The Chemistry of 1,3,5-Triazacyclohexane Complexes, 4[◇]

Strained 1,3,5-Triazacyclohexane Complexes of Copper(I) and Copper(II)

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In this paper we report on the synthesis and the crystallographic characterization of η^3-1,3,5-triazacyclohexane (R_3TAC) complexes of copper(I) and copper(II). The complexes [{(Me_3TAC)$CuCl_2$}$_2$] (**1**), [($i$$Pr_3$TAC)$CuCl_2$] (**2**), [{$(PhCH_2)_3$TAC}Cu($PPh_3$)]($BF_4$) (**3**), and [($i$$Pr_3$TAC)Cu($PPh_3$)]($BF_4$) (**4**) were characterized by X-ray crystallography. The highly strained and bent Cu–N bonds are longer than in the corresponding complexes of other amine ligands. One methylene carbon atom of the ring comes close to the copper atom (2.55–2.65 Å). However, investigation of the ring deuterated complexes by IR and X-ray crystallography ([D_6]**2**) showed no clear evidence for attractive C–H–Cu interactions.

Copper(I)/(II) complexes with three facially coordinating nitrogen atoms play an important role in the biological binding and activation of dioxygen[2]. A large number of copper complexes containing ligands binding with three or more nitrogen atoms were described as models for the biological systems, but only a few were structurally identified as peroxo or superoxo complexes[3]. However, most of the complexes are unable to serve as functional models, especially for the oxidation of aliphatic C–H bonds, and only recently the dicopper(II)-μ-η^2:η^2-peroxo complex [$(LCu)_2$ (O_2)]$(CF_3SO_3)_2$ (L = 1,4,7-triisopropyl-1,4,7-triazacyclononane) was shown to cleave such a C–H bond[4]. Deuteration of the *i*Pr groups of the ligand showed that first an aliphatic C–H/D bond of the ligand close to the Cu_2O_2 core is cleaved. In order to increase the reactivity of such triaza complexes, we started to explore the coordination chemistry of triaza ligands where the three nitrogen atoms are "pulled together" by a smaller ring size, i.e. 1,3,5-triazacyclohexanes R_3TAC[5a–c], or by a central carbon atom, i.e. trisaminomethanes[5d]. We showed that complexes of $CrCl_3$ and $FeCl_3$ with *N*-alkylated 1,3,5-triazacyclohexanes as ligands can be prepared where the ring strain caused by the small N–metal–N angle (60°) leaves a less shielded metal center. UV/Vis spectra reveal that the ligand field strength is indeed much smaller than in other amine complexes[5a,b]. However, no other crystallographically investigated η^3-R_3TAC complexes with transition metal atoms are known so far.

In this paper we report on the preparation and crystal structures of several copper(I) and copper(II) complexes with triazacyclohexane ligands.

Copper(II) Complexes

Treatment of a concentrated solution of $CuCl_2$ in EtOH with an equimolar amount of Me_3TAC or *i*Pr_3TAC causes precipitation of the green complexes [{(Me_3TAC)$CuCl_2$}$_2$][6] (**1**) and [($i$$Pr_3$TAC)$CuCl_2$] (**2**). Large crystals of **2** can be grown by preparation of the compound in $CHCl_3$. The solution above the insoluble $CuCl_2$ turns deep green and after a few hours large crystals begin to grow swimming on the surface. Similarly, green crystals containing **1** were grown from a brown solution. Due to the much lower solubility of **1** in $CHCl_3$ crystallization required a few weeks, and water and 1,3,5-trioxane generated by hydrolysis of the ligand were built into the crystals. In contrast to an analogous 1,4,7-triazacyclononane complex[7], the triazacyclohexane complexes cannot be prepared from aqueous solutions and decompose in water. Thus, triazacyclohexanes are much weaker ligands than triazacyclononanes.

The molecular structure of **2** is shown in Figure 1 and selected bond lengths and angles are given in Table 1. The coordination environment around the copper atom is a distorted square pyramid. The basal plane is occupied by two chlorine [Cu–Cl = 2.218(1) Å] and two nitrogen atoms [Cu–N = 2.103(3) Å] with an angle between the nitrogen atoms of only 65.5(1)° and the copper atom lying in the plane within the standard deviation. The third nitrogen atom of the triazacyclohexane approaches the axial position [Cu–N = 2.390(3)

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Scheme 1. Preparation of R_3TAC copper complexes

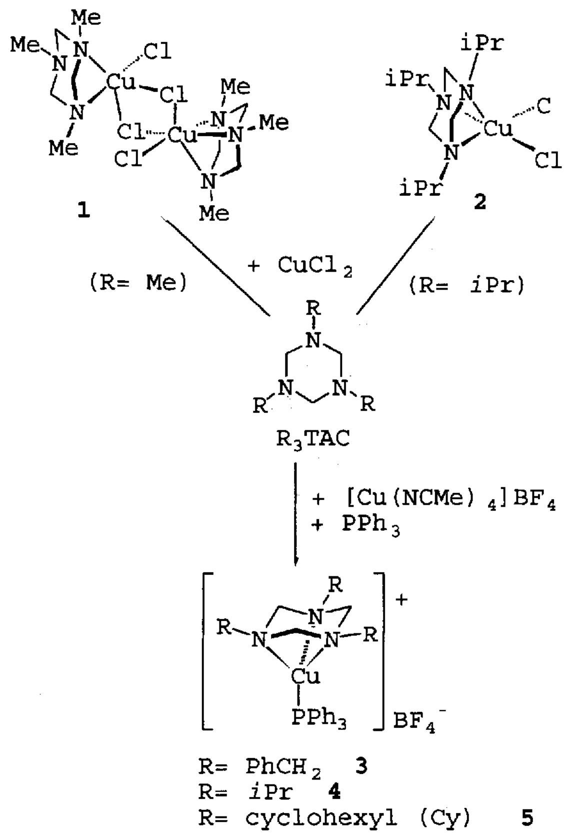
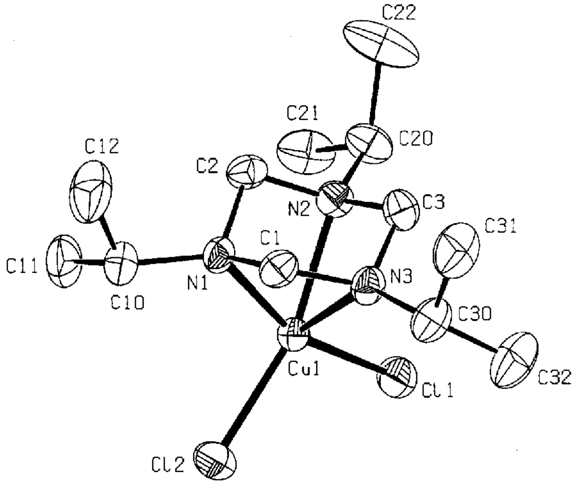
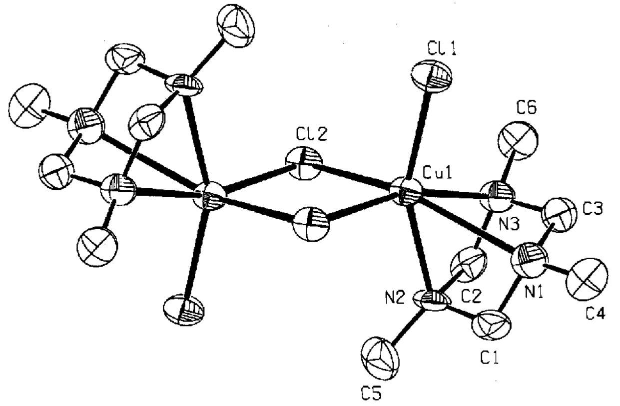


Figure 1. Molecular structure of **2** (and $[D_6]$**2**)



Å] with an angle of only 57° with respect to the basal plane. In the closely related 1,4,7-triazacyclononane complex[7] the Cu−Cl distances are longer [2.268(1) and 2.312(1) Å] and the Cu−N distances shorter [2.038(4), 2.063(4), and 2.246(4) Å], indicating a weaker coordination by the R_3TAC ligand. On the opposite side of the N_2CuCl_2 plane a carbon atom (C2) of the triazacyclohexane ring comes close to the copper atom [Cu−C2 = 2.592(3) Å] with one C−H bond nearly side-on [Cu−C2−H(refined) = 100(3)°]. This distance is similar to the agostic Cu−C distance of 2.78 Å in the cationic Cu^I complex $[(norbornadiene)Cu(dien)]^+$ (Cu−N 2.08−2.25 Å)[8] and to the agostic Co−C distance of 2.52 Å in $[Co^{III}(dacoda)(SO_3)]^-$ (Co−N 1.93−1.96 Å)[9]. In the latter case the C−H bond is also part of an alkyl bridge between two coordinating nitrogen atoms in the basal plane of a square pyramid, and this activated hydrogen atom could be deprotonated by a base. In order to test the effect of the possible Cu−(C−H) interaction, we obtained the crystal structure of the fully ring-deuterated compound $[D_6]$**2**. The bond lengths and angles (in parentheses of Table 1) show no significant differences as compared to the non-deuterated structure and therefore show no evidence for an interaction of the C−H bond close to the copper atom.

Figure 2. Molecular structure of **1**



The structure of **1** in the crystal is shown in Figure 2. The coordination geometry is square-pyramidal as in **2** [Cu−Cl 2.235(6), 2.261(3) Å; $Cu-N_{eq}$ 2.064(8), 2.151(10), and $Cu-N_{ax}$ 2.597(12) Å]. Due to the smaller nitrogen substituents two complexes are associated by two chlorine bridges [Cu−Cl 2.707(5) Å]. This causes the copper atom to move out of the basal plane by 0.19 Å towards the extra chlorine atom and elongates the trans-oriented $Cu-N_{ax}$ bond. However, the close Cu−C2 contact [2.557(10) Å] is unchanged and shorter than the longest Cu−N bond.

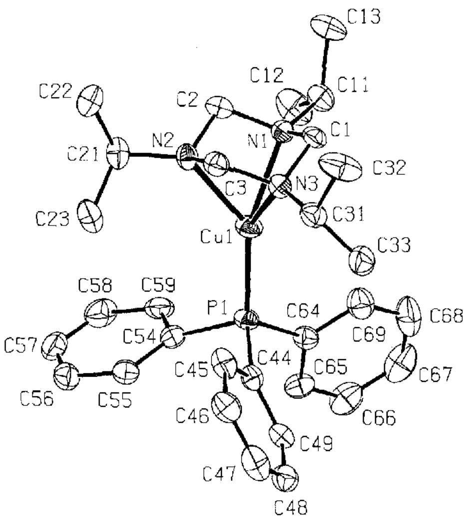
The IR spectra of the compounds does not reveal any stretching vibrations outside of the 2800−3100 cm^{-1} region, thus indicating C−H bond weakening. The IR spectrum of $[D_6]$**2** shows two C−D stretching vibrations, one at 2263 and a stronger one at 2077 cm^{-1}, and that of the partially ring deuterated $[D_{2.4}]$**2** shows four C−D vibrations at 2259, 2235, 2106, and 2081 cm^{-1}. Thus, only two absorptions (2235 and 2106 cm^{-1}) are found for the isolated C−D stretching vibrations of the CHD groups. The corresponding CHD vibrations in [D]**1** are similar but much weaker. A comparison with the vibrational analysis of $[D_6]$-1,3,5-trioxane[10] (C−D stretching vibrations at ca. 2280 and 2090 cm^{-1}) shows that this is the normal vibrational splitting of the C−D stretching vibrations of a methylene unit in this environment without inferring any agostic C−D bond. The splitting of the isolated CHD vibrations is probably due to the different force constants in the axial and equatorial position.

We were unable to obtain useful ^1H- or ^3C-NMR spectra due to the paramagnetism of **1** and **2**. However, the ^2H-NMR spectrum of the ring-deuterated [$D_{2.4}$]**2** shows two 500 Hz wide signals at $\delta = 97$ and 60 in a ratio of 1:2. We assign these to one set of either the *endo*- or *exo*-deuterium atoms of the ring with the other set broadened beyond detectability. ^{2}H-NMR spectra of **1** are difficult to interpret due to low solubility even in the best solvent $MeNO_2$ and show narrow signals at $\delta = 2.8$ and 7.8 as well as broad signals at $\delta = 71$ and 30. This may indicate a monomer-dimer equilibrium in $MeNO_2$ solution.

Copper(I) Complexes

Treatment of **1** with R_3TAC in CH_2Cl_2 gives highly oxygen-sensitive complexes $[(R_3TAC)Cu(NCMe)](BF_4)$[11]. After addition of PPh_3, the more stable adducts $[(R_3TAC)Cu(PPh_3)](BF_4)$ (R = $PhCH_2$, **3**, *i*Pr, **4**, and *c*-C_6H_{11}, **5**) can be isolated. Crystallization from CH_2Cl_2/toluene gave colorless crystals of **3** · $(C_7H_8)_{0.5}$ and **4**.

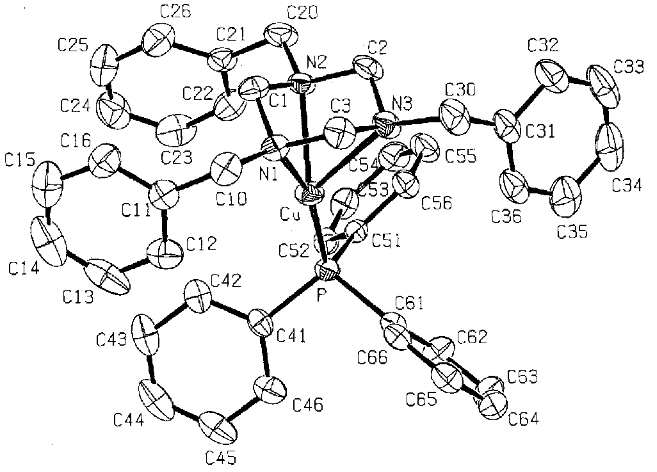
Figure 3. Molecular structure of one of the two independent cations of **4**



The molecular structure of **4** shows two independent molecules with distorted tetrahedral coordination environment at the Cu centers. One contain the triazacyclohexane bonded in the η^3 mode with almost equal Cu−N distances [2.176(5), 2.201(5), and 2.202(4) Å], the other has one nitrogen atom moved somewhat closer to the copper atom [2.150(4), 2.234(4), and 2.237(4) Å]. As in the Cu^{II} complexes the shortest $Cu-C_{ring}$ distance of 2.652(5) is shorter than in the "agostic" Cu^I complex[8] mentioned above. However, there is no structural indication of an attractive interaction of the C−H bond with the copper atom.

Surprisingly, the molecular structure of the closely related benzyl substituted complex **3** is quite different. One nitrogen atom is closer [2.122(2) Å], the second one at a similar distance [2.210(2) Å] and the third one is much farther away [2.446(3) Å] from the copper atom than in **4**. The three benzyl substituents of the ligand are directed towards the metal atom and some interaction between the phenyl groups and the copper atom may be responsible for the distorted coordination geometry around the copper atom. However, the nearest aromatic carbon atom is 3.49 Å away from the copper center and therefore much farther away than the closest carbon atom of the triazacyclohexane ring [2.600(3) Å]. In contrast to the other Cu^I complexes (R = *i*Pr, Cy), the IR spectrum of **3** exhibits a rather strong absorption at 2786 cm^{-1} which is shifted upon complete deuteration of the ring positions to 2026 cm^{-1}. The intensity and the difference to the other still observable much weaker C−D stretching vibrations at 2233, 2219, and 2075 cm^{-1} indicate, that an agostic C−H/D bond might be responsible for the distorted coordination geometry.

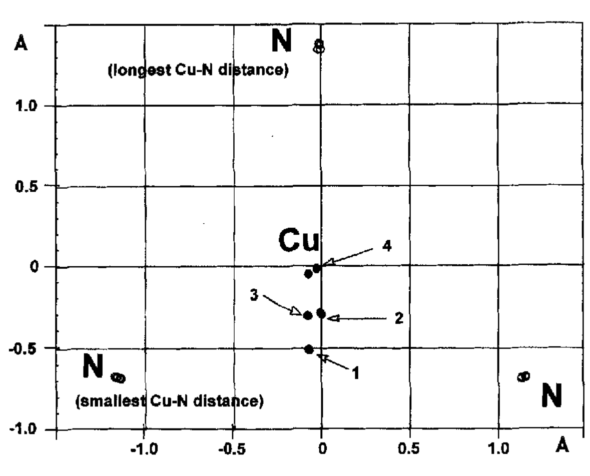
Figure 4. Molecular structure of the cation of **3**



The distances to the phosphorus atoms on the fourth coordination site are nearly equal [2.1431(9) ain **3** and 2.124(2) and 2.137(2) Å in **4**] and smaller than the Cu−N bond lengths. These are short compared to the normal range of Cu(I)−P bond lengths of 2.15−2.30 Å[12−15].

The ^{1}H-NMR spectrum shows two doublets for the ring protons − one *exo* and one *endo* with respect to the copper atom. However, the signal pair for **3** is broadened, indicating some unsymmetrical bonding even on the NMR time scale. The ^{31}P-NMR signals of $\delta = 9-12$ are similar to that found in $[\{HB(3,5-Me_2pz)_3\}Cu(PPh_3)]$ ($\delta = 11.87$)[13]. The ^{13}C-NMR shifts of the PPh_3 are comparable to other Cu^I-PPh_3 complexes[14,15].

Figure 5. Projection of the copper atoms onto the plane of the three nitrogen atoms



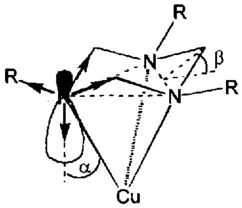
Comparison of the Structures

Superposition of the N_3 planes of the crystallographically investigated copper complexes shows that the positions of the three donor atoms are virtually superimposable.

Thus, the triazacyclohexane ligand is a rigid ligand whose ring structure is little changed by the substituents R or different mode of coordination to the metal atoms. A projection of the copper positions onto these planes shows coordination modes between nearly η^3 in the center of the three nitrogen atoms for **4** and almost η^2 between two of the three nitrogen atoms for **1**. The distance of the copper atom from this plane has only a narrow range of 1.724–1.789 Å with a slight difference between the tetracoordinated Cu^I and penta-/hexacoordinated Cu^{II}. Thus, the copper is able to move above the N_3 plane to meet the electronic requirement similar to the ring slippage of cyclic π complexes. Indeed, the similarity of R_3TAC and Cp* was noticed before because of similar ligand field strength, similar metal-donor atomic bond length, and similarly bent metal-donor atomic bond[5b]. Thus, the R_3TAC can provide easy change of the coordination number and could therefore assist in redox reactions.

Comparison of all structures shows that the copper–nitrogen distance depends on the angle α by which the nitrogen lone pair deviates from the direct Cu–N bond. The angular position of the nitrogen lone pair was constructed from the three normalized N–C bonds around the nitrogen atom as indicated in Scheme 2. A plot of the Cu–N bond lengths vs. $\sin^2\alpha$ shows a linear dependence. This corresponds to the dependence of the orbital interaction energy of bent metal–ligand bonds on α[16]. Therefore, the spread of Cu–N distances is largely due to electronic effects.

Scheme 2. Definition of the angles α (lone pair-N–Cu) and β (between the N_3 and N_2C planes)



The distance of the ring carbon atoms from the copper atom are short in all structures. There is a dependence of the tilt angle of the CH_2 group in the ring out of the plane of the three nitrogen atoms (Figure 7).

As the Cu–C distance decreases below 260 pm the CH_2 group is bent away from the copper atom and out of the N_3 plane by almost 45° instead of the normal range of 30–40°. Therefore, the closest methylene groups are rather repelled than attracted by the copper atom in the Cu^I and Cu^{II} complexes.

Conclusion

The 1,3,5-triazacyclohexanes R_3TAC can serve as tridentate ligands for copper(I) and copper(II). Due to the ring strain and misdirection of the nitrogen lone pairs, the Cu–N

Table 1. Selected bond lengths and angles in **1**, **2**, [D$_6$]**2**, **3**, and **4**. The angles α and β are defined in Scheme 2

Complex	**1**·[(C$_3$H$_6$O$_3$)(H$_2$O)]$_{0.33}$	**2**·(CHCl$_3$)	[D$_6$]**2**·(CHCl$_3$)	**3**·(toluene)$_{0.5}$	**4**
Formula	$C_{6.5}H_{16.33}Cl_2CuN_3O_{0.67}$	$C_{13}H_{28}Cl_5CuN_3$	$C_{13}H_{22}D_6Cl_5CuN_3$	$C_{45.5}H_{42}BCuF_4N_3P$	$C_{30}H_{42}BCuF_4N_3P$
M_t	281.67	467.18	473.23	812.15	626.0
Crystal system	trigonal	orthorhombic	orthorhombic	triclinic	orthorhombic
Space group	$R\bar{3}$ (no. 148)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)	$Pna2_1$ (no. 33)
Z	6	4	4	2	8
a [Å]	16.775(5)	11.167(2)	11.184(4)	8.904(2)	20.359(2)
b [Å]		12.554(3)	12.539(4)	11.743(2)	10.198(2)
c [Å]		15.239(5)	15.233(7)	20.452(4)	30.121(2)
α [deg]	117.89(2)			84.87(2)	
β [deg]				83.83(2)	
γ [deg]				75.08(2)	
V [Å^3]	1759.9(8)	2136.4(9)	2136.2(13)	2050.1(7)	6253.9(11)
$D_{calcd.}$ [g cm^{-3}]	1.595	1.453	1.472	1.316	1.330
F(000)	860	964	964	842	2624
μ(Mo-*K*α) [mm^{-1}]	2.245	1.625	1.625	0.614	0.783
Data collection:					
T [K]	166(2)	163(2)	163(2)	163(2)	190(2)
Radiation (Mo-*K*α) [Å]	0.71069	0.71069	0.71069	0.71069	0.71073
2 $\Theta_{min,max}$ [deg]	3, 55	4, 50	4, 56	2, 52	4, 50
Total data	1124	2155	2977	8544	6154
Unique data	1115, *R*(int)=0.0591	2132	2468	7995, *R*(int)=0.0215	5625
Refinement:					
No. of reflections	971 [$I>4\sigma(I)$]	2118 [$I>2\sigma(I)$]	2461 [$I>4\sigma(I)$]	7978 [$I>2\sigma(I)$]	5608 [$I>2\sigma(I)$]
No. of refined param.	128	207	223	538	721
Aborption corr.	DIFABS	ψ-scan	DIFABS		ψ-scan
min,max	0.74, 1.15	0.90, 1.00	0.82, 1.11		0.83, 1.00
Min,max density [eÅ^{-3}]	–0.466, 0.751	–0.386, 0.341	–0.399, 0.367	–0.474, 1.727	–0.346, 0.447
R_1 (observed data)	0.0619	0.0248	0.0296	0.0478	0.0391
wR_2 (observed Data)	0.1657	0.0625	0.0680	0.1214	0.0890
GOF	1.129	1.077	1.071	1.026	1.025

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

bonds are weaker than in 1,4,7-triazacyclononane complexes.

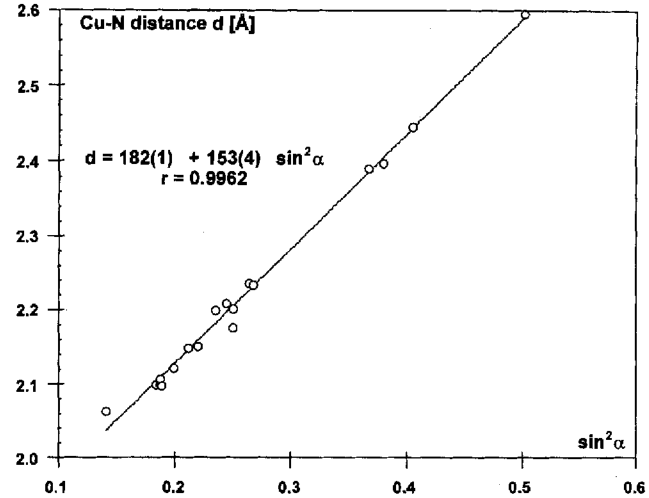


Figure 6. Dependence of the Cu–N distance on $\sin^2\alpha$

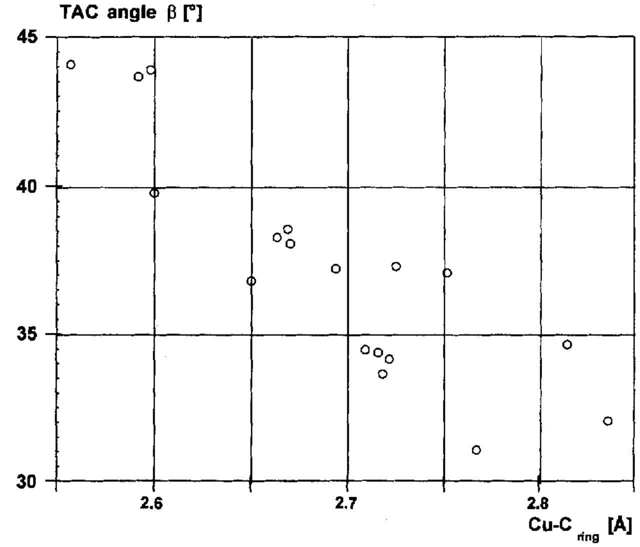


Figure 7. Dependence of β on the Cu–C_{ring} distance

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Experimental

General Considerations: All manipulations were carried out by standard Schlenk, vacuum, and glove box techniques unless stated otherwise. THF, toluene (dried and stored over Na/benzophenone), CH_2Cl_2 and $CDCl_3$ (dried, degassed, and stored over CaH_2) were freshly condensed into the reaction flasks. – Me_3TAC, $(CD_2O)_x$, iPrNH_2, PPh_3, $CuBr_2$, and $CuCl_2$ were purchased from Aldrich. $[Cu(NCMe)_4](BF_4)$, all other R_3TAC were prepared according to literature procedures[17]. – For IR spectra a Perkin Elmer 580 B, for UV/Vis spectra a Beckman DU 650, for ^1H-, ^{13}C-, ^{19}F- and ^{31}P-NMR spectra a Bruker WP-80 SY (80 MHz) or Bruker ARX 200 (200 MHz), and for ^2H-NMR spectra a Bruker ARX 400 (400 MHz) were used. Elemental analyses were performed with a Perkin-Elmer Series II CHN/O analyzer 2400 or at the analytical facility of the Humboldt Universität zu Berlin. Melting points were determined with a HWS-SG 2000 and are uncorrected.

2-Deuterio-1,3,5-trimethyl-1,3,5-triazacyclohexane ([D]Me_3TAC): To a solution of Me_3TAC (12 ml, 85 mmol) in hexane (120 ml), a solution of nBuLi in hexane (1.6 M, 55 ml, 88 mmol) was added. Colorless 2-Li-Me_3TAC precipitated. After 2 d, D_2O (2 ml, 100 mmol) was added. After 1 h at room temp. and 30 min at 50 °C, the solution was decanted and the residue extracted several times with Et_2O. The combined organic extracts were concentrated and the residue was distilled at 60–70 °C/20 Torr to yield 10.1 g (91%) of colorless [D]Me_3TAC. – ^1H NMR ($CDCl_3$): δ = 3.17 (br, 5 H, CH_2/CHD), 2.28 (s, 9 H, Me). – ^2H NMR (neat): δ = 2.96. – ^{13}C NMR ($CDCl_3$): δ 77.12 (s, CH_2), 76.67 (t, J_{CD} = 22 Hz, CHD), 40.19 (Me).

2,4,6-Hexadeuterio-1,3,5-triisopropyl-1,3,5-triazacyclohexane ([D_6]$i$$Pr_3TAC$): Deuterated paraformaldehyde $(CD_2O)_x$ (1.246 g) was treated with 10 ml of iPrNH_2 containing little KOH with cooling in a water bath. After 15 min more iPrNH_2 (15 ml) and KOH were added until the mixture was saturated. After 2 h, all volatile components were distilled off at 100 °C and the residue was treated with water and pentane. The organic layer was separated, washed with water, and the solvent removed in vacuo. At 50 °C/0.01 Torr 0.588 g (21%) of [D_6]$i$$Pr_3TAC$ was distilled. – ^1H NMR ($CDCl_3$): δ = 2.85 (sept, J = 6.5 Hz, 3 H, C$H$$Me_2$), 1.06 (d, J = 6.5 Hz, 18 H, CHMe_2). – ^2H NMR (neat): δ = 3.09.

Partially Deuterated 2,4,6-Deuterio-1,3,5-triisopropyl-1,3,5-triazacyclohexane ([$D_{2.4}$]$i$$Pr_3TAC$): Partially deuterated formaldehyde was prepared by equilibrating $(py_2CH_2)Br_2$ with one equivalent of D_2O in 1,4-dioxane and subsequent hydrolysis by refluxing with K_2CO_3. The formed formaldehyde was distilled off into water. This solution was treated with an excess of iPrNH_2 and [$D_{2.4}$]$i$$Pr_3TAC$ was isolated as described above. The deuterium content was determined by ^1H-NMR analysis. – ^1H NMR ($CDCl_3$): δ = 3.41 (ca. 2.5 H, NCH_2N), 3.36 (ca. 1.1 H, NCHDN), 2.74 (sept, J = 6.5 Hz, 3 H, C$H$$Me_2$), 0.95 d ($J$ = 6.5 Hz, 18 H, CHMe_2).

2,4,6-Hexadeuterio-1,3,5-tribenzyl-1,3,5-triazacyclohexane {[D_6]$(PhCH_2)_3TAC$}: Deuterated paraformaldehyde $(CD_2O)_x$ (2.666 g) and 16 g of $PhCH_2NH_2$ were heated in toluene (20 ml) and water/toluene was distilled off until a constant boiling point of 110 °C was reached. The remaining toluene was removed in vacuo (10^{-2} Torr) and the residue recrystallized from hexane (–20 °C). Thus, 8.0 g of colorless crystals was obtained (80%). – ^1H NMR ($CDCl_3$): δ = 7.20–7.33 (15 H, Ph), 3.67 (s, 6 H, PhCH_2). – ^{13}C NMR ($CDCl_3$): δ = 138.35 (*ipso*-Ph), 128.79 (m, *o*-Ph), 128.13 (*o,m*-Ph), 126.91 (*p*-Ph), 72.73 (quint, J = 21.6 Hz, NCD_2N), 56.86 (PhCH_2N).

[{(Me₃TAC)CuCl}₂(μ-Cl)₂] $[\{(Me_3TAC)CuCl\}_2(\mu\text{-}Cl)_2]$ (**1**): $CuCl_2$ (1.5 g, 11.2 mmol) was dissolved in ethanol (20 ml), then Me_3TAC (2 ml, 14.2 mmol) was added to the solution. The green precipitate was filtered off after 5 minutes, washed twice with EtOH (10 ml), and dried in vacuo to yield 2.4 g (81%) of green **1**, m.p. 117 °C (dec.). – $C_{12}H_{30}Cl_4Cu_2N_6$ (527.31): calcd. C 27.33, H 5.73, N 15.94; found C 27.51, H 5.83, N 16.24. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 930 nm (1.90), 720 (1.78), 386 (3.41), 315 (4.00), 280 (4.48); in KBr: 870, 630 (1.5:1).

$[\{([D]Me_3TAC)CuCl_2\}_2]$ was prepared analogously from $CuCl_2$ and [D]Me_3TAC. – IR (KBr): $\tilde{\nu}$ = 2200 cm^{-1}, 2100 (C–D).

$[(iPr_3TAC)CuCl_2]$ (**2**): $CuCl_2$ (3.4 g, 25.3 mmol) was dissolved in ethanol (20 ml), then $i$$Pr_3TAC$ (7 ml, 29.2 mmol) was added to the solution. The green precipitate was filtered off after 5 min, washed three times with EtOH (10 ml), and dried in vacuo to yield 7.6 g (86%) of green $[(iP_3TAC)CuCl_2]$, m.p. 91 °C (dec.). Alternatively, large crystals containing $CHCl_3$ could be grown within 2 h by adding *i*Pr$_3$TAC (0.2 ml) to $CuCl_2$ (100 mg) and $CHCl_3$ (2.3 ml) in a thin tube. The crystals swimming on the surface were removed, washed with hexane and dried in vacuo to give the solvent-free **2** in 54% yield. – $C_{12}H_{27}Cl_2CuN_3$ (347.82): calcd. C 41.44, H 7.82, N 12.08; found C 41.60, H 8.30, N 12.25. – UV/Vis (CH_2Cl_2): λ_{max} (lg ε) = 930 nm (1.90), 700 (1.85), 394 (3.18), 334 (3.59), 276 (4.34).

[([D$_6$]iPr$_3$TAC)CuCl$_2$] was prepared analogously from [D$_6$]*i*Pr$_3$TAC and $CuCl_2$. – IR (CsCl) (rel. intensity): $\tilde{\nu}$ = 2263 cm^{-1} (1), 2077 (2) (C–D).

[([D$_{2.4}$]iPr$_3$TAC)CuCl$_2$] was prepared analogously from [D$_{2.4}$]*i*Pr$_3$TAC and $CuCl_2$. – IR (CsCl) (rel. intensity): $\tilde{\nu}$ = 2259(1) cm^{-1}, 2235(1.2), 2106(6), 2081(1.3). – ^{2}H NMR (CH_2Cl_2): δ = +96.8 ($\Delta\nu_{1/2}$ = 490(14) Hz), +60.4 ($\Delta\nu_{1/2}$ = 650(16) Hz) (rel. intensity 1:2).

[{(PhCH$_2$)$_3$TAC}Cu(PPh$_3$)](BF$_4$) (**3**): [Cu(MeCN)$_4$](BF$_4$) (5.07 g, 16.1 mmol), PPh_3 (4.20 g, 16.0 mmol), and $(PhCH_2)_3$TAC (5.78 g, 16.2 mmol) were stirred in CH_2Cl_2 (30 ml). After 12 h, the solvent was removed in vacuo and the residue was washed with THF until the solution remained colorless. The remaining colorless solid was dried in vacuo to yield 10.6 g (87%) of **3**, m.p. 146–149 °C. – $C_{42}H_{42}BCuF_4N_3P$ (770.14): calcd. C 65.50, H 5.49, N 5.46; found C 64.59, H 5.52, N 5.49. – ^{1}H NMR ($CDCl_3$): δ = 7.52–7.49, 7.38–7.31, 7.17–6.87 (m, 30 H, C_6H_5), 4.22 (br, 3 H, NCH_2N), 3.67 ("s", 9 H, NCH_2N + PhC*H*$_2$). – ^{13}C NMR ($CDCl_3$): δ = 135.03 (*ipso-Ph*CH$_2$), 133.51 (d, *J* = 13.8 Hz, *o*-PPh$_3$), 131.00 (*p*-PPh$_3$), 130.8 (d, *J* = 21 Hz, *ipso*-PPh$_3$), 129.70 (*m-Ph*CH$_2$), 129.23 (d, *J* = 9.5 Hz, *m*-PPh$_3$), 128.60 (*o-Ph*CH$_2$), 128.06 (*p-Ph*CH$_2$), 75.39 (NCH_2N), 55.98 (PhC*H*$_2$). – ^{19}F NMR ($CDCl_3$): δ = –74.66 (BF$_4$). – ^{31}P ($CDCl_3$): δ = 9.79 (PPh$_3$).

[([D$_6$](PhCH$_2$)$_3$TAC)Cu(PPh$_3$)](BF$_4$) was prepared analogously. IR (KBr): $\tilde{\nu}$ = 2233 cm^{-1}, 2219, 2075, 2026.

[(iPr$_3$TAC)Cu(PPh$_3$)](BF$_4$) (**4**). [Cu(MeCN)$_4$](BF$_4$) (4.98 g, 15.8 mmol) and PPh_3 (4.15 g, 15.8 mmol) were suspended in CH_2Cl_2 (30 ml), then *i*Pr$_3$TAC (6 g, 28 mmol) was added to the suspension. After 12 h of stirring, the solvent was removed in vacuo and the residue was washed with THF until the solution remained colorless. The remaining slightly yellowish solid was dried in vacuo to yield 6.54 g (66%) of **4**, m.p. 133–135 °C. – $C_{30}H_{42}BCuF_4N_3P$ (626.07): calcd. C 57.56, H 6.76, N 6.71; found C 57.21, H 6.86, N 6.53. – ^{1}H NMR ($CDCl_3$): δ = 7.48–7.27 (m, 15 H, Ph), 4.34 (d, *J* = 8.7 Hz, 3 H, NCH_2N), 3.70 (d, *J* = 8.7 Hz, 3 H, NCH_2N), 3.13 (sept, *J* = 6.6 Hz, 3 H, C*H*Me$_2$), 1.08 (d, *J* = 6.6 Hz, 18 H, CH*Me*$_2$). – ^{13}C NMR ($CDCl_3$): δ = 133.32 (d, *J* = 14.7 Hz, *o*-PPh$_3$), 130.98 (*p*-PPh$_3$), 130.8 (d, *J* = 42 Hz, *ipso*-PPh$_3$), 129.23 (d, *J* = 9.8 Hz, *m*-PPh$_3$), 71.06 (CH$_2$), 52.43 (*C*HMe$_2$), 19.44 (CH*Me*$_2$). – ^{19}F NMR ($CDCl_3$): δ = –76.14 (BF$_4$). – ^{31}P NMR ($CDCl_3$): δ = 11.66 (PPh$_3$).

[(Cy$_3$TAC)Cu(PPh$_3$)](BF$_4$) (**5**). [Cu(MeCN)$_4$](BF$_4$) (0.47 g, 1.5 mmol), PPh_3 (0.40 g, 1.5 mmol), and Cy$_3$TAC (0.50 g, 1.5 mmol) were stirred in CH_2Cl_2 (30 ml). After 12 h, the solvent was removed in vacuo and the residue was washed with THF until the solution remained colorless. The remaining colorless solid was dried in vacuo to yield 1.05 g (94%) of **5**, m.p. 141 °C. – $C_{39}H_{54}BCuF_4N_3P$ (746.20): calcd. C 62.77, H 7.29, N 5.63; found C 62.05, H 7.41, N 5.39. – ^{1}H NMR ($CDCl_3$): δ = 7.55–7.30 (m, 15 H, Ph), 4.33 (d, *J* = 8.6 Hz, 3 H, NCH_2N), 3.81 (d, *J* = 8.6 Hz, 3 H, NCH_2N), 2.64 [m, 3 H, NC*H*(CH$_2$)$_5$], 1.81–1.53, 1.28–0.99 [m, 30 H, NCH(C*H*$_2$)$_5$]. – ^{13}C NMR ($CDCl_3$): δ = 133.29 (d, *J* = 14.8 Hz, *o*-PPh$_3$), 130.93 (*p*-PPh$_3$), 130.69 (d, *J* = 42 Hz, *ipso*-PPh$_3$), 129.12 (d, *J* = 10.1 Hz, *m*-PPh$_3$), 71.70 (N*C*H$_2$N), 60.63 (NCH), 29.96, 25.23 [NCH(*C*H$_2$)$_5$]. – ^{19}F NMR ($CDCl_3$): δ = –76.09 (BF$_4$). – ^{31}P NMR ($CDCl_3$): δ = 11.77 (PPh$_3$).

Crystal-Structure Determinations: Crystals were grown by crystallization from $CHCl_3$ (green: **1**: 1.0 × 0.99 × 0.55 mm; **2**: 0.27 × 0.18 × 0.75 mm; [D$_6$]**2**: 0.1 × 0.3 × 1.0 mm) or by slow diffusion of a CH_2Cl_2 solution into toluene (colorless: **3**: 0.2 × 0.25 × 0.8 mm; **4**: 0.46 × 0.34 × 0.23 mm).

A compilation of the crystal data, data collection, and refinement for **1**, **2**, [D$_6$]**2**, **3**, and **4** is given in Table 2. Crystals suitable for X-ray structure determination were selected by using a modified device, similar to that of Veith and Bärninghausen[18]. The crystals were mounted on a glass fiber and transferred to an Enraf-Nonius CAD4 four-circle diffractometer (STOE STADI4 four-circle diffractometer for 4) equipped with a low temperature device. Lattice parameters derived from the setting angles of 25 reflections in the range of 8° < 2Θ < 14° (from 20 reflections in the range of 26° < 2Θ < 33° for **4**) were obtained. Data were collected in the $\bar{\omega}$-2Θ scan mode. Every 200 reflections (after every three hours for **4**) three standard reflections were monitored and the crystal was reoriented if deviations between 0.1° and 0.15° occurred. Intensity data were corrected for Lorentz and polarization effects. Structure solution was performed by use of the Patterson method for **1**, **2**, and [D$_6$]**2** and direct methods for **3** and **4** (SHELXS-86)[19] and subsequent difference Fourier synthesis (SHELXL-93)[20]. Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included by using a riding model with d_{CH} = 0.96 Å and U_{iso} = 0.08 Å^2 (U_{iso} = 0.06 Å^2 for **3**). Neutral atomic scattering factors were taken from Cromer and Mann[21]. Geometrical calculations and illustrations were performed with Platon[22].

Structural Details for Complex **1**: Complex **1** crystallizes with two molecules of water and trioxane in the unit cell. The hydrogen atoms of the water molecule could not be found in the difference Fourier map and were not included in the least-squares refinement. The trioxane molecule was isotropically refined by using a split model of two rings with each oxygen and carbon position very close together. Furthermore, the C–O distance and the O–C–O, C–O–C angles had to be set to the values found in the crystal structure of trioxane[23]. A test was made to switch the carbon and oxygen atoms which worsened the wR_2 value and the goodness-of-fit to wR_2 = 0.1751 and *GOF* = 1.14. No attempt was undertaken to calculate missing hydrogen atoms of the trioxane molecule.

To test a possible influence of the copper atom on the hydrogen positions (H2A, H2B) of the CH_2 group closest to the metal atom, these position were refined isotropically.

Structural Details for Complexes **2** *and* [D$_6$]**2**: Both complexes crystallize with one molecule of $CHCl_3$ in the non-centrosymmetric space group $P2_12_12_1$. The Flack parameters for both structures are χ = 0.02(2) and confirmed the most probable structure[24]. To test a possible influence of the copper atom on the hydrogen positions (H2A, H2B) of the CH_2 group closest to the metal atom these position were refined isotropically. In [D$_6$]**2** all D atoms were refined isotropically.

Structural Details for Complex **3**. Each unit cell contains one molecule of toluene which is located around a center of inversion (–*x*, 2 – *y*, –*z*). Though disordered, its positions could be anisotropically refined by using a split atom model related by the center of inversion. No attempt was undertaken to calculate missing hydrogen atoms on the toluene molecule. To test a possible influence of the copper atom on the hydrogen positions of the methylene groups of the TAC ligand, H1A, H1B, H2A, H2B, H3A, and H3B were refined isotropically.

Structural Details for Complex **4**: Complex **4** crystallizes in the non-centrosymmetric space group $Pna2_1$ with two independent mol-

Table 2. Crystallographic data of **1**, **2**, [D$_6$]**2**, **3**, and **4**

Complex	Cu–N	α	Cu–C$_{ring}$	β	other bond lengths	other bond angles	
1	N1 2.60(1)	45.1	C2 2.557(10)	44.1	Cu–Cl1 2.235(6)	N1–Cu–N2 59.0(4)	N2–Cu–Cl2 92.9(4)
	N2 2.15(1)	27.9	C3 2.763(11)	31.1	Cu–Cl2′ 2.261(3)	N1–Cu–N3 59.7(3)	Cl1–Cu–Cl2′ 101.7(2)
	N3 2.064(8)	22.0	C1 2.84(2)	32.1	Cu–Cl2 2.707(5)	N2–Cu–N3 65.4(4)	Cl1–Cu–Cl2 102.2(3)
					Cu–Cu 3.511(2)	N1–Cu–Cl2 1 46.7(2)	Cl2–Cu–Cl2′ 90.5(2)
2	N1 2.101(3)	25.9	C3 2.718(3)	33.6	Cu–Cl1 2.219(1)	N1–Cu–N2 65.5(1)	N1–Cu–Cl2 98.03(8)
[[D$_6$]**2**]	[2.101(3)]	[25.6]	[2.722(4)]	[34.2]	[2.218(1)]	[65.4(1)]	[98.27(9)]
	N2 2.104(3)	24.9	C1 2.712(4)	34.5	Cu–Cl2 2.218(1)	N1–Cu–N3 62.4(1)	N3–Cu–Cl2 114.77(8)
	[2.101(3)]	[25.4]	[2.715(5)]	[34.4]	[2.218(1)]	[62.4(1)]	[114.82(8)]
	N3 2.390(3)	37.2	C2 2.592(3)	43.5		N2–Cu–N3 62.5(1)	Cl1–Cu–Cl2 100.56(4)
	[2.398(3)]	[38.0]	[2.597(3)]	[43.9]		[62.6(1)]	[100.41(5)]
3	N1 2.122(2)	26.5	C2 2.813(4)	34.7	Cu–P 2.1431(9)	N1–Cu–N2 64.7(1)	N1–Cu–P 158.33(7)
	N2 2.210(2)	29.6	C3 2.752(3)	37.1	P–C41 1.810(3)	N1–Cu–N3 61.2(1)	N2–Cu–P 135.41(7)
	N3 2.446(3)	39.5	C1 2.600(3)	39.8		N2–Cu–N3 60.46(9)	N3–Cu–P 131.24(7)
4 Cu1:	N1 2.176(5)	30.0	C3 2.693(5)	37.2	Cu1–P1 2.124(2)	N1–Cu–N2 64.3(2)	N1–Cu–P1 150.1(1)
	N2 2.201(5)	29.0	C1 2.662(5)	38.3	P1–C64 1.812(6)	N1–Cu–N3 64.3(2)	N2–Cu–P1 140.7(1)
	N3 2.202(4)	30.0	C2 2.669(6)	38.1		N2–Cu–N3 63.9(2)	N3–Cu–P1 134.3(1)
Cu2:	N4 2.234(4)	31.1	C6 2.652(5)	36.8	Cu2–P2 2.137(2)	N4–Cu–N5 63.1(2)	N4–Cu–P2 142.9(1)
	N5 2.237(4)	30.9	C4 2.668(6)	38.6	P2–C80 1.819(6)	N4–Cu–N6 63.9(2)	N5–Cu–P2 135.1(1)
	N6 2.150(4)	27.4	C5 2.725(5)	37.3		N5–Cu–N6 63.8(2)	N6–Cu–P2 148.4(1)

ecules. The absolute structure parameter of −0.004(14) confirmed the correct positions for the atoms in the structure.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-405407 (**1**), −405406 (**2**), −405408 ([D$_6$]**2**), −405409 (**3**), and −405410 (**4**), the names of the authors, and the journal citation.

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