Evidence for an Equilibrium between an N-heterocyclic Carbene and Its Dimer in Solution**

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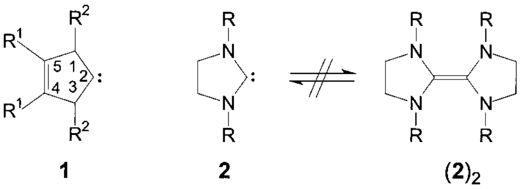
Dedicated to Professor Wolf-Peter Fehlhammer
on the occasion of his 60th birthday

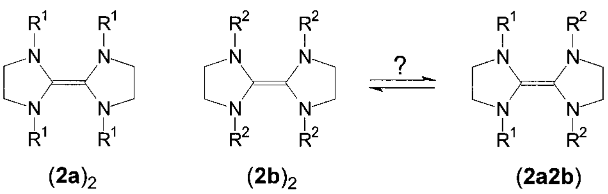
Shortly after the isolation of the first stable N-heterocyclic carbene **1** (derived from imidazole),[1] the synthesis and characterization of saturated carbenes **2** (derived from imidazoline and postulated by Wanzlick more than 40 years ago[2]) was successfully carried out.[3] However, carbenes of type **2** were not prepared by the dissociation of electron-rich enetetramines $(\mathbf{2})_2$ as suggested by Wanzlick (Scheme 1); they were obtained by deprotonation of imidazolinium salts[3a] or by reduction of imidazoline-2-thiones.[3b]



Scheme 1.

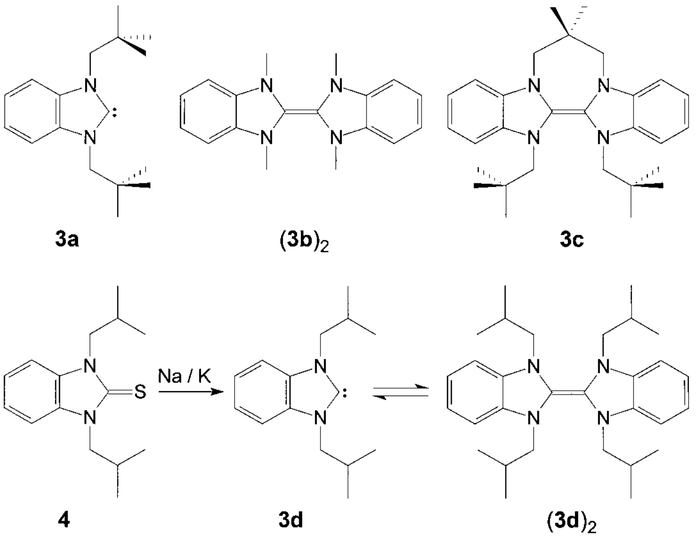
Numerous carbene complexes $\mathbf{2}{=}\mathrm{ML}_n$ have been prepared by the reaction of enetetramines $(\mathbf{2})_2$ with coordinatively unsaturated transition metal complexes by cleavage of the C–C double bond.[4] However, no evidence for the formation of free carbene intermediates **2** has been observed in these reactions.

On the contrary, investigations of the metathesis reaction between cyclic and acyclic enetetramines by Winberg et al.[5] did not lead to the corresponding cross products. Lemal and co-workers[6] showed that the metathesis reaction between $(\mathbf{2a})_2$ and $(\mathbf{2b})_2$ leading to mixed olefins **2a2b** (Scheme 2) only proceeds in the presence of electrophiles. On the basis of these findings the existence of the free carbenes and the equilibrium between **2** and $(\mathbf{2})_2$ postulated by Wanzlick was excluded. In addition, subsequent investigations by Lappert et al. led to the same result.[7] In contrast to this, Denk et al. recently showed by NMR spectroscopy that metathesis products of type **2a2b** can be obtained from two different enetetramines at elevated temperatures.[8]



Scheme 2. Metathesis experiment using two different enetetramines.

While the detection of these metathesis products indicates the existence of the "Wanzlick-equilibrium" between enetetramine and carbene, it can not be regarded as proof of such. Denk et al. have already pointed out that the formation of the metathesis product **2a2b** from $(\mathbf{2a})_2$ and $(\mathbf{2b})_2$ can also be explained by a [2+2] cycloaddition/cycloreversal.[8] Only the detection of **2** and $(\mathbf{2})_2$ at the same time in the absence of any electrophile can be regarded as unequivocal proof for an equilibrium between carbene and enetetramine. In this paper we describe dibenzotetraazafulvalene $(\mathbf{3d})_2$ which at ambient temperature is already in equilibrium with the corresponding annelated N-heterocyclic carbene **3d**. In addition, we present the opening of the bridged compound **3c** to form a molybdenum dicarbene complex (Scheme 3).



Scheme 3.

We recently described the first stable annelated N-heterocyclic carbene **3a**.[9] Despite the unsaturated nature of the N-heterocyclic ring, this carbene shows structural and spectroscopical properties which are typical for saturated carbenes of type **2**. In addition, the fast dimerization of the N-methylated derivative, which is sterically less crowded, to form $(\mathbf{3b})_2$[9, 10] is characteristic for saturated N-heterocyclic carbenes. Unsaturated derivatives of type **1** seldom form enetetramines,[1b] or only after suitable double bridging.[11] Since derivatives of type **3** are stable as either N-heterocyclic carbenes, such as **3a**, or as enetetramines, such as $(\mathbf{3b})_2$, due to the bulky substituents at the nitrogen atoms,[12] we felt this was a chance to find evidence of the sought-after equilibrium betweeen carbene and enetetramine, by adaptation of the N substituents.

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The first clues towards a carbene/enetetramine equilibrium were provided by the reduction of a C_3-linked dithione to give the enetetramine **3c** (Scheme 3). Despite considerable steric bulk at the N-substituents the bridge leads to the immediate formation of the enetetramine **3c**. The analogous dimerization was not observed for **3a** or for a number of single-bridged imidazoline-2-ylidenes by Chen et al.[11] The formation of enetetramine **3c** in solution was established by ^{13}C NMR spectroscopy ($\delta(C2) = 119.5$) and in the solid state by X-ray diffraction analysis (Figure 1).[19a)] In the crystal the enetetramine **3c** is twisted along the C2–C2* axis. However, the N–C=C–N torsion angles differ, most likely due to the C_3 bridge (N2-C2-C2*-N2* 21.6(1)°, N1-C2-C2*-N1* 1.4(1)°). A similar twist of the double bond was found in the enetetramine $(\mathbf{3b})_2$, although the twist angles were nearly identical (16.8(1)° and 14.4(1)°, respectively).[10] On the other hand, both molecules show a regular length for the double bond (**3c**: 1.345(2); $(\mathbf{3b})_2$ 1.344(4) Å). NMR spectroscopic studies did not indicate the dissociation of **3c** into two bridged N-heterocyclic carbenes.

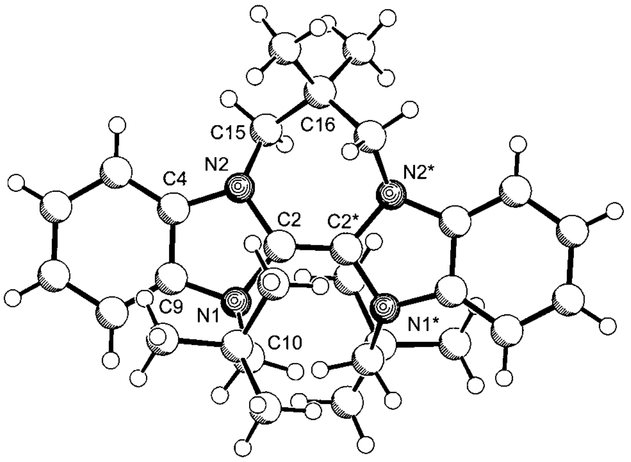

Figure 1. Molecular structure of **3c** in the crystal (SCHAKAL-depiction). Selected bond lengths [Å] and angles [°]: N1-C2 1.4212(11), N1-C9 1.3992(12), N1-C10 1.4640(12), N2-C2 1.4214(11), N2-C4 1.3981(12), C2-C2* 1.345(2), C4-C9 1.4001(14); C2-N1-C9 107.13(7), C2-N1-C10 121.40(8), C9-N1-C10 121.43(8), C2-N2-C4 107.17(7), N1-C2-N2 107.64(8), N1-C2-C2* 125.81(5), N2-C2-C2* 125.94(5). Symmetry (*) $1-x, y, 1/2-z$.

The decrease of steric bulk at the N substituents leads to the formation of enetetramines after reduction of the corresponding thiones, even without a bridge. Such behavior has never previously been observed for unbridged Arduengo-type carbenes.[11] The enetetramine $(\mathbf{3d})_2$ was obtained in 50% yield by reduction of the diisobutyl-substituted thione **4** with Na/K alloy in toluene. After workup (careful separation of K_2S), compound $(\mathbf{3d})_2$ can be collected from the solution as yellow crystals. The X-ray diffraction analysis[19b)] (Figure 2) again showed a twisted olefin (torsion angle N1-C2-C12-N2 15.7(2)°) with a regular C=C bond length of 1.332(5) Å.

While crystallization experiments with **3d** always resulted in the isolation of the enetetramine $(\mathbf{3d})_2$, ^{13}C NMR spectroscopic investigations of the reaction mixture indicated the presence of both the carbene **3d** ($\delta(C2) = 227.8$, compare to **3a**[9] $\delta(C2) = 231.5$) and the entetramine $(\mathbf{3d})_2$ ($\delta(C2) = 119.0$, compare to $(\mathbf{3b})_2$[10] $\delta(C2) = 121.0$). This surprising result prompted us to start detailed NMR spectroscopic studies. Crystalline enetetramine $(\mathbf{3d})_2$ was dissolved in dry, deoxygenated [D$_8$]toluene and ^1H NMR spectra were recorded at intervals of one hour. The use of crystalline $(\mathbf{3d})_2$ and carefully purified toluene makes the presence of the electrophile (K_2S) very unlikely. The first spectrum (Figure 3), which

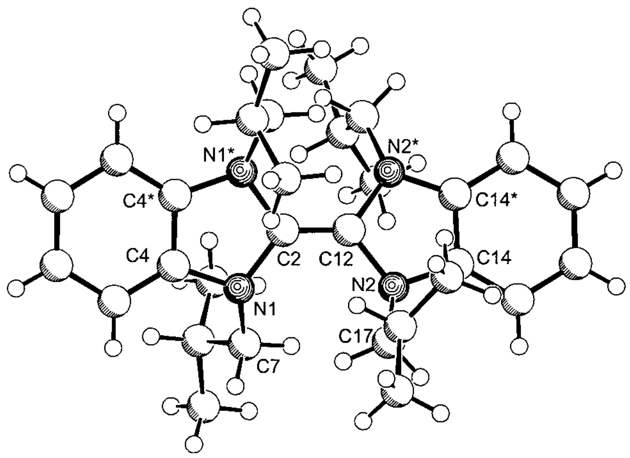

Figure 2. Molecular structure of $(\mathbf{3d})_2$ in the crystal (SCHAKAL-depiction). Selected bond lengths [Å] and angles [°]: N1-C2 1.439(3), N1-C4 1.405(4), N1-C7 1.476(4), N2-C12 1.432(3), N2-C14 1.384(4), N2-C17 1.480(4), C2-C12 1.332(5), C4-C4* 1.389(6), C14-C14* 1.393(6); C2-N1-C4 107.3(2), C2-N1-C7 122.2(2), C4-N1-C7 118.4(2), C12-N2-C14 108.0(2), C12-N2-C17 121.7(2), C14-N2-C17 118.3(2), N1-C2-N1* 107.0(3), N1-C2-C12 126.51(15), N2-C12-N2* 106.2(3), N2-C12-C2 126.9(2). Symmetry (*) $y, x, -z$.

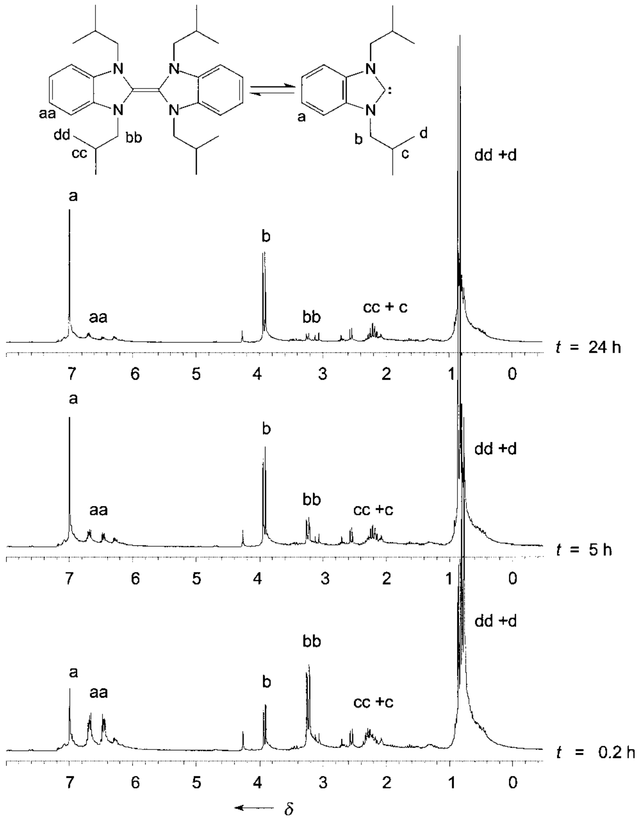

Figure 3. Time-resolved ^1H NMR spectra (200 MHz, [D$_8$]toluene) of $(\mathbf{3d})_2$ at 298 K.

is still dominated by resonance signals of the enetetramine (**3d**)$_2$ (bb: $\delta(\mathrm{NCH_2}) = 3.23$, aa: $\delta(\mathrm{Ar{-}H}) = 6.66$ and 6.48), already indicates the formation of carbene **3d** (b: $\delta(\mathrm{NCH_2}) = 3.92$, a: $\delta(\mathrm{Ar{-}H}) = 7.08$). The appearance of signals for **3d** in the first spectrum is attributed to the time elapsed between the preparation of the sample and the first data being acquired (0.2 h). With time, the intensities of the **3d** resonance signals increase and the intensities of (**3d**)$_2$ resonance signals decrease. After 24 h no more changes can be detected and the system equilibrates at a ratio of 90% **3d** and 10% (**3d**)$_2$. When the starting concentration of (**3d**)$_2$ is higher, the equilibrium establishes at a ratio of 85:15. Identical results were obtained from ^{13}C NMR spectroscopy by the disappearance of the C2 resonance signal of the enetetramine at $\delta = 119.0$ and by the increase of the carbene C2 resonance signal at $\delta = 227.8$. However, the signal intensities in ^{13}C NMR spectra did not not allow a quantitative estimation of the equilibrium.

The simultaneous detection of **3d** and (**3d**)$_2$ by NMR spectroscopy in a solution prepared from pure (**3d**)$_2$ constituted evidence of the equilibrium between the N-heterocyclic carbene and the corresponding enetetramine as well as the dissociation of the enetetramine into two carbenes in a direct route, rather than the indirect route via the metathesis products. We are convinced that catalytically active electrophiles were absent under the reaction conditions specified.

The dissociation of the double bond in (**3d**)$_2$ at ambient temperature can be rationalized in terms of the binding model developed by Carter, Goddard, Malrieu, and Trinquier (CGMT Model[13a]), which was also used by Chen[13b] to discuss the weakness of the double bond in electron-rich olefins. In formal dimers of singlet carbenes **1**–**3** the strength of the C–C double bond can be approximated by the bond strength of a regular double bond (usually the $(\mathrm{sp^2{-}sp^2})\sigma/(\mathrm{p{-}p})\pi$-double bond of ethylene of 172 kcal mol^{-1}[14]) minus the sum of the singlet–triplet energy gap for both carbene parts. The singlet–triplet energy gap amounts to approximately 85 kcal mol^{-1}[15] per "Arduengo" carbene of type **1**, which has been used to explain the weakness of the C=C bond in molecules of type (**1**)$_2$ and the difficulties in their preparation. The singlet–triplet gap is smaller for carbenes of type **2** due to the saturation of the N-heterocyclic ring; the entetramines (**2**)$_2$ are readily formed but difficult to dissociate into carbenes.[13b] Annelated N-heterocyclic carbenes of type **3** obviously have an intermediate singlet–triplet energy gap; the formation and dissociation of dibenzotetraazafulvalenes (**3**)$_2$ are primarily determined by the steric bulk of the N substituents. This behavior emphasizes the unusual properties of the carbenes of type **3**, which have the topology of unsaturated N-heterocyclic carbenes (type **1**) but show the reactivity of saturated derivatives (type **2**). However, the energy gap between the singlet and triplet states must also be considerable for carbenes of type **3**, as can be seen from the strong twist of the C–C double bond (N–C=C–N torsion angle 15.7(2)°; relative to torsion angles of 16.8(1) and 14.3(1)° in (**3b**)$_2$[10] and 6 and 8° in N-methylated (**2**)$_2$.[3b])

Even so, **3c** is more sterically hindered than (**3d**)$_2$; opening of the C–C double bond in **3c** can not be observed under regular conditions, which we have attributed to the C$_3$ bridge. However, in analogy to reactions already reported,[4, 16] the dibenzotetraazafulvalene can be opened by coordinatively unsaturated transition metal complexes (acting as Lewis acids) to form a dicarbene complex. Treatment of **3c** with [Mo(nor)(CO)$_4$] (nor = norbornadiene) yields the dicarbene complex **5** after 1 h. The X-ray diffraction analysis[19c)] of **5** (Figure 4) shows an approximately octahedral complex. The Mo–C(carbene) bond length (2.324(3) Å) is, within experimental error, the same as the equivalent bond length in *fac*-[Mo(Im)$_3$(CO)$_3$] (Im = *N*,*N'*-dimethylimidazolin-2-ylidene).[17] The C$_3$ bridge between the two carbene donors in **5** allows a C(carbene)-Mo-C(carbene) bond angle of 95.77(14)° in the octahedral complex **5**, whereas the C$_1$ bridge between two benzimidazolin-2-ylidene groups, at least in the PdI$_2$ complex, leads to an acute C-Pd-C-angle of 83.7(3)°.[18] The excellent donor ability of the carbene groups in **5** is also illustrated by the different Mo–CO bond lengths for the CO ligands which are *cis* and *trans* to the carbene ligands (2.035(3) and 1.963(3) Å).[20]

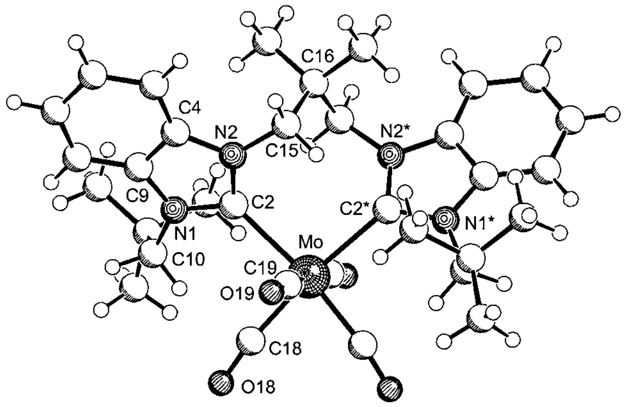

Figure 4. Molecular structure of **5** in the crystal (SCHAKAL depiction). Selected bond lengths [Å] and angles [°]: Mo-C2 2.234(3), Mo-C18 1.963(3), Mo-C19 2.035(3), N1-C2 1.385(4), N1-C9 1.387(4), N1-C10 1.452(4), N2-C2 1.367(4), N2-C4 1.392(3), N2-C15 1.462(3), C4-C9 1.372(5), C18-O18 1.160(3), C19-O19 1.135(4); C2-Mo-C2*, 95.77(14), C2-Mo-C18 92.03(10), C2-Mo-C18* 170.98(10), C2-Mo-C19 99.77(12), C2-Mo-C19* 82.51(12), C18-Mo-C18* 80.57(15), C18-Mo-C19 91.72(12), C18-Mo-C19* 85.71(12), C18*-Mo-C19 85.71(12), C18*-Mo-C19* 91.72(12), C19-Mo-C19* 176.6(2), C2-N1-C9 111.4(3), C2-N1-C10 124.7(3), C9-N1-C10 123.8(3), C2-N2-C4 112.3(2), C2-N2-C15 124.7(2), C4-N2-C15 122.4(2), N1-C2-N2 103.3(2), Mo-C18-O18 173.1(2), Mo-C9-O19 174.1(3). Symmetry (*) $1/2 - y$, $1/2 - x$, $1/2 - z$.

Experimental Section

All work was performed in an atmosphere of dry argon with thoroughly dried reagents and solvents. All of the carbenes and dibenzotetraazafulvalens were obtained by reduction of the corresponding benzimidazole-2-thiones[9] with Na/K alloy in toluene. ^{1}H and ^{13}C NMR spectra were obtained at 200 or 50.3 MHz, respectively.

4: yellow oil. ^{1}H NMR ([D$_8$]THF): $\delta = 6.98$ (m, 4H; Ar–H), 3.88 (d, 4H; NCH$_2$), 2.26 (m, 2H; C*H*Me$_2$), 0.73 (d, 12H; CH$_3$); ^{13}C NMR ([D$_8$]THF): $\delta = 169.3$ (C=S), 131.6, 121.8, 108.6 (Ar–C), 51.1 (NCH$_2$), 27.0 (*C*HMe$_2$), 19.5 (CH$_3$).

Mixture of **3d** and (**3d**)$_2$: solid yellow crystals of (**3d**)$_2$ (m.p. 32 °C); ^{1}H NMR ([D$_8$]toluene): $\delta = 7.08$ (m, 4H; Ar–H **3d**), 6.66 (m, 4H; Ar–H (**3d**)$_2$), 6.48 (m, 4H; Ar–H (**3d**)$_2$, 3.92 (d, 4H; NCH$_2$ **3d**), 3.23 (d, 8H; NCH$_2$ (**3d**)$_2$), 2.33 (m, 2H; C*H*Me$_2$ **3d**), 2.36 (m, 4H; C*H*Me$_2$ (**3d**)$_2$), 0.80

(d, 12H; CH_3 **3d**), 0.89 (d, 24H; CH_3 (**3d**)$_2$); ^{13}C NMR ([D$_8$]toluene): $\delta =$ 227.8 (carbene-C **3d**), 119.0 ($N_2C{=}CN_2$ (**3d**)$_2$), 135.8, 121.2, 110.3 (Ar–C **3d**), 142.3, 120.2, 110.1 (Ar–C (**3d**)$_2$), 55.6 (NCH_2 **3d**), 55.8 (NCH_2 (**3d**)$_2$), 29.4 (CHMe$_2$ **3d**), 26.1 (CHMe$_2$ **3d** = **3d**), 20.5 (CH_3 **3d**), 20.9 (CH_3 (**3d**)$_2$).

3c: Yellow crystals (m.p. 37 °C); ^1H NMR (C_6D_6): $\delta = 7.18$ (m, 4H; Ar–H), 6.08 (m, 4H; Ar–H), 4.52 (s, br, 4H; NCH_2), 4.11 (s, 4H; NCH_2), 0.97 (s, 18H; $C(CH_3)_3$), 0.81 (s, 6H; $C(CH_3)_2$); ^{13}C NMR (C_6D_6): $\delta = 119.5$ ($N_2C{=}CN_2$), 141.9, 141.8, 120.1, 119.4, 108.8, 105.8 (Ar–C), 58.6 (NCH_2), 22.4 (NCH_2), 36.7 (CMe$_3$), 33.6 (CMe$_2$), 29.4 ($C(CH_3)_3$), 25.0 ($C(CH_3)_2$).

5: A solution of [Mo(nor)(CO)$_4$] (300 mg, 1.0 mmol) was added dropwise to a solution of **3c** (336 mg, 0.80 mmol) in THF (30 mL) under argon. The yellow reaction solution was stirred for 12 h at ambient temperature. The solvent was removed in vacuo and the residue was dissolved in ethyl acetate (3 mL). This solution was purified by chromatography (SiO_2, hexane/ethyl acetate 5/1) and the product solution was reduced in volume, yielding yellow crystals of **5**. Yield 402 mg (80%). ^1H NMR ($CDCl_3$): $\delta = 7.53-7.22$ (m, 8H; Ar–H), 5.55, 4.93, 4.32, 3.91 (d, 2H; NCH_2), 1.10 (s, 18H; $C(CH_3)_3$), 0.88 (s, 6; $C(CH_3)_2$); ^{13}C NMR ($CDCl_3$): $\delta = 219.9$ (*trans*-CO), 210.0 (*cis*-CO), 208.2 (carbene-C), 136.4, 135.9, 122.6, 122.2, 113.2, 110.8 (Ar–C), 59.1, 52.4 (NCH_2), 41.0 (CMe$_2$), 35.0 (CMe$_3$), 29.6 ($C(CH_3)_3$), 24.8 ($C(CH_3)_2$).

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[12] Imidazoline-based carbenes with sterically demanding N-substituents are also stable as monomers, whereas sterically less-demanding N-substituents lead to enetetramines.[3b]

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[19] X-ray structure analysis: All data sets were collected on a Enraf-Nonius CAD4 or a Nonius Kappa-CCD diffractometer with a rotating anode FR591 (Nonius) used as a radiation source. The following programs were used: EXPRESS and COLLECT for data collection; MolEN and Denzo-SMN for data reduction; SORTAV for absorption correction of CCD-Data; SHELXS-97 for structure solution; SHELXL-97 for structure refinement; and SCHAKAL-92 for molecular graphics. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-124994 (**3c**), -124995 (**3d**)$_2$ and -124996 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk). a) **3c** ($C_{29}H_{40}N_4$): $M_r = 444.65$, colorless crystals $0.30 \times 0.30 \times 0.15$ mm, $a = 19.155(1)$, $b = 0.534(1)$, $c = 15.439(1)$ Å, $\beta = 123.92(1)^\circ$, $V = 1585.1(3)$ Å^3, $\rho_{calcd} = 1.142$ g cm^{-3}, $\mu = 0.68$ cm^{-1}, empirical absorption correction ($0.980 \le T \le 0.990$), $Z = 4$ (C16 and midpoint of the C2–C2* bond on a twofold axis), monoclinic, space group $C2/c$ (No. 15), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 9982 measured reflections ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.71$ Å^{-1}, 3884 unique and 3070 observed reflections $[I \ge 2\sigma(I)]$, 184 refined parameters, $R = 0.047$, $wR^2 = 0.117$, max. (min.) residual electron density 0.28 (-0.17) e Å^{-3}, positional disorder of the bridging atoms C15, C16 and C17, hydrogen atoms calculated and refined as riding atoms. b) **3d** ($C_{30}H_{44}N_4$): $M_r = 460.69$, yellow crystals, $0.30 \times 0.20 \times 0.10$ mm, $a = 10.558(3)$, $c = 24.577(7)$ Å, $V = 2739.6(13)$ Å^3, $\rho_{calcd} = 1.117$ g cm^{-3}, $\mu = 4.99$ cm^{-1}, no absorption correction ($0.865 \le T \le 0.952$), $Z = 4$ (C2–C12 bond on twofold axis), tetragonal, space group $P4_32_12$ (No. 96), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega/2\theta$ scans, 3162 measured reflections ($+h$, $-k$, $-l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 2802 unique and 1953 observed reflections $[I \ge 2\sigma(I)]$, 160 refined parameters, $R = 0.060$, $wR^2 = 0.160$, max. (min.) residual electron density 0.32 (-0.27) e Å^{-3}, Flack parameter 0.0(11), hydrogen atoms calculated and refined as riding atoms. c) **5** ($C_{33}H_{40}N_4O_4Mo$): $M_r = 652.63$, yellow crystals, $0.35 \times 0.30 \times 0.25$ mm, $a = 17.637(1)$, $c = 20.517(1)$ Å, $V = 6382.1(6)$ Å^3, $\rho_{calcd} = 1.358$ g cm^{-3}, $\mu = 4.53$ cm^{-1}, empirical absorption correction ($0.858 \le T \le 0.895$), $Z = 8$ (C16 and Mo on a twofold axis), tetragonal, space group $P4_2/nbc$ (No. 133), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ-scans, 17302 measured reflections ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.71$ Å^{-1}, 4888 unique and 3515 observed reflexions $[I \ge 2\sigma(I)]$, 195 refined parameters, $R = 0.055$, $wR^2 = 0.126$, max. (min.) residual electron density 0.50 (-0.76) e Å^{-3}, hydrogen atom positions calculated and refined as riding atoms.

[20] Note added in proof (December 21, 1999): The thermal dissociation of sterically less-demanding dibenzotetraazafulvalenes was recently demonstrated by Lemal et al. on the basis of NMR data. See Y. Liu, P. E. Linder, D. M. Lemal, *J. Am. Chem. Soc.* **1999**, *121*, 10626.

Chromophore Alignment in a Chiral Host Provides a Sensitive Test for the Orientation–Intensity Rule of Induced Circular Dichroism**

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Circular dichroism is an essential spectral property for probing chirality.[1, 2] An interesting effect arises when an achiral guest chromophore is complexed in a chiral host. The guest becomes optically active, a phenomenon referred to as "induced" circular dichroism (ICD).[3–5] The spectroscopic information resulting from this interaction is unique, since sign and magnitude of the ICD signal depend on the relative orientation of the chromophore in the host. Harata et al. have

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