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LIGAND REDISTRIBUTION REACTIONS AS A ROUTE TO CYCLOPENTADIENYL- OR 1-AZA-ALLYLZIRCONIUM(IV) TRICHLORIDES AND THE X-RAY STRUCTURES OF $[\{\overline{\mathrm{Zr(LL')}}\mathrm{Cl_2}(\mu\text{-}\mathrm{Cl})\}_2]$ AND $[\overline{\mathrm{Zr(LL')}}_2\mathrm{Cl_2}]$ [LL′ = N(R)C(Bu^t)CHR, R = SiMe$_3$]*

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Abstract—Mixing equimolar portions of $ZrCl_4$ and $[Zr(Cp^x)_2Cl_2]$ in toluene at ambient temperature rapidly gave, in a very high yield, a precipitate of $ZrCp^xCl_3$ [$Cp^x = C_5H_5$ (**1**), $C_5H_4Bu^t$ (**2**) or $C_5H_3Bu^t_2-1,3$ (**3**)]. Addition of tetrahydrofuran (THF) to each of **2** or **3** at *ca* 20°C caused the bright yellow colour to be discharged and the solid to dissolve, due to the formation of $[Zr(Cp^x)_2Cl_2]$ and $[ZrCl_4(THF)_2]$; this was established by preparative scale experiments and also by ^{91}Zr NMR spectroscopic studies. The 1-aza-allylzirconium(IV) chloride $[\{\overline{\mathrm{Zr(LL')}}\mathrm{Cl_2}(\mu\text{-}\mathrm{Cl})\}_2]$ (**4**) was obtained by a similar redistribution reaction as **1**–**3**, from *rac*-$[\overline{\mathrm{Zr(LL')}}_2\mathrm{Cl_2}]$ (**5**) and $ZrCl_4$ [LL′ = N(R)C(Bu^t)CHR, R = SiMe$_3$]. The X-ray structures of **4** and **5** have been determined.

The 12-electron monocyclopentadienylzirconium(IV) halides, or titanium and hafnium analogues, provide useful starting materials for the preparation of a wide range of η-cyclopentadienyl-group 4 metal derivatives,[1,2] including alkyl, allyl,[3,4] diene[5–7] and aryl[8] complexes. Several group 4 metallocenes containing mixed cyclopentadienyl rings have been obtained from monocyclopentadienyl precursors.[9–13] Their Lewis acidity has been demonstrated in the formation of 16-electron adducts such as $[Zr(\eta\text{-}Cp)Cl_3L_2]$ (L represents a range of two-electron donors), and in their use as catalysts in organic synthesis.[14–18]

Several synthetic methods have been explored in attempts to find a convenient preparative route to the group 4 metal (M) compounds $MCpCl_3$ and substituted cyclopentadienyl analogues. Nucleophilic substitution of the chloride in MCl_4 (M = Zr or Hf) by treatment with an equimolar portion of the appropriate lithium cyclopentadienide gave $M(\eta\text{-}C_5Me_5)Cl_3$ (M = Zr or Hf),[19] $Zr\{\eta\text{-}C_5H_2Bu^t_3\text{-}1,2,4\}Cl_3$[12] or $[Zr\{\eta\text{-}C_5H_3(SiMe_2CH_2PPr^i_2)_2\text{-}1,3\}Cl_3]$.[20] In all other cases thus far reported, using variously substituted cyclopentadienyls, this procedure resulted in the formation of the appropriate metallocene(IV) dichloride. Indeed, it has been stated that "$ZrCpCl_3$ is difficult to obtain by the usual *nucleophilic* routes via substitution of chloride from $ZrCl_4$ by $\bar{C}p$ from various sources".[8] Di(cyclopentadienyl)magnesium was, however, a convenient ligand transfer reagent for the preparation of $Zr(\eta\text{-}C_5H_5)Cl_3$ and $Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}Cl_3$, using xylene as solvent.[21] The reaction of $ZrCl_4$ with half an equivalent of $Tl(C_5H_5)$ in dimethoxyethane (DME) gave $[Zr(\eta\text{-}C_5H_5)Cl_3(DME)]$, which has been X-ray authenticated.[14] Treatment of $ZrCl_3(PEt_3)_2$ with $2Tl(C_5H_5)$ gave thallium metal and the X-ray-characterized $[Zr(\eta\text{-}C_5H_5)Cl_3(PEt_3)_2]$.[22]

The photo-induced chlorination of [Zr(η-

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*Dedicated to Prof. Edward Abel. We, and especially M. F. L. (who has enjoyed his friendship for four decades), pay tribute to his many contributions to chemistry and education.

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$C_5H_5)_2Cl_2]$ yielded $Zr(\eta\text{-}C_5H_5)Cl_3$ using Cl_2 in CCl_4,[8] or with Bu^tCl as the chlorine atom source.[14] The silyl cleavage reaction of the appropriate silylated cyclopentadiene with MCl_4 (M = Zr or Hf) readily gave $M(\eta\text{-}C_5Me_5)Cl_3$[23,24] or $M\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}Cl_3$.[25]

The structure of crystalline cyclopentadienylziconium(IV) chloride has been shown to be $[\{Zr(\eta\text{-}C_5H_5)Cl(\mu\text{-}Cl)_2\}_\infty]$ (**A**),[26] while the pentamethyl analogue is a dimer, $[\{Zr(\eta\text{-}C_5Me_5)Cl_2(\mu\text{-}Cl)_2\}_2]$ (**B**).[24]

We have recently described the synthesis, structure and some reactions of the lithium β-diketinimate $[\{\overline{Li(LL)}\}_2]$ [LL = N(R)C(Ph)C(H)C(Ph)NR, R = $SiMe_3$], and shown that the $[LL]^-$ ligand is sterically extremely demanding and is able to bond to a metal (Sn^{4+}) in a quasi-η^5-manner.[27] A related ligand is the aza-allyl $[N(R)C(Bu^t)CHR]^-$ (abbreviated as $[LL']^-$); crystalline $[\{\overline{Li(LL')}\}_2]$ is binuclear, while crystalline *rac*-$[\overline{Zr(LL')}_2Cl_2]$ was believed to be a monomer.[28]

We now report the selective synthesis of a series of monocyclopentadienylzirconium(IV) chloride complexes $ZrCp^xCl_3$ [Cp^x = C_5H_5 (**1**), $C_5H_4Bu^t$ (**2**) or $C_5H_3Bu^t_2$-1,3 (**3**)] and $[\{\overline{Zr(LL')}Cl_2(\mu\text{-}Cl)\}_2]$ (**4**) via a solvent-dependent ligand redistribution reaction from $ZrCl_4$ and the corresponding Zr^{IV} dichloride. Also described are the X-ray structures of crystalline **4** and of *rac*-$[\overline{Zr(LL')}_2Cl_2]$ (**5**).

RESULTS AND DISCUSSION

The monocyclopentadienylzirconium(IV) chlorides $Zr(\eta\text{-}C_5H_{5-n}R_n)Cl_3$ [R = Bu^t and $n = 1$ (**2**) or 2 (**3**); or R = H, $n = 0$ (**1**)] were prepared by the ligand redistribution reaction in toluene at room temperature of $[Zr(\eta\text{-}C_5H_{5-n}R_n)_2Cl_2]$ and the metal tetrachloride:

$$[Zr(\eta\text{-}C_5H_{5-n}R_n)_2Cl_2] + ZrCl_4 \xrightarrow[20^\circ C]{PhMe} 2Zr(\eta\text{-}C_5H_{5-n}R_n)Cl_3 \quad \begin{array}{ll} \mathbf{1}\, n = 0, & R = H \\ \mathbf{2}\, n = 1, & R = Bu^t \\ \mathbf{3}\, n = 2, & R = Bu^t. \end{array} \qquad (1)$$

Addition of solid $ZrCl_4$ to the appropriate zirconocene(IV) dichloride dissolved in toluene (no reaction occurred in hexane) resulted in the immediate formation of a bright yellow precipitate in each case. A small excess (*ca* 2–3%) of the zirconocene(IV) dichloride was used to ensure complete consumption of the $ZrCl_4$. The air- and moisture-sensitive yellow solid $Zr(\eta\text{-}C_5H_{5-n}R_n)Cl_3$ (**1–3**) was washed with successively toluene and pentane to remove unreacted $[Zr(\eta\text{-}C_5H_{5-n}R_n)_2Cl_2]$, in preparation for analysis. No reaction was observed between $ZrCl_4$ and $[Zr\{\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$ or between $HfCl_4$ and $[Hf\{\eta\text{-}C_5H_3Bu^t_2\text{-}1,3\}_2Cl_2]$ under these similar mild conditions.

In an effort to prepare X-ray-quality crystals of $Zr(\eta\text{-}C_5H_4Bu^t)Cl_3$ (**2**) or $Zr\{\eta\text{-}C_5H_3Bu^t_2\text{-}1,3\}Cl_3$ (**3**), both sublimation and crystallization from toluene were considered. Each compound decomposed upon attempted sublimation and the low solubility of **2** or **3** in toluene prevented our obtaining X-ray quality single crystals. The X-ray structures of $[\{Zr(\eta\text{-}C_5H_5)Cl(\mu\text{-}Cl)_2\}_\infty]$ (**1** = **A**),[26] and **2** and **3** are likely to be similar. Their yellow colour, not so obvious for **1**, is probably due to a ligand → metal charge transfer.

With the literature preparation of $Zr(\eta\text{-}C_5Me_5)Cl_3$ in mind,[19] attempts were made to prepare **2** by the reaction of $ZrCl_4$ with one equivalent of $LiC_5H_4Bu^t$ in diethyl ether; but $[Zr(\eta\text{-}C_5H_4Bu^t)_2Cl_2]$ was the only identified product. The reaction between $ZrCl_4$ and one equivalent of $Li[C_5H_3Bu^t_2\text{-}1,3]$ in toluene gave the desired product **3**, but its limited solubility in toluene prevented its ready separation from the LiCl residue.

The monocyclopentadienylzirconium(IV) chlorides **1**,[22] **2** and **3** were identified by microanalysis and ^1H NMR spectroscopy, the latter data being available for comparison with those for the corresponding zirconocene dichloride (Table 1). Their low solubility in benzene or toluene prevented a ^{91}Zr spectroscopic study being carried out.

Addition of tetrahydrofuran (THF) to the solid trichloride **2** or **3** caused the bright yellow colour to be instantly discharged and the solid to dissolve. Removal of THF followed by extraction into toluene yielded a crystalline solid which was identified by ^1H NMR spectroscopy as the white $[Zr(\eta\text{-}C_5H_4Bu^t)_2Cl_2]$ or the pale yellow $[Zr(\eta\text{-}C_5H_3Bu^t_2\text{-}1,3)_2Cl_2]$, respectively. The residual solids after extraction were found to contain $ZrCl_4(THF)_2$ together with unextracted zirconocene(IV) chloride, but there was no evidence of any remaining **2** or **3**. The zirconocene(IV) chlorides were obtained in *ca* 80% yield, but the zirconium tetrachloride-THF adducts were not cleanly isolated. We conclude that addition of THF to the yellow solids caused the redistribution reaction of eq. (1) to reverse; eq. (2) illustrates this process for the case of **2**:

$$\underset{\mathbf{2}}{2Zr(\eta\text{-}C_5H_4Bu^t)Cl_3} \xrightarrow[20^\circ C]{THF} [Zr(\eta\text{-}C_5H_4Bu^t)_2Cl_2] + ZrCl_4(THF)_2. \qquad (2)$$

Table 1. ^{1}H NMR spectroscopic chemical shift (δ) data and assignments for the zirconium monocyclopentadienyls and their zirconocene(IV) precursors

Complex	δ^a	
	Ring protons	Bu^t
$Zr(\eta\text{-}C_5H_4Bu^t)Cl_3$	6.07 (t, 2H) 5.75 (t, 2H)	1.29 (s, 9H)
$Zr(\eta\text{-}C_5H_3Bu^t_2\text{-}1,3)Cl_3$	6.39 (t, 1H) 6.03 (d, 2H)	1.10 (s, 18H)
$[Zr(\eta\text{-}C_5H_4Bu^t)_2Cl_2]$	6.42 (t, 4H) 6.31 (t, 4H)	1.33 (s, 18H)
$[Zr(\eta\text{-}C_5H_3Bu^t_2\text{-}1,3)_2Cl_2]$	6.62 (t, 2H) 5.82 (d, 4H)	1.29 (s, 36H)

[a] Chemical shifts (δ) in ppm relative to $SiMe_4$, calibrated with respect to internal solvent. Spectra recorded in C_6H_6 at *ca* 298 K and 360 MHz.

In addition to ^{1}H NMR spectroscopy, ^{91}Zr NMR spectroscopy was also used to identify the products of this reaction. As a starting point, $^{91}Zr\{^1H\}$ NMR spectra were recorded at 305 K for standard samples of $ZrCl_4(THF)_2$, $[Zr(\eta\text{-}C_5H_4Bu^t)_2Cl_2]$[29] and $[Zr(\eta\text{-}C_5H_3Bu^t_2\text{-}1,3)_2Cl_2]$[30] dissolved in THF. As expected for molecules with relatively low symmetry, the signals were very broad and poorly defined at room temperature, with the band-width at half-height ($w_{1/2}$) being in the region of 3500 Hz; warming to 338 K resulted in a significant sharpening of the signals and all spectra were subsequently recorded at this temperature.

The spectrum of $ZrCl_4(THF)_2$ comprised a single resonance centred at δ 623, $w_{1/2}$ 1250 Hz, with that of $[Zr(\eta\text{-}C_5H_4Bu^t)_2Cl_2]$ showing a single resonance centred at δ -73.4, $w_{1/2}$ 1500 Hz (cf. δ -60.0, $w_{1/2}$ 2900 Hz reported in ref. 32). The ^{91}Zr NMR spectrum of the products of the reaction between **1** and THF indicated that in solution there were two distinct zirconium atom magnetic environments (δ 624 and -65.9). Comparison of the two signals with the reference spectra confirmed the products to be $ZrCl_4(THF)_2$ and $[Zr(\eta\text{-}C_5H_4Bu^t)_2Cl_2]$, respectively. The spectrum of $[Zr(\eta\text{-}C_5H_3Bu^t_2\text{-}1,3)_2Cl_2]$ comprised a single resonance centred at δ -12.4, $w_{1/2}$ 1800 Hz, while that for $ZrCl_4(THF)_2$ was as described above. The ^{91}Zr NMR spectrum of the actual products of the reaction again showed two signals (δ 624 and -7.6), in agreement with the reference spectra, confirming the products to be $ZrCl_4(THF)_2$ and $[Zr(\eta\text{-}C_5H_3Bu^t_2\text{-}1,3)_2Cl_2]$. Selected data are shown in Table 2 and Figs 1 and 2.

It is evident that earlier failures to obtain satisfactory results for the preparation of all but highly hindered compounds $ZrCp^xCl_3$ from $ZrCl_4$ by $\overline{Cl}/\overline{Cp}^x$ exchange failed because of the choice of solvent; in a non-polar medium, the reactions are sluggish, while in an ethereal solvent, rapid metathesis occurs [eq. (2)] unless the donor solvent is such as to form a substitution-inert six-coordinate complex such as $[ZrCp^xCl_3(DME)]$.

The ligand redistribution reaction in toluene has also proved to be a convenient method to prepare

Table 2. Selected $^{91}Zr\{^1H\}$ NMR spectral chemical shifts (δ) and linewidths at half-height ($w_{1/2}$)

Complex	δ^a	$w_{1/2}$ (Hz)	Temp. (K)	Ref.
$[Zr(C_5H_5)_2Cl_2]^b$	-121.9	276	298	33
	-113.0	250	333	32
$[Zr(C_5H_5)_2Br_2]^b$	0.0	19	298	33
$[Zr(C_5H_4Et)_2Cl_2]^b$	-74.4	600–630	333	32
$[Zr(C_5H_4Pr^i)_2Cl_2]^b$	-75.7	840–880	333	32
$[Zr(\eta\text{-}C_5H_4Bu^t)_2Cl_2]^c$	-73.4	1500	338	This work
$[Zr(\eta\text{-}C_5H_3Bu^t_2\text{-}1,3)_2Cl_2]^c$	-12	1800	338	This work
$ZrCl_4(THF)_2^c$	623	1250	338	This work

[a] Chemical shifts (δ) in ppm relative to $[Zr(C_5H_5)_2Br_2]$.

[b] In C_6H_6, but values corrected for data in THF: $\delta_{corr} = \delta\ (C_6H_6)\text{-}5.44$.[31]

[c] Spectra recorded in THF (20% deuterated and 80% protonated solvent) in 10 mm tubes at 46.49 MHz.

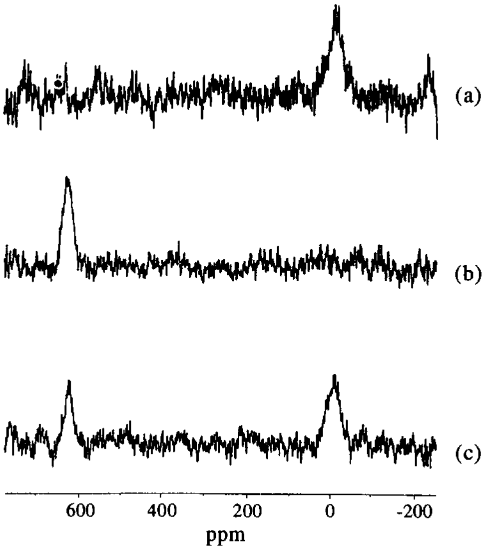

Fig. 1. ^{91}Zr{^{1}H} NMR spectra of: (a) $[\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_4Bu^t})_2\mathrm{Cl_2}]$, (b) $\mathrm{ZrCl_4(THF)_2}$ and (c) products of the reaction between $\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_4Bu^t})\mathrm{Cl_3}$ and THF, at 338 K and 46.49 MHz.

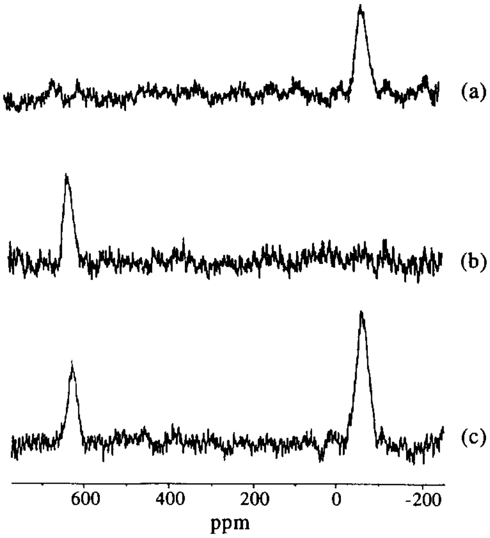

Fig. 2. ^{91}Zr{^{1}H} NMR spectra of: (a) $[\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_3Bu^t_2}\text{-}1,3)\mathrm{Cl_3}]$, (b) $\mathrm{ZrCl_4(THF)_2}$ and (c) products of the reaction between $\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_3Bu^t_2}\text{-}1,3)\mathrm{Cl_3}$ and THF, at 338 K and 46.49 MHz.

a mono(aza-allyl)zirconium complex. Treatment of *rac*-$[\overline{\mathrm{Zr(LL')}}_2\mathrm{Cl_2}]$ (**5**) with $\mathrm{ZrCl_4}$ in toluene at 50°C for 4 h led to $[\{\overline{\mathrm{Zr(LL')}}\mathrm{Cl_2}(\mu\text{-}\mathrm{Cl})\}_2]$ (**4**) in 80% yield, eq. (3). Furthermore, the reaction of Li(LL′) with one equivalent of $\mathrm{ZrCl_4}$ in diethyl ether only afforded **5**. We conclude that the ether causes the reverse of reaction (3) to take place, by a process analogous to eq. (2).

$$\underset{\mathbf{5}}{[\overline{\mathrm{Zr(LL')}}_2\mathrm{Cl_2}]} + \mathrm{ZrCl_4} \xrightarrow[50^\circ\mathrm{C}]{\text{toluene}} \underset{\mathbf{4}}{[\{\overline{\mathrm{Zr(LL')}}\mathrm{Cl_2}(\mu\text{-}\mathrm{Cl})\}_2]}. \quad (3)$$

The X-ray molecular structures of $[\{\overline{\mathrm{Zr(LL')}}\mathrm{Cl_2}(\mu\text{-}\mathrm{Cl})\}_2]$ (4) *and* rac-$[\overline{\mathrm{Zr(LL')}}_2\mathrm{Cl_2}]$ (5)

The molecular structures and atom numbering scheme for **4** and **5** are shown in Figs 3 and 4, respectively; selected bond distances and angles are presented in Tables 3 and 4, respectively.

The molecular structure of the crystalline **4** shows it to be a dimer. Each zirconium atom is bridged by two chlorine atoms and is coordinated to a 1-aza-allyl group in an η^3-bonding mode, thus forming around the metal a square (four chlorine atoms)-based pyramid with the centroid of the η^3-1-aza-all ligand occupying the apical site. The Zr—C contacts are such that with the terminal carbon it is shorter [Zr—C(2) 2.387(5) Å] than with the central carbon [Zr—C(1) 2.525(4) Å].

The molecular structure of crystalline **5** shows it to be a monomer. Each zirconium is coordinated to two chlorine atoms and in an η^3-bonding mode to two 1-aza-allyl groups. Taking the aza-allyl group as occupying a single site, the coordination geometry may be regarded as distorted tetrahedral around the metal. The Zr—C bond distances relating to the 1-aza-allyl groups are similar as for **4**, the terminal contact [Zr—C(1) 2.387(5) Å] being shorter than the central [Zr—C(2) 2.525(4) Å].

The structures of complexes **4** and **5** may be compared with those of $[\{\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_5})\mathrm{Cl_2}(\mu\text{-}\mathrm{Cl})_2\}_\infty]$,[26] $[\{\mathrm{Zr}(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Cl_2}(\mu\text{-}\mathrm{Cl})_2\}_2]$,[27] $[\overline{\mathrm{Zr\{N(R)C(Bu^t)C(H)C(Ph)NR\}}}\mathrm{Cl_3}]$ ($\mathrm{R = SiMe_3}$; **C**)[29] and $[\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Cl_2}]$;[34] some pertinent bond lengths are given in Table 5. From their states of molecular aggregation, we conclude that the η^3-1-aza-allyl ligand $[\mathrm{N(R)C(Bu^t)CHR}]^-$ ($= [\mathrm{LL'}]^-$) is sterically demanding, probably to a similar extent as $[\eta^5\text{-}\mathrm{C_5Me_5}]^-$, but not as much as the β-diketinimato ligand found in **C**.

EXPERIMENTAL

All manipulations were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over potassium–sodium alloy under argon prior to use. The following compounds were prepared by known procedures: $[\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_4Bu^t})_2\mathrm{Cl_2}]$,[30] $[\mathrm{Zr}(\eta\text{-}\mathrm{C_5H_3Bu^t_2}\text{-}1,3)_2\mathrm{Cl_2}]$[31] and *rac*-$[\overline{\mathrm{Zr\{N(R)C(Bu^t)CHR\}}}_2\mathrm{Cl_2}]$.[29] Microanalyses were

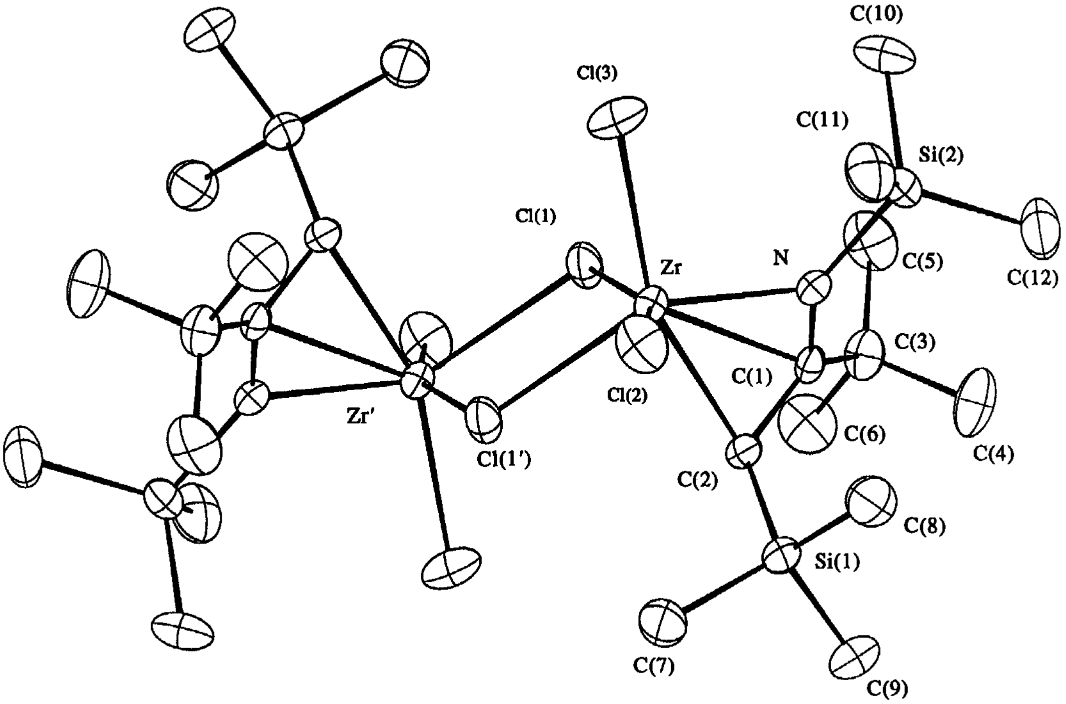

Fig. 3. The X-ray molecular structure of [{$\overline{\mathrm{Zr(LL}'}$)Cl$_2$($\mu$-Cl)}$_2$] (**4**) and atom numbering.

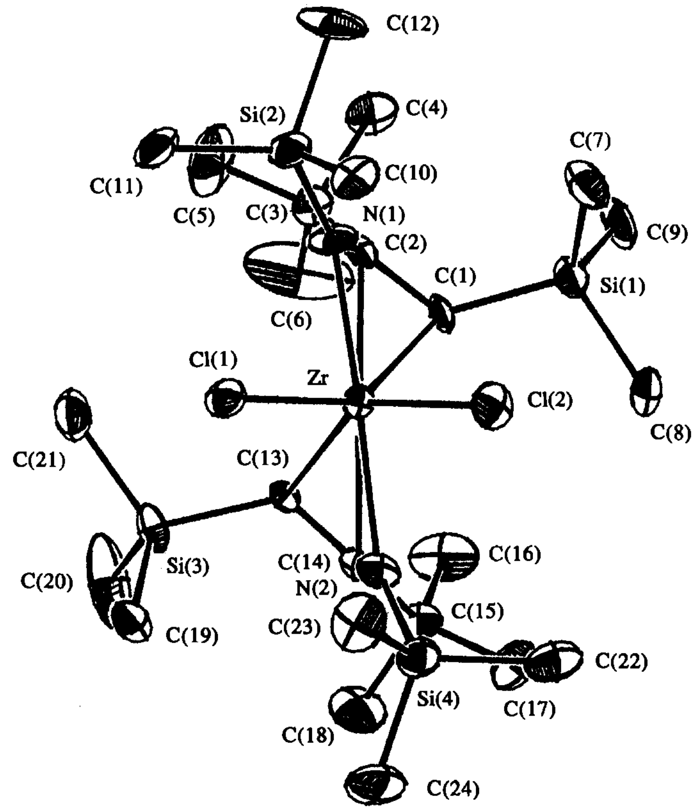

Fig. 4. The X-ray molecular structure of *rac*-[$\overline{\mathrm{Zr(LL}'}$)$_2Cl_2$] (**5**) and atom numbering.

Table 3. Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for $[\{Zr(LL')Cl_2(\mu\text{-}Cl)\}_2]$ (**4**)

Zr—Cl(1)	2.629(2)	N—Zr—Cl(1)	97.70(11)
Zr—Cl(1′)	2.566(2)	N—Zr—C(2)	61.1(2)
Zr—Cl(2)	2.360(2)	C(1)—Zr—Cl(1)	80.21(11)
Zr—Cl(3)	2.393(2)	C(1)—Zr—Cl(2)	118.93(11)
Zr—C(1)	2.525(4)	Cl(1)—Zr—Cl(1′)	117.09(12)
Zr—C(2)	2.387(5)	Cl(1′)—Zr—Cl(2)	85.44(6)
Zr—N	2.115(4)	Cl(2)—Zr—Cl(3)	95.05(8)
C(1)—C(2)	1.405(7)	Cl(3)—Zr—Cl(1)	81.85(7)

Table 4. Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for $[Zr(LL')_2Cl_2]$ (**5**)

Zr—Cl(1)	2.405(4)	N(1)—Zr—Cl(1)	87.3(3)
Zr—Cl(2)	2.401(5)	N(1)—Zr—C(1)	59.2(5)
Zr—C(1)	2.379(13)	Cl(1)—Zr—Cl(2)	97.4(2)
Zr—C(2)	2.554(14)	C(2)—Zr—Cl(1)	97.5(2)
Zr—N(1)	2.225(12)	C(2)—Zr—Cl(2)	114.3(5)
C(1)—C(2)	1.38(2)	C(2)—Zr—C(14)	113.4(5)

Table 5. Selected bond lengths (Å) in some crystalline organozirconium(IV) chlorides

Compound	Zr—C	Zr—N	$Zr—Cl_t$	$Zr—Cl_{br}$	Ref.
$[\{Zr(\eta\text{-}C_5H_5)Cl_2(\mu\text{-}Cl)_2\}_\infty]$	2.19^a	—	2.419(3)	2.623^a	26
$[\{Zr(\eta\text{-}C_5Me_5)Cl_2(\mu\text{-}Cl)_2\}_2]$	2.175^a	—	2.394^a	2.588^a	24
$[Zr\{N(R)C(Bu^t)C(H)C(Ph)NR\}Cl_3]$	2.58^a	2.163^a	2.416^a		28
$[Zr(\eta\text{-}C_5H_5)_2Cl_2]$	2.49^a	—	2.44^a	—	33
$[\{Zr\{N(R)C(Bu^t)CHR\}Cl_2(\mu\text{-}Cl)\}_2]$ (**4**)	2.525(4) 2.387(5)	2.115(4)	2.37^a	2.60^a	This work
rac-$[Zr\{N(R)C(Bu^t)CHR\}_2Cl_2]$ (**5**)	2.554(14) 2.379(13)	2.225(12)	2.40^a	—	This work

[a] Mean value.

carried out by Medac Ltd (Brunel University). NMR spectra were recorded using Bruker WM 250, WM 360 or WM 500 spectrometers.

Preparation of $Zr(\eta\text{-}C_5H_5)Cl_3$ (**1**)

Solid $ZrCl_4$ (1.02 g, 4.38 mmol) was added to a stirring solution of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ (1.30 g, 4.45 mmol) in toluene (50 cm^3) at room temperature. The initially colourless solution became bright yellow and a very bright yellow suspension appeared after *ca* 2 min. Stirring was continued for 1 h followed by filtration to recover the yellow solid (2.05 g, 7.80 mmol, 89%), which was then washed with toluene followed by pentane and dried *in vacuo.*

Preparation of $Zr(\eta\text{-}C_5H_3Bu^t_2-1,3)Cl_3$ (**2**)

Solid $ZrCl_4$ (0.60 g, 2.57 mmol) was added to a stirring solution of $[Zr(\eta\text{-}C_5H_3Bu^t_2\text{-}1,3)_2Cl_2]$ (1.43 g, 2.77 mmol) in toluene (50 cm^3) at room temperature. The initially colourless solution became bright yellow and a very bright yellow suspension appeared after *ca* 10 min. Stirring was continued for 1 h followed by filtration to recover the yellow solid (1.80 g, 4.80 mmol, 95%), which was then washed with toluene followed by pentane and dried *in vacuo*. Found: C, 42.1; H, 5.8. $Zr(\eta\text{-}C_5H_3Bu^t_2)Cl_3$ requires: C, 41.6; H, 5.7%.

Preparation of $Zr(\eta\text{-}C_5H_4Bu^t)Cl_3$ (3)

Solid $ZrCl_4$ (0.72 g, 3.09 mmol) was added to a stirring solution of $[Zr(\eta\text{-}C_5H_4Bu^t)_2Cl_2]$ (1.26 g, 3.13 mmol) in toluene (50 cm^3) at room temperature. The initially colourless solution became bright yellow and a very bright yellow suspension appeared after *ca* 2 min. Stirring was continued for 1 h followed by filtration to recover the yellow solid (1.85 g, 5.80 mmol, 93%), which was then washed with toluene followed by pentane and dried *in vacuo*. Found: C, 33.9; H, 4.1. $Zr(\eta\text{-}C_5H_4Bu^t)Cl_3$ requires: C, 33.9; H, 4.2%.

Preparation of $[\{\overline{Zr(LL')}Cl_2(\mu\text{-}Cl)\}_2]$ [**4**; LL′ = N(R)C(Bu^t)CHR, R = $SiMe_3$]

Solid $ZrCl_4$ (1.20 g, 3.73 mmol) was added to *rac*-$[\overline{Zr(LL')}_2Cl_2]$ (**5**)[29] in toluene (*ca* 35 cm^3) at ambient temperature. The stirred mixture was heated at 50°C for 4 h and was then filtered. Concentration of the filtrate afforded white crystals of **4** (2.90 g, 80%). Found: C, 32.8; H, 6.43; N, 3.18. $Zr(LL')Cl_3$ requires: C, 32.8; H, 6.41; N, 3.18%. ^1H NMR (360 MHz, $CDCl_3$), δ: 0.25 and 0.56 (s, 9H), 1.29 (s, 9H), 5.25 (s, 1H); ^{13}C (125 MHz, $CDCl_3$), δ: 0.95, 3.42, 29.50, 41.64, 105.39, 192.01.

X-ray structure determinations of $[\{\overline{Zr(LL')}Cl_2(\mu\text{-}Cl)\}_2]$ (**4**) *and* rac-$[\overline{Zr(LL')}_2Cl_2]$ (**5**)

In each case, unique data sets were collected at room temperature from a crystal sealed in a capillary under argon on an Enraf–Nonius CAD4 diffractometer with monochromated Mo-K_α radiation. The data set for **5** was corrected for a 2.9% change in the standard reflections during the data collection. Data were corrected for Lorentz and polarization effects and for absorption using psi-scan data for **4** and DIFABS[34] for **5**.

Each structure was solved using the heavy atom routines of SHELXS-86[35] and refined by full matrix least-squares with non-hydrogen atoms anisotropic. Refinement of **4** was carried out with SHELXS-93 based on F^2 and using all unique data, and with hydrogen atoms in riding mode with $U_{iso}(H) = 1.5\ U_{eq}(C)$ for methyl groups and 1.2 $U_{eq}(C)$ otherwise. Refinement of **5** was carried out with programs from the Enraf–Nonius MOLEN package based on F, using only reflections with $I > 2\sigma(I)$ and with hydrogen atoms at fixed calculated position with $U_{iso} = 1.2\ U_{eq}(C)$.

Further details are given in Table 6. Tables of atom positions and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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Table 6. X-ray crystal structure details for compounds **4** and **5**

	$[\{\overline{Zr(LL')}Cl_2(\mu\text{-}Cl)\}_2]$ (**4**)	$[\overline{Zr(LL')}_2Cl_2]$ (**5**)
Formula	$C_{24}H_{56}Cl_6N_2Si_4Zr_2$	$C_{24}H_{56}Cl_2N_2Si_4Zr$
M	880.2	647.2
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $Pbca$
a, b, c (Å)	9.916(5), 15.083(4), 13.993(5)	16.441(8), 25.218(12), 17.434(6)
β (°)	93.83(3)	90
U (Å^3), Z, D_c (g cm^{-3})	2088, 2, 1.40	7228, 8, 1.19
F(000)	904	2752
μ(Mo-K_α) (cm^{-1})	10.2	5.9
Crystal size (mm^3)	0.3 × 0.2 × 0.15	0.15 × 0.15 × 0.1
θ_{max} for data (°)	28	25
Total unique reflections ($2 < \theta < 28°$)	5013	6993
Reflections with $I > 2\sigma\ (I)$	3171	2009
R [for $I > 2\sigma\ (I)$][a]	0.062	0.089
Max parameter shift/e. s. d.	0.005	0.02
Number of variables	172	298
($\Delta\rho$) max., min. (e Å^{-3})	+1.51, −0.93	+0.58, −0.28

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$.

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REFERENCES

1. Cf. D. J. Cardin, M. F. Lappert and C. L. Raston, *Chemistry of Organo-zirconium and -hafnium Compounds*, Ch. 2. Ellis Horwood, Chichester (1986).
2. P. T. Wolczanski and J. E. Bercaw, *Organometallics* 1982, **1**, 793.
3. E. J. Larson, P. C. van Dort, J. S. Dailey, J. R. Lakanen, L. M. Pederson, M. E. Silver, J. C. Huffman and S. O. Russo, *Organometallics* 1987, **6**, 2141.
4. J. Blenkers, H. J. de Liefde Meijer and J. H. Teuben, *J. Organomet. Chem.* 1981, **218**, 383.
5. J. Blenkers, B. Hessen, F. van Bolhuis, A. J. Wagner and J. H. Teuben, *Organometallics* 1987, **6**, 459.
6. Y. Wielstra, S. Gambarotta and A. L. Spek, *Organometallics* 1990, **9**, 572.
7. K. P. Reddy and J. L. Petersen, *Organometallics* 1989, **8**, 2107.
8. G. Erker, K. Berg, L. Treschanke and K. Engel, *Inorg. Chem.* 1982, **21**, 1277.
9. C. J. Curtis and R. C. Haltiwanger, *Organometallics* 1991, **10**, 3220.
10. P. G. Gassman and C. H. Winter, *Organometallics* 1991, **10**, 1592.
11. S. Jüngling, R. Mülhaupt and H. Plenio, *J. Organomet. Chem.* 1993, **460**, 191.
12. H. Sitzmann, P. Zhou and G. Wolmershäuser, *Chem. Ber.* 1994, **127**, 3.
13. H. G. Alt, J. S. Han and U. Thewalt, *J. Organomet. Chem.* 1993, **456**, 89.
14. N. J. Wells, J. C. Huffman and K. G. Caulton, *J. Organomet. Chem.* 1981, **213**, C17.
15. G. Erker, C. Sarter, M. Albrecht, S. Dehnicke, C. Krüger, E. Raabe, R. Schlund, R. Benn, A. Rufińska and R. Mynott, *J. Organomet. Chem.* 1990, **382**, 89.
16. G. Erker, *J. Organomet. Chem.* 1990, **400**, 185.
17. G. Erker, C. Sarter, S. Werner and C. Krüger, *J. Organomet. Chem.* 1989, **377**, C55.
18. G. Erker, J. Schamberger, A. A. H. van der Zeijden, S. Dehnicke, C. Krüger, R. Goddard and M. Nolte, *J. Organomet. Chem.* 1993, **459**, 107.
19. J. H. Wengrovius and R. R. Schrock, *J. Organomet. Chem.* 1981, **205**, 319.
20. M. D. Fryzuk, S. S. H. Mao, P. B. Duval and S. J. Rettig, *Polyhedron* 1995, **14**, 11.
21. A. W. Duff, P. B. Hitchcock, M. F. Lappert R. G. Taylor and J. A. Segal, *J. Organomet. Chem.* 1985, **293**, 271.
22. J. H. Wengrovius, R. R. Schrock and C. S. Day, *Inorg. Chem.* 1981, **20**, 1844.
23. G. H. Llinás, M. Mena, F. Palacios, P. Royo and R. Serrano, *J. Organomet. Chem.* 1988, **340**, 37.
24. A. Martín, M. Mena and F. Palacios, *J. Organomet. Chem.* 1994, **480**, C10.
25. C. H. Winter, X. X. Zhou, D. A. Dobbs and M. J. Heeg, *Organometallics* 1991, **10**, 210.
26. L. M. Engelhardt, R. I. Papasergio, C. L. Raston and A. H. White, *Organometallics* 1984, **3**, 18.
27. P. B. Hitchcock, M. F. Lappert and D. S. Liu, *J. Chem. Soc., Chem. Commun.* 1994, 1699.
28. P. B. Hitchcock, M. F. Lappert and D. S. Liu, *J. Chem. Soc., Chem. Commun.* 1994, 2637.
29. L. A. Nekhaeva, G. N. Bondarenko, S. V. Rykov, A. I. Nekhaev, B. A. Krentsel, V. P. Mar'in, L. I. Vyshinskaya, L. M. Khrapova, A. V. Polonskii and N. N. Korneev, *J. Organomet. Chem.* 1991, **406**, 139.
30. I. F. Urazowski, V. I. Ponomaryev, I. F. Nifant'ev and D. A. Lemenovskii, *J. Organomet. Chem.* 1989, **368**, 287.
31. U. Böhme, K.-H. Thiele and A. Rufinska, *Z. Anorg. Allg. Chem.* 1994, **620**, 1455.
32. B. G. Sayer, N. Hao, G. Dénès, D. G. Bickley and M. J. McGlinchey, *Inorg. Chim. Acta* 1981, **48**, 53.
33. K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton and G. V. Rees, *Acta Cryst.* 1974, **B30**, 2290.
34. N. Walker and D. Stuart, *Acta Cryst.* 1983, **A39**, 158.
35. G. M. Sheldrick, in *Crystallographic Computing* 3 (Edited by G. M. Sheldrick, C. Krüger and R. Goddard), pp. 175–189. Oxford University Press (1985).