

Triazamethylenemethane complexes of zirconium and tantalum

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Abstract

Addition of $[\text{Li}_2(\text{THF})_4][\text{C}(\text{NPh})_3]$ (**2**) to a THF solution of Cp^*ZrCl_3 ($\text{Cp}^* = \text{C}_5\text{Me}_5$) yields, after recrystallization in Et_2O , the zwitterionic species $\text{Cp}^*[\text{C}(\text{NPh})_3]\text{ZrCl}_2\text{Li}(\text{Et}_2\text{O})(\text{THF})$ (**3**). Treating **3** with excess methylaluminoxane (MAO) affords a homogeneous Ziegler–Natta catalyst for ethylene polymerization. Addition of LiNPh_2 to **3** allows for Cl substitution to give the new product $\text{Cp}^*[\text{C}(\text{NPh})_3]\text{Zr}(\text{NPh}_2)\text{ClLi}(\text{THF})_2$ (**4**). A single crystal diffraction study of **4** reveals that the $[\text{C}(\text{NPh})_3]$ ligand is η^2 -bound. The group 5 complex $\text{Cp}^*[\text{C}(\text{NPh})_3]\text{TaMe}_2$ (**5**) was prepared by addition of **2** to $\text{Cp}^*\text{TaMe}_2\text{Cl}(\text{OSO}_3\text{CF}_3)$. The X-ray diffraction structure of **5** shows that the $[\text{C}(\text{NPh})_3]$ ligand is η^2 -bound to tantalum and that, when compared to **4**, there is less electron delocalization across the inner core of $[\text{C}(\text{NPh})_3]$. © 1998 Elsevier Science B.V.

Keywords: Ziegler–Natta polymerization; Zirconium catalysts; Metallocene mimics; Dianionic ligands

1. Introduction

The discovery of new metallocene-based polymerization catalysts rests on the development and application of new ligands for electrophilic transition metals ¹. Modification of the metallocene ligand environment leads to different catalysts and ultimately different product structures ². Chiral and C_2 -symmetric modifications of the cyclopentadienyl (Cp) ligand are sought for stereoregular polymerization. The ansa-motif, whereby two Cp cores are joined by a transannular bridge, imparts considerable stability and rigidity to the catalytic site. Ansa-metallocenes can be used in the synthesis of polyolefins with highly isotactic, syndiotactic or hemiisotactic structures. Exchanging amides for Cp has been shown to reduce the steric congestion about the metal and increase the electrophilic behavior. Amide containing catalysts [8,9] have special propensity for copolymerizing 1-alkenes with ethylene [10] and for living polymerization of 1-alkenes [11].

Despite the successes in improving and modulating polymerization activity and specificity by changes in the ligand environment, the menu of ancillary ligands remains relatively restricted. One

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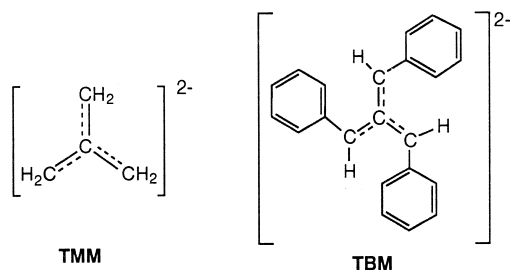
¹ For a recent overview, see [1].

² Comprehensive reviews: Refs. [2–7].

strategy to expand the list of available choices consists of using dianionic fragments that donate six π electrons to the metal. As Jordan originally pointed out, replacing a Cp ligand in a metallocene for one of these mimics leaves gross structural and orbital features intact but changes the overall charge [12]. It is possible with these metallocene mimics to probe the effect of charge on reactivity. Group 4 complexes containing the dicarbollide ($[\text{C}_2\text{B}_9\text{H}_{11}]^{-2}$) [12–15], aminoborollide ($[\text{C}_4\text{H}_4\text{BN}^i\text{Pr}_2]^{-2}$) [16], and carborane (i.e., nido-[2,3- $\text{R}_2\text{C}_2\text{B}_4\text{H}_4]^{-2}$ where $\text{R} = \text{H}$ or SiMe_3) [17] ligands³ have been prepared in this context. Ligand functionalities which are nonessential for metal bonding, such as the exocyclic nitrogen in aminoborollides and the Lewis-basic B–H bonds in carborane cages, have the potential of binding to the metal and inhibiting substrate approach.

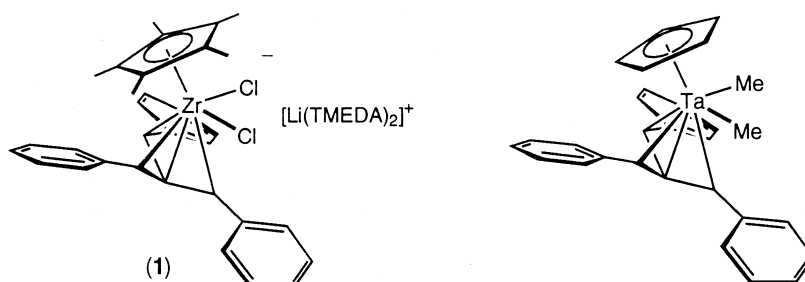
Substitution of a cyclopentadienyl ligand for a dianionic six electron ligand also permits the synthesis of metallocene-like complexes incorporating group 5 metals. To this end, $(\text{C}_5\text{H}_4\text{Me})(\text{C}_2\text{B}_9\text{H}_{11})\text{TaMe}_2$, [14] $\text{Cp}^*(\eta^4\text{-1,3-butadiene})\text{TaMe}_2$ [19] and $\text{Cp}^*(\text{C}_4\text{H}_4\text{B-N}^i\text{Pr}_2)\text{TaMe}_2$ [20], containing the dianionic dicarbollide, diene and aminoborollide ligands, respectively, have been prepared. The aminoborollide ligand is ‘ambivalent’ and allows for a Ta(III) resonance contribution [21]. This electronic feature, coupled with the more covalent Ta–C bond, accounts for the lower activity of aminoborollide–Ta complexes. The diene–Ta combination is especially interesting since it allows for the living polymerization of ethylene [22].

Our group has been interested in exploring the utility of trimethylenemethane (TMM) and tribenzylidenemethane (TBM) dianions as Cp-mimics [23]. These fragments do not contain heteroatom functionalities and are strictly dianionic. They therefore enforce only high oxidation state characteristics to the metal.

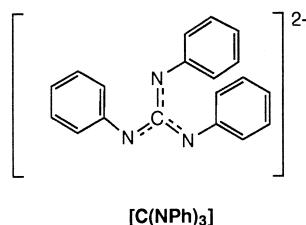


Group 4 complexes such as $[\text{Cp}^*(\text{TBM})\text{ZrCl}_2][\text{Li}(\text{TMEDA})_2]$ (**1**), are zwitterionic and catalyze the polymerization of olefins when mixed with a large excess of methylaluminoxane (MAO) [24]. The TBM ligand in **1** is η^4 -bound to zirconium thereby donating six electrons. Complexes of general composition $\text{Cp}(\text{TBM})\text{TaMe}_2$ also have a metallocene-like geometry and an η^4 -bound TBM fragment [25]. These tantalum complexes are chemically robust and have shown polymerization activity when treated with MAO. The catalytic species however, are shorter lived than in the case of standard group 4 metallocenes.

³ For related work refer to Ref. [18].



It was of interest to us to examine how the triazamethylenemethane analog of TBM, $[\text{C}(\text{NPh})_3]^{-2}$, binds to early transition metals.



Only two transition metal complexes with the ligand type $[\text{C}(\text{NPh})_3]^{-2}$ have been previously reported. In $\mu^2\text{-}[\text{C}(\text{NCy})_3]\text{Fe}_2(\text{CO})_6$ (Cy = cyclohexyl), the triazamethylenemethane fragment uses two of its nitrogen atoms to bridge the two tricarbonyl–iron cores [26]. Mononuclear $(\text{cod})\text{Pt}[\text{C}(\text{NPh})_3]$ (cod = cyclooctadiene) contains the $[\text{C}(\text{NPh})_3]$ fragment bound in an η^2 -fashion, forming an essentially planar four-membered PtNCN metallacycle⁴. The inner carbon forms a double bond to the exo-cyclic nitrogen and two single bonds to the nitrogen atoms at the α sites of the metallacycle. The X-ray structure of $\{\text{Li}_4[\text{C}(\text{NPh})_3]_2(\text{THF})_6\}$ shows two dianionic units bridged by two lithiums cations [35]. Metrical parameters within the core of $[\text{C}(\text{NPh})_3]$ suggest delocalization through the inner carbon and are consistent with ‘Y-conjugation’ [36,37]. It is also interesting to note that the relative disposition of phenyl groups in $[\text{C}(\text{NPh})_3]$ generates local C_s symmetry whereas for $[\text{TBM}][\text{Li}(\text{TMEDA})_2]$ the more symmetric C_{3h} arrangement is found [38].

In view of the few examples available and the variation of coordination modes, we started a study of the bonding between $[\text{C}(\text{NPh})_3]$ and early transition metals. The results of this study are disclosed in this communication.

2. Results and discussion

As previously reported, *N,N',N''*-triphenylguanidene ($[\text{C}(\text{NPh})(\text{NHPh})_2]$) may be doubly deprotonated using *n*-BuLi in THF [28–34]. Quick removal of solvent followed by pentane wash gives a white microcrystalline product of composition $[\text{Li}_2(\text{THF})_4][\text{C}(\text{NPh})_3]$ (**2**) which can be used without further purification. Reaction of **2** in THF with Cp^*ZrCl_3 results in a color change from colorless to

⁴ Similarly, amidinate ligands form a MNCN type metallacycle with a variety of early and late transition metals. See Refs. [27–34].

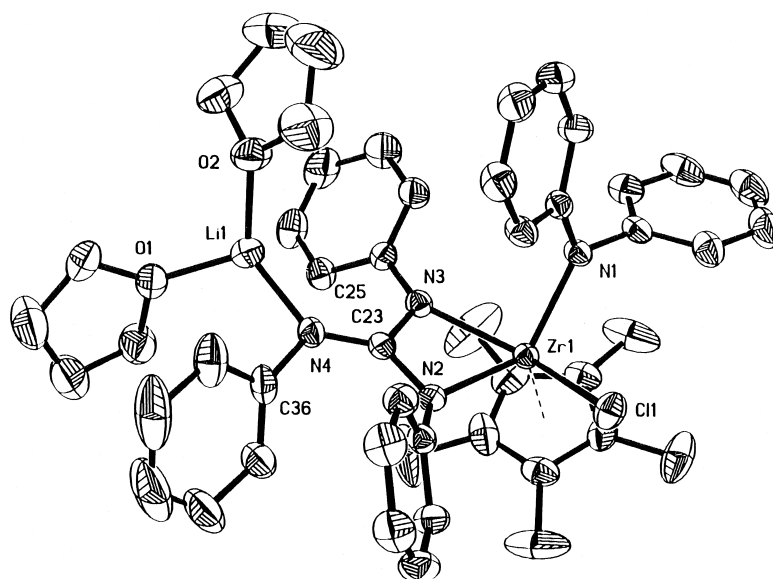
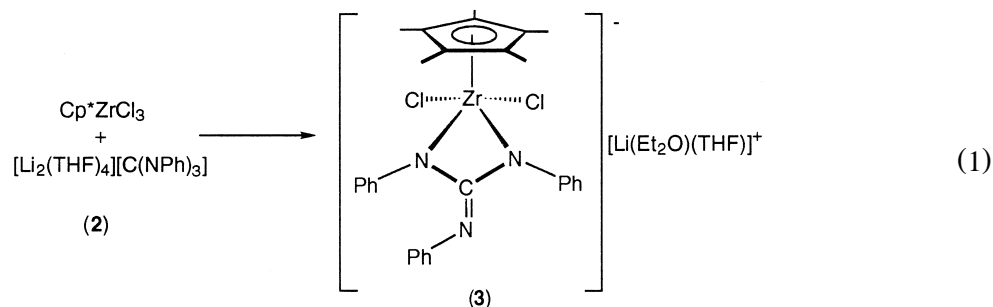


Fig. 1. ORTEP structure of **4** shown at 50% probability.

yellow. After solvent removal, extraction with diethyl ether and cooling to -30°C for 12 hours, a yellow solid is obtained, which, by ^1H NMR spectroscopy and elemental analysis, is consistent with a single product of formula $[\text{Cp}^*[\text{C}(\text{NPh})_3]\text{ZrCl}_2][\text{Li}(\text{Et}_2\text{O})(\text{THF})]$ (**3** in Eq. (1)).



The propensity to keep the Et_2O and THF suggests a charged zirconium core that keeps Li^+ as its counteranion. X-ray quality crystals of **3** were not obtainable and the relationship between the Zr core and Li^+ remains undetermined.

Addition of one equivalent of LiNPh_2 to a THF solution of **3** results in the formation of $[\text{Cp}^*[\text{C}(\text{NPh})_3]\text{ZrCl}(\text{NPh}_2)][\text{Li}(\text{THF})_2]$ (**4** in Eq. (2)). This reaction is nearly quantitative by ^1H NMR spectroscopy.

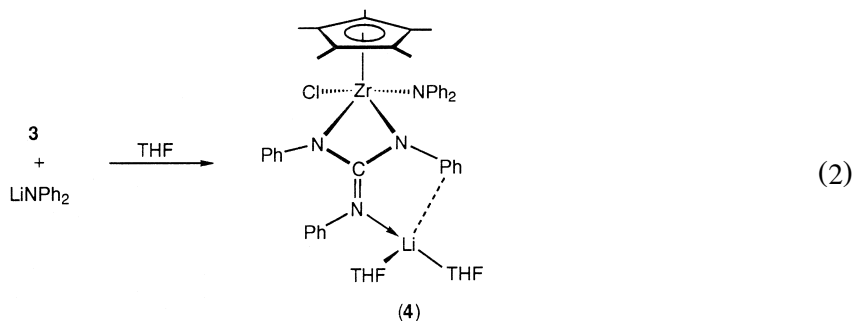


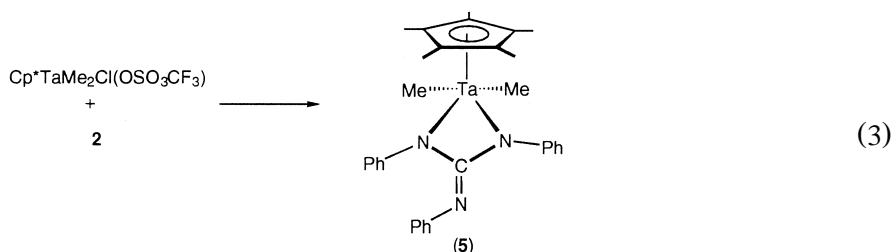
Table 1
Selected bond lengths (Å) and angles (°) for **4**

Atoms	Distance (Å)	Atoms	Angles (°)
Zr(1)–Cl(1)	2.4671(6)	Cl(1)–Zr(1)–N(1)	91.61(6)
Zr(1)–N(1)	2.137(2)	Cl(1)–Zr(1)–N(2)	84.61(5)
Zr(1)–N(3)	2.192(2)	N(1)–Zr(1)–N(3)	90.22(7)
Zr(1)–N(2)	2.228(2)	N(2)–C(23)–N(3)	106.6(2)
Zr(1)–C(23)	2.736(2)	N(2)–C(23)–N(4)	131.5(2)
C(23)–N(2)	1.373(3)	N(3)–C(23)–N(4)	121.9(2)
C(23)–N(3)	1.378(3)	O(1)–Li(1)–O(2)	112.3(2)
C(23)–N(4)	1.320(3)		
Li(1)–N(4)	1.979(5)		
Li(1)–O(1)	1.190(5)		
Li(1)–O(2)	1.874(5)		
Li(1)–C(25)	2.483(6)		
Li(1)–C(36)	2.760(5)		

Crystals of **4** suitable for crystallography were obtained by slowly evaporating a concentrated benzene solution, and the results of this study are shown in Fig. 1. Bond distances and angles are given in Table 1. As seen in Fig. 1, the [C(NPh)₃] ligand is η^2 -coordinated forming an α, α' -diazametallacycle. The inner carbon of the [C(NPh)₃] ligand is nearly equidistant to the three nitrogen atoms (C(23)–N(2) 1.373(3) Å, C(23)–N(3) 1.378(3) Å, C(23)–N(4) 1.320(3) Å). However, C(23)–N(4) is statistically shorter by about 0.05 Å. The lithium countercation is coordinated via two THF molecules and N(4). Additional electron density to the Li, at least in the solid state, is provided by the phenyl rings on N(3) and N(4). The geometry at Zr resembles a four-legged piano stool with the Cp* ligand forming the ‘seat’. The Zr–N(2) distance is slightly longer than that of Zr–N(3) perhaps as a result of the stronger trans effect of NPh₂ relative to Cl.

Reaction of **3** with excess MAO and ethylene results in the formation of polyethylene (PE). The activity of the **3**/MAO mixture was measured at 26 kg (PE/Zr) mol l atm. Under identical conditions, Cp₂ZrCl₂/MAO gave an activity of 90 kg (PE/Zr) mol l atm while **1**/MAO gave 15 kg (PE/Zr) mol l atm. Thus, if we assume that MAO serves its standard role of alkylation followed by heterolytic ligand extraction, the [C(NPh)₃] ligand leads to neutral catalysts that are more reactive than their TBM counterparts yet less active than standard cationic metallocenes⁵.

To expand the scope of this investigation, a Group 5 complex containing the [C(NPh)₃] ligand was synthesized. Addition of **2** to a THF solution of Cp*TaMe₂Cl(OSO₃CF₃) results in the formation of Cp*[C(NPh)₃]TaMe₂ (**5** in Eq. (3)).



⁵ This also holds true for the related benzamidinate early transition metal complexes. See for example Ref. [39].

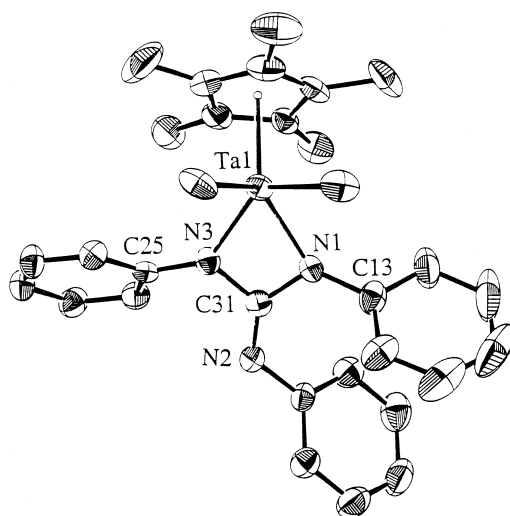


Fig. 2. ORTEP structure of **5** shown at 50% probability.

This red-orange product is readily crystallized from a concentrated ether solution vapor diffused with pentane at -35°C . The X-ray crystal structure of **5** is shown in Fig. 2. Bond distances and angles are given in Table 2. The geometry at the Ta in **5** is similar to the Zr environment in **4**. The molecule resembles a four-legged piano stool with the $[\text{C}(\text{NPh})_3]$ ligand coordinated in an η^2 fashion giving a α, α' -diazametallocyclobutane. The distances of the nitrogens to the inner core carbon of the $[\text{C}(\text{NPh})_3]$ ligand show significant disparity. The $\text{C}(31)\text{--N}(2)$ distance ($1.268(7)$ Å) is consistent with double bond character whereas the $\text{C}(31)\text{--N}(1)$ ($1.398(7)$ Å) and $\text{C}(31)\text{--N}(3)$ ($1.407(7)$ Å) distances indicate single bond character. The bond angles for N(1) and N(3) ($\text{Ta}(1)\text{--N}(1)\text{--C}(13)$ $137.9(4)^{\circ}$, $\text{Ta}(1)\text{--N}(3)\text{--C}(25)$ $139.0(4)^{\circ}$) indicate that these nitrogens are sp^2 hybridized.

Mixing **5** and MAO (at $[\text{Zr}]$ to $[\text{Al}]$ ratios of approximately 500 and 1000) does not result in an ethylene polymerization catalyst.

3. Conclusion

In summary, we have shown that $[\text{C}(\text{NPh})_3]$ can be used in the synthesis of early transition metal complexes. The electron density within the inner core of the ligand is more delocalized in **4** than in **5**.

Table 2
Selected bond lengths (Å) and angles ($^{\circ}$) for **5**

Atoms	Distance (Å)	Atoms	Angles ($^{\circ}$)
Ta(1)–N(1)	2.116(5)	C(11)–Ta(1)–C(12)	85.8(3)
Ta(1)–N(3)	2.058(5)	N(1)–C(31)–N(2)	133.8(5)
Ta(1)–C(11)	2.178(7)	N(1)–C(31)–N(3)	101.9(5)
Ta(1)–C(12)	2.205(7)	N(2)–C(31)–N(3)	124.3(5)
N(1)–C(31)	1.398(7)	Ta(1)–N(1)–C(13)	137.9(4)
N(2)–C(31)	1.268(7)	Ta(1)–N(3)–C(25)	139.0(4)
N(3)–C(31)	1.407(7)		

This difference is probably a result of Li^+ coordination to the exo-cyclic N atom. It is interesting that η^4 -coordination was not observed in either **4** or **5**. This coordination mode is observed for the isoelectronic TBM ligand and allows for donation of up to six π electrons. The structural parameters of **5** show clear evidence that the two Ta-bound N atoms are sp^2 hybridized suggesting that in addition to the two Ta–N σ bonds, there is an additional π component. The $[\text{C}(\text{NPh})_3]$ core can thus donate up to eight electrons to the metal center. A more complete survey of the reactivity patterns of **3** and **5** will be the subject of future studies.

Table 3
Crystal and structure refinement data for **4** and **5**

Crystal parameters	4	5
Chemical formula	$\text{C}_{49}\text{H}_{56}\text{ClN}_4\text{LiO}_4\text{Zr}$	$\text{C}_{30}\text{H}_{36}\text{N}_3\text{Ta}$
Formula weight	866.66	619.58
Crystal system	triclinic	monoclinic
Space group (No.)	$P\bar{1}(\#2)$	$C2/c(\#15)$
Z	2	8
a (Å) ^a	11.7636(1)	31.2878(4)
b (Å)	12.4384(1)	7.9181(1)
c (Å)	17.9531(1)	23.003(3)
α (°)	86.732(1)	
β (°)	71.238(1)	101.687(1)
γ (°)	89.372(1)	
Volume (Å ³)	2483.2(4)	2483.2(4)
ρ_{calc} (mg/m ³)	1.263	1.480
Crystal dims. (mm)	$0.20 \times 0.25 \times 0.35$	$0.20 \times 0.40 \times 0.20$
Temperature (°C)	–50	–50
Measurement of intensity data and structure refinement	4	5
Diffractionmeter	Siemens SMART	Siemens SMART
Radiation, λ (Å)	Mo, 0.71073	Mo, 0.71073
2θ range for data collection (°) ^b	4–56	3–56
Limiting indices	$-14 \leq h \leq 15$ $-14 \leq k \leq 16$ $0 \leq l \leq 23$	$0 \leq h \leq 40$ $-10 \leq k \leq 9$ $-28 \leq l \leq 24$
Total reflections	15510 (to 45°) ^c	30025
Independent reflections	10983 ($R_{\text{int}} = 0.0255$)	13565 ($R_{\text{int}} = 0.061$)
No. of observed data	10980 ($I > 2\sigma(I)$)	4575 ($I > 3\sigma(I)$)
No. of parameters varied	577	316
μ (mm ⁻¹)	3.19	3.95
Absorption correction	empirical (SADABS)	semiempirical
Range of trans. factors	0.50600–0.55791	0.5900–0.8840
$R_1(F_o)$, $wR_2(F_o^2)$ %, ($I > 2\sigma(I)$) ^d	4.41, 13.17	4.2, 3.9
$R_1(F_o)$, $wR_2(F_o^2)$ %, all data	5.65, 14.69	NA
Goodness-of-fit on F^2	1.085	1.85

^aIt has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at $10 \times$ the listed values.

^bThe SMART CCD crystal-to-detector distance is set to 5.094 cm which equates to a maximum 2θ angle of 56.52°.

^cAlthough data are routinely collected to 56°, these crystals were weak diffractors and therefore data greater than 45° were omitted from the refinement.

^d $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$, $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1 / [\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$ and $P = [f \cdot (\text{Maximum of } 0 \text{ or } F_o^2) + (1 - f) \cdot F_c^2]$.

4. Experimental

4.1. General considerations

All manipulations were carried out using either high-vacuum or glovebox techniques as previously described [40]. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer at 400.1 and 100.6 MHz, respectively. Toluene, pentane, diethyl ether and tetrahydrofuran were distilled from benzophenone ketyl prior to use. The preparations of $[\text{C}(\text{NPh})_3][\text{Li}_2(\text{THF})_4]$ [27], $\text{Cp}^* \text{Zr}(\text{CH}_2\text{Ph})\text{Cl}_2$ and $\text{Cp}^* \text{ZrCl}_3$ [41] are available in the literature.

4.2. $\text{Cp}^*([\text{C}(\text{NPh})_3])\text{ZrCl}_2\text{Li}(\text{Et}_2\text{O})(\text{THF})$ (3)

A THF solution of **2** (1.23 g, 2.78 mmol) was added dropwise to a THF solution of $\text{Cp}^* \text{ZrCl}_3$ (0.925 g, 2.78 mmol). After stirring for 30 min the solvent was replaced with 20 ml of Et_2O and the LiCl removed by filtration leaving a clear bright yellow solution. The volume was reduced by 50% and the solution cooled at -30°C for 12 h. This provided the product as a fluorescent yellow solid which was isolated by filtration and dried under reduced pressure (1.43 g, 70%). The added THF-d_8

Table 4
Crystallographic data for **4**

Crystal parameters	
Chemical formula	$\text{ZrC}_{49}\text{H}_{56}\text{ClN}_4\text{LiO}_2$
Formula weight	866.66
Crystal system	triclinic
Space group (No.)	$P\bar{1}(\#2)$
Z	2
a (Å)	11.7636(1)
b (Å)	12.4384(1)
c (Å)	17.9531(1)
α (°)	86.732(1)
β (°)	71.238(1)
γ (°)	89.372(1)
Volume (Å ³)	2483.2(4)
ρ_{calc} (g cm ⁻³)	1.263
Crystal dims. (mm ³)	$0.20 \times 0.25 \times 0.35$
Temperature (°C)	-50
Measurement of intensity data	
Diffractometer	Siemens SMART
Radiation	$\text{Mo}, 0.71073 \text{ \AA}$
2θ range (°)	3.4–56.0
No. of data collected	15510
No. of unique data	10983
No. of observed data ($F_o > 4\sigma(F_o)$)	10980
Agreement between equivalent data (R_{int})	0.0255
No. of parameters varied	577
μ (mm ⁻¹)	3.19
Absorption correction	empirical (SADABS)
Range of trans. factors	0.50600–0.55791
$R_1(F_o), wR_2(F_o), (F_o > 4\sigma(F_o))$	0.0441, 0.1317
$R_1(F_o), wR_2(F_o)$ (all data)	0.0565, 0.1469
Goodness of fit	1.085

Table 5

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
Zr(1)	−3001(1)	−2690(1)	1814(1)	23(1)
Li(1)	−2373(4)	−6919(4)	2488(3)	42(1)
Cl(1)	−2930(1)	−1196(1)	2645(1)	39(1)
N(1)	−4917(2)	−2756(2)	2269(1)	28(1)
N(2)	−1735(2)	−3493(2)	2359(1)	26(1)
N(3)	−2929(2)	−4452(2)	1920(1)	26(1)
N(4)	−1756(2)	−5464(2)	2549(1)	30(1)
O(1)	−1190(2)	−8013(2)	2173(1)	46(1)
O(2)	−3855(2)	−7476(2)	3141(1)	51(1)
C(1)	−3078(2)	−1887(2)	443(2)	39(1)
C(2)	−2387(2)	−1178(2)	709(2)	36(1)
C(3)	−1348(2)	−1714(2)	733(2)	41(1)
C(4)	−1399(3)	−2766(3)	503(2)	49(1)
C(5)	−2469(3)	−2879(2)	325(2)	48(1)
C(6)	−4102(3)	−1559(4)	160(2)	78(1)
C(7)	−2664(4)	−9(2)	850(2)	67(1)
C(8)	−314(4)	−1197(4)	911(2)	85(2)
C(9)	−446(4)	−3620(4)	406(2)	96(2)
C(10)	−2834(5)	−3823(3)	−44(2)	99(2)
C(12)	−4770(2)	−3460(2)	3529(1)	34(1)
C(13)	−5268(3)	−3973(2)	4267(2)	40(1)
C(14)	−6458(3)	−4292(2)	4531(2)	45(1)
C(15)	−7147(3)	−4104(2)	4045(2)	44(1)
C(16)	−6663(2)	−3602(2)	3301(2)	37(1)
C(11)	−5455(2)	−3268(2)	3024(1)	28(1)
C(18)	−6325(2)	−2702(2)	1509(2)	41(1)
C(19)	−7127(3)	−2115(3)	1211(2)	53(1)
C(20)	−7352(3)	−1067(3)	1363(2)	58(1)
C(21)	−6788(3)	−557(3)	1812(2)	57(1)
C(22)	−5987(3)	−1124(2)	2106(2)	44(1)
C(17)	−5742(2)	−2196(2)	1956(1)	32(1)
C(23)	−2074(2)	−4528(2)	2295(1)	26(1)
C(25)	−2537(2)	−6136(2)	1224(2)	35(1)
C(26)	−2969(3)	−7000(2)	939(2)	47(1)
C(27)	−4174(3)	−7096(3)	1040(2)	58(1)
C(28)	−4956(3)	−6311(3)	1422(2)	56(1)
C(29)	−4543(2)	−5457(2)	1727(2)	39(1)
C(24)	−3328(2)	−5353(2)	1636(1)	28(1)
C(31)	−196(2)	−2587(2)	2728(2)	35(1)
C(32)	363(3)	−2354(2)	3272(2)	43(1)
C(33)	−75(3)	−2795(2)	4033(2)	45(1)
C(34)	−1094(3)	−3442(2)	4255(2)	43(1)
C(35)	−1661(2)	−3652(2)	3713(2)	34(1)
C(30)	−1205(2)	−3247(2)	2935(1)	27(1)
C(37)	404(3)	−5178(3)	2317(2)	53(1)
C(38)	1410(4)	−5407(3)	2537(4)	87(2)
C(39)	1344(5)	−6034(4)	3188(4)	104(2)
C(40)	251(5)	−6458(4)	3647(3)	91(2)
C(41)	−778(4)	−6234(3)	3443(2)	57(1)
C(36)	−720(3)	−5585(2)	2776(2)	38(1)
C(42)	−81(3)	−7882(3)	1541(2)	61(1)
C(43)	857(4)	−8365(4)	1841(3)	100(2)
C(44)	261(4)	−9083(4)	2506(3)	81(1)
C(45)	−1047(3)	−8832(3)	2738(2)	57(1)

Table 5 (continued).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
C(46)	−4477(3)	−8413(3)	3050(2)	65(1)
C(47)	−5793(4)	−8149(4)	3379(3)	97(2)
C(48)	−5834(4)	−7310(5)	3922(4)	124(2)
C(49)	−4654(4)	−6837(4)	3711(3)	86(1)
C(101)	1837(6)	−401(6)	−5547(4)	132(3)
C(102)	1590(4)	384(4)	−5029(4)	100(2)
C(103)	2284(5)	535(4)	−4588(2)	78(1)
C(104)	3233(7)	−59(6)	−4649(4)	131(2)
C(105)	3510(9)	−878(7)	−5165(5)	171(4)
C(106)	2800(8)	−1039(5)	−5624(4)	144(3)

displaced the coordinated THF and Et₂O. ¹H NMR (C₆D₆/THF-*d*₈; 1:1): δ 7.41, 7.08, 6.93, 6.78, 6.58 (15H, [C₆H₅N]₃C), 2.09 (s, 15H, C₅(CH₃)₅). ¹³C NMR (C₆D₆/THF-*d*₈; 1:1): δ 162.4 ([C₆H₅N]₃C), 150.0, 149.12, 127.8, 125.8, 124.7, 123.8, 121.9, 120.0([C₆H₅N]₃C, C₅(CH₃)₅), 12.5 (C₅(CH₃)₅). Anal. Calcd. for ZrC₃₇H₄₈Cl₂LiN₃O₂: C, 60.38; H, 6.58; N, 5.71; Found: C, 60.37; H, 6.39; N, 5.64.

Table 6

Bond lengths (Å) and angles (°) for **4**

Zr(1)–N(1)	2.137(2)
Zr(1)–N(3)	2.192(2)
Zr(1)–N(2)	2.228(2)
Zr(1)–Cl(1)	2.4671(6)
Zr(1)–C(4)	2.503(3)
Zr(1)–C(3)	2.524(3)
Zr(1)–C(5)	2.566(3)
Zr(1)–C(2)	2.585(2)
Zr(1)–C(1)	2.631(2)
Zr(1)–C(23)	2.736(2)
Li(1)–O(2)	1.874(5)
Li(1)–O(1)	1.910(5)
Li(1)–N(4)	1.979(5)
Li(1)–C(25)	2.483(6)
Li(1)–C(36)	2.760(5)
N(1)–C(11)	1.415(3)
N(1)–C(17)	1.427(3)
N(2)–C(23)	1.373(3)
N(2)–C(30)	1.416(3)
N(3)–C(23)	1.378(3)
N(3)–C(24)	1.403(3)
N(4)–C(23)	1.320(3)
N(4)–C(36)	1.408(3)
O(1)–C(42)	1.430(4)
O(1)–C(45)	1.443(4)
O(2)–C(49)	1.421(4)
O(2)–C(46)	1.428(4)
C(1)–C(2)	1.406(4)
C(1)–C(5)	1.412(4)
C(1)–C(6)	1.496(4)
C(2)–C(3)	1.398(4)
C(2)–C(7)	1.504(4)
C(3)–C(4)	1.401(4)

Table 6 (continued).

C(3)–C(8)	1.511(4)
C(4)–C(5)	1.405(5)
C(4)–C(9)	1.512(4)
C(5)–C(10)	1.511(5)
C(12)–C(13)	1.385(4)
C(12)–C(11)	1.403(3)
C(13)–C(14)	1.380(4)
C(14)–C(15)	1.379(4)
C(15)–C(16)	1.387(4)
C(16)–C(11)	1.405(3)
C(18)–C(17)	1.390(4)
C(18)–C(19)	1.405(4)
C(19)–C(20)	1.353(5)
C(20)–C(21)	1.379(5)
C(21)–C(22)	1.388(4)
C(22)–C(17)	1.384(4)
C(25)–C(26)	1.384(4)
C(25)–C(24)	1.408(3)
C(26)–C(27)	1.376(5)
C(27)–C(28)	1.385(5)
C(28)–C(29)	1.383(4)
C(29)–C(24)	1.392(3)
C(31)–C(32)	1.386(4)
C(31)–C(30)	1.387(3)
C(32)–C(33)	1.378(4)
C(33)–C(34)	1.386(4)
C(34)–C(35)	1.383(4)
C(35)–C(30)	1.391(3)
C(37)–C(38)	1.386(5)
C(37)–C(36)	1.396(4)
C(38)–C(39)	1.348(8)
C(39)–C(40)	1.376(8)
C(40)–C(41)	1.395(5)
C(41)–C(36)	1.389(4)
C(42)–C(43)	1.484(5)
C(43)–C(44)	1.438(6)
C(44)–C(45)	1.493(5)
C(46)–C(47)	1.509(6)
C(47)–C(48)	1.458(7)
C(48)–C(49)	1.439(6)
C(101)–C(102)	1.352(7)
C(101)–C(106)	1.352(10)
C(102)–C(103)	1.328(7)
C(103)–C(104)	1.310(7)
C(104)–C(105)	1.381(10)
C(105)–C(106)	1.372(11)
N(1)–Zr(1)–N(3)	90.22(7)
N(1)–Zr(1)–N(2)	126.32(7)
N(3)–Zr(1)–N(2)	59.90(7)
N(1)–Zr(1)–Cl(1)	91.61(6)
N(3)–Zr(1)–Cl(1)	136.18(5)
N(2)–Zr(1)–Cl(1)	84.61(5)
N(1)–Zr(1)–C(4)	137.64(10)
N(3)–Zr(1)–C(4)	87.74(9)
N(2)–Zr(1)–C(4)	88.25(9)
Cl(1)–Zr(1)–C(4)	118.10(8)

Table 6 (continued).

N(1)–Zr(1)–C(3)	139.73(8)
N(3)–Zr(1)–C(3)	117.89(9)
N(2)–Zr(1)–C(3)	93.63(8)
Cl(1)–Zr(1)–C(3)	86.87(7)
C(4)–Zr(1)–C(3)	32.36(10)
N(1)–Zr(1)–C(5)	105.49(9)
N(3)–Zr(1)–C(5)	86.53(8)
N(2)–Zr(1)–C(5)	114.86(9)
Cl(1)–Zr(1)–C(5)	134.49(7)
C(4)–Zr(1)–C(5)	32.15(11)
C(3)–Zr(1)–C(5)	52.99(10)
N(1)–Zr(1)–C(2)	108.21(8)
N(3)–Zr(1)–C(2)	137.78(8)
N(2)–Zr(1)–C(2)	124.09(8)
Cl(1)–Zr(1)–C(2)	82.32(6)
C(4)–Zr(1)–C(2)	52.92(9)
C(3)–Zr(1)–C(2)	31.73(8)
C(5)–Zr(1)–C(2)	52.41(9)
N(1)–Zr(1)–C(1)	90.97(8)
N(3)–Zr(1)–C(1)	114.78(8)
N(2)–Zr(1)–C(1)	140.65(8)
Cl(1)–Zr(1)–C(1)	108.97(7)
C(4)–Zr(1)–C(1)	52.57(9)
C(3)–Zr(1)–C(1)	52.23(8)
C(5)–Zr(1)–C(1)	31.50(9)
C(2)–Zr(1)–C(1)	31.26(8)
N(1)–Zr(1)–C(23)	109.55(7)
N(3)–Zr(1)–C(23)	29.97(7)
N(2)–Zr(1)–C(23)	29.95(7)
Cl(1)–Zr(1)–C(23)	110.86(5)
C(4)–Zr(1)–C(23)	88.43(8)
C(3)–Zr(1)–C(23)	108.51(8)
C(5)–Zr(1)–C(23)	102.63(9)
C(2)–Zr(1)–C(23)	139.37(8)
C(1)–Zr(1)–C(23)	134.13(8)
O(2)–Li(1)–O(1)	112.3(2)
O(2)–Li(1)–N(4)	124.5(3)
O(1)–Li(1)–N(4)	115.9(2)
O(2)–Li(1)–C(25)	110.9(2)
O(1)–Li(1)–C(25)	103.8(2)
N(4)–Li(1)–C(25)	82.8(2)
O(2)–Li(1)–C(36)	131.8(3)
O(1)–Li(1)–C(36)	90.7(2)
N(4)–Li(1)–C(36)	29.05(10)
C(25)–Li(1)–C(36)	103.1(2)
C(11)–N(1)–C(17)	114.1(2)
C(11)–N(1)–Zr(1)	118.0(2)
C(17)–N(1)–Zr(1)	127.2(2)
C(23)–N(2)–C(30)	121.1(2)
C(23)–N(2)–Zr(1)	95.98(13)
C(30)–N(2)–Zr(1)	136.3(2)
C(23)–N(3)–C(24)	122.1(2)
C(23)–N(3)–Zr(1)	97.43(14)
C(24)–N(3)–Zr(1)	139.6(2)
C(23)–N(4)–C(36)	122.4(2)
C(23)–N(4)–Li(1)	128.6(2)
C(36)–N(4)–Li(1)	107.9(2)

Table 6 (continued).

C(42)–O(1)–C(45)	109.0(2)
C(42)–O(1)–Li(1)	124.7(2)
C(45)–O(1)–Li(1)	120.7(3)
C(49)–O(2)–C(46)	109.2(3)
C(49)–O(2)–Li(1)	120.8(3)
C(46)–O(2)–Li(1)	128.5(3)
C(2)–C(1)–C(5)	107.6(2)
C(2)–C(1)–C(6)	124.9(3)
C(5)–C(1)–C(6)	126.0(3)
C(2)–C(1)–Zr(1)	72.54(14)
C(5)–C(1)–Zr(1)	71.71(14)
C(6)–C(1)–Zr(1)	132.1(2)
C(3)–C(2)–C(1)	108.2(2)
C(3)–C(2)–C(7)	126.4(3)
C(1)–C(2)–C(7)	125.1(3)
C(3)–C(2)–Zr(1)	71.76(14)
C(1)–C(2)–Zr(1)	76.2(2)
C(7)–C(2)–Zr(1)	123.2(2)
C(2)–C(3)–C(4)	108.3(3)
C(2)–C(3)–C(8)	124.7(3)
C(4)–C(3)–C(8)	126.8(3)
C(2)–C(3)–Zr(1)	76.5(2)
C(4)–C(3)–Zr(1)	73.0(2)
C(8)–C(3)–Zr(1)	120.7(2)
C(5)–C(4)–C(3)	108.1(3)
C(5)–C(4)–C(9)	125.0(4)
C(3)–C(4)–C(9)	126.9(4)
C(5)–C(4)–Zr(1)	76.4(2)
C(3)–C(4)–Zr(1)	74.6(2)
C(9)–C(4)–Zr(1)	118.2(2)
C(4)–C(5)–C(1)	107.8(3)
C(4)–C(5)–C(10)	126.8(4)
C(1)–C(5)–C(10)	124.8(4)
C(4)–C(5)–Zr(1)	71.5(2)
C(1)–C(5)–Zr(1)	76.8(2)
C(10)–C(5)–Zr(1)	124.5(2)
C(13)–C(12)–C(11)	120.9(2)
C(14)–C(13)–C(12)	120.9(3)
C(15)–C(14)–C(13)	119.0(2)
C(14)–C(15)–C(16)	121.1(3)
C(15)–C(16)–C(11)	120.7(3)
C(16)–C(11)–C(12)	117.5(2)
C(16)–C(11)–N(1)	122.9(2)
C(12)–C(11)–N(1)	119.6(2)
C(17)–C(18)–C(19)	119.6(3)
C(20)–C(19)–C(18)	120.8(3)
C(19)–C(20)–C(21)	120.2(3)
C(20)–C(21)–C(22)	119.7(3)
C(17)–C(22)–C(21)	121.1(3)
C(22)–C(17)–C(18)	118.6(2)
C(22)–C(17)–N(1)	119.7(2)
C(18)–C(17)–N(1)	121.7(2)
N(4)–C(23)–N(2)	131.5(2)
N(4)–C(23)–N(3)	121.9(2)
N(2)–C(23)–N(3)	106.6(2)
N(4)–C(23)–Zr(1)	173.2(2)
N(2)–C(23)–Zr(1)	54.07(11)

Table 6 (continued).

N(3)–C(23)–Zr(1)	52.60(11)
C(26)–C(25)–C(24)	120.5(3)
C(26)–C(25)–Li(1)	102.1(2)
C(24)–C(25)–Li(1)	89.7(2)
C(27)–C(26)–C(25)	120.6(3)
C(26)–C(27)–C(28)	119.4(3)
C(27)–C(28)–C(29)	120.7(3)
C(28)–C(29)–C(24)	120.6(3)
C(29)–C(24)–N(3)	119.2(2)
C(29)–C(24)–C(25)	118.2(2)
N(3)–C(24)–C(25)	122.5(2)
C(32)–C(31)–C(30)	121.4(2)
C(33)–C(32)–C(31)	119.8(3)
C(32)–C(33)–C(34)	119.8(2)
C(35)–C(34)–C(33)	120.0(3)
C(34)–C(35)–C(30)	121.0(2)
C(31)–C(30)–C(35)	118.0(2)
C(31)–C(30)–N(2)	119.9(2)
C(35)–C(30)–N(2)	122.1(2)
C(38)–C(37)–C(36)	120.4(4)
C(39)–C(38)–C(37)	121.6(5)
C(38)–C(39)–C(40)	119.5(4)
C(39)–C(40)–C(41)	120.1(4)
C(36)–C(41)–C(40)	120.8(4)
C(41)–C(36)–C(37)	117.6(3)
C(41)–C(36)–N(4)	119.0(3)
C(37)–C(36)–N(4)	123.1(3)
C(41)–C(36)–Li(1)	89.3(2)
C(37)–C(36)–Li(1)	133.7(2)
N(4)–C(36)–Li(1)	43.0(2)
O(1)–C(42)–C(43)	106.2(3)
C(44)–C(43)–C(42)	107.2(3)
C(43)–C(44)–C(45)	107.0(3)
O(1)–C(45)–C(44)	106.8(3)
O(2)–C(46)–C(47)	105.4(3)
C(48)–C(47)–C(46)	104.0(4)
C(49)–C(48)–C(47)	107.9(4)
O(2)–C(49)–C(48)	108.0(4)
C(102)–C(101)–C(106)	120.0(7)
C(103)–C(102)–C(101)	120.6(6)
C(104)–C(103)–C(102)	121.3(5)
C(103)–C(104)–C(105)	120.0(7)
C(106)–C(105)–C(104)	119.2(7)
C(101)–C(106)–C(105)	118.8(6)

4.3. $Cp^*([C(NPh)_3]ZrCl(NPh_2)Li(THF)_2)$ (**4**)

To a THF solution of **3** (0.084 g, 0.113 mmol), a solution of $LiNPh_2$ (0.020 g, 0.113 mmol) was added and the reaction mixture was stirred for 30 min at which time the solvent was replaced with C_6D_6 and filtered. This bright yellow solution was used to acquire the 1H and ^{13}C NMR spectroscopy data. Allowing the solvent to evaporate inside a nitrogen containing glove box overnight gave X-ray quality crystals which were also used for elemental analysis. A deuterated benzene molecule of recrystallization was determined by both X-ray and elemental analysis. The added $THF-d_8$ displaced

Table 7

Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2 U_{11} + \dots + 2hka^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zr(1)	22(1)	25(1)	22(1)	0(1)	-7(1)	1(1)
Li(1)	37(2)	35(2)	51(3)	-1(2)	-10(2)	-3(2)
Cl(1)	49(1)	30(1)	40(1)	-8(1)	-17(1)	1(1)
N(1)	23(1)	32(1)	27(1)	2(1)	-8(1)	2(1)
N(2)	26(1)	26(1)	29(1)	-1(1)	-11(1)	0(1)
N(3)	24(1)	28(1)	27(1)	-2(1)	-11(1)	2(1)
N(4)	30(1)	28(1)	37(1)	-1(1)	-17(1)	3(1)
O(1)	42(1)	39(1)	52(1)	4(1)	-10(1)	5(1)
O(2)	44(1)	45(1)	54(1)	-11(1)	-3(1)	-6(1)
C(1)	32(1)	57(2)	26(1)	8(1)	-8(1)	-5(1)
C(2)	44(2)	33(1)	28(1)	7(1)	-8(1)	1(1)
C(3)	31(1)	56(2)	33(1)	13(1)	-9(1)	-7(1)
C(4)	49(2)	54(2)	26(1)	11(1)	8(1)	20(1)
C(5)	73(2)	45(2)	20(1)	3(1)	-7(1)	-10(1)
C(6)	41(2)	149(4)	45(2)	39(2)	-20(2)	-16(2)
C(7)	108(3)	34(2)	47(2)	9(1)	-13(2)	8(2)
C(8)	62(2)	135(4)	64(2)	47(2)	-34(2)	-57(2)
C(9)	91(3)	101(3)	55(2)	25(2)	28(2)	64(3)
C(10)	196(6)	69(3)	32(2)	-2(2)	-35(3)	-43(3)
C(12)	29(1)	41(1)	28(1)	1(1)	-6(1)	4(1)
C(13)	44(2)	46(2)	29(1)	6(1)	-11(1)	7(1)
C(14)	49(2)	46(2)	33(1)	11(1)	-6(1)	4(1)
C(15)	35(1)	45(2)	44(2)	7(1)	-5(1)	-5(1)
C(16)	30(1)	42(1)	38(1)	6(1)	-11(1)	-4(1)
C(11)	27(1)	28(1)	27(1)	-1(1)	-6(1)	4(1)
C(18)	36(1)	51(2)	36(1)	4(1)	-14(1)	-2(1)
C(19)	33(2)	90(3)	40(2)	4(2)	-17(1)	0(2)
C(20)	39(2)	79(2)	55(2)	17(2)	-16(1)	15(2)
C(21)	51(2)	55(2)	63(2)	6(2)	-17(2)	22(2)
C(22)	41(2)	45(2)	45(2)	1(1)	-15(1)	10(1)
C(17)	24(1)	41(1)	28(1)	4(1)	-7(1)	4(1)
C(23)	24(1)	28(1)	25(1)	-2(1)	-7(1)	2(1)
C(25)	38(1)	35(1)	34(1)	-9(1)	-12(1)	5(1)
C(26)	70(2)	35(2)	45(2)	-16(1)	-27(2)	9(1)
C(27)	79(2)	40(2)	74(2)	-15(2)	-49(2)	-4(2)
C(28)	51(2)	52(2)	82(2)	-14(2)	-44(2)	-3(1)
C(29)	35(1)	37(1)	52(2)	-7(1)	-23(1)	1(1)
C(24)	32(1)	27(1)	27(1)	-1(1)	-14(1)	0(1)
C(31)	33(1)	37(1)	38(1)	3(1)	-14(1)	-7(1)
C(32)	37(1)	46(2)	53(2)	-2(1)	-24(1)	-9(1)
C(33)	51(2)	53(2)	43(2)	-13(1)	-29(1)	4(1)
C(34)	51(2)	51(2)	30(1)	-3(1)	-17(1)	1(1)
C(35)	33(1)	37(1)	32(1)	1(1)	-9(1)	-1(1)
C(30)	26(1)	27(1)	29(1)	-4(1)	-12(1)	2(1)
C(37)	39(2)	44(2)	82(2)	-13(2)	-28(2)	6(1)
C(38)	51(2)	66(2)	169(5)	-41(3)	-65(3)	20(2)
C(39)	100(4)	87(3)	175(6)	-49(4)	-110(4)	44(3)
C(40)	148(5)	70(3)	100(4)	-31(3)	-98(4)	51(3)
C(41)	84(2)	47(2)	54(2)	-12(2)	-41(2)	23(2)
C(36)	45(2)	29(1)	50(2)	-13(1)	-29(1)	13(1)
C(42)	55(2)	58(2)	57(2)	1(2)	-1(2)	12(2)
C(43)	50(2)	93(3)	136(5)	44(3)	-10(3)	15(2)
C(44)	74(3)	84(3)	84(3)	6(2)	-28(2)	31(2)
C(45)	64(2)	37(2)	68(2)	11(2)	-18(2)	0(1)

Table 7 (continued).

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(46)	69(2)	54(2)	66(2)	−1(2)	−14(2)	−17(2)
C(47)	58(3)	115(4)	111(4)	5(3)	−19(3)	−34(3)
C(48)	56(3)	110(4)	173(6)	−36(4)	15(3)	7(3)
C(49)	77(3)	86(3)	74(3)	−32(2)	8(2)	3(2)
C(101)	105(4)	136(5)	148(6)	−65(5)	−20(4)	−45(4)
C(102)	65(3)	96(4)	131(5)	−49(3)	−11(3)	−6(2)
C(103)	97(3)	65(3)	57(2)	−13(2)	−1(2)	−4(2)
C(104)	168(7)	145(6)	86(4)	1(4)	−52(4)	56(5)
C(105)	221(10)	135(7)	128(7)	10(5)	−22(6)	112(7)
C(106)	201(9)	62(3)	109(5)	−37(3)	38(5)	−10(4)

the coordinated THFs. ^1H NMR δ ($\text{C}_6\text{D}_6/\text{THF}-d_8$; 1:1) 7.24–6.26 (m, 25H, phenyls), 1.55 ($\text{C}_5(\text{CH}_3)_5$). ^{13}C NMR ($\text{C}_6\text{D}_6/\text{THF}-d_8$; 1:1): δ 163.9 ($[\text{C}_6\text{H}_6\text{N}]_3\text{C}$), 153.8, 152.7, 150.1, 128.7, 127.8, 127.5, 124.0, 122.5, 120.9, 118.6, 116.03, ($[\text{C}_6\text{H}_5\text{N}]_3\text{C}$, $\text{C}_5(\text{CH}_3)_5$, $(\text{C}_6\text{H}_5)_2\text{N}$), 11.5 ($\text{C}_5(\text{CH}_3)_5$). Anal. Calcd for $\text{ZrC}_{49}\text{H}_{56}\text{ClLiN}_4\text{O}_2\text{C}_6\text{D}_6$: C, 69.47; H, 6.59; N, 5.89; Found: C, 68.84; H, 6.50; N, 5.94.

Table 8
Crystallographic data for **5**

Crystal parameters	
Chemical formula	$\text{TaC}_{31}\text{H}_{36}\text{N}_3$
Formula weight	619.58
Crystal system	monoclinic
Space group (No.)	$C2/c$ (#9)
Z	8
a (Å)	31.2878 (4)
b (Å)	7.9181 (1)
c (Å)	23.003 (3)
β (°)	101.687 (1)
Volume (Å ³)	2483.2(4)
ρ_{calc} (g cm ^{−3})	1.480
Crystal dimens. (mm ³)	0.20 × 0.40 × 0.20
Temperature (°C)	−50
Measurement of intensity data	
Diffractometer	Siemens SMART
Radiation	Mo, 0.71073 Å
2θ range, (°)	3.4–56.0
No. of data collected	30025
No. of unique data	13565
No. of observed data ($F_o > 3\sigma(F_o)$)	4575
Agreement between equivalent data (R_{int})	0.0415
No. of parameters varied	316
μ (mm ^{−1})	39.5
Absorption correction	semiempirical
Range of trans. factors	0.5900–0.8840
$R_1(F_o)$, $wR_2(F_o)$, ($F_o > 3\sigma(F_o)$)	0.042, 0.039
Goodness of fit	1.85

4.4. Cp* $[C(NPh)_3]TaMe_2$ (**5**)

A THF solution of **2** (0.835 g, 1.88 mmol) was added to a benzene:THF (9:1) solution of Cp*TaMe₂Cl(OSO₃CF₃) (1.0 g, 1.88 mmol). The reaction was stirred for 45 min at which point the solvent was replaced with diethyl ether/toluene (9:1). The resulting mixture was filtered and the solvent removed to give a red-orange solid. The solid was then washed with pentane and placed under vacuum to give 1.02 g (86%) of product. ¹H NMR δ (C₆D₆) 6.99 (b, 8H), 6.94 (t, 2H), 6.84 (d, 2H), 6.81 (t, 2H), 6.61 (t, 1H) ([C₆H₅N]₃C), 1.60 (s, 15H, C₅(CH₃)₅), 0.39 (s, 6H, TaMe₂). ¹³C NMR (C₆D₆) 147.6 ([C₆H₅N]₃C), 153.0, 149.4, 127.9, 127.8, 127.0, 126.8, 124.0, 123.7, 123.2, 123.0, 120.9, 120.1 ([C₆H₅N]₃C, C₅(CH₃)₅), 69.0 Ta(CH₃)₂, 11.2 (C₅(CH₃)₅).

4.5. Ethylene polymerization

Compound **3** (0.020 g) was activated with methylalumoxane (MAO, 6.4 wt% Al) and stirred for 10 min. The reaction flask was then evacuated and 2 atm of ethylene were introduced. The reaction is

Table 9
Positional parameters and B_{iso}/B_{eq} for **5**

Atom	x	y	z	B_{eq}
Ta(1)	0.088312(8)	0.20691(3)	0.44096(1)	2.521(5)
N(1)	0.1122(2)	0.1406(6)	0.5308(2)	2.8(1)
N(2)	0.1638(2)	-0.0953(6)	0.5523(2)	2.7(1)
N(3)	0.1324(2)	0.0114(6)	0.4572(2)	2.4(1)
C(1)	0.1341(2)	0.4469(7)	0.4423(3)	2.7(1)
C(2)	0.0916(2)	0.5153(7)	0.4324(3)	3.2(2)
C(3)	0.0683(2)	0.4572(8)	0.3767(3)	3.8(2)
C(4)	0.0976(3)	0.3592(9)	0.3507(3)	4.0(2)
C(5)	0.1380(2)	0.3521(8)	0.3907(3)	3.3(2)
C(6)	0.1713(2)	0.4815(8)	0.4927(3)	3.8(2)
C(7)	0.0752(2)	0.6368(8)	0.4732(4)	4.8(2)
C(8)	0.0237(3)	0.509(1)	0.3481(4)	6.5(3)
C(9)	0.0874(4)	0.287(1)	0.2887(3)	7.1(3)
C(10)	0.1794(3)	0.2832(9)	0.3780(4)	4.7(2)
C(11)	0.0329(2)	0.2777(9)	0.4798(3)	4.0(2)
C(12)	0.0408(2)	0.0605(8)	0.3765(3)	3.7(2)
C(13)	0.0998(2)	0.1624(8)	0.5865(3)	3.2(2)
C(14)	0.0824(2)	0.0325(10)	0.6141(3)	4.3(2)
C(15)	0.0711(3)	0.061(1)	0.6687(4)	6.2(3)
C(16)	0.0766(3)	0.216(2)	0.6945(4)	7.9(3)
C(17)	0.0928(3)	0.346(1)	0.6668(4)	7.0(3)
C(18)	0.1051(3)	0.3212(9)	0.6124(3)	4.7(2)
C(19)	0.1765(2)	-0.0810(8)	0.6145(2)	2.5(1)
C(20)	0.1744(2)	-0.2232(8)	0.6491(3)	3.2(1)
C(21)	0.1891(2)	-0.2149(10)	0.7105(3)	4.1(2)
C(22)	0.2059(3)	-0.067(1)	0.7372(3)	4.4(2)
C(23)	0.2089(2)	0.0740(9)	0.7026(3)	4.2(2)
C(24)	0.1947(2)	0.0673(8)	0.6419(3)	3.3(2)
C(25)	0.1603(2)	-0.0832(7)	0.4265(2)	2.4(1)
C(26)	0.2048(2)	-0.1001(7)	0.4477(3)	2.8(1)
C(27)	0.2301(2)	-0.1879(8)	0.4142(3)	3.2(1)
C(28)	0.2105(2)	-0.2574(7)	0.3600(3)	3.4(2)
C(29)	0.1664(2)	-0.2398(8)	0.3392(3)	3.2(2)
C(30)	0.1413(2)	-0.1538(8)	0.3721(3)	2.8(1)
C(31)	0.1393(2)	0.0093(7)	0.5195(3)	2.4(1)

quenched with 100 ml of a 10% HCl methanolic solution. After stirring this mixture for 6 h, the solid polyethylene (PE, $T_m = 125^\circ\text{C}$) is filtered, washed four times with methanol, and dried to constant weight (2.95 g).

4.6. Structure determination of **4** and **5**

Slow evaporation of a benzene solution for **4** and an ether solution for **5** afforded crystals that were suitable for X-ray diffraction. Fragments of both **4** and **5** were cut and mounted on glass fibers under Paratone-8277 and placed on the X-ray diffractometer in a cold nitrogen stream supplied by a Siemens LT-2A low temperature device. The X-ray intensity data were collected on a standard Siemens SMART-CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 1.5 kW (50 kV, 30 mA). A total of 1.3 hemispheres of data were collected using a narrow frame method with scan widths of 0.3° in ω , and exposure times of 10 s/frame. Frames were integrated to 0.75 \AA for **4** and 0.90 \AA for **5** with the Siemens SAINT program yielding a total of 15510 reflections for **4** and 30025 reflections for **5**. The unit cell parameters were based upon the least-squares refinement of three dimensional centroids of 10980 reflections and 4575 reflections at -50°C for **4** and **5**, respectively. The space groups were assigned on the basis of systematic absences by using the XPREP program (SHELXTL 5.04 [42]). The structure of **4** was solved by direct methods (SHELXTL) and the structure of **5** was determined by heavy-atom Patterson methods (TEXSAN [43]). Both structures were refined by full-matrix least-squares on F^2 . All non-hydrogen atoms for both structures were refined with anisotropic thermal parameters. H atoms were included in

Table 10
Intramolecular distances involving the nonhydrogen atoms of **5**

Atom	Atom	Distance	Atom	Atom	Distance
Ta(1)	N(1)	2.116(5)	C(4)	C(5)	1.41(1)
Ta(1)	N(3)	2.058(5)	C(4)	C(9)	1.51(1)
Ta(1)	C(1)	2.377(6)	C(5)	C(10)	1.488(9)
Ta(1)	C(2)	2.454(6)	C(13)	C(14)	1.376(9)
Ta(1)	C(3)	2.476(6)	C(13)	C(18)	1.387(9)
Ta(1)	C(4)	2.469(6)	C(14)	C(15)	1.39(1)
Ta(1)	C(5)	2.410(6)	C(15)	C(16)	1.36(1)
Ta(1)	C(11)	2.178(7)	C(16)	C(17)	1.36(1)
Ta(1)	C(12)	2.205(7)	C(17)	C(18)	1.39(1)
N(1)	C(13)	1.425(7)	C(19)	C(20)	1.389(8)
N(1)	C(31)	1.398(7)	C(19)	C(24)	1.398(8)
N(2)	C(19)	1.409(7)	C(20)	C(21)	1.394(9)
N(2)	C(31)	1.268(7)	C(21)	C(22)	1.38(1)
N(3)	C(25)	1.437(7)	C(22)	C(23)	1.386(9)
N(3)	C(31)	1.407(7)	C(23)	C(24)	1.378(9)
C(1)	C(2)	1.412(8)	C(25)	C(26)	1.386(8)
C(1)	C(5)	1.429(8)	C(25)	C(30)	1.390(8)
C(1)	C(6)	1.493(9)	C(26)	C(27)	1.397(8)
C(2)	C(3)	1.417(9)	C(27)	C(28)	1.387(9)
C(2)	C(7)	1.505(9)	C(28)	C(29)	1.373(9)
C(3)	C(4)	1.421(9)	C(29)	C(30)	1.375(8)
C(3)	C(8)	1.48(1)			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 11
Intramolecular bond angles involving the nonhydrogen atoms of **5**

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
N(1)	Ta(1)	N(3)	62.9(2)	C(3)	Ta(1)	C(4)	33.4(2)
N(1)	Ta(1)	C(1)	95.3(2)	C(3)	Ta(1)	C(5)	56.0(2)
N(1)	Ta(1)	C(2)	108.2(2)	C(3)	Ta(1)	C(11)	85.0(3)
N(1)	Ta(1)	C(3)	141.1(2)	C(3)	Ta(1)	C(12)	88.0(2)
N(1)	Ta(1)	C(4)	149.7(2)	C(4)	Ta(1)	C(5)	33.5(2)
N(1)	Ta(1)	C(5)	116.8(2)	C(4)	Ta(1)	C(11)	117.3(3)
N(1)	Ta(1)	C(11)	79.4(2)	C(4)	Ta(1)	C(12)	82.5(3)
N(1)	Ta(1)	C(12)	125.7(2)	C(5)	Ta(1)	C(11)	135.9(2)
N(3)	Ta(1)	C(1)	102.6(2)	C(5)	Ta(1)	C(12)	109.9(2)
N(3)	Ta(1)	C(2)	136.5(2)	C(11)	Ta(1)	C(12)	85.8(3)
N(3)	Ta(1)	C(3)	142.1(2)	Ta(1)	N(1)	C(13)	137.9(4)
N(3)	Ta(1)	C(4)	109.3(2)	Ta(1)	N(1)	C(31)	96.4(3)
N(3)	Ta(1)	C(5)	88.3(2)	C(13)	N(1)	C(31)	122.9(5)
N(3)	Ta(1)	C(11)	132.8(2)	C(19)	N(2)	C(31)	124.3(5)
N(3)	Ta(1)	C(12)	93.6(2)	Ta(1)	N(3)	C(25)	139.0(4)
C(1)	Ta(1)	C(2)	33.9(2)	Ta(1)	N(3)	C(31)	98.8(3)
C(1)	Ta(1)	C(3)	56.4(2)	C(25)	N(3)	C(31)	120.8(5)
C(1)	Ta(1)	C(4)	56.4(2)	Ta(1)	C(1)	C(2)	76.0(4)
C(1)	Ta(1)	C(5)	34.7(2)	Ta(1)	C(1)	C(5)	73.9(3)
C(1)	Ta(1)	C(11)	108.5(2)	Ta(1)	C(1)	C(6)	122.0(4)
C(1)	Ta(1)	C(12)	138.7(2)	C(2)	C(1)	C(5)	107.7(6)
C(2)	Ta(1)	C(3)	33.4(2)	C(2)	C(1)	C(6)	128.0(6)
C(2)	Ta(1)	C(4)	55.4(2)	C(5)	C(1)	C(6)	123.9(6)
C(2)	Ta(1)	C(5)	56.3(2)	Ta(1)	C(2)	C(1)	70.1(3)
C(2)	Ta(1)	C(11)	80.0(2)	Ta(1)	C(2)	C(3)	74.2(4)
C(2)	Ta(1)	C(12)	120.2(2)	Ta(1)	C(2)	C(7)	124.1(4)
C(1)	C(2)	C(3)	108.5(6)	C(15)	C(16)	C(17)	120.2(8)
C(1)	C(2)	C(7)	125.0(6)	C(16)	C(17)	C(18)	120.8(9)
C(3)	C(2)	C(7)	126.5(7)	C(13)	C(18)	C(17)	118.6(8)
Ta(1)	C(3)	C(2)	72.4(4)	N(2)	C(19)	C(20)	118.7(5)
Ta(1)	C(3)	C(4)	73.0(4)	N(2)	C(19)	C(24)	122.0(5)
Ta(1)	C(3)	C(8)	126.3(5)	C(20)	C(19)	C(24)	119.0(6)
C(2)	C(3)	C(4)	107.5(6)	C(19)	C(20)	C(21)	119.9(6)
C(2)	C(3)	C(8)	125.3(7)	C(20)	C(21)	C(22)	120.7(6)
C(4)	C(3)	C(8)	126.7(7)	C(21)	C(22)	C(23)	119.6(6)
Ta(1)	C(4)	C(3)	73.6(4)	C(22)	C(23)	C(24)	120.3(7)
Ta(1)	C(4)	C(5)	70.9(4)	C(19)	C(24)	C(23)	120.5(6)
Ta(1)	C(4)	C(9)	124.9(5)	N(3)	C(25)	C(26)	122.9(5)
C(3)	C(4)	C(5)	108.5(6)	N(3)	C(25)	C(30)	117.5(5)
C(3)	C(4)	C(9)	124.9(8)	C(26)	C(25)	C(30)	119.5(5)
C(5)	C(4)	C(9)	126.4(7)	C(25)	C(26)	C(27)	119.6(5)
Ta(1)	C(5)	C(1)	71.4(3)	C(26)	C(27)	C(28)	119.9(6)
Ta(1)	C(5)	C(4)	75.6(4)	C(27)	C(28)	C(29)	120.2(6)
Ta(1)	C(5)	C(10)	126.3(4)	C(28)	C(29)	C(30)	120.3(6)
C(1)	C(5)	C(4)	107.8(6)	C(25)	C(30)	C(29)	120.5(6)
C(1)	C(5)	C(10)	125.5(7)	N(1)	C(31)	N(2)	133.8(5)
C(4)	C(5)	C(10)	126.0(7)	N(1)	C(31)	N(3)	101.9(5)
N(1)	C(13)	C(14)	122.0(6)	N(2)	C(31)	N(3)	124.3(5)
N(1)	C(13)	C(18)	117.7(6)	C(14)	C(13)	C(18)	120.3(6)
C(13)	C(14)	C(15)	119.4(8)	C(14)	C(15)	C(16)	120.7(9)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

idealized positions for both structures. Data collection and refinement parameters for **4** and **5** are given in Table 3. Additional information is given in Appendices A and B.

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Table 12
Anisotropic displacement parameters for **5**

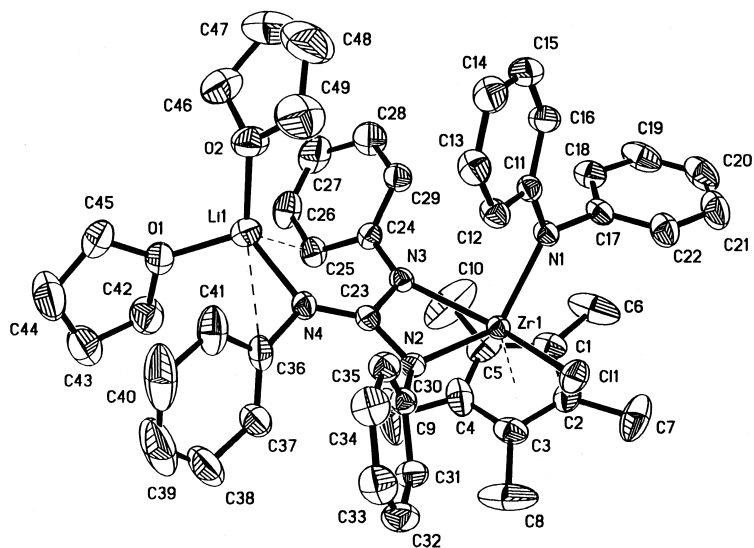
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta(1)	0.0280(1)	0.0297(1)	0.0376(1)	0.0011(1)	0.00546(9)	0.0019(1)
N(1)	0.043(3)	0.030(3)	0.036(3)	0.008(2)	0.014(3)	-0.001(2)
N(2)	0.041(3)	0.033(3)	0.027(3)	0.004(2)	0.006(2)	-0.001(2)
N(3)	0.029(3)	0.032(3)	0.031(3)	0.000(2)	0.005(2)	-0.004(2)
C(1)	0.036(4)	0.026(3)	0.041(4)	-0.001(3)	0.012(3)	0.002(3)
C(2)	0.046(4)	0.021(3)	0.056(4)	0.004(3)	0.012(4)	0.004(3)
C(3)	0.044(4)	0.042(4)	0.053(4)	0.000(3)	-0.004(4)	0.015(3)
C(4)	0.069(5)	0.044(4)	0.040(4)	0.005(4)	0.017(4)	0.012(3)
C(5)	0.048(4)	0.030(3)	0.055(4)	-0.001(3)	0.028(4)	0.009(3)
C(6)	0.042(4)	0.039(4)	0.061(5)	-0.010(3)	0.005(4)	0.000(3)
C(7)	0.059(5)	0.030(4)	0.105(6)	0.008(4)	0.043(5)	-0.006(4)
C(8)	0.066(6)	0.079(6)	0.092(7)	0.014(5)	-0.008(5)	0.034(5)
C(9)	0.130(9)	0.109(7)	0.029(4)	-0.019(7)	0.008(5)	0.005(5)
C(10)	0.070(5)	0.047(4)	0.076(5)	0.003(4)	0.047(5)	0.009(4)
C(11)	0.031(4)	0.054(4)	0.071(5)	0.004(3)	0.015(3)	0.015(4)
C(12)	0.026(4)	0.037(4)	0.070(5)	0.005(3)	-0.012(3)	0.003(3)
C(13)	0.031(3)	0.056(5)	0.038(4)	0.007(3)	0.010(3)	-0.004(3)
C(14)	0.039(4)	0.081(6)	0.044(4)	-0.001(4)	0.007(3)	0.009(4)
C(15)	0.035(5)	0.150(10)	0.051(5)	0.009(5)	0.009(4)	0.025(6)
C(16)	0.059(6)	0.20(1)	0.039(5)	0.047(8)	0.016(4)	0.007(7)
C(17)	0.088(7)	0.122(9)	0.053(6)	0.047(6)	0.006(5)	-0.039(6)
C(18)	0.070(6)	0.060(5)	0.049(4)	0.013(4)	0.012(4)	-0.022(4)
C(19)	0.029(3)	0.041(4)	0.027(3)	0.005(3)	0.005(3)	-0.002(3)
C(20)	0.041(4)	0.044(4)	0.036(3)	-0.005(3)	0.007(3)	0.000(3)
C(21)	0.055(5)	0.062(5)	0.041(4)	0.006(4)	0.018(3)	0.012(4)
C(22)	0.061(5)	0.074(6)	0.031(4)	0.010(4)	0.009(4)	-0.006(4)
C(23)	0.048(5)	0.063(5)	0.045(4)	0.002(4)	0.000(4)	-0.015(4)
C(24)	0.038(4)	0.046(4)	0.041(4)	0.003(3)	0.008(3)	0.002(3)
C(25)	0.037(4)	0.023(3)	0.030(3)	0.002(3)	0.006(3)	0.006(3)
C(26)	0.032(3)	0.039(4)	0.032(3)	0.005(3)	0.001(3)	0.001(3)
C(27)	0.037(4)	0.051(4)	0.036(3)	0.008(3)	0.010(3)	0.004(3)
C(28)	0.054(5)	0.040(4)	0.040(4)	0.004(3)	0.019(3)	-0.003(3)
C(29)	0.043(4)	0.045(4)	0.034(3)	0.002(3)	0.006(3)	-0.011(3)
C(30)	0.030(3)	0.042(4)	0.032(3)	-0.002(3)	0.002(3)	-0.001(3)
C(31)	0.030(3)	0.028(3)	0.035(3)	-0.005(3)	0.010(3)	0.000(3)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$.

Appendix A. X-ray report for $\text{ZrC}_{49}\text{H}_{56}\text{ClN}_4\text{LiO}_4$

A.1. X-ray data collection

A yellow fragment crystal of approximate dimensions of $0.20 \times 0.25 \times 0.35$ mm was selected for X-ray analysis. The crystal was mounted on a glass fiber with epoxy under nitrogen and immediately placed in a cold nitrogen stream at -50°C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 1.5 kW (50 kV, 30 mA). A total of 1321 frames of data were collected using a narrow frame method with scan widths of $0.3^\circ \omega$ and exposure times of 10 s/frame using a crystal-to-detector distance of 5.094 cm. (maximum 2θ angle of 56.52°). The total data collection time was approximately 8 h. Frames were integrated with the Siemens SAINT program to yield a total of 15510 reflections, of which 10983 were independent ($R_{\text{int}} = 2.55\%$) and 10980 were above 4σ (F). The unit cell parameters (at -50°C) of $a = 11.7636$ (1) Å, $b = 12.4384$ (1) Å, and $c = 17.9531$ (1) Å, $\alpha = 86.732$ (1), $\beta = 71.238$ (1), $\gamma = 89.372$ (1), were based upon the least-squares refinement of three dimensional centroids of 10980 reflections. The space group was assigned as $P\bar{1}(\#2)$ the basis of systematic absences and intensity statistics using XPREP, and the crystal solved and refined using direct methods included in the SHELXTL 5.04 package. For a Z value of 2 there is one independent molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (on F^2), with hydrogens included in idealized locations. The structure was refined to $R_1 = 0.0441$. $wR_2 = 0.1317$. Fractional coordinates and thermal parameters are given in the supplementary material (Tables 4–7).



Appendix B. X-ray report for TaC₃₁H₃₆N₃

B.1. X-ray data collection

A parallelepiped red crystal of approximate dimensions of 0.20 × 0.40 × 0.20 mm was selected for X-ray analysis. The crystal was mounted under nitrogen and immediately placed in a cold nitrogen stream at −50°C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 1.5 kW (50 kV, 30 mA). A total of 1321 frames of data were collected using a narrow frame method with scan widths of 0.3° ω and exposure times of 10 s/frame using a crystal-to-detector distance of 5.094 cm. (maximum 2θ angle of 56.52°). The total data collection time was approximately 8 h. Frames were integrated with the Siemens SAINT program to yield a total of 30025 reflections, of which 13565 were independent ($R_{\text{int}} = 4.15\%$) and 4575 were above 3σ (F). The unit cell parameters (at −50°C) of $a = 31.2878$ (4) Å, $b = 7.9181$ (1) Å, and $c = 23.003$ (3) Å, $\beta = 101.687$ (1), were based upon the least-squares refinement of three dimensional centroids of 4575 reflections.

B.2. Data reduction

The data were integrated with the SAINT program using an algorithm proposed by Kabsch [47]. SAINT was used to perform the integration of intensity of reflections and scaling, absorption and time decay correction and statistical analysis of the data. The data were corrected for Lorentz and polarization effects. Of the 30025 reflections which were collected, 13565 were unique ($R_{\text{int}} = 0.0415$); equivalent reflections were merged. The minimum and maximum transmission factors were 0.5900 and 0.8840. The linear absorption coefficient, μ , for Mo-K α radiation is 39.5 cm^{−1}. XPREP was used for space group and empirical absorption corrections.

B.3. Structure solution and refinement

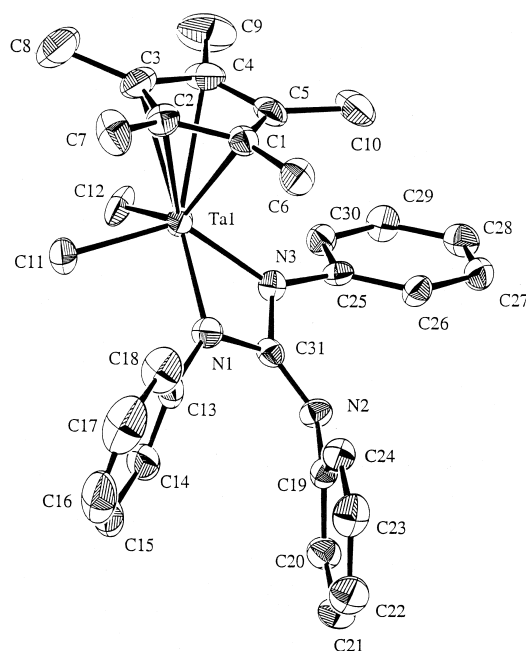
The structure was solved by heavy-atom Patterson methods (SAPI91 [44]) and expanded using Fourier techniques (DIRDIF92 [45]). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions. The final cycle of full-matrix least-square refinement⁶ was based on 4575 observed reflections ($I > 3.00\sigma(I)$) and 316 variable parameters and converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of:

$$R = \sum ||F_o| - |F_c|| \sum |F_o| = 0.042, \quad R_w = \sqrt{\sum F_o - F_c^2 / \sum w F_o^2} = 0.039$$

The standard deviation of an observation of unit weight⁷ was 1.54. The weighting scheme was based on counting statistics and included a factor ($p = 0.010$) to downweight the intense reflections. All calculations were performed using the teXSan [46] crystallographic software package of Molecular Structure Corporation (Tables 8–12).

⁶ Least-squares: Function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma^2(F_o)) = (4F_o^2)/(\sigma^2(F_o^2))$, $\sigma^2(F_o^2) = (S^2(C + R^2B) + (pF_o^2)^2)/L_p^2$, S = Scan rate, C = total integrated peak count, R = Ratio of scan time to background counting time, B = total background count, L_p = Lorentz-polarization factor, p = p -factor.

⁷ Standard deviation of an observation of unit weight: $\sqrt{\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)}$, where N_o = number of observations, N_v = number of variables.



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