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Syntheses of 2,4-Disubstituted 1,3,5-Triazapentadienyl Ligands Having Two Guanidinato Moieties and Their Use in the Isolation of Copper(I) Complexes

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2,4-N,N′-Disubstituted 1,3,5-triazapentadienyl ligands as their lithium salts $[\mathrm{Li}\{(\mathrm{N(R)C(R')})_2\mathrm{N}\}]_2$ [where R = $\mathrm{SiMe_3}$ here and hereafter and R′ = dimethylamino (**1**) or 1-piperidino (**2**)] were synthesized via the reactions of $\mathrm{LiN(SiMe_3)_2}$ with 2 equiv of the α-hydrogen-free carbonitrile dimethylcyanamide or 1-piperdinecarbonitrile and used in the isolation of the two-coordinate copper(I) complexes $[\mathrm{Cu}\{(\mathrm{N(R)C(R')})_2\mathrm{N}\}]_2$ [R′ = dimethylamino (**3**) and 1-piperidino (**4**)]. Complex **2** features a twisted W-shaped ligand backbone in the solid state. Complexes **3** and **4** show an unusual 12-membered ring dinuclear copper(**I**) triazapentadienyl and a less expressed ability to form a stable delocalized triazapentadienyl system.

Both β-diketiminato (1,5-diazapentadienyl) and 1,3,5-triazapentadienyl ligands are monoanionic, nitrogen-based donors capable of forming six-membered metallacycles with metal ions. Over the past few years, β-diketiminato ligands and their metal complexes have received significant increasing attention,[1] especially *N*,*N*′-bis(trimethylsilyl)-β-diketiminates, which have been extensively investigated.[2,3] Recently, we reported that addition reactions of the reagent $\mathrm{Li[CHR_2]}$ (R = $\mathrm{SiMe_3}$) or the derived 1-azaallyllithium $\mathrm{[LiN(R)C(Bu^t)CHR]_2}$ with α-hydrogen-free nitriles led to a β-diketiminatolithium and further to derived transition-metal complexes.[4,5] However, the isoelectronic 1,3,5-triazapentadienyl ligands have not been paid as much attention as β-diketiminato ligands probably because of the lack of versatile methods for the ligand synthesis.[6] Recently, groups led by Dias and Siedle reported the synthesis of a series of fluorinated 1,3,5-triazapentadienyl ligands $[\mathrm{N}\{(\mathrm{C_3F_7})\mathrm{C(R')N}\}_2]^-$ (R′ = H, Ph, 2,6-$^i\mathrm{Pr_2C_6H_3}$, $\mathrm{C_6F_5}$, 2-F,6-$(\mathrm{CF_3})$-$\mathrm{C_6H_3}$, and 2,4,6-$\mathrm{Me_3C_6H_2}$) and some of their metal complexes.[7–15] Other related literature in this area concerned the use of $[\mathrm{N}\{(\mathrm{R'})\mathrm{C(H)N}\}_2]^-$ (R′ = 2-, 3-, or 4-pyridyl) as a ligand for nickel and palladium.[16,17] Some 1,3,5-triazaheptatrienyllithium and 1,3,5,7-tetraazaheptatrienyllithium compounds were also described.[18,19] Because of rare information on 1,3,5-triazapentadienyl-metal complexes and interesting results that we obtained from the reaction of an N-centered anion to an α-hydrogen-free nitrile, we were attracted to the 2,4-N,N′-disubstituted 1,3,5-triazapentadienyl ligands and their metal coordination chemistry. The new system with a

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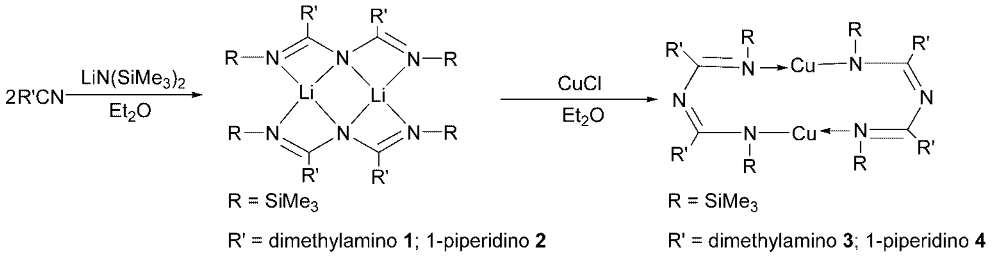
Scheme 1. Synthetic Routes to Complexes **1**−**4**



guanidinato moiety in the backbone exhibits substantial scope and diversity in its coordination chemistry and provides synthetic utility in organic and organometallic chemistry. In addition, its metal complexes have similar potential applications as catalysts, or magnetic materials as metal β-diketiminates[20,21] or amidinates.[22,23]

In this paper, we report the syntheses of the lithium salts of 2,4-N,N′-disubstituted 1,3,5-triazapentadienyl ligands $[Li\{N(N(R)C(R'))_2\}]_2$ [where R = $SiMe_3$ and R′ = NMe_2 (**1**) and 1-piperidino (**2**)] and their utility in copper(I) chemistry. The 1,3,5-triazapentadienyllithium **2** was prepared by the reaction of $LiN(SiMe_3)_2$ and 1-piperdinecarbonitrile in a 1:2 molar ratio in diethyl ether. It was isolated as colorless crystals; single crystals of **2** suitable for X-ray diffraction studies were obtained by recrystallization from Et_2O. Complex **1** was not isolated but was generated in situ in the same manner as complex **2**. To our knowledge, except for the U-shaped triazapentadienyllithium $[\{N\{(C_3F_7)C(Mes)N\}_2\}Li(THF)_2]$ and $[\{N\{(C_3F_7)C(Dipp)N\}_2\}Li(THF)]$ (where Mes = 2,4,6-$Me_3C_6H_2$ and Dipp = 2,6-$Pr^i{}_2C_6H_3$),[12] complex **2** is the first structurally characterized dimeric triazapentadienyllithium complex in which the NCNCN backbone adopts a W-shaped conformation. The new procedure for preparing 1,3,5-triazapentadienyl ligands is practical and can be used in the synthesis of a series of lithium salts of 1,3,5-triazapentadienyl ligands having two guanidinato moieties and their transition-metal complexes.

The copper(I) triazapentadienyl compounds **3** and **4** were synthesized by treatment of **1** and **2** with anhydrous CuCl in a 1:1 molar ratio, respectively, in diethyl ether at low temperature. **3** and **4** were isolated as colorless crystalline solids in poor yields (18% for **3** and 19% for **4**), and suitable single crystals were obtained by recrystallization from dichloromethane. The overall process is illustrated in Scheme 1.

The molecular structure of crystalline **2** is illustrated in Figure 1. $[Li\{(N(SiMe_3)C(NMe_2))_2N\}]_2$ **2** crystallizes in the $P\bar{1}$ space group. The molecule **2** is a dimer built around a planar LiNLiN ring; the angles at the nitrogen atom [79.6(2) and 79.9(2)°] are narrower than those at the Li atom [99.9(3) and 100.1(3)°]. Each lithium atom is coordinated with four nitrogen atoms from two ligands. Each ligand NCNCN backbone adopts a twisted W-shaped conformation. The dihedral angles between the two LiNCN moieties linked by N3 and N8 are 51.8 and 52.3°, respectively, while the dihedral angles between the two LiNCN moieties linked by Li1 and Li2 are 59.6 and 62.3°, respectively. The molecule **2** has two fused back-to-back tricyclic boat motifs comprising a central planar N3Li1N8Li2 (mean deviation 0.048 Å) ring flanked by planar N3Li1N5C10 and N8Li2N6C22, N8Li1N10C28, and N3Li2N1C4, respectively. The dihedral angle between the core N3Li1N8Li2 and the adjacent four-membered rings Li2N1C4N3 and Li1N8C28N10 are 44.0 and 41.8°, respectively. The dihedral angle (82.5°) between Li1N3C10N5 and Li2N6C22N8 is slightly smaller than that between Li1N8C28N10 and Li2N1C4N3 (85.8°). The bond distances N1−C4, C4−N3, N3−C10, and C10−N5 are 1.309(4), 1.367(4), 1.362(4), and 1.304(4) Å, respectively, indicating a short–long−long–short pattern of C−N bond lengths in the NCNCN backbone.

The molecular structure of crystalline **3** is shown in Figure 2; it is dimeric. The two 1,3,5-triazapentadienyl ligands in the complex are equivalent and bridge the copper atoms in a $\mu,\kappa^1{:}\kappa^1$ fashion. For the ligand NCNCN backbone, a short–long–short–long pattern of C−N bond lengths can be seen: d(N1−C1) and d(N2−C2) are 1321(5) and 1.315(5) Å, respectively, while d(C1−N2) and d(C2−N5′) are 1.371(5) and 1.360(6) Å, respectively. This pattern indicates C═N characteristics of a conjugated system. However, the N_3C_2 framework is not coplanar. The dihedral angle between the N1−C1−N2 and N2−C2−N5′ planes is 64.1°. Therefore,

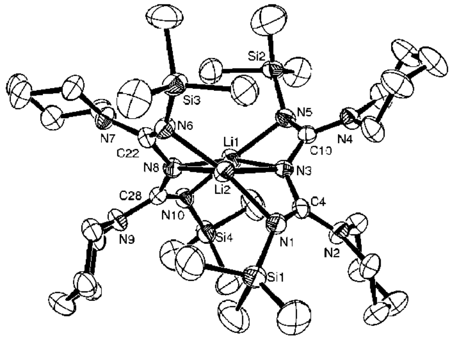


Figure 1. Molecular structure of **2**. Selected bond distances (Å) and angles (deg): Li1−N3 2.075(6), Li1−N5 2.013(6), Li1−N8 2.062(7), Li1−N10 2.039(6), Li2−N1 2.050(6), Li2−N3 2.065(6), Li2−N6 2.054(6), Li2−N8 2.066(6), N1−C4 1309(4), N2−C4 1.371(4), N3−C4 1.367(4), N3−C10 1.362(4), N4−C10 1.374(4), N5−C10 1.304(4), N6−C22 1.302(4), N7−C22 1.374(4), N8−C22 1.368(4), N8−C28 1.370(4), N9−C28 1.371(4), N10−C28 1.302(4); N3−Li1−N8 99.9 (3), N3−Li2−N8 100.1(3), Li1−N3−Li2 79.6(2), Li1−N8−Li2 79.9(2), N1−C4−N3 115.9(3), C4−N3−C10 130.2(3), N3−C10−N5 116.0(3), N6−C22−N8 115.2(3), C22−N8−C28 128.8(3), N8−C28−N10 116.2(3), Li1−N3−C10 86.3(2), Li2−N8−C22 88.0(2).

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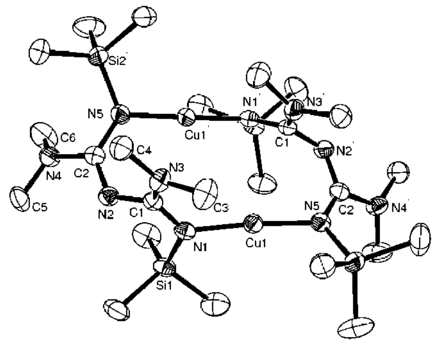


Figure 2. Molecular structure of **3**. Selected bond distances (Å) and angles (deg): Cu1−N1 1.896(4), N1−C1 1321(5), C1−N2 1.371(5), C1−N3 1.339(5), C3−N3 1.454(6), C4−N3 1.455(6), Cu1−N5 1.883(4), C2−N2 1.315(5), C2−N4 1.385(4), C2−N5′ 1.360(6), N4−C5 1.457(6), N4−C6 1.458(6); N1−Cu1−N5 174.07(15), Cu1−N1−C1 126.5(3), N1−C1−N2 118.1(4), C1−N2−C2 122.7(4), N2−C2−N5′ 126.0(4), C2−N5′−Cu1 120.2(3).

this framework adopts a twisted W-shaped conformation and the conjugated system is finally impaired to some extent. For the C1N1N2N3 and C2N2N4N5′ guanidinato moieties, the dihedral angles between N1C1N2 and C3N3C4 and between N2C2N5′ and C5N4C6 are 15.6 and 86.7°, respectively. The distance between the copper atoms is 3.636 Å, which is much longer than the "normal" Cu−Cu bond distance of 2.65–2.70 Å and hence does not exhibit some bonding interaction between the Cu−Cu atoms.[22–24]

In complex **4** (Figure 3), there are two chemically similar, crystallographically independent molecules in the crystal lattice, and the bond distances and angles show no significant differences. The molecule **4** has a structure similar to that of complex **3** except for the replacement of NMe$_2$ by 1-piperidino. The NCNCN backbone in **4** is not coplanar, but atoms N5, C10, N3, and C4 are in a plane (mean deviation 0.0072 Å). There is a dihedral angle of 68.4° between N1C4N3 and N3C10N5 planes. The dihedral angles between N1C4N3 and C5N2C9 and between N3C10N5 and C11N4C15 are 31.3 and 50.8°, respectively. The distance between the copper atoms is 3.536 Å, indicating no interaction between the two copper atoms.

In contrast to the copper(I) 1,3,5-triazapentadienyl adducts **3** and **4** described in this paper, several 1,3,5-triazapentadienylcopper(I) complexes of fluorinated ligands such as $[\mathrm{N}\{(\mathrm{C_3F_7})\mathrm{C}(\mathrm{C_6F_5})\mathrm{N}\}_2]^{-}$[11] and $[\mathrm{N}\{(\mathrm{C_3F_7})\mathrm{C}(\mathrm{Dipp})\mathrm{N}\}_2]^{-}$[15] featured a κ^2-bonded ligand with a U-shaped ligand backbone and thus gave six-membered metallacycles, while in both **3** and **4** the twisted U-shaped ligands bond with Cu$^{\mathrm{I}}$ in a κ^1 mode, forming an unusual 12-membered ring. The Cu−N bond distances in **3** [1.896(3) and 1.883 (4) Å] and **4** [1.888(3) and 1.871(3) Å] are shorter than those reported values on triazapentadienylcopper(I) complexes (1.939−2.049 Å), but they are similar to data on dinuclear copper(I) amidinate compounds.[25,26]

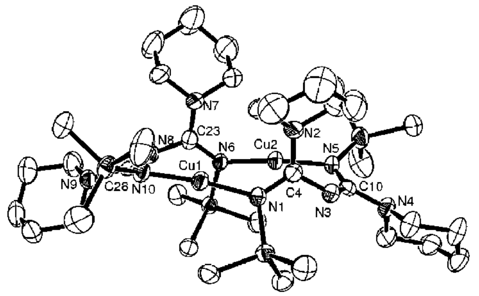
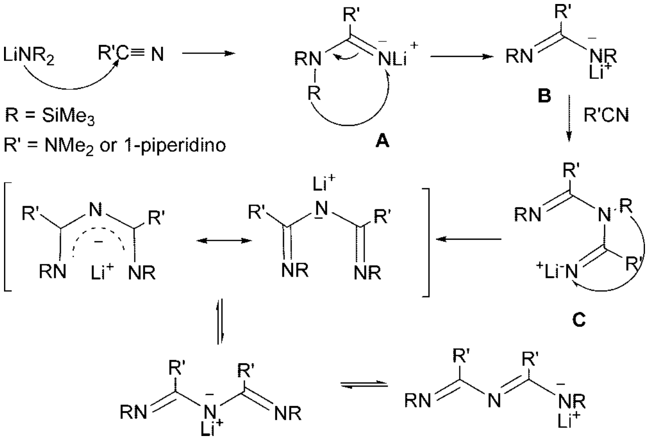


Figure 3. Molecular structure of **4**. Selected bond distances (Å) and angles (deg): Cu1−N1 1.888(3), Cu2−N5 1.871(3), N1−C4 1327(4), C4−N2 1.354(5), C4−N3 1.369(4), C10−N3 1.308(4), Cu1−N10 1.881(3), Cu2−N6 1.880(3), C10−N4 1.398(4), C10−N5 1.353(4), N4−C11 1.464(5), N4−C15 1.456(5); N1−Cu1−N10 172.05(12), Cu1−N1−C4 127.6(2), N1−C4−N3 118.6(3), C4−N3−C10 122.3(3), N3−C10−N5′ 126.3(3), C10−N5′−Cu2 119.5(2).

Scheme 2. Proposed Pathway for the Formation of **1** and **2**



The proposed pathway for the formation of **1** and **2** is outlined in Scheme 2. The initial step is an attack of the N-centered nucleophile on R′CN to yield the intermediate ketimide **A**, en route to its rearrangement product **B**. **B** then attacks a second R′CN molecule to give **C**, undergoing a further isomerization to give the final W-shaped product or a U-shaped 1,3,5-triazapentadienyl product. The pathway involved 1,3-Me$_3$Si migrations of N → N and concomitant N−C bond formation.

In conclusion, we described the synthesis of two novel dimeric 2,4-N,N′-disubstituted 1,3,5-triazapentadienyllithium compounds and their derived copper(I) complexes. A synthetic pathway for the lithium complexes **1** and **2** is put forward. We are currently exploring the coordination chemistry of this interesting class of 1,3,5-triazapentadienato ligands with guanidinato moieties and the applications of their metal complexes.

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Supporting Information Available: X-ray crystallographic data and experimental details for **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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