

Synthesis of Secondary, Tertiary and Quaternary 1,3,5-Triazapenta-1,3-dienes and Their Co^{II} , Zn^{II} , Pd^{II} , Cu^{II} and BF_2 Coordination Compounds^[‡]

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The secondary and tertiary 1,3,5-triazapenta-1,3-dienes **2** and **3** are easily obtained by the reaction of *N*-imidoyl chlorides with amidines or from ethyl *N*-imidoylimidoates **5** and primary amines. In a new synthetic pathway the compounds **5** were prepared by the reaction of imidoates in their protonated or free form with *N*-imidoyl chlorides. A quaternary 1,3,5-triazapenta-1,3-diene **4a** is obtained by the reaction of the imidoate **5b** with pyrrolidine. X-ray diffraction studies of the tertiary 1,3,5-triazapenta-1,3-diene **3c** and its protonated form **3c·HCl** allow the comparison of different patterns of intermolecular hydrogen bonding in the solid state. Two equivalents of a secondary 1,3,5-triazapenta-1,3-diene **2** were treated at room temperature after deprotonation with potassium *tert*-butoxide with CuCl_2 , $\text{Ni}(\text{ClO}_4)_2$ or with $\text{Pd}(\text{ac})_2$ (without deprotonation) to give the corresponding neutral 2:1 chelate complexes **(2a)₂·Cu**, **(2a)₂·Ni** and **(2b)₂·Pd**, respectively. A fluorescent boron complex **2b·BF₂** was obtained by

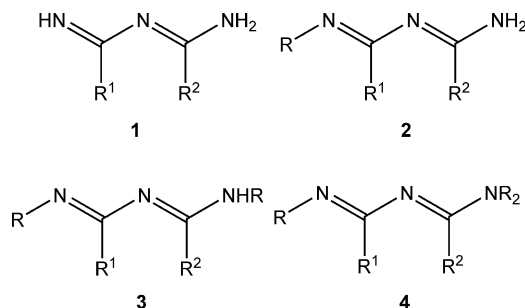
reacting **2b** with boron trifluoride–diethyl ether. From the tertiary triazapentadiene **3c** and CoCl_2 or ZnCl_2 the six-membered 1:1 chelate complexes **3c·CoCl₂** and **3c·ZnCl₂**, respectively, were obtained. In these cases a proton shift from the terminal nitrogen atom of the free ligand to the central nitrogen atom of the complex was observed. Two equivalents of **3c** reacted at room temperature with $\text{Cu}(\text{ac})_2$ or $\text{Pd}(\text{ac})_2$ to form the neutral 2:1 chelate complexes **(3c)₂·Cu** and **(3c)₂·Pd**, respectively. A fluorescent 1:1 boron complex **3c·BF₂** was obtained from **3c** and boron trifluoride–diethyl ether. In all cases the triazapentadienes act as neutral or anionic bidentate ligands to form six-membered chelates with the metal ion or the boron centre. Most of the complexes were completely characterized, which included X-ray crystallography.

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Introduction

Primary (**1**), secondary (**2**), tertiary (**3**) and quaternary (**4**) 1,3,5-triazapenta-1,3-dienes are interesting as nitrogen-rich bidentate ligands for metal ion and Lewis acid coordination forming six-membered chelates (Scheme 1).^[1] In comparison to β -diimines, the additional central nitrogen atom influences the electronic properties of the ligand by its electronegativity and its lone pair, and allows cyclic conjugation not only in its anionic but also in its neutral form. Furthermore, 1,3,5-triazapenta-1,3-dienes offer a potential third coordination site at the central nitrogen atom. There is a close relationship of their chemistry to that of oligonitriles, i.e. they may be considered as amino-substituted dimers of nitriles.^[2]

Several different synthetic routes for primary, secondary and tertiary 1,3,5-triazapentadienes **1–3** have been disclosed. Ley and Müller were the first to prepare secondary triazapentadienes already in 1907 by the reaction of amidines with imidoyl halides.^[3] Subsequently, this method was modified by our group.^[4,5] Tertiary 1,3,5-triazapenta-1,3-



Scheme 1. General structure of 1,3,5-triazapenta-1,3-dienes **1–4**.

dienes **3** were first synthesized by Cooper, Partridge, Oxley and Short using various reaction paths.^[6,7] The synthesis of tertiary perfluoroalkyl-triazapentadienes was achieved by Siedle et al. in 2003.^[8]

Quaternary 1,3,5-triazapenta-1,3-dienes **4** have rarely been reported. By methylation of **3** Cooper, Partridge and Short obtained such a penta-substituted example.^[6] Starting with a *N*-acylamidine, Breslin et al. replaced the $\text{C}=\text{O}$ group by a $\text{C}=\text{S}$ group using Lawesson's reagent. After methylation, the SCH_3 group was exchanged by primary and secondary amines to give the corresponding triazapentadienes.^[9]

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Coordination compounds of triazapentadienes have been known since 1907 from the work of Ley and Müller.^[3] They reported that the formation of neutral 2:1 metal complexes was achieved by reacting secondary 1,3,5-triazapentadienes (**2**) with cobalt(II) acetate, copper(II) acetate and nickel(II) acetate.^[3] However, at that time the nature of these complexes was unclear. Several examples of metal-mediated conversions of nitriles and oximes or imines into 1,3,5-triazapentadiene complexes have been reported by Kukushkin et al.^[10] Zhou et al. reported on the addition reaction of $\text{PhN}(\text{SiMe}_3)\text{M}$ ($\text{M} = \text{Li}$ or Na) or $(\text{Dipp})\text{N}(\text{SiMe}_3)\text{Li}$ with two equivalents of dimethylcyanamide, which led to the corresponding 1,3,5-triazapentadienyl ligand and subsequently to transition metal complexes with nickel(II) and copper(II) ions.^[11]

Some neutral 2:1 complexes with primary 1,3,5-triazapentadienyl ligands were reported by Guo et al. using a multi-step procedure. In 2004 they synthesized a bis(2,4-dipyridyl-1,3,5-triazapentadienato)nickel(II) complex starting from two equivalents of cyanopyridine and $\text{LiN}(\text{SiMe}_3)_2$.^[12]

By ring opening of tri(2-pyridyl)triazine in the presence of the Lewis acid copper(II) acetate and sodium perchlorate in methanol Kajiware et al. obtained a complex chain structure, which was converted to a bis[2,4-di(2-pyridyl)-1,3,5-triazapentadienyl]copper(II) complex by the addition of EDTA.^[13] Access to a neutral copper complex from 4-cyanopyridine, $\text{Cu}(\text{OH})_2$ and $(\text{NH}_4)_2\text{CO}_3$, as an ammonia source, was achieved by Zhang et al. in 2005.^[14]

Tertiary 1,3,5-triazapentadienes **3** as anionic ligands are scarcely investigated. The first neutral 2:1 complex was prepared by Siedle et al. in 2003 by the deprotonation of a tertiary perfluoralkyl-substituted 1,3,5-triazapenta-1,3-diene **3** with potassium hydride and subsequent reaction with metal salts to produce neutral metal ion complexes.^[8] The group of Diaz also reported on fluorinated examples and metal complexes thereof.^[15]

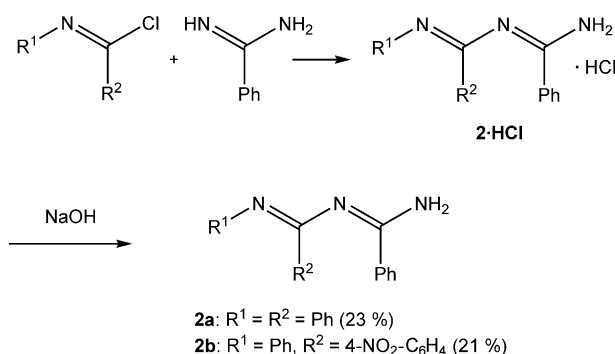
Neutral 1:1 boron complexes containing a 1,3,5-triazapentadienyl ligand are rarely found in the literature. In some of the examples the two terminal, coordinating nitrogen atoms are part of a cyclic system.^[16] The only known neutral boron 1:1 six-membered chelate complex with a primary 1,3,5-triazapentadienyl ligand was prepared by Anderson et al. by adding tris(dimethylamino)borane to a solution of biguanidine in pyridine.^[17]

In this report we describe the synthesis of one novel secondary (**2b**), four new tertiary (**3a–d**) and one new quaternary (**4a**) 1,3,5-triazapentadienes using different reaction pathways. For this purpose a new synthetic route for *N*-imidoylimidoates **5** was developed, which were easily converted into triazapentadienes. We report on the structural properties of imidoate **5a** and the triazapentadiene in its free and protonated form (**3c**, **3c·HCl**) as determined by X-ray diffraction. Furthermore, we present several novel coordination compounds prepared by reactions of **2** and **3** in their neutral or anionic forms with various metal salts and with BF_3 .

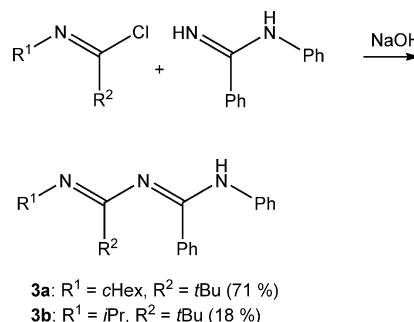
Results and Discussion

Synthesis of 1,3,5-Triazapentadienes

In order to synthesize secondary and tertiary 1,3,5-triazapenta-1,3-dienes **2** and **3** we adapted a procedure used by Ley and Müller^[3] and later modified by HeBe et al.^[4,5] (see Schemes 2 and 3) using imidoyl chlorides and amidines. In the case of benzamidine the use of equimolar amounts of amidine and imidoyl chloride led to the triazapentadienyl cation chlorides **2·HCl**, which were converted into the free forms **2a** and **2b** by treatment with a 2 N sodium hydroxide solution.



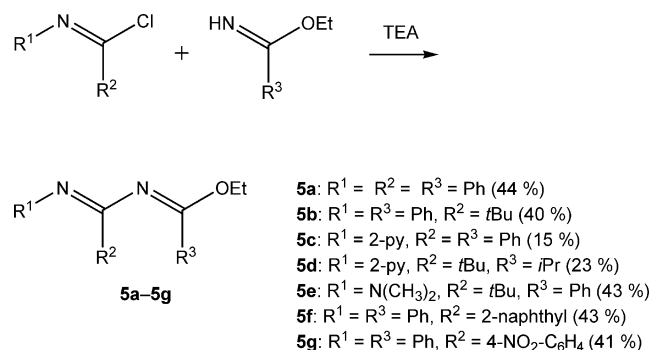
Scheme 2. Synthesis of secondary 1,3,5-triazapenta-1,3-dienes **2**.



Scheme 3. Synthesis of tertiary 1,3,5-triazapenta-1,3-dienes **3**.

Similarly, the reaction of *N*-phenylbenzamidinium with imidoyl chlorides gave the compounds **3a** and **3b** after treatment with a sodium hydroxide solution. However, in the case of tertiary triazapentadienes **3** this method is only effective for derivatives bearing an aliphatic substituent at the imidoyl position since the corresponding aromatic imidoyl chlorides proved to be quite unreactive.

Therefore, for the synthesis of 1,3,5-triazapenta-1,3-dienes with aromatic substituents a new reaction pathway based on *N*-imidoylimidoates **5**, the nitrogen analogues of *N*-acylimidoates,^[18] was developed (Scheme 4). Up to now only one synthetic route for them is known. By ring opening of 2-methyl-3,5-diphenyl-1,2,4-thiadiazolium fluorosulfate with sodium ethanolate in ethanol Crook and Sykes obtained the first *N*-imidoylimidoate **5**.^[19] The protonated form of this substance was characterized by X-ray diffraction in 1977.^[20]

Scheme 4. New synthetic pathway for *N*-imidoylimidoates **5**.

We have since found that the *N*-imidoylimidoates **5** can be obtained much easier by the reaction of imidoates or imidoate hydrochlorides with *N*-imidoyl chlorides in the presence of an excess of base.

Compound **5a** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell (Figure 1). The lengths of the interesting central C4–N5–C6–N7 bonds are 1.272 Å, 1.399 Å, and 1.284 Å, whereas the bond angle C4–N5–C6 around the central nitrogen atom amounts to 124.11°. The two planes around the C atoms C4 and C6 intersecting at nitrogen atom N5 form an angle of 76.7° (C6 is out of the plane of N5, N7 and C61 by 0.03 Å). The phenyl substituent at C6 is twisted by only 0.9° relative to the C6=N7 bond, while the imidoate phenyl group adopts a dihedral angle of 34.53°. The ethoxy group adopts a cisoid conformation (angle C2–O3–C4–N5: 3.78°).

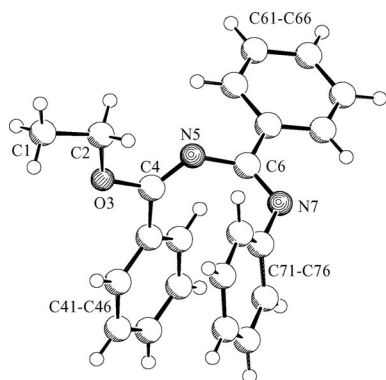
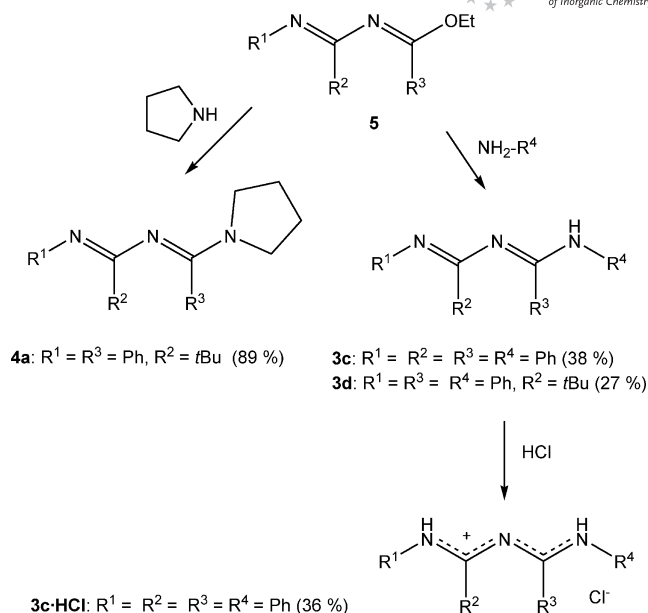


Figure 1. Molecular structure of **5a** in the crystalline state as obtained by an X-ray diffraction study (Schakal plot^[21]). Crystallographic numbering. Selected structural parameters: bond lengths [Å]: C(1)–C(2) 1.497(3), C(2)–O(3) 1.443(2), O(3)–C(4) 1.345(2), C(4)–N(5) 1.272(2), N(5)–C(6) 1.399(2), C(6)–N(7) 1.284(2), N(7)–C(71) 1.416(3); bond angles [°]: C(1)–C(2)–O(3) 107.11(16), C(2)–O(3)–C(4) 116.76(14), O(3)–C(4)–N(5) 120.27(16), C(4)–N(5)–C(6) 124.11(16), N(5)–C(6)–N(7) 125.81(18), C(6)–N(7)–C(71) 120.87(18); torsional angles [°]: C(1)–C(2)–O(3)–C(4) 179.18(18), C(2)–O(3)–C(4)–N(5) –3.78(26), C(2)–O(3)–C(4)–C(41) 175.65(16), O(3)–C(4)–N(5)–C(6) 170.87(16), C(4)–N(5)–C(6)–N(7) –67.33(26), N(5)–C(6)–N(7)–C(71) 8.15(27).

The reaction of compound **5** with primary amines leads to the compounds **3c** and **3d**, whereas the reaction with secondary amines gives the quaternary triazapentadiene **4a** (Scheme 5).

Scheme 5. Synthesis of tertiary (**3**) and quaternary (**4**) 1,3,5-triazapenta-1,3-dienes from *N*-imidoylimidoates **5**.

Crystal Structures and Hydrogen Bonding of **3c** and **3c·HCl**

Compounds **3c** and **3c·HCl** form intermolecular hydrogen bonds in the solid state. Thus, the amine hydrogen atom of the tertiary triazapentadiene **3c** (Figure 2, bottom) takes part in an intermolecular hydrogen bond to a terminal nitrogen of another triazapentadiene molecule leading to a helical structure. The N–H···N distance amounts to 2.244 Å while the corresponding N···N distance is 3.096 Å.

The X-ray structure of **3c** (Figure 2, top) shows that the phenyl substituent at the nitrogen atom N5 and the atoms N5, C4 and N3 are located on a common plane. The C4=N3 bond (1.286 Å) is *E*-configured while the C2=N1 bond (1.291 Å) adopts a *Z* configuration. The C2–N3 bond (1.381 Å) has a (+)-*gauche* conformation with a torsional angle of 61.2°, indicating a significant interaction of the lone pair of the nitrogen atom N1 and the π electrons of the C=N bond.

As seen in Figure 3 the protonation of the triazapentadiene **3c** takes place at the terminal imine function to form the triazapentadienylium salt **3c·HCl**. This site of protonation provides the best possible delocalization. Along the N–C–N–C–N backbone of **3c·HCl** the four C–N bond lengths vary very little between 1.328 and 1.330 Å with bond angles of 120.9°, 123.3° and 120.5°. The N1–C2–N3–C4 dihedral angle of –152.58° indicates that the conformation of the C2–N3 bond has changed from a (+)-*gauche* confirmation in **3c** to a (+)-*anticlinal* conformation.

Compound **3c·HCl** aggregates through N–H···Cl···H–N hydrogen bridges to form linear polymers (Figure 4). Thus, the chloride anion interconnects two triazapentadienylium ions through hydrogen bonding, building a one-dimensional chain. The H–Cl distances are 2.26–2.31 Å (N···Cl distances: 3.164–3.195 Å).

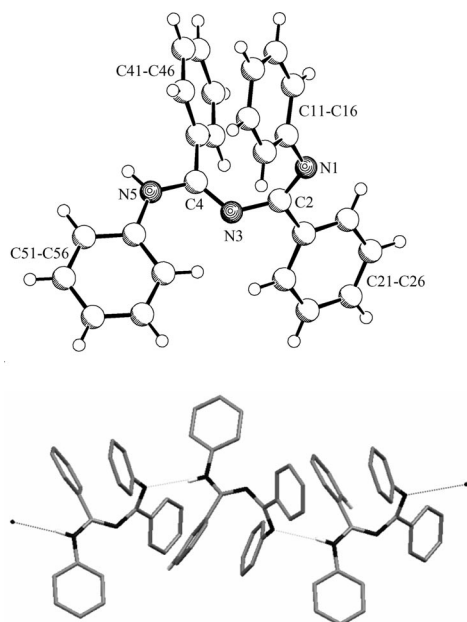


Figure 2. Molecular structure of **3c** in the crystalline state as obtained by an X-ray diffraction study. Top: single molecule (SCHAKAL plot^[21]); bottom: ensemble of three molecules, formed by hydrogen bonding (MERCURY plot^[22]). Crystallographic numbering. Selected structural parameters: bond lengths [Å]: N(1)–C(2) 1.291(2), C(2)–N(3) 1.381(2), N(3)–C(4) 1.286(2), C(4)–N(5) 1.359(2), N(1)–C(11) 1.417(2), C(4)–C(41) 1.493(2), N(5)–C(51) 1.413(2); bond angles [°]: N(1)–C(2)–C(3) 126.91(16), C(2)–N(3)–C(4) 124.01(15), N(3)–C(4)–N(5) 122.16(16), C(11)–N(1)–C(2) 121.61(15), N(3)–C(4)–C(41) 124.24(16), C(4)–N(5)–C(51) 129.59(16); torsional angles [°]: N(1)–C(2)–N(3)–C(4) 61.15(26), C(2)–N(3)–C(4)–N(5) –168.15(17), C(11)–N(1)–C(2)–N(3) –5.25(28), C(21)–C(2)–N(3)–C(4) –126.23(18), C(2)–N(3)–C(4)–C(41) 16.39(27), N(3)–C(4)–N(5)–C(51) –3.18(29).

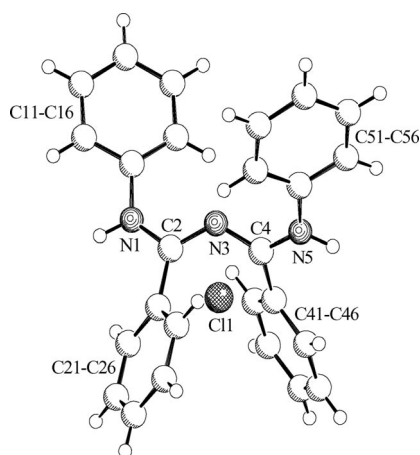


Figure 3. Molecular structure of **3c·HCl** in the crystalline state as obtained by an X-ray diffraction study. The chloride ion is situated well above the plane of the cation (SCHAKAL plot^[21]). Crystallographic numbering. Selected structural parameters: bond lengths [Å]: N(1)–C(2) 1.328(3), C(2)–N(3) 1.330(3), N(3)–C(4) 1.329(3), C(4)–N(5) 1.328(3), N(5)–C(51) 1.426(4), N(1)–C(11) 1.427(4), C(2)–C(21) 1.485(4), C(4)–C(41) 1.486(4); bond angles [°]: N(1)–C(2)–N(3) 120.9(3), C(2)–N(3)–C(4) 123.3(2), N(3)–C(4)–N(5) 120.5(3), C(2)–N(1)–C(11) 129.2(3), N(3)–C(2)–C(21) 122.6(3), N(3)–C(4)–C(41) 123.1(3), C(4)–N(5)–C(51) 128.0(3); torsional angle [°]: N(1)–C(2)–C(3)–C(4) 152.58(27), C(21)–C(2)–N(3)–C(4) 34.69(42), C(11)–N(1)–C(2)–N(3) 8.27(47).

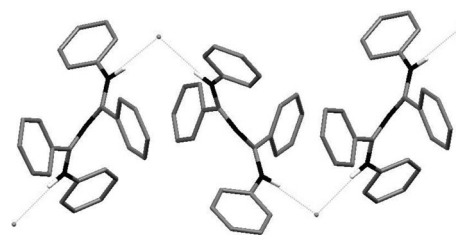
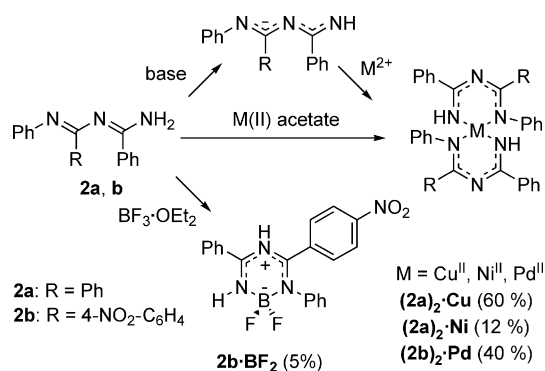


Figure 4. Ensemble of three molecules of **3c·HCl**, formed by hydrogen bonding (MERCURY plot^[22]).

Coordination Compounds

The neutral 2:1 metal complexes of secondary triazapentadienes (**2a**)₂·Cu, (**2a**)₂·Ni and (**2b**)₂·Pd were obtained either by reacting the respective ligand **2** with metal ion acetates or by deprotonating the ligand **2** with potassium *tert*-butoxide first and then reacting the triazapentadienyl anion with a metal salt. The 1:1 boron complex **2b·BF₂** was obtained by the reaction of the ligand **2b** with boron trifluoride–diethyl ether (Scheme 6).



Scheme 6. Synthesis of 2:1 metal complexes and of a 1:1 boron complex of secondary triazapentadienes **2**.

The reaction of the ligand **2a** with copper(II) acetate in a 2:1 ratio in tetrahydrofuran led to a brown solution, from which dark red crystals were obtained in 60% yield upon diffusion of diethyl ether. The complex (**2a**)₂·Cu crystallizes in the orthorhombic space group *Pna*2₁ with four molecules in the unit cell. Figure 5 shows the neutral 2:1 complex, where the two triazapentadienyl ligands form two six-membered chelate rings coordinating the copper ion. The two ligands are slightly twisted against each other and adopt a *trans* position so that the phenyl groups at N5B and N5A are at the maximal distance. Within the N–C–N–C–N chain of the triazapentadienyl ligand extensive delocalization is observed with bond lengths of 1.303, 1.345, 1.347 and 1.320 Å.

For the synthesis of a neutral Ni^{II} complex the ligand **2a** was deprotonated with potassium *tert*-butoxide in anhydrous tetrahydrofuran at 0 °C under argon. A half equivalent of nickel(II) perchlorate hexahydrate was added. From the brown clear solution red crystals could be obtained in 12% yield after overlaying the reaction solution with diethyl

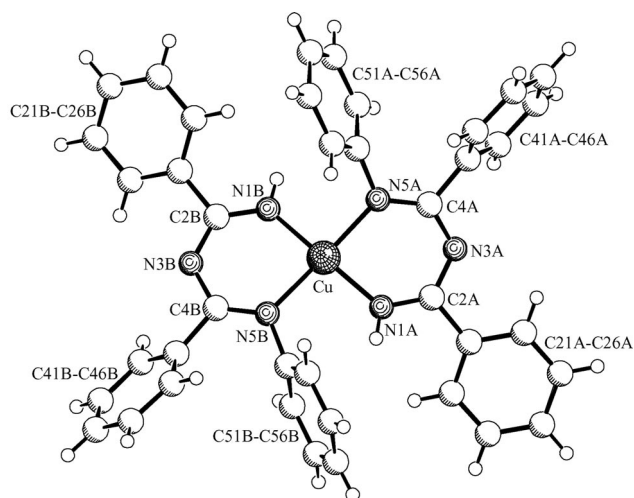


Figure 5. Molecular structure of **(2a)₂·Cu** in the solid state (crystallographic numbering). Selected structural parameters: bond lengths [Å] Cu–N1A 1.9122(17), Cu–N5A 2.0057(15), N1A–C2A 1.303(3), C2A–N3A 1.345(2), N3A–C4A 1.347(3), C4A–N5A 1.320(2); bond angles [°] N1A–Cu–N5A 88.44(7), N1A–Cu–N1B 158.83(10), N5A–Cu–N1B 93.69(6), N1A–Cu–N5B 95.47(7), N1B–Cu–N5B 163.22(7), N1A–C2A–N3A 125.62(19), C2A–N3A–C4A 122.88(17), N3A–C4A–N5A 127.35(16); torsional angles (°) Cu–N1A–C2A–N3A 11.57, N1A–C2A–N3A–C4A 4.55, C2A–N3A–C4A–N5A –7.71, N3A–C4A–N5A–Cu –4.57, N5A–Cu–N1A–C2A –17.13, N5A–C4A–C41A–C42A –124.59, N1A–C2A–C21A–C22A 12.24, N5B–Cu–N1A–C2A 179.23, N1B–Cu–N5A–C4A –145.48.

ether. Compound **(2a)₂·Ni** crystallizes in the monoclinic space group *C2/c*. The X-ray structure shows the formation of a 2:1 chelate complex (Figure 6), where the nickel centre is perfectly square-planar and coordinated by two triazapentadienyl ligands.

The neutral Pd^{II} complex **(2b)₂·Pd** was obtained after addition of a solution of palladium(II) acetate in tetrahydrofuran to a solution of the ligand **2b** in tetrahydrofuran. Yellow crystals were formed in 40% yield upon diffusion of diethyl ether. The compound crystallizes in the monoclinic space group *P2₁/n* with two molecules in the unit cell. Figure 7 shows that the two triazapentadienyl ligands coordinate with their terminal nitrogen atoms at the palladium centre resulting in a perfect square-planar coordination.

For the preparation of a BF₂ complex under argon, boron trifluoride–diethyl ether was added to a solution of the ligand **2b** in dry toluene. After 3 h of heating at 80 °C the corresponding neutral B^{III} complex **2b·BF₂** was obtained. Yellow crystals were formed in 5% yield after recrystallization from dichloromethane/heptane in a ratio of 1:1. In solution this compound displays a strong yellow fluorescence (see below). Compound **2b·BF₂** crystallizes in the monoclinic space group *P2₁/c* with four molecules in the unit cell. The X-ray structure determination shows a 1:1 boron complex, where the boron has a tetrahedral coordination sphere (Figure 8). The triazapentadienyl ligand coordinates to the boron centre with its terminal nitrogen atoms. Within the N–C–N–C–N network different bond lengths were

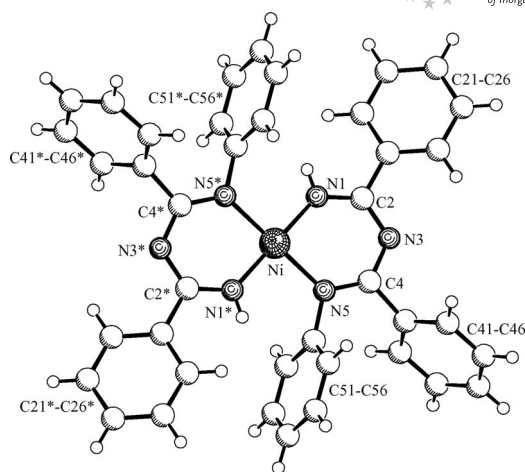


Figure 6. Molecular structure of **(2a)₂·Ni** in the solid state (crystallographic numbering). Selected structural parameters: bond lengths [Å] Ni–N1 1.8492(13), Ni–N5 1.9358(12), N1–C2 1.3013(19), C2–N3 1.3364(19), N3–C4 1.3385(19), C4–N5 1.3308(18); bond angles [°] N1–Ni–N5 88.01(5), N1–Ni–N1* 180.00(7), N5–Ni–N1* 91.99(5), N1–Ni–N5* 91.99(5), N1*–Ni–N5* 88.01(5), N5–Ni–N5* 180.00(5), N1–C2–N3 125.37(19), C2–N3–C4 120.42(13); torsional angles [°] Ni–N1–C2–N3 3.72, N1–C2–N3–C4 3.11, C2–N3–C4–N5 –3.57, N3–C4–N5–Ni –2.32, N5–Ni–N1–C2 –6.95, N5–C4–C41–C42 –118.21, N1–C2–C21–C22 153.21, N5*–Ni–N1–C2 173.05, N1*–Ni–N5–C4 –173.99.

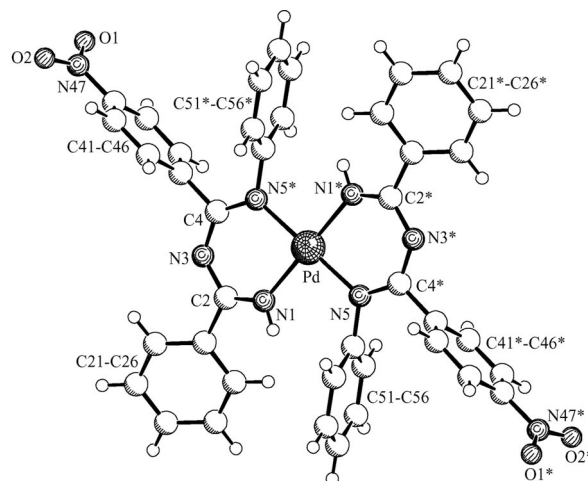


Figure 7. Molecular structure of **(2b)₂·Pd** in the solid state (crystallographic numbering). Selected structural parameters: bond lengths [Å] Pd–N1 1.992(2), Pd–N5* 2.037(2), N1–C2 1.305(3), C2–N3 1.347(3), N3–C4 1.341(3), C4–N5* 1.323(3); bond angles [°] N1–Pd–N5* 87.22(9), N1–Pd–N1* 180, N5*–Pd–N1* 92.78(9), N1–Pd–N5 92.78(9), N1*–Pd–N5 87.22(9), N5*–Pd–N5 180, N1–C2–N3 126.1(2), C2–N3–C4 122.6(2), N3–C4–N5* 129.4(2); torsional angles [°] Pd–N1–C2–N3 –12.86, N1–C2–N3–C4 –0.76, N5*–Pd–N1–C2 14.23, N5*–C4–C41–C42 –77.34, N1–C2–C21–C22 –31.84, N1–Pd–N5–C4* –172.63.

found. While the N1–C2 and C2–N3 bonds (1.33 Å) show approximately equal lengths, the bonds N3–C4 (1.353 Å) and C4–N5 (1.31 Å) are different in length, reflecting the asymmetry of the ligand.

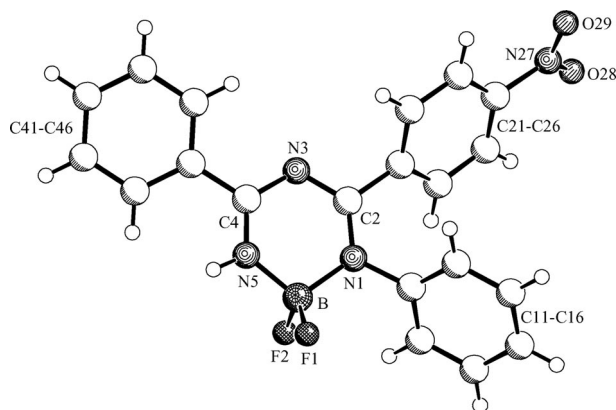


Figure 8. Molecular structure of **2b·BF₂** in the solid state (crystallographic numbering). Selected structural parameters: bond lengths [Å] N1–N2 1.3333(19), C2–N3 1.3337(19), N3–C4 1.3528(19), C4–N5 1.309(2), B–N5 1.516(2), B–N1 1.557(2); bond angles [°] N5–B–N1 106.05(12), N1–C2–N3 125.05(13), C2–N3–C4 118.62(13), C4–N5–B 124.84(14), F2–B–F1 108.41(13), F2–B–N5 111.98(15); torsional angles [°] N5–B–N1–C2 –13.91, B–N1–C2–N3 5.68, N1–C2–N3–C4 3.80, C2–N3–C4–N5 –2.39, N5–C4–C41–C42 –22.03, N3–C4–N5–B –8.99.

Figure 9 shows the UV/Vis and fluorescence spectra of the complex **2b·BF₂**, which exhibits an intense absorption band (dashed) at 301 nm with a shoulder at 275 nm. In the corresponding fluorescence spectrum a single band with a maximum at 417 nm is observed; the Stokes shift amounts to ca. 142 nm (the line at 395 nm is device-specific). It should be noted that luminescent 1,3,5-triazapenta-1,3-diene platinum(II) was prepared and investigated by Kulkushkin et al.^[10b,10f]

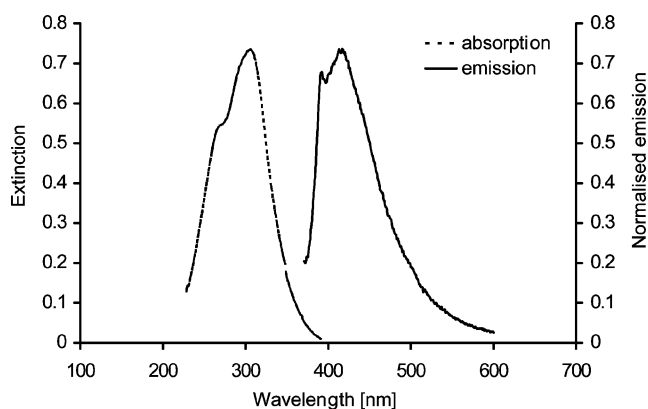
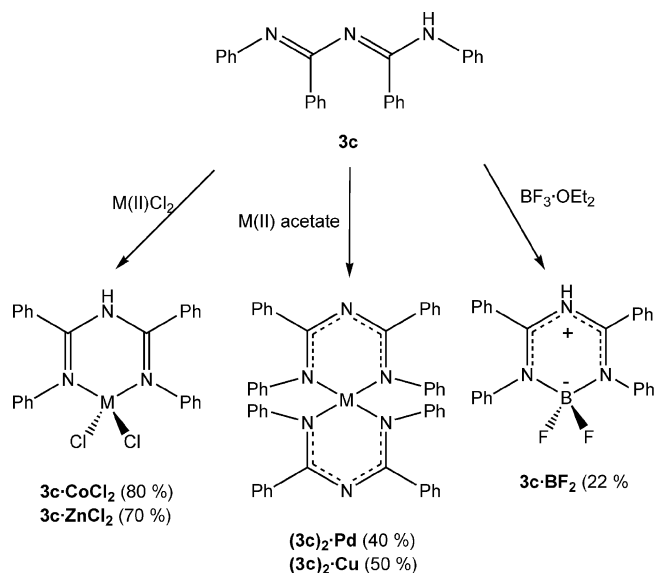


Figure 9. UV/Vis absorption and fluorescence spectra of compound **2b·BF₂**.

The tertiary triazapentadienes **3** were also used for various complexation experiments. The 1:1 metal complexes **3c·CoCl₂** and **3c·ZnCl₂** were obtained by reacting the ligand with metal chlorides, while the neutral 2:1 complexes (**3c**)₂·Pd (no X-ray diffraction) and (**3c**)₂·Cu were obtained by adding the corresponding metal acetates to **3c**. A 1:1 boron complex **3c·BF₂** was obtained by the reaction of the ligand **3c** with boron trifluoride–diethyl ether (Scheme 7).



Scheme 7. Synthesis of 2:1 and 1:1 metal complexes and a 1:1 boron complex from the tertiary triazapentadiene **3c**.

The cobalt complex **3c·CoCl₂** was synthesised by dissolving the ligand **3c** in acetonitrile and adding a solution of cobalt(II) chloride hexahydrate in ethanol dropwise. Blue crystals were formed in 80% yield upon diffusion of diethyl ether. The compound **3c·CoCl₂** crystallizes in the triclinic space group *P* $\bar{1}$ with two units of C₂₆H₂₁Cl₂CoN₃·2C₂H₅N in the unit cell. As shown in Figure 10, **3c** acts as a chelating ligand forming a planar six-membered 1:1 chelate with Co^{II}. The NH proton of the free 1,3,5-triazapentadiene **3c** has moved from the terminal nitrogen N1 to the central nitrogen atom N3 in the complex. Now, the ligand adopts the tautomeric structure of a triazapenta-1,4-diene.

In the solid state complex **3c·CoCl₂** forms a homodimer by self-organization of two complementary species via hydrogen bonding (Figure 11). The two complexes are tilted by 180° against each other. On the one hand hydrogen bonds are formed between the hydrogen at the central nitrogen atom N3 of the ligand and the chloride ion of the second structure. (H...Cl-distance: 3.339 Å, N–Cl distance: 3.248 Å). On the other hand the same hydrogen atom forms one more hydrogen bond with the solvent acetonitrile (H...Cl distance: 2.220 Å) so that a bifurcated system with two acceptors is formed.

From equimolar amounts of **3c** and zinc chloride in ethanol colourless crystals were formed upon diffusion of diethyl ether in 70% yield. The zinc complex **3c·ZnCl₂** crystallizes in the tetragonal space group *P* $\bar{4}$ ₂/m with four molecules in the unit cell. As depicted in Figure 12, a six-membered 1:1 chelate complex is formed which is not planar. The zinc ion and the nitrogen atom N3 deviate from the plane so that a slight distortion towards a boat shape is observed. Again, a proton shift from the terminal to the central nitrogen atom took place in the ligand. The Zn^{II} ion displays tetrahedral coordination; the metal complex has a mirror plane along the zinc and the nitrogen N3 atom.

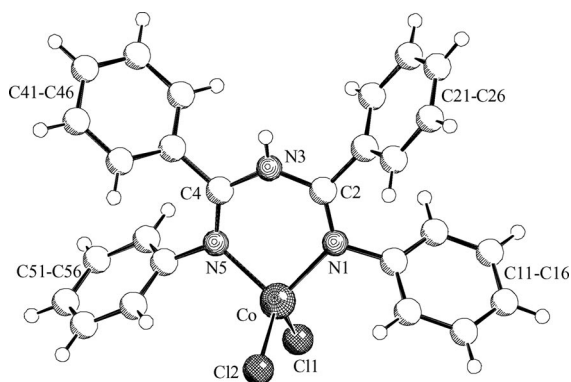


Figure 10. Molecular structure of **3c·CoCl₂** in the solid state (crystallographic numbering). Selected structural parameters: bond lengths [Å] Co–Cl1 2.2527(5), Co–Cl2 2.2307(5), Co–N1 1.9997(14), Co–N5 1.9948(13), N1–C2 1.292(2), C2–N3 1.377(2), N3–C4 1.374(2), C4–N5 1.296(2); bond angles [°] N1–Co–Cl1 112.30(4), N5–Co–Cl1 111.10(4), N1–Co–Cl2 116.10(4), N5–Co–Cl2 113.04(4), Cl1–Co–Cl2 110.358(18), N1–C2–N3 123.04(14), C4–N3–C2 131.61(14), N5–C4–N3 122.31(14); torsional angles [°] Co–N1–C2–N3 –4.07, N1–C2–N3–C4 –5.54, C2–N3–C4–N5 5.46, N3–C4–N5–Co 4.24, N5–Co–N1–C2 9.19, N1–C2–C21–C22 –58.26, N5–C4–C41–C42 52.20, C4–N5–C51–C52 –118.61.

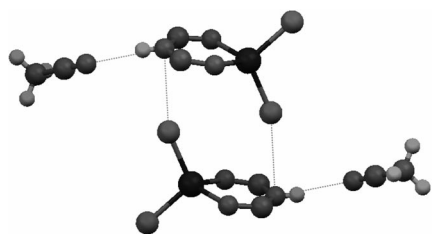


Figure 11. Molecular structure of the homodimer of **3c·CoCl₂** in the crystalline state as obtained by an X-ray diffraction study, with two molecules of acetonitrile connected by hydrogen bonding. The phenyl rings are omitted for clarity (MERCURY plot^[22]).

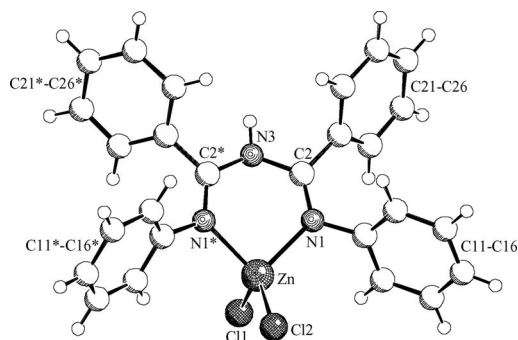


Figure 12. Molecular structure of **3c·ZnCl₂** in the solid state (crystallographic numbering). Selected structural parameters: bond lengths [Å] Zn–Cl1 2.2334(14), Zn–Cl2 2.1915(14), Zn–N1* 2.039(3), Zn–N1 2.039(3), N1–C2 1.285(5), C2–N3 1.393(4), N3–C2* 1.374(2); bond angles [°] N1–Zn–Cl1 110.35(9), N1*–Zn–Cl1 110.35(9), N1–Zn–Cl2 113.09(9), N1*–Zn–Cl2 113.09(9), Cl2–Zn–Cl1 116.14(6), N1–C2–N3 122.2(3), C2–N3–C2* 130.4(5); torsional angles [°] Zn–N1–C2–N3 8.83, N1–C2–N3–C2* 19.67, N1*–Zn–N1–C2 –24.46.

Reaction of the ligand **3c** with copper(II) acetate in a molar ratio of 2:1 in tetrahydrofuran leads to a brown solution, from which black crystals were obtained in 50% yield upon diffusion of diethyl ether. The complex (**3c**)₂·Cu crystallizes in the orthorhombic space group *Pbcn* with four molecules of C₅₂H₄₀CuN₆·C₄H₈O in the unit cell. As shown in Figure 13, the two triazapentadienyl ligands are connected with their terminal nitrogen ligands to the copper centre forming two six-membered chelates. The torsional angles indicate an approximately planar structure of both these chelate rings. Within the N–C–N–C–N chain of the triazapentadienyl ligand a complete delocalization is observed with bond lengths of 1.3285, 1.3430, 1.3449 and 1.3247 Å. The 2:1 copper complex with secondary triazapentadienyl ligands (**2a**)₂·Cu shows similar distances (see above).

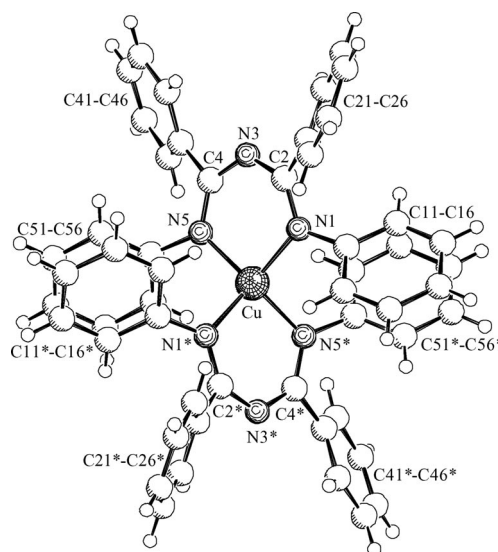


Figure 13. Molecular structure of (**3c**)₂·Cu in the solid state (crystallographic numbering). Selected structural parameters: bond lengths [Å] Cu–N1 1.9486(18), Cu–N5 1.9416(17), N1–C2 1.310(2), C2–N3 1.351(3), N3–C4 1.347(3), C4A–N5A 1.330(3); bond angles [°] N1–Cu–N5 94.82(7), N5–Cu–N5* 128.58(11), N5*–Cu–N1 102.83(7), N1–C2–N3 125.63(19), C4–N3–C2 126.67(18), N5–C4–N3 125.19(19); torsional angles [°] Cu–N1–C2–N3 –20.94, N1–C2–N3–C4 15.33, C2–N3–C4–N5 7.26, N3–C4–N5–Cu –18.68, N5–Cu–N1–C2 7.99, N5*–Cu–N1–C2 150.27, N1*–Cu–N5–C4 141.68, N5–C4–C41–C42 –37.23.

For the preparation of a BF₂ complex boron trifluoride–diethyl ether is added to a solution of the ligand **3c** in dry toluene under argon. The reaction mixture was heated for 3 h at 80 °C. Yellow crystals were formed in 22% yield after recrystallization from dichloromethane/heptane in a ratio of 1:1. In the solid state the boron complex shows strong blue fluorescence while in solution no fluorescence is observed. Complex **3c·BF₂** crystallizes in the monoclinic space group *P2₁/n* with four molecules in the unit cell (Figure 14).

Again, the triazapentadienyl ligand coordinates with its terminal nitrogen atoms to the boron centre showing a tetrahedral coordination sphere. Different bond lengths within the N–C–N–C–N network are observed. Compared to the C2–N3 and N3–C4 distances, which are approximately

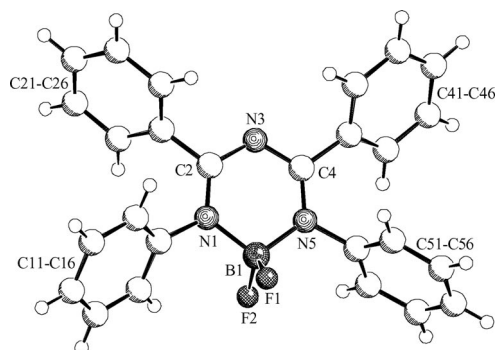


Figure 14. Molecular structure of **3c**·**BF₂** in the solid state (crystallographic numbering). Selected structural parameters: bond lengths [Å] N1–C2 1.3285(13), C2–N3 1.3430(13), N3–C4 1.3449(13), C4–N5 1.3247(13), B1–N5 1.5522(14), B1–N1 1.5539(14); bond angles [°] N5–B1–N1 107.57(8), N1–C2–N3 124.38(9), C2–N3–C4 119.88(9), C4–N5–B1 122.83(9), F2–B1–F1 109.32(9), F2–B1–N5 109.73(9); torsional angles [°] N5–B1–N1–C2 –1.73, B1–N1–C2–N3 –1.68, N1–C2–N3–C4 –0.46, C2–N3–C4–N5 2.48.

equally long (1.3430 Å and 1.3449 Å, respectively), the bonds between N1–C2 and C4–N5 are much shorter (1.3285 Å and 1.3247 Å, respectively). This slightly unsymmetrical arrangement might be caused by crystal packing effects. Dihedral angles between –2.20° and 2.48° within the six-membered chelate indicate an almost planar complex.

Conclusions

We have described the synthesis of novel secondary, tertiary and quaternary 1,3,5-triazapentadienes **2**, **3** and **4** by the reaction of *N*-imidoyl chlorides with amidines or from *N*-imidoylimidoates **5** with primary and secondary amines. A new synthetic route for seven new derivatives **5a–g**, starting from imidoates or their hydrochlorides and imidoyl chlorides, was developed. X-ray diffraction studies of the tertiary 1,3,5-triazapentadiene **3c** and its protonated form **3c**·**HCl** shows different types of hydrogen bonding in the solid state. The triazapentadienes **2**, **3** and **4** are excellent ligands for metal-ion complexation. Thus, from the reaction of two equivalents of secondary 1,3,5-triazapenta-1,3-dienes **2**, after deprotonation with potassium *tert*-butoxide, with CuCl₂, Ni(ClO₄)₂ or with Pd(ac)₂ (without deprotonation) the corresponding neutral 2:1 chelate complexes (**2a**)₂·**Cu**, (**2a**)₂·**Ni** and (**2b**)₂·**Pd**, respectively, were isolated. A fluorescent boron complex **2b**·**BF₂** was obtained by reacting **2b** with boron trifluoride–diethyl ether. Similarly, from the tertiary triazapentadiene **3c** and CoCl₂ or ZnCl₂ the six-membered 1:1 chelate complexes **3c**·**CoCl₂** and **3c**·**ZnCl₂**, respectively, were obtained. Two equivalents of **3c** reacted at room temperature with Cu(ac)₂ or Pd(ac)₂ to give the neutral 2:1 chelate complexes (**3c**)₂·**Cu** and (**3c**)₂·**Pd**, respectively. A fluorescent 1:1 boron complex **3c**·**BF₂** was obtained from **3c** and boron trifluoride–diethyl ether. We have demonstrated that 1,3,5-triazapentadienes act as potent neutral or anionic bidentate ligands forming stable six-membered chelates with various metal ions or with a BF₂ fragment.

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 solvents. MS MAT C 312, Finnigan (70 eV). ESI-MS: Quattro LC-Z, Micromass. MALDI (16–19 kV), nitrore (337 nm, 3 ns); matrix DTBC {2-[(*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]-malononitrile}. UV/Vis: Varian Cary 1 Bio. CHN elemental analysis: Elementar Vario El III. Fluorescence spectra: AMINO-BOWMAN Series-2. Melting points were measured with a Paterno–Büchi melting point B-450 apparatus and are uncorrected. DC: SIL G/UV₂₅₄, Macherey–Nagel and silica gel F₂₅₄, Merck. Column chromatography: silica gel 60, Merck. All solvents were rigorously dried by standard methods. When necessary, the experiments were carried out with complete exclusion of moisture (argon, septum and syringe technique) in glassware, which was thoroughly dried by repeated heating under argon and subsequent evacuation.

1,2,4-Triphenyl-1,3,5-triazapenta-1,3-diene (2a): In analogy to the literature procedure,^[4] benzamidine (2.09 g, 17.5 mmol) was suspended in diethyl ether (10 mL). The suspension was then added dropwise to *N*-phenylbenzimidoyl chloride^[23] in diethyl ether (20 mL). The reaction mixture was stirred for 2 h before being heated to reflux for 1 h. The precipitated triazapentadiene hydrochloride was separated and transferred into its free form by adding a sodium hydroxide solution (30 mL, 2 N) and then extracted with dichloromethane until no residue was observed. The combined organic layers were dried with magnesium sulfate and the solvent was removed under reduced pressure; yield 1.19 g (4 mmol, 23%), light yellow solid; m.p. 140–142 °C, ref.^[4] 143 °C. IR (KBr): $\tilde{\nu}$ = 3437 (vs, NH₂), 3315 (vs, NH₂), 3066 (s, CH_{arom.}), 3060 (m, CH_{arom.}), 1643 (vs, C=N), 1591 (vs, C=C_{arom.}), 1370 (s), 1279 (s), 1105 (s), 1056 (s), 1012 (s) 1009 (s), 875 (s), 867 (vs), 838 (vs), 813 (s), 756 (s), 758 (vs) 699 (vs) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 4.76 (br., 2 H, NH₂), 6.76 (m, 1 H, CH_{arom.}), 6.96–7.07 (m, 2 H, CH_{arom.}), 7.20–7.23 (m, 2 H, CH_{arom.}), 7.33–7.42 (m, 4 H, CH_{arom.}), 7.56–7.57 (m, 3 H, CH_{arom.}), 7.92 (m, 1 H, CH_{arom.}), 8.05–8.06 (m, 2 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 121.2, 122.9, 126.7, 128.4, 129.5, 130.8 (C_{arom.}), 134.0 (*i*-C_{arom.}), 135.6 (*i*-C_{arom.}), 149.8 (*i*-C_{arom.}), 152.7 (C=N), 161.2 (C=N) ppm. MS (70 eV): *m/z* (%) = 300 (18) [M⁺(¹³C)], 299 (96) [M⁺], 298 (79) [M⁺ – 1], 196 (27) [M⁺ – PhCN], 180 (100) [PhCNPh⁺], 104 (64) [PhCN⁺ + 1], 103 (36) [PhCN⁺], 93 (41) [PhNH⁺ + 2], 77 (82) [Ph⁺], 51 (12) [C₄H₃⁺].

2-(4-Nitrophenyl)-1,4-diphenyl-1,3,5-triazapenta-1,3-diene (2b): In analogy to the procedure described for **2a**, the reaction of benzamidine (3.60 g, 30 mmol) and *N*-phenyl-4-nitrobenzimidoyl chloride^[24] (7.23 g, 30 mmol) led to an orange solid; yield 2.19 g (6.37 mmol, 21%); m.p. 146–148 °C. IR (KBr): $\tilde{\nu}$ = 3425 (vs, NH₂), 3315 (vs, NH₂), 3066 (s, CH_{arom.}), 3060 (m, CH_{arom.}), 1643 (vs, C=N), 1591 (vs, C=C_{arom.}), 1346 (vs, NO), 1170 (s), 1139 (s), 1105 (s), 1066 (s), 1029 (s) 1014 (s), 875 (s), 867 (vs), 844 (vs), 813 (s), 756 (s), 748 (vs) 696 (vs), 514 (s) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 4.89 (s, 2 H, NH₂), 6.73–6.75 (m, 1 H, CH_{arom.}), 6.96–7.30 (m, 4 H, CH_{arom.}), 7.73–7.61 (m, 5 H, CH_{arom.}), 7.93–8.06 (m, 2 H, CH_{arom.}), 7.93–8.06 (m, 2 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 126.8, 128.4, 130.4 (C_{arom.}), 136.0 (*i*-C_{arom.}), 142.3 (*i*-C_{arom.}), 142.3 (*i*-C_{arom.}), 153.6 (C=N), 159.2 (C=N) ppm. MS (70 eV): *m/z* (%) = 345 (24) [M⁺(¹³C)], 344 (94) [M⁺], 343 (100) [M⁺ – 1], 225 (62) [C₆H₄NO₂CNPh⁺], 104 (55) [M⁺].

[PhCN⁺ + 1], 103 (26) [PhCN⁺], 93 (36) [PhCN⁺ + 2], 77 (55) [Ph⁺]. C₂₀H₁₆N₄O₂ (344.37): calcd. C 69.76, H 4.68, N 16.27; found C 69.40, H 4.57, N 16.06.

General Procedure for the Synthesis of *N*-Imidoilymidoates 5: Imidoate or imidoate hydrochloride (10 mmol) was suspended in dry dichloromethane (20 mL). Whilst stirring triethylamine (11 mmol for imidoate or 22 mmol for imidoate hydrochloride) was added at room temperature. The suspension was stirred for 1 h and afterwards cooled down to 0 °C. At this temperature equimolar amounts of the corresponding *N*-imidoilyl chlorides were very slowly added. After warming to room temperature the reaction mixture was stirred for a further 20 h. After filtration of the triethylammonium salt the residue was treated with warm pentane until the solid became colourless. The combined organic layers were dried with magnesium sulfate. After removal of the solvent the crude product was purified by column chromatography.

Ethyl *N*-[(*Z*)-Phenyl(phenylimino)methyl]benzenecarboximidoate (5a): From ethyl benzimidoate hydrochloride^[18,25] (1.86 g, 10.0 mmol) and *N*-phenylbenzimidoyl chloride^[18,26] (2.16 g, 10.0 mmol) a yellow solid was obtained. The crude product was purified by column chromatography (pentane/ethyl acetate, 2:1 + 3% triethylamine); yield 1.43 g (4.35 mmol, 44%); m.p. 81–83 °C. IR (KBr): $\tilde{\nu}$ = 3300 (w), 3163 (w), 3105 (w), 3088 (m), 3059 (s), 3026 (m), 2976 (s), 2955 (m), 2934 (m), 2897 (m), 2864 (m), 2774 (m), 2718 (m), 2600 (w), 2448 (w), 2336 (w), 2311 (w), 1960 (w), 1944 (w), 1813 (w), 1771 (w), 1622 (s), 1603 (vs), 1661 (vs), 1589 (vs), 1572 (vs), 1493 (s), 1481 (s), 1472 (s), 1448 (vs), 1391 (s), 1366 (s), 1325 (s), 1310 (vs), 1279 (vs), 1223 (s), 1186 (m), 1169 (m), 1148 (vs), 1115 (s), 1061 (vs), 1024 (vs), 1001 (s), 988 (m), 970 (m), 922 (s), 891 (s), 881 (s), 847 (m), 829 (m), 795 (w), 779 (vs), 737 (vs), 712 (vs), 692 (vs), 671 (vs), 615 (m), 573 (m), 530 (s), 444 (m) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): δ = 1.31–1.35 (t, ³*J* = 7.2 Hz, 3 H, OCH₂CH₃), 4.27–4.34 (q, ³*J* = 7.2 Hz, 2 H, OCH₂CH₃), 6.53–6.57 (m, 2 H, CH_{arom.}), 6.86–6.92 (m, 1 H, CH_{arom.}), 7.06–7.11 (m, 2 H, CH_{arom.}), 7.17–7.22 (m, 4 H, CH_{arom.}), 7.23–7.28 (m, 1 H, CH_{arom.}), 7.31–7.36 (m, 3 H, CH_{arom.}), 7.43–7.47 (m, 2 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 14.2 (OCH₂CH₃), 63.1 (OCH₂CH₃), 121.4 (2 C, C_{arom.}), 122.4 (C_{arom.}), 127.7 (2 C, C_{arom.}), 127.9 (2 C, C_{arom.}), 128.1 (2 C, C_{arom.}), 128.3 (2 C, C_{arom.}), 130.6 (2 C, C_{arom.}), 130.9 (2 C, C_{arom.}), 131.3 (*i*-C_{arom.}), 136.4 (*i*-C_{arom.}), 149.6 (*i*-C_{arom.}), 157.7 (N–C=N), 158.1 (O–C=N) ppm. MS (ESI, methanol): *m/z* (%) = 351 (6) [M + Na⁺], 329 (100) [M + H⁺]. C₂₂H₂₀N₂O (328.41): calcd. C 80.46, H 6.14, N 8.53; found C 80.12, H 5.93, N 8.54.

X-ray Crystal Structure Analysis for 5a:^[27,28] Empirical formula: C₂₂H₂₀N₂O, *M_r* = 328.40 g mol⁻¹, colourless crystal 0.35 × 0.20 × 0.10 mm, *a* = 8.096(1) Å, *b* = 11.043(1) Å, *c* = 11.537(1) Å, *α* = 67.02(1)°, *β* = 83.99(1)°, *γ* = 74.57(1)°, *V* = 915.4(2) Å³, *ρ*_{calc} = 1.191 g cm⁻³, *μ* = 0.74 mm⁻¹, empirical absorption correction (0.975 ≤ *T* ≤ 0.993), *Z* = 2, triclinic, space group *P* $\bar{1}$ (No. 2), *λ* = 0.71073 Å, *T* = 223(2) K, *ω* and *φ* scans, 9406 reflections collected (*±h*, *±k*, *±l*), [(sin *θ*)/*λ*] = 0.66 Å⁻¹, 4270 independent (*R*_{int} = 0.049) and 2056 observed reflections [*I* ≥ 2σ(*I*)], 227 refined parameters, *R* = 0.059, *wR*₂ = 0.159, max. (min.) residual electron density 0.17 (–0.21) e Å⁻³, hydrogen atoms calculated and refined as riding atoms.

Ethyl Benzenecarboximidoate Derivative 5b: This compound was obtained from ethyl benzimidoate hydrochloride^[18,25] (1.86 g, 10.0 mmol) and *N*-phenyl-pivalimidoyl chloride^[29] (1.96 g, 10.0 mmol). The crude product was purified by column chromatography (pentane/ethyl acetate, 5:1 + 5% triethylamine); yield 1.28 g (4.0 mmol, 40%), yellow oil. IR (NaCl): $\tilde{\nu}$ = 3076 (m), 3061 (m),

3028 (m), 3017 (m), 2972 (s), 2932 (m), 2901 (m), 2868 (m), 1674 (vs), 1614 (vs), 1591 (vs), 1524 (w), 1493 (m), 1477 (s), 1448 (s), 1391 (m), 1364 (s), 1317 (m), 1300 (s), 1271 (vs), 1246 (s), 1209 (m), 1186 (m), 1167 (m), 1151 (m), 1111 (s), 1090 (vs), 1032 (s), 1001 (w), 926 (s), 893 (w), 843 (m), 799 (w), 779 (m), 754 (s), 694 (vs), 644 (w), 467 (vs), 457 (vs), 444 (vs), 419 (s), 413 (s) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 1.28–1.32 (m, 3 H, OCH₂CH₃), 1.31 [s, 9 H, (CH₃)₃], 4.05–4.27 (m, 2 H, OCH₂CH₃), 6.56–6.58 (m, 2 H, CH_{arom.}), 6.78–6.83 (m, 1 H, CH_{arom.}), 7.00–7.06 (m, 2 H, CH_{arom.}), 7.24–7.29 (m, 2 H, CH_{arom.}), 7.35–7.41 (m, 3 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 14.2 (OCH₂CH₃), 28.8 [C(CH₃)₃], 39.3 [C(CH₃)₃], 62.5 (OCH₂CH₃), 121.4 (2 C, C_{arom.}), 121.8 (C_{arom.}), 127.6 (2 C, C_{arom.}), 128.0 (2 C, C_{arom.}), 128.1 (2 C, C_{arom.}), 130.7 (C_{arom.}), 131.3 (*i*-C_{arom.}), 149.9 (*i*-C_{arom.}), 153.7 (N–C=N), 169.0 (O–C=N) ppm. MS (ESI, methanol): *m/z* (%) = 309 (100) [M + H⁺]. C₂₀H₂₄N₂O (308.43): calcd. C 77.89, H 7.84, N 9.08; found C 77.78, H 7.85, N 9.14.

Ethyl Benzimidoate Derivative 5c: This compound was obtained from ethyl pyridine-2-imidoate^[30] (1.50 g, 10 mmol) and *N*-phenylbenzimidoyl chloride^[26] (2.16 g, 10.0 mmol). The crude product was purified by column chromatography (pentane/ethyl acetate, 10:1 + 3% triethylamine); yield 0.49 g (1.5 mmol, 15%), slight yellow solid. IR (KBr): $\tilde{\nu}$ = 3566 (s), 3379 (s), 3215 (m), 3069 (m), 3053 (m), 3038 (m), 3026 (m), 3009 (m), 2978 (s), 2957 (m), 2937 (m), 2926 (m), 2901 (m), 2870 (m), 1680 (vs), 1665 (vs), 1616 (vs), 1591 (vs), 1578 (vs), 1479 (s), 1470 (s), 1445 (s), 1429 (s), 1393 (m), 1367 (s), 1312 (vs), 1285 (vs), 1248 (vs), 1229 (s), 1165 (vs), 1113 (s), 1094 (s), 1065 (vs), 1043 (s), 1024 (s), 995 (s), 924 (s), 907 (m), 889 (s), 881 (s), 806 (m), 795 (m), 775 (s), 739 (vs), 702 (vs), 687 (s), 677 (s), 665 (s), 523 (m) cm⁻¹. ¹H NMR (300.13 MHz, CDCl₃): δ = 1.26–1.33 (t, ³*J* = 7.1 Hz, 3 H, OCH₂CH₃), 4.27–4.34 (q, ³*J* = 7.1 Hz, 2 H, OCH₂CH₃), 6.59–6.62 (m, 2 H, CH_{arom.}), 6.86–6.91 (m, 1 H, CH_{arom.}), 7.05–7.10 (m, 2 H, CH_{arom.}), 7.21–7.26 (m, 1 H, CH_{arom.}), 7.37–7.39 (m, 3 H, CH_{arom.}), 7.47–7.50 (m, 1 H, CH_{arom.}), 7.59–7.65 (m, 1 H, CH_{arom.}), 7.98–8.01 (m, 2 H, CH_{arom.}), 8.46–8.48 (m, 1 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 14.0 (OCH₂CH₃), 63.3 (OCH₂CH₃), 121.2 (3 C, C_{arom.}), 122.3 (C_{arom.}), 122.9 (2 C, C_{arom.}), 125.1 (2 C, C_{arom.}), 129.4 (2 C, C_{arom.}), 136.5 (2 C, C_{arom.}), 136.9 (*i*-C_{arom.}), 147.7 (*i*-C_{arom.}), 148.8 (2 C, C_{arom.}), 150.2 (*i*-C_{arom.}), 154.5 (N–C=N), 159.2 (O–C=N) ppm. MS (ESI, methanol): *m/z* (%) = 330 (100) [M + H⁺]. C₂₁H₁₉N₃O (329.40): calcd. C 76.57, H 5.81, N 12.76; found C 76.16, H 5.79, N 12.52.

Ethyl (1*E*)-*N*-[(1*E*)-2,2-Dimethyl-*N*-(2-pyridyl)propanimidoyl]-2-methylpropanimidoate (5d): A yellow oil was obtained from ethyl pyridine-2-carboximidoate^[30] (1.50 g, 10 mmol) and *N*-isopropylpivalimidoyl chloride^[31] (1.12 g, 10.0 mmol). The crude product was purified by column chromatography (pentane/ethyl acetate, 10:1 + 3% triethylamine); yield 0.87 g (3.2 mmol, 23%). IR (NaCl): $\tilde{\nu}$ = 3346 (w), 3244 (w), 3057 (m), 2963 (vs), 2926 (s), 2901 (s), 2868 (s), 1682 (vs), 1632 (vs), 1582 (s), 1479 (s), 1470 (s), 1462 (s), 1431 (s), 1387 (m), 1358 (s), 1337 (m), 1306 (vs), 1277 (vs), 1246 (s), 1194 (m), 1169 (m), 1140 (s), 1117 (s), 1086 (vs), 1047 (m), 1030 (m), 995 (m), 961 (w), 907 (s), 887 (m), 849 (w), 802 (m), 768 (m), 744 (s), 671 (m), 621 (w), 484 (vs), 465 (vs), 453 (vs), 444 (vs), 434 (vs), 409 (s) cm⁻¹. ¹H NMR (300.13 MHz, CDCl₃): δ = 0.67–0.68 [d, 3 H, CH(CH₃)₂], 0.94–0.96 [d, 3 H, CH(CH₃)₂], 1.40 [s, 9 H, (CH₃)₃], 1.40–1.45 (t, ³*J* = 7.1 Hz, 3 H, OCH₂CH₃), 0.94–0.96 [quint, 1 H, CH(CH₃)₂], 4.29–4.36 (q, ³*J* = 7.2 Hz, 2 H, OCH₂CH₃), 7.28–7.32 (m, 1 H, CH_{arom.}), 7.73–7.75 (m, 2 H, CH_{arom.}), 8.57–8.90 (m, 1 H, CH_{arom.}) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 13.7 (OCH₂CH₃), 19.9 [CH(CH₃)₂], 20.1 [CH(CH₃)₂], 28.5 [C(CH₃)₃], 40.2 [CH(CH₃)₃], 48.3 [C(CH₃)₂], 65.9 (OCH₂CH₃),

123.9, 127.5, 138.2 ($C_{\text{arom.}}$), 143.4 ($i-C_{\text{arom.}}$), 148.9 ($C_{\text{arom.}}$), 153.8 ($N-C=N$), 182.4 ($O-C=N$) ppm. MS (ESI, methanol): m/z (%) = 276 (100) [$M + H^+$]. $C_{16}H_{25}N_3O$ (275.39): calcd. C 69.78, H 9.15, N 15.26; found C 69.44, H 9.27, N 15.15.

Ethyl *N*-(*N*-Phenylpivalimidoyl)(dimethylamino)formimidoate (5e):

The *N*-imidoylimidoate **5e** was obtained from ethyl (dimethylamino)formimidoate^[30] (1.18 g, 10.2 mmol) and *N*-phenylpivalimidoyl chloride^[29] (1.98 g, 10.2 mmol). The crude product was purified by column chromatography (pentane/ethyl acetate, 2:1 + 5% triethylamine); yield 1.20 g (4.4 mmol, 43%), orange oil. IR (NaCl): $\tilde{\nu}$ = 3074 (m), 3059 (m), 3024 (m), 2976 (s), 2953 (s), 2928 (s), 2868 (m), 1626 (vs), 1572 (vs), 1477 (vs), 1447 (s), 1400 (s), 1381 (s, ν_s CH_3), 1352 (s), 1313 (s), 1246 (s), 1207 (vs), 1173 (s), 1153 (m), 1109 (m), 1094 (m), 1069 (m), 1051 (s), 1028 (m), 993 (s), 926 (s), 893 (m), 841 (m), 808 (m), 785 (m), 756 (s), 700 (s), 521 (m), 467 (vs), 457 (vs), 434 (s), 420 (vs), 407 (s) cm^{-1} . 1H NMR (300.13 MHz, $CDCl_3$): δ = 1.18–1.23 (t, 3 H, OCH_2CH_3), 1.33 [s, 9 H, $(CH_3)_3$], 2.47 [s, 6 H, $N(CH_3)_2$], 3.94–4.14 (m, 2 H, OCH_2CH_3), 6.75–6.78 (m, 2 H, $CH_{\text{arom.}}$), 6.83–6.89 (m, 1 H, $CH_{\text{arom.}}$), 7.15–7.21 (m, 2 H, $CH_{\text{arom.}}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.6 (OCH_2CH_3), 29.1 [$C(CH_3)_3$], 37.0 $N(CH_3)_2$, 38.9 [$C(CH_3)_3$], 62.9 (OCH_2CH_3), 121.1 (2 C, $C_{\text{arom.}}$), 121.3 ($C_{\text{arom.}}$), 128.1 (2 C, $C_{\text{arom.}}$), 151.1 ($i-C_{\text{arom.}}$), 153.1 ($N-C=N$), 169.2 ($O-C=N$) ppm. MS (ESI, methanol): m/z (%) = 276 (100) [$M + H^+$]. $C_{16}H_{25}N_3O$ (275.39): calcd. C 69.78, H 9.15, N 15.26; found C 70.06, H 9.19, N 15.12.

Ethyl *N*-(*Z*)-(2-Naphthyl)(phenylimino)methylbenzenecarboximidoate (5f):

A light yellow solid was obtained from ethyl benzimidate hydrochloride^[18,25] (3.60 g, 19.4 mmol) and *N*-phenyl-2-naphthoyl chloride^[32] (5.15 g, 19.4 mmol). The crude product was purified by column chromatography (pentane/ethyl acetate, 20:1 + 3% triethylamine); yield 3.18 g (8.40 mmol, 43%); m.p. 83–85 °C. IR (KBr): $\tilde{\nu}$ = 3312 (m), 3182 (m), 3080 (s), 3059 (s), 3028 (s), 2978 (vs), 2955 (s), 2936 (s), 2922 (s), 2897 (s), 2868 (s), 2720 (m), 2621 (m), 2529 (m), 2440 (m), 2382 (m), 2291 (m), 2129 (m), 1987 (m), 1963 (m), 1946 (m), 1931 (m), 1919 (m), 1896 (m), 1834 (m), 1811 (m), 1796 (m), 1665 (vs), 1611 (vs), 1591 (vs), 1576 (vs), 1487 (vs), 1470 (vs), 1448 (vs), 1389 (s), 1360 (vs), 1350 (s), 1325 (s), 1308 (s), 1292 (vs), 1265 (vs), 1244 (vs), 1238 (vs), 1223 (vs), 1192 (s), 1173 (s), 1148 (vs), 1121 (vs), 1109 (vs), 1086 (s), 1070 (s), 1055 (vs), 1034 (vs), 1018 (vs), 1001 (s), 980 (s), 972 (s), 959 (m), 949 (s), 916 (vs), 899 (s), 891 (s), 868 (s), 856 (vs), 827 (s), 810 (m), 783 (s), 771 (vs), 758 (vs), 731 (s), 696 (vs), 687 (vs), 665 (vs), 636 (s), 617 (m), 606 (s), 548 (m), 509 (s), 474 (vs), 463 (s), 442 (m) cm^{-1} . 1H NMR (400.13 MHz, $CDCl_3$): δ = 1.34–1.39 (t, 3J = 7.1 Hz, 3 H, OCH_2CH_3), 4.33–4.41 (q, 3J = 7.1 Hz, 2 H, OCH_2CH_3), 6.57–6.60 (m, 2 H, $CH_{\text{arom.}}$), 6.88–6.94 (m, 1 H, $CH_{\text{arom.}}$), 7.08–7.19 (m, 4 H, $CH_{\text{arom.}}$), 7.27–7.34 (m, 3 H, $CH_{\text{arom.}}$), 7.47–7.56 (m, 2 H, $CH_{\text{arom.}}$), 7.86–7.99 (m, 3 H, $CH_{\text{arom.}}$), 8.26–8.24 (m, 1 H, $CH_{\text{arom.}}$), 8.51 (s, 1 H, $CH_{\text{arom.}}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.2 (OCH_2CH_3), 63.2 (OCH_2CH_3), 121.4, 122.4, 124.9, 126.2, 127.1, 127.7, 127.8, 128.1, 128.1, 128.2, 128.3, 128.9, 130.9 (17 C, $C_{\text{arom.}}$), 131.4, 132.9, 133.8, 134.6, 149.6 ($i-C_{\text{arom.}}$), 158.0, 158.2 ($C=N$) ppm. MS (ESI, methanol): m/z (%) = 1158 (3) [$3M + Na^+$], 779 (6) [$2M + Na^+$], 401 (6) [$M + Na^+$], 379 (100) [$M + H^+$]. $C_{26}H_{22}N_2O$ (378.47): calcd. C 82.51, H 5.86, N 7.40; found C 82.35, H 5.70, N 7.34.

Ethyl *N*-(*Z*)-(4-Nitrophenyl)(phenylimino)methylbenzenecarboximidoate (5g):

The compound was obtained from ethyl benzimidate hydrochloride^[18,25] (8.83 g, 47.6 mmol) and *N*-phenyl-4-nitrobenzimidoyl chloride^[33] (12.40 g, 47.6 mmol) in dry chloroform. The crude product was purified by column chromatography (pen-

tane/ethyl acetate, 10:1 + 3% triethylamine); yield 7.34 g (19.7 mmol, 41%), yellow solid; m.p. 121 °C. IR (KBr): $\tilde{\nu}$ = 3078 (w), 3069 (w), 3061 (w), 2978 (m), 2937 (w), 2899 (w), 2440 (w), 1948 (w), 1647 (vs), 1609 (m), 1574 (vs), 1518 (vs), 1485 (s), 1472 (m), 1448 (m), 1406 (w), 1391 (m), 1367 (m), 1344 (vs), 1325 (s), 1281 (vs), 1219 (m), 1175 (w), 1144 (m), 1105 (m), 1063 (s), 1026 (m), 1011 (m), 984 (w), 932 (w), 922 (m), 891 (m), 878 (m), 868 (m), 851 (s), 833 (w), 791 (m), 771 (m), 739 (s), 717 (s), 702 (s), 692 (s), 530 (w), 473 (w), 424 (vw) cm^{-1} . 1H NMR (300.13 MHz, $CDCl_3$): δ = 1.35–1.39 (t, 3J = 7.1 Hz, 3 H, OCH_2CH_3), 4.32–4.39 (q, 3J = 7.1 Hz, 2 H, OCH_2CH_3), 6.58–6.61 (m, 2 H, $CH_{\text{arom.}}$), 6.91–6.97 (m, 1 H, $CH_{\text{arom.}}$), 7.10–7.25 (m, 6 H, $CH_{\text{arom.}}$), 7.33–7.39 (m, 1 H, $CH_{\text{arom.}}$), 8.21–8.29 (m, 4 H, $CH_{\text{arom.}}$) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 14.2 (OCH_2CH_3), 63.6 (OCH_2CH_3), 121.2 (2 C, $C_{\text{arom.}}$), 123.1 ($C_{\text{arom.}}$), 123.5 (2 C, $C_{\text{arom.}}$), 127.5 (2 C, $C_{\text{arom.}}$), 128.27 (2 C, $C_{\text{arom.}}$), 128.31 (2 C, $C_{\text{arom.}}$), 128.8 (2 C, $C_{\text{arom.}}$), 130.97 ($i-C_{\text{arom.}}$), 131.3 ($C_{\text{arom.}}$), 142.4, 148.7, 149.0 ($i-C_{\text{arom.}}$), 156.3 ($N-C=N$), 159.3 ($O-C=N$) ppm. MS (ESI, methanol): m/z (%) = 769 (9) [$2M + Na^+$], 396 (13) [$M + Na^+$], 374 (100) [$M + H^+$]. $C_{22}H_{19}N_3O_3$ (373.40): calcd. C 70.76, H 5.13, N 11.25; found C 70.69, H 4.93, N 11.28.

2-tert-Butyl-1-cyclohexyl-4,5-diphenyl-1,3,5-triazapenta-1,3-diene (3a):

On the basis of a literature procedure^[4] *N*-phenylbenzamidine^[34] (2.94 g, 15.0 mmol) was treated with *N*-cyclohexylpivalimidoyl chloride^[35] (3.03 g, 15.0 mmol) to form the product **3a** as a yellow solid. The crude product was purified by column chromatography (pentane/ethyl acetate, 2:1 + 3% triethylamine); yield 3.82 g (10.6 mmol, 71%), yellow solid; m.p. 92 °C. IR (KBr): $\tilde{\nu}$ = 3352 (s), 3076 (s), 3061 (s), 3028 (s), 3017 (s), 2963 (vs), 2934 (vs), 2851 (vs), 2793 (m), 2667 (m), 2660 (m), 2480 (m), 2405 (m), 2353 (m), 2235 (m), 2147 (w), 1956 (w), 1919 (m), 1811 (w), 1776 (m), 1659 (vs), 1651 (vs), 1645 (vs), 1634 (vs), 1589 (vs.), 1556 (vs.), 1514 (vs), 1493 (vs), 1481 (vs), 1447 (vs), 1396 (s), 1366 (vs), 1321 (vs), 1300 (vs), 1279 (vs), 1258 (s), 1234 (s), 1219 (s), 1196 (s), 1186 (s), 1167 (vs), 1151 (s), 1094 (s), 1070 (s), 1059 (s), 1024 (s), 1001 (m), 968 (m), 930 (vs), 901 (s), 891 (s), 876 (vs), 845 (s), 816 (s), 791 (s), 773 (s), 748 (vs), 717 (m), 696 (vs), 667 (s), 625 (s), 609 (m), 573 (s), 555 (m), 521 (s), 509 (m), 490 (m), 467 (m), 442 (m), 411 (m) cm^{-1} . 1H NMR (599.59 MHz, $CDCl_3$): δ = 0.75–1.01 (m, 4 H, CH_2), 1.17 [s, 9 H, $(CH_3)_3$], 1.26–1.33 (m, 3 H, CH_2), 1.47–1.49 (m, 1 H, CH_2), 1.67–1.70 (m, 2 H, CH_2), 3.46–3.47 (m, 1 H, CH), 4.36–4.37 (br., 1 H, NH), 6.93–6.95 (m, 1 H, $CH_{\text{arom.}}$), 7.02–7.03 (m, 2 H, $CH_{\text{arom.}}$), 7.22–7.25 (m, 2 H, $CH_{\text{arom.}}$), 7.36–7.40 (m, 3 H, $CH_{\text{arom.}}$), 7.99–8.01 (m, 2 H, $CH_{\text{arom.}}$) ppm. ^{13}C NMR (125.70 MHz, $CDCl_3$): δ = 24.3 (3 C, CH_2), 27.6 (2 C, CH_2), 28.5 [$C(CH_3)_3$], 28.4 [$C(CH_3)_3$], 58.5 (CH), 122.0 ($C_{\text{arom.}}$), 122.2 (2 C, $C_{\text{arom.}}$), 127.8 (2 C, $C_{\text{arom.}}$), 127.9 (2 C, $C_{\text{arom.}}$), 128.0 (2 C, $C_{\text{arom.}}$), 129.9 ($C_{\text{arom.}}$), 137.5 ($i-C_{\text{arom.}}$), 150.8 ($i-C_{\text{arom.}}$), 158.1, 160.5 ($C=N$) ppm. MS (ESI, methanol): m/z (%) = 362 (100) [$M + H^+$]. $C_{24}H_{31}N_3$ (361.52): calcd. C 79.73, H 8.64, N 11.62; found C 79.43, H 8.70, N 11.40.

2-tert-Butyl-1-isopropyl-4,5-diphenyl-1,3,5-triazapenta-1,3-diene (3b):

The triazapentadiene **3b** was synthesised in the same manner as that described for **3a** from of *N*-phenylbenzamidine^[34] (2.94 g, 15.0 mmol) and an equimolar amount of *N*-isopropylpivalimidoyl chloride^[31] as a yellow solid. The crude product was purified by column chromatography (pentane/ethyl acetate, 2:1 + 3% triethylamine); yield 0.89 g (2.8 mmol, 18%), yellow solid; m.p. 105 °C. IR (KBr): $\tilde{\nu}$ = 3381 (vs), 3074 (s), 3055 (s), 3026 (s), 2995 (s), 2968 (vs), 2926 (s), 2910 (s), 2868 (s), 2718 (m), 2469 (m), 367 (m), 1774 (w), 1647 (vs), 1585 (vs), 1551 (vs), 1506 (vs), 1481 (vs), 1466 (vs), 1450 (vs), 1398 (s), 369 (vs), 1350 (vs), 1339 (vs), 1315 (s), 1254 (vs), 1217 (vs), 1196 (vs), 1165 (vs), 1128 (s), 1065 (vs), 1024 (s),

1001 (s), 976 (m), 959 (s), 918 (vs), 889 (s), 851 (m), 831 (m), 814 (s), 787 (s), 766 (vs), 710 (vs), 698 (vs), 671 (vs), 621 (m), 571 (s), 527 (s), 480 (m), 447 (w) cm^{-1} . ^1H NMR (400.13 MHz, CDCl_3): δ = 0.78–0.99 (br., 6 H, CH_3), 1.04 [s, 9 H, (CH_3)₃], 3.85–3.87 (m, 1 H, CH), 4.33 (br., NH), 6.92–6.97 (m, 1 H, $\text{CH}_{\text{arom.}}$), 7.03–7.05 (m, 2 H, $\text{CH}_{\text{arom.}}$), 7.22–7.26 (m, 2 H, $\text{CH}_{\text{arom.}}$), 7.36–7.42 (m, 3 H, $\text{CH}_{\text{arom.}}$), 7.99–8.02 (m, 2 H, $\text{CH}_{\text{arom.}}$) ppm. ^{13}C NMR (100.62 MHz, CDCl_3): δ = 23.6 [2 C, $\text{CH}(\text{CH}_3)_2$], 28.4 [3 C, $\text{C}(\text{CH}_3)_3$], 38.4 [$\text{C}(\text{CH}_3)_3$], 42.9 [$\text{CH}(\text{CH}_3)_2$], 122.1 ($\text{C}_{\text{arom.}}$), 122.3 (2 C, $\text{C}_{\text{arom.}}$), 128.1 (4 C, $\text{C}_{\text{arom.}}$), 128.2 (2 C, $\text{C}_{\text{arom.}}$), 135.4 ($\text{C}_{\text{arom.}}$), 150.6 ($i\text{-C}_{\text{arom.}}$), 158.4, 159.9 (C=N) ppm. MS (ESI, methanol): m/z (%) = 322 (100) [$\text{M} + \text{H}^+$]. $\text{C}_{21}\text{H}_{27}\text{N}_3$ (321.46): calcd. C 78.46, H 8.47, N 13.07; found C 78.46, H 8.50, N 12.96.

1,2,4,5-Tetraphenyl-1,3,5-triazapenta-1,3-diene (3c): Aniline (12.80 g, 137.0 mmol), dissolved in dry tetrahydrofuran, was deprotonated with an equimolar amount of *n*-butyllithium at -78°C . After stirring for 10 min imidoate **5a** (45.00 g, 137.0 mmol), dissolved in dry tetrahydrofuran, was slowly added. The reaction mixture was stirred overnight at room temperature. The organic layer was washed three times with water before being dried with magnesium sulfate. Finally, the solvent was removed in vacuo. The crude product was recrystallized from chloroform to form yellow crystals; yield 19.6 g (52.2 mmol, 38%); m.p. 187°C , ref.^[6] $183\text{--}184^\circ\text{C}$. IR (KBr): $\tilde{\nu}$ = 3265 (s), 3244 (m), 3211 (s), 3196 (s), 3055 (s), 3034 (s), 3026 (s), 2596 (w), 2496 (w), 2361 (w), 1632 (vs), 1597 (vs), 1583 (vs), 1560 (vs), 539 (vs), 1497 (vs), 1489 (vs), 1441 (vs), 1360 (s), 1313 (vs), 1296 (vs), 1265 (vs), 1217 (vs), 1177 (s), 1169 (s), 1140 (s), 1074 (m), 1053 (vs), 1022 (s), 1001 (m), 970 (m), 922 (s), 903 (m), 845 (w), 835 (w), 826 (m), 785 (s), 766 (s), 754 (vs), 735 (s), 716 (vs), 690 (vs), 673 (s), 663 (s), 617 (m), 590 (s), 571 (m), 523 (s), 511 (m) cm^{-1} . ^1H NMR (499.84 MHz, CDCl_3): δ = 6.52 (br., 1 H, NH), 6.67–6.68 (m, 2 H, $\text{CH}_{\text{arom.}}$), 6.91–6.96 (m, 3 H, $\text{CH}_{\text{arom.}}$), 7.11–7.16 (m, 3 H, $\text{CH}_{\text{arom.}}$), 7.20–7.23 (m, 2 H, $\text{CH}_{\text{arom.}}$), 7.35–7.38 (m, 3 H, $\text{CH}_{\text{arom.}}$), 7.43–7.48 (m, 3 H, $\text{CH}_{\text{arom.}}$), 7.53–7.55 (m, 2 H, $\text{CH}_{\text{arom.}}$), 8.14–8.16 (m, 2 H, $\text{CH}_{\text{arom.}}$) ppm. ^{13}C NMR (125.70 MHz, CDCl_3): δ = 120.0 (2 C, $\text{C}_{\text{arom.}}$), 122.1 (3 C, $\text{C}_{\text{arom.}}$), 123.7 ($\text{C}_{\text{arom.}}$), 126.7 (2 C, $\text{C}_{\text{arom.}}$), 128.15 (2 C, $\text{C}_{\text{arom.}}$), 128.16 (2 C, $\text{C}_{\text{arom.}}$), 128.2 (2 C, $\text{C}_{\text{arom.}}$), 128.5 (2 C, $\text{C}_{\text{arom.}}$), 128.9 (2 C, $\text{C}_{\text{arom.}}$), 130.25 (2 C, $\text{C}_{\text{arom.}}$), 130.27 (2 C, $\text{C}_{\text{arom.}}$), 135.1 ($i\text{-C}_{\text{arom.}}$), 137.9 ($i\text{-C}_{\text{arom.}}$), 139.4 ($i\text{-C}_{\text{arom.}}$), 149.8 ($i\text{-C}_{\text{arom.}}$), 153.4, 159.6 (C=N) ppm. MS (ESI, methanol): m/z (%) = 376 (100) [$\text{M} + \text{H}^+$]. $\text{C}_{26}\text{H}_{21}\text{N}_3$ (375.47): calcd. C 83.17, H 5.64, N 11.19; found C 82.94, H 5.54, N 11.03.

X-ray Crystal Structure Analysis for 3c·HCl:^[27,28] Empirical formula: $\text{C}_{26}\text{H}_{21}\text{N}_3\cdot\text{HCl}$, M_r = 494.83 g mol^{-1} , light yellow crystal $0.20 \times 0.20 \times 0.20$ mm, a = 11.335(1) Å, b = 12.790(1) Å, c = 17.575(1) Å, β = 102.13(1)°, V = 2491.0(3) Å³, ρ_{calc} = 1.319 g cm^{-3} , μ = 3.481 mm^{-1} , empirical absorption correction ($0.543 \leq T \leq 0.543$), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 20132 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60 \text{ Å}^{-1}$, 4353 independent (R_{int} = 0.035) and 4200 observed reflections [$I \geq 2\sigma(I)$], 302 refined parameters, R = 0.048, wR_2 = 0.129, max. (min.) residual electron density 0.62 (–0.51) e Å^{-3} , hydrogen atom at N5 from difference Fourier calculations, others calculated and refined as riding atoms.

1,2,4,5-Tetraphenyl-1,3,5-triazapenta-1,3-dienylium Hydrochloride (3c·HCl): The hydrochloride of compound **3c** was obtained by adding hydrochloric acid (0.3 mL, c = 2 mol L^{-1}) to a solution of **3c** (0.60 g, 1.6 mmol). The light yellow precipitate was filtered off and dried under high vacuum for 5 h at 100°C ; yield 0.24 g (0.6 mmol, 36%); m.p. 265°C . IR (KBr): $\tilde{\nu}$ = 3568 (w), 3424 (w), 3051 (m), 3026 (m), 3005 (m), 2918 (m), 2822 (s), 2785 (s), 2363 (w), 1701

(w), 1686 (w), 1605 (s), 1583 (s), 1572 (s), 1516 (vs), 1497 (vs), 1447 (vs), 1364 (m), 1348 (m), 1296 (w), 1275 (m), 1232 (w), 1184 (w), 1157 (w), 1078 (w), 1063 (w), 1026 (w), 1001 (w), 935 (w), 903 (w), 847 (w), 771 (s), 752 (m), 690 (s), 615 (w), 575 (w), 509 (m) cm^{-1} . MS (ESI, methanol): m/z (%) = 376 (100) [M^+]. $\text{C}_{26}\text{H}_{21}\text{N}_3\cdot\text{HCl}$ (411.93): calcd. C 75.81, H 5.38, N 10.20; found C 75.43, H 5.23, N 10.10.

X-ray Crystal Structure Analysis for 3c·HCl:^[27,28] Empirical formula: $\text{C}_{26}\text{H}_{21}\text{N}_3\cdot\text{HCl}$, M_r = 411.92 g mol^{-1} , colourless crystal $0.35 \times 0.20 \times 0.03$ mm, a = 11.098(1) Å, b = 13.240(1) Å, c = 15.561(1) Å, β = 110.18(1)°, V = 2146.1(3) Å³, ρ_{calc} = 1.275 g cm^{-3} , μ = 0.196 mm^{-1} , empirical absorption correction ($0.935 \leq T \leq 0.994$), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 6582 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.60 \text{ Å}^{-1}$, 3701 independent (R_{int} = 0.059) and 2034 observed reflections [$I \geq 2\sigma(I)$], 279 refined parameters, R = 0.053, wR_2 = 0.134, max. (min.) residual electron density 0.22 (–0.29) e Å^{-3} , hydrogen atom at N1 from difference Fourier calculations, others calculated and refined as riding atoms.

2-tert-Butyl-1,4,5-triphenyl-1,3,5-triazapenta-1,3-diene (3d): As described for **3c**, aniline (0.60 g, 6.6 mmol) was deprotonated with an equimolar amount of *n*-butyllithium before adding **5b** (1.02 g, 3.3 mmol) to give the triazapentadiene **3d** as a yellow solid; yield 0.31 g (0.9 mmol, 27%); m.p. $151\text{--}153^\circ\text{C}$. IR (KBr): $\tilde{\nu}$ = 3250 (m), 3225 (m), 3213 (m), 3194 (m), 3121 (m), 3069 (s), 3055 (s), 3034 (s), 3018 (s), 2990 (s), 2957 (s), 2930 (s), 2901 (m), 2866 (m), 1653 (s), 1638 (vs), 1618 (s), 1599 (vs), 1574 (vs), 1541 (vs), 1497 (vs), 1485 (vs), 1458 (s), 1441 (vs), 1389 (m), 1340 (s), 1327 (s), 1310 (s), 1296 (s), 1265 (s), 1240 (s), 1205 (s), 1180 (s), 1086 (s), 1074 (s), 1020 (m), 999 (m), 947 (s), 926 (m), 916 (w), 899 (m), 839 (w), 795 (m), 775 (m), 754 (vs), 729 (m), 692 (vs), 665 (m), 617 (w), 588 (m), 521 (m), 511 (m) cm^{-1} . ^1H NMR (400.13 MHz, CDCl_3): δ = 1.19 [25%, s, 9 H, (CH_3)₃], 1.37 [75%, s, 9 H, (CH_3)₃], 6.09 (25%, br., 1 H, NH), 6.31 (75%, br., 1 H, NH), 6.63–7.78 (25%, m, 15 H, $\text{CH}_{\text{arom.}}$, 75%, m, 15 H, $\text{CH}_{\text{arom.}}$) ppm. ^{13}C NMR (100.61 MHz, CDCl_3): δ = 28.3 [25%, 3 C, $\text{C}(\text{CH}_3)_3$], 28.7 [75%, 3 C, $\text{C}(\text{CH}_3)_3$], 39.2 [$\text{C}(\text{CH}_3)_3$], 120.6, 121.6, 121.9, 123.4, 127.3, 127.3, 127.8, 128.3, 128.4, 128.89, 129.9 ($\text{C}_{\text{arom.}}$), 134.7, 146.3, 150.5 ($i\text{-C}_{\text{arom.}}$), 163.9, 171.1 (C=N) ppm. MS (ESI, methanol): m/z (%) = 356 (100) [$\text{M} + \text{H}^+$]. $\text{C}_{24}\text{H}_{25}\text{N}_3$ (355.48): calcd. C 81.09, H 7.09, N 11.82; found C 80.91, H 7.11, N 11.73.

2-tert-Butyl-1,4-diphenyl-5-pyrrolidine-1,3,5-triazapenta-1,3-diene (4a): In analogy to the procedure described for **3c** by deprotonation of pyrrolidine (0.88 g, 12.3 mmol) with *n*-butyllithium (12.3 mmol) and subsequent conversion with **5b** (1.90 g, 6.2 mol). The crude product was purified by column chromatography (pentane/ethyl acetate, 5:1 + 3% triethylamine); yield 0.18 g (5.5 mmol, 89%), yellow oil. IR (KBr): $\tilde{\nu}$ = 3059 (m), 3026 (m), 2968 (s), 2951 (s), 2924 (s), 2868 (s), 1597 (vs), 1576 (vs), 1495 (s), 1479 (s), 1448 (s), 1431 (s), 1385 (s), 1354 (m), 1340 (s), 1286 (s), 1277 (s), 1252 (s), 1229 (s), 1200 (m), 1169 (m), 1119 (m), 1096 (s), 1070 (m), 1024 (m), 972 (w), 943 (m), 914 (m), 878 (m), 818 (m), 777 (m), 750 (s), 694 (s), 523 (m), 474 (vs), 461 (vs), 451 (vs), 432 (s), 420 (s), 409 (vs) cm^{-1} . ^1H NMR (400.13 MHz, CDCl_3): δ = 1.25 [s, 9 H, (CH_3)₃], 1.82 (br., 4 H, NCH_2CH_2), 3.16 (br., 4 H, NCH_2CH_2), 6.55–6.58 (m, 2 H, $\text{CH}_{\text{arom.}}$), 6.63–6.65 (m, 2 H, $\text{CH}_{\text{arom.}}$), 6.79–6.83 (m, 1 H, $\text{CH}_{\text{arom.}}$), 7.05–7.09 (m, 2 H, $\text{CH}_{\text{arom.}}$), 7.12–7.15 (m, 2 H, $\text{CH}_{\text{arom.}}$), 7.21–7.23 (m, 1 H, $\text{CH}_{\text{arom.}}$) ppm. ^{13}C NMR (75.47 MHz, CDCl_3): δ = 25.42 (4 C, NCH_2CH_2), 29.3 [$\text{C}(\text{CH}_3)_3$], 39.0 [$\text{C}(\text{CH}_3)_3$], 48.2 (4 C, NCH_2CH_2), 120.8, 122.8, 127.1, 127.7, 128.0, 128.7 (10 C, $\text{C}_{\text{arom.}}$), 135.6, 151.2 (2 C, $i\text{-C}_{\text{arom.}}$), 154.4, 171.1 (C=N) ppm. MS (ESI, methanol): m/z (%) = 356 (100) [$\text{M} + \text{H}^+$].

C₂₂H₂₇N₃ (333.47): calcd. C 79.24, H 8.16, N 12.60; found C 79.08, H 8.06, N 12.39.

Bis(1,2,4-triphenyl-1,3,5-triazapenta-1,3-dienyl)copper(II) [(2a)₂·Cu]: Compound **2a** (0.1 mmol, 30 mg) was dissolved in anhydrous tetrahydrofuran in a dry Schlenk tube under argon. The solution was cooled to 0 °C. An equimolar amount of potassium *tert*-butoxide was then added whilst stirring. After a colour change from yellow to orange, the reaction mixture was warmed to room temperature and stirred for 10 min. Water-free copper(II) chloride (0.05 mmol, 9 mg), dissolved in anhydrous tetrahydrofuran (1.5 mL), was then added. After a short while of shaking, diethyl ether was allowed to diffuse into the solution. After 4 d dark red crystals had formed; yield 19 mg (0.03 mmol, 60%), dark red rods; m.p. 220 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3350 (vs), 3334 (vs), 3080 (s, CH_{arom.}), 3057 (s), 3030 (s), 1589 (s), 1539 (vs), 1218 (vs), 1180 (s), 1153 (s), 1074 (s), 1062 (s), 1024 (s), 999 (s), 939 (s), 910 (s), 852 (s), 783 (s), 719 (vs), 694 (vs), 586 (s) cm⁻¹. MS (ESI, methanol): m/z (%) = 662–664 [C₄₀H₃₂N₆Cu + H⁺]. C₄₀H₃₂CuN₆ (660.26): calcd. C 72.76, H 4.88, N 12.73; found C 72.69, H 4.85, N 12.55.

X-ray Crystal Structure Analysis for (2a)₂·Cu:^[27,28] Empirical formula: C₄₀H₃₂CuN₆, M_r = 660.26 g mol⁻¹, red crystal 0.40 × 0.40 × 0.30 mm, a = 18.942(1) Å, b = 17.249(1) Å, c = 9.915(1) Å, V = 3239.5(4) Å³, ρ_{calc} = 1.354 g cm⁻³, μ = 0.713 mm⁻¹, empirical absorption correction (0.763 ≤ T ≤ 0.815), Z = 4, orthorhombic, space group *Pna*2₁ (No. 33), λ = 0.71073 Å, T = 198(2) K, ω and ϕ scans, 12449 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/ λ] = 0.67 Å⁻¹, 6781 independent (R_{int} = 0.018) and 6173 observed reflections [$I \geq 2\sigma(I)$], 432 refined parameters, R = 0.029, wR_2 = 0.072, max. (min.) residual electron density 0.28 (–0.33) e Å⁻³, Flack parameter –0.022(8), hydrogen atoms at N1 from difference Fourier calculations, others calculated and refined as riding atoms.

Bis(1,2,4-triphenyl-1,3,5-triazapenta-1,3-dienyl)nickel(II) [(2a)₂·Ni]: This nickel complex was prepared using the same reaction conditions as those used for (2a)₂·Cu from the triazapentadiene **2a** (0.1 mmol, 30 mg) and nickel(II) perchlorate hexahydrate (0.05 mmol, 19 mg). Red crystals were obtained after 10 d; yield 4 mg (0.006 mmol, 12%), red rods; m.p. 288 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3350 (vs), 3055 (s), 3026 (m), 2952 (m), 1587 (s), 1541 (vs), 1454 (vs), 1417 (vs), 1382 (vs), 1346 (s), 1274 (s), 1220 (s), 1182 (m), 1159 (m), 1107 (m), 1068 (m), 1026 (m), 1001 (m), 954 (m), 921 (m), 873 (m), 852 (m), 794 (m), 781 (m), 723 (s), 969 (s) cm⁻¹. MS (MALDI): m/z (%) = 654–657 [C₄₀H₃₂N₆Ni + H⁺]. C₄₀H₃₂N₆Ni (665.43): calcd. C 73.30, H 4.92, N 12.82; found C 72.97, H 4.85, N 13.31.

X-ray Crystal Structure Analysis for (2a)₂·Ni:^[27,28] Empirical formula: C₄₀H₃₂N₆Ni, M_r = 655.43 g mol⁻¹, red crystal 0.35 × 0.25 × 0.12 mm, a = 14.877(1) Å, b = 6.012(1) Å, c = 18.205(1) Å, β = 98.28(1)°, V = 1611.3(3) Å³, ρ_{calc} = 1.351 g cm⁻³, μ = 0.641 mm⁻¹, empirical absorption correction (0.807 ≤ T ≤ 0.927), Z = 2, monoclinic, space group *P2*₁/*n* (No. 14), λ = 0.71073 Å, T = 198(2) K, ω and ϕ scans, 10446 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/ λ] = 0.66 Å⁻¹, 3828 independent (R_{int} = 0.043) and 3201 observed reflections [$I \geq 2\sigma(I)$], 218 refined parameters, R = 0.033, wR_2 = 0.085, max. (min.) residual electron density 0.30 (–0.63) e Å⁻³, hydrogen atom at N1 from difference Fourier calculations, others calculated and refined as riding atoms.

Bis[2-(4-nitrophenyl)-1,4-biphenyl-1,3,5-triazapenta-1,3-dienyl]palladium(II) [(2b)₂·Pd]: A solution of palladium(II) acetate (0.05 mmol, 12 mg) in tetrahydrofuran (1 mL) was added to **2b** (0.1 mmol, 34 mg) in tetrahydrofuran (1 mL). After a short while of shaking, diethyl ether was allowed to diffuse into the yellow reaction mixture. After 6 d yellow crystals were obtained; yield 20 mg

(0.02 mmol, 40%), yellow needles; m.p. 310 °C (decomp.). IR (KBr): $\tilde{\nu}$ = 3338 (vs), 3060 (s), 2970 (m), 2852 (m), 1600 (m), 1587 (s), 1543 (vs), 1519 (vs), 1454 (vs), 1417 (vs), 1346 (vs), 1255 (s), 1224 (vs), 1157 (m), 1107 (m), 1068 (m), 1026 (m), 1014 (m), 945 (m), 920 (w), 833 (w), 854 (s), 792 (m), 756 (s), 702 (vs) cm⁻¹. MS (MALDI): m/z (%) = 791–797 [C₄₀H₃₀N₈O₄Pd + H⁺]. C₄₀H₃₀N₈O₄Pd (793.13): calcd. C 60.57, H 3.81, N 14.13; found C 60.83, H 3.60, N 13.51.

X-ray Crystal Structure Analysis for (2b)₂·Pd:^[27,28] Empirical formula: C₄₀H₃₀N₈O₄Pd·C₄H₈O, M_r = 865.22 g mol⁻¹, yellow crystal 0.50 × 0.15 × 0.07 mm, a = 6.493(1) Å, b = 17.149(1) Å, c = 17.876(1) Å, β = 93.19(1)°, V = 1987.4(3) Å³, ρ_{calc} = 1.446 g cm⁻³, μ = 0.524 mm⁻¹, empirical absorption correction (0.780 ≤ T ≤ 0.964), Z = 2, monoclinic, space group *P2*₁/*n* (No. 14), λ = 0.71073 Å, T = 198(2) K, ω and ϕ scans, 13170 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/ λ] = 0.66 Å⁻¹, 4735 independent (R_{int} = 0.040) and 3483 observed reflections [$I \geq 2\sigma(I)$], 264 refined parameters, R = 0.039, wR_2 = 0.113, max. (min.) residual electron density 0.74 (–0.74) e Å⁻³, disordered solvent molecule and NO₂ group refined with geometrical and thermal restraints, hydrogen atom at N1 from difference Fourier calculations, others calculated and refined as riding atoms.

[2-(4-Nitrophenyl)-1,4-diphenyl-1,3,5-triazapenta-1,3-dienyl]boron(III) Difluoride (2b·BF₂): Boron trifluoride–diethyl ether (12.6 mmol, 1.79 g) was slowly added dropwise to a solution of triazapentadiene **2b** (5 mmol, 1.72 g) in dry toluene (15 mL). The reaction mixture was heated for 3 h at 80 °C. Afterwards the mixture was cooled to room temperature, diluted with chloroform (20 mL) and washed with water (10 mL). The organic layer was separated and dried with magnesium sulfate. Finally, the solvent was removed in vacuo. The crude product was recrystallized from dichloromethane/heptane; yield 93 mg (0.2 mmol, 5%), yellow crystals; m.p. 246 °C. IR (KBr): $\tilde{\nu}$ = 3354 (s), 3044 (w), 1603 (s), 1591 (s), 1572 (vs), 1522 (vs), 1510 (s), 1487 (vs), 1462 (vs), 1441 (vs), 1408 (s), 1348 (vs), 1327 (m), 1310 (s), 1236 (m), 1186 (w), 1165 (m), 1136 (m), 1105 (s), 1072 (m), 1040 (m), 1018 (s), 1003 (m), 962 (s), 922 (w), 876 (m), 854 (s), 841 (w), 812 (w), 800 (w), 777 (w), 760 (m), 737 (s), 714 (m), 698 (m), 631 (w), 617 (w) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.18–7.31 (m, 5 H, CH_{arom.}), 7.54–7.59 (m, 3 H, CH_{arom.}), 7.64–7.72 (m, 2 H, CH_{arom.}), 8.08–8.1 (m, 2 H, CH_{arom.}), 8.28–8.29 (m, 2 H, CH_{arom.}), 10.65 (br, 1 H, NH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 122.7 (2 C, C_{arom.}), 127.1 (C_{arom.}), 127.3 (2 C, C_{arom.}), 128.5 (2 C, C_{arom.}), 128.6 (4 C, C_{arom.}), 130.7 (2 C, C_{arom.}), 132.4 (*i*-C_{arom.}), 132.9 (C_{arom.}), 139.7, 141.8, 147.6 (3 C, *i*-C_{arom.}), 164.6 (C=N), 165.6 (C=N) ppm. ¹¹B NMR (96.29 MHz, [D₆]DMSO): δ = 0.43 (t, 1:2:1, J = 26.8 Hz) ppm. ¹⁹F NMR (282.38 MHz, [D₆]DMSO): δ = –125.0 (q, 1:1:1:1, J = 23.4 Hz) ppm. MS (ESI, methanol): m/z (%) = 807 [2M + Na⁺], 415 [M + Na⁺], 393 [M + H⁺]. UV/Vis (dichloromethane): λ_{max} ($\tilde{\nu}$, ϵ) = 306 (32679 cm⁻¹, 16356 M⁻¹ cm⁻¹), 274 (36496 cm⁻¹, sh, 12267 M⁻¹ cm⁻¹) nm. Fluorescence (dichloromethane, concentration: 4.5 × 10⁻⁵ mol l⁻¹): λ_{max} = 417 nm (excitation at 350 nm). C₂₀H₁₅BF₂N₄O₂ (392.17): calcd. C 61.25, H 3.86, N 14.29; found C 61.27, H 3.82, N 14.23.

X-ray Crystal Structure Analysis for 2b·BF₂:^[27,28] Empirical formula: C₂₀H₁₅BF₂N₄O₂, M_r = 392.17 g mol⁻¹, yellow crystal 0.50 × 0.40 × 0.20 mm, a = 12.3632(3) Å, b = 15.2904(3) Å, c = 9.7003(1) Å, β = 97.302(1)°, V = 1818.86(6) Å³, ρ_{calc} = 1.432 g cm⁻³, μ = 0.108 mm⁻¹, empirical absorption correction (0.948 ≤ T ≤ 0.979), Z = 4, monoclinic, space group *P2*₁/*c* (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 13653 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/ λ] = 0.66 Å⁻¹, 3988 independent (R_{int}

= 0.092) and 3016 observed reflections [$I \geq 2\sigma(I)$], 265 refined parameters, $R = 0.056$, $wR_2 = 0.157$, max. (min.) residual electron density 0.30 (–0.35) $\text{e}\cdot\text{\AA}^{-3}$, hydrogen atom at N5 from difference Fourier calculations, others calculated and refined as riding atoms.

(1,2,4,5-Tetraphenyl-1,3,5-triazapenta-1,3-diene)cobalt(II) Chloride ($3\text{c}\cdot\text{CoCl}_2$): 1,2,4,5-Tetraphenyl-1,3,5-triazapenta-1,3-diene (**3c**) (38 mg, 0.1 mmol) was solved in acetonitrile (2 mL) before adding an equimolar amount of cobalt(II) chloride hexahydrate in ethanol (1 mL). Diethyl ether was allowed to diffuse into the blue reaction mixture. After 3 d blue crystals were obtained; yield 40 mg (0.08 mmol, 80%); m.p. 301 °C. IR (KBr): $\tilde{\nu} = 3425$ (m), 3410 (w), 3055 (w), 3034 (w), 3024 (w), 3005 (w), 2953 (w), 2924 (m), 2853 (m), 1632 (s), 1593 (m), 1576 (m), 1560 (w), 1543 (w), 1524 (w), 1479 (vs), 690 (m), 638 (w), 600 (w), 511 (w) cm^{-1} . MS [ESI (negative), acetonitrile] m/z (%) = 503 (100) [$\text{C}_{26}\text{H}_{21}\text{Cl}_2\text{CoN}_3 - \text{H}^+$], 410 (12), 374 (40) [$\text{C}_{26}\text{H}_{21}\text{N}_3 - \text{H}^+$]. UV/Vis (acetonitrile): λ_{max} ($\tilde{\nu}$, ϵ) = 270 (37037 cm^{-1} , 44355 $\text{M}^{-1}\text{cm}^{-1}$), 194 (51546 cm^{-1} , 129032 $\text{M}^{-1}\text{cm}^{-1}$) nm. $\text{C}_{26}\text{H}_{21}\text{Cl}_2\text{CoN}_3$ (505.3): calcd. C 61.80, H 4.19, N 8.32; found C 61.48, H 4.09, N 8.19.

X-ray Crystal Structure Analysis for $3\text{c}\cdot\text{CoCl}_2$:^[27,28] Empirical formula: $\text{C}_{26}\text{H}_{21}\text{Cl}_2\text{CoN}_3\cdot 2\text{C}_2\text{H}_5\text{N}$, $M_r = 587.40$ $\text{g}\cdot\text{mol}^{-1}$, blue crystal $0.40 \times 0.30 \times 0.15$ mm, $a = 10.5693(1)$ Å, $b = 11.9625(1)$ Å, $c = 13.6393(2)$ Å, $\alpha = 114.126(1)^\circ$, $\beta = 92.085(1)^\circ$, $\gamma = 110.343(1)^\circ$, $V = 1443.23(3)$ Å³, $\rho_{\text{calc}} = 1.352$ $\text{g}\cdot\text{cm}^{-3}$, $\mu = 0.807$ mm^{-1} , empirical absorption correction ($0.738 \leq T \leq 0.889$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198(2)$ K, ω and ϕ scans, 14493 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å^{–1}, 6837 independent ($R_{\text{int}} = 0.053$) and 5763 observed reflections [$I \geq 2\sigma(I)$], 348 refined parameters, $R = 0.035$, $wR_2 = 0.089$, max. (min.) residual electron density 0.35 (–0.56) $\text{e}\cdot\text{\AA}^{-3}$, hydrogen atom at N3 from difference Fourier calculations, others calculated and refined as riding atoms.

(1,2,4,5-Tetraphenyl-1,3,5-triazapenta-1,3-diene)zinc(II) Chloride ($3\text{c}\cdot\text{ZnCl}_2$): Zinc chloride (14 mg, 0.01 mmol) was added to a solution of 1,2,4,5-tetraphenyl-1,3,5-triazapenta-1,3-diene (**3c**) (38 mg, 0.1 mmol) dissolved in ethanol (2 mL). Diethyl ether was allowed to diffuse into the reaction mixture at room temperature. After 6 h colourless crystals were obtained; yield 37 mg (0.07 mmol, 70%). IR (KBr): $\tilde{\nu} = 3448$ (vw), 3236 (m), 3148 (m), 3055 (s, CH), 2824 (m), 1622 (s), 1605 (s), 1583 (s), 1572 (vs), 1531 (vs), 1514 (vs), 1506 (vs), 1495 (vs), 1445 (vs), 1360 (s), 1340 (s), 1329 (s), 1298 (m), 1275 (m), 1231 (m), 1180 (m), 1155 (m), 1074 (w), 1026 (m), 1001 (m), 905 (m), 766 (s), 754 (s), 689 (vs), 615 (m), 571 (m), 513 (m) cm^{-1} . MS [ESI (negative), acetonitrile] m/z (%) = 508–514 (24) [$\text{C}_{26}\text{H}_{21}\text{Cl}_2\text{ZnN}_3 - \text{H}^+$], 410–374 (100) [$\text{C}_{26}\text{H}_{21}\text{N}_3 - \text{H}^+$]. $\text{C}_{26}\text{H}_{21}\text{Cl}_2\text{N}_3\text{Zn}\cdot 0.5\text{EtOH}$ (534.79): calcd. C 60.64, H 4.52, N 7.86; found C 60.45, H 4.42, N 7.79.

X-ray Crystal Structure Analysis for $3\text{c}\cdot\text{ZnCl}_2$:^[27,28] Empirical formula: $\text{C}_{26}\text{H}_{21}\text{Cl}_2\text{N}_3\text{Zn}$, $M_r = 511.73$ $\text{g}\cdot\text{mol}^{-1}$, colourless crystal $0.30 \times 0.30 \times 0.20$ mm, $a = 19.9528(6)$ Å, $c = 6.7140(1)$ Å, $V = 2672.9(1)$ Å³, $\rho_{\text{calc}} = 1.272$ $\text{g}\cdot\text{cm}^{-3}$, $\mu = 1.135$ mm^{-1} , empirical absorption correction ($0.727 \leq T \leq 0.805$), $Z = 4$, tetragonal, space group $P4m2_1$ (No. 113), $\lambda = 0.71073$ Å, $T = 198(2)$ K, ω and ϕ scans, 10256 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å^{–1}, 3288 independent ($R_{\text{int}} = 0.042$) and 2862 observed reflections [$I \geq 2\sigma(I)$], 153 refined parameters, $R = 0.045$, $wR_2 = 0.145$, max. (min.) residual electron density 1.72 (–0.39) $\text{e}\cdot\text{\AA}^{-3}$ around 0,0.5, z could not be refined in a chemically meaningful manner, refined as racemic twin, hydrogen atom at N3 from difference Fourier calculations, others calculated and refined as riding atoms.

Bis(1,2,4,5-tetraphenyl-1,3,5-triazapenta-1,3-dienyl)palladium(II) [$(3\text{c})_2\cdot\text{Pd}$]: A solution of palladium(II) acetate (0.05 mmol, 12 mg)

in tetrahydrofuran (2 mL) was added to **3c** (0.1 mmol, 38 mg) in tetrahydrofuran (1 mL). After a short while of shaking diethyl ether was allowed to diffuse into the yellow reaction mixture at room temperature. After 10 d a yellow precipitate was filtered off and dried at 100 °C; yield 16 mg (0.02 mmol, 40%); m.p. 245 °C (decomp.). IR (KBr): $\tilde{\nu} = 3449$ (w), 3076 (vw), 3055 (w), 3026 (w), 2924 (vw), 2853 (vw), 1593 (w), 1580 (w), 1528 (s), 1491 (m), 1454 (s), 1418 (vs), 1377 (s), 1333 (m), 1323 (m), 1312 (m), 1283 (w), 1242 (m), 1180 (w), 1094 (w), 1070 (w), 1028 (w), 999 (vw), 939 (w), 885 (vw), 831 (w), 795 (w), 771 (m), 750 (m), 700 (s), 658 (w), 602 (w), 546 (w), 515 (w), 449 (w) cm^{-1} . MS (ESI, methanol): m/z (%) = 853–860 (19) [$\text{C}_{52}\text{H}_{40}\text{N}_6\text{Pd} + \text{H}^+$], 428 (17), 376 (100) [$\text{C}_{26}\text{H}_{21}\text{N}_3$], 180 (19) [$\text{C}_{13}\text{H}_{10}\text{N}^+$]. $\text{C}_{52}\text{H}_{40}\text{N}_6\text{Pd}$ (855.33): calcd. C 73.02, H 4.7, N 9.83; found C 72.78, H 4.87, N 9.73.

Bis(1,2,4,5-tetraphenyl-1,3,5-triazapenta-1,3-dienyl)copper(II) [$(3\text{c})_2\cdot\text{Cu}$]: In analogy to the procedure described for (**2a**)₂·Cu, the reaction of **3c** (38 mg, 0.01 mmol) and copper(II) acetate hydrate (10 mg, 0.05 mmol) led to black crystals; yield 44 mg (0.05 mmol, 50%); m.p. 237 °C. IR (KBr): $\tilde{\nu} = 3441$ (w), 3059 (w), 3022 (w), 2970 (w), 2924 (w), 2853 (w), 1593 (w), 1580 (w), 1506 (s), 1489 (s), 1450 (vs), 1418 (vs), 1333 (w), 1313 (w), 1285 (w), 1225 (m), 1175 (w), 1153 (w), 1092 (w), 1069 (w), 1026 (w), 999 (w), 934 (w), 907 (w), 793 (m), 777 (m), 752 (m), 716 (w), 700 (m), 690 (m), 677 (w), 590 (w), 542 (w), 519 (w) cm^{-1} . MS (ESI, methanol): m/z (%) = 812 (4) [$\text{C}_{52}\text{H}_{40}\text{CuN}_6 + \text{H}^+$], 376 (100) [$\text{C}_{26}\text{H}_{21}\text{N}_3 + \text{H}^+$]. UV/Vis (acetonitrile): λ_{max} ($\tilde{\nu}$, ϵ) = 235 (42553 cm^{-1} , 15422 $\text{M}^{-1}\text{cm}^{-1}$), 197 (51282 cm^{-1} , 34844 $\text{M}^{-1}\text{cm}^{-1}$) nm. $\text{C}_{52}\text{H}_{40}\text{N}_6\text{Cu}\cdot\text{C}_4\text{H}_8\text{O}$ (884.57) calcd. C 76.04, H 5.47, N 9.50; found C 75.88, H 5.37, N 9.42.

X-ray Crystal Structure Analysis for $(3\text{c})_2\cdot\text{Cu}$:^[27,28] Empirical formula: $\text{C}_{52}\text{H}_{40}\text{CuN}_6\cdot\text{C}_4\text{H}_8\text{O}$, $M_r = 884.54$ $\text{g}\cdot\text{mol}^{-1}$, black crystal $0.35 \times 0.20 \times 0.20$ mm, $a = 19.2753(3)$ Å, $b = 14.4552(2)$ Å, $c = 16.6923(2)$ Å, $V = 4650.95(11)$ Å³, $\rho_{\text{calc}} = 1.263$ $\text{g}\cdot\text{cm}^{-3}$, $\mu = 0.516$ mm^{-1} , empirical absorption correction ($0.840 \leq T \leq 0.904$), $Z = 4$, orthorhombic, space group $Pbcn$ (No. 60), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and ϕ scans, 27340 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å^{–1}, 5540 independent ($R_{\text{int}} = 0.053$) and 4040 observed reflections [$I \geq 2\sigma(I)$], 287 refined parameters, $R = 0.051$, $wR_2 = 0.162$, max. (min.) residual electron density 1.70 (–0.57) $\text{e}\cdot\text{\AA}^{-3}$, hydrogen atoms calculated and refined as riding atoms.

(1,2,4,5-Tetraphenyl-1,3,5-triazapenta-1,3-dienyl)boron(III) Difluoroboride ($3\text{c}\cdot\text{BF}_2$): Boron trifluoride-diethyl ether (25.2 mmol, 3.58 g) was added dropwise to a solution of **3c** (10 mmol, 3.75 g) in dry toluene (25 mL). The reaction mixture was heated for 3 h at 80 °C. Afterwards the mixture was cooled to room temperature, diluted with chloroform (40 mL) and washed with water (20 mL). The organic layer was separated and dried with magnesium sulfate. Finally, the solvent was removed in vacuo. The crude product was recrystallized from dichloromethane/heptane; yield 0.91 g (2.2 mmol, 22%), colourless crystals; m.p. 237 °C. IR (KBr): $\tilde{\nu} = 3061$ (m), 3030 (w), 1599 (m), 1583 (s), 1537 (vs), 1493 (s), 1456 (vs), 1443 (vs), 1427 (vs), 1385 (s), 1317 (s), 1288 (m), 1248 (m), 1229 (s), 1182 (m), 1157 (m), 1132 (s), 1115 (s), 1070 (vs), 1051 (vs), 1001 (s), 972 (s), 918 (m), 868 (m), 851 (m), 799 (m), 779 (s), 764 (s), 752 (m), 743 (s), 710 (s), 694 (vs), 663 (m), 565 (m), 542 (m), 519 (m) cm^{-1} . ¹H NMR (300 MHz, CDCl_3): $\delta = 7.14$ – 7.31 (m, 16 H, CH_{arom}), 7.47 – 7.50 (m, 4 H, CH_{arom}) ppm. ¹³C NMR (75.47 MHz, CDCl_3): $\delta = 127.0$ (2 C, C_{arom}), 127.2 (4 C, C_{arom}), 127.9 (4 C, C_{arom}), 128.7 (4 C, C_{arom}), 130.1 (4 C, C_{arom}), 130.4 (2 C, C_{arom}), 135.1 (2 C, $i\text{-C}_{\text{arom}}$), 140.9 (2 C, $i\text{-C}_{\text{arom}}$), 166.6 (2 C, C=N) ppm. ¹¹B NMR (96.29 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 0.93$ (t, 1:2:1, $J = 27.3$ Hz) ppm. ¹⁹F NMR (282.38 MHz, $[\text{D}_6]\text{DMSO}$): δ

= -129.1 (q, 1:1:1:1) ppm. MS (ESI, methanol): m/z (%) = 869 (20) [2 M + Na⁺], 446 (30) [M + Na⁺], 424 (100) [M + H⁺]. UV/Vis (dichloromethane): λ_{max} (ϵ) = 297 (33667 cm⁻¹, 24412 M⁻¹ cm⁻¹) nm. C₂₆H₂₀BF₂N₃ (423.26): calcd. C 73.78, H 4.76, N 9.93; found C 73.62, H 4.88, N 9.90.

X-ray Crystal Structure Analysis for 3c·BF₂:^[27,28] Empirical formula: C₂₆H₂₀BF₂N₃, M_r = 423.26 g mol⁻¹, colourless crystal 0.55 × 0.40 × 0.40 mm, a = 12.1904(1) Å, b = 11.6666(1) Å, c = 14.7293(1) Å, β = 98.503(1)°, V = 2071.78(4) Å³, ρ_{calc} = 1.357 g cm⁻³, μ = 0.093 mm⁻¹, empirical absorption correction (0.951 ≤ T ≤ 0.964), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 198(2) K, ω and ϕ scans, 13628 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin \theta)/\lambda] = 0.66$ Å⁻¹, 4897 independent (R_{int} = 0.037) and 4213 observed reflections [$I \geq 2\sigma(I)$], 289 refined parameters, R = 0.038, wR_2 = 0.103, max. (min.) residual electron density 0.28 (−0.19) e Å⁻³, hydrogen atoms calculated and refined as riding atoms.

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