Syntheses and Structures of 13-Substituted 1,5,9-Triazatricyclo[7.3.1.$0^{5,13}$]-tridecanes and Their Copper(II) Chloride Complexes

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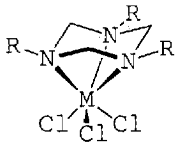
Received March 21, 1995

Key Words: Orthoamides / Trisaminomethanes, tricyclic / Guanidinium cation, alkylation / Copper(II) complexes

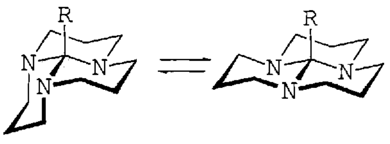
The orthoamides **2a**, **b** (R = Ph and $PhCH_2$) have been prepared by alkylation of the guanidinium salt $\mathbf{4}^+BPh_4^-$ with PhNa and $PhCH_2Na$, respectively. The crystal structures of the two orthoamides have been determined by X-ray crystallography. Their reaction with $CuCl_2$ gives 1:1 complexes. The crystal structure of the complex with **2a** shows a square planar geometry around the copper atom with η^2-**2a** and two chlorides and weak interactions two the third nitrogen atom and a C–H bond of **2a** in the axial positions.

Ligand Synthesis

The reactivity of complexes with chelating ligands can be increased by pulling together the coordinating donor atoms. Therefore, we are interested in ligands having three tertiary amines in close proximity. Simple complexes with η^3-bound 1,3,5-triazacyclohexanes **1** were synthesized that showed highly strained metal–nitrogen bonds[1].

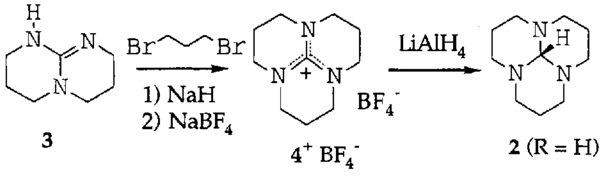


1
(M = Cr, Fe)



trans-trans-cis **2** *all-trans*

The all-*trans* isomer of 13-substituted 1,5,9-triazacyclotridecane or shorter orthoamides **2** have the three nitrogen atoms at a similar position connected through only one central carbon atom. A lengthy synthetic route[2] to this ligand via triazacyclododecane (R = H, Me, and Et) and the structures of the ligands **2** with R = H (only the *all-trans* isomer)[3] and with R = Me (both isomers)[4] are known. The crystal structures of two $Mo(CO)_3$ complexes[5] with R = H and Me have been described. Later, Weisman et al. reported an apparently much easier synthesis for **2** which is, however, restricted to R = H[6]. They prepared the guanidinium salt $\mathbf{4}^+BF_4^-$ from **3** and 1,3-dibromopropane/NaH and reduced it with $LiAlH_4$ to **2** (R = H).

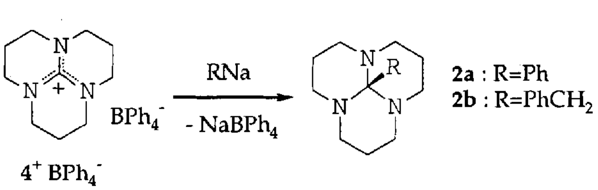


3 $\mathbf{4}^+\ BF_4^-$ **2** (R = H)

In a similar reaction the alkylation of the cation $\mathbf{4}^+$ should yield **2** with a variety of aryl or alkyl substituents. However, all attempts to alkylate $\mathbf{4}^+BF_4^-$ with alkyllithium, Grignard or alkylcopper reagents failed and only $\mathbf{4}^+$ salts could be isolated. However, the anion BF_4^- was attacked and we decided to change the anion.

In the synthesis of $\mathbf{4}^+$ a hygroscopic bromide $\mathbf{4}^+Br^-$ is obtained which could not be recrystallized. Drying at 0.01 mbar for a few days yielded a crude bromide which can be used directly for metallation but in low yields. Alternatively, treatment of an aqueous solution of the crude bromide with $NaBPh_4$ and subsequent Soxhlet extraction of the precipitate gave pure colorless non-hygroscopic $\mathbf{4}^+BPh_4^-$. However, no alkylation of the bromide or BPh_4^- salt was observed when using lithium reagents except for a low yield of **2** (R = Me) when using $LiCH_2SiMe_3$ and hydrolysis of the C–Si bond during aqueous work-up.

Much better results were obtained by using potassium or even better sodium reagents. Refluxing benzyl or phenyl sodium with $\mathbf{4}^+$ BPh_4^- gave nearly a 50% yield of the benzyl and phenyl substituted **2**. Using a mixture of alkyllithium with Na*Ot*Bu or K*Ot*Bu or the use of the crude bromide also gave the alkylated products but in poorer yields.



$\mathbf{4}^+\ BPh_4^-$

2a : R=Ph
2b : R=$PhCH_2$

The compounds **2a**, **b** are colorless solids which can be sublimed. The NMR spectra show only the symmetric pattern consistent with a fast equilibrium between the *all-trans* and *trans-trans-cis* isomers. The C–N bonds are not hydrolyzed by water.

Slow evaporation of hexane solutions of **2a** and **2b** gave colorless crystals suitable for X-ray crystallography.

2a crystallizes with three independent molecules in the unit cell. They are all present in the *cis-trans-trans* conformation (Figure 1).

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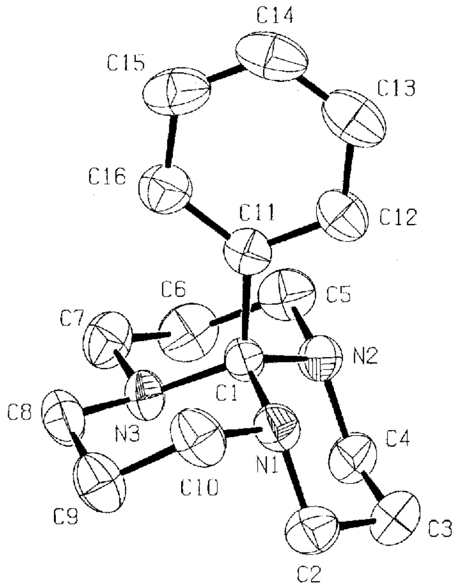
Figure 1. PLATON[7] plot of one of the three independent molecules of **2a**

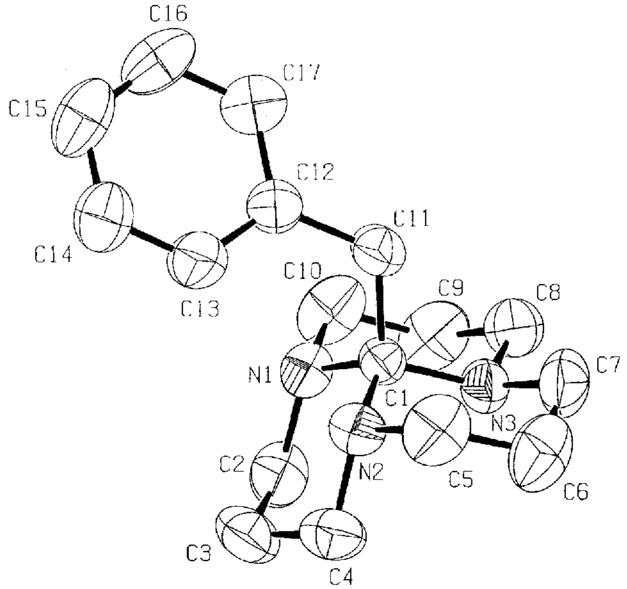


Selected bond lengths [Å] and angles [°] (average of three independent molecules): C1–C(Ph) 1.551(5), C(Ph)–C(Ph) 1.381(10), all other C–C 1.505(11), C1–N3 1.488(4), all other C–N 1.466(5); N3–C1–C(Ph) 117.4(5), N2/3–C1–C(Ph) 105.5(5), N–C1–N 109.4(4), C(*trans* ring)–N–C1 111.2(6), C(*cis* ring)–N–C1 116.1(7), C1–C11–C12 116.8(3), C1–C11–C16 125.4(3).

2b crystallizes also in the *cis-trans-trans* conformation, however, with only one independent molecule in the unit cell (Figure 2).

Both **2a** and **2b** have very similar structures which are similar to the *trans-trans-cis* form of **2** (R = Me)[4]. The bond of the central carbon atom to the alkyl substituent is longer than all other C–C single bonds [1.551(5) Å for **2a**, 1.559(3) Å for **2b** and 1.540 Å for **2** (R = Me)]. The C–N bond between the two *trans* rings is longer than all other C–N bonds by 0.02 to 0.03 Å which expresses some ring strain in this bond. The alkyl substituent is bent away from that bond and causes the corresponding N–C–C angle to be larger than the tetrahedral angle depending on the steric requirement of the substituent [117.4(5)° in **2a**, 112.0(2)° in **2b** and 113.5° in **2** (R = Me)].

Figure 2. PLATON[7] plot of **2b**

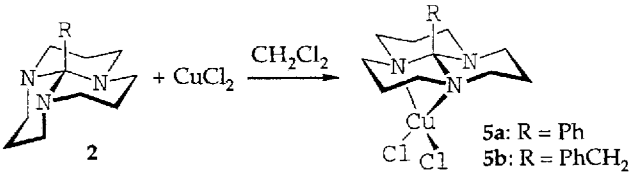


Selected bond lengths [Å] and angles [°]: C1–C11 1.559(3), C11–C12 1.510(3), C(Ph)–C(Ph) 1.373(13), all other C–C 1.499(17), C1–N3 1.494(2), all other C–N 1.465(7); N3–C1–C11 112.0(2), N2/3–C1–C11 107.9(2), N–C1–N 109.7(3), C(*trans* ring)–N–C1 113.2(8), C(*cis* ring)–N–C1 115.7(3), C1–C11–C12 116.8(2).

Copper(II) Chloride Complexes

We investigated the Ligand properties of **2** towards copper. Copper(I)/(II) complexes with three facially coordinating nitrogen atoms play an important role in the biological binding and activation of dioxygen[8]. A large number of copper complexes containing ligands binding with three or more nitrogen atoms have been described as models for biological systems, but only a few have been structurally identified as peroxo or superoxo complexes[9]. 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 $[(LCu)_2(O_2)]^{2+}$ (L = 1,4,7-triisopropyl-1,4,7-triazacyclo-nonane) has been shown to cleave such a C–H bond[10]. By deuteration of the *i*Pr groups of the ligand, it has been shown that first an aliphatic C–H/D bond of the ligand close to the Cu_2O_2 core is broken.

Treatment of $CuCl_2$ with **2a**, **b** in CH_2Cl_2 gave the air-sensitive green complexes **5a**, **b**.



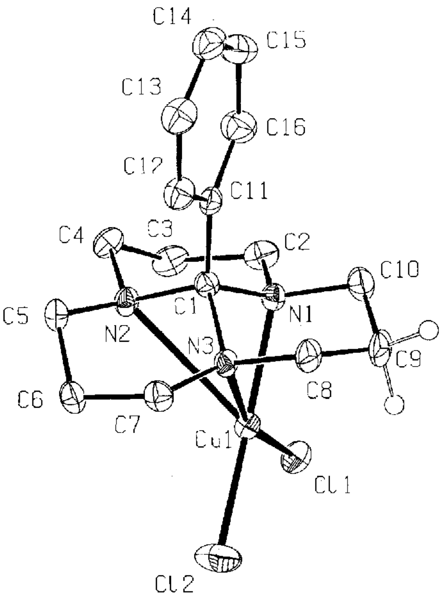
2

5a: R = Ph
5b: R = $PhCH_2$

Slow evaporation of a solution of **5a** in CH_2Cl_2 under argon by contacting it with a flask containing toluene gave large green crystals of **5a**. The crystal structure is shown in Figure 3.

When compared to the structure of the corresponding 1,3,5-triazacyclononane complex [data in parentheses][11], **5a** shows a high degree of distortion due to the ring strains. The copper atom is square planarly coordinated by the two chlorine (Cu–Cl = 2.210(1) and 2.216(1) Å) [2.268(1) and 2.312(1) Å] and two nitrogen atoms (Cu–N = 2.069(2) and 2.073(2) Å) [2.038(4) and 2.063(4) Å] with an angle between the nitrogen atoms of only 66.16(9)° [82.2(2)°] and the copper atom lying 0.10 Å [0.20 Å] above the plane towards the third nitrogen atom of the orthoamide which approaches the axial position with a much longer distance Cu–N of 2.754(3) Å [2.246(4) Å]. However, the copper lies directly between the two close nitrogen atoms when projected onto the plane defined by the three nitrogen atoms of the orthoamide and the ligand must be considered as η^2-bonded although the ligand has the correct all-*trans* conformation for η^3-coordination. On the opposite side of the N_2CuCl_2 plane a C–H bond (C9–H9A) of the propylene bridge comes close to the copper atom [Cu–C9 = 2.856(4) Å, Cu–H9A = 2.58(3)]. This distance is not much longer than the agostic Cu–CH distance in the cationic copper(I) complex $[(norbonadiene)Cu(dien)]^+$ (Cu–C = 2.78 Å and Cu–H 2.01 Å with Cu–N 2.08–2.25 Å)[12] and the agostic Co–C distance of 2.52 Å in $[Co(III)(dacoda)(SO_3)]^-$ (Co–N 1.93–1.96 Å)[13]. In the latter case the C–H bond is also part of a propylene bridge be-

Figure 3. PLATON[7] plot of **5a**



Selected bond lengths [Å] and angles [°]: Cu–N1 2.073(2), Cu–N2 2.754(3), Cu–N3 2.069(2), Cu–Cl1 2.2098(12), Cu–Cl2 2.2164(12), Cu–H9A 2.58(3), N1–Cu–N3 66.16(9), Cl1–Cu–Cl2 98.48(5).

tween two coordinating nitrogen atoms in the basal plane of a square pyramid and this activated group could be deprotonated by a base.

However, the distortion in the chair of the diazacyclohexane rings of the ligand suggests a repulsion rather than attraction of this C–H bond. The angles between the plane defined by the two nitrogen atoms and the adjacent methylene carbon atoms and the two planes defined by the three methylene carbon atoms or the two nitrogen atoms and the central carbon atom lie all in the range of 46–49° in the two "non-agostic" diazacyclohexane rings. The corresponding angles in the "agostic" diazacyclohexane ring deviate considerably from this range {[N1–C1–N3]/[N1–C10–C8–N3] 61.24(16)° and [C8–C9–C10]/[N1–C10–C8–N3] 42.66(18)°}. Both deviations lead to a larger Cu–C9 distance and are therefore an indication that C9 is repelled from the copper atom.

Conclusion

A more general route to 13-substituted orthoamides **2** from the guanidinium salt **4** and sodium alkyls and aryls is described. Complexation with $CuCl_2$ showed that these compounds can serve as ligands with unusually distorted coordination geometries.

We thank the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and Prof. *H. Schumann* for the support of this work. R. D. K. thanks the *Deutsche Forschungsgemeinschaft* for a habilitation fellowship.

Experimental

All reactions were performed under dry argon and in dry solvents distilled from Na/benzophenone or CaH_2 (CH_2Cl_2). – Melting points were determined with an HWS-SG 2000, HWS Mainz, and are uncorrected. – NMR (Bruker ARX 200): ^1H NMR (200 MHz): ext. TMS; $^{13}C\{^1H\}$ NMR (50.26 MHz): ext. TMS. – Elemental analyses: Perkin-Elmer Series II CHNS/O analyser and the analytical facilities of the FU and HU Berlin.

1,5,9-Triazatridecylium Tetraphenylborate ($\mathbf{4}^+BPh_4^-$): 1,5,7-triazabicyclo[4.4.0]dec-5-ene (**3**) (15.0 g, 108 mmol) was dissolved in THF (250 ml) and NaH (2.6 g, 108 mmol) was added. 1,3-Dibromopropane (21.75 g, 108 mmol), dissolved in 25 ml of THF, was added dropwise at –78°C. After slow warming to ambient temperature and stirring for 24 h, the solution was decanted from the solids which were washed with Et_2O (100 ml). Extraction with 150 ml of CH_2Cl_2 in several portions and removal of the solvent yielded 19 g of impure $\mathbf{4}^+Br^-$ which was dissolved in 150 ml of water. Addition of an aqueous solution of 25 g (73 mmol) of $NaBPh_4$ precipitated $\mathbf{4}^+BPh_4^-$ which was dried in vacuo and Soxhlet-extracted with acetone. 20 g (37%) of colorless $\mathbf{4}^+BPh_4^-$ was obtained, m.p. 269°C. – ^1H NMR ($CDCl_3$): δ = 7.7–7.0 (m, 20H, BPh_4^-), 3.29 (t, 12H, NCH_2), 2.00 (tt, 6H, CCH_2C). – $C_{34}H_{38}N_3B$ (499.51): calcd. C 81.75, H 7.67, N 8.41; found C 81.25, H 7.75, N 8.44.

13-Phenyl-1,5,9-triazatridecane (**2a**): $\mathbf{4}^+BPh_4^-$ (4.0 g, 8.0 mmol) and phenyl sodium (1.6 g, 16.0 mmol) were refluxed in hexane for three days. The suspension became light brown during that time. The solids were filtered off and extracted with hexane. The solvent of the combined hexane extracts was removed in vacuo. The remaining waxy solid was redissolved in ether and filtered through neutral alumina. The solvent was removed in vacuo and the remaining crude **2a** sublimed at 90°C/10^{-2} Torr. 0.97 g (48%) of colorless crystalline **2a** were obtained, m.p. 97–98°C. – ^1H NMR ($CDCl_3$): δ = 7.8–7.2 (m, 5H, Ph), 2.96 (m, 12H, NCH_2), 2.11 (m, 3H, CCH_2C), 1.48 (m, 3H, CCH_2C). – ^{13}C NMR ($CDCl_3$): δ = 145.6 (1-Ph), 130.4 (2-Ph), 127.0 (3-Ph), 126.6 (4-Ph), 86.9 (Ph-CN_3), 48.1 (NCH_2), 20.9 (CCH_2C). – $C_{16}H_{23}N_3$ (257.38): calcd.C 74.67, H 9.01, N 16.33; found C 74.64, H 9.58, N 15.94.

13-Benzyl-1,5,9-triazatridecane (**2b**): $\mathbf{4}^+BPh_4^-$ (10.0 g, 20.0 mmol) and benzyl sodium (3.1 g, 19.9 mmol) were refluxed in toluene for three days. The suspension became light brown during that time. Work-up analogous to **2a** and sublimation at 100°C/10^{-2} Torr yielded 2.51 g (46%) of colorless crystalline **2b**, m.p. 117–119°C. – ^1H NMR ($CDCl_3$): δ = 7.6–7.3 (m, 5H, Ph), 3.43 (s, 2H, $PhCH_2$), 2.96 (m, 12H, NCH_2), 2.13 (m, 3H, CCH_2C), 1.50 (m, 3H, CCH_2C). – ^{13}C NMR ($CDCl_3$): δ = 139.05 (1-Ph), 130.18 (2-Ph), 127.39 (3-Ph), 125.39 (4-Ph); 86.8 ($PhCH_2CN_3$), 48.59 (NCH_2), 25.84 ($PhCH_2$), 21.36 (CCH_2C). – $C_{17}H_{25}N_3$ (271.41): calcd. C 75.23, H 9.28, N 15.48; found C 75.03, H 9.66, N 15.34.

Dichloro(13-phenyl-1,5,9-triazatridecane)copper(II) (**5a**): **2a** (520 mg, 2.02 mmol) and anhydrous $CuCl_2$ (540 mg, 4.01 mmol) were stirred in CH_2Cl_2 (30 ml) for 12 hrs. The green solution was filtered and the solvent removed in vacuo yielding 430 mg (54%) of green crystalline **5a**, m.p. 123–124°C (dec.). – $C_{16}H_{23}N_3CuCl_2$ (391.83): calcd. C 49.05, H 5.92, N 10.72; found C 48.75, H 5.74, N 10.98.

Dichloro(13-benzyl-1,5,9-triazatridecane)copper(II) (**5b**): Analogously to **5a**, **2b** (740 mg, 2.54 mmol) and anhydrous $CuCl_2$ (390 mg, 2.71 mmol) yielded 720 mg (70%) of green crystalline **5b**, m.p. 100°C (dec.). – $C_{17}H_{25}N_3CuCl_2$ (405.86): calcd. C 50.31, H 6.21, N 10.35; found C 50.43, H 5.73, N 10.79.

Crystal Structure Determinations: The crystals of **2a**, **2b**, and **5a** were mounted on a glass fiber and transferred to an Enraf-Nonius CAD4 four circle diffractometer (Mo-K_α radiation). Data were collected with ω-2Θ scans. Every 200 reflections intensity data were monitored through the measurement of three standard reflections. All data were corrected for Lorentz, polarization, and for absorption effects (DIFABS[14]). The structures were solved using Direct Methods (SHELX-86)[15] and the refinement of the molecules using difference-fourier methods (SHELX-93)[16]. The molecules were refined against F_o^2 by full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed on calculated positions with d_{CH} = 0.98 Å and U_{iso} = 0.08 Å^2. The hydrogen atoms H(9a) and H(9b) of the structure **5a** were refined isotropically. Compound **2a** crystallizes with three independent molecules per asymmetric unit. More details on structure solution and refinement are collected in Table 1.

Table 1. Crystal data and details of the structure analysis for compounds **2a**, **2b** and **5a**

	2a	**2b**	**5a**
Formula	$C_{16}H_{23}N_3$	$C_{17}H_{25}N_3$	$C_{16}H_{23}N_3CuCl_3$
Mol. mass [g mol^{-1}]	257.37	271.40	391.82
Crystal size [mm]	0.7 × 0.45 × 1.1	0.5 × 0.25 × 0.7	0.35 × 0.45 × 1.1
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$ (No. 4)	$P2_1/a$ (No. 14)	$P2_1/c$ (No. 14)
a [Å]	14.116(4)	7.996(2)	8.896(4)
b [Å]	7.7234(13)	17.708(2)	12.082(4)
c [Å]	19.599(4)	11.027(3)	16.087(8)
β [°]	96.64(2)	104.92(2)	103.03(4)
V [Å^3]	2122.4(8)	1508.8(6)	1684.5(13)
Z	6	4	4
$D_{calcd.}$ [g cm^{-3}]	1.208	1.195	1.545
F(000)	840	592	812
μ(Mo-K_α) [mm^{-1}]	0.073	0.072	1.586
Temperature [K]	293(2)	293(2)	163(2)
Scan range (2Θ) [°]	2, 47	4, 50	4, 48
hkl range	+15, +8, ±21	+9, +21, ±13	±8, +13, +18
Measured reflections	3260 (R_{int} = 0.0185)	3333 (R_{int} = 0.01)	2638 (R_{int} = 0.0647)
Unique refl.	3117	1924	2120
Data for refinement(n)	3112	1903	2106
Parameters refined (p)	513	181	207
Absorption corr.: max./min.	DIFABS 1.21/0.81;	DIFABS 1.07/0.76	DIFABS 1.14/0.84
ρ_o[a]; max./min [eÅ^{-3}]	0.11/−0.12	0.18/−.16	0.32/−0.26
R_1[b]	0.0341	0.0483	0.0276
wR_2[c] [$I > 2\sigma(I)$]	0.0851	0.1259	0.0714
GOF[d]	1.034	1.094	1.056

[a] Largest difference peak and hole.

[b] $R_1 = (\Sigma \|F_o|-|F_c\|)/\Sigma |F_o|$.

[c] $wR_2 = [\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_o^2)^2]]^{1/2}$.

[d] Goodness of fit = $[\Sigma [w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

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-404269 (**2a**), CSD-404270 (**2b**) and CSD-404268 (**5a**), the names of the authors and the journal citation.

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