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On the Advantage of Cyclic over Acyclic Carbenes to Access Isolable Capto-Dative C-Centered Radicals

Janell K. Mahoney,^a Rodolphe Jazzar,^a Guy Royal,^b David Martin^{*,b} and Guy Bertrand^{*,a}

Dedication ((optional))

Abstract: A cyclic and an acyclic di(amino)carbene as well as a cyclic and an acyclic (alkyl)(amino)carbene cleanly react with benzoyl chloride to give the corresponding adducts 1_{cyc}^{+} , 1_{acy}^{+} , 2_{cyc}^{+} and $\mathbf{2}^{+}_{acy}$, respectively. The reduction of $\mathbf{1}^{+}_{cyc}$ and $\mathbf{2}^{+}_{cyc}$ derived from cyclic carbenes affords the corresponding radicals 1_{cyc} and 2_{cyc} that are stable at room temperature. In contrast, radicals 1_{acy} and 2_{acy}, derived from acyclic carbenes, cannot be isolated. It is shown that 1_{acy} is as thermodynamically stabilized as its cyclic counterpart 1_{cyc} , but its instability is the result β-hydrogens of the nitrogen substituent, along with the enhanced flexibility around C-N bonds, which allow for a H•-migration-elimination process. Radical 2_{acy} is thermodynamically unstable, and disproportionates into the corresponding iminium 2^{+}_{acy} and enolate 2^{-}_{acy} . This is due to the excessive steric hindrance, which prevents electron-delocalization on the NCCO fragment, and thus the capto-dative stabilization. This work suggests general guidelines for the design of highly persistent (amino)(carboxy)radicals, especially by emphasizing the key advantage of cyclic patterns.

Introduction

In recent years, stable carbenes^[1,2] have emerged as powerful tools^[3] for the design of stable paramagnetic metal complexes^[4] and main-group derivatives.^[5] They have also allowed for an insightful reinvestigation into the stabilization of C-centered radicals,^[6] using the synergistic combination of electron donating and withdrawing substituents, the so-called capto-dative effect.^[7] However, while this substitution pattern weakens the C–C bond of the corresponding dimer, the monomer typically remains thermodynamically disfavoured.^[8] For instance, (dimethylamino)-(carboxy)radical I exists in the solid state as the diamagnetic dimer II (Figure 1).^[8a] Interestingly, sufficient amounts of the radical are formed in solution at 140 °C, which allowed for both the detection of I by EPR and the determination of the dimerization enthalpy (-25 kcal.mol⁻¹ versus about -80 kcal.mol⁻¹ for typical C–C bonds).

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Figure 1. Dimerization of (dimethylamino)(carboxy) radical I.

Stable N-substituted carbenes are ideal precursors for captodative radicals such as Illa-e (Figure 2). Fukuzumi et al. reacted thiazolylidene^[9] with benzaldehyde in the presence of a base and performed a one-electron electrochemical oxidation of the resulting enolate to afford capto-dative radical IIIa.[10] EPR monitoring showed that the compound decayed within hours at room temperature. More recently, we demonstrated that cyclic (alkyl)(amino)carbenes (CAACs)^[11,12] allow for a simple two-step synthesis of the first structurally characterized monomeric Ccentered (amino)(carboxy)radicals IIIb, as well as related bi- and tri-radicals.^[13] These molecules were found to be perfectly stable in solution at room temperature. In addition, we found that carbonyl substituents with strong electronegative inductive effects afford remarkably air-persistent radicals.^[14] Hudnall et al. also reported that radicals IIIc, IIId and IIIe, which are based on stable imidazol-2-ylidene,^[15] cyclic(amido)(amino) carbene ^[16] and cyclic(diamido)carbene,^[17] respectively, are also isolable at room temperature.^[18] Strikingly, only cyclic carbenes have been used so far, and it has already been shown that their acyclic versions differ significantly in terms of electronic properties, and consequently chemical behaviour.^[19] Herein, we explore stable acyclic di(amino)carbene^[20] and (alkyl)(amino) carbene^[21] as building blocks for (amino)(carboxy)radicals 1_{acy} and 2_{acy} , respectively, and we discuss their stability compared to their cyclic counterparts 1_{cyc} and 2_{cyc}.





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Results and Discussion

Using the strategy previously employed,^[13] the saturated cyclic diaminocarbene (imidazolidin-2-ylidene)^[22] and its acyclic counterpart, the bis(diisopropylamino)carbene,^[20] were reacted with benzoyl chloride to afford iminiums 1^{+}_{cyc} and 1^{+}_{acy} in 66 and 78 % yield, respectively (Scheme 1).



Scheme 1. Synthesis of radicals 1_{cyc} and 1_{acy} .

The cyclic voltammograms of $\mathbf{1}_{cyc}^{+}$ and $\mathbf{1}_{acy}^{+}$ feature two reversible reduction waves, which were assigned to the formation of the radical and enolate species, respectively (Figure 3).

In both cases, the corresponding potentials were separated by 0.5-0.7 V, indicating that disproportionation of the redoxamphoteric radicals could be excluded. Therefore, we undertook the synthesis of radicals $\mathbf{1}_{cyc}$ and $\mathbf{1}_{acy}$ by electrochemical reduction of $\mathbf{1^+}_{cyc}$ and $\mathbf{1^+}_{acy},$ respectively, while monitoring the reaction by UV-Vis. In both cases, the stoichiometry (one coulomb per mole of reagent) was consistent with a one-electron process. Cyclic voltammograms, as well as rotating disk electrode (RDE) voltammetry were similar for the product and the starting material, demonstrating that neither 1_{cyc} nor 1_{acy} underwent further chemical transformations after the electron transfer. The isotropic EPR spectra of 1_{cyc} and 1_{acy} (Figure 4) and UV-Vis spectroscopy gave definitive evidence for the identity of the radicals. Indeed DFT calculations reproduced experimental $a(^{15}N)$ isotropic hyperfine coupling constants^[23] (1_{cvc}: exp., 6.6 and 5.4 MHz; calc. 5 and 4 MHz; 1_{acv}: exp., 11.6 and 6.0 MHz; calc. 13 and 7 MHz), as well as the large UV-Vis absorptions (1cyc: exp., 358 and 539 nm; calc. 350 and 515 nm; 1_{acy}: exp., 504 nm; calc. 496 nm). Note that the chemical reduction of $\mathbf{1}_{cyc}^{+}$ and $\mathbf{1}_{acy}^{+}$ with a stoichiometric amount of cobaltocene similarly afforded radicals $\mathbf{1}_{cyc}$ and $\mathbf{1}_{acy}$ in 67 and 63% yield, respectively.



Figure 4. Isotropic X-band EPR spectra of 1_{eyc} and 1_{acy} (top) and corresponding simulated band shapes (bottom) with the following hyperfine coupling constants: 1_{eyc} , $a(^{15}N) = 6.6$ and 5.4 MHz, $a(^{1}H) = 10.66$ (2), 8.30 (2), 1.49, 2.08 and 3.21 MHz; 1_{acy} , $a(^{15}N) = 11.6$ and 6.0 MHz, $a(^{1}H) = 8.9$, 6.1, 7.9 3.9 and 3.2 MHz.

Under an inert atmosphere, and similarly to most (amino)(carboxy)radicals that are derived from stable cyclic carbenes, 1_{cyc} was found to be stable at room temperature for weeks in solution. In contrast, under the same conditions, radical 1_{acy} decomposes within a few days. Attempts to obtain crystals of 1_{acv} from a cooled concentrated hexane solution led to the isolation of the C-C dimer 4 of the (amino)(carboxy)radical 3 (Scheme 2).²⁴ Clearly, **1**_{acy} undergoes a 1,3-H⁻-migration and a yielding subsequent fragmentation, 3 and Nisopropylacetonimine. Interestingly, the EPR spectrum of a THF solution of 4 gives a strong isotropic X-band absorption (Figure 5, left), which is fully consistent with radical 3 as it features large isotropic hyperfine coupling constants with one nitrogen (20.6 MHz) and one hydrogen (22.8 MHz). Note that dimer II (Figure



Figure 3. Cyclovoltammetric and UV-Vis studies of 1_{acy}^* (top) and 1_{cyc}^* (bottom). a) Cyclic voltammogram in CH₃CN + (*n*-Bu)₄NPF₆ 0.1 mol·L⁻¹ (carbon electrode, $\Phi = 3$ mm; *E* vs Fc/Fc^{*}) before (black) and after (red) electrolysis. b) UV-Vis monitoring (1 scan every 50 seconds) of the electrochemical reduction on a reticulated vitreous electrode. c) Rotating disk electrode voltammetry (RDE; 10 mV/s; 600 rpm) before electrolysis. d) RDE (10 mV/s; 600 rpm) after one-electrolysis.

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1) only releases detectable amounts of radical **I** at high temperatures,^[8a] which is due to the difference of steric hindrance. DFT calculations confirmed this assumption with a computed dissociation enthalpy of only +2 kcal·mol⁻¹ for **4** (experimental value reported for **II** in diphenyl ether at 140 °C: +25 kcal·mol⁻¹).

Radicals $\mathbf{1}_{cyc}$ and $\mathbf{1}_{acy}$ are both air-sensitive, just like previously reported **IIIa-e**. The resulting decay of the latter has been attributed to a reaction with dioxygen, although products of the reaction have never been clearly identified. Interestingly, while briefly exposing $\mathbf{1}_{acy}$ to air, we detected a transient paramagnetic compound. Its EPR spectrum featured a 1:1:1 triplet of 1:2:1 triplets indicating coupling with one nitrogen ($a_N = 42.7$ MHz) and two hydrogens ($a_H = 12.2$ MHz), respectively (Figure 5, right). These values perfectly match those of the known di(isopropyl)nitroxide radical.^[25] The formation of this compound is the first evidence of oxidative cleavage of N-C bonds resulting from the air-oxidation of such capto-dative radicals (Scheme 2).



Scheme 2. In contrast to cyclic radical 1_{cyc} , which is stable at room temperature for weeks, radical 1_{acy} undergoes fragmentation into 3, which is in equilibrium in solution with its dimer 4; Air oxidation of 1_{acy} leads to the di(isopropyl)nitroxide radical.



Figure 5. Isotropic X-band EPR spectra in acetonitrile (experimental and simulated) of radicals 3 and iPr_2NO .

Next, we reacted the acyclic (diisopropylamino)(*tert*butyl)carbene^[21] with benzoyl chloride and isolated iminium 2^{+}_{acy} (Scheme 3). The cyclovoltammogram of 2^{+}_{acy} at a scan rate of 0.2 V.s⁻¹ features an irreversible reduction wave at $E_p = -1.30$ V versus Fc/Fc⁺, with the corresponding re-oxidation wave at $E_p = -$ 0.28 V (Figure 6a). These data are indicative of an electron transfer, followed by a chemical transformation. When increasing the scan rate, the reduction of 2^{+}_{acy} at $E_p = -1.30$ V turned progressively reversible ($E_{1/2} = -1.22$ V; $\Delta E_p = 300$ mV at scan rate = 6.4 V·s⁻¹, see Figure 6b) as the cyclovoltammetry time scale surpassed the rate of the chemical transformation. The complete electrochemical reduction of 2^+_{acy} required two coulombs per mole. This ruled out the possibility for the isolation of the desired radical 2_{acy} and, instead indicated the formation of enolate 2^-_{acy} through a two-electron transfer. Evaporation of volatiles and extraction of the residue with diethylether led to the isolation of enol 2_{acy} H [²⁶] as the final compound, and thus identified protonation of 2^-_{acy} as the chemical transformation that was previously evidenced by cyclovoltammetry experiments.



Scheme 3. A two-electron reduction occurs with $\mathbf{2^{*}}_{acy}$ giving the corresponding enolate $\mathbf{2^{*}}_{acy}$



Figure 6. a) Cyclic voltammogram of 2^*_{acy} (1 mmol·L⁻¹) in CH₃CN + (*n*-Bu)₄NPF₆ 0.1 mol·L⁻¹ (carbon electrode, $\Phi = 3$ mm; *E* vs Fc/Fc⁺) with scan rate v = 0.2 V.s⁻¹; the dashed line corresponds to scan on a -1.6 – 1 V range. b) Cyclic voltammogram of 2^*_{acy} in same conditions with scan rate v = 6.4 V.s⁻¹

Among other metrics,^[27] a recognized measurement of the π accepting capabilities of stable carbenes is the ³¹P NMR chemical shift of the corresponding (phenyl)phosphinidene adducts (>C=PPh).^[19c,d] Accordingly, the π -accepting properties of cyclic carbenes increase from entry 1 to 6 of Table 1. Concomitantly, the redox potential of the corresponding cyclic cations/radicals follows the same trend, in line with recent results from Hudnall et al.[18] Surprisingly, cations/radicals derived from acyclic carbenes (entry 7 and 8) stand out abnormally from the series. Indeed, acyclic di(amino)carbenes and (alkyl)(amino)carbenes are among the most electron πaccepting carbenes, and therefore one would have expected the reduction of corresponding iminiums $\mathbf{1}_{acy}^{+}$ ($E_{1/2} = -1.24$ V) and 2_{acy}^{+} (E_{1/2} = -1.22 V) to occur at more weakly negative potentials than those of the very weakly π -acceptor NHCs 1_{cyc}^{+} ($E_{1/2}$ = -1.32 V) and 2^{+}_{cyc} ($E_{1/2}$ = -1.21 V).

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Entry	Carbene	δ^{31} P NMR ^[a]	Cation	E _{1/2} (mV) ^[b]			
1	Dipp, N N N Dipp	-18.9	llic⁺	-1.32			
2	Dipp N N N Dipp	-10.2	1 ⁺ _{cyc}	-1.21			
3	Mes O N N Mes	37.7	IIId⁺	-0.98			
4	Bn N S	57	Illa⁺	-0.95			
5	Dipp, N •	68.9	2 ⁺ _{сус}	-0.93			
6	Mes O N N Mes	83	llle⁺	-0.48			
7	iPr iPr ^{∕N} ↓• iPr ^{∕N} √iPr	69.5	1 ⁺ _{acy}	-1.24			
8	iPr iPr-N•	126.3	2 [*] _{acy}	(-1.22) ^[c]			

 Table 1. Experimental measures of electronic properties of free carbenes and of the corresponding radicals.

[a] ³¹P NMR chemical shift (ppm) for carbene•PPh adducts as a measure of the π -accepting properties of carbenes according to reference 19c. [b] Redox potential for cation/radical. [c] Reduction potential for $2^{+}_{acy}/2^{-}_{acy}$.

We performed DFT calculations in order to have more insight into the singular reduction behavior of acyclic cations 1^{+}_{acy} and 2^{+}_{acy} , especially with respect to their cyclic counterparts 1^{+}_{cyc} and 2^{+}_{cyc} . There is no unambiguous way to define radical stabilization energy (RSE). However, numerous studies have shown that the enthalpy of the hydrogen atom exchange of a Ccentered radical with CH₄ is a conceptually simple and insightful method for the study of the capto-dative effect.^[28] For instance, isodesmic reaction (1) provides a relevant estimate for the effect on RSE of a set of (X,Y) substituents. It is well known that RSEs hardly benefit from the combination of substituents is expected to have a synergetic effect, resulting in a strong deviation (DARSE) from the additivity of the RSE of each substituent, as defined by equation (2):

•CHXY + CH₄ \rightarrow CH₂XY + •CH₃ Δ H=RSE_(X,Y) (1) DARSE_(X,Y) = RSE_(X,Y) - RSE_(X,H) - RSE_(H,Y) (2)

(DARSE).				
Entry	radical	RSE (kcal.mol ⁻¹)	DARSE (kcal.mol ⁻¹)	
1	1 _{cyc}	41.9	9.7	
2	1 _{acy}	41.6	11.9	
3	2 _{cyc}	36.5	6.3	
4	2 _{acy}	21.4	-2.6	
5	3	37.7	6.8	

Table 2. Calculated radical stabilization energy RSE for 1_{cyc} , 1_{acy} , 2_{cyc} , 2_{acy}

and 3 (relative to H_3C) and corresponding deviation from additivity of RSE

As expected strong DARSE values were found for 1_{cyc} , 1_{acy} and 2_{cyc} (Table 2, entries 1-3), but surprisingly the capto-dative combination in 2_{acy} has a clear detrimental effect (entry 4); in addition the RSE for 2_{acy} is much smaller than for the other three radicals. We hypothesized that the mediocre thermodynamic stabilization of radical 2_{acy} was due to the excessive steric hindrance around the radical center. Indeed, as shown in Figure 7, in contrast to 2_{cyc} which features a nearly-planar conjugated π -system (NC1C2O torsion angle: 6.7 °), there is a strong torsion around the C1–C2 bond of 2_{acy} (37.8 °) that prevents the electron-delocalization on the NCCO fragment. The calculated RSE (37.7 kcal.mol⁻¹) and DARSE (6.8 kcal.mol⁻¹) for radical 3 (Scheme 2), a much less bulky analogue of 2_{acy} , confirmed our assessment.



Figure 7. View along the C1–C2 axis of the optimized geometry of 2_{cyc} , 2_{acy} and 3 at the B3LYP/TZVP level of theory.

Conclusions

We have shown that the substitution pattern of stable acyclic (amino)carbenes is detrimental for the stability of the corresponding radicals $\mathbf{1}_{acy}$ and $\mathbf{2}_{acy},$ but for different reasons. Radical thermodynamically unstable, 2_{acy} is and disproportionates into the corresponding iminium $\mathbf{2}^{+}_{acy}$ and enolate 2⁻acy. This is due to the excessive steric hindrance, which prevents the electron-delocalization on the NCCO fragment, and thus capto-dative stabilization. In contrast, 1acy is as thermodynamically stabilized as its cyclic counterpart 1cyc, but suffers from the presence of β-hydrogens on the N-substituent along with the enhanced flexibility around C-N bonds, which allow for a H•-migration-elimination process. This work suggests

general guidelines for the design of highly persistent (amino)(carboxy)radicals, especially by emphasizing the key advantage of cyclic patterns. Their rigidity prevents rearrangements, and offers an optimal +M donation of the amino group allowing for a fully conjugated NCCO fragment, with a planar local environment. The recent assumption^[18] that the π -accepting properties of carbenes parallel the reduction potential of the corresponding (amino)(carboxy)radicals is in agreement with our findings in the cyclic series. However, the acyclic carbenes considered in this study seem to be out of range, but other acyclic carbenes should be considered before drawing a conclusion.

Experimental Section

General Considerations: All manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk and drybox techniques. Dry and oxygen-free solvents were employed. Benzoyl chloride was purified by distillation before use. Stable carbenes were prepared as previously reported,^[22,20,21] as well as radical 2_{cyc} .^[13] ¹H, ¹³C, and ¹⁹F NMR spectra were recorded on Bruker Advance 300, Varian VX 500 and Jeol ECA 500 spectrometers. Chemical shifts are given relative to SiMe₄ and referenced to the residual solvent signal (¹H, ¹³C) or relative to an external standard (¹⁹F: CFCI₃). Melting points were measured with Büchi Melting Point B-545 apparatus. Electrochemical experiments were carried out with a Bio-logic SP-300 potentiostat. An Ag/0.01M AgNO_{3} reference electrode in CH₃CN + 0.1M [Bu₄N]PF₆ was used. Cyclic voltammetry experiments were performed in CH₃CN + 0.1M [Bu₄N]PF₆ a vitreous carbon disk (3 mm in diameter) as working electrode and a platinum wire as auxiliary electrode. Ferrocene was used as standard, and all reduction potentials are reported with respect to the E_{1/2} of the Fc/Fc⁺ redox couple. Electrochemical reductions were performed using reticulated vitreous carbon electrode, and were monitored with a Zeiss MCS 501 UV-NIR Plus spectrometer. EPR spectra were obtained using an X-band Bruker EMX Plus spectrometer.

Synthesis of iminium 1^{+}_{cyc} : Benzoyl chloride (0.37 mL, 3.17 mmol) was added slowly to a toluene solution of the imidazolidin-2-ylidene (1.027 g, 2.88 mmol). The solution was stirred for 20 minutes and then filtered. The solid was then washed with hexanes (3 x 20mL) to yield a white powder. Recrystallization by diffusion of diethyl ether into a dichloromethane solution of the product yielded 1_{cyc}^{+} as colorless crystals. Yield: 942 mg (66 %). mp: 261–263 °C. MS (m/z): [M⁺] calc. for $C_{34}H_{43}N_2O^{+}$, 495.3375; found, 495.3372. UV-Vis: Absorbance [nm] (ϵ) = 269 (12,285). ¹H NMR (CDCl₃, 300 MHz): δ = 7.96 (d, J = 6 Hz, 2H), 7.62 (t, J = 6 Hz, 1H), 7.45 (t, J = 6 Hz, 2H), 7.32 (t, J = 6 Hz, 2H), 7.12 (d, J = 6 Hz, 4H), 5.07 (bs, 4H), 3.45 (sept, J = 3Hz, 4H), 1.33 (d, J = 3 Hz, 12H), 1.12 (d, J = 3 Hz, 12H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ = 180.6 (C). 162.1 (C), 147.1 (C), 137.1 (CH), 131.7 (CH), 131.3 (C), 130.0 (CH), 129.9 (CH), 128.7 (C). 125.4 (CH), 55.7 (CH₂), 29.4 (CH), 26.9 (CH₃), 23.1 (CH₃) ppm.

Synthesis of iminium 1⁺_{acy}: Benzoyl chloride (0.122mL, 0.965 mmol) was added to a hexane solution of bis(diisopropylamino)carbene (194 mg, 0.804 mmol) and the solution stirred for 20 minutes. The solvent was filtered off and the solid washed with diethyl ether (2x10mL). Recrystallization from diffusion of diethyl ether into a dichloromethane solution of the product yielded a yellow crystalline material. Yield: 284 mg (78%). mp: 209–210 °C. MS (m/z): [M⁺] cale. for C₂₀H₃₃N₂O⁺, 317.2587; found, 317.2590. UV-Vis: Absorbance [nm] (ϵ) = 272 (12,676), 367 (838). ¹H NMR (CDCl₃, 400 MHz): δ = 8.11 (bd, 2H, J = 7.2 Hz), 7.70-7.61 (m, 3H), 4.19 (sept, 4H, J = 6.8 Hz), 1.41 (d, 12H, J = 6.8 Hz), 1.37 (d, 12H, J = 6.8 Hz) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 189.5 (C), 168.0 (C), 136.8 (CH), 133.8 (CH), 130.3 (CH), 56.9 (CH), 22.9 (CH₃), 22.6 (CH₃) ppm.

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Synthesis of iminium **2⁺**acy: A solution of the acvclic (amino)(alkyl)carbene in THF was prepared in situ from the corresponding amidinium triflate (0.50 g, 1.64 mmol) and lithium 2,2,6,6tetramethylpiperidine (0.24 g, 1.64 mmol). The solution was cooled to -78 °C, and benzoyl chloride (0.20 mL, 1.99 mmol) was added dropwise. The solution was stirred at -78 °C for 30 minutes, warmed to room temperature and stirred an additional 30 minutes. The supernatant was removed via filtration, and the solid was then washed with diethyl ether (2 x 10 mL) and dried in vacuo. Extraction of the product in chloroform and removal of the solvent in vacuo yielded a white solid. Yield: 255 mg (38 %). mp: 179–180 °C. MS (m/z): $[M^{\star}]$ calc. for $C_{18}H_{28}NO^{\star},\,274.2165;$ found, 274.2169. UV-Vis: Absorbance [nm] (ε) = 263 (9,058), 268 (9,427). ¹H NMR (CDCl₃, 500 MHz): δ = 8.10 (bs, 1H), 7.80 (bs, 3H), 7.71 (bs, 1H), 5.32 (sept, J = 6.6 Hz, 1H), 4.62 (sept., J = 7.0 Hz, 1H), 1.88 (d, J = 6.6 Hz, 3H), 1.71 (d, J = 6.6 Hz, 3H), 1.54 (s, 9H), 1.51 (d, J = 7.0 Hz, 3H), 1.30 (d, J = 7.0 Hz, 3H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ = 197.8 (C), 189.0 (C), 137.3 (CH), 131.9 (C), 130.7 (CH), 127.5 (CH), 62.4 (CH), 40.5 (C), 29.3 (CH₃), 23.7 (CH₃) ppm. ^{19}F NMR (CDCl₃, 376 MHz): δ = -78.18 (s) ppm.

Radical 1_{cyc}: Iminium salt 1⁺_{cyc} (0.400 g, 0.75 mmol) and cobaltocene (0.14 g, 0.75 mmol) were combined under argon. Dichloromethane was added to the flask, and the solution stirred for 30 minutes. Removal of the solvent *in vacuo* and extraction in diethyl ether yielded 1_{cyc} as a dark purple solid. Yield: 250 mg (67 %). mp: 104–106 °C. The electrochemical reduction of iminium salt 1⁺_{cyc} (6.9 mg, 0.013 mmol), in 10.0 mL of acetonitrile containing 0.1M [Bu₄N]PF₆, was performed on a reticulated vitreous carbon electrode at a potential of -1.50 V under an argon atmosphere. Complete electrolysis (one electron exchanged per molecule) yielded a purple solution. Absorbance [nm] (ϵ) =242 (9,120), 359 (5,643), 541 (2,991).

Radical 1_{acy}: Iminium salt 1_{acy}^{+} (0.200 g, 0.57 mmol) and cobaltocene (0.097 g, 0.52 mmol) were combined under argon. Dichloromethane was added to the flask, and the solution stirred for 20 minutes. Removal of the solvent *in vacuo* and extraction in hexanes yielded 1_{acy} as a dark reddish-purple solid. Yield: 62 mg (63 %). mp: 102–104 °C. The electrochemical reduction of iminium salt 1_{acy}^{+} (3.7 mg, 0.012 mmol), in 10.0 mL of acetonitrile containing 0.1M [Bu₄N]PF₆, was performed on a reticulated vitreous carbon electrole at a potential of -1.40 V under an argon atmosphere. Complete electrolysis (one electron exchanged per molecule) yielded a reddish-purple solution. UV-Vis: Absorbance [nm] (ϵ) = 236 (6,026), 505 (3,515). Crystallization of 1_{acy} by cooling a concentrated hexane solution yielded crystals of **4** as yellow blocks. mp: 109-111°C

Electrochemical Synthesis of 2_{acy} **H**: Iminium salt 2_{acy}^{+} (4.5 mg, 0.011 mmol), in 10.0 mL of acetonitrile containing 0.1M [Bu₄N]PF₆, was reduced on a reticulated vitreous carbon electrode at -1.60V under an argon atmosphere. Complete electrolysis (two electrons exchanged per molecule) yielded a yellow solution. Removal of the solvent in vacuo and extraction in diethyl ether yielded a yellow oil. UV-Vis: Absorbance [nm] (ϵ) = 248 (13,561), 394 (618). ¹H NMR (C₆D₆, 400 MHz): δ = 8.06 (s, 1H), 7.31-7.29 (m, 2H), 7.08-7.00 (m, 3H), 3.29 (sept, J = 6.4 Hz, 2H), 1.05 (d, J = 6.4 Hz, 12H), 0.95 (s, 9H) ppm. ¹³C NMR (C₆D₆, 100 MHz): δ = 153.5 (C), 138.8 (C), 130.3 (CH), 129.7 (CH), 129.0 (CH), 124.3 (C), 49.3 (CH), 36.5 (C), 32.7 (CH₃), 22.9 (CH₃), 22.6 (CH₃) ppm.

Computational methods

The DFT calculations were carried at the B3LYP/TZVP level of theory, unless otherwise stated, using the program package Gaussian09.^[29] Optimized structures were identified as energy minima by calculating the vibrational frequencies. The solvent (acetonitrile) was taken into account only for TD-DFT calculations, using the Polarizable Continuum Model (PCM) method.

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Keywords: Carbene • Radical • Capto-dative effect • EPR

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FULL PAPER

Stable or unstable capto-dative radicals: The relative stability of carbene derived cyclic and acyclic capto-dative radicals is discussed in the light of electrochemical measurements, EPR and DFT calculations. Decomposition pathways are observed with acylic capto-dative radicals. isolated ? X $X \rightarrow N$ $Y \rightarrow N$ $X \rightarrow N$ $Y \rightarrow N$ $Y \rightarrow$