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Preparation of new zirconium benzamidinates: alkyl derivatives and low-valent chemistry yielding metallacycles *via* coupling of alkynes and ethylene †

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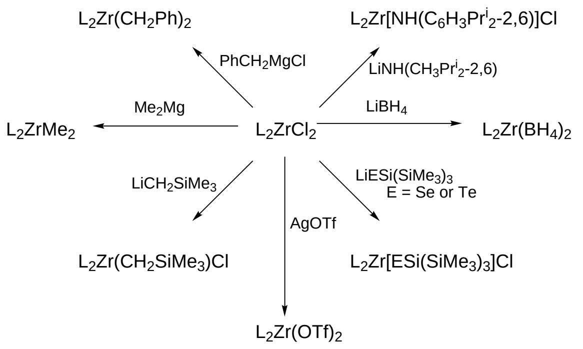
A wide range of new zirconium(IV) derivatives utilizing the *N,N′*-bis(trimethylsilyl)benzamidinato ligand are reported. The previously reported dichloride, L_2ZrCl_2 [L = $PhC(NSiMe_3)_2$], reacted cleanly with 1 equivalent of Me_2Mg in Et_2O to give L_2ZrMe_2 which was isolated as colorless crystals from CH_2Cl_2 or Et_2O. Attempting to prepare the methyl chloride derivative using 0.5 equivalent of Me_2Mg yielded mixtures of dichloride, dimethyl and methyl chloride derivatives. The compound L_2ZrCl_2 reacted cleanly with 1 equivalent of the bulkier alkyl $LiCH_2SiMe_3$ giving $L_2Zr(CH_2SiMe_3)Cl$. Reactivity of methyl derivatives with a variety of small molecules (CO, CO_2 or acetone) is reported. The dimethyl compound, L_2ZrMe_2, reacted cleanly with $B(C_6F_5)_3$ to form the methyltriarylborate complex $L_2Zr[MeB(C_6F_5)_3]Me$ which is moderately active towards ethylene polymerization. Additionally, several other derivatives are conveniently prepared by salt-metathesis reactions with the dichloride including: $L_2Zr(CH_2Ph)_2$, $L_2Zr(OSO_2CF_3)_2$, $L_2Zr[NH(C_6H_3Pr^i_2\text{-}2,6)]Cl$, $L_2Zr(BH_4)_2$, $L_2Zr[ESi(SiMe_3)_3]Cl$ (E = Se or Te). The 1% Na–Hg amalgam reduction of L_2ZrCl_2 in the presence of diphenylacetylene or trimethylsilylacetylene yielded orange zirconacyclopentadienes $L_2Zr(C_4Ph_4)$ and $L_2Zr[C_4H_2(SiMe_3)_2\text{-}2,4]$ in moderate yields. The compound $L_2Zr(C_4Ph_4)$ reacted readily with CO to give the dark red η^2-cyclopentadienone $L_2Zr[\eta^2\text{-}C(O)C_4Ph_4]$. Analogous to the formation of the zirconacyclopentadienes, reduction in the presence of ethylene gave the zirconacyclopentane, $L_2Zr(C_4H_8)$, in good yield. When the reduction is carried out in the absence of any trapping ligands, however, a benzamidinate ligand is oxidatively cleaved and the dimeric imido-iminoacyl compound, $[LZr(\eta^2\text{-}PhCNSiMe_3)(\mu\text{-}NSiMe_3)]_2$, is isolated as orange crystals in moderate yield. Single-crystal X-ray diffraction data are reported for L_2ZrCl_2, L_2ZrMe_2 and $L_2Zr(C_4H_8)$.

Recently, there has been growing interest in the use of N-donor ligands as Cp ($Cp = \eta\text{-}C_5H_5$) alternatives for early-transition-metal chemistry.[1] Driving much of this research is the tremendous success that metallocenes have enjoyed in important reactions including olefin polymerization, heterocycle formation and organic transformations.[2–4] A number of workers have explored the use of bulky amido,[5–9] porphyrin,[10] N_4-macrocycles,[11–15] and other ligands with much success. We were attracted to the *N,N′*-bis(trimethylsilyl)benzamidinate ligand due to its ease of preparation and derivatization and its proven synthetic utility for transition metal, main group and f-block element derivatives throughout the periodic table.[16–18] We[19] and others[20–22] have published results on a variety of zirconium amidinates; much of the interest has been in their ability to support electrophilic, olefin polymerization catalysts. Sterically, the bis(trimethylsilyl)benzamidinate ligand appears to be intermediate to Cp and Cp* ($Cp^* = \eta\text{-}C_5Me_5$) ligands, although the shape of the ligand sphere is quite different.[23] Electronically, the hard three-electron donor ligands are expected to generate a highly Lewis-acidic metal. Indeed, reactivity differences between bis(amidinate) and bis(cyclopentadienyl) systems have been attributed[23] to the highly polarized nature of the metal–nitrogen bonds leading to increased metal ionicity. In this paper, we report the full experimental details of a range of new Zr derivatives and their reaction chemistry, as well as details of some previously communicated work.[19]

Results and Discussion

Salt-metathesis reactions of L_2ZrCl_2



Scheme 1 L = $PhC(NSiMe_3)_2$, OTf = OSO_2CF_3

As shown in Scheme 1, L_2ZrCl_2[24] has proven to be an excellent starting material for the preparation of a wide range of derivatives *via* salt metathesis. Dimethyl and dibenzyl derivatives were easily prepared by the addition of Me_2Mg or $PhCH_2MgCl$ solutions to the dichloride in Et_2O. Typical isolated yields following work-up and crystallization were over 80%. Similarly, Rausch and co-workers[21] have recently reported preparing the dimethyl compound from L_2ZrCl_2 and MeLi. The compound L_2ZrMe_2 is a high melting, colorless crystalline solid that displays no sign of decomposition after 1 year in a N_2-filled drybox. The yellow dibenzyl derivative is likewise thermally stable. In contrast to the titanium system, attempts to prepare the methyl chloride derivative, $L_2Zr(Me)Cl$, by the addition of 0.5 equivalent of Me_2Mg to an homogeneous tetrahydrofuran (thf) solution of L_2ZrCl_2 gave a mixture of dimethyl, methyl chloride and dichloride derivatives (12, 73 and 15% respectively; based on ^1H NMR analysis of the crude solution). Purification by crystallization from Et_2O proved impossible due to co-crystallization of the three species. While $Cp_2Zr(Me)Cl$ is commonly prepared[25,26] by heating an equimolar mixture of Cp_2ZrMe_2 and Cp_2ZrCl_2 in toluene, only *ca.* 15% conversion to $L_2Zr(Me)Cl$ was observed upon heating a $[^2H_8]$toluene solution

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† Dedicated to the memory of Professor Sir Geoffrey Wilkinson, FRS.

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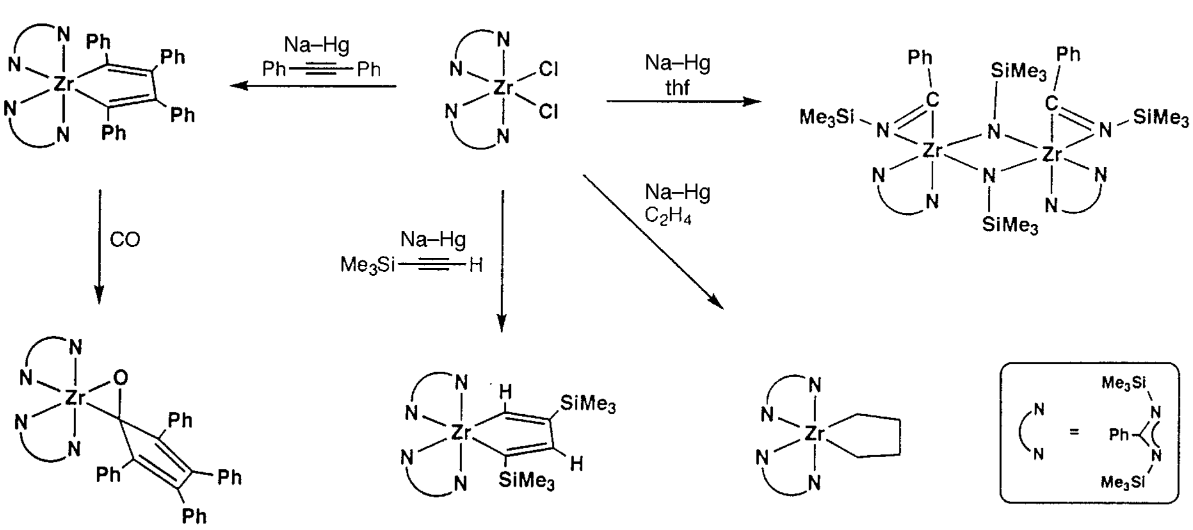

Scheme 2

of the dimethyl and dichloride compounds to 130 °C for 3 d. Further heating only resulted in slow decomposition of the dimethyl. Additional attempts using milder reagents (Me_2Zn or Me_3Al) led to no reaction with the dichloride. Although pure $L_2Zr(Me)Cl$ could not be obtained, samples of *ca.* 90% purity could be obtained by the thermolysis of L_2ZrMe_2 in CCl_4. Reaction progress was monitored periodically by ^1H NMR spectroscopy. After 17 h at 53 °C, a mixture with the composition 87% methyl chloride, 8% dimethyl and 5% dichloride was obtained. Attempts to use a stoichiometric amount of CCl_4 in C_6D_6 only led to 23% conversion to the methyl chloride after 7 d at 53 °C. With the use of a bulkier substituent, however, it was possible to prepare an alkyl chloride derivative. Reaction of 0.5 equivalent of $Mg(CH_2SiMe_3)_2$ with L_2ZrCl_2 in Et_2O followed by crystallization from hexamethyldisiloxane (HMDSO) yielded analytically pure crystals of $L_2Zr(CH_2SiMe_3)Cl$ in 52% yield.

[$^2H_6$]Benzene solutions of L_2ZrMe_2 were found to react cleanly and readily (<1 h) with O_2, CO_2 or acetone (1 equivalent) giving $L_2Zr(OMe)_2$, $L_2Zr(O_2CMe)Me$ and $L_2Zr(OCMe_3)Me$ respectively. Although $L_2Zr(OMe)_2$ did not react with additional equivalents of O_2, the acetate and alkoxide derivatives were found to react with excess CO_2 and acetone within 12 h giving complex mixtures of products. Unlike Cp_2ZrMe_2, which reacts with CO to cleanly form $Cp_2Zr[\eta^2\text{-}C(O)Me]Me$,[27,28] L_2ZrMe_2 rapidly gave forest green solutions from which we were unable to characterize any products. When CO was reacted with $L_2Zr(Me)Cl$ in C_6D_6, however, clean conversion to $L_2Zr[\eta^2\text{-}C(O)Me]Cl$ occurred within 12 h. The acyl functionality was characterized by $^{13}C\text{-}\{^1H\}$ NMR spectroscopy which revealed a downfield signal at δ 325 and by IR spectroscopy which showed the CO stretch at 1589 cm^{-1}. Insertion of acetone into the Zr–C bond of $L_2Zr(Me)Cl$ yielding $L_2Zr(OCMe_3)Cl$ proceeded similarly to that of the dimethyl, but required longer to go to completion.

Recently, several workers have utilized zirconium amidinates to support olefin polymerization catalysts.[20–22] Rausch and co-workers reported[21] reacting L_2ZrMe_2 with $Ph_3C[B(C_6F_5)_3]$ to presumably form a cationic zirconium alkyl, with the loss of Ph_3CMe. Surprisingly, this derivative was found to be inactive for ethylene polymerization, whereas the L_2ZrCl_2–methylaluminoxane (MAO) mixture displayed moderate activity. We found that L_2ZrMe_2 readily reacts with $B(C_6F_5)_3$, which has been shown by Marks and co-workers[29] to be an effective co-catalyst, in C_6D_6 to give a single product that displays spectroscopic data consistent with $L_2Zr[MeB(C_6F_5)_3]Me$. Similar to the aforementioned L_2ZrCl_2–MAO system, the 'cation-like' derivative readily polymerizes ethylene, with an activity of *ca.* 20 kg of polyethylene mol Zr per atm (atm = 101 325 Pa) per h, giving a polymer which melts just below 140 °C.§

Several other derivatives were prepared from L_2ZrCl_2 by salt-metathesis reactions. Reaction of the dichloride with AgOTf in thf gave $L_2Zr(OTf)_2$ in good yield. The solubility of the bis(triflate) in hexanes and the observation of a single signal in the ^{19}F NMR spectrum (in C_6D_6) are consistent with covalently bonded triflates. The compound L_2ZrCl_2 reacted cleanly with $LiBH_4$ in Et_2O giving $L_2Zr(BH_4)_2$ in 79% yield following hexanes work-up. Infrared spectroscopy reveals multiple bands attributable to B–H stretches a factor which complicates determination of hapticity. One major feature is a strong singlet at 2511 cm^{-1} assignable[30] to the B–H (terminal) stretch of an $\eta^3\text{-}BH_4$ ligand. The tetrahydroborate derivative is fairly unreactive compared to the zirconocene analogue,[31–33] failing to react with diphenylacetylene or CO in C_6D_6 at room temperature. Also, attempts to generate a terminal Zr hydride by the addition of Lewis bases (PMe_3, pyridine, Ph_3PO, Et_3N or 4-dimethylaminopyridine) failed to give any reaction. The selenolate and tellurolate derivatives, $L_2Zr[ESi(SiMe_3)_3]Cl$ (E = Se or Te), were prepared by the reaction of the dichloride with $(thf)_2LiESi(SiMe_3)_3$ in hexanes. Both are highly soluble in hydrocarbon solvents yet can be isolated from HMDSO in *ca.* 65% yield. By comparison to known zirconocene compounds,[34] the failure of $L_2Zr[ESi(SiMe_3)_3]Cl$ to react with a second equivalent of $(thf)_2LiESi(SiMe_3)_3$ is consistent with the qualitative view of the $PhC(NSiMe_3)_2$ ligand as being more sterically demanding than Cp.[35]

Reduction chemistry of L_2ZrCl_2

The reductive coupling of alkynes by generated 'Cp_2Zr' is well known and has proven to be a useful technique for the preparation of a wide range of dienes and heterocycles.[36–38] Our exploration of alkyne and ethylene coupling by reduced zirconium amidinates has likewise shown promising results. As shown in Scheme 2, reduction of L_2ZrCl_2 by 1% Na–Hg in thf in the presence of alkynes and ethylene yielded the expected zirconacyclopentadiene and zirconacyclopentane products. Reduction of the dichloride in the presence of 2 equivalents of diphenylacetylene, followed by hexanes work-up, gave $L_2Zr(C_4Ph_4)$ as orange crystals in 20% yield. When only 1 equivalent of the alkyne is used, the zirconacyclopentadiene is still formed along with $[LZr(\eta^2\text{-}PhCNSiMe_3)(\mu\text{-}$

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§ Full details of polymerization studies will be published separately. Preliminary studies were carried out in toluene in a Fischer–Porter apparatus under the following conditions: $T = 25$ °C, 4 atm ethylene, [catalyst] = 6.7 mM.

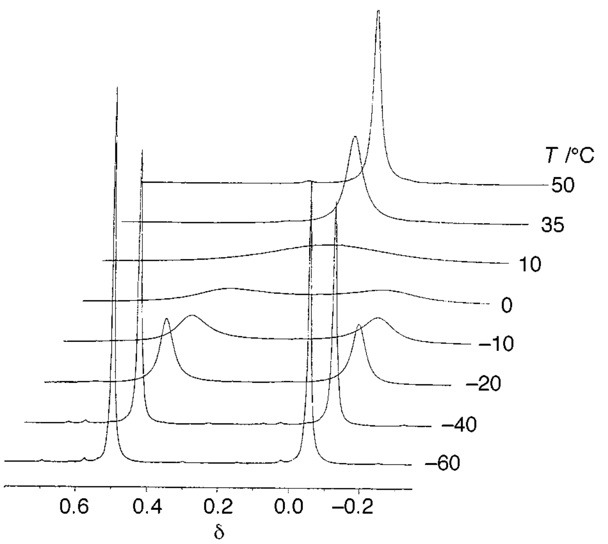

Fig. 1 Variable-temperature ^{1}H NMR spectra of $L_2Zr(C_4Ph_4)$ taken in C_6D_6 showing the $SiMe_3$ peaks

$NSiMe_3)]_2$ (see later) indicating that the zirconacyclopropene is not likely to be isolated. The zirconacyclopentadiene displays a broadened signal in the ^{1}H NMR (C_6D_6) spectrum for the trimethylsilyl group which at low temperature ($T_c = 10$ °C) splits into two signals of equal intensity (Fig. 1). The activation parameter for this fluxional process, which we attribute to being simple ligand rotation, is calculated to be 13(1) kcal mol^{-1} (cal = 4.184 J). When the asymmetric alkyne Me_3SiCCH was used, the 2,4 substituted zirconacyclopentadiene, $L_2Zr[C_4H_2(SiMe_3)_2\text{-}2,4]$, was isolated in 39% yield. No evidence for the formation of other regioisomers was found upon ^{1}H NMR analysis of the crude reaction solution. Hydrolysis of Zr–C bonds by the addition of several equivalents of H_2O to C_6D_6 solutions of $L_2Zr(C_4Ph_4)$ and $L_2Zr[C_4H_2(SiMe_3)_2\text{-}2,4]$ cleanly gave (1*E*, 3*E*)-1,2,3,4-tetraphenylbuta-1,3-diene and (1*E*)-1,3-bis(trimethylsilyl)buta-1,3-diene (along with an uncharacterized white precipitate). Reaction of $L_2Zr(C_4Ph_4)$ with CO in toluene occurs immediately (Scheme 2) forming the η^2-cyclopentadienone, $L_2Zr[\eta^2\text{-}C(O)C_4Ph_4]$, which was isolated in 61% yield. The dark red zirconacyclopentadienone was characterized analytically and displays a parent ion in the electron impact (EI) mass spectrum. Although indefinitely stable in C_6D_6, it was found to decompose rapidly in $CDCl_3$. Similar to its precursor zirconacyclopentadiene, $L_2Zr[\eta^2\text{-}C(O)C_4Ph_4]$ also displays a broadened signal in the ^{1}H NMR spectrum (C_6D_6) for the trimethylsilyl groups which decoalesce into two singlets of equal intensity ($T_c = -23$ °C) giving a calculated activation parameter [$\Delta G^\ddagger = 12(1)$ kcal mol^{-1}] which is slightly lower than that of the zirconacyclopentadiene.

Carrying out the reduction under ethylene (100 psi, 1 psi = 6894.76 Pa) gave the zirconacyclopentane product, $L_2Zr(C_4H_8)$, which was isolated as orange crystals from hexanes in 67% yield. This improved yield relative to the zirconacyclopentadienes is possibly due to a higher concentration of alkene (compared to alkyne) in solution or possibly just better crystallization properties. The compound $L_2Zr(C_4H_8)$ is remarkably stable, showing no decomposition (by ^{1}H NMR spectroscopy) after 1 year in a fluorescent-lit dry box. Unlike the hindered zirconacyclopentadienes, reactivity with CO (in C_6D_6) is messy, apparently forming multiple products.

Carrying out the Na–Hg reduction in the absence of trapping ligands afforded a new orange product which displayed four trimethylsilyl signals of equal intensity in the ^{1}H NMR spectrum (in C_6D_6). At elevated temperatures ($T_c = 75$ °C), two of the signals coalesced [$\Delta G^\ddagger = 17(1)$ kcal mol^{-1}] revealing a very sterically hindered metal center(s). Infrared spectroscopy revealed a stretch at 1518 cm^{-1} which is consistent with either a C–N or a C–C double bond, and X-ray crystallography showed the compound to be the dimeric imido-iminoacyl complex, $[LZr(\eta^2\text{-}PhCNSiMe_3)(\mu\text{-}NSiMe_3)]_2$, formed *via* the oxidative cleavage of an amidinate ligand. Details of the crystal structure have been communicated[19] and a line drawing is shown in Scheme 2. The metallacycle reactions imply that the reaction proceeds *via* a 'L_2Zr' intermediate which must undergo C–N cleavage of an amidinate ligand and dimerization to afford the isolated product. Attempts to trap intermediates formed after ligand cleavage (with phosphines, CO or thf) failed implying that ligand cleavage may occur after a bimetallic intermediate is formed. We have also recently reported similar ligand cleavage in a related Ti system.[39] Additionally, Cotton and co-workers have reported[40,41] C–N bond cleavages of formamidinate ligands by reduced Ti and Ta systems.

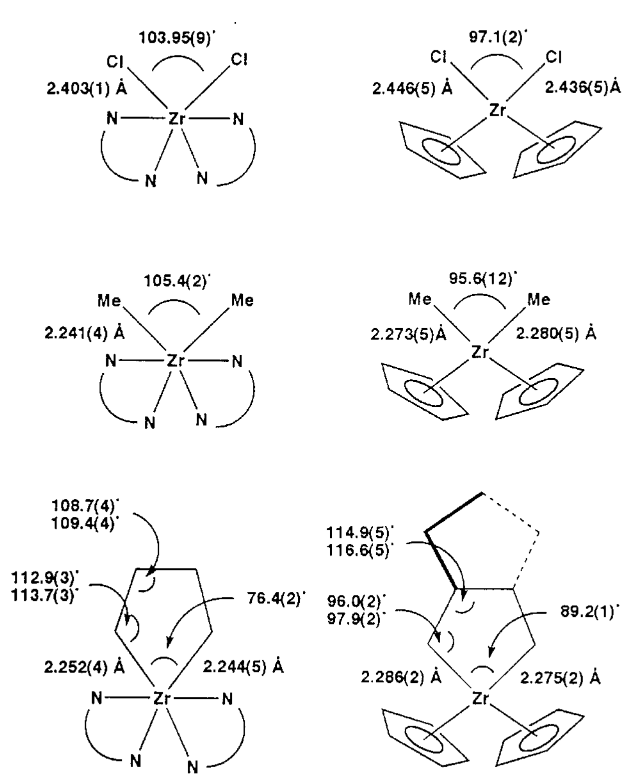

Fig. 2 Comparison of structural features of crystallographically characterized derivatives with related zirconocenes[42–44]

Crystal structure descriptions

Structural data and collection parameters can be found in Table 1. While this manuscript was in preparation, the structures of L_2ZrCl_2 and L_2ZrMe_2 were reported by Walther *et al.*,[20] so their descriptions will be appropriately brief. Comparisons will be made to the related zirconocene derivatives Cp_2ZrCl_2,[42] Cp_2ZrMe_2,[43] and $Cp_2Zr[C_5H_8(CH_2)_2\text{-}1,2]$[44] shown in Fig. 2.

L_2ZrCl_2. An ORTEP[45] view is shown in Fig. 3 with selected bond lengths and angles in Table 2. The solid-state structure contains a crystallographically imposed two-fold axis which splits the Cl–Zr–Cl angle. As expected, the amidinates are coordinated to the Zr center *cis* to one another. The Zr–N bond lengths are similar [2.251(4), 2.208(4) Å], with a slight elongation of the Zr–N bond *trans* to N. The Zr–Cl bond length of 2.403(1) Å is relatively short compared to those in Cp_2ZrCl_2[43] [2.436(5), 2.446(5) Å] perhaps reflecting the ionic bonding of the amidinate ligands relative to the soft Cp ligands. The broad Cl–Zr–Cl angle [103.95(9)°] compared to that in Cp_2ZrCl_2 [97.1(2)°] implies a sterically unhindered Zr center in the solid state.

Table 1 Crystal data and collection parameters

	L_2ZrCl_2	L_2ZrMe_2	$L_2Zr(C_4H_8)$
Formula	$C_{26}H_{46}Cl_2N_4Si_4Zr$	$C_{28}H_{52}N_4Si_4Zr$	$C_{30}H_{54}N_4Si_4Zr$
M	689.15	648.31	674.35
Space group	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)	*P*2$_1$/*n* (no. 14)
T/°C	−105	−104	−160
a/Å	20.941(3)	21.416(6)	10.5075(1)
b/Å	9.2798(15)	9.312(2)	12.6696(1)
c/Å	17.867(3)	17.670(3)	28.2416(3)
U/Å^3	3453.3(17)	3506(2)	3706.33(7)
β/°	95.963(15)	95.77(2)	99.665(1)
Z	4	4	4
D/g cm^{-3}	1.28	1.23	1.208
Diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4	Siemens SMART
Radiation (λ/Å)	Mo-Kα (0.71 073)	Mo-Kα (0.71 073)	Mo-Kα (0.71 073)
Monochromator	Graphite	Graphite	Graphite
Detector	Crystal scintillation counter	Crystal scintillation counter	CCD area detector
Scan type, width	θ–2θ, $\Delta\theta = 0.70 + 0.35 \tan\theta$	θ–2θ, $\Delta\theta = 0.70 + 0.35 \tan\theta$	ω, 0.3°
Scan speed	5.49 (θ, ° min^{-1})	5.49 (θ, ° min^{-1})	30 s per frame
Reflections measured	$+h, +k, \pm l$	$+h, \pm k, \pm l$	Hemisphere
2θ range/°	3–45	3–45	3–46.5
μ/cm^{-1}	6.20	4.64	4.49
T_{min}, T_{max}	0.91, 1.35	0.94, 1.00	0.910, 0.997
Crystal dimensions/mm	0.17 × 0.28 × 0.35	0.30 × 0.40 × 0.40	0.20 × 0.15 × 0.15
Reflections measured	2420	4945	15 242
Unique reflections	2250	2278	5614
Observations ($I > 3\sigma$)	1897	1917	3752
Parameters	168	168	568
R	0.0443	0.0267	0.0376
R′	0.0537	0.0363	0.0405
S	2.397	1.501	1.51

Table 2 Selected bond lengths (Å) and angles (°) for L_2ZrCl_2

Zr–Cl	2.403(1)	N(2)–Si(2)	1.763(4)
Zr–N(1)	2.208(4)	N(1)–C(1)	1.315(6)
Zr–N(2)	2.251(4)	N(2)–C(1)	1.326(6)
N(1)–Si(1)	1.765(4)	C(1)–C(2)	1.518(7)
Cl–Zr–Cl	103.95(9)	N(1)–Zr–N(1′)	90.5(2)
N(1)–Zr–Cl	91.22(10)	N(1)–Zr–N(2′)	111.54(14)
N(1)–Zr–Cl′	147.82(11)	N(2)–Zr–N(2′)	169.9(2)
N(1)–Zr–N(2)	60.58(14)		

Table 3 Selected bond lengths (Å) and angles (°) for L_2ZrMe_2

Zr–C(1)	2.241(4)	N(2)–Si(2)	1.744(2)
Zr–N(1)	2.319(2)	N(1)–C(2)	1.320(4)
Zr–N(2)	2.237(2)	N(2)–C(2)	1.340(4)
N(1)–Si(1)	1.752(2)	C(2)–C(3)	1.507(4)
C(1)–Zr–C(1)	105.36(22)	N(1)–Zr–N(1′)	176.15(13)
N(1)–Zr–C(1)	96.33(11)	N(1)–Zr–N(2′)	117.57(9)
N(1)–Zr–C(1′)	87.71(11)	N(2)–Zr–N(2′)	92.84(13)
N(1)–Zr–N(2)	59.39(9)		

L_2ZrMe_2. An ORTEP view is shown in Fig. 4 with selected bond lengths and angles in Table 3. Like the dichloride, the isomorphous dimethyl contains a crystallographically imposed two-fold axis splitting the Me–Zr–Me angle. The Zr–N bond lengths [2.319(2), 2.237(2) Å] show an elongation of the Zr–N bond *trans* to N. Sharing the trends observed for the dichloride, the Zr–Me bond length of 2.241(4) Å is short compared to those in Cp_2ZrMe_2[44] (2.273, 2.280 Å), and the Me–Zr–Me bond angle of 105.4(2)° is large relative to that of Cp_2ZrMe_2 (95.6°).

$L_2Zr(C_4H_8)$. The ORTEP views are shown in Figs. 5 and 6 with selected bond lengths and angles in Table 4. Geometry at the Zr center is pseudo-octahedral, with the amidinate ligands bonded *cis* in typical fashion. The Zr–N bond lengths [2.215(3), 2.317(3), 2.250(3), 2.315(3) Å] display the same *trans* influence observed in the aforementioned dichloride and dimethyl struc-

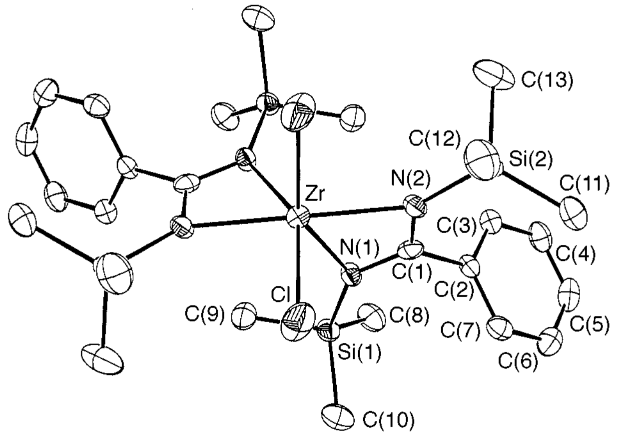

Fig. 3 An ORTEP view of L_2ZrCl_2 down the C_2 axis drawn with 50% thermal ellipsoids. Hydrogens omitted for clarity

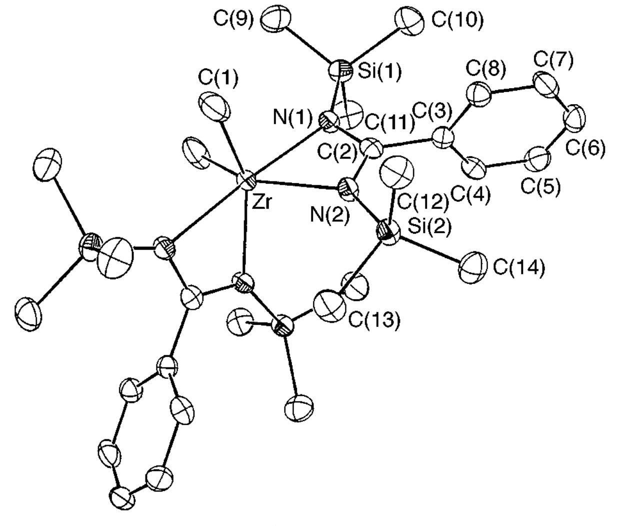

Fig. 4 An ORTEP view of L_2ZrMe_2 drawn with 50% thermal ellipsoids. Hydrogens omitted for clarity

Table 4 Selected bond lengths (Å) and angles (°) for $L_2Zr(\eta^2-C_4H_8)$

Zr–N(1)	2.215(3)	C(3)–C(4)	1.525(6)
Zr–N(2)	2.317(3)	C(1)–H(1)	1.09(4)
Zr–N(3)	2.250(3)	C(1)–H(2)	0.95(4)
Zr–N(4)	2.315(3)	C(2)–H(3)	0.97(4)
Zr–C(1)	2.252(4)	C(2)–H(4)	0.94(4)
Zr–C(4)	2.244(5)	C(3)–H(5)	0.93(4)
Zr–H(2)	2.41(4)	C(3)–H(6)	1.03(4)
Zr–H(7)	2.48(4)	C(4)–H(7)	0.96(4)
C(1)–C(2)	1.526(7)	C(4)–H(8)	0.96(4)
C(2)–C(3)	1.528(7)		
N(1)–Zr–N(2)	60.1(1)	N(3)–Zr–C(4)	100.0(2)
N(1)–Zr–N(3)	102.4(1)	N(4)–Zr–C(1)	94.9(1)
N(1)–Zr–N(4)	111.6(1)	N(4)–Zr–C(4)	103.0(1)
N(1)–Zr–C(1)	94.3(1)	C(1)–Zr–C(4)	76.4(2)
N(1)–Zr–C(4)	144.8(2)	Zr–C(1)–H(2)	88(3)
N(2)–Zr–N(3)	102.4(1)	Zr–C(4)–H(7)	93(2)
N(2)–Zr–N(4)	159.8(1)	Zr–C(1)–C(2)	113.7(3)
N(2)–Zr–C(1)	103.8(1)	Zr–C(4)–C(3)	112.9(3)
N(2)–Zr–C(4)	88.9(1)	C(1)–C(2)–C(3)	109.4(4)
N(3)–Zr–N(4)	59.9(1)	C(2)–C(3)–C(4)	108.7(4)
N(3)–Zr–C(1)	153.4(1)		

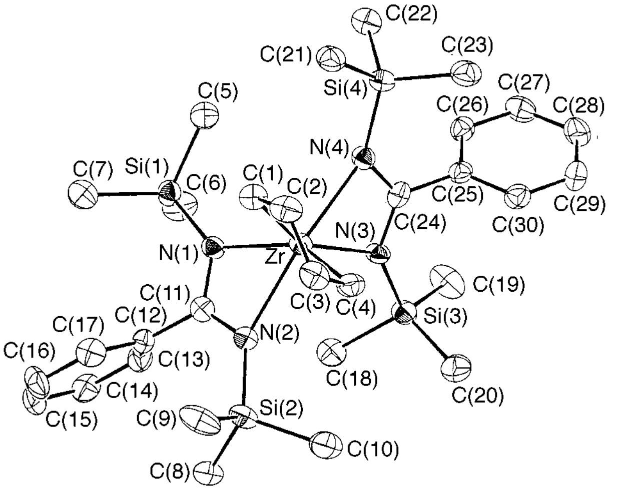

Fig. 5 An ORTEP view of $L_2Zr(C_4H_8)$ drawn with 50% thermal ellipsoids. Hydrogens omitted for clarity

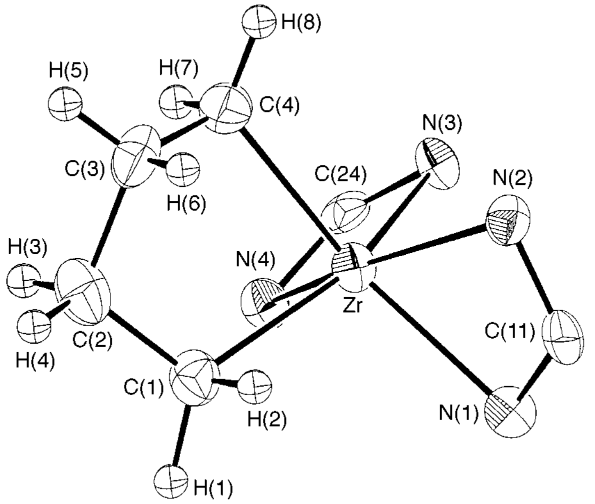

Fig. 6 An ORTEP view of the core of $L_2Zr(C_4H_8)$ drawn with 50% thermal ellipsoids

tures. The zirconacyclopentane moiety is twisted. The Zr–C bond distances [2.252(4), 2.244(5) Å] are virtually identical to that of the dimethyl derivative [2.241(4) Å] but are shorter than those of $Cp_2Zr[C_5H_8(CH_2)_2-1,2]$[44] [2.275(2), 2.286(2) Å]. The C–Zr–C angle of 76.4(2)° is exceptionally acute relative to that of the dimethyl [105.4(2)°] and compared to the related parameter of $Cp_2Zr[C_5H_8(CH_2)_2-1,2]$ [89.2(1)°]. The high quality of the data set allowed for the location of the metallacycle hydrogens in a Fourier-difference map and their subsequent isotropic refinement. This revealed close contacts between Zr–H(2) and Zr–H(7) at distances of 2.41(4) and 2.48(4) Å respectively. In addition, the acute Zr–C(1)–H(2) and Zr–C(4)–H(7) angles of 88(3) and 93(2)° respectively lend additional support to the presence of agostic interactions with the formally 12-electron metal center.[46]

Experimental

General considerations

Standard Schlenk-line and glove box techniques were used throughout the preparative procedures. Tetrahydrofuran, diethyl ether, hexamethyldisiloxane and hexanes were distilled from sodium–benzophenone under nitrogen. Dichloromethane was distilled from CaH_2 under nitrogen; $CDCl_3$ was predried over 4 Å molecular sieves, degassed with three freeze–pump–thaw cycles, and vacuum transferred from CaH_2; C_6D_6 and [$^2H_8$]toluene were predried over 4 Å molecular sieves, degassed with three freeze–pump–thaw cycles, and vacuum transferred from sodium–benzophenone; CO, CO_2 (bone dry) and H_2 were used directly from gas cylinders without purification. The dichloride L_2ZrCl_2 was prepared by reaction of $ZrCl_4(thf)_2$ with (tmen)Li[PhC(NSiMe$_3$)$_2$] (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) in thf following a procedure similar to that reported for the Ti analogue.[47] The compounds Me_2Mg,[48,49] $(thf)_2LiSeSi(SiMe_3)_3$,[50] $(thf)_2LiTeSi(SiMe_3)_3$[50] and $B(C_6F_5)_3$[51,52] were prepared according to literature procedures. The compound $LiCH_2SiMe_3$ was prepared by the addition of Me_3SiCH_2Cl to a Li dispersion in Et_2O. Methyllithium (halide free) and $PhCH_2MgCl$ solutions were used as purchased from Aldrich. Lithium tetrahydroborate and AgOTf were purchased from Strem and used as received. The compound $LiNHC_6H_3Pr^i{}_2$-2,6 was prepared by addition of the primary amine to *n*-butyllithium in hexanes–diethyl ether. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. Proton and $^{13}C-\{^1H\}$ NMR spectra were recorded at ambient temperatures. Chemical shifts (δ) are given relative to residual protium in the deuteriated solvent at δ 7.24, 7.15, 2.09 for $CDCl_3$, C_6D_6 and [$^2H_8$]toluene (methyl) respectively. Selenium-77 spectra were indirectly referenced to Me_2Se at δ 0 by direct reference to KSeCN in ethanol at δ −322. Fluorine-19 spectra were referenced to $PhCF_3$ at δ 0.0. Infrared samples were prepared as Nujol mulls and spectra taken using KBr plates. Elemental analyses and mass spectral data were determined within the College of Chemistry, University of California, Berkeley. Single crystal X-ray structure determination was performed at CHEXRAY, University of California, Berkeley.

L_2ZrMe_2

A diethyl ether solution of Me_2Mg (42.7 cm^3, 14.5 mmol) was added dropwise to L_2ZrCl_2 (10.0 g, 14.5 mmol) in diethyl ether (200 cm^3) forming a cloudy, light beige solution. After stirring overnight, the ether was removed under reduced pressure affording a light beige solid. The solid was extracted with CH_2Cl_2 (150 cm^3) and filtered through a Celite pad on a fritted disc. Concentration to 100 cm^3 followed by cooling to −40 °C gave the product as analytically pure, colorless crystals (7.7 g, 82%). M.p. 190–201 °C. ^1H NMR (C_6D_6, 300 MHz): δ 7.22–7.17 (m, 4 H), 7.03–6.97 (m, 6 H), 1.02 (s 6 H), 0.12 (s, 36 H). $^{13}C-\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 184.4, 140.9, 128.8, 126.2, 44.8, 2.2. IR (KBr): 1391s, 1261m, 1247m, 1167w, 1113w, 980m, 920w, 841s, 787m, 759m, 720m, 702m, 494m cm^{-1} (Found: C, 51.76; H, 7.77; N, 8.87. Calc. for $C_{28}H_{52}N_4Si_4Zr$: C, 51.87; H, 8.08; H, 8.64%).

Reaction of L_2ZrCl_2 with Me_2Mg

Tetrahydrofuran (30 cm^3) was added to L_2ZrCl_2 (0.50 g, 0.72 mmol) forming a clear, colorless solution. A diethyl ether solution of Me_2Mg (1.5 cm^3, 0.36 mmol) was added dropwise over 15 min. After stirring overnight, the volatile materials were removed under reduced pressure producing a white solid. The solid was extracted with CH_2Cl_2 (20 cm^3) and filtered. Removal of the CH_2Cl_2 under reduced pressure produced a white solid which was found to be composed of 73% $L_2Zr(Me)Cl$, 15% L_2ZrCl_2 and 12% L_2ZrMe_2 by ^1H NMR spectroscopy. Attempts to isolate pure $L_2Zr(Me)Cl$ by crystallization have been unsuccessful. ^1H NMR (C_6D_6, 300 MHz): δ 7.2–7.1 (m, 6 H), 7.0–6.9 (m, 8 H), 1.31 [s, 3 H, $L_2Zr(Me)Cl$], 1.02 (s, 1 H, L_2ZrMe_2), 0.18 (s, 7 H, L_2ZrCl_2), 0.15 [s, 36 H, $L_2Zr(Me)Cl$], 0.12 (s, 6 H, L_2ZrMe_2).

Reaction of L_2ZrMe_2 with CCl_4

A solution of L_2ZrMe_2 (2.00 g, 3.08 mmol) in CCl_4 (30 cm^3) was heated to 53 °C for 17 h. At this time, ^1H NMR analysis of the reaction mixture indicated a mixture with the composition 87% $L_2Zr(Me)Cl$, 8% L_2ZrMe_2 and 5% L_2ZrCl_2. The volatiles were removed under reduced pressure, and the residue crystallized from Et_2O. The resulting colorless crystals (1.6 g, 78%) had similar composition to the crude solution and were used in subsequent reaction studies.

Reaction of L_2ZrMe_2 with $B(C_6F_5)_3$

[$^2H_6$]Benzene was added to L_2ZrMe_2 (2.4 mg, 3.7 μmol) and $B(C_6F_5)_3$ (1.9 mg, 3.7 μmol) forming a clear colorless solution. Within 30 min, a single product {$L_2Zr[MeB(C_6F_5)_3]Me$} had formed. ^1H NMR (C_6D_6, 400 MHz): δ 7.1–7.0 (m, 4 H), 7.0–6.8 (m, 6 H), 2.06 (br, 3 H), 1.07 (s, 3 H), −0.15 (s, 36 H). ^{19}F NMR (C_6D_6, 57.2 MHz): δ −132.0 (d, $J = 23$, 6 F), −160.9 (t, $J = 21$, 3 F), −165.1 (t, $J = 19$ Hz, 6 F).

$L_2Zr(CH_2SiMe_3)Cl$

Diethyl ether (40 cm^3) was added to L_2ZrCl_2 (2.00 g, 2.90 mmol) and $Mg(CH_2SiMe_3)_2$ (0.303 g, 1.52 mmol) forming a cloudy colorless solution. After stirring overnight, the volatile materials were removed under reduced pressure affording an oily residue. The residue was extracted with hexanes (50 cm^3) and filtered through a pad of Celite on a fritted disc. The hexanes were removed *in vacuo* and the white residue taken up in HMDSO. Concentration of this solution to 5 cm^3 followed by cooling to −40 °C afforded the analytically pure product as large colorless crystals (1.1 g, 52%). M.p. 105–108 °C. ^1H NMR (C_6D_6, 300 MHz): δ 7.33–7.28 (m, 4 H), 7.00–6.95 (m, 6 H), 1.52 (s, 2 H), 0.51 (s, 9 H), 0.17 (s, 36 H). ^{13}C-{^1H} NMR (C_6D_6, 75.5 MHz): δ 185.1, 140.1, 129.3, 126.4, 68.7, 3.9, 2.7. IR (KBr): 1400s (br), 1262m, 1248s, 1160w, 1074w, 1010w, 982s, 915m, 836s (br), 786m, 763m, 743m, 714m, 499m cm^{-1} (Found: C, 48.93; H, 7.67; N, 7.96. Calc. for $C_{30}H_{57}ClN_4Si_5Zr$: C, 48.63; H, 7.75; N, 7.56%).

$L_2Zr(CH_2Ph)_2$

To a colorless slurry of L_2ZrCl_2 (3.00 g, 4.35 mmol) and Et_2O (45 cm^3) was added an ether solution of $PhCH_2MgCl$ (5.00 cm^3, 8.71 mmol) forming a cloudy yellow solution. After stirring overnight, the volatiles were removed under reduced pressure and the yellow solid was extracted with CH_2Cl_2 (60 cm^3). The extract was filtered through a pad of Celite on a fritted disc and concentrated to 30 cm^3. Pentane (20 cm^3) was added and the solution was filtered again. Cooling to −40 °C yielded the product as yellow crystals (2.7 g, 78%). Recrystallization from hexanes gave analytically pure product. M.p. 200 °C (decomp.). ^1H NMR (C_6D_6, 300 MHz): δ 7.44 (d, $J = 8.1$, 4 H), 7.30 (t, $J = 7.4$ Hz, 4 H), 7.05–6.95 (m, 12 H), 2.85 (s, 4 H), 0.02 (s, 36 H). ^{13}C-{^1H} NMR (C_6D_6, 75.5 MHz): δ 187.4, 150.0, 140.5, 129.0, 128.8, 128.2, 127.6, 126.2, 121.2, 78.3, 2.8. IR (KBr): 1594m, 1391s, 1260 (sh), 1248m, 1203m, 1178w, 1075w, 1028w, 1006m, 982s, 920w, 837s (br), 787m, 765m, 743m, 714m, 699m, 552w, 529w, 501m cm^{-1} (Found: C, 59.93; H, 7.49; N, 6.96. Calc. for $C_{40}H_{60}N_4Si_4Zr$: C, 60.02; H, 7.55; H, 7.00%).

$L_2Zr[SeSi(SiMe_3)_3]Cl$

At −10 °C, hexanes (40 cm^3) were added to L_2ZrCl_2 (0.35 g, 0.50 mmol) and $(thf)_2LiSeSi(SiMe_3)_3$ (0.25 g, 0.53 mmol) forming a cloudy yellow solution. After stirring overnight at room temperature, the volatile materials were removed under reduced pressure affording a light yellow solid. Extraction of the solid with HMDSO (25 cm^3) followed by filtration gave a clear, yellow solution. Concentration of the solution to 10 cm^3 and cooling to −40 °C gave 0.21 g of product as small yellow crystals. A second crop (0.11 g) was isolated from the mother-liquor. Total yield: 0.32 g, 65%. M.p. 179–184 °C. ^1H NMR (C_6D_6, 300 MHz): δ 7.32–7.28 (m, 4 H), 7.01–6.96 (m, 6 H), 0.54 (s, 27 H), 0.23 (s, 36 H). ^{13}C-{^1H} NMR (C_6D_6, 75.5 MHz): δ 183.7, 140.3, 129.3, 128.2, 126.5, 2.9, 1.8. ^{77}Se NMR (C_6D_6, 57.2 MHz): δ −2.92. IR (KBr): 1378s (br), 1243m, 1002m, 979m, 841s (br), 765m, 706m, 494m cm^{-1} (Found: C, 43.05; H, 7.22; N, 6.01. Calc. for $C_{35}H_{73}ClN_4SeSi_8Zr$: C, 42.88; H, 7.51; N, 5.72%).

$L_2Zr[TeSi(SiMe_3)_3]Cl$

At −10 °C, toluene (40 cm^3) was added to $[PhC(NSiMe_3)_2]_2$-$ZrCl_2$ (0.50 g, 0.73 mmol) and $(thf)_2LiTeSi(SiMe_3)_3$ (0.38 g, 0.73 mmol) forming a cloudy yellow-orange solution. After warming to ambient temperature, the solution became dark orange. After stirring overnight, the volatile materials were removed under reduced pressure. Extraction with HMDSO (40 cm^3) followed by filtration gave a clear orange solution. Concentration of the solution to 5 cm^3 and cooling to −40 °C gave 0.10 g of product as orange crystals. A second crop (0.40 g) was isolated from the mother-liquor. Total yield: 0.50 g, 67%. M.p. 144–149 °C. ^1H NMR (C_6D_6, 300 MHz): δ 7.31–7.27 (m, 4 H), 6.99–6.94 (m, 6 H), 0.57 (s, 27 H), 0.22 (s, 36 H). ^{13}C-{^1H} NMR (C_6D_6, 75.5 MHz): δ 183.2, 140.0, 129.4, 128.3, 126.4, 3.0, 2.3. IR (KBr): 1378s (br), 1243m, 1008m, 979m, 838s (br), 761m, 709m, 626m cm^{-1} (Found: C, 41.22; H, 7.05; N, 5.73. Calc. for $C_{35}H_{73}ClN_4Si_8TcZr$: C, 40.86; H, 7.15; N, 5.45%).

$L_2Zr(NHC_6H_3Pr^i{}_2\text{-}2,6)Cl$

At −10 °C, toluene (110 cm^3) was added to L_2ZrCl_2 (2.00 g, 2.90 mmol) and $LiNHC_6H_3Pr^i{}_2$-2,6 (0.55 g, 3.0 mmol) forming a cloudy, dull yellow solution. The mixture was warmed to room temperature over 2 h. After stirring overnight, the toluene was removed under reduced pressure affording a light yellow solid. The solid was extracted with hexanes (75 cm^3) and filtered. Concentration of the clear yellow solution to 20 cm^3 followed by cooling to −40 °C produced 1.25 g of product as yellow crystals. A second crop (0.12 g) was isolated from the mother-liquor. Total yield: 1.37 g, 58%. Analytically pure crystals were obtained by recrystallization in hexanes. M.p. 197–200 °C. ^1H NMR (C_6D_6, 300 MHz): δ 7.37–7.31 (m, 4 H), 7.22 (d, $J = 7.6$, 2 H), 7.18 (s, 1 H), 7.07 (t, $J = 7.6$, 1 H), 7.01–6.96 (m, 6 H), 4.07 (br, 2 H), 1.52 (d, $J = 6.7$ Hz, 6 H), 0.11 (s, 36 H). ^{13}C-{^1H} NMR (C_6D_6, 75.5 MHz): δ 184.6, 140.3, 129.3, 128.2, 127.8, 126.7, 122.9, 28.6, 25.1, 2.5. IR (KBr): 1400s (br), 1248s, 1189s, 1161w, 1114w, 1075w, 1032w, 1009m, 984s, 927w, 843s (br), 788m, 762m, 742m, 716m, 499m cm^{-1} (Found: C, 54.96; H, 7.89; N, 8.60. Calc. for $C_{38}H_{64}ClN_5Si_4Zr$: C, 54.99; H, 7.77; N, 8.44%).

$L_2Zr(OTf)_2$

To a 100 cm^3 round-bottomed flask containing $[PhC(N\text{-}SiMe_3)_2]_2ZrCl_2$ (0.50 g, 0.73 mmol) and AgOTf (0.41 g, 1.6 mmol) was added thf (30 cm^3) forming a milky white slurry. After stirring overnight, the volatiles were removed under reduced pressure and the residue was extracted with Et_2O (40 cm^3). The extract was filtered through Celite on a fritted disc and concentrated to 10 cm^3. The addition of hexanes (10 cm^3) followed by concentration to 10 cm^3 and cooling to −40 °C yielded 0.24 g of product as large colorless crystals. A second crop of crystals yielded 0.17 g of product. Total yield: 0.41 g, 62%. M.p. 195–198 °C. ^1H NMR (C_6D_6, 300 MHz): δ 7.40 (br, 4 H), 7.00–6.86 (m, 6 H), 0.11 (s, 36 H). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 189.0, 138.0, 130.4, 128.2, 1.7. ^{19}F NMR (C_6D_6, 57.2 MHz): δ −13.7. IR (KBr): 1364s, 1255m, 1240m, 1201s, 1154m, 981s (br), 836s (br), 788w, 765m, 745w, 708w, 691w, 632m, 594w, 508m cm^{-1} (Found: C, 36.89; H, 5.02; N, 6.02. Calc. for $C_{28}H_{46}F_6N_4O_6S_2Si_4Zr$: C, 36.70; H, 5.06; N, 6.11%.

$L_2Zr(BH_4)_2$

Diethyl ether (50 cm^3) was added to a 100 cm^3 round-bottomed flask containing L_2ZrCl_2 (4.00 g, 5.80 mmol) and $LiBH_4$ (0.320 g, 14.5 mmol). After stirring overnight, the volatiles were removed under reduced pressure giving a white solid. The solid was extracted with warm hexanes (130 cm^3) and filtered through a pad of Celite on a fritted disc giving a clear colorless solution. Concentration to 90 cm^3 followed by cooling to −40 °C afforded analytically pure product as long colorless needles. Total yield from two crops: 3.0 g, 79%. M.p. 226–228 °C. ^1H NMR (C_6D_6, 400 MHz): δ 7.13–7.08 (m, 4 H), 6.98–6.82 (m, 6 H), 2.14 (br, 8 H), 0.10 (s, 36 H). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 183.9, 140.0, 129.2, 126.5, 2.5. IR (KBr): 2511m, 2441w, 2400w, 2362m, 2340w, 2199w (br), 2144m (br), 1249s, 1163w, 1116w, 1075w, 1031w, 1008m, 984s, 924w, 838s (br), 784w, 764m, 718m, 498m cm^{-1} (Found: C, 47.88; H, 8.33; N, 8.55. Calc. for $C_{26}H_{54}B_2N_4Si_4Zr$: C, 48.20; H, 8.40; N, 8.65%).

Reaction of L_2ZrMe_2 with O_2

A Teflon-capped NMR tube containing L_2ZrMe_2 (*ca.* 5 mg) and C_6D_6 was degassed by freeze–pump–thaw techniques then backfilled with O_2 (5 psi). Within 1.5 h, the reaction had reached completion with only a single product $[L_2Zr(OMe)_2]$ observed by ^1H NMR spectroscopy. ^1H NMR (C_6D_6, 400 MHz): δ 7.25–7.20 (m, 4 H), 7.05–7.00 (m, 6 H), 4.08 (s, 6 H), 0.13 (s, 36 H).

Reaction of L_2ZrMe_2 with CO_2

Reaction carried out similarly to that of L_2ZrMe_2 with O_2. The only differences are that 15 psi of CO_2 were used and the reaction time was 1 h. $L_2Zr(OAc)Me$, 100% by ^1H NMR. ^1H NMR (C_6D_6, 400 MHz): δ 7.32–7.25 (m, 4 H), 6.05–6.97 (m, 6 H), 1.98 (s, 3 H), 1.09 (s, 3 H), 0.16 (36 H). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 183.9, 140.7, 128.8, 138.1, 126.5, 124.7, 47.7, 23.5, 2.8. IR (CsI, neat): 2953m, 2898w, 1554m (br), 1498w, 1400s (br), 1247s, 1170w, 1124w, 1074w, 1032w, 985s, 945w, 920w, 839s (br), 761m, 721m, 702m, 610w, 496m cm^{-1}.

Reaction of L_2ZrMe_2 with acetone

To a toluene (20 cm^3) solution of L_2ZrMe_2 (0.71 g, 1.1 mmol) was added acetone (84 μl, 1.1 mmol). After 45 min, the volatiles were removed under reduced pressure producing the product $L_2Zr(OCMe_3)Me$ as a colorless oil that solidified upon standing overnight (0.61 g, 79%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.34–7.29 (m, 6 H), 7.21–7.16 (m, 4 H), 1.45 (s, 9 H), 0.19 (s, 3 H), −0.11 (s, 36 H). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 182.7, 141.6, 128.3, 128.0, 125.9, 77.8, 32.5, 32.1, 2.2.

Reaction of $L_2Zr(Me)Cl$ with acetone

A procedure similar to that for the reaction of L_2ZrMe_2 with acetone was followed excepting that the reaction was carried out overnight and 5 equivalents of acetone were added to $L_2Zr(Me)Cl$ giving the product $L_2Zr(OCMe_3)Cl$ in 75% yield. ^1H NMR (C_6D_6, 300 MHz): δ 7.28–7.20 (m, 4 H), 7.00–6.90 (m, 6 H), 1.57 (s, 9 H), 0.17 (s, 36 H). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 182.5, 140.8, 128.7, 128.0, 126.1, 79.4, 32.1, 2.2.

Reaction of $L'_2Zr(Me)Cl$ with CO [$L' = 4\text{-}MeC_6H_4C(NSiMe_3)_2$]

A C_6D_6 (*ca.* 0.5 cm^3) solution of $L'_2Zr(Me)Cl$ (*ca.* 5 mg) was transferred into a Teflon-capped NMR tube. The solution was freeze–pump–thawed and charged with CO (20 psi). After a few minutes, the solution became yellow and within 12 h, complete conversion to a single product $[L'_2Zr(\eta^2\text{-}C(O)Me)Cl]$ had occurred. ^1H NMR (C_6D_6, 300 MHz); δ 7.17 (d, $J = 8.4$, 4 H), 6.85 (d, $J = 7.8$ Hz, 4 H), 2.75 (s, 3 H), 1.99 (s, 6 H), 0.17 (s, 36 H). $^{13}C\text{-}\{^1H\}$ NMR (C_6D_6, 75.5 MHz): δ 325.3, 183.3, 138.8, 138.5, 128.9, 126.5, 33.1, 21.2, 2.5. IR (KBr, neat film): 3061w, 2954m, 2897w, 1589w, 1577w, 1499m, 1446s, 1393s (br), 1247s, 1167w, 1008 (sh), 984s, 920w, 838s (br), 762m, 703m, 496m cm^{-1}.

$L_2Zr(\eta^2\text{-}C_4Ph_4)$

To a 250 cm^3 round-bottomed flask containing L_2ZrCl_2 (2.50 g, 3.63 mmol), 1% Na–Hg amalgam (0.33 g Na, 15 mmol Na), and Ph_2C_2 (1.36 g, 7.62 mmol) was added thf (100 cm^3) cooled to −78 °C. The mixture was stirred at −10 °C for 4 h, then allowed to warm to ambient temperature. After stirring overnight, the volatile materials were removed under reduced pressure leaving an orange residue. This residue was extracted with hexanes (120 cm^3) and filtered, giving a clear orange solution. Concentration of the solution to 30 cm^3, warming to *ca.* 50 °C, and cooling to room temperature resulted in small orange crystals of the product forming within 2 h (0.70 g, 20%). M.p. 215–218 °C (decomp.). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.32–7.20 (m, 6 H), 7.11 (t, $J = 7.6$, 4 H), 6.94 (d, $J = 7.4$, 4 H), 6.89 (t, $J = 7.3$ Hz, 4 H), 6.82–6.70 (m, 12 H), −0.09 (br, 36 H). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 205.8, 189.0, 153.2, 149.5, 141.0, 139.9, 130.6, 128.9, 127.7, 127.6, 127.2, 126.4, 124.5, 122.7, 2.5 (br). EI mass spectrum: *m/z* (relative intensity) 973 (M^+, 36), 796 ($M^+ - Ph_2C_2$, 4), 647 (4), 616 (L_2Zr^+, 4), 382 (26), 305 (8), 249 (8), 180 (100), 165 (26), 146 (14). IR (KBr): 1588w, 1387s (br), 1248m, 1164w, 1075w, 1006w, 981m, 843s (br), 768m, 698m, 500m cm^{-1} (Found: C, 66.88; H, 6.96; N, 5.71. Calc. for $C_{54}H_{66}N_4Si_4Zr$: C, 66.54; H, 6.82; N, 5.75%).

$L_2Zr[\eta^2\text{-}C_4H_2(SiMe_3)_2\text{-}2,4]$

To a 100 cm^3 round-bottomed flask containing L_2ZrCl_2 (0.75 g, 1.1 mmol) and 1% Na–Hg amalgam (0.053 g Na, 2.3 mmol Na) was added thf (30 cm^3) and trimethylsilylacetylene (0.46 cm^3, 3.3 mmol) cooled to −50 °C. The mixture was stirred at −10 °C for 3 h, then allowed to warm to ambient temperature. After stirring overnight, the volatile materials were removed under reduced pressure. The oily residue was extracted with hexanes (40 cm^3) and filtered. The hexanes were removed under reduced pressure and the orange oil was taken up in HMDSO. Concentration of the solution to 5 cm^3 and cooling to −40 °C gave the product as an orange solid (0.32 g, 39%). Recrystallization from HMDSO gave analytically pure product. M.p. 115 °C (decomp.). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.94 (d, $J = 2.1$, 1

H), 8.49 (d, $J = 2.1$ Hz, 1 H), 7.36–7.30 (m, 6 H), 7.21–7.15 (m, 4 H), 0.14 (s, 9 H), 0.13 (s, 9 H), −0.16 (s, 36 H). ^{13}C-{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 213.9, 209.2, 185.4, 155.4, 150.6, 140.9, 128.5, 127.9, 125.9, 2.1, 0.9, −1.6. IR (KBr): 1410s (br), 1246s, 1168w, 1074w, 1031w, 1008w, 983s, 913m, 843s (br), 786m, 758m, 719m, 700m, 615w, 555w, 498m cm^{-1}.

$L_2Zr[\eta^2\text{-}C(O)C_4Ph_4]$

In a Schlenk tube, toluene (10 cm^3) was added to $L_2Zr(\eta^2\text{-}C_4Ph_4)$ (0.19 g, 0.20 mmol) forming a clear orange solution. The tube was briefly evacuated and then backfilled with CO (2 psi). Almost immediately, the solution became dark red. After 20 min, the volatiles were removed under reduced pressure, and to the oily residue was added pentane (15 cm^3) causing dark red microcrystals to form (0.12 g, 61%). M.p. 220–222 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.67 (d, $J = 7.0$, 4 H), 7.49 (d, $J = 7.0$, 4 H), 7.17 (t, $J = 7.7$, 4 H), 7.09 (t, $J = 7.5$ Hz, 4 H), 6.99 (m, 14 H), 0.05 (s, 36 H). ^{13}C-{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 185.4, 140.2, 139.0, 137.9, 132.5, 130.9, 129.6, 129.0, 127.5, 124.6, 120.4, 3.0. EI mass spectrum: m/z (relative intensity) 1001 (M^+, 12), 986 (10), 916 (13), 898 (100), 882 (13), 808 (10), 723 (10), 704 (10), 635 (10), 546 (10), 531 (25), 458 (80), 442 (15), 305 (22), 289 (15), 176 (20), 146 (20). IR (KBr): 1592m, 1248m, 1168w, 984m, 835s (br), 763m, 740m, 712m, 702m, 656w, 638w, 606w, 542w, 500m cm^{-1} (Found: C, 65.56; H, 6.82; N, 5.49. Calc. for $C_{55}H_{66}N_4OSi_4Zr$: C, 65.88; H, 6.63; N, 5.59%).

$L_2Zr(\eta^2\text{-}C_4H_8)$

Tetrahydrofuran (30 cm^3) cooled to −78 °C was added to L_2ZrCl_2 (2.00 g, 2.90 mmol) and 1% Na–Hg amalgam (0.267 g Na, 11.6 mmol Na) in a Fischer–Porter bottle. Immediately, ethene (100 psi) was added and the reaction mixture was slowly allowed to warm to ambient temperature while stirring rapidly. After stirring for 2 d, the volatiles were removed under reduced pressure and the orange-gray residue was extracted with hexanes (50 cm^3). Filtration followed by concentration to 4 cm^3 afforded the product as orange crystals overnight (1.3 g, 67%). Recrystallization from hexanes gave analytically pure product. M.p. 115 °C (decomp.). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.24–7.18 (m, 4 H), 7.03–6.97 (m, 6 H), 2.89 (qnt, $J = 3.4$ Hz, 4 H), 1.73 (m, 4 H), 0.11 (s, 36 H). ^{13}C-{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 185.9, 140.7, 128.8, 126.5, 73.3, 33.8, 2.5. IR (KBr): 1425s, 1399s, 1248s, 1167w, 1074w, 1031w, 1008w, 982s, 920w, 842s (br), 785w, 761m, 744w, 719m, 686w, 500m cm^{-1} (Found: C, 53.21; H, 8.12; N, 8.20. Calc. for $C_{30}H_{54}N_4Si_4Zr$: C, 53.43; H, 8.07; N, 8.31%).

$[LZr(\eta^2\text{-}PhCNSiMe_3)(\mu\text{-}NSiMe_3)]_2\cdot 0.5C_6H_4$

To a 100 cm^3 round-bottomed flask charged with L_2ZrCl_2 (1.00 g, 1.45 mmol) and 1% Na–Hg amalgam (0.13 g Na, 5.8 mmol Na) was added thf (45 cm^3) cooled to −78 °C. The mixture was stirred at −10 °C for 4 h, then allowed to warm to ambient temperature. After stirring overnight, the volatile materials were removed under reduced pressure leaving a brown residue. Extraction with hexanes (50 cm^3) followed by filtration gave a clear red-orange solution. Concentration of the solution to 5 cm^3 and cooling to −40 °C produced the product as small, orange crystals (0.23 g, 26%). M.p. 220–223 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.42 (d, $J = 7.7$, 4 H), 7.32–7.20 (m, 8 H), 7.18–7.07 (m, 4 H), 6.99 (t, $J = 7.4$ Hz, 4 H), 1.25 (m, hexane, 4 H), 0.86 (m, hexane, 3 H), 0.42 (s, 18 H), 0.18 (s, 18 H), 0.06 (s, 18 H), −0.48 (s, 18 H). ^{13}C-{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 279.5, 184.6, 141.7, 140.6, 129.6, 128.8, 128.3, 127.5, 127.4, 127.3, 126.3, 31.6 (hexane), 22.7 (hexane), 14.1 (hexane), 7.1, 4.2, 3.3, 2.7. IR (KBr): 1518m, 1440s (br), 1244s, 1004m, 989m, 884s, 842s (br), 752m, 722m, 690w, 604w, 584s, 507w, 486m cm^{-1} (Found: C, 51.20; H, 7.69; N, 8.65. Calc. for $C_{55}H_{99}N_8Si_8Zr_2$: C, 51.63; H, 7.80; N, 8.76%).

X-Ray crystallography

Table 1 lists a summary of crystallographic data for all structurally characterized compounds.

L_2ZrCl_2. Crystals suitable for X-ray diffraction studies were grown from Et_2O at −15 °C. A small crystal was mounted[53] on a glass fiber using Paratone-N hydrocarbon oil. The crystal was then transferred to an Enraf-Nonius CAD-4 diffractometer and centered in the beam. It was cooled to −105 °C by a nitrogen flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the sample position. Crystal quality was evaluated *via* measurement of intensities and inspection of peak scans. Automatic peak search and indexing procedures yielded a triclinic reduced primitive cell. Inspection of the Niggli values revealed a C-centered monoclinic cell. The final cell parameters and specific data collection parameters for this data set are given in Table 1.

The 2420 raw intensity data were converted to structure factor amplitudes and their estimated standard deviations (e.s.d.s) by correction for scan speed, background and Lorentz and polarization effects. Inspection of intensity standards revealed a reduction of 10% of the original intensity. The data were corrected for this decay. Inspection of the azimuthal scan data[¶] showed variations which did not agree from reflection to reflection, indicating possible orientation problems during collection of the azimuthal scans. An empirical correction was made to the data based on the combined differences of F_o and F_c following refinement of all atoms with isotropic thermal parameters ($T_{max} = 1.35$, $T_{min} = 0.91$, no θ dependence). Inspection of the systematic absences indicated possible space groups *Cc* and *C*2/*c*. The choice of the centric group was confirmed by the successful solution and refinement of the structure. Removal of the systematically absent data left 2250 unique data in the final data set.

The structure was solved by comparison to the isomorphous Ti structure and refined *via* standard least-squares and Fourier techniques. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.3 times the B_{eq} of the calculations, but not refined. The final residuals ($R = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}$, $S = \{[\Sigma w(|F_o| - |F_c|)^2]/(n_o - n_v)\}^{\frac{1}{2}}$, where n_o is the number of observations, n_v the number of variable parameters, and the weights w were given by: $w = 1/\sigma^2(F_o)$, $\sigma(F_o^2) = [\sigma_o^2(F_o^2) + (pF_o^2)^2]^{\frac{1}{2}}$, where $\sigma^2(F_o)$ is calculated as above from $\sigma(F_o)^2$ and where p is the factor used to lower the weight of intense reflections) for 168 variables refined against the 1897 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0443$, $R' = 0.0537$ and $S = 2.397$. The R value for all 2250 data was 0.0541.

The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_o|)^2$, where w is the weight of a given observation. The p factor, used to reduce the weight of intense reflections, was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used[54] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[55]

L_2ZrMe_2. Crystals suitable for X-ray diffractions studies were grown from Et_2O at −15 °C. Data collection was performed analogously to that for L_2ZrCl_2.

The 4945 raw intensity data were converted to structure factor amplitudes and their e.s.d.s by correction for scan speed, background and Lorentz and polarization effects. Inspection of

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[¶] Reflections used for azimuthal scans were located near χ = 90° and the intensities measured at 10° increments of rotation of the crystal about the diffraction vector.

intensity standards revealed negligible reduction in intensities (0.8%) over data collection. Inspection of the azimuthal scan data¶ showed a variation $I_{min}/I_{max} = 0.94$ for the average curve. An empirical correction based on the observed variation was applied to the data.

Inspection of the systematic absences indicated possible space groups *Cc* and *C*2/*c*. The choice of the centric group was confirmed by the successful solution and refinement of the structure. Removal of the systematically absent data left 2278 unique data in the final data set.

The structure was solved by comparison to the isomorphous Ti structure and refined *via* standard least-squares and Fourier techniques. Hydrogen atoms were assigned idealized locations and values of B_{iso} approximately 1.3 times the B_{eq} of the calculations, but not refined. The final residuals (as for L_2ZrCl_2) for 168 variables refined against the 1917 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0267$, $R' = 0.0363$ and $S = 1.501$. The *R* value for all 2278 data was 0.0333.

$L_2Zr(\eta^2\text{-}C_4H_8)$. Crystals suitable for X-ray diffraction studies were grown from hexanes at −40 °C. A large crystal was cut to appropriate size and mounted[53] on a glass capillary using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector,[56] centered in the beam, and cooled to −160 °C by nitrogen-flow low-temperature apparatus which had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrix and cell constants were determined by collection of 60 10-second frames, followed by spot integration and least-squares refinement. A hemisphere of data was collected using 0.3° ω scans at 30-seconds per frame. The raw data were integrated (XY spot spread = 1.60°; Z spot spread = 0.60°) and the unit cell parameters refined (7373 reflections with $I > 5\sigma$) using SAINT.[57] Data analysis and absorption correction ($T_{min} = 0.910$, $T_{max} = 0.997$) were performed using Siemens XPREP.[58] The unit-cell parameters indicated a primitive monoclinic cell and systematic absences indicated space group $P2_1/c$ (no. 14). The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied.

The 15 242 reflections measured were averaged ($R_{int} = 0.0578$) yielding 5614 unique reflections. The structure was solved and refined with the TEXSAN[59] software package using direct methods[60] and expanded using Fourier techniques.[61] All non-hydrogen atoms were refined anisotropically. Hydrogens were located in a Fourier-difference map and were refined isotropically. The final residuals (as for L_2ZrCl_2) for the 568 variables refined against the 3752 data for which $F^2 > 3\sigma(F^2)$ were $R = 0.0376$, $R' = 0.0405$ and $S = 1.51$. The quantity minimized by the least-squares program was $\Sigma w(|F_o| - |F_c|)^2$, where *w* is the weight of a given observation. The *p* factor was set to 0.03 throughout the refinement. The analytical forms of the scattering factor tables for the neutral atoms were used[54] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[55]

CCDC reference number 186/640.

Acknowledgements

We thank the Petroleum Research Fund, administered by the ACS, for funding and the Sloan Foundation for the award of a fellowship (to J. A.).

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Received 5th May 1997; *Paper* 7/03109B