155 Å).[17]

If we view the conjugate acid (**2**) of the cyclopropenylidene **4** as a proton/carbene complex we can clearly see several structural and spectroscopic trends (Table 1). Upon comparison of the exocyclic C-N bonds, an elongation is observed through the series **2** < **3** < **4**, which corresponds to decreased π-donation from the amino groups. This is confirmed by the observed rotational barriers about the NC bond, as deduced from variable temperature NMR experiments. The carbene bond angle 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**, indicating a certain amount of ionic character in the lithium carbene bond.

To test the lability of cyclopropenylidene **4** from Li^+ we attempted, unsuccessfully, solvent extraction of the free carbene with several non-polar solvents. We then tried to sequester the metal ion into a strong complexing agent. Upon addition of an excess of 12-crown-4-ether to a diethyl ether solution of **3**, a yellow solid precipitated immediately. After recrystallization from a THF/diethyl ether solution, the compound was isolated as yellow crystals (mp. 105−107 °C, dec.) 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 and the other two ring carbons remained essentially the same ($\Delta\delta$ = 3 and <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** (Fig. 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-ether to the N,N-diisopropyl-tetrahydropyrimid-2-ylidene lithium BF_4 complex induces the liberation of the free carbene. This suggests that cyclopropenylidene **4** coordinates lithium cations very strongly compared to *N*-heterocyclic carbenes.

We then turned our attention to the deprotonation route. When *n*-BuLi is used as a base, as Yoshida did,[8a,b] but the cyclopropenium **2** with BF_4- instead of ClO_4- as a counteranion, the reaction appeared to be very clean. The ^{1}H and ^{13}C NMR data of the resulting product are identical to those of the lithium complex **3** obtained by the lithium-halogen exchange reaction. Interestingly, when *n*-BuLi is replaced by potassium bis(trimethylsilyl)amide, under identical exper imental 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 using *n*-BuLi or any other lithium-containing bases. In contrast to Li^+, the presence of potassium cations 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 cyclopropenylidene lithium complexes. In fact, in our hands, all attempts to isolate the lithium cyclopropenylidene complex featuring BPh_4^- 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

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{7}Li and ^{13}C NMR spectra were recorded on Bruker Avance 300 and 600 spectrometers. ^{7}Li chemical shifts are reported in ppm relative to a solution of LiCl in D_2O as external standard. **1** (X = BF_4). This compound was obtained from **1** (X = Cl) by the reported procedure,[19] but using $NaBF_4$ for the anion exchange instead of HBF_4 (30.00 g, 90%). m.p. 120−121 °C; ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ = 4.13 (sept, 2H, C*H*CH_3, *J* = 6.7), 3.87 (sept, 2H, C*H*CH_3, *J* = 6.8), 1.41 (d, 24H, CHC*H*$_3$, *J* = 6.7) ppm; ^{13}C NMR ($CDCl_3$, 25 °C, 75 MHz): δ = 131.9 (C_{ring}), 93.1 (CCl), 57.9 (CH), 48.3 (CH), 22.3 (CH_3), 20.4 (CH_3) ppm. **2** (X = BF_4). This compound was obtained from **2** (X = Cl) by the reported procedure,[10] but using $NaBF_4$ for the anion exchange instead of $NaBPh_4$ (33.50 g, 90%). m.p. 121−122 °C; ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz): δ = 7.47 (s, 1H, CH_{ring}), 4.03 (sept, 2H, C*H*CH_3, *J* = 6.7), 3.87 (sept, 2H, C*H*CH_3, *J* = 6.7), 1.39 (d, 12H, CH_3, *J* = 6.7), 1.37 (d, 12H, CH_3, *J* = 6.6) ppm; ^{13}C NMR ($CDCl_3$, 25°C, 75 MHz): δ = 133.6 (C_{ring}), 99.1 (CH_{ring}), 57.1 (*C*HCH_3), 48.9 (*C*HCH_3), 20.6 (CH_3), 20.6 (CH_3) ppm. **3** (X = BF_4). 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) was added at −78 °C *n*-butyllithium (1 eq). The reaction was

stirred for 15 minutes and then warmed to room temperature. After concentration under 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 (1.59 g, 45% from **1**, and 1.88 g, 48% from **2**). m.p. 88−90 °C, dec.; ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ = 3.62 (broad m, 4H, CH), 1.21 (very broad m, 24H, CH_3) ppm; ^{13}C NMR (THF-d_8, 25 °C, 75 MHz): δ = 166.8 (CLi), 154.9 (C_{ring}), 50.4 (br, CH), 21.1 (CH_3) ppm; ^{7}Li NMR (THF-d_8, 25 °C, 233 MHz): δ = 0.27 ppm. **5**. At room temperature, to a solution of **3** (2.00 g, 4.72 mmol) in diethyl ether (60 mL) was added 12-crown-4-ether (2 eq) and a precipitate immediately formed. The yellow solid was washed with hexane (40 mL) and dried under vacuum. The residue was recrystallized from a THF/ether solution at −25 °C, and yellow crystals were obtained (1.43 g, 60%). m.p. 105−107 °C, dec.; ^{1}H NMR (THF-d_8, 25 °C, 300 MHz): δ = 4.00 (sept, 4H, CH, J = 6.7), 3.57 (s, 16H, CH_2), 1.41 (d, 24H, CH_3, J = 6.7) ppm; ^{13}C NMR (THF-d_8, 25 °C, 75 MHz): δ = 164.6 (CLi), 154.6 (C_{ring}), 52.1 (br, CH), 48.8 (br, CH), 20.9 (CH_3) ppm; ^{7}Li NMR (THF-d_8, 25 °C, 233 MHz): δ = −0.10 ppm.

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

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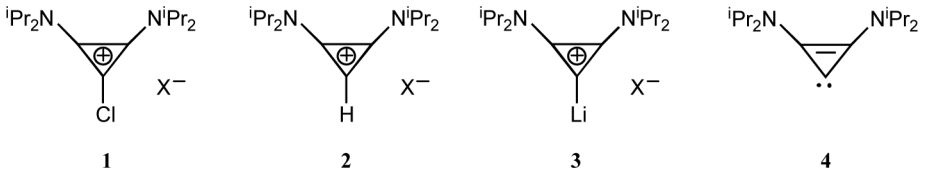

Figure 1.

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

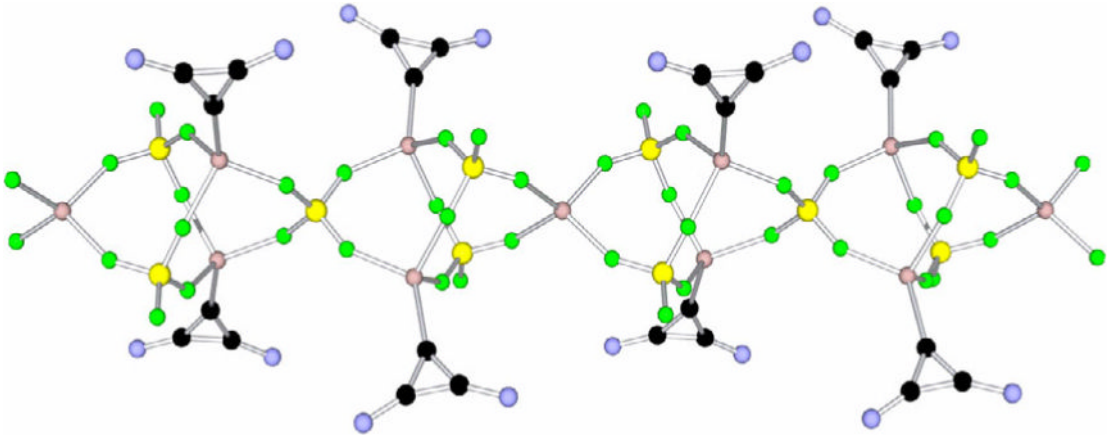

Figure 2.
Molecular view of a crystal structure of polymeric cyclopropenylidene-Li adduct **3**. The isopropyl groups on nitrogen have been omitted for clarity. Color code: C (black), N (blue), Li (pink), B (yellow), F (green).

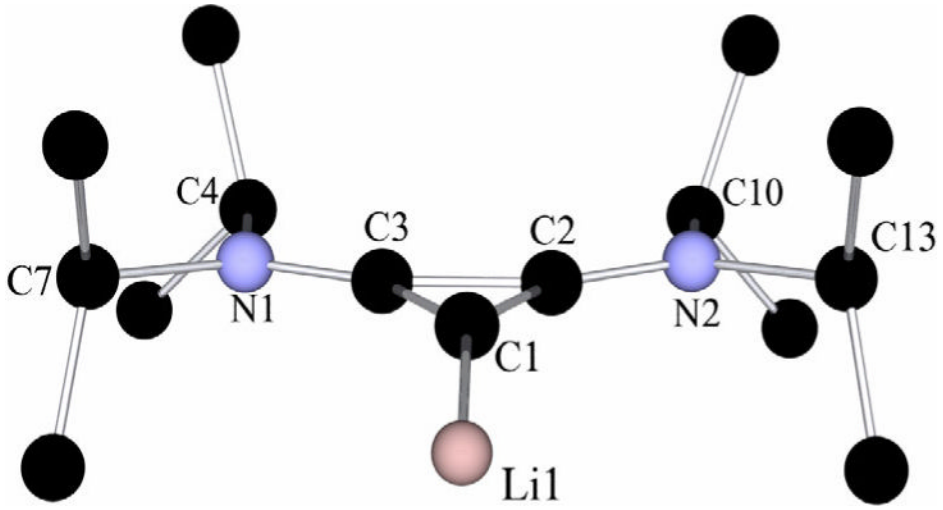

Figure 3.

Molecular view of a crystal structure of the cyclopropenylidene-lithium portion of **3**. Color code: C (black), N (blue), Li (pink). 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).

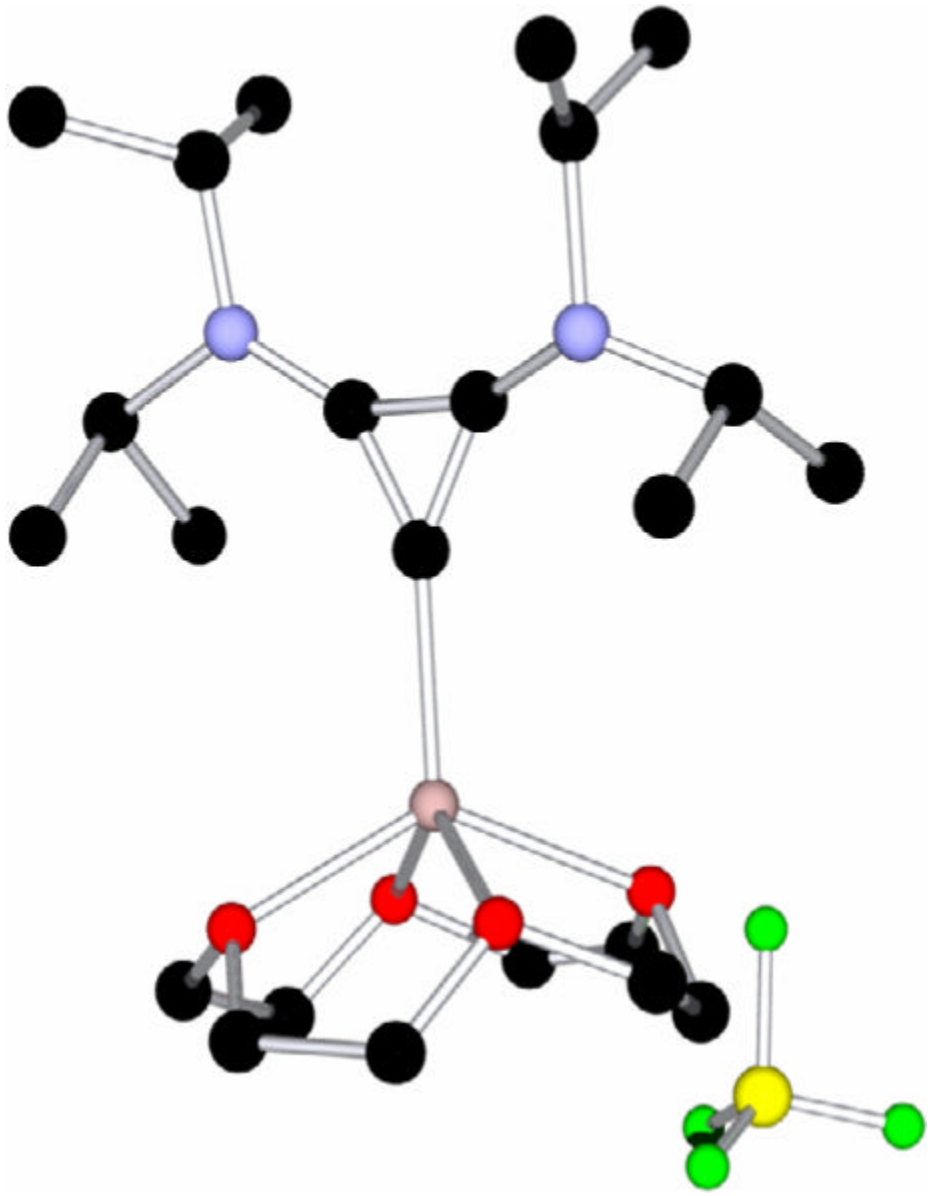

Figure 4.
Molecular view of a crystal structure of **5**. Color code: C (black), N (blue), Li (pink), B (yellow), F (green), O (red). Due to the presence of thermal disorder, geometric parameters cannot be accurately discussed.

Table 1

Comparison of the geometric parameters, rotational barrier about the $C_{ring}N$ bonds, and spectroscopic data for compounds **2, 3** and **4**.

Compound	C_{ring}-N Bond Length[a] (Å)	Carbene Angle (°)	Rotational Barrier[b] (kJ/mol)	^{13}C NMR[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 and the corresponding carbon in **2** and **3**.