RESEARCH ARTICLE

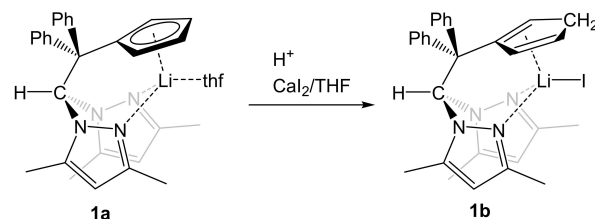# Synthesis and Structure of a New Bulky Hybrid Scorpionate/Cyclopentadienyl Ligand and its Lithium Complex

Miles J. Mandel,[a] Helmar Görls,[a] and Matthias Westerhausen*[a]

Dedicated to Professor Cameron Jones on the occasion of his 60th birthday.

The reaction of 5-(1-adamantyl)-3-methyl-1H-pyrazole with dibromomethane yields a product mixture of bis(3-adamantyl-5-methylpyrazolyl)methane ($H_2C(Pz^{Ad,Me})_2$, **2a**), (3-adamantyl-5-methylpyrazolyl)-(3-methyl-5-adamantylpyrazolyl)methane (($H_2C(Pz^{Ad,Me})(Pz^{Me,Ad})$, **2b**) and bis(3-methyl-5-adamantylpyrazolyl)methane ($H_2C(Pz^{Me,Ad})_2$, **2c**). Lithiation of sterically congested $H_2C(Pz^{Ad,Me})_2$ (**2a**) and subsequent addition of diphenylfulvene yields lithium 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*pentadienide, [(thf)Li{Cp—CPh₂—CHPz^{Ad,Me}}] (**3**) which is unable to form a thf adduct but can be hydrolyzed to H_5C_5—CPh₂—CHPz^{Ad,Me} (**4**). Adamantyl groups in 5-position of bis(pyrazolyl)methane, i.e. **2b** and **2c**, prohibit formation of a fulvene adduct. For comparison reasons, [{H₅C₅—CPh₂—CHPz^{Me2}}LiI] (**1b**) has been prepared via protolysis of (thf)lithium 1,1-bis(3,5-dimethylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*pentadienide, [(thf)Li{Cp—CPh₂—CHPz^{Me2}}] (**1a**), in the presence of calcium iodide.

1. Introduction

Substituted tris(pyrazolyl)boranates (homoscorpionates) are a widely used ligand system with a facial $\kappa^3 N$-binding mode to metal ions.[1,2] Isoelectronic tris(pyrazolyl)methanes and -methanides (*C*-homoscorpionates) have been studied less intensively.[2,3] The facial binding behavior, the monoanionic charge and the mode of action as a 6-electron donor make these ligand systems comparable to the *cyclo*pentadienide anion. Substitution of one pyrazolyl side-arm by another functionality produces heteroscorpionates (based on bis(pyrazolyl)boranates) and *C*-heteroscorpionates (by substitution of the central BH_2^- unit by the CH^- fragment). A combination of the bis(pyrazolyl)methyl building block with a *cyclo*pentadienyl moiety has only been performed applying the sterically undemanding 3,5-dimethylpyrazolyl bases as depicted in Scheme 1. Furthermore, it has been shown that these *cyclo*pentadienyl/*C*-heteroscorpionate ligands could be transferred to transition metal ions via a metathetical approach of the lithium complexes with halides of these metals.[4] In (tetrahydrofuran)lithium 1,1-bis(3,5-dimethylpyrazolyl)-2,2-di-

Scheme 1. Conversion of 1,1-bis(3,5-dimethylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*pentadienide, [(thf)Li{Cp—CPh₂—CHPz^{Me2}}] (**1a**), to the lithium iodide adduct [{H₅C₅—CPh₂—CHPz^{Me2}}LiI] (**1b**).

phenyl-2-ethyl-*cyclo*pentadienide, [(thf)Li{Cp—CPh₂—CHPz^{Me2}}] (**1a**), the lithium atom binds to both pyrazolyl bases, the thf molecule and shows a η^5-coordination to the anionic *cyclo*pentadienide ring, altogether a distorted tetrahedral arrangement of four ligands.

Protonation of [(thf)Li{Cp—CPh₂—CHPz^{Me2}}] in THF in the presence of calcium iodide leads to formation of [{H₅C₅—CPh₂—CHPz^{Me2}}LiI] (**1b**) as depicted in Scheme 1. For clarity reasons, in all schemes the overlain pyrazolyl moiety is shown in grey whereas the pyrazolyl substituent at the front is drawn in black. The lithium atom of **1b** binds to the iodine atom, both pyrazolyl bases and shows a η^4-coordination to the diene-system of the cyclopentadiene ring.[5] Reduced electrostatic attraction leads to enlarged Li—C distances (Li—C > 255.6(8)–323.7(8) pm) compared to the lithium *cyclo*pentadienide complex [(thf)Li{Cp—CPh₂—CHPz^{Me2}}] (**1a**) (Li—C 225(1)–244(1) pm).[4b]

We became interested in sterically crowded *cyclo*pentadienyl/*C*-heteroscorpionate ligands with bulky adamantyl instead of small methyl groups in 3-positions of both pyrazolyl rings. Sterically crowded homoscorpionates HB(Pz^{Ad,R})₃ gained tremen-

[a] M. J. Mandel, Dr. H. Görls, Prof. Dr. M. Westerhausen
Friedrich Schiller University Jena
Institute of Inorganic and Analytical Chemistry
Humboldtstraße 8, D-07743 Jena
E-mail: m.we@uni-jena.de

dous interest several years ago with the HB(3-Ad-5-*i*PrPz)₃ anion being the most crowded homoscorpionate up to now. This ligand has been studied as tridentate ligand at e.g. copper,[6] iron,[7] manganese,[8] calcium,[9] barium,[10] and ytterbium.[11] Significantly enhanced preparative challenges limited the access to the corresponding isoelectronic *C*-homoscorpionate [C(Pz^{Ad,R})₃]⁻ anions and only the magnesium and ytterbium complexes have been investigated so far.[12] Furthermore, bis(3,5-diadamantylpyrazolyl)methane, H₂C(Pz^{Ad2})₂, has been employed as bidentate ligand at Pd(II).[13] in addition, this base could be converted to the aldehyde (Pz^{Ad2})₂CH—CHO, but attempts to oxidize this aldehyde to the carboxylic acid failed due to steric protection and starting substrate was recovered.[14]
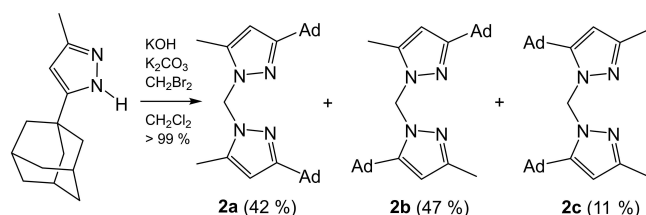
We intended the preparation of a bulky *C*-heteroscorpionate with a cyclopentadiene side-arm and to subsequently synthesize the lithium complex for comparison with the less congested congeners **1a** and **1b**.

2. Results and Discussion

2.1. Syntheses

Starting 5-(1-adamantyl)-3-methyl-1*H*-pyrazole can be prepared with high yield *via* the reaction of 1-(1-adamantyl)butane-1,3-dione with hydrazine hydrate according to a published protocol.[15] Thereafter, this pyrazole was quantitatively converted to bis(pyrazolyl)methane *via* the reaction with dibromomethane in the presence of potassium hydroxide and potassium carbonate in refluxing dichloromethane according to Scheme 2. Different substituents in 3- and 5-positions of the pyrazole substrate led to a mixture of three different isomers of bis(3,5-dialkylpyrazolyl)methane: bis(3-adamantyl-5-methylpyrazolyl)methane (H₂C(Pz^{Ad,Me})₂, **2a**, 42%), bis(3-methyl-5-adamantylpyrazolyl)methane (H₂C(Pz^{Me,Ad})₂, **2c**, 11%) and the mixed isomer (3-adamantyl-5-methylpyrazolyl)-(3-methyl-5-adamantylpyrazolyl)methane ((H₂C(Pz^{Ad,Me})(Pz^{Me,Ad}), **2b**, 47%). Bis(3-methyl-5-adamantylpyrazolyl)methane (H₂C(Pz^{Me,Ad})₂, **2c**) was the minor component in this product mixture due to significant intramolecular steric repulsion between the bulky adamantyl groups in 5,5'-positions.

Separation of the isomers succeeded by fractional crystallization from different solvents. Recrystallization from hot
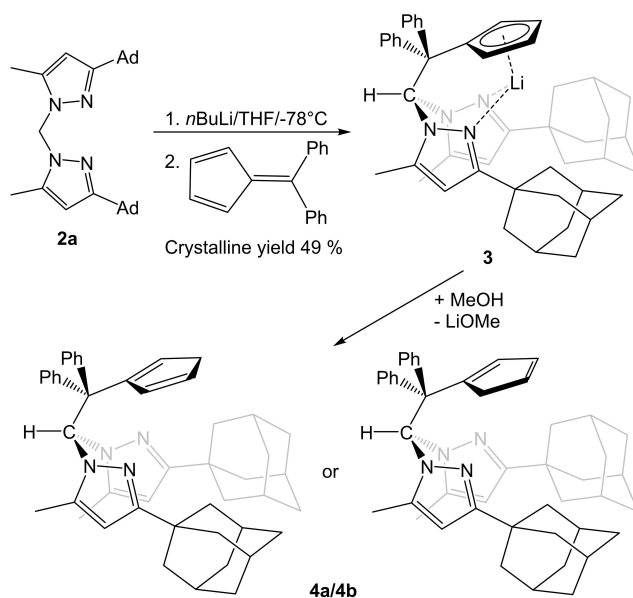
ethanol gave 36% of desired bis(3-adamantyl-5-methylpyrazolyl)methane (H₂C(Pz^{Ad,Me})₂, **2a**). Repeated recrystallization of the remaining product mixture from isopropanol yielded 3% of bis(3-methyl-5-adamantylpyrazolyl)methane (H₂C(Pz^{Me,Ad})₂, **2c**). Finally, the mixed isomer (3-adamantyl-5-methylpyrazolyl)-(3-methyl-5-adamantylpyrazolyl)methane ((H₂C(Pz^{Ad,Me})(Pz^{Me,Ad}), **2b**) could be isolated from the combined filtrates after recrystallization from acetone with an isolated crystalline yield of 29%.

Bis(3-adamantyl-5-methylpyrazolyl)methane (H₂C(Pz^{Ad,Me})₂, **2a**) was lithiated with *n*-butyllithium in THF at −78°C. The colorless suspension was warmed to 0°C and then, one equivalent of diphenylfulvene was added, yielding an intensively red reaction solution. Work-up of this reaction mixture and recrystallization from THF gave colorless crystals of lithium 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*pentadienide, [(thf)Li{Cp–CPh₂–CHPz^{Ad,Me}}] (**3**) according to Scheme 3. Under similar reaction conditions, the other isomers **2b** and **2c** did not yield the analogous cyclopentadienyl/*C*-heteroscorpionate systems; the bulky adamantyl group in 5-position impeded the reaction with diphenylfulvene. Nevertheless, complexes of asymmetric 3-adamantyl-5-methylpyrazolyl)-(3-methyl-5-adamantylpyrazolyl)methane ((H₂C(Pz^{Ad,Me})(Pz^{Me,Ad}), **2b**) could be formed with cobalt(II) chloride ([(**2b**)CoCl₂], see Supporting Information).

Protolysis of **3** with an aqueous ammonium chloride solution in tetrahydrofuran at 0°C yielded a mixture of two tautomeric forms of 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-

Scheme 3. Lithiation of bis(3-adamantyl-5-methylpyrazolyl)methane (H₂C(Pz^{Ad,Me})₂, **2a**) in THF at −78°C and subsequent addition reaction with diphenylfulvene at 0°C yielding lithium 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*pentadienide, [(thf)Li{Cp–CPh₂–CHPz^{Ad,Me}}] (**3**). Hydrolysis yields a mixture of the tautomeric forms of 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-diphenyl-2-*cyclo*pentadienylethane, **4a** and **4b**.

Scheme 2. Synthesis of the regioisomeric product mixture of bis(3-adamantyl-5-methylpyrazolyl)methane (H₂C(Pz^{Ad,Me})₂, **2a**), (3-adamantyl-5-methylpyrazolyl)-(3-methyl-5-adamantylpyrazolyl)methane ((H₂C(Pz^{Ad,Me})(Pz^{Me,Ad}), **2b**) and bis(3-methyl-5-adamantylpyrazolyl)-methane (H₂C(Pz^{Me,Ad})₂, **2c**); yields are given in brackets.

diphenyl-2-*cyclo*pentadienylethane, **4a** and **4b**. Reaction of this mixture with butyllithium reformed the lithium complex **3**.

2.2. Molecular Structures

The molecular structures and atom labelling schemes of **2a**, **2b** and **2c** are depicted in Figures 1, 2 and 3. Derivative **2a** crystallized with three half molecules A, B and C and an
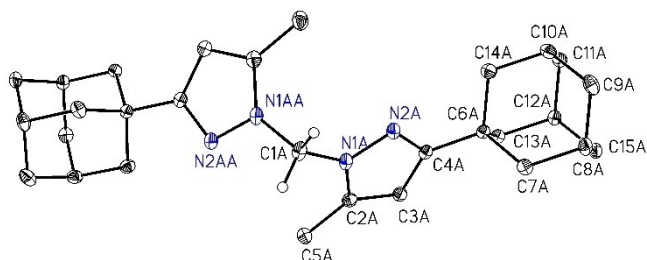

Figure 1. Molecular structure and atom labelling scheme of molecule A of bis(3-adamantyl-5-methylpyrazolyl)methane ($H_2C(Pz^{Ad,Me})_2$, **2a**). Symmetry-related atoms are marked with a second letter "A". The ellipsoids represent a probability of 30%, H atoms are neglected for clarity reasons except those at C1. Selected bond lengths (pm): N1 A–N2 A 136.38(19), N1 A–C1 A 144.68(19), N1 A–C2 A 135.8(2), N2 A–C4 A 133.1(2), C2 A–C3 A 137.6(2), C3 A–C4 A 141.0(2), C2 A–C5 A 149.3(2), C4 A–C6 A 151.1(2); angles (deg.): N1 A–C1 A–N1AA 114.1(2), C1 A–N1 A–N2 A 118.50(12), C1 A–N1 A–C2 A 128.52(13), C2 A–N1 A–N2 A 112.83(14).
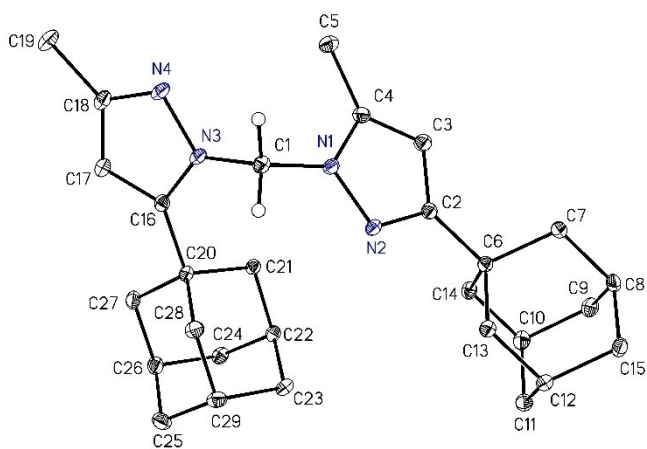

Figure 2. Molecular structure and atom labelling scheme of asymmetric 3-adamantyl-5-methylpyrazolyl)-(3-methyl-5-adamantylpyrazolyl)methane (($H_2C(Pz^{Ad,Me})(Pz^{Me,Ad})$, **2b**). The ellipsoids represent a probability of 30%, H atoms are omitted for the sake of clarity except those at C1. Selected bond lengths (pm): N1–N2 136.80(14), N1–C1 144.84(16), N1–C4 135.95(17), N2–C2 133.23(17), C2–C3 141.06(18), C3–C4 137.27(19), C2–C6 151.18(17), C4–C5 149.69(18), N3–N4 137.61(15), N3–C1 145.97(16), N3–C16 138.04(16), N4–C18 132.30(18), C16–C17 138.03(18), C17–C18 140.85(19), C16–C20 151.32(17), C18–C19 149.43(18); angles (deg.): N1–C1–N3 115.54(11), C1–N1–N2 118.78(10), C1–N1–C4 128.94(11), N2–N1–C4 112.19(10), C1–N3–N4 113.81(10), C1–N3–C16 133.38(11), N4–N3–C16 111.62(10).
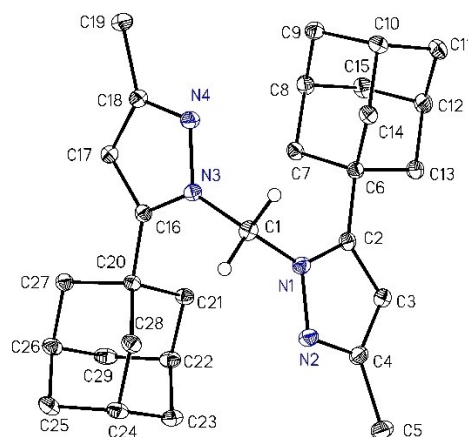

Figure 3. Molecular structure and atom labelling scheme of bis(3-methyl-5-adamantylpyrazolyl)methane ($H_2C(Pz^{Me,Ad})_2$, **2c**). The ellipsoids represent a probability of 30%, H atoms are omitted for clarity reasons except those at C1. Only molecule A of three molecules is depicted, symmetry-equivalent atoms are marked with an additional letter "A". Selected bond lengths (pm): N1–N2 137.53(13), N1–C1 145.77(14), N1–C2 138.08(14), N2–C4 132.78(15), C2–C3 138.33(16), C3–C4 140.59(17), C2–C6 151.71(15), C4–C5 149.73(16), N3–N4 137.44(13), N3–C1 145.68(14), N3–C16 137.72(14), N4–C18 132.83(15), C16–C17 138.45(15), C17–C18 140.77(16), C16–C20 151.57(15), C18–C19 149.89(16); angles (deg.): N1–C1–N3 116.33(9), C1–N1–N2 113.83(9), C1–N1–C2 133.92(9), N2–N1–C2 111.99(9), C1–N3–N4 113.95(9), C1–N3–C16 133.76(9), N4–N3–C16 112.25(9).

intercalated adamantane molecule, the molecules are completed by crystallographic C_2 symmetry. Only molecule A is depicted in Figure 1. In all compounds steric pressure, which could be induced by the demanding adamantyl groups, is minimized by rotation around the C1–N1 and C1–N3 bonds. Nevertheless, some characteristic common features can be recognized. The C1–N bond lengths to pyrazole rings with the adamantyl substituent in 3-position are slightly elongated. In addition, the C–C bond lengths between the Ad group and the pyrazolyl ring are larger than those of the methyl substituent. However, in the cobalt complex [(**2b**)CoCl$_2$] both C1–N1/N3 distances with values of 145.1(3) and 145.4(3) pm, respectively, are identical within the estimated standard deviation. In all bis(pyrazolyl)methanes, the proximal C1–N–N and distal C1–N–C bond angles differ significantly due to steric repulsion between the methylene unit and the alkyl groups bonded in 5-position regardless of the size of this substituent.

Molecular structure and atom labelling scheme of the lithium iodide adduct [{H_5C_5–CPh_2–$CHPz^{Me2}$}LiI] (**1b**) is shown in Figure 4. The lithium cation is in a severely distorted tetrahedral environment of an iodide ion, two pyrazolyl bases and a butadiene π-system. Due to steric requirements, the N2–Li1–N4 bond angle of 90.9(3)° is very narrow whereas the I1–Li1–N2/N4 angles of 122.4(3)° and 129.(3)°, respectively, are strongly widened. The Li–C distances to the butadiene π-system vary from 255.6(8) to 323.7(8) pm and are significantly larger than observed for lithium *cyclo*pentadienides due to lack of electro-
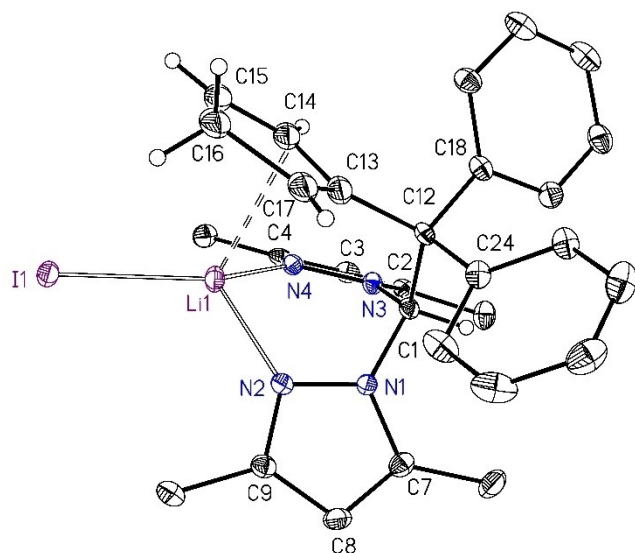
Figure 4. Molecular structure and atom labelling scheme of the lithium iodide adduct [{H_5C_5–CPh_2–$CHPz^{Me2}$}LiI] (**1 b**). The ellipsoids represent a probability of 30%, hydrogen atoms are neglected except those at C1 and those of the cyclopentadienyl moiety. Selected bond lengths (pm): Li1–I1 263.2(6), Li1–N2 204.4(7), Li1–N4 203.4(8), Li1–C13 272.9(8), Li1–C14 255.6(8), Li1–C15 300.3(8), Li1–C17 323.7(8), N1–N2 136.9(4), N3–N4 137.2(4), C1–N1 145.4(5), C1–N3 145.5(5), C1–C12 160.5(5), C12–C13 153.9(5), C12–C18 154.3(5), C12–C24 154.9(5), C13–C14 146.5(7), C13–C17 136.7(7), C14–C15 134.7(6), C15–C16 146.9(7), C16–C17 157.7(6); angles (deg.): N1–C1–N3 109.6(3), C1–N1–N2 121.4(3), C1–N1–C7 127.0(3), N2–N1–C7 111.7(3), C1–N3–N4 120.3(3), C1–N3–C2 127.7(3), N4–N3–C2 111.0(3), I1–Li1–N2 122.4(3), I1–Li1–N4 129.3(3).

Figure 5. Molecular structure and atom labelling scheme of lithium 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*-pentadienide, [(thf)Li{Cp–CPh_2–$CHPz^{Ad,Me}$}] (**3**). The ellipsoids represent a probability of 30%, hydrogen atoms are neglected except those at C1. Selected bond lengths (pm): Li1–N2 212.0(3), Li1–N4 200.5(3), Li1–C31 218.0(3), Li1–C32 229.4(3), Li1–C33 232.9(3), Li1–C34 226.3(3), Li1–C35 218.0(3), N1–N2 137.36(16), N3–N4 137.17(16), C1–N1 147.43(18), C1–N3 146.29(18), C1–C30 160.24(19), C30–C31 152.53(19), C30–C36 156.30(19), C30–C42 155.3(2), C31–C32 141.7(2), C31–C35 142.4(2), C32–C33 140.3(2), C33–C34 140.6(3), C34–C35 140.7(2); angles (deg.): N1–C1–N3 107.23(11), C1–N1–N2 118.34(11), C1–N1–C2 127.40(12), N2–N1–C2 110.87(12), C1–N3–N4 120.72(11), C1–N3–C16 128.00(12), N4–N3–C16 110.90(11), N2–Li1–N4 83.07(10).

static attraction.[16] Thus, the Li–C bond lengths in complex **1 a** range from 225(1) to 244(1) pm.[4a,b]
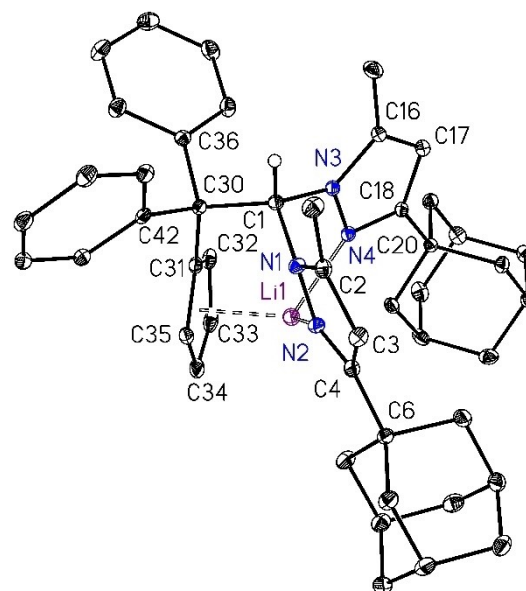
Molecular structure and atom labelling scheme of lithium 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*pentadienide, [(thf)Li{Cp–CPh_2–$CHPz^{Ad,Me}$}] (**3**), is depicted in Figure 5. Despite the fact that this compound has been prepared in tetrahydrofuran, no such solvent molecule is bound at the lithium cation. The lithium atom Li1 is bound to both pyrazolyl Lewis bases with a very narrow N2–Li1–N4 bond angle of 83.07(10)°. The small coordination number of Li1 leads to short Li1–C bonds to the *cyclo*pentadienide substructure, ranging from 218.0(3) (Li1–C31 and Li1–C35) to 232.9(3) pm (Li1–C33).

2.3. NMR Spectroscopy

Selected NMR parameters of the bis(pyrazolyl)methanes **2 a**, **2 b** and **2 c** are listed in Table 1; the substituent in 3-position is named firstly as superscript, the second superscript denominates the substituent in 5-position. Note that **2 b** contains two differently substituted pyrazolyl rings. Expectedly, the NMR parameters of 3-adamantyl-5-methyl- ($Pz^{Ad,Me}$) and 3-methyl-5-adamantylpyrazolyl groups ($Pz^{Me,Ad}$) are quite similar but none-

Table 1. Selected NMR data of the bis(pyrazolyl)methanes **2 a**, **2 b** and **2 c**.[a]

	2 a $Pz^{Ad,Me}$	**2 b** $Pz^{Ad,Me}$	**2 b** $Pz^{Me,Ad}$	**2 c** $Pz^{Me,Ad}$
^{1}H NMR				
CH_2	6.15	6.36		6.52
CH_3	2.38	2.23	2.19	2.19
$CHPz$	5.83	5.85	5.85	5.88
$^{13}C\{^1H\}$ NMR				
CH_2	62.0	64.7		66.8
CH_3	11.4	11.6	13.6	13.6
$C3_{Pz}$	161.4	161.1	147.3	146.7
$C4_{Pz}$	102.7	103.0	105.0	105.6
$C5_{Pz}$	139.9	140.3	154.2	154.1
$C1_{Ad}$	33.9	34.0	34.5	34.2
$C2_{Ad}$	42.7	42.7	41.2	40.7
$C3_{Ad}$	28.8	28.8	28.7	28.6
$C4_{Ad}$	37.0	37.1	36.6	36.5

[a] The assignment of the NMR parameters of **2 b** was performed in analogy to the symmetric derivatives **2 a** and **2 c**.

theless, characteristic trends can be elucidated. Exchange of $Pz^{Ad,Me}$ by $Pz^{Me,Ad}$ leads to an increasing low field shift for the

methylene fragment in the ^{1}H and ^{13}C{^{1}H} NMR spectra. Furthermore, the adamantyl group causes a stronger low field shift of the pyrazolyl carbon atom than the methyl substituent. The chemical shifts of the adamantyl groups remain nearly unaffected whether they are bonded at 3- or 5-positions of the pyrazolyl rings.

Lithiation of **2a** and addition of diphenylfulvene leads to significantly low field shifted resonances of the methylene moieties in the ^{1}H and ^{13}C{^{1}H} NMR spectra. This reaction leads to substitution of a hydrogen atom by a triarylmethyl functionality. The chemical shifts of the pyrazolyl carbon atoms remain nearly uninfluenced by coordination to a lithium atom.

3. Conclusions

The substitution of the bromine atoms in dibromomethane by 5-(1-adamantyl)-3-methyl-1*H*-pyrazole quantitatively yields a product mixture of bis(3-adamantyl-5-methylpyrazolyl)methane (H$_2$C(Pz^{Ad,Me})$_2$, **2a**), (3-adamantyl-5-methylpyrazolyl)-(3-methyl-5-adamantylpyrazolyl)methane ((H$_2$C(Pz^{Ad,Me})(Pz^{Me,Ad}), **2b**) and bis(3-methyl-5-adamantylpyrazolyl)methane (H$_2$C(Pz^{Me,Ad})$_2$, **2c**) with a ratio of 42:47:11. Lithiation and subsequent reaction of **2a** with diphenylfulvene leads to formation of lithium 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*penta-dienide, [(thf)Li{Cp—CPh$_2$—CHPz^{Ad,Me}}] (**3**). Due to steric repulsion compound **2c** is the minor component. The bulky adamantyl groups shield the lithium atom in **3** and therefore, this complex crystallizes from THF solution without formation of a thf adduct. The rather small coordination number of the lithium atom leads to short Li—N bond lengths of 200.5(3) and 212.0(3) pm to the pyrazolyl bases whereas these bonds are elongated in the thf adduct (tetrahydrofuran)lithium 1,1-bis(3,5-dimethylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*pentadienide, [(thf)Li{Cp—CPh$_2$—CHPz^{Me2}}] (**1a**) (Li—N 213(1) and 237(1) pm). In the lithium chloride derivative [{H$_5$C$_5$—CPh$_2$—CHPz^{Me2}}LiI] (**1b**), however, comparable Li—N distances of 203.4(8) and 204.4(7) pm are observed. In all these complexes the C—C bond lengths between the bis(pyrazolyl)methyl and triarylmethyl moieties are significantly elongated (**1a**: 158.1(7),[4b] **1b**: 160.5(5) and **3**: 160.24(19) pm).

Experimental Section

General. All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques, if not otherwise noted. The solvents were dried over KOH and subsequently distilled over sodium/benzophenone under a nitrogen atmosphere prior to use. All substrates were purchased from Alfa Aesar, abcr, Sigma Aldrich or TCI and used without further purification. The yields given are not optimized. Purity of the compounds was verified by NMR spectroscopy. Deuterated solvents were dried over sodium, distilled, degassed, and stored under nitrogen. ^{1}H, ^{7}Li and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance III 400 (BBO, BBFO probes), Avance II HD 500 (BBO Prodigy probe) or Avance neo 500 (BBFO Prodigy probe) spectrometers. Chemical shifts are reported in parts per million relatively to SiMe$_4$ as an external standard referenced to the solvents residual proton signal using

xiref AU program for ^{13}C NMR spectra. Elemental analyses were performed with an ELEMENTAR Vario EL III instrument. Mass spectra were obtained with the mass spectrometer Finnigan MAT SSQ 710. Starting 5-(1-adamantyl)-3-methyl-1*H*-pyrazole was prepared according to a literature protocol.[15]

Synthesis of (tetrahydrofuran)lithium 1,1-bis(3,5-dimethylpyrazolyl)-2,2-diphenyl-2-ethyl-cyclopentadienide, [(thf)Li{Cp—CPh$_2$—CHPz^{Me2}}] (1a). The synthesis of **1a** was performed according to a literature procedure.[4b] Bis(3,5-dimethylpyrazolyl)methane (1 equiv.; 29.4 mmol; 6.00 g) was dissolved in 300 mL of THF at −78 °C. Within 15 min a 2.5 M n-BuLi solution (1 equiv.; 129.4 mmol; 11.7 mL) in n-hexane was added dropwise. After one hour the suspension was warmed to 0 °C and diphenylfulvene (1 eq.; 29.4 mmol; 6.77 g) was added. Thereafter, the intensively red solution was warmed to r.t. and the solvent removed under reduced pressure. Addition of 150 mL of n-hexane to the oily residue yielded 11,14 g of colorless **1a** (74 %) which was washed twice with hexane. ^{1}**H NMR** (C$_6$D$_6$; 400 MHz; 297 K): $\delta = 7.14, 7.04, 6.92, 6.50, 5.95, 5.49, 3.52$(THF), 1.88, 1.62, 1.36(THF). ^{13}**C{^{1}H} NMR** (C$_6$D$_6$; 151 MHz; 297 K): $\delta = 149.6$, 146.7, 139.8, 131.0, 127.6, 125.8, 114.4, 105.7, 102.1, 74.0, 67.8(THF), 63.4, 25.6 (THF), 13.4, 11.2. ^{7}**Li NMR** (C$_6$D$_6$; 156 MHz; 297 K): $\delta = −5.35$.

Synthesis of (1,1-bis(3,5-dimethylpyrazolyl)-2,2-diphenyl-2-ethyl-cyclopentadiene)lithium iodide, [{H$_5$C$_5$—CPh$_2$—CHPz^{Me2}}LiI] (1b). The thf adduct of lithium 1,1-bis(3,5-dimethylpyrazolyl)-2,2-diphenyl-2-ethyl-*cyclo*pentadienide, [(thf)Li{Cp—CPh$_2$—CHPz^{Me2}}] (**1a**) (1 equiv., 500 mg; 0.98 mmol) was dissolved in 35 mL of THF giving a clear brownish solution. At r.t. 46 mL of a colorless 0.032 M CaI$_2$/THF solution (1.5 equiv., 1.46 mmol) was added. After 4 days the solvent of this orange suspension was removed in vacuo and 40 mL of toluene were added. Solid materials were removed by filtration and 60 mg of **1b** crystallized at −20 °C from this filtrate. Yield: 9 %. ^{1}**H NMR** (C$_6$D$_6$; 400 MHz; 297 K): $\delta = 7.06–7.01$ (m, 6H, C(*m*-/p-11-Ph)-H)-H); 6.92 (d, 4H, C(*o*-11-Ph)-H)-H); 6.70 (s, 1H, C(4)-H); 6.37 (bs, 1H, C(7)-H); 5.95–5.93 (m, 2H, C(10+9)-H); 5.24 (s, 2H, C(2)-H); 3.13 (s, 2H, C(8)-H); 2.53 (s, 6H, C(12/13)-H); 1.52 (s, 6H, C(12/13)-H). ^{7}**Li NMR** (C$_6$D$_6$; 156 MHz; 297 K): $\delta = 1.83$. **IR** (solid): $\tilde{\nu}$ [cm^{-1}] = 2963(w); 1595(m); 1556(m); 1411(m); 1260(s); 1016(s); 956(m); 937(m); 896(m); 792(s); 757(m); 740(m); 721(s); 695(s); 688(s); 662(m). **Elemental analysis** (C$_{36}$H$_{38}$ILiN$_4$): calcd.: C 65.46; H 5.80; N 8.48; found: C 65.63, H 5.82, N 8.47.

Synthesis of bis(3-adamantyl-5-methylpyrazolyl)methane, H$_2$C(Pz^{Ad,Me})$_2$ (2a): 3-Adamantyl-5-methylpayrazole (2 equiv., 0.231 mmol; 50.00 g), KOH (3 equiv., 0.693 mol; 38.88 g) and K$_2$CO$_3$ (3 equiv., 0.693 mol; 95,78 g) were suspended in dibromomethane (0.116 mol; 20.09 g) and 600 mL of dichloromethane and refluxed under vigorous stirring. Thereafter the precipitate was removed by filtration and washed 3 times with 30 mL of dichloromethane each. The organic phases were combined and 200 mL of water were added. After 30 min of stirring, the organic phase was separated and dried over anhydrous sodium sulfate. Then the solvent was removed under reduced pressure and the resulting yellow oil was dissolved in 200 mL of n-pentane. Finally, a colorless product mixture of three isomers was isolated with a yield of 99 % (50,83 g). An isomeric ratio of 42 % of bis(3-adamantanyl-5-methyl-pyrazolyl)methane (**2a**), of 47 % of (3-adamantyl-5-meth-ylpyrazolyl)-(3-methyl-5-adamantylpyrazolyl)methane ((H$_2$C-(Pz^{Ad,Me})(Pz^{Me,Ad}), (**2b**) and of 11 % of bis(5-adamantantyl-3-methyl-pyrazolyl)methane (**2c**) was determined by NMR spectroscopy. Purity of the bulk product was verified by mass spectrometry [*m/z* (%) = 444 (62) [M$^+$]; 228 (100) [M-pz]; 217 (16); 215 (14); 185 (4); 171 (12); 135 (24)] and elemental analysis (C$_{35}$H$_{44}$N$_4$O: calcd.: C 78.33; H 9.07; N 12.60; found: C 78.07, H 9.04, N 12.43). Separation of these isomers succeeded by fractional crystallization from different solvents. The first crystal batch from hot ethanol gave analytically

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pure **2a** with a crystalline yield of 36% (18,47 g). Removal of the solvent of the filtrate and subsequent recrystallization from isopropanol gave an enhanced amount of **2c**. Repeated recrystallization from isopropanol yielded 1.46 g of **2c** (3%). The mixed isomer **2b** was obtained by combining of all filtrates and repeated recrystallization from acetone yielding 14.63 g of pure **2b** (29%). *Physical data of bis(3-adamantyl-5-methylpyrazolyl)methane, H_2C-(Pz^{Ad,Me})$_2$ (2a)*: **^{1}H NMR** (CDCl$_3$; 400 MHz; 297 K): $\delta = 6.15$ (s, 2H, C(4)-H); 5.83 (s, 2H, C(2)-H); 2.38 (s, 6H, C(5)-H); 2.03 (s, 6H, C(8)-H); 1.89 (s, 12H, C(7)-H); 1.75 (s, 12H, C(9)-H). **^{13}C{^{1}H} NMR** (CDCl$_3$; 101 MHz; 297 K): $\delta = 161.4$ (C-3); 139.9 (C-1); 102.7 (C-2); 62.0 (C-4); 42.7 (C-7); 37.0 (C-9); 33.9 (C-6); 28.8 (C-8); 11.4 (C-5). **IR** (solid): $\tilde{\nu}$ [cm^{-1}] = 2897(s); 2844(m); 1550(m); 1454(m); 1391(w); 1365(w); 1344(m); 1330(s); 1312(m); 1271(m); 1181(w); 1148(w); 1100(m); 1075(w); 1000(m); 977(w); 961(m); 851(m); 812(w); 763(m); 718(w); 681(w); 638(m); 630(m); 506(w); 406(w). *Physical data of (3-adamantyl-5-methylpyrazolyl)-(3-methyl-5-adamantylpyrazolyl)methane, H_2C-(Pz^{Ad,Me})(Pz^{Me,Ad}) (2b)*: **^{1}H NMR** (CDCl$_3$; 400 MHz; 297 K): $\delta = 6.36$ (s, 2H, C(4)-H); 5.85 (s, 2H, C(2/2')-H); 2.23 (s, 3H, C(5)-H); 2.19 (s, 3H, C(5')-H); 2.02 (s, 6H, C(8/8')-H); 1.96 (s, 6H, C(7')-H); 1.89 (s, 6H, C(7)-H); 1.74 (s, 12H, C(9/9')-H). **^{13}C{^{1}H} NMR** (CDCl$_3$; 101 MHz; 297 K): $\delta = 161.1$ (C-3); 154.2 (C-1'); 147.3 (C-3'); 140.3 (C-1); 105.0 (C-2'); 103.0 (C-2); 64.7 (C-4); 42.7 (C-7); 41.2 (C-7'); 37.1 (C-9); 36.6 (C-9'); 34.5 (C-6'); 34.0 (C-6); 28.8 (C-8); 28.7 (C-8'); 13.6 (C-5'); 11.6 (C-5). **IR** (solid): $\tilde{\nu}$ [cm^{-1}] = 2897(s); 2844(s); 2676(w); 1548(m); 1479(w); 1450(m); 1420(m); 1403(w); 1365(w); 1342(m); 1328(s); 1310(s); 1273(m); 1255(m); 1187(w); 1167(w); 1151(w); 1100(m); 1073(w); 1038(w); 1020(w); 991(w); 975(m); 963(m); 936(w); 853(w); 814(w); 804(w); 785(s); 761(m); 716(w); 683(m); 641(m); 624(w); 516(w); 502(w); 467(w); 453(w); 443(w); 424(w). *Physical data of bis(5-adamantyl-3-methylpyrazolyl)methane, H_2C(Pz^{Me,Ad})$_2$ (2c)*: **^{1}H NMR** (CDCl$_3$; 400 MHz; 297 K): $\delta = 6.52$ (s, 2H, C(4)-H); 5.88 (s, 2H, C(2')-H); 2.19 (s, 6H, C(5')-H); 1.99 (s, 6H, C(8')-H); 1.84 (s, 12H, C(7')-H); 1.70 (s, 12H, C(9')-H). **^{13}C{^{1}H} NMR** (CDCl$_3$; 101 MHz; 297 K): $\delta = 154.1$ (C-1'); 146.7 (C-3'); 105.6 (C-2'); 66.8 (C-4); 40.7 (C-7'); 36.5 (C-9'); 34.2 (C-6'); 28.6 (C-8'); 13.6 (C-5'). **IR** (solid): $\tilde{\nu}$ [cm^{-1}] = 3904(w); 2899(s); 2844(s); 2656(w); 1550(m); 1473(w); 1446(m); 1422(m); 1399(w); 1365(w); 1342(m); 1332(m); 1310(s); 1271(w); 1246(m); 1181(w); 1167(w); 1151(w); 1100(m); 1069(w); 1038(w); 1016(w); 975(w); 959(m); 936(w); 851(m); 814(w); 781(s); 761(m); 716(w); 704(w); 679(m); 641(m); 626(m); 508(w); 465(w); 457(w); 426(w); 414(w).

Synthesis of lithium 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-diphenyl-2-ethyl-cyclopentadienide, [(thf)Li{Cp—CPh$_2$—CHPz^{Ad,Me}}] (3): Bis(3-adamantyl-5-methylpyrazolyl)methane **2a** (1 equiv.; 11.4 mmol; 5.00 g) was dissolved at $-78\,°C$ in 130 mL of THF and within 10 min a 2.5 M n-BuLi solution (1 equiv.; 11.4 mmol; 4.5 mL) in n-hexane was added dropwise. After 1 h the colorless suspension was warmed to $0\,°C$ and diphenylfulvene (1 equiv.; 11.4 mmol; 2.59 g) was added. An intensively red reaction mixture formed. All volatiles were removed under reduced pressure leaving a brown oily residue. Addition of 150 mL of n-hexane gave a colorless solid of **3** (49%, 3.86 g) which was washed twice with 20 mL of hexane. Recrystallization from THF yielded single crystals suitable for X-ray diffraction experiments. **^{1}H NMR** (C$_6$D$_6$; 400 MHz; 297 K): $\delta = 7.65$ (d, H, C(o-11-Ph)-H); 7.15 (s, 1H, C(4)-H); 7.05 (t, 4H, C(m-11-Ph)-H); 6.94 (t, 2H, C(p-11-Ph)-H); 6.63 (t, 2H, C(7/10)-H); 5.91 (t, 2H, C(8/9)-H); 5.57 (s, 2H, C(2)-H); 1.93 (bs, 6H, C(15)-H); 1.86 (bs, 12H, C(14)-H); 1.64 (bs, 18H, C(12/16)-H). **^{13}C{^{1}H} NMR** (C$_6$D$_6$; 101 MHz; 297 K): $\delta = 160.1$ (C-3); 149.0 (qC-11-Ph); 139.9 (C-1); 130.9 (o-11-Ph); 127.7 (m-11-Ph); 126.1 (p-11-Ph); 114.9 (C-8/9); 110.0 (C-6); 102.8 (C-7/10); 102.0 (C-2); 74.0 (C-4); 63.2 (C-5); 42.9 (C-14); 37.0 (C-16); 34.1 (C-13); 28.9 (C-15); 11.4 (C-12). **^{7}Li NMR** (C$_6$D$_6$; 156 MHz; 297 K): $\delta = -5.65$. **IR** (solid): $\tilde{\nu}$ [cm^{-1}] = 3049(w); 2902(s); 2846(m); 1564(m); 1554(m); 1493(w); 1450(m); 1442(m); 1420(m); 1379(m); 1357(w); 1329(m); 1303(m); 1226(w); 1206(w); 1185(w); 1163(w); 1103(w); 1081(w); 1072(w); 1053(w); 1032(w); 1001(w); 977(m); 850(w); 824(m); 814(m);

785(m); 770(m); 762(m); 755(m); 736(s); 723(s); 716(s); 708(s); 695(s); 656(m). **MS (EI)**: m/z (%) = 680 (8) [M]; 674 (100) [bpz^{Ad,Me}cpH].

Synthesis of [(2b)CoCl$_2$]: Compound **2b** (1 equiv.; 0.56 mmol; 250 mg) and cobalt(II) chloride hexahydrate (1 equiv.; 0,56 mmol; 133 mg) were dissolved in 5 mL of diethyl ether and heated under reflux for 2 h. Then the intensively blue suspension was filtered. The solvent was removed from the filtrate and the residual solid recrystallized from dichloromethane yielding 110 mg of crystalline [(2b)CoCl$_2$] (34%). **IR** (solid): $\tilde{\nu}$ [cm^{-1}] = 2919(s); 2905(s); 2882(s); 2846(s); 2678(w); 1550(s); 1452(s); 1428(s); 1395(m); 1383(m); 1371(m); 1361(m); 1344(m); 1316(m); 1291(w); 1273(s); 1248(s); 1220(w); 1187(m); 1173(w); 1122(w); 1104(m); 1085(m); 1057(m); 1026(m); 1006(m); 991(m); 975(m); 961(w); 938(w); 855(w); 832(m); 814(m); 798(s); 783(m); 757(m); 738(w); 716(w); 687(w); 679(m); 655(w); 641(m); 614(w); 530(w); 520(w); 473(w); 447(w); 435(w); 422(w); 410(w).

Synthesis of the tautomeric mixture of 1,1-bis(3-adamantyl-5-methylpyrazolyl)-2,2-diphenyl-2-cyclopentadienylethane, H_5C_5—CPh$_2$—CHPz^{Ad,Me} (4a) and (4b): [(thf)Li{Cp—CPh$_2$—CHPz^{Ad,Me}}] (3, 1.00 g; 1.47 mmol) was dissolved in 20 mL of THF at $0\,°C$ and within 5 min, 20 mL of a saturated aqueous NH$_4$Cl solution was added. This 2-phase system was stirred for 30 min at r.t. and then the organic phase was separated. The aqueous phase was washed twice with 10 mL of diethyl ether and the combined organic phases were dried over anhydrous MgSO$_4$. Removal of the solvent under reduced pressure yielded the tautomeric mixture of **4a** and **4b** as yellow solid (76%, 750 mg). **^{1}H NMR** (C$_6$D$_6$; 400 MHz; 297 K): Tautomer a: $\delta = 8.11$ (s, 1H, C(4)-H); 7.54 (d, 4H, C(o-11-Ph)-H); 7.13 (t, 4H, C(m-11-Ph)-H); 7.03 (t, 2H, C(p-11-Ph)-H); 6.53 (s, 1H, C(CpH)-H); 6.48 (s, 1H, C(CpH)-H); 6.09 (s, 1H, C(CpH)-H); 5.63 (s, 2H, C(2)-H); 2.80 (s, 2H, C(CpH$_2$)-H); 1.98 (s, 6H, C(15)-H); 1.89 (s, 12H, C(14)-H); 1.72 (s, 12H, C(16)-H); 1.41 (s, 6H, C(12)-H). Tautomer b: $\delta = 7.88$ (s, 1H, C(4)-H); 7.38 (d, 4H, C(o-11-Ph)-H)-H); 7.11–7.03 (m, 6H, C(m/p-11-Ph)-H)-H); 6.50 (bs, 1H, C(CpH)-H); 6.30–6.26 (m, 2H, C(CpH)-H); 5.65 (s, 2H, C(2)-H); 3.50 (s, 2H, C(CpH$_2$)-H); 1.98 (s, 6H, C(15)-H); 1.89 (s, 12H, C(14)-H); 1.72 (s, 12H, C(16)-H); 1.32 (bs, 6H, C(12)-H). **^{13}C{^{1}H} NMR** (C$_6$D$_6$; 101 MHz; 297 K): Tautomer a: $\delta = 159.5$ (C-3); 151.0 (C-6); 142.9 (qC-11-Ph); 141.1 (C-1); 136.0 (C—CpH); 132.1 (o-11-Ph); 131.1 (C—CpH); 127.9 (C—CpH); 126.9 (m-11-Ph); 126.3 (p-11-Ph); 102.7 (C-2); 78.2 (C-4); 61.3 (C-5); 43.1 (C-14); 41.2 (C—CpH$_2$); 37.3 (C-16); 34.2 (C-13); 29.2 (C-15); 10.5 (C-12). Tautomer b: $\delta = 159.8$ (C-3); 154.8 (C-6); 143.6 (qC-11-Ph); 141.1 (C-1); 133.1 (C—CpH); 132.3 (o-11-Ph); 131.6 (C—CpH); 130.2 (C—CpH); 126.7 (m-11-Ph); 126.3 (p-11-Ph); 102.7 (C-2); 78.3 (C-4); 62.8 (C-5); 43.1 (C-14); 42.9 (C—CpH$_2$); 37.3 (C-16); 34.2 (C-13); 29.2 (C-15); 10.4 (C-12). **IR** (solid): $\tilde{\nu}$ [cm^{-1}] = 2901(s); 2846(s); 1736(w); 1718(w); 1685(w); 1636(m); 1577(w); 1558(m); 1507(w); 1450(s); 1418(m); 1373(m); 1357(m); 1340(m); 1306(m); 1289(m); 1253(m); 1179(m); 1102(m); 1071(m); 1038(m); 998(m); 977(m); 963(m); 900(m); 881(m); 830(m); 785(s); 718(s); 700(s); 638(m); 626(m); 612(m); 518(m); 492(m); 457(m); 439(w); 418(m); 406(m). **MS (ESI)**: m/z (%) = 674 (10) [M]; 458 (10); 444 (54) [bpz^{Ad,Me}]; 394 (12); 304 (12); 229 (100); 215 (28). **Elemental analysis** (C$_{47}$H$_{54}$N$_4$): calcd.: C 83.63; H 8.06; N 8.30; found: C 82.10, H 8.37, N 7.14.

Crystal structure determinations: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.[17–19] The structures were solved by intrinsic phases (SHELXT)[20] and refined by full-matrix least squares techniques against F$_o$^{2}.[21] Compound **2a** crystallized with three half molecules in the asymmetric unit. The methane carbon atoms of the three molecules lie on a two-fold axis of rotation. One molecule of **2a** has a disordered adamantyl group. The disordering could be resolved. The hydrogen atoms bonded to

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the cyclopentadienyl carbon atoms C14 and C15 of **1b** and to the methane group C1 of compounds **2b** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[21] Crystallographic data as well as structure solution and refinement details are summarized in Table S1. XP and POV-Ray were used for structure representations.

Supporting Information

NMR spectra as well as crystal structure and refinement details are given in the Supporting Information in pdf format. In addition, crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2128411 for **1b**, CCDC-2128412 for **2a**, CCDC-2128551 for **2b**, CCDC-2128413 for **2c**, CCDC-2128414 for **3**, and CCDC-2128415 for (**2b**) $CoCl_2$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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