

1,3,5-Triazapentadienes as Chelating Ligands: 1,2,4-Triphenyl-1,3,5-triazapentadiene Complexes of Cobalt(II), Nickel(II), Palladium(II), Copper(II) and Zinc(II)^[‡]

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Dedicated to Prof. Paul v. R. Schleyer on the occasion of his 75th birthday

Keywords: Chelates / Ligand design / Triazapentadienes / N ligands / Tautomerism / DFT calculations

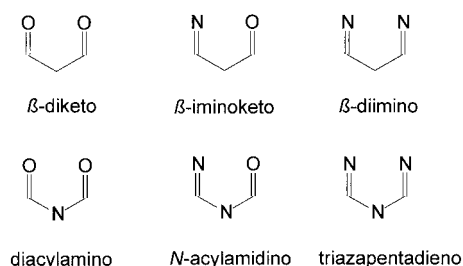
1,2,4-Triphenyl-1,3,5-triazapentadiene (**1a**), prepared from benzamidine and *N*-phenylbenzimidoyl chloride, was treated at room temperature with CoCl₂, Ni(NO₃)₂, Na₂PdCl₄, CuCl₂ and ZnCl₂ to form the corresponding six-membered 1:1 chelate complexes **1a**·CoCl₂, **1a**·Ni(NO₃)₂, **1a**·PdCl₂, **1a**·CuCl₂, and **1a**·ZnCl₂. In the solid state **1a**·Ni(NO₃)₂ forms infinite linear chains, bridged by nitrate ions. From **1a** and Cu(OTf)₂ a 2:1 copper complex was obtained [(**1a**)₂·Cu(OTf)₂]. In all cases a proton shift from nitro-

gen atom N1 in the free ligand to N3 in the complex was observed. All complexes were completely characterized including X-ray crystallography. Quantum chemical DFT calculations indicate that triazapentadiene is a better ligand for ZnCl₂, PdCl₂ and CuCl₂ compared to β-diimines and *N*-acylamidines.

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Introduction

1,3-Dicarbonyl derivatives and their nitrogen analogues (β-iminoketones and β-diimines) present valuable ligands for metal-ion chelation, either as neutral or as anionic species. Our synthetic interest is directed towards the development of analogous ligands, which bear a nitrogen atom in the central position instead of a carbon atom. From this point of view, diacylamines ("imides" in organic nomenclature) may be regarded as nitrogen analogues of β-diketones, *N*-acylamidines as nitrogen analogues of β-iminoketones (β-ketimino) and 1,3,5-triazapentadienes^[1] (tap) as nitrogen analogues of β-diimines (Scheme 1). Some of these compounds have found intensive application in coordination chemistry, as they are quite potent bidentate chelating ligands [see, for example (β-diketiminato)metal complexes^[2]]. The three nitrogen analogues deserve special attention of coordination chemists as they offer an additional coordination site at the central nitrogen atom, especially in their anionic form.



Scheme 1. Chelating ligands.

1,3,5-Triazapentadienes have rarely been used for the synthesis of metal complexes. However, already in 1907 Ley and Müller reported on the preparation of triazapentadienes and their successful complexation with cobalt(II) acetate, copper(II) acetate and nickel(II) acetate.^[3] However, the nature of these complexes remained unclear. Many years later, Breuer and Small prepared a 1,3,5-triazapentadiene ligand starting from benzylamine, ethyl orthoformate and *N,N*-dibenzylformamide.^[4] They obtained a blue (1,3,5-triazapentadiene)copper(II) chelate complex after treatment with copper(II) acetate in methanol. Siedle et al. treated a perfluorated imidoyl fluoride with 2 mol-equiv. of aniline to obtain a perfluorated 1,3,5-triazapentadiene derivative, which may be converted into the corresponding 1,3,5-triazapentadienyl anion using *n*-butyllithium.^[5] Treatment with silver oxide afforded the respective six-membered ring chelate silver complex, which in turn could be transmetallated to the

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corresponding Pd^{II}, Ir^{III} and Rh^{III} chelate complexes. Similarly, Fe^{II}, Co^{II} and Cu^{II} complexes were obtained by transmetallation of the corresponding potassium compound. Copper(I) and silver(I) complexes of fluorinated triazapentadienyl ligands were recently reported by Dias and Singh.^[6,7]

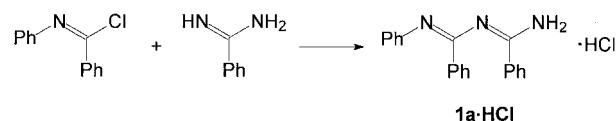
However, there are several examples in the literature, where 1,3,5-triazapentadienes have been formed in situ from simpler amino compounds in the course of template reactions. For instance, Turnbull et al. treated Cu(ClO₄)₂·6H₂O with triazine in 95% methanol.^[8] They obtained in 25% yield a 2:1 six-membered chelate Cu^{II} complex of the parent 1,3,5-triazapenta-1,4-diene, which was interpreted to be the result of copper(II)-catalyzed hydrolysis of triazine.^[9] Analogously, tris(2-pyridyl)triazine may be hydrolyzed in the presence of copper(II) acetate to give bis[2,4-di(2-pyridyl)-1,3,5-triazapentadienyl]copper(II) complexes, either employing the corresponding triazapentadienes as neutral ligands or as anions after deprotonation.^[10] Interestingly, the two nitrogen atoms in 1 and 5 position of the triazapentadiene act as coordination sites, not the 2-pyridyl subunits. Barker et al. reported on the in situ formation of the 2,4-diphenyl-1,3,5-triazapentadienyl ligand, when lithiobenzamidine was treated with Pt(PhCN)₂Cl₂ in ethereal solution. They isolated the 2:1 Pt^{II} chelate complex as a result of a nucleophilic attack of the benzamidine anion on the complexed benzonitrile. Similarly, a Pd^{II} complex was obtained from lithiobenzamidine and Pd(PhCN)₂Cl₂.^[11] Acetamidine undergoes a self-condensation reaction to form a 2,4-dimethyl-1,3,5-triazapentadiene ligand when treated with nickel(II) chloride hexahydrate in methanol. The resulting Ni^{II} chloride chelate complex contains two neutral tautomers of the triazapentadiene units each with a proton at the central N3 position.^[12] Nickel(II) chloride reacts with nitriles in the presence of oximes to form 2:1 chelate complexes.^[13]

In this report we describe our experiments on the synthesis and thorough structural characterization of (1,3,5-triazapentadiene)metal complexes, of which some examples already were obtained by Ley and Müller in 1907.^[3] These studies were part of an extended project concerning the application of 1,3,5-triazapentadienes for the synthesis of longer oligonitriles of the general formula R₂N–(CR=N)_n–CR=NR.^[14]

Results and Discussion

As a typical, stable example 1,2,4-triphenyl-1,3,5-triazapentadiene (**1a**) was chosen as starting material for various complexation experiments. Its preparation is based on a procedure given by Ley and Müller,^[3] according to which benzamidine is treated with *N*-phenylbenzimidoyl chloride. These authors used an equimolar surplus of amidine to trap the formed hydrochloride. In our experiments, this procedure did not work very successfully because of severe separation problems. We found it easier to use equimolar amounts of amidine and imidoyl chloride. Under these con-

ditions mixtures of amidine hydrochloride and triazapentadienyl chloride **1a**·HCl are formed. However, the amidine hydrochloride was easily removed by washing with hot water in an ultrasonic bath. The free triazapentadiene **1a** was subsequently obtained in 29% yield after treatment with 2 N sodium hydroxide solution and repeated extraction with dichloromethane.



Triazapentadienes are expected to be subject of tautomerism.^[14] However, in our NMR, IR and X-ray studies all evidence is in favor for the indicated 1,3,5-triazapenta-1,3-diene structure **1a**. Indications for a tautomeric 1,3,5-triazapenta-1,4-diene structure were not observed.

Metal Complexes

Various metal complexes of triazapentadiene **1a** were easily obtained by co-dissolving metal salts with the ligand **1a** and crystallization, which was usually induced by adding less polar solvents to the reaction mixture.

Complex **1a**·CoCl₂

The deep blue complex **1a**·CoCl₂ is obtained from **1a** and cobalt(II) chloride hexahydrate after stirring of the components in acetonitrile in 72% yield as a fine precipitate. Recrystallisation from acetonitrile/DMF (1:1) and little diethyl ether produced a single crystal, suitable for X-ray analysis. The crystal system is triclinic (*P* $\bar{1}$) with two molecules in the unit cell. As Figure 1 shows, the ligand adopts now the tautomeric structure of a triazapenta-1,4-diene acting as a chelating ligand forming a six-membered 1:1 chelate with a tetrahedral Co^{II} moiety (compare ref.^[15]).

Complex **1a**·Ni(NO₃)₂

From equimolar amounts of **1a**, dissolved in DMF, and nickel(II) nitrate hexahydrate, dissolved in ethanol, an amorphous lilac precipitate **1a**·Ni(NO₃)₂ is formed upon diffusion of diethyl ether. Dissolving in acetonitrile and repeated diffusion of diethyl ether yields turquoise needles in 76% yield, which are monoclinic (*P*2₁/*c*) and contain four molecules and four ethanol molecules in a unit cell. As Figures 2 and 3 display, a six-membered 1:1 chelate complex is formed and again a proton shift in the ligand from N1 to N3 is observed. In addition to ligand **1a**, one nitrate unit is coordinated in a bidentate fashion and two other ones are coordinated in a monodentate fashion to the Ni^{II} ion, forming an infinite chain structure with octahedral coordination sphere around Ni^{II}. A 2:1 nickel complex of another triazapentadiene system (acetimidoylacetamidine) has been reported by Norrestam.^[12] Some of the corresponding diiminonickel complexes (β -iminoamino complexes) are known.^[16]

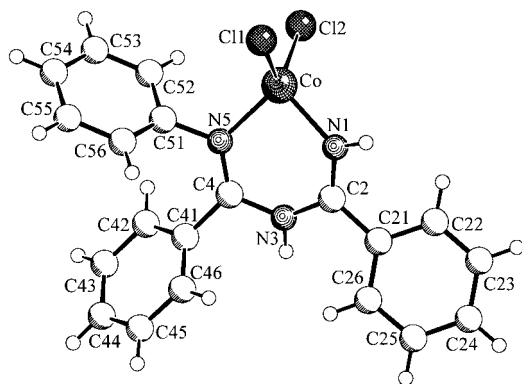


Figure 1. Molecular structure of complex **1a·CoCl₂** in the solid state (crystallographic numbering). Selected structural parameters: Bond lengths [Å] Co–Cl1 2.2472(5), Co–Cl2 2.2543(5), Co–N1 1.9785(14), Co–N5 2.0067(13), N1–C2 1.290(2), C2–N3 1.3836(19), N3–C4 1.3878(19), C4–N5 1.2923(19); bond angles [°] N1–Co–N5 91.68(5), N1–Co–Cl1 109.87(4), N5–Co–Cl1 115.55(4), N1–Co–Cl2 114.59(4), N5–Co–Cl2 109.25(4), Cl1–Co–Cl2 114.03(2), N1–C2–N3 121.34(14), C2–N3–C4 129.87(13), N3–C4–N5 121.88(13); torsional angles [°] Co–N1–C2–N3 –7.19, N1–C2–N3–C4 –15.96, C2–N3–C4–N5 21.57, N3–C4–N5–Co –3.18, N5–Co–N1–C2 16.83, N1–C2–C21–C22 –24.73, N5–C4–C41–C42 48.87, C4–N5–C51–C52 59.23.

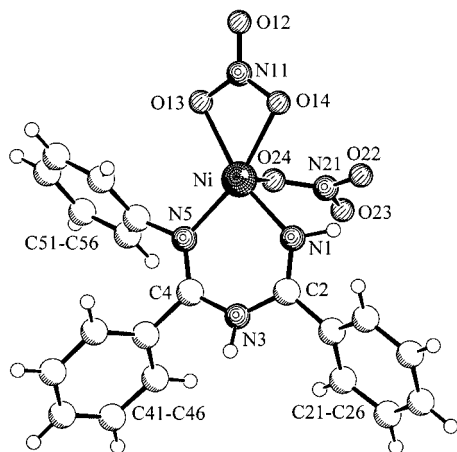


Figure 2. Molecular structure of one independent unit of **1a·Ni(NO₃)₂** in the solid state (crystallographic numbering). Selected structural parameters: Bond lengths [Å] Ni–O13 2.117(2), Ni–O14 2.124(2), Ni–O23* 2.090(2), Ni–O24 2.112(2), Ni–N1 1.969(3), Ni–N5 2.037(2), N1–C2 1.280(4), C2–N3 1.382(4), N3–C4 1.382(4), C4–N5 1.286(4); bond angles [°] N1–Ni–N5 90.69(11), N1–Ni–O23* 96.89(10), N5–Ni–O23* 86.26(10), N1–Ni–O24 90.62(10), N5–Ni–O24 86.42(9), O23*–Ni–O24 169.57(8), N1–Ni–O13 164.70(10), N5–Ni–O13 104.15(10), N1–Ni–O14 104.16(10), N5–Ni–O14 165.02(10), O13–Ni–O14 61.19(9), N1–C2–N3 121.5(3), C2–N3–C4 130.3(3), N3–C4–N5 123.2(3); torsional angles [°] O12–N11–O13–Ni –179.47, O13–Ni–N1–C2 –168.54, O13–Ni–N5–C4 –176.35, Ni–N1–C2–N3 –3.53, N1–C2–N3–C4 7.59, C2–N3–C4–N5 –2.10, N3–C4–N5–Ni –6.41, N5–Ni–N1–C2 –2.50, N1–C2–C21–C26 38.18, N5–C4–C41–C46 –61.27, C4–N5–C51–C52 –60.09.

Complex **1a·PdCl₂**

A Pd^{II} complex was obtained from equimolar amounts of **1a** and Na₂PdCl₄ in DMF as solvent upon diffusion of diethyl ether into the reaction mixture. Orange small tiles

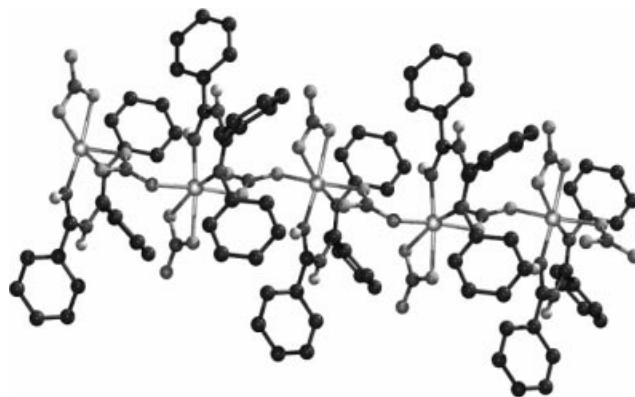


Figure 3. Plot of a part of the infinite chain structure of **1a·Ni(NO₃)₂** in the solid state.

were formed in 66% yield. They form a triclinic lattice (*P* $\bar{1}$) with two molecules and four DMF molecules in the unit cell. The X-ray diffraction of **1a·PdCl₂** (Figure 4) shows again the formation of a six-membered chelate 1:1 complex with a proton at the central nitrogen atom as a result of a proton shift. The chelate ring is not exactly planar, but slightly distorted with torsional angles up to 10° in a boat-shape fashion. As expected, Pd^{II} is square-planar coordinate. The corresponding (β -diimino)Pd^{II} complexes are reported to have catalytic activity in ethylene polymerization reactions.^[17]

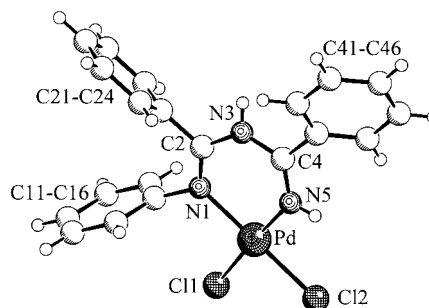


Figure 4. Molecular structure of one independent unit of **1a·PdCl₂** in the solid state (crystallographic numbering). Selected structural parameters: Bond lengths [Å] Pd–Cl1 2.2968(6), Pd–Cl2 2.3087(6), Pd–N1 2.0421(17), Pd–N5 1.9809(18), N1–C2 1.293(3), C2–N3 1.376(3), N3–C4 1.368(3), C4–N5 1.280(3); bond angles [°] N1–Pd–N5 89.49(7), N1–Pd–Cl1 93.51(5), N5–Pd–Cl1 176.96(6), N1–Pd–Cl2 175.85(5), N5–Pd–Cl2 87.70(6), Cl1–Pd–Cl2 89.33(2), N1–C2–N3 124.41(19), C2–N3–C4 129.36(18), N3–C4–N5 121.49(19); torsional angles [°] Pd–N1–C2–N3 0.78, N1–C2–N3–C4 –9.96, C2–N3–C4–N5 5.01, N3–C4–N5–Pd 8.79, N5–Pd–N1–C2 7.55, C2–N1–C11–C12 93.78, N1–C2–C21–C22 –66.94, N5–C4–C41–C46 39.49.

Complexes **1a·CuCl₂** and **(1a)₂·Cu(OTf)₂**

Equimolar amounts of ligand **1a** and copper(II) chloride dihydrate in ethanol yielded dark green little tiles in 46% yield after diffusion of diethyl ether. They crystallize in the triclinic space group *P* $\bar{1}$ with two molecules and two molecules of ethanol in the unit cell. Figure 5 shows the 1:1 chelate complex formed, again with a proton at N3 after a shift from position N1 of the free ligand. The six-membered

chelate ring has a clear boat shape with Cu^{II} and N3 significantly above the plane of the four other atoms. The Cu^{II} ion displays a distorted tetrahedral coordination as a result of a Jahn–Teller distortion in this d⁹ copper compound.

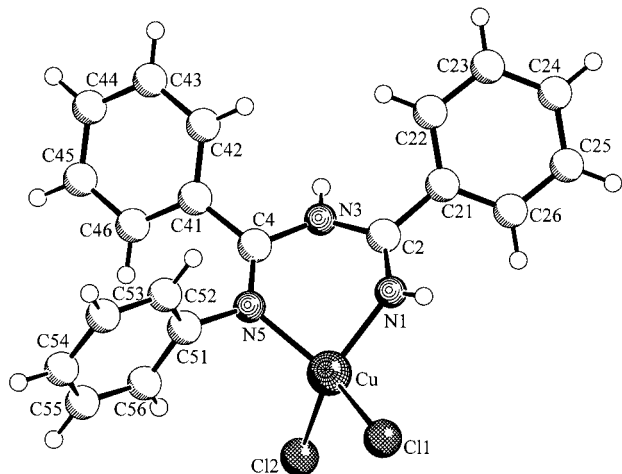


Figure 5. Molecular structure of one independent unit of **1a**·CuCl₂ in the solid state (crystallographic numbering). Selected structural parameters: Bond lengths [Å] Cu–Cl1 2.2290(8), Cu–Cl2 2.2281(8), Cu–N1 1.928(2), Cu–N5 1.986(2), N1–C2 1.278(3), C2–N3 1.372(3), N3–C4 1.386(3), C4–N5 1.298(3); bond angles [°] N1–Cu–N5 87.90(9), N1–Cu–Cl1 97.87(8), N5–Cu–Cl1 142.89(7), N1–Cu–Cl2 138.42(8), N5–Cu–Cl2 99.28(7), Cl1–Cu–Cl2 100.21(3), N1–C2–N3 121.2(2), C2–N3–C4 126.5(2), N3–C4–N5 119.9(2); torsional angles [°] Cu–N1–C2–N3 19.50, N1–C2–N3–C4 19.74, C2–N3–C4–N5 –26.38, N3–C4–N5–Cu –5.96, N5–Cu–N1–C2 –35.97, N1–C2–C21–C26 37.39, N5–C4–C41–C46 –41.60, C4–N5–C51–C52 –70.68.

Reaction of ligand **1a** with copper(II) triflate in the molar ratio 2:1 in acetonitrile yielded a dark green solution, from which blue-violet rod-like crystals were obtained in 54% yield after diffusion of diethyl ether.^[18] They crystallize in the triclinic space group *P* $\bar{1}$ with two molecules and two molecules of diethyl ether in the unit cell. From Figure 6 a 2:1 chelate complex can be derived. The ligands from two six-membered chelate rings with the mobile protons at position N3/N3*. Cu^{II} is square-planar coordinate with two additional longer contacts to the triflate counterions (2.498 Å). A 2:1 chelate complex of the parent 1,3,5-triazapentadiene, which was formed in situ by hydrolysis of triazine, has been reported by Turnbull et al.^[8]

Complex **1a**·ZnCl₂

Addition of a solution of zinc(II) chloride hydrate in ethanol to an ethanolic solution of triazapentadiene **1a** leads to a fine, colorless precipitate, from which a few single crystals **1a**·ZnCl₂ were obtained after dissolving in little DMF and infusion of diethyl ether. **1a**·ZnCl₂ crystallizes in the triclinic space group *P* $\bar{1}$ with two molecules in the unit cell. The X-ray analysis indicates the formation of a 1:1 chelate complex (Figure 7). The Zn^{II} ion displays a tetrahedral coordination. The complex **1a**·ZnCl₂ is not planar, but shows a weak distortion towards boat shape. As in the other examples discussed before, a proton shift from the terminal amino group of **1a** to nitrogen atom N3 accompanies the

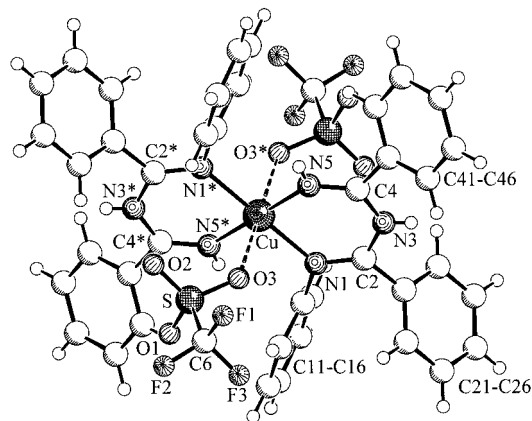


Figure 6. Molecular structure of one independent unit of (**1a**)₂·Cu(OTf)₂ in the solid state (crystallographic numbering). Selected structural parameters: Bond lengths [Å] Cu–N1 2.0613(17), Cu–N5 1.9466(18), Cu–O3(18), 2.498(18), N1–C2 1.291(3), C2–N3 1.376(3), N3–C4 1.371(3), C4–N5 1.286(3); bond angles [°] N1–Cu–N5 86.36(7), N1–Cu–N1* 180.00(10), N5–Cu–N1* 93.64(7), N1–Cu–N5* 93.46(7), N5–Cu–N5* 180.00(10), N1*–Cu–N5* 86.36(7), N1–C2–N3 123.29(18), C2–N3–C4 127.62(18), N3–C4–N5 121.45(19); torsional angles [°] Cu–N1–C2–N3 9.89, N1–C2–N3–C4 2.08, C2–N3–C4–N5 –3.99, N3–C4–N5–Cu –7.47, N5–Cu–N1–C2 –14.13, C2–N1–C11–C12 –73.41, N1–C2–C21–C22 –63.75, N5–C4–C41–C42 –41.03, N1*–Cu–N5–C4 –166.64, N5*–Cu–N1–C2 165.87.

complexation. 2,4,6,8,8-Pentakis(dimethylamino)-1-oxa-3,5,7-aza-1,3,5,7-octatetraene, which may be regarded to include a triazapentadiene subunit, forms with ZnCl₂ a six-membered chelate complex, where ZnCl₂ bridges oxygen and nitrogen atoms.^[19] (β-Diimino)Zn complexes are well known for their catalytic activity in CO₂/oxirane copolymerisations.^[20]

Quantum Chemical Calculations

In order to rationalize the ability of the triazapentadiene ligand to coordinate to metal ions in comparison with similar systems (β-diimines, *N*-acylamidines) and to investigate their propensity for proton shifts in going from the free ligand to the chelate complex quantum chemical model calculations on the DFT level were performed. Zn^{II} and Pd^{II} complexes were investigated as typical (diamagnetic) examples of the complexes experimentally studied. The B3LYP hybrid functional was used together with the basis sets 6-31G*, 6-31+G(d,p), and MP2 and SCS-MP2^[21] single points for the Zn^{II} compounds, and 6-31G*, 6-31+G(d,p) for C, H, N, O, Cl and the Stuttgart-Dresden Pd-ECP MWB^[22] for the Pd^{II} complexes. All structures were completely optimized. The energies reported include zero point correction (no scaling). The G98 program^[23] was employed using the build-in basis sets. BSSE effects^[24] were considered using the counterpoise method as implemented in G03.^[25]

As a measure for the tendency of the ligand to form chelate complexes simply the reaction energy of the complexation reaction was calculated, starting from free ZnCl₂ or

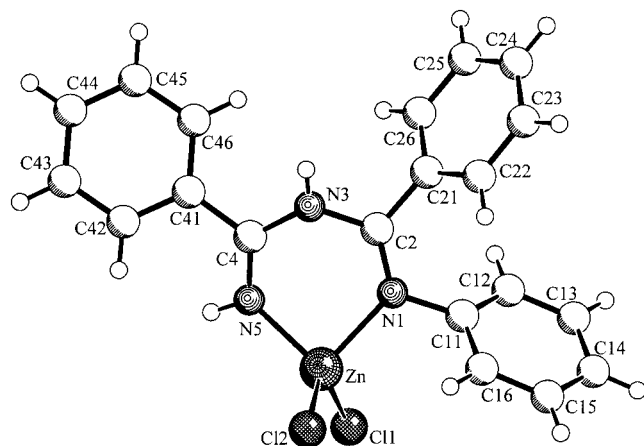
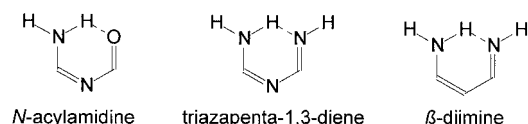


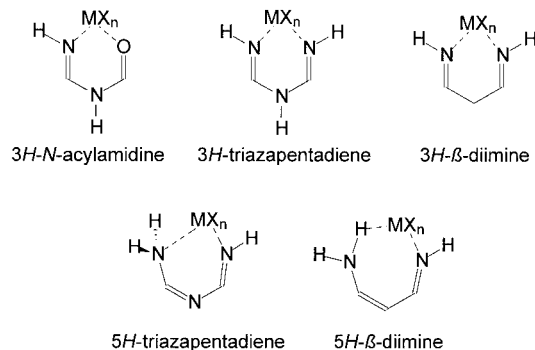
Figure 7. Molecular structure of one independent unit of **1a**· ZnCl_2 in the solid state (crystallographic numbering). Selected structural parameters: Bond lengths [Å] $\text{Zn}-\text{Cl1}$ 2.2221(4), $\text{Zn}-\text{Cl2}$ 2.2394(5), $\text{Zn}-\text{N1}$ 2.0615(12), $\text{Zn}-\text{N5}$ 1.9818(12), $\text{N1}-\text{C2}$ 1.2935(17), $\text{C2}-\text{N3}$ 1.3903(18), $\text{N3}-\text{C4}$ 1.3816(18), $\text{C4}-\text{N5}$ 1.2856(18); bond angles [°] $\text{N1}-\text{Zn}-\text{N5}$ 90.48(5), $\text{N1}-\text{Zn}-\text{Cl1}$ 109.12(4), $\text{N5}-\text{Zn}-\text{Cl1}$ 112.90(4), $\text{N1}-\text{Zn}-\text{Cl2}$ 109.73(4), $\text{N5}-\text{Zn}-\text{Cl2}$ 114.23(4), $\text{Cl1}-\text{Zn}-\text{Cl2}$ 117.030(16), $\text{N1}-\text{C2}-\text{N3}$ 121.88(12), $\text{C2}-\text{N3}-\text{C4}$ 130.92(12), $\text{N3}-\text{C4}-\text{N5}$ 120.93(12); torsional angles [°] $\text{Zn}-\text{N1}-\text{C2}-\text{N3}$ 3.05, $\text{N1}-\text{C2}-\text{N3}-\text{C4}$ -20.12, $\text{C2}-\text{N3}-\text{C4}-\text{N5}$ 12.14, $\text{N3}-\text{C4}-\text{N5}-\text{Zn}$ 12.15, $\text{N5}-\text{Zn}-\text{N1}-\text{C2}$ 11.87, $\text{C2}-\text{N1}-\text{Cl1}-\text{Cl2}$ -55.12, $\text{N1}-\text{C2}-\text{C21}-\text{C22}$ -49.66, $\text{N5}-\text{C4}-\text{C41}-\text{C42}$ 22.42.

PdCl_2 in the gas phase and the free ligands in their lowest energy hydrogen-bonded conjugated form (Scheme 2).^[16] For triazapentadiene and β -diimine two types of complexes were considered: first, the chelate complex involving a ligand after proton shift (“3H ligand”), second, a complex with a ligand in its original enolized form (“5H ligand”) (Scheme 3). For the latter structures, at higher levels of DFT theory, the geometry optimizations opened the chelate structure in favor of hydrogen bonds from the chlorine atoms to the amino groups. In substituted derivatives as studied experimentally 5H-type structures were not observed (see above).



Scheme 2. Free ligands in their best gas phase structure (reference structures).

Among the ZnCl_2 compounds on all levels of theory triazapentadiene forms the strongest complexes acting as symmetrical ligand after proton shift from N1 to N3 (3H form) (Table 1). Indeed, this kind of coordination is experimentally observed (see above). The β -diimino ligand comes second in its two tautomeric forms, whereas (*N*-acylamidine) ZnCl_2 complexes are significantly less stable (by 5.0–5.7 kcal/mol). The β -diimino ligand is surprisingly differently treated by the theoretical methods employed. The DFT methods predict a better complexation energy for the ligand in its 5H form compared to the 3H form, probably



Scheme 3. Types of complexes (first row involving 3H ligands, second row 5H ligands).

due to the hydrogen bond formed. The MP2 single points, however, strongly favor the 3H form, which is known from many complexes.^[2] The reason for this special behavior of the DFT methods remains unclear. For triazapentadiene, all methods prefer the 3H complexes over the 5H forms by 2.2–7 kcal/mol.

In the PdCl_2 series of chelate complexes (Table 2) a similar superiority of the triazapentadiene complex in its 3H form is found in accordance with the experimental findings (see above). Here, the β -diimine complexes come second (3.7–6.5 kcal/mol), whereas *N*-acylamidine forms the weakest complexes towards PdCl_2 .^[26,27] Both 5H forms of triazapentadiene and β -diimine bind significantly weaker than their 3H isomers and are therefore not expected to coordinate without tautomerism.

(*N*-Acylamidine)-^[26] and (β -diimine) PdCl_2 ^[17] complexes have found interest due to their potential as catalyst precursors.

For CuCl_2 preliminary UB3LYP/6-31+G(d,p) calculations (including ZPE and BSSE), which may probably be insufficient for such open-shell systems, indicate again best binding to triazapentadiene (−19.5 kcal/mol), whereas *N*-acylamidine and β -diimine coordinate weaker (−15.8 and −12.9 kcal/mol, respectively).

It is interesting to note that according to the gas-phase calculations triazapentadiene generally is a better ligand for ZnCl_2 , PdCl_2 and CuCl_2 compared to β -diimine. Besides the electron-donating influence of the central nitrogen atom its ability to allow π -conjugation over all five centers of the neutral ligand may be the reason for this observation. Thus, the introduction of the nitrogen atom in 3-position of β -diimine enhances the coordination ability of such chelating systems. This conclusion may be of importance with regard to the catalytic properties of such chelate complexes, e.g. as polymerization catalysts.

The comparison of the ZnCl_2 , PdCl_2 and CuCl_2 complexation energies at similar levels of theory quantifies the common experience of significantly higher values for the PdCl_2 complexes as metal ion of the second transition row, whereas CuCl_2 and ZnCl_2 are coordinated with similar strength.

Table 1. Quantum chemical complexation energies for ZnCl₂ model complexes at various computational levels including ZPE+BSSE [kcal/mol].

Ligand at ZnCl ₂	B3LYP/6-31G(d) ^[a]	B3LYP/6-31+G(d,p) ^[a]	MP2/6-31+G(d,p) ^[b]	SCS-MP2/6-31+G(d,p) ^[b]
<i>N</i> -Acylamidine	−12.74	−13.95	−16.28	−16.22
3 <i>H</i> -Triazapentadiene	−18.23	−19.64	−21.47	−21.21
5 <i>H</i> -Triazapentadiene	−16.05	−17.35	−15.92	−14.88
3 <i>H</i> -β-Diimine	−13.27	−12.33	−18.12	−18.68
5 <i>H</i> -β-Diimine, H-bridged	−14.72	−17.19	−14.14	−13.01

[a] Fully geometry optimized. [b] Single points on B3LYP/6-31+G(d,p) geometries.

Table 2. Quantum chemical complexation energies for PdCl₂ model complexes at various computational levels including ZPE and BSSE (only column 4) [kcal/mol].

Ligand at PdCl ₂	B3LYP/6-31G(d)/MWB ^[a]	B3LYP/6-31+G(d,p)/MWB ^[a]	B3LYP/6-31+G(d,p)/MWB ^[a] +BSSE
<i>N</i> -Acylamidine	−45.90	−40.19	−37.23
3 <i>H</i> -Triazapentadiene	−63.37	−58.20	−54.51
5 <i>H</i> -Triazapentadiene	−47.14	−41.08	−37.67
3 <i>H</i> -β-Diimine	−59.73	−51.67	−48.19
5 <i>H</i> -β-Diimine	−53.95	−47.53	−43.90

[a] Fully geometry optimized.

Conclusions

Triazapentadienes, easily prepared from amidines and imidoyl halides, are potent chelating ligands for metal complexation. 1,2,4-Triphenyl-1,3,5-triazapentadiene (**1a**) forms 1:1 six-membered chelate complexes with CoCl₂, Ni(NO₃)₂, Na₂PdCl₄, CuCl₂ and ZnCl₂, and additionally one 2:1 complex with Cu(OTf)₂. In the case of the Ni^{II} complex, a linear chain structure resulting from NO₃ bridging was observed. All new complexes have been fully characterized including X-ray crystallography.

By use of DFT-B3LYP calculations the relative complexation energies of model triazapentadiene, *N*-acylamidine and β-diimino ligands binding to ZnCl₂, CuCl₂ and PdCl₂ in the gas phase were evaluated. According to these theoretical results triazapentadiene binds stronger to these metal salts than β-diimine and *N*-acylamidine. For β-diimine and triazapentadiene, tautomeric complexes, characterized by the 3*H* and 5*H* form of the ligand, respectively, are discussed.

Experimental Section

Materials and Methods: IR: Nicolet 5DXC. ¹H NMR: Bruker WM 300 (300.13 MHz), Bruker AM 360 (360.13 MHz), Bruker AMX 400 (400.13 MHz) and Varian Unity plus (599.86 MHz), internal reference tetramethylsilane. ¹³C NMR: Bruker WM 300 (75.47 MHz), Bruker AMX 400 (100.61 MHz) and Varian Unity 600 plus (150.85 MHz), internal reference tetramethylsilane or solvent. MS: MAT C 312, Finnigan (70 eV). ESI-MS: Quattro LC-Z, Micromass. MALDI (16–19 kV), nitrogen (337 nm, 3 ns); matrix: DTBC (2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene] malononitrile). UV/Vis: Cary 1 Bio, Varian. CHN: Elementar Vario El III. Melting points are uncorrected.

1,2,4-Triphenyl-1,3,5-triazapenta-1,3-diene (1a): In analogy to a literature procedure,^[3] 7.73 g (64.7 mmol) of benzamidine was suspended in 20 mL of diethyl ether. 13.88 g (64.7 mmol) of *N*-phenylbenzimidoyl chloride,^[28] dissolved in 40 mL of diethyl ether, was

added dropwise. After stirring at room temperature for 2 h, the reaction mixture was heated to reflux for 1 h. The precipitate was removed by filtration and was treated with hot water in an ultrasonic bath in order to remove benzamidine hydrochloride. The remaining light yellow residue was separated and treated with 50 mL of 2 N sodium hydroxide solution. The suspension was extracted with portions of dichloromethane as long as solid was present in the reaction mixture. The combined organic layers were dried with magnesium sulfate. The solvent was removed under reduced pressure. Yield 5.54 g (18.5 mmol, 29%), light yellow solid, m.p. 143 °C (ref.^[3] 152 °C). IR (KBr): $\tilde{\nu}$ = 3483, (s, NH₂), 3379 (s, NH₂), 3057 (m, CH_{arom.}), 3026 (w, CH_{arom.}), 2997 (w, CH_{arom.}), 1645 (vs, C=N), 1599 (vs, C=C_{arom.}), 1586 (vs, C=C_{arom.}), 1483 (m), 1448 (m), 1367 (s), 1315 (m), 1269 (m), 1227 (m), 1175 (w), 1074 (w), 1013 (m), 935 (w), 921 (w), 837 (m), 810 (m), 787 (m), 758 (s), 702 (vs) cm^{−1}. ¹H NMR (300 MHz, CDCl₃): δ = 6.80 (br., 2 H, NH₂), 6.93–6.99 (m, 1 H, CH_{arom.}), 7.05–7.08 (m, 2 H, CH_{arom.}), 7.22–7.28 (m, 2 H, CH_{arom.}), 7.41–7.51 (m, 6 H, CH_{arom.}), 7.78–7.81 (m, 2 H, CH_{arom.}), 8.01–8.05 (m, 2 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 122.0, 123.1, 128.0, 128.7, 128.9, 131.0, 131.3 (C_{arom.}), 135.4 (*i*-C_{arom.}), 136.9 (*i*-C_{arom.}), 151.8 (*i*-C_{arom.}), 154.7 (C=N), 161.7 (C=N) ppm. MS (70 eV): m/z (%) = 300 (14) [M⁺ (¹³C)], 299 (77) [M⁺], 298 (83) [M⁺ − 1], 196 (18) [M⁺ − PhCN], 180 (100) [PhCNPh⁺], 104 (57) [PhCN⁺ + 1], 103 (25) [PhCN⁺], 93 (32) [PhNH⁺ + 2], 77 (84) [Ph⁺], 51 (11) [C₄H₃⁺]. C₂₀H₁₇N₃ (299.36): calcd. C 80.24 H 5.72 N 14.04; found C 80.13 H 5.38 N 14.03.

(1,2,4-Triphenyl-1,3,5-triazapenta-1,4-diene)cobalt(II) Chloride (1a·CoCl₂): 30 mg (0.10 mmol) of triazapentadiene **1a** and 24 mg (0.10 mmol) of cobalt(II) chloride hexahydrate were dissolved in 1 mL of acetonitrile. The resulting blue precipitate was filtered off. Yield 34 mg (0.07 mmol, 72%), blue powder, m.p. 208 °C. IR (KBr): $\tilde{\nu}$ = 3244 (s, NH), 3202 (m, NH), 3088 (m, CH_{arom.}), 3063 (m, CH_{arom.}), 3034 (m, CH_{arom.}), 1630 (vs, C=N), 1578 (s, C=C_{arom.}), 1504 (vs, C=C_{arom.}), 1493 (s, C=C_{arom.}), 1450 (m), 1375 (m), 1299 (m), 1275 (m), 1211 (m), 1138 (m), 852 (w), 781 (w), 752 (m), 696 (s) cm^{−1}. MS (MALDI, Matrix DCTB): m/z (%) = 393–397 [C₂₀H₁₆N₃CoClH⁺], 358 [C₂₀H₁₆N₃CoH⁺], 300 [C₂H₁₇N₃H⁺]. UV/Vis (dichloromethane): $\lambda_{\max}$ ($\tilde{\nu}$, ϵ) = 621 (16103, 436), 542 (18450, 129), 364 (27473, 1124), 302 (33113, sh, 2351), 244 (40984,

20346), 227 (44053 cm⁻¹, sh, 14526 m⁻¹ cm⁻¹) nm. C₂₀H₁₇ClCoN₃·CH₃CN (470.25): calcd. C 55.97 H 3.99 N 9.79; found C 55.66 H 3.82 N 9.73.

X-ray Crystal Structure Analysis for 1a·CoCl₂:^[29] Formula C₂₀H₁₇Cl₂CoN₃·CH₃CN, *M* = 470.25, blue crystal 0.30 × 0.20 × 0.15 mm, *a* = 10.064(1), *b* = 10.833(1), *c* = 11.996(1) Å, *a* = 105.12(1), *β* = 104.20(1), *γ* = 112.27(1)°, *V* = 1078.2(2) Å³, *ρ*_{calcd.} = 1.448 g cm⁻³, *μ* = 10.59 cm⁻¹, empirical absorption correction (0.742 ≤ *T* ≤ 0.857), *Z* = 2, triclinic, space group *P* $\bar{1}$ (No. 2), *λ* = 0.71073 Å, *T* = 198 K, *ω* and *φ* scans, 12583 reflections collected (*±h*, *±k*, *±l*), [(sin *θ*)/*λ*] = 0.66 Å⁻¹, 5107 independent (*R*_{int} = 0.033) and 4512 observed reflections [*I* ≥ 2σ(*I*)], 269 refined parameters, *R* = 0.029, *wR*₂ = 0.069, max. residual electron density 0.28 (−0.41) e·Å⁻³, hydrogen atoms at N1 and N3 from difference Fourier calculations, others calculated and all refined as riding atoms.

(1,2,4-Triphenyl-1,3,5-triazapenta-1,4-diene)nickel(II) Nitrate [1a·Ni(NO₃)₂]: 30 mg (0.10 mmol) of triazapentadiene **1a** was dissolved in 0.5 mL of DMF and treated with 29 mg (0.10 mmol) of nickel(II) nitrate hexahydrate, dissolved in 1 mL of ethanol. After short shaking, a light-blue clear solution was formed. Diethyl ether was allowed to diffuse into the reaction mixture. After 1 d, a lilac precipitate was formed. It was filtered off and dissolved in 1 mL of acetonitrile. The solution turned blue. After repeated diffusion with diethyl ether, crystals were obtained. Yield 40 mg (0.08 mmol, 76%), turquoise needles, m.p. 209 °C (decomp.) IR (KBr): *ν* = 3350 (br., OH/NH), 1657 (s, C=N), 1614 (s, C=C_{arom.}), 1587 (s, C=C_{arom.}), 1555 (s, C=C_{arom.}), 1490 (s), 1441 (s), 1385 (vs), 1221 (m), 1024 (m), 779 (m), 752 (m), 696 (s) cm⁻¹. MS (MALDI, Matrix DCTB): *m/z* (%) = 655–661 (100) [C₄₀H₃₂N₆NiH⁺], 300 (11) [C₂₀H₁₇N₃H⁺]. UV/Vis (dichloromethane): *λ*_{max} (*ν*, *ε*) = 342 (29240, sh, 651), 272 (36765, sh, 6897), 236 (42373, sh, 22873), 224 (44643 cm⁻¹, 23234 m⁻¹ cm⁻¹) nm. C₂₀H₁₇N₃NiO₆·C₂H₅OH (528.16): calcd. C 50.03 H 4.39 N 13.26; found C 50.84 H 4.53 N 13.25.

X-ray Crystal Structure Analysis for [1a·Ni(NO₃)₂]: Formula C₂₀H₁₇N₃NiO₆·C₂H₅OH, *M* = 528.16, light green crystal 0.50 × 0.15 × 0.05 mm, *a* = 11.961(1), *b* = 9.829(1), *c* = 22.025(1) Å, *β* = 100.63(1)°, *V* = 2544.9(4) Å³, *ρ*_{calcd.} = 1.378 g cm⁻³, *μ* = 8.11 cm⁻¹, empirical absorption correction (0.687 ≤ *T* ≤ 0.961), *Z* = 4, monoclinic, space group *P*2₁/*c* (No. 14), *λ* = 0.71073 Å, *T* = 198 K, *ω* and *φ* scans, 22808 reflections collected (*±h*, *±k*, *±l*), [(sin *θ*)/*λ*] = 0.68 Å⁻¹, 6386 independent (*R*_{int} = 0.037) and 5315 observed reflections [*I* ≥ 2σ(*I*)], 311 refined parameters, *R* = 0.058, *wR*₂ = 0.179, max. residual electron density 1.98 (−0.85) e·Å⁻³ close to solvent molecule, hydrogen atoms at N1 and N3 from difference Fourier calculations, others calculated and all refined as riding atoms, mixture of different solvents refined as disordered ethanol with isotropic thermal displacement parameters.

(1,2,4-Triphenyl-1,3,5-triazapenta-1,4-diene)palladium(II) Chloride (1a·PdCl₂): A mixture of 30 mg (0.10 mmol) of triazapentadiene **1a** and 29 mg (0.10 mmol) of disodium tetrachloropalladate(II) was dissolved in 1.7 mL of DMF. The orange solution was kept in a closed vial until a colorless precipitate was formed, which was filtered off. To the filtrate diethyl ether was allowed to diffuse. After 1 d, orange crystals had formed. Yield 41 mg (0.07 mmol, 66%), orange little tiles, m.p. 220 °C (decomp.). IR (KBr): *ν* = 3352 (m, NH), 3194 (m, NH), 3059 (m, CH_{arom.}), 2999 (m, CH_{arom.}), 2931 (m, CH_{arom.}), 1649 (vs, C=N), 1632 (vs, C=N), 1580 (m, C=C_{arom.}), 1516 (s, C=C_{arom.}), 1487 (s, C=C_{arom.}), 1444 (m), 1387 (s), 1312 (m), 1255 (m), 1217 (m), 1156 (m), 1105 (m), 1026 (w), 868 (w), 773 (m), 719 (m), 700 (s) cm⁻¹. MS (MALDI, Matrix DCTB): *m/z* (%)

= 436–447 [C₂₀H₁₆N₃ClPdH⁺], 404 [C₂₀H₁₇N₃⁺ + DCTB], 300 [C₂₀H₁₇N₃⁺]. UV/Vis (dichloromethane): *λ*_{max} (*ν*, *ε*) = 388 (25773, 308), 276 (36232, sh, 9829), 241 (41494, 31043), 228 (42860 cm⁻¹, sh, 27870 m⁻¹ cm⁻¹) nm. C₂₀H₁₇Cl₂N₃Pd·2 C₃H₇NO (622.86): calcd. C 50.13 H 5.02 N 11.24; found C 49.88 H 5.07 N 11.13.

X-ray Crystal Structure Analysis for 1a·PdCl₂: Formula C₂₀H₁₇Cl₂N₃Pd·2 C₃H₇NO, *M* = 622.86, yellow crystal 0.30 × 0.25 × 0.15 mm, *a* = 10.575(1), *b* = 11.341(1), *c* = 13.196(1) Å, *a* = 67.62(1), *β* = 82.38(1), *γ* = 71.68(1)°, *V* = 1389.1(2) Å³, *ρ*_{calcd.} = 1.489 g cm⁻³, *μ* = 8.92 cm⁻¹, empirical absorption correction (0.776 ≤ *T* ≤ 0.878), *Z* = 2, triclinic, space group *P* $\bar{1}$ (No. 2), *λ* = 0.71073 Å, *T* = 198 K, *ω* and *φ* scans, 11495 reflections collected (*±h*, *±k*, *±l*), [(sin *θ*)/*λ*] = 0.66 Å⁻¹, 6419 independent (*R*_{int} = 0.035) and 5904 observed reflections [*I* ≥ 2σ(*I*)], 335 refined parameters, *R* = 0.029, *wR*₂ = 0.073, max. residual electron density 0.72 (−0.84) e·Å⁻³, hydrogen atoms at N3 and N5 from difference Fourier calculations, others calculated and all refined as riding atoms.

(1,2,4-Triphenyl-1,3,5-triazapenta-1,4-diene)copper(II) Chloride (1a·CuCl₂): A solution of 0.10 mmol (17 mg) of copper(II) chloride dihydrate in 1 mL of ethanol was added dropwise to a solution of 30 mg (0.10 mmol) of triazapentadiene **1a** in 5 mL of ethanol. The mixture turned dark green. After 1 d, dark green crystals had formed upon diffusion with diethyl ether. Yield 22 mg (0.05 mmol, 46%), green little tiles, m.p. 154 °C (decomp.). IR (KBr): *ν* = 3429 (br., s, OH), 3248 (s, NH), 3192 (sh, m, NH), 3061 (m, CH_{arom.}), 3034 (m, CH_{arom.}), 2962 (m, CH_{aliph.}), 2932 (m, CH_{aliph.}), 2883 (br., CH_{aliph.}), 1654 (s, C=N), 1630 (vs, C=C_{arom.}), 1580 (m, C=C_{arom.}), 1497 (vs), 1447 (m), 1381 (m), 1319 (m), 1306 (m), 1281 (m), 1219 (m), 1138 (m), 1076 (m), 1055 (m), 1030 (m), 865 (sh), 854 (m), 787 (m), 771 (m), 750 (m), 716 (m), 700 (s) cm⁻¹. MS (MALDI, Matrix DCTB): *m/z* (%) = 362–365 [C₂₀H₁₆N₃CuH⁺], 300 [C₂₀H₁₇N₃H⁺]. UV/Vis (dichloromethane): *λ*_{max} (*ν*, *ε*) = 407 (24570, 1415), 281 (35587, sh, 10370), 243 (41152 cm⁻¹, 24796 m⁻¹ cm⁻¹) nm. C₂₀H₁₇Cl₂CuN₃·C₂H₅OH (479.87): calcd. C 55.06 H 4.83 N 8.76; found C 54.69 H 4.49 N 8.70.

X-ray Crystal Structure Analysis for 1a·CuCl₂: Formula C₂₀H₁₇Cl₂CuN₃·C₂H₅OH, *M* = 479.87, green crystal 0.25 × 0.10 × 0.05 mm, *a* = 9.562(1), *b* = 10.099(1), *c* = 11.909(1) Å, *a* = 76.21(1), *β* = 78.15(1), *γ* = 83.05(1)°, *V* = 1089.9(2) Å³, *ρ*_{calcd.} = 1.462 g cm⁻³, *μ* = 12.65 cm⁻¹, empirical absorption correction (0.743 ≤ *T* ≤ 0.939), *Z* = 2, triclinic, space group *P* $\bar{1}$ (No. 2), *λ* = 0.71073 Å, *T* = 198 K, *ω* and *φ* scans, 11413 reflections collected (*±h*, *±k*, *±l*), [(sin *θ*)/*λ*] = 0.66 Å⁻¹, 5134 independent (*R*_{int} = 0.043) and 3844 observed reflections [*I* ≥ 2σ(*I*)], 272 refined parameters, *R* = 0.041, *wR*₂ = 0.085, max. residual electron density 0.36 (−0.51) e·Å⁻³, hydrogen atoms at N1 and N3 from difference Fourier calculations, others calculated and all refined as riding atoms.

[Bis(1,2,4-triphenyl-1,3,5-triazapenta-1,4-diene)]copper(II) Triflate [(1a)₂·Cu(OTf)₂]: 30 mg (0.10 mmol) of triazapentadiene **1a** and 18 mg (0.05 mmol) of copper(II) triflate were dissolved in 1 mL of acetonitrile. Then diethyl ether was allowed to diffuse into the green solution. After 4 d, crystals were removed by filtration. Yield 30 mg (0.03 mmol, 54%), blue-violet rods, m.p. 211 °C (decomp.). IR (KBr): *ν* = 3339 (s, NH), 3204 (m, NH), 3099 (m, CH_{arom.}), 3061 (m, CH_{arom.}), 1655 (s, C=N), 1581 (m, C=C_{arom.}), 1520 (vs, C=C_{arom.}), 1447 (m), 1396 (m), 1313 (s), 1283 (vs), 1257 (vs), 1225 (vs), 1167 (s), 1155 (s), 1032 (vs), 921 (w), 852 (m), 810 (w), 783 (m), 721 (m), 696 (s) cm⁻¹. MS (MALDI, Matrix DCTB): *m/z* (%) = 660–664 (28) [C₄₀H₃₂N₆CuH⁺], 362 (22) [C₂₀H₁₆N₃CuH⁺], 300 (100) [C₂₀H₁₇N₃H⁺]. UV/Vis (dichloromethane): *λ*_{max} (*ν*, *ε*) = 373 (26810, 3117), 315 (31746, 11573), 248 (40323, 91178), 228

(43860 cm⁻¹, sh, 59688 M⁻¹ cm⁻¹) nm. C₄₂H₃₄CuF₆N₆O₆S₂·2C₄H₁₀O (1108.65): calcd. C 52.52 H 3.57 N 8.75; found C 52.49 H 3.30 N 8.74.

X-ray Crystal Structure Analysis for [(1a)₂·Cu(OTf)₂]: Formula C₄₀H₃₄CuN₆CF₃SO₃·2C₄H₁₀O, *M* = 1108.65, blue-purple crystal 0.35 × 0.30 × 0.25 mm, *a* = 10.607(1), *b* = 11.703(1), *c* = 12.758(1) Å, *a* = 99.27(1), *β* = 108.30(1), *γ* = 113.76(1)°, *V* = 1298.6(2) Å³, *ρ*_{calcd.} = 1.418 g cm⁻³, *μ* = 5.81 cm⁻¹, empirical absorption correction (0.823 ≤ *T* ≤ 0.868), *Z* = 1, triclinic, space group *P* $\bar{1}$ (No. 2), *λ* = 0.71073 Å, *T* = 198 K, *ω* and *φ* scans, 9438 reflections collected (*±h*, *±k*, *±l*), [(*sinθ*)/*λ*] = 0.68 Å⁻¹, 6383 independent (*R*_{int} = 0.025) and 5446 observed reflections [*I* ≥ 2σ(*I*)], 341 refined parameters, *R* = 0.048, *wR*₂ = 0.131, max. residual electron density 1.05 (−0.47) e·Å⁻³ close to the ether molecules, hydrogen atoms at N3 and N5 from difference Fourier calculations, other calculated and all refined as riding atoms.

(1,2,4-Triphenyl-1,3,5-triazapenta-1,4-diene)zinc(II) Chloride (1a·ZnCl₂): 30 mg (0.10 mmol) of triazapentadiene **1a** was dissolved in 4 mL of ethanol. Insoluble residues were filtered off. Then the solution was treated dropwise with a solution of 14 mg (0.10 mmol) of zinc(II) chloride hydrate in 0.4 mL of ethanol. A light colorless precipitate formed, which was dissolved by addition of as little as possible of DMF. After filtration, diethyl ether was allowed to diffuse, until colorless crystals formed. Low yield, not sufficient for complete analysis and spectroscopy. M.p. 193 °C. MS (MALDI, Matrix DTCB): *m/z* (%) = 398–404 (8) [C₂₀H₁₆N₃ZnClH⁺], 300 (100) [C₂₀H₁₇N₃H⁺].

X-ray Crystal Structure Analysis for 1a·ZnCl₂: Formula C₂₀H₁₇Cl₂N₃Zn, *M* = 435.64, colourless crystal 0.50 × 0.35 × 0.20 mm, *a* = 9.884(1), *b* = 10.390(1), *c* = 11.032(1) Å, *a* = 110.13(1), *β* = 98.74(1), *γ* = 107.80(1)°, *V* = 970.0(2) Å³, *ρ*_{calcd.} = 1.492 g cm⁻³, *μ* = 15.50 cm⁻¹, empirical absorption correction (0.511 ≤ *T* ≤ 0.747), *Z* = 2, triclinic, space group *P* $\bar{1}$ (No. 2), *λ* = 0.71073 Å, *T* = 198 K, *ω* and *φ* scans, 7412 reflections collected (*±h*, *±k*, *±l*), [(*sinθ*)/*λ*] = 0.67 Å⁻¹, 4720 independent (*R*_{int} = 0.016) and 4409 observed reflections [*I* ≥ 2σ(*I*)], 241 refined parameters, *R* = 0.024, *wR*₂ = 0.061, max. residual electron density 0.33 (−0.40) e·Å⁻³, hydrogen atoms at N3 and N5 from difference Fourier calculations, others calculated and all refined as riding atoms.

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