

Synthesis, Structure, Tautomerism and Reactivity of Methanetrisamidines

Benjamin Gutschank, Stephan Schulz,* Michael Marcinkowski, Georg Jansen, Heinz Bandmann, Dieter Bläser, Christoph Wölper

N,N'-chelating monoanionic amidinate ligands have been studied in detail within the last decades due to the easy tunability of their steric and electronic properties,^[1] which allows the synthesis of *tailor made* 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 were investigated in cancer research due to their anti-proteinase activity.^[3] Unfortunately, only very few polyamidines, almost exclusively 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 Me₂Si- and CH₂-bridged derivatives.^[4,5] In contrast, isoelectronic tetranitromethane C(NO₂)₄ and tetramethylmethane-tetracarboxylate C(COOMe)₄ are well known.^[6]

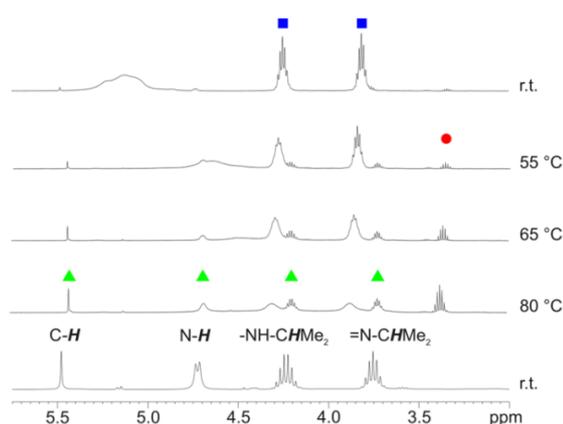


Figure 1. Temperature-dependent ¹H NMR monitoring showing the hydrolysis of **1a** with water in C₆D₆ (**1a** ■, **2a** ▲, C(Ni-Pr)₂ ●).

We recently reported on the synthesis of tetraamidinatomet methane complexes {C[C(NR)₂ZnMe]₄} (R = *i*-Pr **1a**; Ph **1b**, Et **1c**, Cy **1d**) by reactions of ZnMe₂ with carbodiimides at elevated temperatures and their reactivity.^[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,

temperature dependent *in situ* ¹H-NMR monitoring (Fig. 1) of the reaction of **1a** with water in C₆D₆ showed a different reaction pathway. **1a** is almost stable against hydrolysis at ambient temperature, whereas heating of the solution to 55 °C exclusively yielded (*i*-PrN)₂C and methanetrisamidine **2a**, respectively. Even though C[C(NR)N(R)H]₄ was not detected by NMR spectroscopy, its formation as reaction intermediate cannot be excluded. Comparable decomposition reactions were found for isoelectronic C(NO₂)₄ and C(COOMe)₄, which react under basic conditions with formation of Ag⁺[C(NO₂)₃]⁻ and HC(COOMe)₃, respectively.^[9] However, an analogous carbodiimide elimination 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 H-migration (SI).

2a was purified by sublimation at 80 °C. The ¹H NMR spectrum shows a singlet (5.37 ppm, toluene-*d*₈) of the central CH group, whereas the NH resonance (4.63 ppm) occurred as a doublet due to ³J_{HH} coupling to CH_{*i*-Pr}. Dynamic ¹H-NMR and DEPT experiments between -40 and +100 °C showed no CH-NH tautomerization reaction of the central C-H group. In contrast, hydrolysis of **1b** yielded both tautomers C[C(NPh)N(Ph)H]₂[C(HNPh)₂] **2b** and HC[C(NHPh)NPh]₃ **2c**. **2b** and **2c** are the first structurally characterized CH-NH tautomers of an acyclic amidine. Even though N,N'-tautomerism in amidines was investigated in detail,^[11] the existence of a CH-NH tautomeric equilibrium was proven only indirectly due to the short-lived ene-1,1-diamine species, which could not be isolated, to date.^[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 forming aminopyridazines.^[14] In addition, the cyclic ketene-N,N acetal is assumed as a key 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/CH₂Cl₂ (**2b**) and from a solution in CH₃CN 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 (r.m.s. deviation of the four C atoms from the best plane is 0.0044 Å), can be considered as sp² hybridized. C1-C2 and C1-C3 are slightly shorter than typical single bonds (1.54 Å) and C1-C4 is longer than a common double bond (1.34 Å), indicating a delocalization of π-electrons. The same is true for both C-N bonds emerging from C4, which are shorter than the expected value for a C(sp²)-N(sp³) single bond (1.43 Å). In contrast, one C-N bond at C2 and C3 shows the typical value of a C-N double bond (1.29 Å), while the other agree well with the mean C-N single bond length as found for RNH-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.

[*] B. Gutschank, Prof. S. Schulz*, M. Marcinkowski, Prof. G. Jansen, Dipl. Ing. H. Bandmann, D. Bläser, Dr. C. Wölper
Faculty of Chemistry, University of Duisburg-Essen
Universitätsstr. 5-7, S07 S03 C30, D-45117 Essen
Fax: (+) 201-183 3830
E-mail: stephan.schulz@uni-due.de

[**] S. Schulz gratefully acknowledges financial support by the University of Duisburg-Essen.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

The central carbon atom (C1) in **2c** binds to three amidine groups and 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 a sp³ hybridization. The enlarged angles compared to the tetrahedron angle can be explained by the steric demand of the residual groups. The C-N bond lengths show typical values of double and single bonds (*vide supra*).

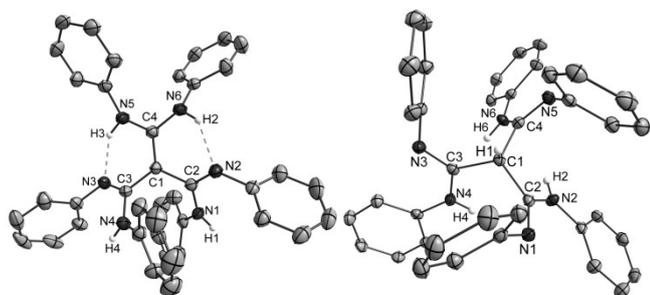


Figure 2. Molecular structure of **2b** (left) and of **2c** (right); thermal ellipsoids at 50% probability levels, hydrogen atoms at arbitrary radii, phenyl hydrogen atoms omitted for clarity. Bond lengths [Å] and angles [°]: **2b**: C(1)-C(2) 1.486(2), C(1)-C(3) 1.476(2), C(1)-C(4) 1.391(2), N(1)-C(2) 1.374(2), N(2)-C(2) 1.294(2), N(5)-C(4) 1.372(2), N(6)-C(4) 1.373(2), C(4)-C(1)-C(3) 121.38(13), C(4)-C(1)-C(2) 120.64(14), C(3)-C(1)-C(2) 117.97(14), N(2)-C(2)-N(1) 122.51(14), N(5)-C(4)-N(6) 119.16(14); N5-H3...N3, d(H...A) 1.93 Å, <(DH...A) 138.6, N6-H2...N2, d(H...A) 1.97 Å, <(DH...A) 137.0; **2c**: C(1)-C(2) 1.5356(14), C(1)-C(3) 1.5345(14), C(1)-C(4) 1.5341(15), N(1)-C(2) 1.2819(14), N(2)-C(2) 1.3644(14), C(4)-C(1)-C(3) 113.04(8), C(4)-C(1)-C(2) 112.37(9), C(3)-C(1)-C(2) 113.21(9), N(1)-C(2)-N(2) 121.88(10).

To elucidate the solvent dependency of the equilibrium between **2b** and **2c**, temperature-dependent NMR experiments were performed in C₆D₆ and CD₃CN. The major form in non-polar C₆D₆ is **2b** (more than 85 %) over the whole temperature range (25 - 75 °C). ¹³C and DEPT90 spectra only showed four broadened phenyl resonances due to a fast intramolecular proton exchange reaction between the amino and imino groups. Consequently, the C-C double bond is delocalized within the planar C₄-moiety, which explains the enhanced stability of **2b**. Characteristic resonances of the ene-1,1-diamidine carbon atom (84.96 ppm), the amidino backbone carbon atoms (153.74 ppm) and the ene-diamine carbon atom (143.53 ppm) could be clearly assigned, whereas NMR spectra of **2b** in polar CD₃CN show an increasing amount of **2c** upon heating from 25 to 75 °C. High temperatures are required due to the poor solubility of **2c**. The formation of **2c** rather points to a solvent (e.g. polarity) than to a temperature dependency, hence allowing to control the equilibrium to some extent via 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 optimizations, **2b** displays C₂ symmetry, while **2c** is C₃ symmetric. Phenyl groups surround the methine group in **2c** with H_{ortho}...C_{meta} distances of 2.87 Å (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}...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), which help to stabilize **2b** over **2c** by 10.6 kJ/mol according to DFT+D3, were found. 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), while the C1-C4 distance of 1.420 Å points to a slightly higher single-bond character in the calculated structure compared to the crystal structure (1.391(2) Å). The DFT+D3 energy difference agrees well with the value of 12.3 kJ/mol as 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 non-polar solvents whereas **2c** dominates in polar solvents (*vide supra*).

Replacement of the phenyl groups by H atoms followed by geometry optimization and vibration frequency calculation at the DFT+D3 level again shows the C₂-symmetrical N-H and the C₃-symmetrical C-H tautomeric forms as true minima on the potential energy surface.^[20] The N-H tautomer is preferred by 23.8 kJ/mol, in good agreement with the MP2 energy difference of 22.1 kJ/mol obtained for the DFT+D3 geometries, which changes only slightly to 23.1 kJ/mol upon re-optimization of the structures 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 2.50 Å, while CH-π contacts obviously no longer exist, which rationalizes the increased energy difference between the tautomeric forms. Upon releasing the C₃ symmetry constraint a second, deeper minimum with C₁ symmetry for the C-H tautomer was found (see SI). This structure is 20.9 kJ/mol higher in energy than the N-H tautomer at the DFT+D3 level of theory, while only 16.1 kJ/mol were obtained with MP2 (17.1 kJ/mol after MP2 re-optimization 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 energetically lowest 12 N-H tautomeric and 15 C-H tautomeric structures were then re-optimized at the DFT+D3 level with a small basis set of split-valence quality, before finally re-optimizing the resulting lowest two conformers for each tautomer at the DFT+D3 level with a triple-zeta basis set. A C₁-symmetrical conformer of **2a** was found to be 1.9 kJ/mol lower in energy than any conformer of the N-H tautomer, the lowest of which was found to display C₂ symmetry. The next conformer of **2a** (C₁ symmetry) was found at 2.0 kJ/mol, while the energy of next conformer (C₁) of the N-H tautomer is 5.6 kJ/mol higher than the lowest conformer of **2a**. The energy difference between the lowest conformers of both tautomers increases to 3.3 kJ/mol on the MP2 level of theory (without re-optimization 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 methanetrissamidines are proton acceptors as was shown by reaction of **2b** with two equivalents of acetic acid, yielding $[C(C(HNPh)_2)_3]^{2+} \{[CH_3COO]^{-}\}_2$ **3** (SI). Crystals of **3**, which crystallizes in the triclinic space group $P\bar{1}$, were obtained from a solution in Et₂O at -30 °C. The most notable structural difference between **2b** and the methanetrissamidinium dication in **3** is reflected by the almost equal C-C bond lengths within the trigonal planar C₄-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 C₄ 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 compared to 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, ampholytic **2a-c** are powerful reagents for the synthesis of multinuclear organometallic complexes due to the presence of acidic N-H groups. Reactions of **2a** with AlMe₃ and *i*-Bu₂AlH occurred with elimination of methane or H₂, respectively, and subsequent formation of HC[C(N*i*-Pr)₂AlR₂]₃ (R = Me **4a**, *i*-Bu **4b**) in quantitative yields. Threefold deprotonation was proven by disappearance of the NH resonances in the ¹H NMR spectra (C₆D₆), whereas the characteristic CH group 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 sp³ hybridization of the central carbon atom and a chelating coordination of the amidinate groups to the AlR₂ units.

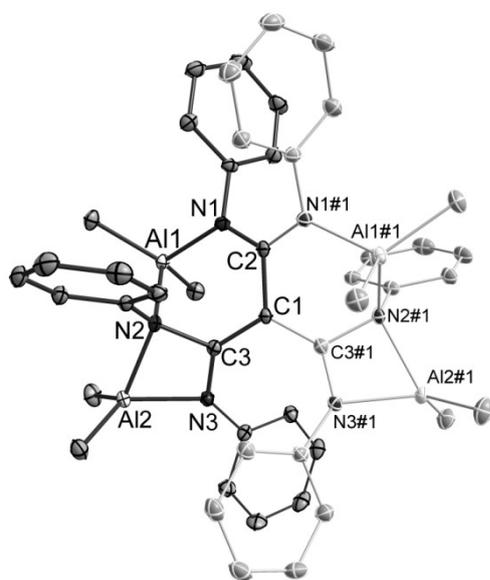


Figure 3. Molecular structure of **4c** (thermal ellipsoids at 50% probability levels, hydrogen atoms omitted for clarity, asymmetric unit shown in dark bonds, C1 and C2 located on a two-fold axis). Bond lengths [Å] and angles [°], #1 -x+1,y,-z+1/2: C(1)-C(2) 1.506(2), C(1)-C(3) 1.4191(15), N(2)-C(3)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

132.96(11), C(3)-N(3)-Al(2) 96.09(8), C(16)-N(3)-Al(2) 129.65(8), N(1)-Al(1)-N(2) 90.67(5), N(3)-Al(2)-N(2) 68.46(4).

In contrast, the reaction of **2b** with a fourfold amount of AlMe₃ gave C[C(NPh)₂AlMe₂]₂[C(N(Ph)AlMe₂)₂] **4c** in quantitative yield. Yellow crystals of **4c** were obtained from a solution in toluene at -30 °C. **4c** crystallizes in the monoclinic space group $C2/c$ with C1 and C2 on a two-fold axis. 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 and one long C-C bonds, 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 due 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 methanetrissamidines {HC[C(NR)NHR]₃ (R = *i*-Pr **2a**, Ph **2c**) and ene-1,1-diamidine-2,2-diamine {C[C(NPh)NPh]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** exhibit 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 compared to the C-H tautomers for Ph- and H-substituted trissamidines, whereas the C-H tautomer of the *i*-Pr substituted complex is slightly lower in energy than the N-H tautomer. Reactivity 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.

Experimental Section

Full details are given in the electronic supplement.

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

Keywords: Tautomerism · X-ray diffraction · ab-initio calculations · Imine · Enamine

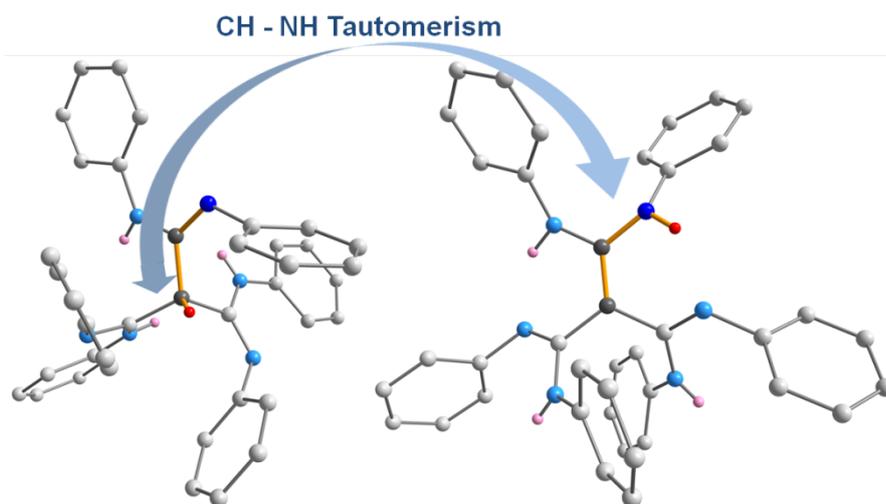
- [1] a) J. Barker, M. Kilner, *Coord. Chem. Rev.* **1994**, 133, 219; b) F. T. Edelmann, *Adv. Organomet. Chem.* **2008**, 57, 1535; c) M. P. Coles, *Dalton. Trans.* **2006**, 118, 985.
- [2] a) K. A. Schug, W. Lindner, *Chem. Rev.* **2005**, 105, 67; b) M. W. Hosseini, *Coord. Chem. Rev.* **2003**, 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* **1976**, 445, 729-738.
- [4] a) J.-A. Gautier, M. Miocque, C. C. Farnoux, in *The Chemistry of Amidines and Imidates*, Vol. 1 (Eds: S. Patai), JOHN WILEY & SONS, London, **1975**, pp. 283-348. b) R. L. Shriner, F. W. Neumann, *Chem. Rev.* **1944**, 35(3), 351.
- [5] a) A. Kraft, R. Fröhlich, *Chem. Commun.* **1998**, 1085; b) A. Kraft, *Perkin Trans.* **1999**, 1, 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. Abeyskera, 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**, *28*, 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. Raczynska, *Perkin Trans. II* **1986**, 1189. c) 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*(8), 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 (MoK α 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 F². Absorption corrections were performed semi-empirically 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 shelXL, *A Qt GUI for SHELXL*. See also: Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, *64*, 112; C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281-1284) **2b**: [C₄₀H₃₄N₆], M = 598.73, colorless crystal (0.42 x 0.32 x 0.26 mm); monoclinic, space group Cc; a = 18.1738(16) Å, b = 10.3046(9) Å, c = 18.983(2) Å; $\alpha = 90^\circ$ $\beta = 113.163(3)^\circ$ $\gamma = 90^\circ$, V = 3268.4(6) Å³; Z = 4; $\mu = 0.073$ mm⁻¹; $\rho_{\text{ber.}} = 1.217$ g cm⁻³; 37607 reflexes ($2\theta_{\text{max}} = 59^\circ$), 8129 unique ($R_{\text{int}} = 0.0333$); 415 parameters, Flack-parameter x = -0.7(15); largest max./min. in the final difference Fourier synthesis 0.249 eÅ⁻³/-0.245 eÅ⁻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**: [C₄₀H₃₄N₆ * C₂H₃N], M = 639.79, colorless crystal (0.24 x 0.18 x 0.13 mm); triclinic, space group P-1; a = 12.3438(7), b = 13.3509(7), c = 13.4235(8) Å; $\alpha = 60.586(2)^\circ$, $\beta = 67.453(3)^\circ$, $\gamma = 66.088(3)^\circ$, V = 1713.77(17) Å³; Z = 2; $\mu = 0.075$ mm⁻¹; $\rho_{\text{ber.}} = 1.240$ g cm⁻³; 28355 reflexes ($2\theta_{\text{max}} = 61^\circ$), 10184 unique ($R_{\text{int}} = 0.0234$); 442 parameters; largest max./min. in the final difference Fourier synthesis 0.394 eÅ⁻³/-0.222 eÅ⁻³; max./min. transmission 0.75/0.67; $R_1 = 0.0460$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1192. **3**: [C₄₀H₃₆N₆, 2(C₂H₃O₂), 2(H₂O)], M = 754.87, pale yellow crystal (0.18 x 0.15 x 0.12 mm); triclinic, space group P-1; a = 10.5079(11) Å, b = 13.5325(15) Å, c = 16.2636(19) Å; $\alpha = 110.849(5)^\circ$, $\beta = 92.152(5)^\circ$, $\gamma = 111.876(5)^\circ$, V = 1966.6(4) Å³; Z = 2; $\mu = 0.086$ mm⁻¹; $\rho_{\text{ber.}} = 1.275$ g cm⁻³; 33622 reflexes ($2\theta_{\text{max}} = 50^\circ$), 6990 unique ($R_{\text{int}} = 0.0405$); 505 parameters; largest max./min. in the final difference Fourier synthesis 0.229 eÅ⁻³/-0.263 eÅ⁻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**: [C₄₈H₅₄Al₄N₆], M = 822.89, yellow crystal (0.25 x 0.10 x 0.08 mm); monoclinic, space group C2/c; a = 17.4755(9) Å, b = 15.5339(8) Å, c = 18.5007(11) Å; $\alpha = \gamma = 90^\circ$, $\beta = 116.831(2)^\circ$, V = 4481.6(4) Å³; Z = 4; $\mu = 1.145$ mm⁻¹; $\rho_{\text{ber.}} = 1.220$ g cm⁻³; 23163 reflexes ($2\theta_{\text{max}} = 61^\circ$), 6861 unique ($R_{\text{int}} = 0.0334$); 263 parameters; largest max./min. in the final difference Fourier synthesis 0.499 eÅ⁻³/-0.235 eÅ⁻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**)" at the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre: CCDC, 12 Union Road, Cambridge, CB21EZ (Fax: (+44)1223/336033; E-mail: deposit@ccdc.cam.ac.uk).
- [17] Detailed informations are given in the electronic supplement.
- [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; S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104/1-18.). The BLYP exchange correlation functional (a) P. A. M. Dirac, *Proc. Roy. Soc. A* **1929**, *123*, 714; b) J. C. Slater, *Phys. Rev.* **1951**, *81*, 385; c) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098. d) 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. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.) were used along with the corresponding auxiliary basis set (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>); a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165; b) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346; c) 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. Letters* **1998**, *294*, 143).
- [20] P. Deglmann, K. May, F. Furche, R. Ahlrichs, *Chem. Phys. Lett.* **2004**, *384*, 103.

Methanetrisamidines

Benjamin Gutschank, Stephan Schulz,*
Michael Marcinkowski, Georg Jansen,
Heinz Bandmann, Dieter Bläser,
Christoph Wölper _____ Page –
Page

Synthesis, Structure, Tautomerism and
Reactivity of Methanetrisamidines



Two tautomeric forms of a methanetrisamidine were structurally characterized for the first time and their reactivity as proton acceptors and multianionic ligand was demonstrated.

DuEPublico

Duisburg-Essen Publications online

UNIVERSITÄT
DUISBURG
ESSEN

Offen im Denken

ub | universitäts
bibliothek

This text is made available via DuEPublico, the institutional repository of the University of Duisburg-Essen. This version may eventually differ from another version distributed by a commercial publisher.

DOI: 10.1002/anie.201205030

URN: urn:nbn:de:hbz:464-20201112-104551-7

This is the **peer reviewed version** of the following article: Angew. Chem. Internat. Ed. 2012, 51, 10893-10897, which has been published in final form at:
<https://doi.org/10.1002/anie.201205030>

All rights reserved.