

An Air-Stable Oxyallyl Radical Cation**

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Regarded as laboratory curiosities at the time of their discovery,^[1] stable carbenes were later recognized as powerful tools in organometallic chemistry since the corresponding complexes led to numerous breakthroughs in homogeneous catalysis.^[2] In main-group chemistry, stable carbenes have only recently found application. Carbenes can coordinate silicon, phosphorus, and their heavier congeners in their zero oxidation state,^[3] and they can stabilize a variety of main-group-element-centered radicals.^[4,5] So far, the applications of stable carbenes in organic chemistry have been limited to merely their role as organocatalysts.^[6] Here we report that stable carbenes can also be used to prepare organic paramagnetic species. We show that oxyallyl radical cations, which were hitherto believed to be only transient intermediates, only observable by mass spectroscopy^[7] or in a glassy matrix at 77 K,^[8] can be isolated at room temperature and are even stable towards air and moisture.

Oxyallyl derivatives **I** (Scheme 1) are non-Kekulé molecules, which have been postulated as intermediates in several rearrangements and cycloaddition reactions,^[9,10] including the in vivo biosynthesis of prostaglandins.^[11] Alkyl-substituted oxyallyl derivatives have been calculated to be singlet biradicals (**Ia**), whose ring closure to give the corresponding cyclopropanones **II** occurs with a negligible barrier.^[12,13] These predictions are in line with a recent report describing

the first observation of a dialkylxyallyl species, which has a half-life at 298 K of 42 min in the solid state, but a few picoseconds in solution.^[14] Importantly, ab initio studies^[15] showed that substituents with a strong +M effect, such as amino groups,^[16] decrease the biradical character and therefore favor the zwitterionic mesomeric form **Ib**, which leads to less reactive species. Indeed, Siemeling et al. reported the isolation of compound **III**,^[17] which they described as a zwitterionic enolate since it features one short and one long C–C_{CO} bond, and a dihedral angle of nearly 90° between the two amidinium units.

Not surprisingly, the redox chemistry of oxyallyl derivatives **I** is terra incognita, and due to the presence of iron centers, the oxidation of **III** is unlikely to occur on the organic fragment. Compound **III** was prepared by the addition of two ferrocene-based diaminocarbenes to CO, but the generalization of this synthetic approach is not straightforward.^[18] Indeed, classical N-heterocyclic carbenes (NHCs) are not electrophilic enough to react with CO.^[19] On the other hand, alkyl(amino)carbenes^[20] and diamidocarbenes^[21] add to carbon monoxide, but afford monocarbene adducts, namely ketenes.^[22] It is quite likely that the addition of a second of these carbenes, and thus the formation of the oxyallyl derivative, is precluded by their steric bulk. Recently, we described a novel type of cyclic diaminocarbene, which features enhanced electrophilicity due to the strained bridge-head position of one of the nitrogen atoms (anti-Bredt NHCs).^[23] We reasoned that the electronic properties of this carbene coupled with virtually no steric hindrance around the bent nitrogen, should make it possible to prepare the desired oxyallyl derivative.

In a first experiment, carbon monoxide was bubbled at –78 °C into a THF solution of the anti-Bredt NHC **2** (prepared by in situ deprotonation of amidinium triflate **1** with potassium hexamethyldisilylazide) (Scheme 2). The reaction mixture immediately turned deep blue; its ¹³C NMR spectrum recorded at –40 °C displayed signals for a new compound **3**, featuring a single type of carbene unit.

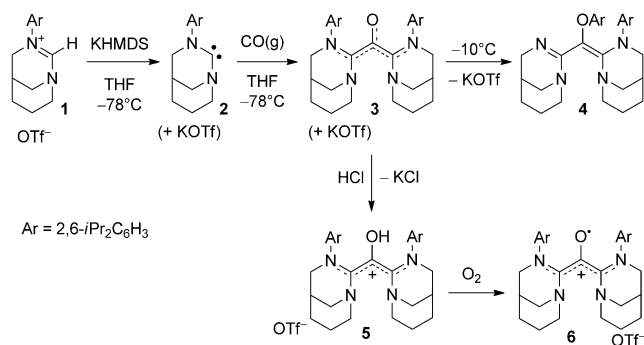
Scheme 1. Oxyallyl **I**, cyclopropanone **II**, and zwitterionic enolate **III**.^[17]

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Scheme 2. Formation and reactivity of oxyallyl **3**.

Table 1: X-ray crystal structures^[a] with selected bond lengths [Å] and angles [°] of **5** (left), *D,L*-**6** (middle), and *meso*-**6** (right).

	O1-C1	C1-C2	N1-C2	N2-C2	C1-C2'	N1'-C2'	N2'-C2'	N1-C2-N2	N1'-C2'-N2'
5	1.3676(19)	1.419(2)	1.3534(19)	1.384(2)	1.424(2)	1.351(2)	1.380(2)	117.70(13)	117.29(13)
<i>D,L</i> - 6	1.287(4)	1.435(5)	1.340(4)	1.388(4)	1.447(5)	1.343(4)	1.378(4)	118.3(3)	117.6(3)
<i>meso</i> - 6	1.2569(18)	1.422(2)	1.3600(18)	1.4060(18)	1.5070(19)	1.3200(17)	1.3498(19)	118.81(12)	119.54(12)

[a] Thermal ellipsoids drawn at 50% probability level. Isopropyl groups, hydrogen atoms, cocrystallized solvents and triflate anions are omitted for clarity.

Importantly no signal above $\delta = 200$ ppm could be observed, demonstrating that **3** was not an aminoketene.^[20] When the solution was warmed to -10°C , it became red, and a new set of ^{13}C NMR signals appeared. After workup, the 3,3-diamino-2-aryloxyacrylimidamide **4** was isolated in 70% yield as a pale yellow solid, and fully characterized (including an X-ray diffraction study).^[24] This result suggests that the deep-blue intermediate was the desired oxyallyl derivative **3**, which rearranged through the migration of the 2,6-diisopropylphenyl (Dipp) group. DFT calculations (B3LYP/6-311g** level of theory) supported this hypothesis by predicting a chemical shift of $\delta = 168$ ppm for the two equivalent NCN carbons of oxyallyl **3**, close to the observed experimental value of $\delta = 160$ ppm; in contrast, the signal of central carbonyl carbon was expected around $\delta = 137$ ppm, among the signals of the quaternary carbons of the Dipp substituents.

In order to ascertain further the formation of oxyallyl **3**, a freshly prepared THF solution of **3** was reacted with one equivalent of HCl at -78°C . After workup, the hydroxycyanine triflate **5** was isolated in 47% yield. X-ray diffraction analysis (Table 1, left) revealed that the CO and carbene fragments are nearly coplanar (dihedral angles: N1-C2-C1-O1: 15° and N1'-C2'-C1-O1: 10°); the C-O bond length (136.8 pm) was in the range observed for related compounds.^[25,26]

Interestingly, compound **5** appeared to be highly sensitive toward oxygen, turning deep green-blue upon brief exposure to air, even in the solid state. A dichloromethane solution of **5** was stirred overnight in a flask opened to air, yielding an NMR-silent product. An X-ray diffraction study revealed the formation of the oxyallyl radical triflate salt *D,L*-**6** (Table 1, middle). The absence of a proton on the central oxygen atom was confirmed by a significantly shorter C-O bond length (*D,L*-**6**: 128.7 pm; **5**: 136.8 pm), and the absence of residual electronic density around the oxygen atom. Cyclic voltammetry showed that **6** is both a weak reducing agent ($E = -0.116$ V vs. Fc^+/Fc , see the Supporting Information) and a weak oxidant ($E = -1.276$ V), illustrating further the thermodynamic stability of this compound.

In line with the experimental results, DFT calculation confirmed that **5** is an excellent hydrogen-radical donor, since the O-H bond dissociation energy was predicted to be only 66 kcal mol $^{-1}$. This value is significantly lower than that for alkyl alcohols (100–110 kcal mol $^{-1}$) and phenols (80–90 kcal mol $^{-1}$), and is even in the range of the value for TEMPO-H (68–71 kcal mol $^{-1}$).^[27] The SOMO of *D,L*-**6** is a bonding combination of the $\pi^*(\text{CO})$ molecular orbital and the LUMO of the carbenes, with significant electronic density on all conjugated atoms (Figure 1, top right). A simple Mulliken analysis confirmed the delocalization of the spin density across the carbonyl moieties (40% on oxygen and 12% on carbon) and the two carbene units (15% on N1 and N1', 11% on N2 and N2', and 19% on C2 and C2').

Interestingly, we have also isolated a few crystals of the *meso* diastereomer of **6** (Table 1, right). In marked contrast

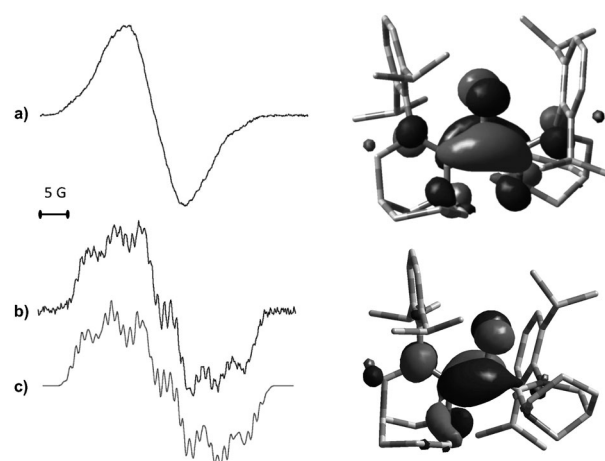


Figure 1. Left: X-band EPR spectra recorded in benzene solution at room temperature for: a) *D,L*-**6** ($g = 2.0051$) and b) *meso*-**6** ($g = 2.0048$). c) Simulated EPR spectrum of *meso*-**6** with the following set of hyperfine coupling constants: $a(^1\text{H}) = 28.3, 20.4, 3.0, 2.9$ (2H), and 2.5 MHz, $a(^{14}\text{N}) = 9.4, 7.9, 3.0$, and 4.0 MHz. Right: Representation of the SOMO of *D,L*-**6** (top) and *meso*-**6** (bottom) with isosurfaces at 0.05 a.u.

with D,L-**6**, the solid-state structure of *meso*-**6** is significantly twisted (dihedral angle: *meso*-**6**: N1-C2-C1-O1: 5° and N1'-C2'-C1-O1: 57°; D,L-**6**: 12° and 16°, respectively). Thus, one carbene unit is only weakly conjugated with the carbonyl moieties, as also shown by the C1-C2' bond length of 150.7 pm, typical of a single CN bond. Furthermore, whereas the hyperfine X-band EPR signal of D,L-**6** is unresolved, the spectrum of *meso*-**6** features a complex pattern, which could be simulated only by assuming two different carbene units (Figure 1, left).^[28] Calculations reveal that the SOMO of *meso*-**6** involves only one carbene unit and confirm that most of the spin density is distributed between the carbonyl moiety (O1: 34%, C1: 14%) and the conjugated carbene unit (46%, i.e. C2: 21%, N1: 21%, and N2: 4%). Interestingly, the difference in energy between *meso*-**6** and D,L-**6** is only +4 kcal mol⁻¹, thus confirming that in such a twisted arrangement the energetic loss due to decreased spin delocalization can be compensated by the reduction of unfavorable steric interactions between the two carbene units.

This work demonstrates that stable carbenes can be used for the preparation and isolation of oxyallyl radical cations under aerobic conditions. Interestingly, the *meso* isomer of **6**, which benefits from the stabilization of only one "carbene" unit, is stable. This suggests that a variety of carbene-stabilized organic radicals should be isolable at ambient temperature.

Experimental Section

Experiments were performed under an atmosphere of dry argon using standard Schlenk techniques, unless otherwise stated. Solvents were dried by standard methods and distilled under argon. ¹H and ¹³C NMR spectra were recorded on Varian Inova 400, 500, and Bruker 300 MHz spectrometers. Low-temperature NMR spectra were recorded on a JEOL 500 MHz spectrometer. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad signal. Melting points (uncorrected) were measured with an Electrothermal MEL-TEMP apparatus. Electrochemical experiments were performed with an analyzer from CH Instruments (Model 620E). EPR spectra were obtained using an X-band Bruker E500 spectrometer. Field calibration was accomplished by using a standard of solid 2,2-diphenyl-1-picrylhydrazyl (DPPH), *g* = 2.0036.

5: A solution of **1** (850 mg, 1.95 mmol) in THF (15 mL) was added dropwise to a stirred solution of KHMDS (430 mg, 2.15 mmol) in THF (3 mL) at -78°C. After 5 min, carbon monoxide was bubbled in the solution for 20 min. Then HCl (0.5 mL, 2 M in diethyl ether) was added dropwise. After the reaction mixture had warmed to room temperature, the volatiles were removed in vacuo and the residue was extracted four times with benzene (10 mL). The solution was concentrated in vacuo. Colorless crystals were obtained by slow diffusion of layered pentane. **5**: 340 mg, 47% yield. M.p.: 190–200°C (decomp.). ¹H NMR (CDCl₃, 400 MHz): δ = 7.23 (t, *J* = 7.5 Hz, 2H), 7.10 (dd, *J* = 2 and 7.5 Hz, 2H), 7.00 (dd, *J* = 2 and 7.5 Hz, 2H), 3.55–3.39 (m, 8H), 3.28 (m, 2H), 2.86 (sept, *J* = 8.4 Hz, 2H), 2.65 (sept, *J* = 8.4 Hz, 2H), 2.58 (m, 2H), 2.09 (m, 2H), 1.81 (broad d, *J* = 13 Hz, 4H), 1.7–1.5 (m, 2H), 1.37–1.28 (m, 2H), 1.23 (d, *J* = 8.4 Hz, 6H), 1.22 (d, *J* = 8.4 Hz, 6H), 1.15 (d, *J* = 8.4 Hz, 6H), 0.58 ppm (d, *J* = 8.4 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): δ = 23.6 (CH₃), 24.3 (CH₃), 24.5 (CH₂), 24.9 (CH₃), 25.3 (CH₃), 28.6 (CH), 29.4 (CH₂), 29.5 (CH), 30.4 (CH), 49.5 (CH₂), 57.6 (CH₂), 60.1 (CH₂), 109.7 (C), 124.2 (CH), 125.2 (CH), 128.9 (CH), 139.1 (C), 142.6 (C), 145.2 (C), 164.6 ppm (C).

6: Compound **5** was prepared in situ from amidinium **1** (693 mg, 1.6 mmol), as described above. The volatiles were removed in vacuo and technical-grade dichloromethane (30 mL) was added. The resulting solution was vigorously stirred overnight in a round-bottom flask opened to air, then washed with water (3 × 10 mL), and dried over anhydrous magnesium sulfate. The volatiles were removed in vacuo, affording a deep green–blue NMR-silent solid. 380 mg, 63% yield. MS (*m/z*): [*M*⁺] calcd. for C₃₉H₅₆N₄O, 596.4454; found, 596.4455. Slow evaporation of a solution of **6** in toluene afforded crystals of D,L-**6** as green–blue needles. 160 mg. M.p.: 204–206°C. Slow diffusion of pentane into the mother liquor afforded a mixture of similar crystals (80 mg), mixed with large red–brown crystalline blocks; 15 mg of the latter was separated manually and identified as *meso*-**6** by X-ray diffractometry. M.p.: 211–213°C.

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