DALTON
FULL PAPER

# Synthesis, structure and molecular dynamics of $\eta^2$-iminoacyl compounds [Cp(ArO)Zr($\eta^2$-Bu$^t$NCCH$_2$Ph)(CH$_2$Ph)] and [Cp(ArO)Zr($\eta^2$-Bu$^t$NCCH$_2$Ph)$_2$]

**Matthew G. Thorn, Jongtaik Lee, Phillip E. Fanwick and Ian P. Rothwell***

*Department of Chemistry, 1393 Brown Building, Purdue University, West Lafayette, IN 47907-1393, USA*

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The reaction of the substrate [CpZr(CH$_2$Ph)$_3$] with the ligands 2,3,5,6-tetraphenyl- **1**, 2-phenyl-4,6-di-*tert*-butyl- **2** or 2-(1-naphthyl)-4,6-di-*tert*-butyl-phenol **3** leads to the corresponding compounds [Cp(ArO)Zr(CH$_2$Ph)$_2$] **4**–**6**. Solution studies show that naphthyl rotation is slow on the NMR timescale at ambient temperatures within **6** leading to non-equivalent benzyl groups with diastereotopic methylene protons. The solid-state structure of **5** shows both benzyl ligands to be $\eta^1$-bound. Compounds **4**–**6** react with *tert*-butylisocyanide in hydrocarbon solvents to initially produce the mono(iminoacyl) derivatives [Cp(ArO)Zr($\eta^2$-Bu$^t$NCCH$_2$Ph)(CH$_2$Ph)] **7**–**9** followed by the bis(iminoacyl) products [Cp(ArO)Zr($\eta^2$-Bu$^t$NCCH$_2$Ph)$_2$] **10**–**12**. In the solution $^{13}$C NMR spectra of the iminoacyl derivatives the Zr–*C*N carbon atom resonates at $\delta$ 242–244 ppm (**7**–**9**) and $\delta$ 229–234 ppm (**10**–**12**) consistent with the $\eta^2$-C,N binding. This was confirmed in the solid state by X-ray diffraction studies of **8**, **11** and **12**. At ambient temperatures only one set of iminoacyl resonances are observed for **10** and **11**, indicating that both iminoacyl rotation and aryloxide rotation are facile. At lower temperatures the iminoacyl ligands in **11** become non-equivalent in the $^1$H NMR spectrum consistent with restricted rotation about the Zr–O–Ar bond. The iminoacyl ligands in the 2-(1-naphthyl) derivative **12** are non-equivalent in solution NMR spectra from −75 to +85 °C. The solution fluxionality of these molecules as determined by NMR studies is discussed in detail.

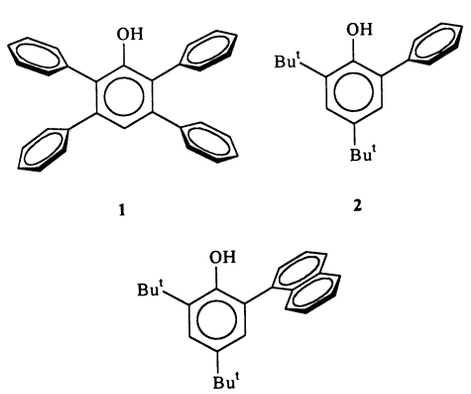
## Introduction

One major focus of our research over the last two decades has been to explore the chemistry of Group 4 metal organometallic compounds containing the bis(aryloxide) fragment [(ArO)$_2$M] (M = Ti, Zr, Hf).[1–3] This was stimulated by the burgeoning amount of exciting chemistry being developed for the corresponding metallocenes [Cp$_2$M][4] combined with the isolobal relationship between O donor ligands such as alkoxides, aryloxides and siloxides and the cyclopentadienyl unit.[5,6] With the correct choice of (typically bulky) aryloxide ligand it is possible to generate both novel and complimentary stoichiometric and catalytic reactivity supported by this metal fragment. Although a number of isostructural motifs are present for stoichiometrically related [Cp$_2$ML$_n$] and [(ArO)$_2$ML$_n$] compounds, the high electronegativity of the aryloxide oxygen combined with its more flexible donating capabilities often lead to stoichiometries (and reactivity) not found for the metallocenes.[7] An important example relates to the reaction of the substrates [Cp$_2$MR$_2$] and [(ArO)$_2$MR$_2$] (M = Ti, Zr, Hf) towards carbon monoxide and isoelectronic organic isocyanides.[8] The metallocene compounds readily form mono-insertion products, *e.g.* [Cp$_2$Ti($\eta^2$-MeCO)(Me)],[9] [Cp$_2$Zr(OAr)($\eta^2$-Bu$^t$NCCH$_2$Ph)][10] and [Cp$_2$Zr($\eta^2$-RCN-*p*-tol)] {R = CH(SiMe$_3$)$_2$}[11] which have a diverse reactivity.[12–15] Further carbonylation can occur but the products do not arise *via* bis(acyl) intermediates.[16] Carbonylation of the aryloxide compounds is complicated by the high reactivity of the ensuing acyl groups, *e.g.* facile acylation of pyridine.[17] However, insertion into both of the metal–alkyl bonds occurs with isocyanides to produce bis(iminoacyls).[18] Subsequent reactivity can include coupling of iminoacyl groups to produce ene-diamide ligands.[19] In the context of these differences we have investigated the reactivity of recently isolated mixed cyclopentadienyl, aryloxide compounds [Cp(ArO)-Zr(CH$_2$Ph)$_2$] towards organic isocyanides. The aryloxides were chosen to give insight into the solution fluxionality of the generated iminoacyl compounds.

## Results and discussion

### Synthesis, characterization and solution fluxionality of compounds

The aryloxide precursors 2,3,5,6-tetraphenyl- **1**,[20] 2-phenyl-4,6-di-*tert*-butyl- **2**,[21] and 2-(1-naphthyl)-4,6-di-*tert*-butyl-phenol **3** (Scheme 1),[22] have been applied to this study. Metallation resistant **1** contains a symmetrically substituted phenoxide nucleus whereas **2** contains non-equivalent *ortho*-substituents. The symmetry is broken down further with the 1-naphthyl ligand, **3**. Restricted rotation about the phenoxy–(1-naphthyl) bond leads




**1** **2**

**3(*dl*)**

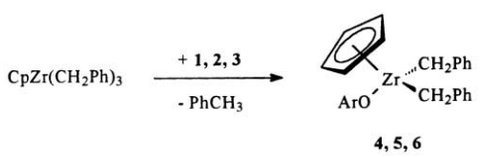
**Scheme 1**

 DOI: 10.1039/b202244n

**Table 1** Selected bond distances (Å) and angles (°) for [CpZr($OC_6H_2$-Ph-2-$Bu^t_2$-4,6)($CH_2Ph)_2$] (**5**)

| | | | |
|---|---|---|---|
| Zr–O(10) | 1.954(2) | Zr–C(30) | 2.262(3) |
| Zr–C(20) | 2.276(3) | Zr–Cp | 2.192(4) |
| Zr–O(10)–C(11) | 159.0(2) | C(20)–Zr–Cp | 110.6(1) |
| O(10)–Zr–C(20) | 106.29(9) | C(30)–Zr–Cp | 107.9(1) |
| O(10)–Zr–C(30) | 108.41(9) | Zr–C(20)–C(21) | 128.8(2) |
| O(10)–Zr–Cp | 115.2(1) | Zr–C(30)–C(31) | 97.4(2) |
| C(20)–Zr–C(30) | 108.3(1) | | |

to a chiral ligand. Previous work has shown that the barrier to this rotation is 18.0(5) kcal $mol^{-1}$ at 67 °C in 2,6-di(1-naphthyl)phenol (*meso–dl* exchange by NMR).[22] This barrier is higher in metal derivatives such as [CpTi($OC_6H_3Np_2$-2,6)$Me_2$] where the methyl groups appear as two sharp singlets at 90 °C in the $^1$H NMR spectrum.[23] The simple addition of these phenols (1 equiv.) to the precursor [$CpZr(CH_2Ph)_3$][24] in hydrocarbon solvents leads to the mono(aryloxides) **4**–**6** respectively (Scheme 2). The solution spectroscopic properties of **4**–**6** are interesting.




**Scheme 2**

All show a single set of Cp and aryloxide resonances in the $^1$H NMR spectrum. In compound **4** the benzyl ligands are equivalent, but diastereotopic methylene protons confirm the lack of a plane of symmetry through this group. A similar pattern is observed for **5** implying that restricted rotation about the Zr–O–Ar bond does not occur on the NMR timescale. In contrast the 1-naphthyl derivative **6** shows non-equivalent benzyl ligands in both the $^1$H (two AB patterns) and $^{13}$C NMR spectra. This clearly shows that restricted rotation about the phenoxy–naphthyl bond occurs on the NMR timescale. The solid-state structure of **5** (Fig. 1, Table 1) shows a three-legged piano stool

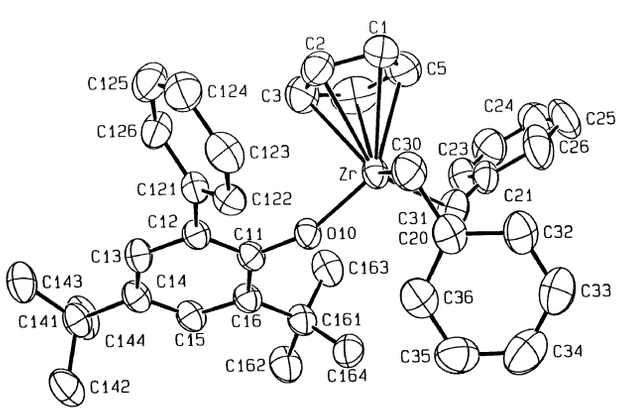



**Fig. 1** ORTEP[35] (50% thermal ellipsoids) view of [$CpZr(OC_6H_2$Ph-2-$Bu^t_2$-4,6)($CH_2Ph)_2$] (**5**).

geometry about the metal center. The aryloxide ligand is oriented so that the phenoxy wedge lies close to coplanar with the Cp group as shown in Scheme 2. Important parameters for the structurally characterized compounds are discussed in a later section.

Reaction of **4**–**6** with *tert*-butylisocyanide proceeds initially to produce mono-insertion products **7**–**9** followed by formation of bis(iminoacyl) derivatives **10**–**12** (Scheme 3). The mono-iminoacyl derivatives **7** and **8** contain a single set of Cp and aryloxide ligand signals. The diastereotopic benzyl protons appear as well resolved AB patterns with the iminoacyl $PhCH_2$

**Table 2** Selected bond distances (Å) and angles (°) for [$CpZr(OC_6H_2$-Ph-2-$Bu^t_2$-4,6)($\eta^2$-$Bu^tNCCH_2Ph$)($CH_2Ph$)] (**8**)

| Molecule 1 | | | |
|---|---|---|---|
| Zr(1)–O(110) | 2.009(5) | Zr(1)–C(18) | 2.186(8) |
| Zr(1)–N(17) | 2.213(7) | Zr(1)–C(19) | 2.319(8) |
| N(17)–C(18) | 1.259(9) | | |
| Zr(1)–O(110)–C(111) | 157.3(5) | N(17)–Zr(1)–C(19) | 91.0(3) |
| O(110)–Zr(1)–N(17) | 93.9(2) | C(18)–Zr(1)–C(19) | 106.2(3) |
| O(110)–Zr(1)–C(18) | 118.4(3) | Zr(1)–N(17)–C(18) | 72.2(5) |
| O(110)–Zr(1)–C(19) | 101.2(2) | N(17)–C(18)–Zr(1) | 74.6(5) |
| N(17)–Zr(1)–C(18) | 33.3(2) | Zr(1)–C(19)–C(191) | 122.2(5) |
| Molecule 2 | | | |
| Zr(2)–O(210) | 1.998(4) | Zr(2)–C(28) | 2.223(8) |
| Zr(2)–N(27) | 2.207(7) | Zr(2)–C(29) | 2.317(8) |
| N(27)–C(28) | 1.293(9) | | |
| Zr(2)–O(210)–C(211) | 158.5(5) | N(27)–Zr(2)–C(29) | 89.9(3) |
| O(210)–Zr(2)–N(27) | 94.2(2) | C(28)–Zr(2)–C(29) | 106.0(3) |
| O(210)–Zr(2)–C(28) | 119.1(3) | Zr(2)–N(27)–C(28) | 73.9(5) |
| O(210)–Zr(2)–C(29) | 100.5(2) | N(27)–C(28)–Zr(2) | 72.1(5) |
| N(27)–Zr(2)–C(28) | 34.0(2) | Zr(2)–C(29)–C(291) | 123.0(5) |

protons exhibiting a significantly larger $^2J$ coupling than the Zr–$CH_2$Ph protons. However, two diastereoisomers of **9** (restricted naphthyl rotation on the NMR timescale, Scheme 3) are clearly present in the solution spectra. Integration of the $C_5H_5$ resonances at $\delta$ 4.88 and 5.15 ppm show a 53/47 mixture of the two isomers in solution. Each isomer gives rise to two separate AB patterns for the benzyl methylene protons. In the solution $^{13}$C NMR spectra of the mono-iminoacyl derivatives **7**–**9** the Zr–*C*N carbon atom resonates at $\delta$ 242–244 ppm. Two well resolved resonances are observed for the two isomers of **9**. The chemical shift of these iminoacyl carbon atoms is consistent with an $\eta^2$-C,N binding of this function in solution,[8] as confirmed in the solid state by a single crystal diffraction study of **8** (Fig. 2, Table 2).

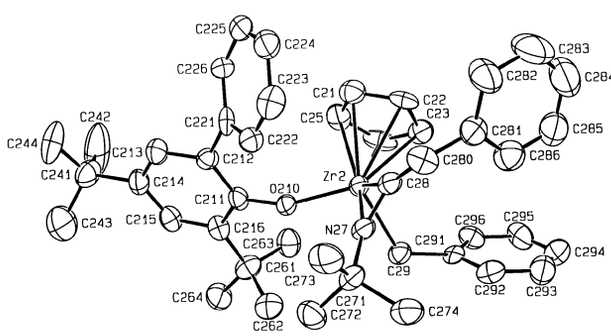
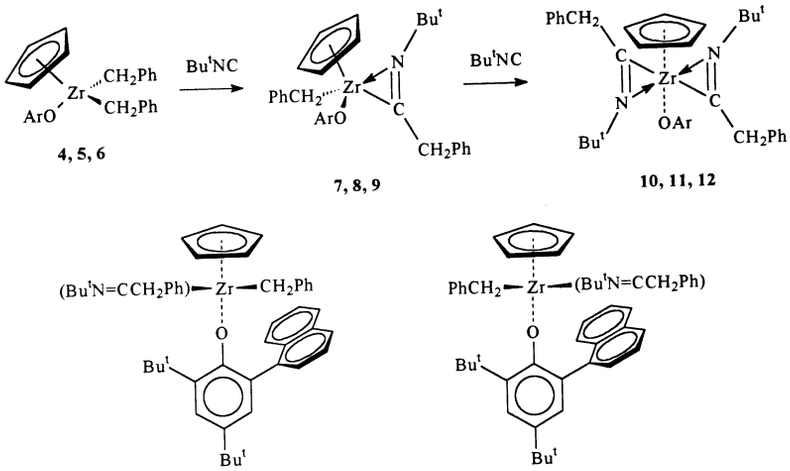



**Fig. 2** ORTEP (50% thermal ellipsoids) view of [$CpZr(OC_6H_2$Ph-2-$Bu^t_2$-4,6)($\eta^2$-$Bu^tNCCH_2Ph$)($CH_2Ph$)] (**8**) (molecule 2).

The spectroscopic properties of the bis-iminoacyl derivatives **10**–**12** are particularly interesting and in some aspects puzzling. In the solid state both **11** and **12** contain both iminoacyl groups $\eta^2$-C,N bound as shown (Fig. 3 and 4, Tables 3 and 4). The CN vectors of the iminoacyl groups are arranged in a head-to-tail fashion, one nitrogen atom is towards the aryloxide oxygen while the other is closer to the Cp group (as represented in Scheme 3). Again the aryloxide wedge lies approximately coplanar with the Cp ring. If this static structure were maintained in solution then one would predict non-equivalent iminoacyl groups for the symmetric 2,3,5,6-tetraphenylphenoxide complex **10**. In the $^1$H NMR spectrum of **10** at −55 °C in toluene-$d_8$ solution, a single, $Me_3$CNC$H_2$Ph singlet and $Me_3$CNC$H_2$Ph AB pattern show that the iminoacyl ligands are equivalent on the NMR timescale at this temperature (Fig. 5). The pattern remains essentially unchanged up to



Scheme 3

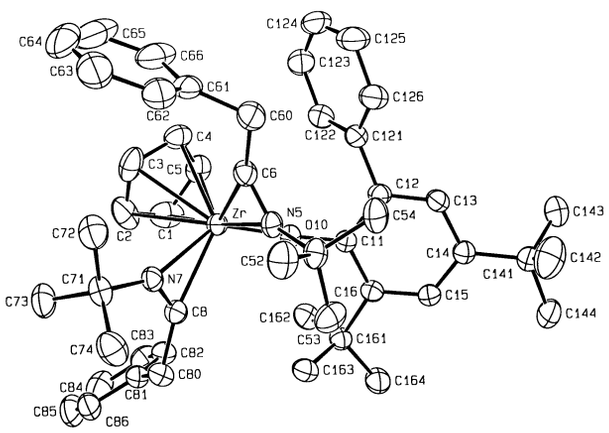


**Fig. 3** ORTEP (50% thermal ellipsoids) view of [CpZr($OC_6H_2$Ph-2-$Bu^t_2$-4,6)($\eta^2$-$Bu^tNCCH_2Ph$)$_2$] (**11**).

**Table 3** Selected bond distances (Å) and angles (°) for [CpZr($OC_6H_2$-Ph-2-$Bu^t_2$-4,6)($\eta^2$-$Bu^tNCCH_2Ph$)$_2$] (**11**)

| | | | |
|---|---|---|---|
| Zr–O(10) | 2.056(2) | Zr–C(8) | 2.257(2) |
| Zr–N(5) | 2.245(2) | Zr–Cp | 2.281(2) |
| Zr–N(7) | 2.267(2) | N(5)–C(6) | 1.275(3) |
| Zr–C(6) | 2.245(2) | N(7)–C(8) | 1.275(3) |
| | | | |
| Zr–O(10)–C(11) | 147.6(1) | N(7)–Zr–C(6) | 90.40(8) |
| O(10)–Zr–N(5) | 86.50(6) | N(7)–Zr–C(8) | 32.75(7) |
| O(10)–Zr–N(7) | 138.19(6) | N(7)–Zr–Cp | 102.06(8) |
| O(10)–Zr–C(6) | 102.94(7) | C(6)–Zr–C(8) | 115.77(8) |
| O(10)–Zr–C(8) | 108.79(7) | C(6)–Zr–Cp | 117.0(1) |
| O(10)–Zr–Cp | 106.4(1) | C(8)–Zr–Cp | 105.45(8) |
| N(5)–Zr–N(7) | 83.84(6) | Zr–N(5)–C(6) | 73.5(1) |
| N(5)–Zr–C(6) | 32.99(7) | N(5)–C(6)–Zr | 73.5(1) |
| N(5)–Zr–C(8) | 95.41(7) | Zr–N(7)–C(8) | 73.2(1) |
| N(5)–Zr–Cp | 149.91(9) | N(7)–C(8)–Zr | 74.0(1) |

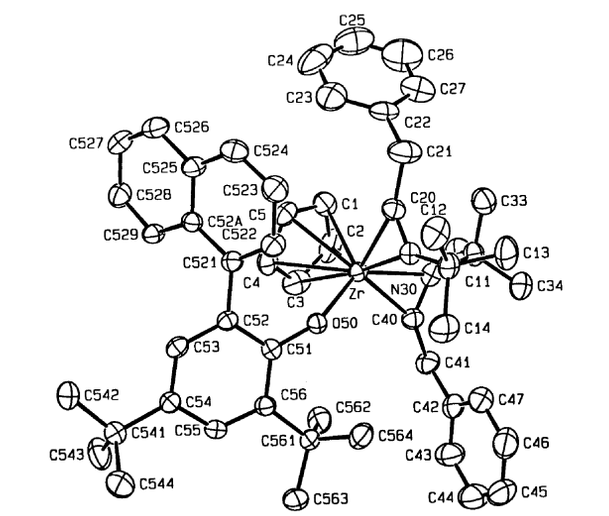
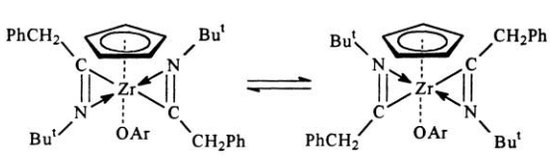


**Fig. 4** ORTEP (50% thermal ellipsoids) view of [CpZr($OC_6H_2$Np-2-$Bu^t_2$-4,6)($\eta^2$-$Bu^tNCCH_2Ph$)$_2$] (**12**).

**Table 4** Selected bond distances (Å) and angles (°) for [CpZr($OC_6H_2$-Np-2-$Bu^t_2$-4,6)($\eta^2$-$Bu^tNCCH_2Ph$)$_2$] (**12**)

| | | | |
|---|---|---|---|
| Zr–O(50) | 2.048(2) | Zr–C(2) | 2.584(3) |
| Zr–N(10) | 2.253(2) | Zr–C(3) | 2.582(3) |
| Zr–N(30) | 2.297(3) | Zr–C(4) | 2.552(3) |
| Zr–C(20) | 2.221(3) | Zr–C(5) | 2.496(3) |
| Zr–C(40) | 2.254(3) | N(10)–C(20) | 1.271(4) |
| Zr–C(1) | 2.532(3) | N(30)–C(40) | 1.273(4) |
| | | | |
| Zr–O(50)–C(51) | 152.1(2) | N(30)–Zr–C(20) | 89.3(1) |
| O(50)–Zr–N(10) | 87.20(9) | N(30)–Zr–C(40) | 32.5(1) |
| O(50)–Zr–N(30) | 136.12(9) | C(20)–Zr–C(40) | 116.0(1) |
| O(50)–Zr–C(20) | 107.7(1) | Zr–N(10)–C(20) | 72.1(2) |
| O(50)–Zr–C(40) | 106.9(1) | N(10)–C(20)–Zr | 74.9(2) |
| N(10)–Zr–N(30) | 86.48(9) | Zr–N(30)–C(40) | 71.9(2) |
| N(10)–Zr–C(20) | 33.0(1) | N(30)–C(40)–Zr | 75.6(2) |
| N(10)–Zr–C(40) | 99.4(1) | | |



Scheme 4

+85 °C although the chemical shifts do vary gradually with temperature. Hence we can conclude that iminoacyl rotation (possibly *via* an $\eta^1$-intermediate) is facile on the NMR timescale, but chemical exchange of iminoacyl environments (which would result in the benzyl protons becoming non-diastereotopic) is not occurring (Scheme 4). A similar situation has been reported for the compound [Zr($OC_6H_3Bu^t_2$-2,6)($\eta^2$-xyNCCH$_2$Ph)$_2$(CH$_2$Ph)].[18] However, at intermediate temperatures there is selective broadening of some of the resonances in the $^1$H NMR spectrum of **10**. This is particularly true at −40 °C where the downfield methylene proton of the benzyl group is broader than the upfield one (Fig. 5). Also the Cp proton signal is broadened at this temperature. At −10 °C the signals are much sharper again and remain so up to +85 °C.

The $^1$H NMR spectrum of 2-phenyl-4,6-di-*tert*-butylphenoxide **11** at −45 °C in toluene-$d_8$ solution shows non-equivalent iminoacyl groups as evidenced by two sharp $Me_3$CNCH$_2$Ph singlets and two well resolved Me$_3$CNC$H_2$Ph AB patterns in the $^1$H NMR spectrum. Only one set of Cp and

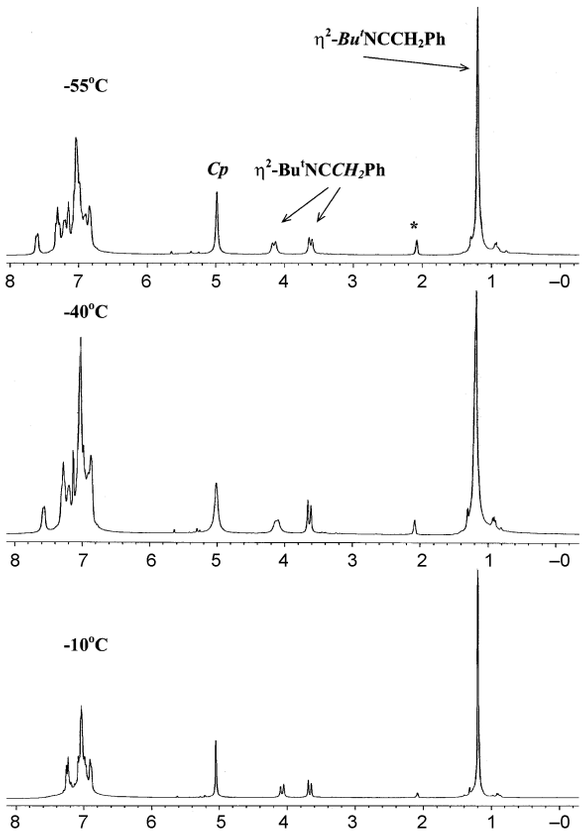
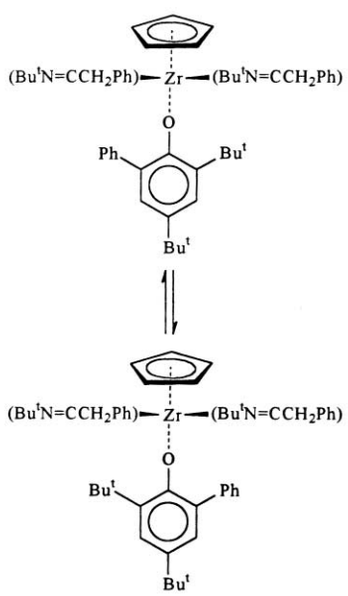



**Fig. 5** $^1$H NMR spectrum (300 MHz, $C_6D_5CD_3$; * protio impurity) of **10** at three different temperatures.

OAr resonances are observed. Hence we can conclude that at this temperature restricted rotation about the Zr–O–Ar bond is occurring leading to the non-equivalence of the iminoacyl groups (Scheme 5). We assume, based upon the data obtained




**Scheme 5**

for **10**, that iminoacyl rotation is facile. As the temperature of the solution is raised the $Me_3CNCH_2Ph$ *tert*-butyl proton resonances broaden and coalesce at +25 °C (300 MHz). By +85 °C a single, sharp resonance is observed. Similarly the two non-equivalent, diastereotopic $Me_3CNCH_2Ph$ AB patterns coalesce to form a single AB pattern at the higher temperature. From the temperature of the coalescence of the *tert*-butyl signals we estimate the barrier to aryloxide rotation to be 14.0(5) kcal mol$^{-1}$ at +25 °C. However, as with **10**, although the Cp resonance is a sharp singlet at −45 and +85 °C, at intermediate temperatures there is some broadening.

The −45 °C $^1$H NMR spectrum of the 1-naphthylphenoxide derivative **12** shows a single set of Cp (sharp singlet) and aryloxide resonances (Fig. 6). Two sharp $Me_3CNCH_2Ph$ singlets

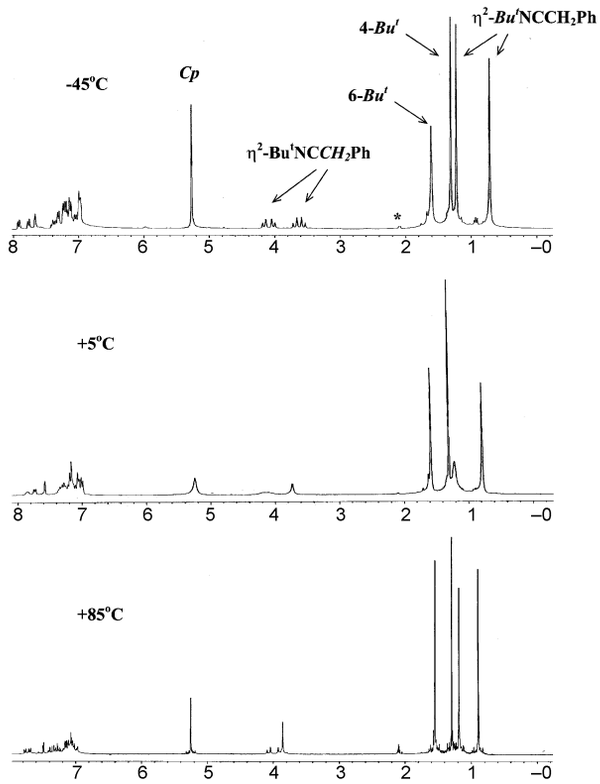



**Fig. 6** $^1$H NMR spectrum (300 MHz, $C_6D_5CD_3$; * protio impurity) of **12** at three different temperatures.

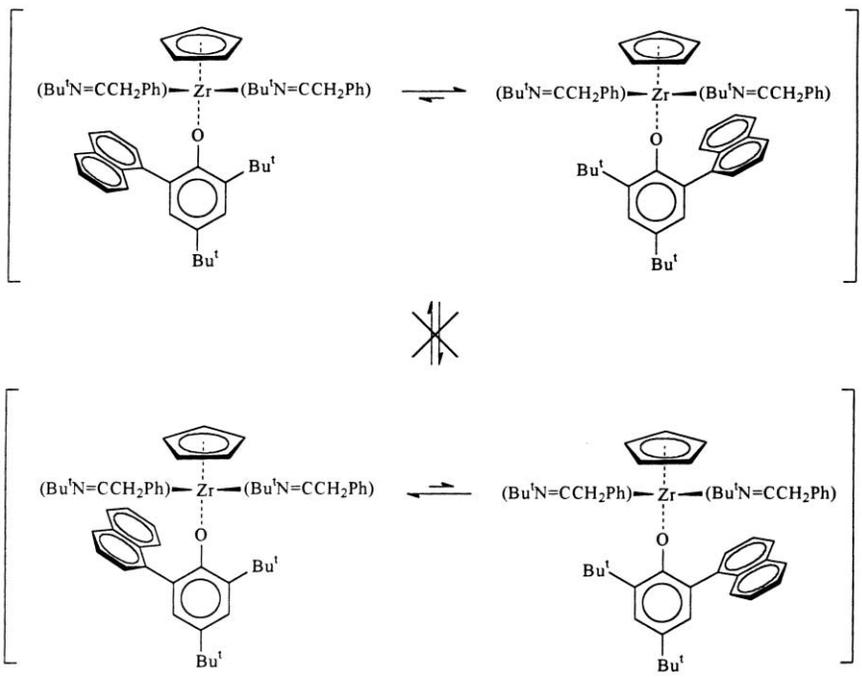
and two well resolved $Me_3CNCH_2Ph$ AB patterns are also present. The solid-state structure of **12** (Fig. 4) shows that the aryloxide wedge is oriented so that the naphthyl group is pointing away from the iminoacyl group (major isomers shown in Scheme 6). It therefore appears that only one enantiomeric pair of the two possible aryloxide rotamers that can be envisaged are detectable by NMR in solution. It seems reasonable that the naphthyl group strongly favors the rotamer with the naphthyl group oriented away from the iminoacyl ligand (Scheme 6) as observed in the solid state. As the temperature of the solution is raised, there is a broadening and then sharpening of some of the $^1$H signals. The Cp and one of the $Me_3CNCH_2Ph$ resonances broaden in the −5 to +45 °C region but then become sharp singlets in essentially the same position at +85 °C (Fig. 6). The two $Me_3CNCH_2Ph$ AB patterns also broaden, change chemical shifts slightly and then sharpen up as two $Me_3CNCH_2Ph$ AB patterns (one pair appearing close to a singlet due to almost identical chemical shifts). The low and high temperature limiting spectra of **12** therefore are consistent with the proposed solution structure and dynamics outlined. What is puzzling is the sometimes selective broadening of resonances at intermediate temperatures for all three of the bis-iminoacyl compounds **10**–**12**.

## Solid state structures

Selected structural parameters for compounds **5**, **8** (pentane solvate, two independent molecules), **11** and **12** are given in Tables 1–4 while Table 5 contains crystal data and data collection parameters. The Zr–OAr distance of 1.954(2) Å in **5** is

**Table 5** Crystal data and data collection parameters

| Compound | **5** | **8** | **11** | **12** |
|---|---|---|---|---|
| Formula | $C_{39}H_{44}OZr$ | $C_{44}H_{53}NOZr \cdot 1/3C_5H_{12}$ | $C_{49}H_{62}N_2OZr$ | $C_{53}H_{64}N_2OZr$ |
| Formula weight | 620.01 | 727.09 | 786.27 | 836.33 |
| Space group | *C*2/*c* (no. 15) | $P2_1/n$ (no. 14) | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| *a*/Å | 27.9412(6) | 16.5371(8) | 12.1678(4) | 11.9950(7) |
| *b*/Å | 13.9072(3) | 17.372(1) | 12.3408(4) | 13.3697(9) |
| *c*/Å | 20.6729(4) | 31.204(1) | 15.8545(3) | 14.9039(5) |
| *α*/° | | | 82.153(2) | 99.974(3) |
| *β*/° | 124.493(1) | 100.265(3) | 88.504(2) | 99.813(3) |
| *γ*/° | | | 63.853(1) | 97.689(2) |
| *V*/Å$^3$ | 6620.9(5) | 8821(1) | 2115.5(2) | 2286.5(4) |
| *Z* | 8 | 8 | 2 | 2 |
| $\rho_{calc}$/g cm$^{-3}$ | 1.244 | 1.095 | 1.234 | 1.215 |
| Temperature/K | 203 | 203 | 203 | 193 |
| Radiation (wavelength) | Mo-Kα (0.71073 Å) | Mo-Kα (0.71073 Å) | Mo-Kα (0.71073 Å) | Mo-Kα (0.71073 Å) |
| *R* | 0.048 | 0.084 | 0.044 | 0.052 |
| $R_w$ | 0.122 | 0.207 | 0.101 | 0.109 |




**Scheme 6**

slightly longer than the values of 1.903(4) and 1.936(4) Å found in the bis(aryloxide) [Zr(OC$_6$H$_3$Bu$^t_2$-2,6)(OC$_6$H$_2$Bu$^t_2$-2,6-OMe-4)(CH$_2$Ph)$_2$][25] indicating a less electron deficient metal center upon replacing OAr with Cp. This interatomic distance also increases slightly as the benzyl ligands are replaced by iminoacyl groups; *cf.* 2.004(5) Å (av.) in **8** and 2.056(2), 2.048(2) Å in **11** and **12**, respectively. As expected, the Zr–O–Ar angles are all large and do not correlate at all with the Zr–OAr distance.[26] A feature of highly electron deficient metal benzyl compounds is the presence of unexpectedly low M–CH$_2$–Ph angles (sometimes less than 90°) observed in many solid state derivatives. These acute angles have been interpreted in terms of $\eta^n$-interactions between the metal center and the benzyl ligand.[27] There is also spectroscopic evidence for some of these $\eta^n$-interactions being maintained in solution.[25] However, the observation of M–CH$_2$–Ph angles lower than 100° in the solid state structures of early transition metal benzyl compounds should not be over interpreted in terms of bonding/reactivity. This is highlighted by a recent study showing dramatically different angles can be observed for different solvates of the same molecule, *i.e.* packing forces may dominate what is apparently a flexible bond angle.[28] Hence, the Zr–C(30)–C(31) angle of 97.4(2)° for one of the benzyl ligands in **5** is not particularly noteworthy. The other benzyl ligands in **5** and **8** have corresponding angles of 128.8(2), 122.2(5) and 123.0(5)°.

The most important structural parameters are those for the zirconium C,N-bound iminoacyl ligands. A large number of simple $\eta^2$-RNCR′ ligands attached to transition metal centers are now known.[8] It is interesting to compare the structural parameters for the compounds obtained in this study with other related zirconium iminoacyl derivatives. One measure of the extent of $\eta^2$-binding which has been applied to both acyl and iminoacyl ligands is the value of the parameter [*d*(M–E) − *d*(M–C)] (E = O, N). This parameter can be used as a measure of the electron deficiency of the metal, with negative values occurring for highly electrophilic metal centers. However, it is important to realize that iminoacyl substituents will undoubtedly influence these parameters. In the bis(aryloxide) compound [Zr(OC$_6$H$_3$Bu$^t_2$-2,6)$_2$($\eta^2$-Bu$^t$NCCH$_2$Ph)$_2$] the Zr–C and Zr–N distances are 2.228(3) and 2.221(3) Å, respectively. The corresponding distances in the Cp derivatives **11** and **12** (which have the same iminoacyl substituents, Tables 3 and 4) are very slightly longer. However, in all three compounds [*d*(M–N) − *d*(M–C)] are close to zero. Analysis of the Cambridge Structural Database shows 14 different compounds containing zirconium–iminoacyl groups.[29] A plot of the values of *d*(Zr–N) *vs.* *d*(Zr–C) for these compounds is shown in Fig. 7. It can be seen that there is an approximately even distribution about the *x* = *y* relationship. The compounds obtained in this study can be seen to be very similar to previously isolated iminoacyls of

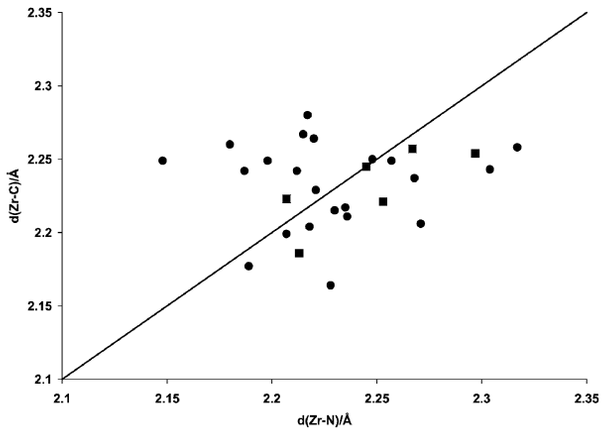



**Fig. 7** Plot of *d*(Zr–N) (Å) *vs*. *d*(Zr–C) (Å) for simple $\eta^2$-iminoacyl derivatives of zirconium (●, ref. 29). Compounds obtained in this study (□).

zirconium. The most negative value for [*d*(M–N) − *d*(M–C)] occurs for the compound [(methoxycalix[4]arene)Zr($\eta^2$-Bu$^t$-NCPh)][29g] (three electron withdrawing phenoxides and a methoxy donor group around the metal) while the most positive value is for the compound [$Cp_2Zr(SC_4N_2Me_2)(\eta^2$-xyNCMe)][29h] (18-electron compound).

## Experimental

### General details

All operations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The hydrocarbon solvents were distilled from sodium/benzophenone and stored over sodium ribbons under nitrogen until use. All organic reagents were purchased from Aldrich Chemical Co., [$CpZrCl_3$] from Strem, and used without further purification. The preparation of phenols **1**, **2**, **3** and [$CpZr(CH_2Ph)_3$] have previously been reported.[20–22,24] The $^1$H and $^{13}$C NMR spectra were recorded on a Varian Associates Gemini-200, Inova-300, or General Electric QE-300 spectrometer and referenced to protio impurities of commercial benzene-$d_6$ or deuterated chloroform as internal standards. Elemental analyses and molecular structures were obtained through Purdue in-house facilities.

### Syntheses

**[CpZr(OC$_6$HPh$_4$-2,3,5,6)(CH$_2$Ph)$_2$] (4).** A sample of [CpZr-($CH_2Ph)_3$] (1.0 g, 2.32 mmol) was dissolved in benzene. One equivalent of 2,3,5,6-tetraphenylphenol (930 mg, 2.33 mmol) **1** was added and the mixture stirred overnight and evacuated to dryness. The resulting crude solid was washed with pentane and dried *in vacuo* to give a yellow solid (1.4 g, 82%). Anal. calc. for $C_{49}H_{40}OZr$: C, 79.96; H, 5.48. Found: C, 79.69; H, 5.48%. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.84–7.31 (aromatics); 6.63 [d, $^3J(^1H–^1H)$ = 7.3 Hz, *ortho*-$CH_2Ph$]; 5.25 (s, *Cp*); 1.58 (d), 1.10 [d, $^2J(^1H–^1H)$ = 10.5 Hz, Zr–$CH_2$]. $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 158.2 (Zr–O–*C*); 114.1 (*Cp*); 64.0 (Zr–*C*H$_2$).

**[CpZr(OC$_6$H$_2$Ph-2-Bu$^t$-4,6)(CH$_2$Ph)$_2$] (5).** A solvent sealed flask was charged with [$CpZr(CH_2Ph)_3$] (750 mg, 1.75 mmol), 2-phenyl-4,6-di-*tert*-butylphenol (493 mg, 1.75 mmol) **2**, and benzene. The yellow mixture was stirred for three days and evacuated to dryness to give a yellow glassy solid. Upon standing in minimal hexane yellow crystals (410 mg, 38%) of **5** formed. Anal. calc. for $C_{39}H_{44}OZr$: C, 75.55; H, 7.15. Found: C, 73.88; H, 7.29%. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.83–7.54 (aromatics); 5.49 (s, *Cp*); 2.23 [d, $^2J(^1H–^1H)$ = 11.0 Hz, Zr–$CH_2$]; 1.55 (s), 1.26 (s, C*Me*$_3$); 1.39 [d, $^2J(^1H–^1H)$ = 11 Hz, Zr–$CH_2$]. Selected $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 157.7 (Zr–O–*C*); 114.2 (*Cp*); 66.2 (Zr–*C*H$_2$); 41.9, 35.4 (*C*Me$_3$); 31.4, 30.5 (C*Me*$_3$).

**[CpZr(OC$_6$H$_2$Np-2-Bu$^t$-4,6)(CH$_2$Ph)$_2$] (6).** A sample of [$CpZr(CH_2Ph)_3$] (1.0 g, 2.3 mmol) was dissolved in benzene. This solution was stirred as 2-(1-naphthyl)-4,6-di-*tert*-butylphenol (493 mg, 1.75 mmol) **3**, was slowly added. The yellow mixture was stirred for thirty minutes and evacuated to dryness affording a yellow solid (1.3 g, 80%). $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.59–7.82 (aromatics); 5.35 (s, *Cp*); 2.04 (d), 1.80 [d, $^2J(^1H–^1H)$ = 10 Hz, Zr–$CH_2$]; 0.97 (d), 0.58 (d, $^2J(^1H–^1H)$ = 11 Hz, Zr–$CH_2$) 1.65 (s), 1.30 (s, C*Me*$_3$); 0.97 (d), 0.58 [d, $^2J(^1H–^1H)$ = 10.7 Hz, Zr–$CH_2$]. Selected $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 159.3 (Zr–O–*C*); 114.6 (*Cp*); 65.0, 64.4 (Zr–*C*H$_2$); 36.2, 35.0 (*C*Me$_3$); 32.2, 31.3 (C*Me*$_3$).

**[CpZr(OC$_6$HPh$_4$-2,3,5,6)($\eta^2$-Bu$^t$NCCH$_2$Ph)(CH$_2$Ph)] (7).** A sample of **4** was placed in a NMR tube and dissolved in $d_6$-benzene. This solution was titrated with *tert*-butylisocyanide forming initially the mono-iminoacyl product **7**. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.51–7.24 (aromatics); 5.02 (s, *Cp*); 3.62 (d), 3.51 [d, $^2J(^1H–^1H)$ = 17 Hz, NCC*H*$_2$Ph]; 2.52 (d), 1.57 [d, $^2J(^1H–^1H)$ = 10 Hz, Zr–C*H*$_2$Ph]; 1.12 (s, NC*Me*$_3$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 244.2 (N*C*CH$_2$Ph); 159.1 (Zr–O–*C*); 111.2 (*Cp*); 62.5 (Zr–*C*H$_2$); 50.7 (N*C*Me$_3$); 43.4 (NC*C*H$_2$Ph); 30.4 (NC*Me*$_3$).

**[CpZr(OC$_6$H$_2$Ph-2-Bu$^t_2$-4,6)($\eta^2$-Bu$^t$NCCH$_2$Ph)(CH$_2$Ph)] (8).** A sample of **5** (220 mg, 0.36 mmol) was dissolved in hexane. One equivalent of *tert*-butylisocyanide was added (40.2 μL, 0.36 mmol) and the mixture stirred overnight and then evacuated to dryness. A minimal amount of pentane was added to this crude solid and upon standing yellow crystals formed. Anal. calc. for $C_{44}H_{53}NOZr$: C, 75.16; H, 7.60. Found: C, 74.31; H, 7.72%. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.81–7.53 (aromatics); 5.32 (s, *Cp*); 3.95 (d), 3.51 [d, $^2J(^1H–^1H)$ = 16.5 Hz, NCC*H*$_2$Ph]; 2.69 (d), 2.19 [d, $^2J(^1H–^1H)$ = 10 Hz, Zr–C*H*$_2$Ph]; 1.59 (s), 1.30 (s), 1.29 (s, CMe$_3$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 243.9 (N*C*CH$_2$Ph); 158.9 (Zr–O–*C*); 111.3 (*Cp*); 61.6 (Zr–*C*H$_2$); 51.5 (N*C*Me$_3$); 43.1 (NC*C*H$_2$Ph); 35.4, 34.1 (*C*Me$_3$); 31.6, 31.0, 29.8 (C*Me*$_3$).

**[CpZr(OC$_6$H$_2$Ph-2-Bu$^t_2$-4,6)($\eta^2$-Bu$^t$NCCH$_2$Ph)(CH$_2$Ph)] (9).** A sample of **6** was placed in a NMR tube and dissolved in $d_6$-benzene. This solution was titrated with *tert*-butylisocyanide forming initially the mono-iminoacyl product **9**. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.73–8.02 (aromatics); 4.88 (s), 5.15 (s, *Cp*); 3.91 (d), 3.86 (d), 3.65 (d), 3.41 (d) [$^2J(^1H–^1H)$ = 16 Hz, NCC*H*$_2$Ph]; 2.59 (d), 2.40 (d), 2.06 (d), 1.68 (d) [$^2J(^1H–^1H)$ = 11 Hz, Zr–C*H*$_2$Ph]; 1.61 (s), 1.52 (s), 1.28 (b), 1.13 (s, CMe$_3$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 242.9, 242.5 (N*C*CH$_2$Ph); 159.8, 158.4 (Zr–O–*C*); 111.5, 110.5 (*Cp*); 62.2, 61.8 (Zr–*C*H$_2$); 51.3, 48.9 (N*C*Me$_3$); 43.3, 43.2 (NC*C*H$_2$Ph); 35.6, 35.4, 34.3, 34.2, 32.2, 31.9 (*C*Me$_3$); 31.7, 31.3, 31.2, 30.1, 29.9, 29.8 (C*Me*$_3$).

**[CpZr(OC$_6$HPh$_4$-2,3,5,6)($\eta^2$-Bu$^t$NCCH$_2$Ph)$_2$] (10).** A sample of **4** was placed in a NMR tube and dissolved in $d_6$-benzene. This solution was titrated with *tert*-butylisocyanide until the bis($\eta^2$-iminoacyl) product was observed to have formed. Layering of the solution with hexane induced the formation of white crystals of **10**. Anal. calc. for $C_{59}H_{58}N_2OZr$: C, 78.53; H, 6.48; N, 3.10. Found: C, 76.44; H, 6.25; N, 2.79%. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 6.90–7.29 (aromatics); 5.07 (s, *Cp*); 4.09 (d), 3.75 [d, $^2J(^1H–^1H)$ = 14.3 Hz, NCC*H*$_2$Ph]; 1.20 (s, NC*Me*$_3$). $^1$H NMR ($C_7D_8$, −55 °C): $\delta$ 6.84–7.61 (aromatics); 4.98 (s, *Cp*); 4.15(d), 3.62 [d, $^2J(^1H–^1H)$ = 13.0 Hz, NCC*H*$_2$Ph]; 1.19 (s,NC*Me*$_3$). $^1$H NMR ($C_7D_8$, +85 °C): $\delta$ 7.06–7.36 (aromatics); 5.24 (s, *Cp*); 4.14(d), 3.86 [d, $^2J(^1H–^1H)$ = 14 Hz, NCC*H*$_2$Ph]; 1.34 (s, NC*Me*$_3$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 233.2 (N*C*CH$_2$Ph); 162.4 (Zr–O–*C*); 107.9 (*Cp*); 59.8 (N*C*Me$_3$); 43.9 (NC*C*H$_2$Ph); 30.8 (NC*Me*$_3$).

**[CpZr(OC$_6$H$_2$Ph-2-Bu$^t_2$-4,6)($\eta^2$-Bu$^t$NCCH$_2$Ph)$_2$] (11).** A sample of **8** (90 mg, 0.13 mmol) was dissolved in benzene. One

equivalent of *tert*-butylisocyanide (16 μL, 0.13 mmol) was added and the mixture allowed to react for two days and then evacuated to dryness affording a white solid. A minimal amount of pentane was added and upon standing colorless crystals formed (50 mg, 50%). Anal. calc. for $C_{49}H_{62}N_2OZr$: C, 73.64; H, 8.33; N, 3.73. Found: C, 73.71; H, 8.12; N, 3.53%. $^1$H NMR ($C_6D_6$, 30 °C): $\delta$ 7.01–7.56 (aromatics); 5.55 (br, *Cp*); 3.91 (br, NCC$H_2$Ph); 1.53 (s), 1.30 (s, C$Me_3$), 1.03 (br, NC$Me_3$). $^1$H NMR ($C_7D_8$, −45 °C): $\delta$ 6.73–7.62 (aromatics); 5.60 (s, *Cp*); 4.19 (d), 3.99 (d), 3.72 (d), 3.63 [d, $^2J(^1H–^1H)$ = 15, 17 Hz, NCC$H_2$Ph]; 1.59 (s), 1.37 (s, C$Me_3$); 1.22 (s), 0.72 (s, NC$Me_3$). $^1$H NMR ($C_7D_8$, +85 °C): $\delta$ 6.9–7.6 (aromatics); 5.59 (s, *Cp*); 4.12 (d), 3.98 [d, $^2J(^1H–^1H)$ = 16 Hz, NCC$H_2$Ph]; 1.50 (s), 1.47 (s, C$Me_3$); 1.08 (s, NC$Me_3$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 231.2 (br, N*C*CH$_2$Ph); 166.7 (Zr–O–*C*); 108.9 (br, Cp); 58.8 (br, N*C*Me$_3$); 42.5 (br, NC*C*H$_2$Ph); 35.6, 33.9 (*C*Me$_3$); 31.8, 30.1, 31.2 (C$Me_3$) and (NC$Me_3$).

**[CpZr(OC$_6$H$_2$Np-2-Bu$^t_2$-4,6)($\eta^2$-Bu$^t$NCCH$_2$Ph)$_2$] (12).** A sample of **6** (300 mg, 0.45 mmol) was dissolved in benzene and *tert*-butylisocyanide (0.10 mL, 0.90 mmol) added. The mixture was stirred overnight and evacuated to dryness affording a yellow solid (370 mg, 67%). Recrystallization from minimal pentane afforded X-ray quality crystals of **12**. Anal. calc. for $C_{53}H_{64}N_2OZr$: C, 76.12; H, 7.72; N, 3.35. Found: C, 76.32; H, 7.70; N, 3.42%. $^1$H NMR ($C_6D_6$, +25 °C): $\delta$ 7.00–8.32 (aromatics); 5.32 (br, *Cp*); 3.75 (br, NCC$H_2$Ph); 1.59 (s), 1.27 (s, C$Me_3$); 1.15 (s), 0.75 (s, NC$Me_3$). $^1$H NMR ($C_7D_8$, −45 °C): $\delta$ 6.97–8.49 (aromatics); 5.28 (s, *Cp*); 4.16 (d), 4.02 (d), 3.69 (d), 3.56 [d, $^2J(^1H–^1H)$ = 15, 17 Hz, NCC$H_2$Ph]; 1.61(s), 1.31 (s, C$Me_3$); 1.23 (s),0.72 (s, NC$Me_3$). $^1$H NMR ($C_7D_8$, +85 °C): $\delta$ 6.97–8.11 (aromatics); 5.25 (s, *Cp*); 4.07 (d), 3.89 (d), 3.89 (d), 3.83 [d, $^2J(^1H–^1H)$ = 17, 17 Hz, NCC$H_2$Ph]; 1.54 (s), 1.29 (s, C$Me_3$); 1.18 (s), 0.89 (s, NC$Me_3$). $^{13}$C NMR ($C_6D_6$, 30 °C): $\delta$ 231.4, 228.9 (N*C*CH$_2$Ph); 161.5 (Zr–O–*C*); 108.8 (*Cp*); 59.8, 57.9 (N*C*Me$_3$); 43.0, 41.5 (NC*C*H$_2$-Ph); 35.7, 33.9 (*C*Me$_3$); 31.7, 31.1, 30.2, 30.1 (C$Me_3$) and (NC$Me_3$).

### X-Ray data collection and reduction

Crystal data and data collection parameters are contained in Table 5. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo-Kα radiation ($\lambda$ = 0.71073 Å) on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the data.[30] An empirical absorption correction using SCALEPACK was applied.[31] Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.[32] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ and the weight $w$ is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$ where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the *International Tables for Crystallography*.[33] Refinement was performed on a AlphaServer 2100 using SHELX-97.[34] Crystallographic drawings were done using ORTEP.[35]

CCDC reference numbers 182088–182091.

See http://www.rsc.org/suppdata/dt/b2/b202244n/ for crystallographic data in CIF or other electronic format.

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