Influence of a [Me₂Si] *ansa* bridge on the barrier to rotation about the Zr–phenyl bond and on the generation and reactivity of benzyne intermediates: comparison of the structures and reactivity of [Me₂Si(C₅Me₄)₂]Zr(Ph)X and Cp*₂Zr(Ph)X (X = H, Cl, Ph)

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Comparison of the chemistry of [Me₂Si(C₅Me₄)₂]ZrPh₂ and Cp*₂ZrPh₂ demonstrates that incorporation of a [Me₂Si] *ansa* bridge reduces the barrier for both (i) rotation about the Zr–Ph bond and (ii) elimination of benzene to generate a benzyne intermediate; furthermore, the [Me₂Si] *ansa* bridge promotes the reaction of *two* equivalents of MeCN with the benzyne intermediate {[Me₂Si(C₅Me₄)₂]-Zr(η²-C₆H₄)}, whereas insertion of only one equivalent is observed with [Cp*₂Zr(η²-C₆H₄)].

Zirconocene aryl complexes have attracted attention due to their ability to generate aryne species which, as exemplified by Buchwald's Cp₂Zr(η²-C₆H₄)(PMe₃),[1] may be isolated in favorable situations. Such benzyne species are not only of intrinsic chemical interest, but have also found considerable application as reactive intermediates in organic synthesis.[2] In this paper, we describe further studies to delineate the *ansa*-effect in metallocene chemistry[3] by reporting the influence of a [Me₂Si] *ansa*-bridge on (i) the barrier to rotation about a Zr–phenyl bond, and (ii) the ability to generate a benzyne intermediate and the impact on its subsequent reactivity.

The *ansa*-zirconocene phenyl complexes [Me₂Si(C₅Me₄)₂]Zr-(Ph)Cl and [Me₂Si(C₅Me₄)₂]ZrPh₂ are obtained by sequential metathesis of [Me₂Si(C₅Me₄)₂]ZrCl₂ with PhLi (Scheme 1), in an analogous manner to the pentamethylcyclopentadienyl derivatives, Cp*₂Zr(Ph)Cl and Cp*₂ZrPh₂.[4] The molecular structures of [Me₂Si(C₅Me₄)₂]Zr(Ph)Cl, [Me₂Si(C₅Me₄)₂]ZrPh₂, Cp*₂Zr(Ph)Cl and Cp*₂ZrPh₂ have been determined by X-ray diffraction (Table 1).[5,6] As has been observed previously for other pairs of [Me₂Si(C₅Me₄)₂]MX₂ and Cp*₂MX₂ derivatives,[3] the [Me₂Si] *ansa* bridge exerts a subtle structural influence
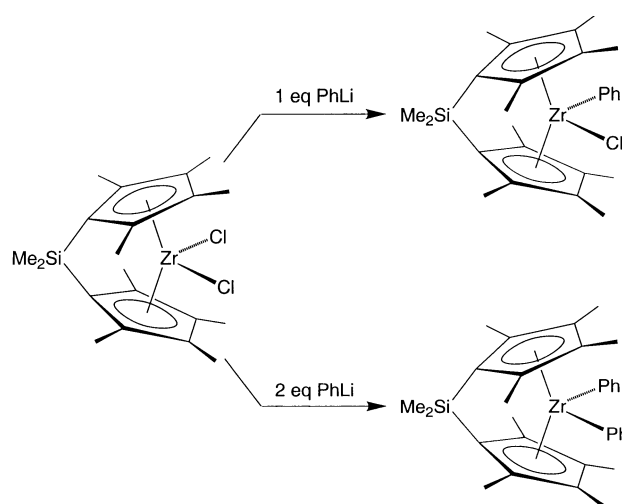

Scheme 1

which forces the cyclopentadienyl groups to tilt by *ca.* 4° such that the ring normals lose coincidence with the Zr–Cp_cent vector and the range of Zr–C bond lengths increases (Table 1); the coordination mode of the ligand thus moves from symmetric η⁵,η⁵-coordination towards η³,η³-coordination.

Interestingly, the subtle structural difference between the *ansa* [Me₂Si(C₅Me₄)₂]Zr(Ph)X and non-*ansa* Cp*₂Zr(Ph)X systems is manifested by a decrease in the barrier to rotation about the Zr–Ph bond for the *ansa* complexes. The latter

Table 1 Geometrical data for Cp*₂Zr(Ph)X and [Me₂Si(C₅Me₄)₂]Zr(Ph)X derivatives
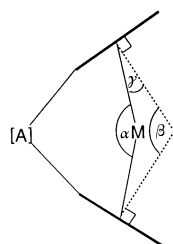
$$\alpha = Cp_{cent}\text{–}M\text{–}Cp_{cent}$$
$$\beta = Cp_{norm}/Cp_{norm}$$
$$\gamma = (\alpha - \beta)/2$$

	$d(Zr\text{–}Cp_{cent})$/Å	$d(Zr\text{–}C)$/Å	$d(Zr\text{–}C)$ range/Å	α/°	β/°	γ/°
Cp*₂Zr(Ph)H	2.233	2.519–2.543	0.024	141.1	141.0	0.05
[Me₂Si(C₅Me₄)₂]Zr(Ph)H	2.224	2.472–2.590	0.188	129.9	122.5	3.7
Cp*₂Zr(Ph)Cl[a]	2.250	2.509–2.589	0.080	139.5	138.1	0.18
[Me₂Si(C₅Me₄)₂]Zr(Ph)Cl	2.234	2.466–2.620	0.154	128.7	120.6	4.1
Cp*₂ZrPh₂[a]	2.279	2.541–2.599	0.058	139.3	137.7	0.8
[Me₂Si(C₅Me₄)₂]ZrPh₂	2.263	2.485–2.644	0.159	127.9	119.1	4.4

[a] Average values for two crystallographically independent molecules.

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process can be conveniently probed by dynamic ^{1}H NMR spectroscopy because all five phenyl protons are chemically inequivalent in the static solid state structure and rotation about the Zr–Ph bond results in coalescence of the signals of the two pairs of *ortho* and *meta* protons.[7] Since a knowledge of the factors that influence the barriers to metal ligand rotations is of relevance to understanding the structure of polymers obtained using metallocene catalysts,[8] we have sought to quantify the effect of a [Me$_2$Si] *ansa* bridge on rotation barriers.

The low temperature (*ca.* 200 K) ^{1}H NMR spectrum of [Me$_2$Si(C$_5$Me$_4$)$_2$]Zr(Ph)Cl is indicative of a static structure, with five different signals for the phenyl group, but upon warming the signals attributed to the two pairs of *ortho* and *meta* protons coalesce.[9] In contrast to the coalescence behavior observed for [Me$_2$Si(C$_5$Me$_4$)$_2$]Zr(Ph)Cl, the non-*ansa* counterpart Cp*$_2$Zr-(Ph)Cl retains a static structure on the NMR time-scale at 350 K.[10] It is, therefore, evident that the barrier for rotation about the Zr–Ph bond in the *ansa* complex [Me$_2$Si(C$_5$Me$_4$)$_2$]Zr(Ph)Cl is substantially less than that in Cp*$_2$Zr(Ph)Cl.[11] The spectroscopic behavior of the pair of phenyl-hydride complexes, [Me$_2$Si(C$_5$Me$_4$)$_2$]Zr(Ph)H and Cp*$_2$Zr(Ph)H, is similar, with only the former exhibiting fluxionality. Likewise, the diphenyl derivatives [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrPh$_2$ and Cp*$_2$ZrPh$_2$ exhibit the same trend, but the barrier for the latter complex is sufficiently low that a quantitative comparison can be made; at 25 °C, rotation about the Zr–Ph bond in [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrPh$_2$ is a factor of *ca.* 400 faster than that of Cp*$_2$ZrPh$_2$.[9] Since the phenyl ligands in the *ansa* zirconocene complexes [Me$_2$Si(C$_5$Me$_4$)$_2$]Zr-(Ph)X (X = H, Cl) exhibit a more pronounced β-agostic interaction, thus providing an additional barrier to rotation than in their non-*ansa* counterparts, Cp*$_2$Zr(Ph)X,[3f] it is evident that the more facile rotation in the *ansa* system may be attributed to the reduction in steric interactions resulting from tilting (γ) of the cyclopentadienyl rings, which increases the distance between the ring methyl substituents and the phenyl ligand.[12]

As with other diphenyl zirconocene complexes,[13] thermal elimination of benzene from [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrPh$_2$ provides a means of generating the benzyne intermediate {[Me$_2$Si-(C$_5$Me$_4$)$_2$]Zr(η^2-C$_6$H$_4$)}. For example, {[Me$_2$Si(C$_5$Me$_4$)$_2$]Zr(η^2-C$_6$H$_4$)} is trapped by ethylene to give [Me$_2$Si(C$_5$Me$_4$)$_2$]Zr-(η^2-C$_6$H$_4$CH$_2$CH$_2$),[5] as illustrated in Scheme 2.[14] While Marks has reported that the non-*ansa* system behaves analogously to [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrPh$_2$ in the presence of ethylene, giving
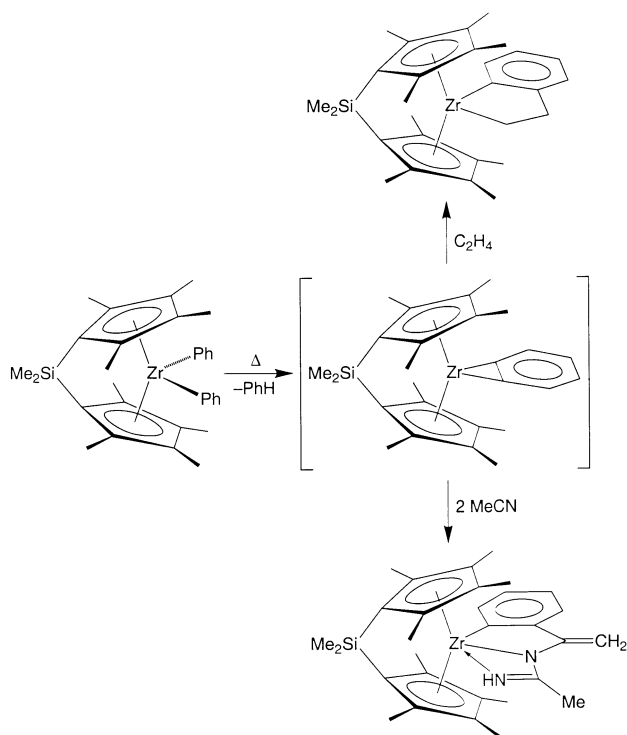
Cp*$_2$Zr(η^2-C$_6$H$_4$CH$_2$CH$_2$),[4b,15] the two systems behave very differently in the presence of acetonitrile. Specifically, whereas [Cp*$_2$Zr(η^2-C$_6$H$_4$)] is trapped by a single molecule of MeCN to give Cp*$_2$Zr[η^2-*C,N*-C$_6$H$_4${C(Me)=N}] (Scheme 3), the *ansa*
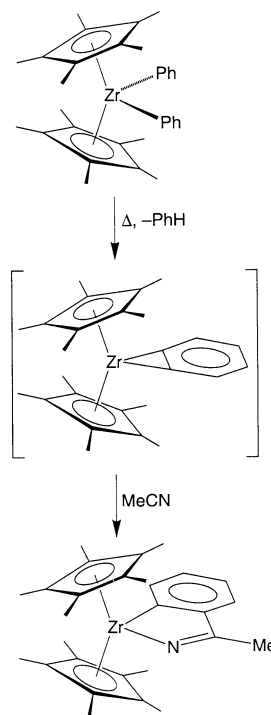
Scheme 3

counterpart {[Me$_2$Si(C$_5$Me$_4$)$_2$]Zr(η^2-C$_6$H$_4$)} is trapped by *two* molecules of MeCN giving [Me$_2$Si(C$_5$Me$_4$)$_2$]Zr[η^3-*C,N,N*-C$_6$H$_4${C(CH$_2$)NC(Me)=NH}] under comparable conditions (Scheme 2). The molecular structures of the acetonitrile insertion products, Cp*$_2$Zr[η^2-*C,N,N*-C$_6$H$_4${C(Me)=N}] and [Me$_2$Si-(C$_5$Me$_4$)$_2$]Zr[η^3-*C,N,N*-C$_6$H$_4${C(CH$_2$)NC(Me)=NH}] have been determined by X-ray diffraction (Fig. 1).[5] Key spectroscopic evidence for the characterization of [Me$_2$Si(C$_5$Me$_4$)$_2$]Zr[η^3-*C,N,N*-C$_6$H$_4${C(CH$_2$)NC(Me)=NH}] is the observation of a triplet resonance at 83.5 ppm ($^1J_{\text{C-H}}$ = 157 Hz) in the ^{13}C NMR spectrum for the CH$_2$ group. In addition to representing an interesting example of an *ansa* effect, the formation of the double insertion product is notable since other zirconocene benzyne species typically only insert a single RCN molecule.[13,16]

Kinetics studies are in accord with the above reactions of [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrPh$_2$ proceeding *via* a benzyne intermediate. Specifically, the rate constants at 40 °C for the reactions with C$_2$H$_4$ [k = 4.3(1) × 10^{-6} s^{-1}] and MeCN [k = 4.0(1) × 10^{-6} s^{-1}] are experimentally indistinguishable and are also independent of the concentration of substrate, as would be expected for rate determining elimination of benzene and the formation of a benzyne intermediate. Interestingly, the rate of elimination of benzene from [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrPh$_2$ is noticeably faster than that from Cp*$_2$ZrPh$_2$ by a factor of 1.7.[17] A possible origin for the enhanced rate may be related to the more facile rotation about the Zr–Ph bond in [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrPh$_2$. Thus, since elimination of benzene would be most favored for a configuration in which the phenyl group that abstracts the hydrogen is perpendicular to the incipient benzyne plane, the rate constant would be expected to be greater for the *ansa* system because of the reduced steric demands.

In summary, comparison of the chemistry of [Me$_2$Si(C$_5$-Me$_4$)$_2$]Zr(Ph)X and Cp*$_2$Zr(Ph)X complexes provides a further illustration of the manner in which an *ansa* bridge may modulate reactivity. Incorporation of a [Me$_2$Si] *ansa* bridge thus facilitates rotation about the Zr–Ph bond in [Me$_2$Si(C$_5$Me$_4$)$_2$]-Zr(Ph)X derivatives and promotes elimination of benzene from [Me$_2$Si(C$_5$Me$_4$)$_2$]ZrPh$_2$. Finally, the benzyne complex so obtained, {[Me$_2$Si(C$_5$Me$_4$)$_2$]Zr(η^2-C$_6$H$_4$)}, reacts with two

Scheme 2
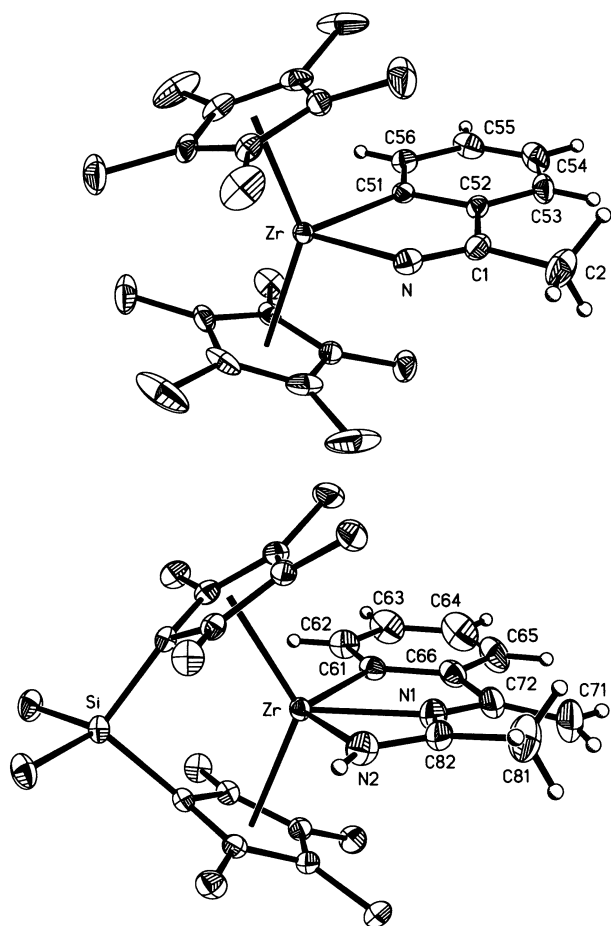
Fig. 1 Molecular structures of $Cp*_2Zr[\eta^2\text{-}C,N\text{-}C_6H_4\{C(Me)=N\}]$ (top) and $[Me_2Si(C_5Me_4)_2]Zr[\eta^3\text{-}C,N,N\text{-}C_6H_4\{C(CH_2)NC(Me)=NH\}]$ (bottom).

equivalents of MeCN, in contrast to the one equivalent that reacts with the non-*ansa* counterpart $[Cp*_2Zr(\eta^2\text{-}C_6H_4)]$.

Acknowledgements

Notes and references

1 S. L. Buchwald, B. T. Watson and J. C. Huffman, *J. Am. Chem. Soc.*, 1986, **108**, 7411.
2 (*a*) S. L. Buchwald and R. D. Broene, *Comprehensive Organometallic Chemistry II*, E. Abel, F. G. A. Stone and G. Wilkinson, (eds), Pergamon, New York, 1995, pp. 771–784; (*b*) S. L. Buchwald and R. D. Broene, *Science*, 1993, **261**, 1696; (*c*) S. L. Buchwald and R. B. Nielsen, *Chem. Rev.*, 1998, **88**, 1047; (*d*) S. L. Buchwald and R. A. Fisher, *Chem. Scr.*, 1989, **29**, 417; (*e*) J.-P. Majoral, P. Meunier, A. Igau, N. Pirio, M. Zablocka, A. Skowronska and S. Bredeau, *Coord. Chem. Rev.*, 1998, **178–180**, 145.
3 For lead articles, see: (*a*) J. C. Green and C. N. Jardine, *J. Chem. Soc., Dalton Trans.*, 1999, 3767; (*b*) J. C. Green, *Chem. Soc. Rev.*, 1998, 263; (*c*) S. L. J. Conway, T. Dijkstra, L. H. Doerrer, J. C. Green, M. L. H. Green and M. L. H. Stephens, *J. Chem. Soc., Dalton Trans.*, 1998, 2689; (*d*) L. Labella, A. Chernega and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1995, 395; (*e*) A. Chernega, J. Cook, M. L. H. Green, L. Labella, S. J. Simpson, J. Souter and A. H. H. Stephens, *J. Chem. Soc., Dalton Trans.*, 1997, 3225; (*f*) H. Lee, P. J. Desrosiers, I. Guzei, A. L. Rheingold and G. Parkin, *J. Am. Chem. Soc.*, 1998, **120**, 3255; (*g*) J. H. Shin and G. Parkin, *Chem. Commun.*, 1999, 887; (*h*) D. Churchill, J. H. Shin, T. Hascall, J. M. Hahn, B. M. Bridgewater and G. Parkin, *Organometallics*, 1999, **18**, 2403; (*i*) D. G. Churchill, B. M. Bridgewater and G. Parkin, *J. Am. Chem. Soc.*, 2000, **122**, 178; (*j*) H. Lee, J. B. Bonanno, J. Cordaro, J. M. Hahn and G. Parkin, *J. Chem. Soc., Dalton Trans.*, 1999, 1365;

(*k*) J. H. Shin, T. Hascall and G. Parkin, *Organometallics*, 1999, **18**, 6.
4 $Cp*_2ZrPh_2$ has been previously reported. See: (*a*) H. S. Tung and C. H. Brubaker, Jr., *Inorg. Chim. Acta*, 1981, **52**, 197; (*b*) L. E. Schock, C. P. Brock and T. J. Marks, *Organometallics*, 1987, **6**, 232.
5 The molecular structures of all new compounds reported in this paper have been determined by single crystal X-ray diffraction.
  $[Me_2Si(C_5Me_4)_2]Zr(Ph)Cl$, $C_{26}H_{35}ClSiZr$, monoclinic, $a = 9.6955(4)$ Å, $b = 12.4482(6)$ Å, $c = 20.4091(9)$ Å, $\beta = 91.194(1)°$, $V = 2462.7(2)$ Å^3, $P2_1/c$, $Z = 4$, $T = 203$ K, $\mu = 0.614$ mm^{-1}, R1 = 0.0320, 5689 reflections.
  $[Me_2Si(C_5Me_4)_2]ZrPh_2$, $C_{35}H_{43}SiZr$, triclinic, $a = 9.899(1)$ Å, $b = 11.497(2)$ Å, $c = 13.928(2)$ Å, $\alpha = 74.67(1)°$, $\beta = 79.25(1)°$, $\gamma = 86.97(1)°$, $V = 1501.9(4)$ Å^3, $P\bar{1}$, $Z = 2$, $T = 298$ K, $\mu = 0.427$ mm^{-1}, R1 = 0.0401, 5130 reflections.
  $Cp*_2Zr(Ph)Cl$, $C_{26}H_{35}ClZr$, triclinic, $a = 8.4788(4)$ Å, $b = 16.1860(8)$ Å, $c = 17.4483(9)$ Å, $\alpha = 89.919(1)°$, $\beta = 85.415(1)°$, $\gamma = 83.084(1)°$, $V = 2369.5(2)$ Å^3, $P\bar{1}$, $Z = 4$, $T = 203$ K, $\mu = 0.586$ mm^{-1}, R1 = 0.0441, 10126 reflections.
  $Cp*_2ZrPh_2$, $C_{32}H_{40}Zr$, monoclinic, $a = 9.3667(1)$ Å, $b = 16.310(2)$ Å, $c = 34.803(4)$ Å, $\beta = 92.765(2)°$, $V = 5310(1)$ Å^3, $P2_1/c$, $Z = 8$, $T = 203$ K, $\mu = 0.431$ mm^{-1}, R1 = 0.0520, 12213 reflections.
  $Cp*_2ZrPh(H)$, $C_{26}H_{36}Zr$, monoclinic, $a = 10.2338(5)$ Å, $b = 13.7292(7)$ Å, $c = 17.2395(9)$ Å, $\beta = 105.576(1)°$, $V = 2333.2(2)$ Å^3, $P2_1/c$, $Z = 4$, $T = 203$ K, $\mu = 0.479$ mm^{-1}, R1 = 0.0410, 5335 reflections.
  $[Me_2Si(C_5Me_4)_2]Zr(\eta^2\text{-}C_6H_4CH_2CH_2)$, $C_{28}H_{38}SiZr$, monoclinic, $a = 10.475(1)$ Å, $b = 13.998(1)$ Å, $c = 16.784(2)$ Å, $\beta = 100.838(2)°$, $V = 2417.1(4)$ Å^3, $P2_1/n$, $Z = 4$, $T = 208$ K, $\mu = 0.517$ mm^{-1}, R1 = 0.0454, 5587 reflections.
  $[Me_2Si(C_5Me_4)_2]Zr(\eta^3\text{-}C,N,N\text{-}C_6H_4\{C(CH_2)NC(Me)=NH\})$, $C_{30}H_{40}N_2SiZr$, triclinic, $a = 9.4411(5)$ Å, $b = 10.2964(6)$ Å, $c = 14.6641(8)$ Å, $\alpha = 83.578(1)°$, $\beta = 78.987(1)°$, $\gamma = 74.495(1)°$, $V = 1345.5(1)$ Å^3, $P\bar{1}$, $Z = 2$, $T = 223$ K, $\mu = 0.474$ mm^{-1}, R1 = 0.0438, 5989 reflections.
  $Cp*_2Zr[\eta^2\text{-}C,N\text{-}C_6H_4\{C(Me)=N\}]$, $C_{28}H_{37}NZr$, triclinic, $a = 8.7032(7)$ Å, $b = 9.6822(8)$ Å, $c = 15.812(1)$ Å, $\alpha = 89.326(1)°$, $\beta = 79.892(2)°$, $\gamma = 70.091(1)°$, $V = 1231.7(2)$ Å^3, $P\bar{1}$, $Z = 2$, $T = 223$ K, $\mu = 0.460$ mm^{-1}, R1 = 0.0470, 5018 reflections. CCDC reference number 186/2213. See http://www.rsc.org/suppdata/dt/b0/b005117i/ for crystallographic files in .cif format.
6 For the molecular structure of Cp_2ZrPh_2, see: W. Clegg, L. Horsburgh, D. M. Lindsay and R. E. Mulvey, *Acta Crystallogr., Sect. C*, 1998, **54**, 315.
7 For other studies concerned with M–aryl rotational barriers as studied by ^{1}H NMR spectroscopy, see: (*a*) P. Courtot, R. Pichon, J. Y. Salaun and L. Toupet, *Can. J. Chem.*, 1991, **69**, 661; (*b*) J. Jeffery, M. F. Lappert, N. T. Luong-Thi, J. L Atwood and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 1978, 1081; (*c*) P. R. Sharp, D. Astruc and R. R. Schrock, *J. Organomet. Chem.*, 1979, **182**, 477; (*d*) W. D. Jones and F. J. Feher, *Inorg. Chem.*, 1984, **23**, 2376.
8 See, for example: J. C. W. Lohrenz, M. Bühl, M. Weber and W. Thiel, *J. Organomet. Chem.*, 1999, **592**, 11 and references therein.
9 $[Me_2Si(C_5Me_4)_2]Zr(Ph)H$: $\Delta G^\ddagger = 12.8(2)$ kcal mol^{-1}, $k = 3(1) \times 10^3$ s^{-1}. $[Me_2Si(C_5Me_4)_2]Zr(Ph)Cl$: $\Delta G^\ddagger = 15.2(1)$ kcal mol^{-1}, $k = 5(1) \times 10^1$ s^{-1}. $[Me_2Si(C_5Me_4)_2]ZrPh_2$: $\Delta G^\ddagger = 13.9(1)$ kcal mol^{-1}, $k = 4(1) \times 10^2$ s^{-1}. $Cp*_2ZrPh_2$: $\Delta G^\ddagger = 17.5(1)$, $k = 9(2) \times 10^{-1}$ s^{-1}. All values at 25 °C determined from a $\Delta G^\ddagger$ *versus* T fit using KINPAR (J. R. Norton, personal communication).
10 It should be noted, however, that although $Cp*_2Zr(Ph)Cl$ exhibits no coalescence behavior, a small temperature dependence of the chemical shifts is observed.
11 For further comparison, the rotational barrier ($\Delta G^\ddagger$) in $(C_5Me_4H)_2$-$Zr(Ph)Cl$ is 20.3 kcal mol^{-1} (unspecified temperature). See reference 7*a*.
12 It is also worth noting that π-interactions may play an additional role in influencing the barrier to rotation. Specifically, π-donation to Zr would be a maximum when the phenyl ring is perpendicular to the equatorial plane, and this stabilizing interaction would be expected to be more influential for the more electron deficient *ansa* system. It would also be expected to provide a more important contribution to lowering the barrier for $[Me_2Si(C_5Me_4)_2]Zr(Ph)H$ than for $[Me_2Si(C_5Me_4)_2]Zr(Ph)Cl$, since π-donation from Cl in the latter complex would effectively compete with that from the phenyl.
13 See, for example: (*a*) S. L. Buchwald, A. Sayers, B. T. Watson and J. C. Dewan, *Tetrahedron Lett.*, 1987, **28**, 3245; (*b*) S. L. Buchwald, B. T. Watson, R. T. Lum and W. A. Nugent, *J. Am. Chem. Soc.*, 1987, **109**, 7137.
14 An additional distinction between the two systems is that thermolysis of $Cp*_2ZrPh_2$ in the absence of a trap generates the fulvene complex $Cp*(C_5Me_4CH_2)ZrPh$ (reference 4*b*), whereas only small quantities of $[Me_2Si(C_5Me_4)(C_5Me_3CH_2)]ZrPh$ may be

observed under comparable conditions. The titanium counterpart has, nevertheless, been isolated (reference 3*j*).

15 For other examples of zirconocene–benzyne trapping by C_2H_4, see: (*a*) G. Erker and K. Kropp, *J. Organomet. Chem.*, 1980, **194**, 45; (*b*) G. Erker and K. Kropp, *J. Am. Chem. Soc.*, 1979, **101**, 3659; (*c*) K. Kropp and G. Erker, *Organometallics*, 1982, **1**, 1246.

16 The mechanism for formation of $[Me_2Si(C_5Me_4)_2]Zr[\eta^3\text{-}C,N,N\text{-}C_6H_4\{C(CH_2)NC(Me)=NH\}]$ may involve a 1,3-hydrogen shift within the mono insertion product $[Me_2Si(C_5Me_4)_2]Zr[\eta^2\text{-}C,N\text{-}C_6H_4\{C(Me)=N\}]$. 1,3-Hydrogen shifts of this type have precedence.

See: S. A. Cohen and J. E. Bercaw, *Organometallics*, 1985, **4**, 1006.

17 Rate constants for elimination of benzene from $Cp*_2ZrPh_2$ at 40 °C: C_2H_4 trap, $k = 2.4(1) \times 10^{-6}$ s^{-1}; MeCN trap, $k = 2.4(1) \times 10^{-6}$ s^{-1}. Marks has reported rate constants for elimination of benzene from $Cp*_2ZrPh_2$ over the range 50–104 °C (reference 4*b*). These data predict a rate constant of $3.6(3) \times 10^{-6}$ s^{-1} at 40 °C (KINPAR). The rate constant comparisons between $[Me_2Si(C_5Me_4)_2]ZrPh_2$ and $Cp*_2ZrPh_2$ reported here are for "side-by-side" kinetics samples in order to minimize systematic error.