ChemComm

Evidence for zirconocene dications in Kaminsky type catalysts

Malcolm L. H. Green and Jörg Saßmannshausen

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR. E-mail: malcolm.green@icl.ox.ac.uk

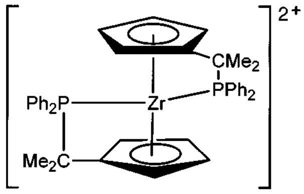
Received (in Cambridge, UK) 22nd October 1998, Accepted 25th November 1998

Low temperature NMR studies indicate that the dicationic salts $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2]^{2+}[MeB(C_6F_5)_3]^-{}_2$ and $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2]^{2+}$ $[MeB(C_6F_5)_3]_2{}^-$ are formed when the neutral compounds $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Me_2]$ and $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2Me_2]$ and $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Me_2]$ are treated with 2 equivalents of $B(C_6F_5)_3$.

Cationic zirconocene complexes are of great interest as catalysts for hydrogenation,[1] isomerisation[2] and especially olefin polymerisation reactions.[3–8] The donor free 14-electron $[Zr(\eta\text{-}C_5H_5)_2R]^+$ cation is believed to be an active species in Ziegler–Natta type olefin polymerisation. However, they are extremely reactive and not isolable. The corresponding 16-electron donor stabilised cations of the type $[Zr(\eta\text{-}C_5H_5)_2R(L)]^+$ or the 18-electron cations $[Zr(\eta\text{-}C_5H_5)_2R(L)_2]^+$ are known where the donor ligands are nitriles, cyclic ethers[9–16] or tertiaryphosphines.[17]

Recently, we described the reactions of the compounds $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2Ph)Me_2]$ **1**, $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)Me_2]$ **2**, $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Me_2]$ **3**, and $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2Me_2]$ **4** with the Lewis acid $B(C_6F_5)_3$ which gave monocations, *e.g.* $[Zr(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4CMe_2Ph)Me_2]^+[MeB(C_6F_5)_3]^-$. The NMR evidence indicated there was intramolecular phenyl coordination to the cationic zirconium centre.[18] These complexes may be regarded as models of solvated cationic zirconocene species presumed to be present in toluene solutions of Kaminsky type olefin polymerisation catalysts.

Metallocene dications $[M(\eta\text{-}C_5H_5)_2L_2]^{2+}X^-{}_2$ have been reported,[19–22] (M = Ti, Zr; L = H_2O or MeCN; X = $CF_3SO_4{}^-$ $ClO_4{}^-$, $BPh_4{}^-$) and notably recent work by Erker and coworkers (**A**).[17]



$2\ MeB(C_6F_5)_3{}^-$

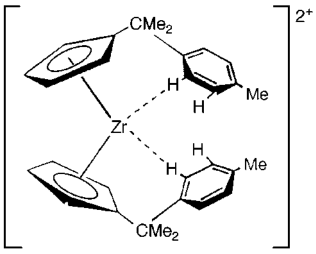
A

Here we report evidence for the formation of dicationic zirconocenes stabilised by metal-arene interactions.

The previously described[18] compounds $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Me_2]$ **3** and $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2Me_2]$ **4** were treated with 2 equivalents of $B(C_6F_5)_3$ in CD_2Cl_2. The reactions were monitored by NMR spectroscopy. At −60 °C the reaction of **4** proceeds cleanly to give a single product, which the NMR data below clearly indicate is the salt $[Zr(\eta\text{-}C_5H_4CMe_2C_6H_4Me\text{-}p)_2]^{2+}[MeB(C_6F_5)_3]_2{}^-$ **5**.

The NMR spectroscopic evidence supporting the structure proposed for **5** is:

(i) A broad signal at δ 0.40 in the ^1H NMR spectrum and a corresponding broad signal at δ 9.58 in the ^{13}C NMR spectrum which can be assigned to the separate $[MeB(C_6F_5)_3]^-$ anion.[23] This observation is further strengthened by the chemical shift difference $\Delta\delta(m,p\text{-}F)$ between the *m*- and *p*-^{19}F of the anion.[24] Values of $\Delta\delta(m,p\text{-}F)$ between 3 and 6 ppm indicate coordination of the anion to the zirconium centre whilst values < 3 ppm indicate non coordination of the anion. The observed value of $\Delta\delta$ 2.8 ppm corresponds to a solvent-separated ion pair.



$2\ MeB(C_6F_5)_3{}^-$

5

(ii) The absence of a Zr*Me* signal in ^1H and ^{13}C NMR together with the integration of the $[\mathit{Me}B(C_6F_5)_3]^-$ anion (6H) indicates the abstraction of *two* rather than *one* methide group from the metal.

(iii) Unlike the reaction product of **4** with *one* equivalent of $B(C_6F_5)_3$ [18] the dication **5** possesses a C_2 axis, which renders the two phenyl groups and the two cyclopentadienyl ligands equivalent. Therefore only four signals for the phenyl group and four signals for the cyclopentadienyl ligand are observed in the ^1H NMR spectrum. Furthermore, unlike the reaction product of **4** with 1 equivalent of $B(C_6F_5)_3$, the signals for the cyclopentadienyl hydrogens are *sharp*, as seen in Fig. 1 showing the ^1H NMR spectrum of the reaction product of **4** with 1 equivalent of $B(C_6F_5)_3$ and Fig. 2, the spectrum of the dication **5** formed with 2 equivalents of $B(C_6F_5)_3$.

(iv) One of the proton signals of each of the cyclopentadienyl ligands of **5** is significantly shifted *upfield* (δ 3.70) which can be explained by the magnetic anisotropy of the phenyl group. In contrast to the ^1H NMR spectrum of the reaction product of $[Zr(\eta\text{-}C_5H_5)(C_5H_4CMe_2C_6H_4Me\text{-}p)Me_2]$ **2** and 1 equivalent of $B(C_6F_5)_3$, where one of the cyclopentadienyl hydrogen signals is shifted *downfield* (δ 6.94), due to a *deshielding* effect of the phenyl ring,

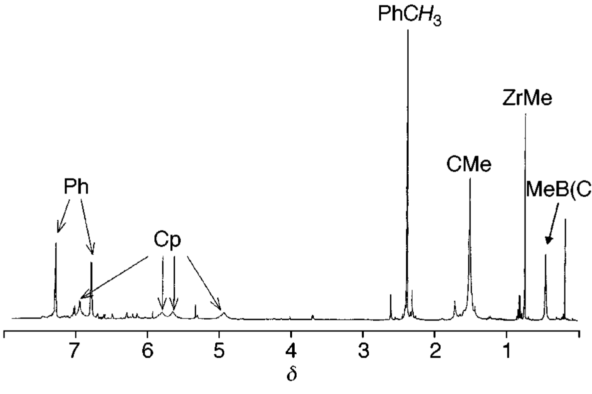


Fig. 1 ^1H NMR spectrum of **4** with 1 equivalent of $B(C_6F_5)_3$ at −60 °C.

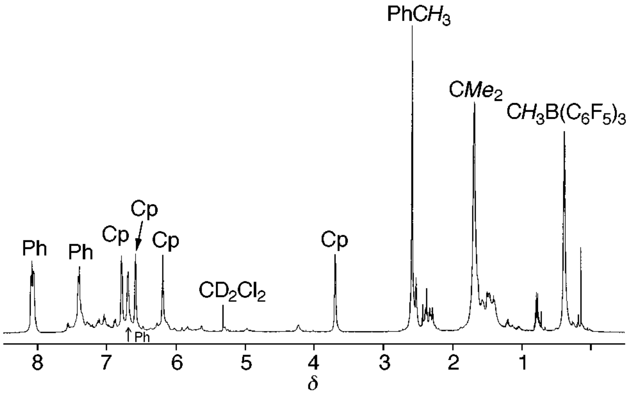


Fig. 2 ^1H NMR spectrum of **4** with 2 equivalents of $B(C_6F_5)_3$ at −60 °C.

here the phenyl ring is located slightly differently probably due to the more sterically crowded environment around the zirconium metal and the cyclopentadienyl hydrogen encounters a *shielding* effect. Interesting is the corresponding ^{13}C signal, which is observed at δ 128.43 (assignment *via* CH correlation spectroscopy).

(v) Similar to the ^1H NMR of the reaction product of **2** with 1 equivalent $B(C_6F_5)_3$, one of the phenyl hydrogen signals is shifted *upfield* to δ 6.69 (*cf.* Fig. 2). This can be assigned to a hydrogen coordinated, or close to, to the zirconium centre. Similar observations of upfield shifts of coordinated phenyl-hydrogen have been made before,[25] notably by Horton *et al.*[26]

(vi) Warming the sample of **5** to −40 °C changes the NMR spectra giving new peaks which are identical to the previously described monocation $[Zr(\eta\text{-}(C_5H_4CMe_2C_6H_4Me\text{-}p)_2Me]^+[MeB(C_6F_5)_3]^-$ [18] and the presence of excess $B(C_6F_5)_3$ also appears in the ^{19}F NMR spectrum. This reaction is reversible and on re-cooling the sample to −60 °C the original spectrum is restored. Further warming above −40 °C increases the amount of the monocation, however some decomposition products are also observed.

The reaction between $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2Me_2]$ **3** and 2 equivalents of $B(C_6F_5)_3$ also gives a product with similar properties to **5**. However it is less soluble than **5** and this restricts investigations at −60 °C. Nonetheless the data are fully consistent with the proposed formulation of the product $[Zr(\eta\text{-}C_5H_4CMe_2Ph)_2]^{2+}$ $[MeB(C_6F_5)_3]^-{}_2$ **6**. Crystals of **6** were not suitable for X-ray crystallography due to twinning. The NMR data for the compounds **5** and **6** are available as supplementary data (see http://www.rsc.org/suppdata/cc/1999/115).

In conclusion the reaction of **3** and **4** with 2 equivalents of $B(C_6F_5)_3$ leads to the formation of dicationic complexes **5** and **6**. These complexes have been characterised by NMR spectroscopy and elemental analysis. The dications of **5** and **6** can be viewed as a model for the cationic species $[Zr(\eta\text{-}C_5H_5)_2(\text{solvent})_2]^{2+}$ and these may well be present in aromatic solutions of Kaminsky-type zirconocene olefin polymerisation catalysts systems.

We would like to thank Dr L. H. Doerrer and Dr D. Häußinger for helpful discussions.

Notes and references

1 Y. Qian, G. Li and Y. Huang, *J. Mol. Catal.*, 1989, **54**, L19.
2 Y. Qian, J. Lu and W. Xu, *J. Mol. Catal.*, 1986, **34**, 31.
3 M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 225.
4 P. C. Möhring, N. Vlachakis, N. E. Grimmer and N. J. Coville, *J. Organomet. Chem.*, 1994, **483**, 159.
5 T. Ushioda, M. L. H. Green, J. Haggitt and X. Yan, *J. Organomet. Chem.*,1996, **518**, 155.
6 W. Kaminsky and M. Arndt, *Adv. Polym. Sci.*, 1995, **127**, 144.
7 H.-H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger and R. Waymouth, *Angew. Chem.*, 1995, **107**, 1255; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143.
8 M. Aulbach and F. Küber, *Chem. Z*, 1994, **28**, 197.
9 R. F. Jordan, C. S. Bajgur, R. Willet and B. Scott, *J. Am. Chem. Soc.*, 1986, **108**, 7410.
10 R. F. Jordan, R. E. LaPointe, C. S. Bajgur, S. F. Echols and R. Willet, *J. Am. Chem. Soc.*, 1987, **109**, 4111.
11 R. F. Jordan, R. E. LaPointe, N. C. Baenzinger and G. D. Hinch, *Organometallics*, 1990, **9**, 1539.
12 J. J. W. Eshuis, Y. Y. Tan, A. Meetsma and J. H. Teuben, *Organometallics*, 1992, **11**, 362.
13 J. J. W. Eshuis, Y. Y. Tan, A. Meetsma and J. H. Teuben, *J. Mol. Catal.*, 1990, **62**, 277.
14 D. M. Amorose, R. P. Lee and J. L. Petersen, *Organometallics*, 1991, **10**, 2191.
15 Y. W. Alelyunas, R. F. Jordan, S. F. Echols, S. L. Borkowsky and P. K. Bradley, *Organometallics*, 1991, **10**, 1406.
16 S. L. Borkowsky, R. F. Jordan and G. D. Hinch, *Organometallics*, 1991, **10**, 1268.
17 B. E. Bosch, G. Erker, R. Fröhlich and O. Meyer, *Organometallics*, 1997, **16**, 5449.
18 L. H. Doerrer, D. Häußinger, M. L. H. Green and J. Saßmannshausen, *J. Chem. Soc., Dalton Trans.*, submitted.
19 Zirconium: L = H_2O, X = $CF_3SO_4^-$, ClO_4^-: W. Lasser and U. Thewalt, *J. Organomet. Chem.*, 1986, **311**, 69; L = H_2O, X = $CF_3SO_4^-$: U. Thewalt and W. Lasser, *J. Organomet. Chem.*, 1984, **276**, 341; L = CH_3CN, X = BPh_4^-: R. F. Jordan and S. F. Echols, *Inorg. Chem.*, 1987, **26**, 383.
20 P. N. Billinger, P. P. K. Claire, H. Collins and G. R. Willey, *Inorg. Chim. Acta*, 1988, **149**, 63.
21 Titanium: L = THF, X = $Co(CO)_4$: J. S. Merola, K.S. Campo, R. A. Gentile and M. A. Modrick, *Inorg. Chim. Acta*, 1989, **165**, 87; L = THF; X = AsF_6: P. Gowik and T. Klapötke, *J. Organomet. Chem.*, 1989, **372**, 33; L = THF, MeCN; X = AsF_6:T. Klapötke, *Polyhedron*, 1989, **8**, 311; L = bipy, X = $CF_3SO_4^-$: U. Thewalt and K. Berhalter, *J. Organomet. Chem.*, 1986, **302**, 193; U. Thewalt and H.-P. Klein, *J. Organomet. Chem.*, 1980, **194**, 297; B. Honold and U. Thewalt *J. Organomet. Chem.*, 1986, **316**, 291; K. Berhalter and U. Thewalt, *J. Organomet. Chem.*, 1987, **322**, 123.
22 For Diels–Alder reactions: T. K. Hollis, N. P. Robinson and B. Bosnich, *J. Am. Chem. Soc.*, 1992, **114**, 5464.
23 D. J. Gillis, M. J. Tudoret and M. C. Baird, *J. Am. Chem. Soc.*, 1993, **115**, 2543.
24 A. D. Horton, J. deWith, J. v. d. Linden and H. v. d. Weg, *Organometallics*, 1996, **15**, 2672.
25 G. G. Hlatky, H. W. Turner and R. R. Eckman, *J. Am. Chem. Soc.*, 1989, **111**, 2728.
26 A. D. Horton and J. H. G. Frijns, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1152.

Communication 8/08197B