Methanetrisamidines

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Synthesis, Structure, Tautomerism, and Reactivity of Methanetrisamidines**

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N,N′-chelating monoanionic amidinate ligands have been studied in detail over the last decades. The easy tunability of their steric and electronic properties[1] allows the synthesis of tailormade metal complexes for technical applications in catalysis and materials sciences.[2] Surprisingly, multifunctional ligands containing two or more amidine moieties, in the following referred to as polyamidines, have been only scarcely investigated. They are of potential interest for the synthesis of (hetero)multimetallic complexes, which may show improved catalytic properties. Moreover, neutral aromatic tetraamidines have been investigated in cancer research owing to their antiproteinase activity.[3] Unfortunately, only very few polyamidines, almost all containing a central phenyl spacer, have been synthesized and multidentate polyamidines, in which the amidine moieties are bound to a single atom, are limited to two Me_2Si- and CH_2-bridged derivatives.[4,5] In contrast, isoelectronic tetranitromethane $C(NO_2)_4$ and tetramethylmethanetetracarboxylate $C(COOMe)_4$ are well known.[6]

We recently reported on the synthesis and reactivity of tetraamidinatomethane complexes $\{C[C(NR)_2ZnMe]_4\}$ (R = *i*Pr (**1a**), Ph (**1b**), Et (**1c**), Cy (**1d**); Cy = cyclohexyl) by reactions of $ZnMe_2$ with carbodiimides at elevated temperatures.[7,8] We now became interested in the neutral multidentate ligands, which were expected to be formed by kinetically controlled hydrolysis of the zinc complexes. However, when we monitored the reaction of **1a** with water in C_6D_6 by temperature-dependent in situ ^{1}H NMR spectroscopy (Figure 1), we found a different reaction pathway. Compound **1a** is almost stable against hydrolysis at ambient temperature, whereas at temperatures above 55 °C $(iPrN)_2C$ and methanetrisamidine **2a** are formed exclusively. Even though the expected tetraamidine $C[C(NR)N(R)H]_4$ was not detected by NMR spectroscopy, its formation as a reaction intermediate cannot be excluded. Comparable decomposition reactions were found for the two isoelectronic compounds $C(NO_2)_4$ and $C(COOMe)_4$, which react under basic conditions to form $Ag^+[C(NO_2)_3]^-$ and $HC(COOMe)_3$, respectively.[9] However, an analogous carbodiimide elimination

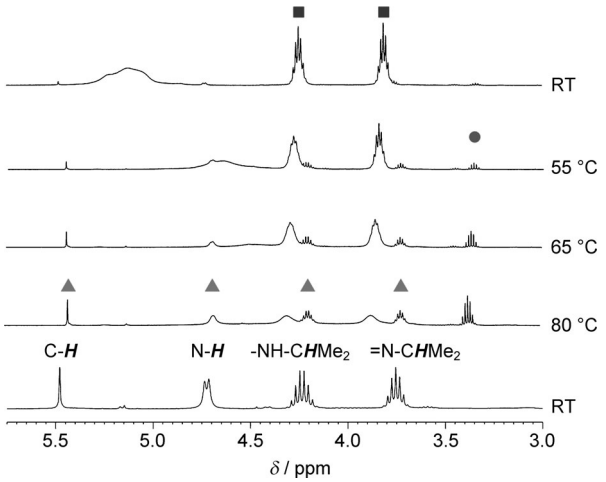

Figure 1. Temperature-dependent ^{1}H NMR spectra monitoring the hydrolysis of **1a** with water in C_6D_6 (**1a** ■, **2a** ▲, $C(NiPr)_2$ ●).

reaction was only observed for metal amidinates (Cu, Al) upon thermal treatment at temperatures higher than 200 °C.[10] Considering the significantly lower reaction temperatures in our experiments, the decomposition of **1a** is expected to proceed by a different reaction pathway, most likely by an intramolecular hydrogen migration (see the Supporting Information).

Compound **2a** was purified by sublimation at 80 °C. The ^{1}H NMR spectrum shows a singlet ($\delta = 5.37$ ppm, [D_8]toluene) for the central CH group, whereas the NH resonance ($\delta = 4.63$ ppm) occurs as a doublet on account of $^3J_{HH}$ coupling to CH_{iPr}. Dynamic ^{1}H NMR and DEPT experiments (DEPT = distortionless enhancement by polarization transfer) between −40 and +100 °C showed no CH–NH tautomerization of the central C–H group. In contrast, hydrolysis of **1b** yielded both tautomeric forms, $C[C(NPh)N(Ph)H]_2[C(HNPh)_2]$ **2b** and $HC[C(NHPh)NPh]_3$ **2c**, which are the first structurally characterized CH–NH tautomers of an acyclic amidine. Even though N,N′-tautomerism in amidines has been investigated in detail,[11] up until now the existence of an equilibrium between CH–NH tautomers has been proven only indirectly for the short-lived ene-1,1-diamine species, which could not be isolated.[12] In contrast, a cyclic ene-1,1-diamine has been previously characterized by NMR spectroscopy.[13] The postulated N–H tautomer of acetamidine plays a crucial role in the Diels–Alder reaction with tetrazine derivatives to form aminopyridazines.[14] In addition, the cyclic ketene *N*,*N*-acetal is assumed as a key

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intermediate in the synthesis of tetraazafulvalenes by oxidative coupling.[15]

Colorless crystals were obtained by slow evaporation of the solvent from a solution in cyclohexane/CH_2Cl_2 (**2b**) and from a solution in CH_3CN upon storage at −10 °C (**2c**).[16] The central carbon atom C1 in **2b**, which binds to three carbon atoms in a trigonal-planar arrangement (root-mean-square deviation of the four C atoms from the best plane is 0.0044 Å), can be considered to be sp^2 hybridized. The C1−C2 and C1−C3 bonds are slightly shorter than typical single bonds (1.54 Å) and C1−C4 is longer than a common double bond (1.34 Å), indicating delocalization of the π-electrons. The same is true for both C−N bonds emerging from C4, which are shorter than the expected length for a C(sp^2)−N(sp^3) single bond (1.43 Å). In contrast, one C−N bond at C2 and C3 shows the typical length of a C−N double bond (1.29 Å), while the other agree well with the mean C−N single-bond length found for R(H)N−CR=NR moieties in the CSD (1.372(28) Å). The structural parameters of the molecule agree well with the hydrogen atom positions found in the difference Fourier synthesis. The conformation of the molecule is supported by two intramolecular hydrogen bonds.

The central carbon atom (C1) in **2c** binds to three amidine groups; one hydrogen position was found next to it in the difference Fourier synthesis, which coincides with the other structural parameters. The C−C bond lengths are in the typical range of C−C single bonds and the C-C1-C bond angles are about 113°. C1 deviates by 0.4180(12) Å from the C2/C3/C4 plane, indicating sp^3 hybridization. The fact that the angles are somewhat greater than the tetrahedral angle can be explained by the steric demand of the residual amidine groups. The C−N bond lengths are typical for double and single bonds (Figure 2).

To elucidate the solvent dependency of the equilibrium between **2b** and **2c**, temperature-dependent NMR experiments were performed in C_6D_6 and CD_3CN. The major form in nonpolar C_6D_6 is **2b** (more than 85%) over the whole temperature range (25–75 °C). The ^{13}C and DEPT90 spectra only show four broadened phenyl resonances due to a fast intramolecular proton exchange reaction between the amino and imino groups. Consequently, the π-electrons of the C=C bond are delocalized within the planar C_4 moiety, which explains the enhanced stability of **2b**. The ^{13}C NMR spectrum of **2b** shows the characteristic resonances of the ene-1,1-diamidine carbon atom ($\delta = 84.96$ ppm), the amidino backbone carbon atoms ($\delta = 153.74$ ppm), and the enediamine carbon atom ($\delta = 143.53$ ppm). In contrast, the NMR spectra of **2b** in polar CD_3CN show an increasing amount of **2c** upon heating from 25 to 75 °C. High temperatures are required owing to the poor solubility of **2c**. The formation of **2c** points to a solvent dependence (e.g. polarity) rather than to a temperature dependence, hence it is possible to control the equilibrium to some extent by the solvent polarity.[17]

Dispersion-corrected density functional theory (DFT + D3) calculations were performed to evaluate the relative stability of the N–H (**2b**) and C–H (**2c**) tautomers in more detail.[18] Upon convergence of the geometry optimization, **2b** displays C_2 symmetry, while **2c** is C_3-symmetric. Phenyl groups surround the methine group in **2c** with $H_{ortho}\cdots C_{meta}$ distances of 2.87 Å (X-ray diffraction analysis (XRD): 2.98, 3.02, 3.13 Å), proving the stabilizing effect of the three CH–π contacts. The calculated C1–C2 distance (1.545 Å) and C2-C1-C3 angle (113.2°) are in excellent agreement with the crystal structure. The remaining three phenyl groups do not show substantial CH–π or π–π stabilizations, but one of their H_{ortho} atoms involved in a nearly planar six-membered H-C-C-N-C-N ring is only 2.28 Å away from the adjacent N atom. A further stabilization of this geometry may be attributed to the three NH···N contacts (2.55 Å) between the different C(NHPh)(NPh) groups. In **2b** only two CH–π contacts were found, with a $H_{ortho}\cdots C_{para}$ distance of 2.87 Å (XRD: 2.87, 2.90 Å). On the other hand, one π–π contact in a typical parallel-displaced arrangement of two phenyl rings of adjacent C(NHPh)(NPh) moieties and two short NH···N bonds of 1.80 Å (XRD 1.93, 1.97 Å) were found which help to stabilize **2b** relative to **2c** by 10.6 kJ mol^{-1} according to DFT + D3. The calculated C1–C2 distance (1.475 Å) agrees very well with experimental values (C1–C2 1.486(2), C1–C3 1.476(2) Å),

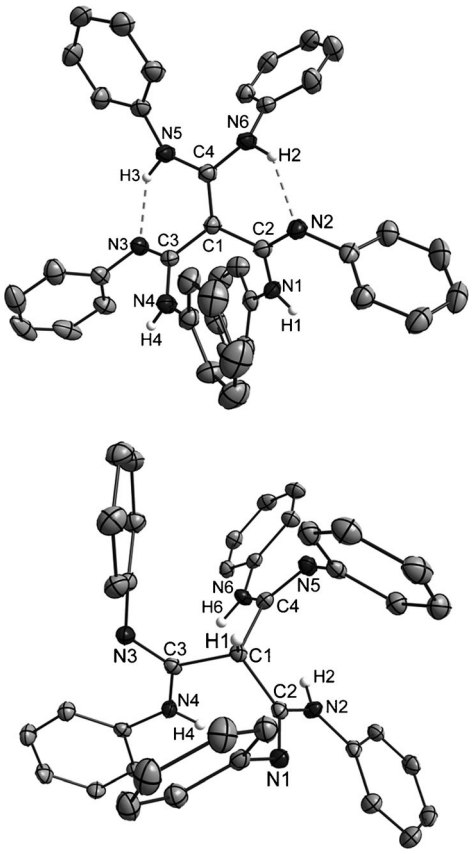

Figure 2. Molecular structure of **2b** (top) and of **2c** (bottom); thermal ellipsoids at the 50% probability level, hydrogen atoms shown as spheres of arbitrary radius, phenyl hydrogen atoms omitted for clarity. Bond lengths [Å] and angles [°]:**2b**: C1–C2 1.486(2), C1–C3 1.476(2), C1–C4 1.391(2), N1–C2 1.374(2), N2–C2 1.294(2), N5–C4 1.372(2), N6–C4 1.373(2), H3···N3 1.93, H2···N2 1.97; C4-C1-C3 121.38(13), C4-C1-C2 120.64(14), C3-C1-C2 117.97(14), N2-C2-N1 122.51(14), N5-C4-N6 119.16(14), N5-H3···N3 138.6, N6-H2···N2 137.0; **2c**: C1–C2 1.5356(14), C1–C3 1.5345(14), C1–C4 1.5341(15), N1–C2 1.2819(14), N2–C2 1.3644(14), C4-C1-C3 113.04(8), C4-C1-C2 112.37(9), C3-C1-C2 113.21(9), N1-C2-N2 121.88(10).

while the C1–C4 distance of 1.420 Å points to slightly higher single-bond character in the calculated structure than in the crystal structure (1.391(2) Å). The DFT + D3 energy difference agrees well with the value of 12.3 kJ mol^{-1} found in ab initio calculations for the DFT + D3 geometries using valence-only second-order Møller–Plesset perturbation theory (MP2).[19] In conjunction with an increase of the dipole moment from 0.97 Debye (**2b**) to 2.42 Debye (**2c**) as obtained from DFT + D3, this energy difference is small enough to explain why **2b** is preferred but not exclusively formed in nonpolar solvents whereas **2c** dominates in polar solvents (vide supra).

Replacement of the phenyl groups by H atoms followed by geometry optimization and calculation of the vibrational frequencies at the DFT + D3 level again shows the C_2-symmetrical N–H and the C_3-symmetrical C–H tautomeric forms to be true minima on the potential energy surface.[20] The N–H tautomer is preferred by 23.8 kJ mol^{-1}, in good agreement with the MP2 energy difference of 22.1 kJ mol^{-1} obtained for the DFT + D3 geometries, which changes only slightly to 23.1 kJ mol^{-1} when the structures are reoptimized at the MP2 level of theory. The π–π contact between adjacent C(NHPh)(NPh) groups observed in **2b** is now replaced with two NH···N contacts with an N···H distance of 2.38 Å, while CH–π contacts obviously no longer exist, which rationalizes the increased energy difference between the tautomeric forms. When the C_3-symmetry constraint was released, a second, lower-lying minimum with C_1 symmetry for the C–H tautomer was found (see the Supporting Information). This structure is 20.9 kJ mol^{-1} higher in energy than the N–H tautomer at the DFT + D3 level of theory, while an anergy difference of only 16.1 kJ mol^{-1} was obtained at the MP2 level (17.1 kJ mol^{-1} after MP2 reoptimization of both structures).

To determine the energy difference between the (unobserved) N–H and C–H (**2a**) tautomers of the *i*Pr-substituted trisamidine, a molecular mechanics force field conformer scan was carried out for both tautomers. The lowest-energy 12 N–H tautomeric and 15 C–H tautomeric structures were then reoptimized at the DFT + D3 level with a small basis set of split-valence quality. Then for each tautomer the two lowest-energy conformers were reoptimized at the DFT + D3 level with a triple-zeta basis set. A C_1-symmetrical conformer of **2a** was found to be 1.9 kJ mol^{-1} lower in energy than any conformer of the N–H tautomer, the lowest of which was found to display C_2 symmetry. The next conformer of **2a** (C_1 symmetry) was found at 2.0 kJ mol^{-1}, while the next conformer (C_1 symmetry) of the N–H tautomer is 5.6 kJ mol^{-1} higher in energy than the lowest conformer of **2a**. The energy difference between the lowest-energy conformers of the two tautomers increases to 3.3 kJ mol^{-1} on the MP2 level of theory (without reoptimization of the DFT + D3 structures), which is too small to explain why only **2a** has been experimentally observed. However, the dipole moment of **2a** is 2.42 Debye (DFT + D3), while that of the two conformers of the N–H tautomer is only 1.02 and 1.07 Debye, respectively. Interactions with neighboring dipole molecules or a polarizable environment may have a stabilizing effect, subsequently favoring the C–H tautomeric form **2a**.

The imino moieties of the methanetrisamidines are proton acceptors as was shown by the reaction of **2b** with two equivalents of acetic acid, yielding $[C(C(HNPh)_2)_3]^{2+}$-$\{[CH_3COO]^-\}_2$ **3** (see the Supporting Information). Crystals of **3**, which crystallizes in the triclinic space group $P\bar{1}$, were obtained from a solution in Et_2O at −30 °C. The most notable structural difference between **2b** and the methanetrisamidinium dication in **3** is reflected by the almost equal C–C bond lengths within the trigonal-planar C_4 moiety (C1–C2 1.417(2) Å, C1–C3 1.4440(19) Å, C1–C4 1.4464(19) Å). The shorter C1–C2 bond can be explained by the orientation of the N-C-N unit relative to the central C_4 unit. The N1/C2/N2 plane is almost coplanar to the C1/C2/C3/C4 plane (26.51(15)°), which allows a more effective π-electron delocalization than that with the other two amidinate groups (40.27(13)°, 43.38(10)°) and explains the slightly elongated C2–N bonds and the slightly shorter C1–C2 bond.

In addition, the ampholytic compounds **2a–c** are powerful reagents for the synthesis of multinuclear organometallic complexes owing to the presence of acidic N–H groups. Reactions of **2a** with $AlMe_3$ and iBu_2AlH occurred with elimination of methane and H_2, respectively, and subsequent formation of $HC[C(NiPr)_2AlR_2]_3$ (R = Me (**4a**), *i*Bu (**4b**)), in quantitative yields. Threefold deprotonation was proven by the disappearance of the NH resonances in the ^{1}H NMR spectra (C_6D_6), whereas the characteristic CH group signal was preserved. Crystals of **4a** and **4b** of low quality were obtained from different solvents, from which the connectivity within the molecules was proven. The models suggest a sp^3 hybridization of the central carbon atom and a chelating coordination of the amidinate groups to the AlR_2 units.

In contrast, the reaction of **2b** with 4 equiv of $AlMe_3$ gave $C[C(NPh)_2AlMe_2]_2[C(N(Ph)AlMe_2)_2]$ **4c** in quantitative yield. Yellow crystals of **4c** were obtained from a solution in toluene at −30 °C. Compound **4c** crystallizes in the monoclinic space group *C*2/*c* with C1 and C2 on a twofold axis (Figure 3). One amidinate group (N1-C1-N1#1) adopts a bridging position, while two serve as chelating units. The C atoms of the amidinate groups bind to trigonal-planar-coordinated C1 with two short bonds and one long C–C bond, showing a delocalized π-electron system within the N3-C3-C1-C3#1-N3#1 unit. The C–N bond lengths within these two amidinate groups differ owing to different coordination numbers of the N atoms, whereas the C–N bond lengths within the N1-C2-N1#1 unit indicate delocalized π-electrons.

To summarize, the methanetrisamidines $\{HC[C(NR)NHR]_3$ (R = *i*Pr (**2a**), Ph (**2c**)) and ene-1,1-diamidine-2,2-diamine $\{C[C(NPh)NHPh)_2]_2[C(NHPh)_2]\}$ (**2b**) were formed by an unforeseen carbodiimide elimination reaction upon hydrolysis of the corresponding tetranuclear zinc complexes. The crystal structures of the N–H and C–H tautomers **2b** and **2c** provide structural evidence of N,C tautomerism in amidines for the first time. In solution, the equilibrium between **2b** and **2c** depends to some extent on the polarity of the solvent. Quantum chemical calculations revealed the N–H tautomers to be energetically favored over the C–H tautomers for Ph- and H-substituted trisamidines, whereas the C–H tautomer of the *i*Pr-substituted complex is slightly lower in energy than the N–H tautomer. Reactivity

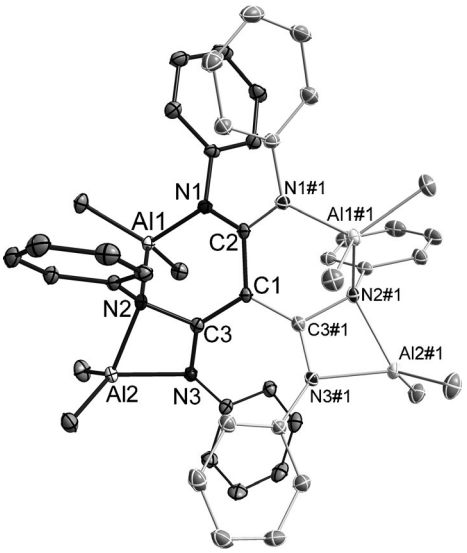

Figure 3. Molecular structure of **4c** (thermal ellipsoids at the 50% probability level, hydrogen atoms omitted for clarity, asymmetric unit shown in dark bonds, C1 and C2 located on a twofold axis). Bond lengths [Å] and angles [°], #1 $-x+1$, y, $-z+1/2$: C1–C2 1.506(2), C1–C3 1.4191(15), N2–C3 1.4470(15), N3–C3 1.3257(16), N1–C2 1.3404(13), Al1–N1 1.9199(11), Al1–N2 1.9984(11), Al2–N3 1.9268(11), Al2–N2 1.9967(11), C3#1-C1-C3 120.55(16), C3#1-C1-C2 119.73(8), C3-C1-C2 119.73(8), N1-C2-N1#1 125.02(16), N1-C2-C1 117.49(8), N3-C3-C1 132.19(12), N3-C3-N2 105.46(10), C1-C3-N2 122.29(11), C2-N1-C4 120.32(11), C2-N1-Al1 125.64(9), C4-N1-Al1 113.22(8), C3-N2-C(10) 120.94(10), C3-N2-Al2 89.32(7), C(10)-N2-Al2 112.40(8), C3-N2-Al1 101.14(7), C(10)-N2-Al1 112.80(8), Al2-N2-Al1 118.29(5), C3-N3-C(16) 132.96(11), C3-N3-Al2 96.09(8), C(16)-N3-Al2 129.65(8), N1-Al1-N2 90.67(5), N3-Al2-N2 68.46(4).

studies showed that these novel ligands can be either protonated at the Lewis basic N centers or metalated by organometallic complexes at the N–H moieties.

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[1] a) J. Barker, M. Kilner, *Coord. Chem. Rev.* **1994**, *133*, 219; b) F. T. Edelmann, *Adv. Organomet. Chem.* **2008**, *57*, 183; c) M. P. Coles, *Dalton Trans.* **2006**, 985.

[2] a) K. A. Schug, W. Lindner, *Chem. Rev.* **2005**, *105*, 67; b) M. W. Hosseini, *Coord. Chem. Rev.* **2003**, *240*, 157.

[3] a) C. Nastruzzi, R. Gambari, *Cancer Lett.* **1990**, *50*, 93–102; b) R. R. Tidwell, L. L. Fox, J. D. Geratz, *Biochim. Biophys. Acta Enzymol.* **1976**, *445*, 729–738.

[4] a) J.-A. Gautier, M. Miocque, C. C. Farnoux, *The Chemistry of Amidines and Imidates*, *Vol. 1* (Eds.: S. Patai), Wiley, London, **1975**, pp. 283–348; b) R. L. Shriner, F. W. Neumann, *Chem. Rev.* **1944**, *35*, 351.

[5] a) A. Kraft, R. Fröhlich, *Chem. Commun.* **1998**, 1085; b) A. Kraft, *Perkin Trans. 1* **1999**, 705; c) S. K. Mandal, L. K. Thompson, M. J. Newland, E. J. Gabe, F. L. Lee, *Chem. Commun.* **1989**, 744; d) S. S. Tandon, L. K. Thompson, J. N. Bridson, J. C. Dewan, *Inorg. Chem.* **1994**, *33*, 54; e) A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, J. V. Waszczak, *J. Am. Chem. Soc.* **1992**, *114*, 5000; f) R. T. Boeré, R. T. Oakley, R. W. Reed, *J. Organomet. Chem.* **1987**, *331*, 161; g) J. Grundy, M. P. Coles, P. B. Hitchcock, *J. Organomet. Chem.* **2002**, *662*, 178; h) J. R. Hagadorn, J. Arnold, *Angew. Chem.* **1998**, *110*, 1813; *Angew. Chem.* Int. Ed. **1998**, *37*, 1729; i) H. Kawaguchi, T. Matsuo, *Chem. Commun.* **2002**, 958; j) J. F. Li, L. H. Weng, X. H. Wei, D. S. Liu, *Dalton Trans.* **2002**, 1401; k) C. T. Chen, L. H. Rees, A. R. Cowley, M. L. H. Green, *Dalton Trans.* **2001**, 1761; l) H. A. Jenkins, D. Abeysekera, D. A. Dickie, J. A. C. Clyburne, *Dalton Trans.* **2002**, 3919; m) S.-D. Bai, J.-P. Guo, D.-S. Liu, W.-Y. Wong, *Eur. J. Inorg. Chem.* **2006**, 4903; n) J. R. Babcock, C. Incarvito, A. L. Rheingold, J. C. Fettinger, L. R. Sita, *Organometallics* **1999**, *18*, 5729.

[6] a) F. D. Chattaway, *J. Chem. Soc. Trans.* **1910**, *97*, 2099–2102; b) R. Scholl, W. Egerer, *Liebigs Ann. Chem.* **1913**, *397*, 301.

[7] a) M. Münch, U. Flörke, M. Bolte, S. Schulz, D. Gudat, *Angew. Chem.* **2008**, *120*, 1535; *Angew. Chem. Int. Ed.* **2008**, *47*, 1512; b) S. Schmidt, S. Gondzik, S. Schulz, D. Bläser, R. Boese, *Organometallics* **2009**, *28*, 4371; c) S. Schmidt, B. Gutschank, S. Schulz, D. Bläser, R. Boese, C. Wölper, *Eur. J. Inorg. Chem.* **2011**, 4464.

[8] a) B. Gutschank, S. Schulz, U. Westphal, D. Bläser, R. Boese, *Organometallics* **2010**, *29*, 2093; b) B. Gutschank, S. Schulz, D. Bläser, R. Boese, C. Wölper, *Organometallics* **2010**, *29*, 6133.

[9] a) M. Göbel, T. M. Klapötke, P. Mayer, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1043; b) R. Scholl, W. Egerer, *Liebigs Ann. Chem.* **1913**, *397*, 301.

[10] a) T. Whitehorne, J. P. Coyle, A. Mahmood, W. H. Monillas, G. Yap, S. Barry, *Eur. J. Inorg. Chem.* **2011**, 3240; b) A. L. Brazeau, Z. Wang, C. N. Rowley, S. T. Barry, *Inorg. Chem.* **2006**, *45*, 2276.

[11] a) C. Berndt, T. Kaempchen, *Chem. Ber.* **1986**, *119*, 1101; b) J. Oszczapowicz, E. Raczynska, J. Osek, *J. Magn. Reson. Chem.* **1986**, *24*, 9; c) E. Raczyńska, *Perkin Trans. 2* **1986**, 1189; d) E. Raczynska, R. Gawinecki, *Trends Org. Chem.* **1998**, *7*, 85.

[12] a) M. Pfau, M. Chiriacescu, G. Revial, *Tetrahedron Lett.* **1993**, *34*, 327; b) K. Sung, S.-H. Wu, R.-R. Wu, S.-Y. Sun, *Org. Chem.* **2002**, *67*, 4298; c) K. Ito, Y. Kizuka, Y. Hirano, *J. Heterocycl. Chem.* **2005**, *42*, 583.

[13] J. Goerdeler, R. Sappelt, *Chem. Ber.* **1967**, *100*, 2064.

[14] H. P. Figeys, A. Mathy, A. Dralants, *Synth. Commun.* **1981**, *11*, 655.

[15] a) J. Brandenburg, C. Käpplinger, R. Beckert, *Synthesis* **1996**, 1302; b) D. Müller, R. Beckert, J. Weston, W. Günther, H. Görls, M. Friedrich, *Eur. J. Org. Chem.* **2001**, 4551.

[16] Bruker AXS D8 Kappa diffractometer with APEX2 detector ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å; $T = 100(1)$ K). The structures were solved by Direct Methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467) and refined by full-matrix least-squares on F^2. Absorption corrections were performed semiempirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). All non-hydrogen atoms were refined anisotropically, methyl hydrogen atoms as rigid groups and others by a riding model. NH and OH hydrogen atoms were taken from the difference Fourier synthesis and constrained. (SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, Universität Göttingen, 1997 and shelXle, *A Qt GUI for SHELXL*. See also: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112; C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284). **2b**: $[C_{40}H_{34}N_6]$, $M = 598.73$, colorless crystal ($0.42 \times 0.32 \times 0.26$ mm); monoclinic, space group Cc; $a = 18.1738(16)$ Å, $b = 10.3046(9)$ Å, $c = 18.983(2)$ Å; $\alpha = 90°$, $\beta = 113.163(3)°$, $\gamma = 90°$, $V = 3268.4(6)$ Å^3; $Z = 4$; $\mu = 0.073$ mm^{-1}; $\rho_{calcd} = 1.217$ g cm^{-3}; 37607 reflections ($2\theta_{max} = 59°$), 8129 unique ($R_{int} = 0.0333$); 415 parameters, Flack parameter $x = -0.7(15)$; largest max./min. in the final difference

Fourier synthesis 0.249 e Å^{-3}/−0.245 e Å^{-3}; max./min. transmission 0.75/0.68; $R_1 = 0.0435$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1076. Due to the high standard deviation of x, the absolute structure could not be determined reliably. **2c**: $[C_{40}H_{34}N_6 \cdot C_2H_3N]$, M = 639.79, colorless crystal (0.24 × 0.18 × 0.13 mm); triclinic, space group $P\bar{1}$; a = 12.3438(7) Å, b = 13.3509(7) Å, c = 13.4235(8) Å; α = 60.586(2)°, β = 67.453(3)°, γ = 66.088(3)°, V = 1713.77(17) Å^3; $Z = 2$; $\mu = 0.075$ mm^{-1}; $\rho_{calcd} = 1.240$ g cm^{-3}; 28355 reflections ($2\theta_{max} = 61°$), 10184 unique ($R_{int} = 0.0234$); 442 parameters; largest max./min. in the final difference Fourier synthesis 0.394 e Å^{-3}/−0.222 e Å^{-3}; max./min. transmission 0.75/0.67; $R_1 = 0.0460$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1192. **3**: $[C_{40}H_{36}N_6 \cdot 2(C_2H_3O_2) \cdot 2(H_2O)]$, M = 754.87, pale yellow crystal (0.18 × 0.15 × 0.12 mm); triclinic, space group $P\bar{1}$; a = 10.5079(11) Å, b = 13.5325(15) Å, c = 16.2636(19) Å; α = 110.849(5)°, β = 92.152(5)°, γ = 111.876(5)°, V = 1966.6(4) Å^3; $Z = 2$; $\mu = 0.086$ mm^{-1}; $\rho_{calcd} = 1.275$ g cm^{-3}; 33622 reflections ($2\theta_{max} = 50°$), 6990 unique ($R_{int} = 0.0405$); 505 parameters; largest max./min. in the final difference Fourier synthesis 0.229 e Å^{-3}/−0.263 e Å^{-3}; max./min. transmission 0.75/0.69; $R_1 = 0.0355$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.0883. The hydrogen atoms of C72 and C82 were refined as idealized disordered methyl group over two positions. **4c**: $[C_{48}H_{54}AL_4N_6]$, M = 822.89, yellow crystal (0.25 × 0.10 × 0.08 mm); monoclinic, space group $C2/c$; a = 17.4755(9) Å, b = 15.5339(8) Å, c = 18.5007(11) Å; $\alpha = \gamma = 90°$, β = 116.831(2)°, V = 4481.6(4) Å^3; $Z = 4$; $\mu = 1.145$ mm^{-1}; $\rho_{calcd} = 1.220$ g cm^{-3}; 23163 reflections ($2\theta_{max} = 61°$), 6861 unique ($R_{int} = 0.0334$); 263 parameters; largest max./min. in the final difference Fourier synthesis 0.499 e Å^{-3}/−0.235 e Å^{-3}; max./min. transmission 0.75/0.66; $R_1 = 0.0398$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1087. The crystallographic data (without structure factors) were deposited as "supplementary publication no. CCDC 868839 (**2b**), CCDC 868842 (**2c**), CCDC 868841 (**3**), and CCDC 868840 (**4c**)" contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] Detailed information is given in the Supporting Information.

[18] Starting from the crystal structures the molecule geometries of **2b** and **2c** were optimized with tightened convergence thresholds and an improved DFT integration grid at the DFT level including a third-generation dispersion energy correction (DFT + D3; a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104). The BLYP exchange correlation functional b) P. A. M. Dirac, *Proc. R. Soc. London Ser. A* **1929**, *123*, 714; c) J. C. Slater, *Phys. Rev.* **1951**, *81*, 385; d) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; e) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785) and a basis set of triple-zeta-valence quality (def2-TZVP; f) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297) were used along with the corresponding auxiliary basis set (g) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057) in the resolution-of-the-identity (RI) approximation as implemented in Turbomole V6.3 (TURBOMOLE V6.3 2009, University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989 – 2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com; h) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165; i) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346; j) M. von Arnim, R. Ahlrichs, *J. Chem. Phys.* **1999**, *111*, 9183.).

[19] Valence-only MP2 calculations were performed in the RI approximation with a larger orbital basis set (def2-TZVPP) and the corresponding auxiliary basis set (F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Lett.* **1998**, *294*, 143).

[20] P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, *384*, 103.

