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Carbyne anions get to work

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Abstract:

The isolation of a rare example of a highly reactive low-valent carbon compound – a carbyne anion complex – enables the discovery of low-valent carbon transfer reactions.

Carbon reactive species are key intermediates in several C–C and C–X bond forming reactions – the basic transformations chemists use to build complex molecules with control of structure and functionality. Over the years, a variety of highly reactive carbon species have been isolated, or at least characterized, enabling progress in synthesis. While trivalent and divalent compounds are now well-known and quite common (Fig. 1a), related monovalent species remain extremely scant. The high degree of unsaturation further enhances the reactivity of anionic, cationic and radical centres, making them attractive species but also challenging compounds to synthesize and stabilize. In 2018, carbyne equivalents¹ (monovalent carbon species with three non-bonded electrons) were generated and their dual radical-carbene reactivity exploited to forge three covalent bonds.

Now, writing in *Nature Synthesis*, Liu and co-workers report a new type of highly reactive carbon compounds – namely, carbyne anions – isolated as copper complexes, and their use in low-valent carbon transfer reactions.² Coordination of low-valent carbon species to metals, and in particular transition metals, is well-established for carbenes and carbynes. The stability, and hence ability to isolate such carbene and carbyne complexes resulted in their widespread use in organic and polymer synthesis – for example, as key reagents in alkene and alkyne metathesis reactions. According to bonding analysis by experimental and computational studies, the copper species prepared by Liu and co-workers are best described as anionic carbyne complexes, rather than metalla carbenes. Reactivity studies show that the complexes engage in unprecedented low-valent carbon transfer reactions.

Design is crucial in the preparation of highly reactive compounds. In the present case, Liu and co-workers leveraged the unique ability of the π -donating phosphino group to stabilize low-valent highly reactive species in their singlet state; that is, with all non-bonding electrons paired in the same orbital(s). The π -donating phosphino group was first used by Bertrand and co-workers in 1988 to isolate the phosphino-silyl-carbene³ ($(\text{Pr}_2\text{N})_2\text{P}-\text{C}-\text{SiMe}_3$ and subsequently nitrenes⁴ and phosphinidenes⁵ (which are isoelectronic to carbynes).

In the method of Liu and co-workers, the carbyne anion is introduced in the coordination sphere of an electropositive metal, to bring stability while imparting $C^{\ominus}\cdots M^{\oplus}$ ionic-type bonding so as to favour carbyne anion reactivity. Particularly judicious was the idea to replace gold, shown in a previous study⁶ to form a metallacarbene species $R_2P-C-AuL$, by copper (see compound **2** in Fig. 1), its lighter electropositive congener. The target complexes were obtained in three steps from the phosphino-silyl-diazo compound **1** (Fig. 1b): A first desilylation step, followed by coordination to copper (with two different ancillary *N*-heterocyclic carbene ligands) and a final step involving dinitrogen release under UV irradiation.

Using this route, the target complexes **2** were isolated in 90% yield as crystalline yellow solids. X-ray diffraction analysis showed substantial π -donation from P to C, as testified by the short P=C bond length (1.541(3) Å) and the trigonal planar environment around the P atom. The P-C-M bond angle is substantially wider in **2** than in the corresponding Au complex (164.5(2)° compared with 144.7(2)°), indicating more carbyne complex and metalla carbene structure, respectively. The electronic structure and bonding situation of the Cu and Au complexes were thoroughly analysed computationally and systematically compared. All data indicate a more ionic $C\cdots M$ bonding with Cu compared with Au.

Having prepared compounds **2**, Liu and co-workers investigated the possibility to achieve carbyne anion transfer reactions. Treatment with chlorotrimethylsilane resulted in the electrophilic silylation of the low-valent carbon atom, with conversion of the carbyne anion complex **2** to a neutral phosphino-silyl-carbene **3a**. Using trifluoromethanesulfonate triphenyl germane as an electrophile, the first phosphino-germyl-carbene **3b** was then prepared and structurally characterized. Upon treatment with methyl trifluoromethanesulfonate, MeOTf, the vinyl phosphine **4** was obtained, most likely as the result of the rearrangement by 1,2-H shift of the first-generated phosphino-methyl-carbene⁷. Finally, the carbyne anion complex **2** was found to add two equivalents of trimethylsilyl cyanide Me_3Si-CN to give the ketenimine **5**. It is remarkable that overall, three bonds are formed at the carbyne centre in the two latter reactions (C-H and $C=CH_2$ for **4**, C-SiMe₃ and $C=CNSiMe_3$ for **5**).

This work represents a real “tour de force”. Free carbyne anions are extremely elusive species, with to date only few reports of their isolation and analysis in the gas phase, using collision-induced dissociation techniques. Anionic carbyne complexes are not unprecedented⁸, but none of the reported compounds showed carbyne anion reactivity as shown here. Moreover, this method enables the synthesis and isolation of a compound behaving as a carbyne anion under normal laboratory conditions, that is, on a preparative scale (up to ~ 100 mg corresponding to ~ 0.1 mmol), in the condensed phase and in the absence of oxygen and moisture.

Of course, the isolation of complexes **2** raises questions and the reported carbyne transfer reactions remain proof-of-concept transformations. More generally, it is not yet known whether complexes **2** are unique examples or the first members of a broader family. It may also be valuable to investigate if the substituent at the C atom can be modified to a functional group other than a phosphino group. In addition, it will be interesting to probe if transition metals other than Cu can be used to host and stabilize the carbyne anion. As for reactivity, the synthetically most significant transformation resulting from this work is the electrophilic functionalization of the carbyne centre to yield carbenes. In the future, the combination of anionic and carbyne features is expected to open the possibility of unprecedented transformations, from addition and insertion reactions, to small molecule and strong bond activations. It is certainly a goal to develop further carbyne anion transfer reactions and to exploit these highly reactive compounds to build complex frameworks that are inaccessible or challenging to achieve by other means.

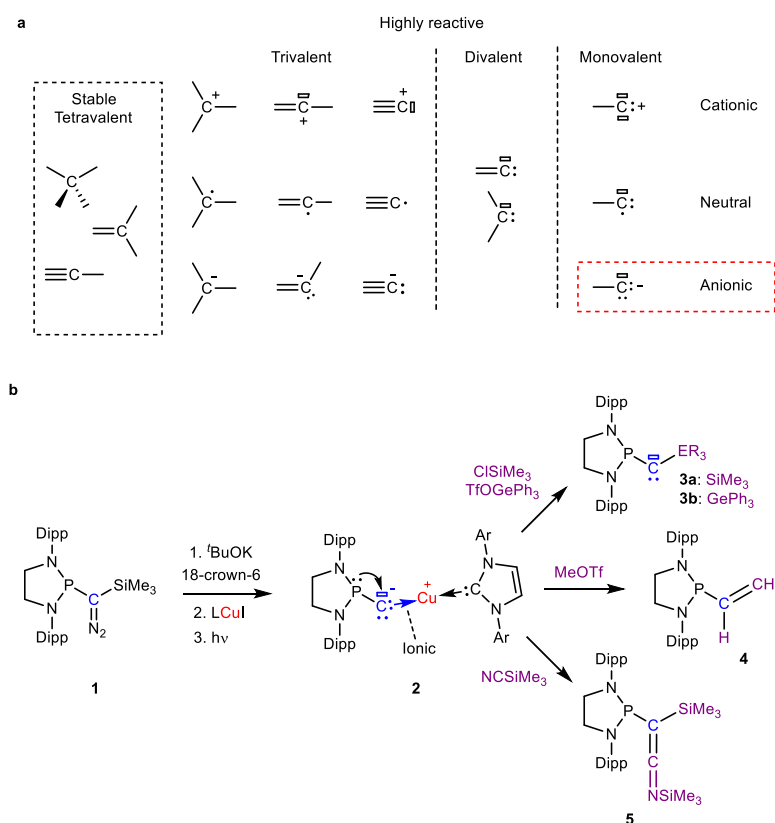


Fig. 1. Overview of the synthesis, structure and reactivity of highly reactive carbon compounds. **a**, The bonding arrangements of stable and highly reactive carbon compounds. A small rectangular box denotes a vacant orbital. **b**, Preparation and C-functionalization of the carbyne anion complex **2**. Ar is either dipp or dipentp. dipp, 2,6-di-*iso*-propylphenyl; dipentp, 2,6-di-(3-pentanyl)phenyl; Me, methyl; Tf, trifluoromethanesulfonyl; *t*Bu, *tert*-butyl.

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