The synthesis and structure of $[Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_5H_3Bu^t{}_2)X]$

Marco M. Corradi, David J. Duncalf, Gerard A. Lawless* and Martin P. Waugh

The Chemistry Laboratory, School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ

Reaction of 1 equiv. of $KC_5H_3Bu^t{}_2$ with $[Zr(\eta\text{-}C_5H_5)_2X_2]$ affords $[Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_5H_3Bu^t{}_2)X]$ (X = Cl 1, Br 2); the molecular structure, and solid- and solution-state ^{13}C NMR data are presented.

There is considerable interest in the catalysis of alkene polymerisation by Zr-based metallocenes. Overwhelming evidence exists supporting the proposal that cationic 14 electron metallocene alkyls $[Zr(\eta\text{-}C_5H_5)_2R]^+$ are the active species.[1–3] Two steps which are crucial to the proposed mechanism are (*i*) the binding of the alkene to the Zr centre and (*ii*) its subsequent insertion into the Zr–R bond. Given that for ethene the entire insertion process may be as fast as 70–170 fs,[4] it is hardly surprising that no examples of a π complex of an alkene and $[Zr(\eta\text{-}C_5H_5)_2R]^+$ have been structurally characterised, despite the synthesis of an ever increasing number of such cations. We now report that this η^2 coordination mode is observable when an alkene may act as a three-electron donor. We present as evidence the structure and ^{13}C NMR spectroscopic data for **2**.

The reaction of $KC_5H_3Bu^t{}_2$ with $[Zr(\eta\text{-}C_5H_5)_2X_2]$ in toluene or thf yields **1** and **2** respectively.† The molecular structure of **2** was determined‡ (Fig. 1). The η^2 coordination mode of the $^-C_5H_3Bu^t{}_2$ is evident from a comparison of the Zr–C(4) and Zr–C(5) bond lengths [2.490(3), 2.539(3) Å, respectively] with those for Zr–C(1), Zr–C(2) and Zr–C(3) [3.462(4), 3.834(5), 3.368(5) Å, respectively]. Zr, Br, C(4) and C(5) are coplanar to within 0.0165 Å. The M(1)–Zr–C(4) and M(1)–Zr–C(5) angles are 118(3) and 107.7(3)° respectively while the corresponding M(2)–Zr–C(4) and M(2)–Zr–C(5) angles are 108.2(3) and 98.6(3)° respectively. The M(1)–Zr–M(2) angle is unexceptional at 128.6(4). The size and asymmetry of the Zr–C(4) and Zr–C(5) interactions are in good agreement with those calculated for the ethene complex $\{Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_2H_4)Me\}$ (2.50, 2.72 Å).[5] **2** may be formulated as a cyclopentadienyl adduct of a 14-electron Zr cation such as $[Zr(\eta\text{-}C_5H_4Bu^t)_2\{CH_2C(Me)C(Me)C(Me)CH_2\}]$[6] or $[Zr(\eta\text{-}C_5H_4Bu^t)_2\{OCMe_2CH_2CH_2CHCH_2\}]$,[7] [for which the η^2 Zr–C bond lengths are 2.602(7)–2.759(7) and 2.68(2), 2.89(2) Å respectively]. In this model the resulting anionic charge is delocalised on C(1), C(2) and C(3) (Scheme 1, **a**). The combination of such anionic and cationic centres within a neutral molecule has been recently demonstrated.[8] The high-frequency shifts exhibited in the ^{13}C NMR spectra of the β, C(1) and C(3) resonances and the corresponding low-frequency shift for C(2) (δ 170.6 and 87.6 respectively, for **2**) indicate, however, that a cationic formulation for C(1) and C(3) is more appropriate (Scheme 1, **b**–**d**). Thus the $^-C_5H_3Bu^t{}_2$ groups of **1** and **2** act as three-electron donors to 15-electron Zr centres resulting in 18-electron complexes. A similar bonding model has been previously proposed to account for the η^2-bonding in $[Ti(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_5H_5)]$.[9] The stability of this coordination mode requires both the availability of a third electron and the concomitant formation of a stable β cationic carbon centre. The Zr–C(4) and Zr–C(5) bond lengths compare well with those reported for the η^2 coordinated butadiene of $[Zr(\eta\text{-}C_5H_5)_2\{\mu\text{-}(1,2\text{-}\eta^2\text{-}Zr):(4\text{-}\eta^1\text{-}Al)\text{-}C_4H_6\}(\mu\text{-}Cl)AlCl_2]$[10] [2.348(2), 2.510(2) Å] and indenyl groups of the *ansa*-bridged systems $[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$ [2.587(8), 2.497(8) Å] and $[Zr\{(CH_2)_5C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$[11] [2.508(5), 2.564(4) Å]. The latter is characterised by a low-frequency ^{13}C NMR shift.§ For $[Zr\{(CH_2)_5C(\eta\text{-}C_5H_5)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$, $[Zr\{Me_2C(\eta\text{-}C_5H_4)(\eta^2\text{-}C_9H_6)\}(\eta\text{-}C_5H_5)Cl]$ and $[Zr(\eta\text{-}C_5H_5)_2\{\mu\text{-}(1,2\text{-}\eta^2\text{-}Zr):(4\text{-}\eta^1\text{-}Al)\text{-}C_4H_6\}(\mu\text{-}Cl)AlCl_2]$ similar shifts have been noted. The long Zr–Br(1), 2.672(1) Å, is also consistent with an 18-electron configuration. A solid-state ^{13}C NMR study of **2** confirmed that the η^2-coordination

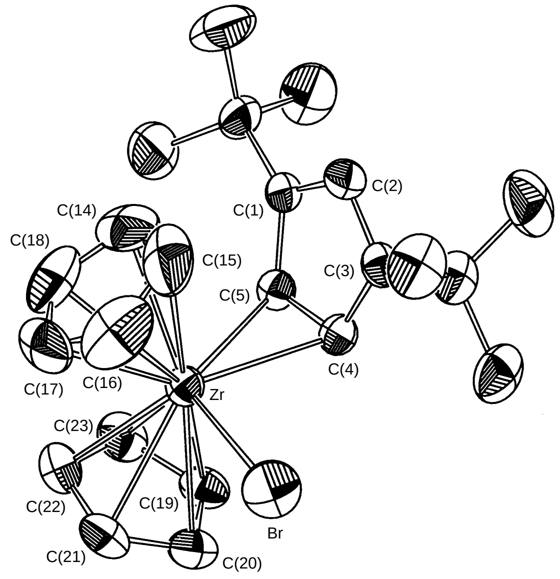
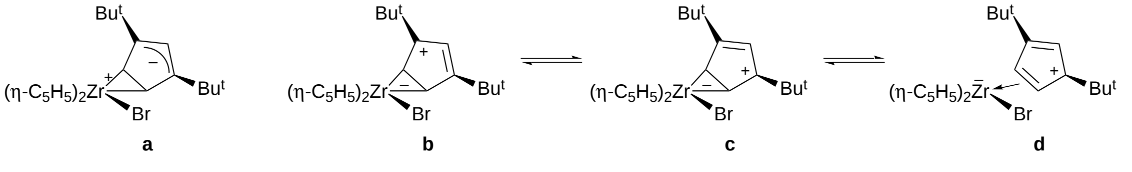


Fig. 1 The molecular structure of $[Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_5H_3Bu^t{}_2)Br]$ **2** and atom numbering scheme with selected bond lengths (Å) and angles (°): Zr–C(1) 3.462(4), Zr–C(2) 3.834(5), Zr–C(3) 3.368(5), Zr–C(4) 2.490(5), Zr–C(5) 2.539(3), Zr–Br 2.672(1), Zr–M(1) 2.21(1), Zr–M(2) 2.24(1), M(1)–Zr–C(4) 118.0(3), M(1)–Zr–C(5) 107.7(3), M(2)–Zr–C(4) 108.2(3), M(2)–Zr–C(5) 98.6(3), M(1)–Zr–M(2) 128.6(4), M(1) denotes the centroid of the ring C(14)–C(18), M(2) denotes the centroid of the ring C(19)–C(23)



Scheme 1 Resonance structures for **2**

mode of the $^{-}C_5H_3Bu^t{}_2$ group is retained in toluene solution at 243 K, as all ^{13}C resonances, C(1)–C(5) are inequivalent. Upon warming to 297 K, however, C(4) and C(5) mutually exchange as do C(1) and C(3). The exchange mechanism may involve either η^2 to η^1 or η^2 to η^5 rearrangements.¶ We favour the latter for **2**, as the former would be extremely unfavourable sterically due to the β-Bu^t substituents, and the twenty electron count associated with such an η^5 rearrangement has precedence in $[Zr(\eta\text{-}C_5H_5)_3(\eta^1\text{-}C_5H_5)]$.[12] For non-cyclopentadienyl based η^2 systems, clearly the former will be of greater importance. A comparison of the ^{13}C NMR data for **1** and **2** corroborates the presence of an η^2 bonding mode for the $^{-}C_5H_3Bu^t{}_2$ ligand of **1**, also. Initial studies indicate that both **1** and **2** are inactive as ethene polymerisation catalysts although the addition of MAO does produce an active system. Finally, a similar three electron interaction between say, ethene or propene, and a 14-electron Zr centre would sufficiently destabilize the corresponding metallocycle permitting facile insertion into a neighbouring Zr–C bond. Furthermore the tacticity of the resulting polymer would be dependent on the rate of insertion in comparison to the rate of η^2 to η^1 exchange.

We thank EPSRC (M. M. C., D. J. D., M. P. W.) for financial support.

Footnotes

† *Syntheses*: $[Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_5H_3Bu^t{}_2)Cl]$. To a Schlenk tube containing $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ (2.84 g, 9.72 mmol) and $KC_5H_3Bu^t{}_2$ (2.1 g, 9.72 mmol) was added 200 ml of dry, degassed toluene. The reaction mixture was stirred for 72 h during which time a gradual colour change from yellow to dark red was observed. After this time the toluene solution was filtered from the off-white precipitate and the toluene removed *in vacuo* to yield **1** as an orange powder, 85.5% (3.6 g, 8.31 mmol). Recrystallisation of **1** from toluene afforded dark orange platelets unsuitable for single-crystal diffraction. Mp (decomp.) 167–169 °C. ^1H NMR ($CDCl_3$, 400.13 MHz) δ 6.05 (s, 10 H) 5.96 [t, 1 H, $^4J(^1H–^1H)$ 1.75 Hz], 5.50 [d, 2 H, $^4J(^1H–^1H)$ 1.75 Hz], 1.28 (s, 18 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.61 MHz) δ 170.2, 115.9 [$^1J(^{13}C–^1H)$ 158 Hz], 113.5 [$^1J(^{13}C–^1H)$ 174 Hz], 88.0 [$^1J(^{13}C–^1H)$ 158 Hz], 34.3, 31.9 [$^1J(^{13}C–^1H)$ 126 Hz].

$[Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_5H_3Bu^t{}_2)Br]$. To a Schlenk tube containing $[Zr(\eta\text{-}C_5H_5)_2Br_2]$ (0.92 g, 2.41 mmol) in thf (40 ml) was added $KC_5H_3Bu^t{}_2$ (0.71 g, 3.29 mmol) slurried in thf (50 ml). An immediate colour change from pale yellow to orange was observed. After stirring for a further 12 h the thf was removed *in vacuo* and the resulting orange powder extracted into hexane. The solvent was removed *in vacuo* to yield **2** as an orange powder, 78%, (0.9 g, 1.88 mmol). Recrystallisation of **2** from toluene afforded dark orange platelets suitable for single-crystal diffraction. Mp (decomp) 139.8 °C. ^1H NMR (C_7D_8, 400.13 MHz) δ 5.96 [t, 1 H, $^4J(^1H–^1H)$ 1.75 Hz], 5.69 (s, 10 H), 5.38 [d, 2 H, $^4J(^1H–^1H)$ 1.75 Hz], 1.33 (s, 18 H); $^{13}C\{^1H\}$ NMR (C_7D_8, 100.61 MHz) δ 170.6, 115.9, 112.8, 87.6, 34.4, 31.6; $^{13}C\{^1H\}$ NMR (C_7D_8, 100.61 MHz, 243 K) δ 172.6, 169.9, 115.4, 112.8, 93.8, 80.9, 35.2, 34.1, 31.7; $^{13}C\{^1H\}$ CP MAS NMR (100.61 MHz) δ 178, 174, 122, 117, 98, 85, 44, 38, 36.

‡ *Crystal data* $[Zr(\eta\text{-}C_5H_5)_2(\eta^2\text{-}C_5H_3Bu^t{}_2)Br]$, $C_{30}H_{39}BrZr$. Crystallographic measurements were made on a Siemens three-circle diffractometer equipped with a SMART CCD area detector, using Mo-Kα radiation, $\lambda = 0.71073$ Å, $2\theta < 57.18°$, $\mu = 2.103\ mm^{-1}$. The heavy atoms were located by the Patterson interpretation of SHELXTL and refined on F^2 by a full-matrix least-squares procedure. Anisotropic thermal parameters were used for all non-H atoms. H atoms were given fixed isotropic temperature factors with the positions constrained by the heavy-atom geometry in the refinement. A molecule of toluene is present within the asymmetric unit. $T = 220(2)$ K. Specimen $0.40 \times 0.35 \times 0.20$ mm, $M = 570.74$, monoclinic, space group $P2_1/n$, $a = 11.082(2)$, $b = 10.224(2)$, $c = 21.675(4)$ Å, $\beta = 96.02(3)°$, $U = 2442.3(8)$ Å^3, $D_c = 1.554$ g cm^{-3}, μ(Mo-Kα) = 2.103 mm^{-1}, $Z = 4$. For reflections with $1.89 < \theta < 28.59°$, $R(F) = 0.0544$ for 4570 observed reflections $[I > 2\sigma(I)]$ and $wR(F^2) = 0.1162$ for all 5724 reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/331.

§ The paramagnetic shift associated with these cations compared with those associated with classical trialkyl carbonium species is diminished due to the resonance stabilisation of the positive charge.

¶ Initial analysis of this lineshape at 298, 273, 253, 243, 233 K yields $\Delta H^\ddagger = 66$ kJ mol^{-1}, $\Delta S^\ddagger = 68$ J K^{-1} mol^{-1}. At 298 K $\Delta G^\ddagger = 46$ kJ mol^{-1}.

References

1 R. F. Jordan, *Adv. Organomet. Chem.*, 1991, **32**, 325.
2 A. S. Guram and R. F. Jordan, in *Comprehensive Organometallic Chemistry*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 4, p. 589.
3 M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255.
4 R. J. Meier, G. H. J. van Doremaele, S. Larlori and F. Buda, *J. Am. Chem. Soc.*, 1994, **116**, 7274.
5 T. K. Woo, L. Fan and T. Ziegler, *Organometallics*, 1994, **13**, 432.
6 A. D. Horton and A. G. Orpen, *Organometallics*, 1992, **11**, 8.
7 Z. Wu, R. F. Jordan and J. L. Petersen, *J. Am. Chem. Soc.*, 1995, **117**, 5867.
8 B. Temme, G. Erker, J. Karl, H. Luftmann, R. Frohlich and S. Kotila, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1755.
9 C. R. Lucas, M. L. H. Green, R. Forder and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1973, 97.
10 G. Erker, R. Noe, C. Kruger and S. Werner, *Organometallics*, 1992, **11**, 4174.
11 G. M. Diamond, M. L. H. Green, P. Mountford, N. A. Popham and A. Chernega, *J. Chem. Soc., Dalton Trans.*, 1996, 921.
12 R. D. Rodgers, R. Vann Bynum and J. L. Atwood, *J. Am. Chem. Soc.*, 1978, **100**, 3238.

Received, 27th September 1996; Com. 6/06638K