

olefin polymerization.^[1] Weakly coordinating anions are required to minimize the ion-pairing interactions, which are crucial in determining the properties of the resulting polymeric materials and the characteristics of the polymerization processes. These counteranions frequently contain fluoro-organic moieties to reduce interactions by dissipating the negative charge and decreasing the nucleophilicity. However, $[\text{RB}(\text{C}_6\text{F}_5)_3]^-$ groups can still be responsible for deactivation processes.

The carbon–fluorine bond is the strongest and least reactive bond found in organic molecules and its activation is a chemical challenge,^[2] whereas the boron–carbon bond is more reactive and C_6F_5 transfer to the cationic metal center is the most commonly observed deactivation pathway for $[\text{L}_2\text{MR}^+][\text{RB}(\text{C}_6\text{F}_5)_3]^-$ catalysts.^[3] Ziegler and co-workers recently reported calculations on different competing thermal deactivation pathways for the $[\text{L}_2\text{MR}^+][\text{RB}(\text{C}_6\text{F}_5)_3]^-$ ion pair.^[4]

We previously reported^[5] Group 4 metal complexes with doubly silyl-amido-bridged chelating tridentate ligands. Complexes of this type, when activated with methylaluminoxane (MAO), are efficient catalysts for ethene polymerization despite generating cationic species free of the alkyl group required for the insertion reaction. Similar observations were made for a related singly silyl- η -amido bridged zirconium dicyclopentadienyl compound^[6] and for cationic Co^I species,^[7] which also show activity towards ethene polymerization.

We report herein the reaction pathways that are followed when the cationic complexes $[\text{Zr}\{\text{C}_5\text{H}_3[\text{SiMe}_2(\eta^1\text{-NtBu})_2\}_2][\text{RB}(\text{C}_6\text{F}_5)_3]$ ($[\text{“Zr”}][\text{RB}(\text{C}_6\text{F}_5)_3]$, $\text{R} = \text{CH}_2\text{Ph}$ (**1**), Me (**2**)) are heated in the presence of triphenylphosphane. Using reported synthetic methods,^[5a] we synthesized the cationic zirconium compounds **1** and **2**^[8] as barely soluble oils or oily solids by adding one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to C_6D_6 solutions of the corresponding alkyl complexes $[\text{“Zr”R}]$ in sealed NMR tubes. The same products were observed when similar reactions were carried out on a preparative scale. Complexes **1** and **2** were thermally stable upon heating them in solution up to 80°C for several hours. However, the addition of one equivalent of PPh_3 to C_6D_6 solutions of **1** and **2** at room temperature gave a suspension of an insoluble solid, which upon heating at 80°C for several days afforded a mixture that contained compounds $[\text{“Zr”F}]$ (**3**) and $[\text{“Zr”}(\text{C}_6\text{F}_5)]$ (**4**). The insoluble solid was separated by filtration, suspended in fresh C_6D_6 , and heated at 80°C for 7 days to give compound **3**.

Compounds **3** and **4** were generated by the transfer of F and C_6F_5 groups, respectively, to the Zr atoms of the starting complexes although their formation and structure were only confirmed when they were obtained by alternative synthetic methods. So compound **3** was prepared by treating $[\text{“Zr”}(\text{CH}_2\text{Ph})]$ with FSnPh_3 ^[9] in toluene at 80°C for 5 h; the product was characterized by elemental analysis and NMR spectroscopy.^[10] The resultant $(\text{PhCH}_2)\text{SnPh}_3$ was also identified by ^1H NMR spectroscopy [$\delta_{\text{CH}_2} = 2.81$ ppm (1s + 2d, 2H, $J_{\text{H,Sn}119} = 68$, $J_{\text{H,Sn}117} = 65$ Hz)].

The reaction of the same benzyl complex with the Lewis acid $\text{Al}(\text{C}_6\text{F}_5)_3$ proceeded at 25°C with abstraction of the benzyl ligand to give the cationic zirconium complex, $[\text{“Zr”}][(\text{PhCH}_2)\text{Al}(\text{C}_6\text{F}_5)_3]$, with simultaneous formation of a small amount of **4**. Quantitative C_6F_5 transfer was completed after

Ion Pairs

DOI: 10.1002/anie.200602694


Evidence of Fluoride Transfer from the Anion of $[\text{Zr}\{\text{C}_5\text{H}_3[\text{SiMe}_2(\eta^1\text{-NtBu})_2\}_2]^+[\text{RB}(\text{C}_6\text{F}_5)_3]^-$ Complexes to the Zirconocenium Cation**

Jesús Cano, María Sudupe, Pascual Royo,* and Marta E. G. Mosquera

Cationic Group 4 metal complexes of the type $[\text{L}_2\text{MR}^+]^+$ generated by activation of the corresponding dialkyl compounds with $\text{B}(\text{C}_6\text{F}_5)_3$ are active homogeneous catalysts for

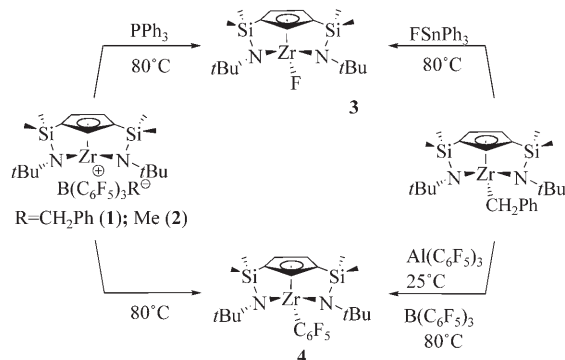
[*] Dr. J. Cano, M. Sudupe, Prof. P. Royo, Dr. M. E. G. Mosquera
Departamento de Química Inorgánica
Universidad de Alcalá
Campus Universitario, 28871 Alcalá de Henares (Spain)
Fax: (+34) 918-854-683
E-mail: pascual.royo@uah.es

[**] Financial support by the Spanish MEC (project MAT2004-02614) and DGUI/CM (program S/0505/PPQ-0328) is acknowledged.
 $\text{R} = \text{Me}, \text{CH}_2\text{Ph}$.

 Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

12 h to give **4** as the unique reaction product,^[11] which was isolated as a crystalline solid.

The chemical shifts in the ¹H NMR spectra for complexes **3** and **4** were identical to those observed for the same products isolated by thermal transformation of **1** and **2** in the presence of PPh₃, which demonstrates that they were formed by F and C₆F₅ transfer to the metal center, respectively (Scheme 1). A



Scheme 1. Thermal transformations observed for complexes **1** and **2**.

significant upfield shift of the signals arising from the *o*-fluorine atoms was observed in the ¹⁹F NMR spectrum of **4** ($\delta=109.1$ ppm) with respect to the corresponding signals observed for B(C₆F₅)₃ ($\delta=132.1$ ppm). The molecular structure of **4** was determined by X-ray diffraction.^[3d,12] The structure agrees with the spectroscopic data and shows clearly the C₆F₅ moiety coordinated to the metal center (see Supporting Information). The Zr coordination sphere is completed by the {C₅H₃[SiMe₂(η^1 -N*t*Bu)]₂} ligand with no other groups bonded to the Zr center. The precision of this study was limited by the poor quality of the crystal set.

Formation of an alkyl-bridged ion-pair system,^[3b] [“Zr”{ μ -RB(C₆F₅)₃}], could be responsible for the intramolecular B–C₆F₅ bond activation and the C₆F₅ transfer to the Zr center with elimination of the neutral borane, RB(C₆F₅)₂.^[13] This reaction is slow when the cationic complexes **1** and **2** are heated at 80°C for 7 days to give complex **4** (Scheme 1).

In the presence of a phosphane, a different deactivation process occurs by transfer of a *p*-fluoro substituent of one of the pentafluorophenyl borate rings to the Zr center. The decomposition of the zirconocenium cation [(1,2-Me₂C₅H₃)₂ZrMe][RB(C₆F₅)₃] has been reported^[3a,14] and two possible pathways for fluoride transfer,^[3a] both based on the same migration of C₆F₅ to the metal center with subsequent activation of the *o*-fluorine atom or direct fluoride migration to the zirconium cation, were proposed although no experimental evidence of the reaction mechanism was given. A similar fluoride transfer was reported very recently for the reaction of the dinuclear hydride complex [(*rac*-(*ebthi*)ZrH(μ -H))₂] with B(C₆F₅)₃.^[15]

The thermal fluoride transfer observed for complexes **1** and **2** may occur by nucleophilic addition of PPh₃ to the *p*-C–F bond of one of the electron-deficient C₆F₅ rings of the metal-coordinated alkylborate counteranion [RB(C₆F₅)₃][–] with immediate transfer of the generated fluoride to the

zirconocenium cation to give **3**.^[16] Supporting this proposal, we note that **4** is not converted into **3**. In addition, we were able to isolate a colorless single crystal of the μ -F complex [(“Zr”)₂(μ -F)][(PhCH₂)B(C₆F₅)₃] (**5**) from the mixture of compounds obtained when an equimolar mixture of **1** and PPh₃ was warmed at 50°C for 7 days.^[17] An X-ray diffraction study (Figure 1) revealed that **5** consists of a separate dinuclear cation, [(“Zr”)₂F]⁺, and the free [(PhCH₂)B(C₆F₅)₃][–] anion.

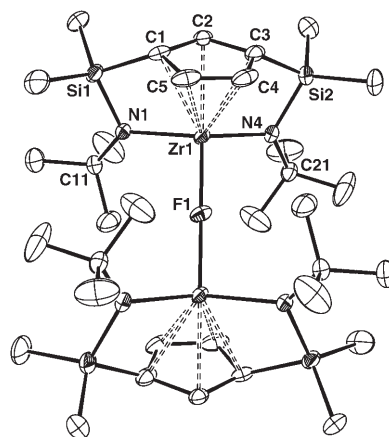


Figure 1. ORTEP view of **5** with thermal ellipsoids set at 30% probability. The complex crystallizes with two independent cations in the unit cell {Zr1-F1-Zr1#} and {Zr2-F2-Zr2#} (not shown). Only half of each cation is present in the asymmetric unit, the other half (Zr#) is generated in each case by crystallographic inversion. The separations Zr1-F1 and Zr2-F2 (2.1393(4), 2.1416(5) Å) are within the range for a Zr–F bond (2.02–2.29 Å). The Zr-F-Zr moiety is linear (180.000(8)° Zr1-F1-Zr1# and 180.000(1)° Zr2-F2-Zr2#), which agrees with results from other complexes with bridging fluorine atoms. The Cp rings are mutually *trans*. The anion is omitted for clarity.

Further confirmation of this reaction pathway was obtained by the isolation of the zwitterionic compound [4-Ph₃P]⁺[C₆F₄{BMe(C₆F₅)₂}][–] (**6**).^[18] Crystals of **6** suitable for X-ray diffraction studies were obtained when equimolar amounts of **2** and PPh₃ were heated at 80°C for 7 days. The molecular structure of compound **6** (Figure 2) demonstrates

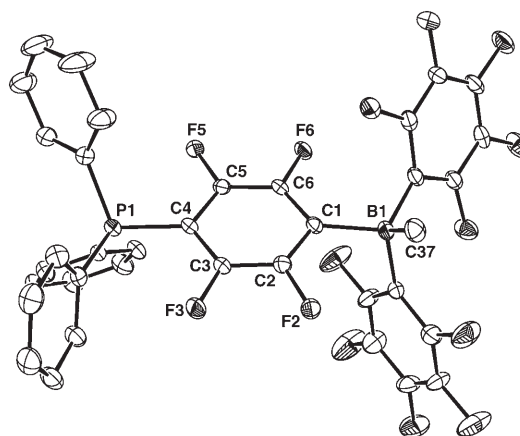


Figure 2. ORTEP view of **6** with thermal ellipsoids set at 30% probability. Both P–C (1.811(3) Å) and B–C (1.680(4) Å) interatomic distances are within the range for single bonds.

that the triphenylphosphonium and the methylbis(pentafluorophenyl)borate fragments are the *para*-substituents of the resulting tetrafluorophenyl activated ring.^[17]

In summary, we have found experimental evidence to support a reaction pathway involving direct fluoride migration to the zirconium cation without previous transfer of C₆F₅. It is noteworthy that the opening of the silyl–amido bridge was not observed in the course of these activations. Experiments with other donor ligands are in progress to investigate the conditions under which the ion pairs **1** and **2** may follow different decomposition routes and the possible mechanisms of these reactions.

Received: July 6, 2006

Published online: October 20, 2006

Keywords: homogeneous catalysis · ion pairs · polymerization · reaction mechanisms · zirconium

- [1] a) M. Bochmann, *J. Chem. Soc. Dalton Trans.* **1996**, 255; b) E. Y. X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 139; c) G. Erker, *Dalton Trans.* **2005**, 1883.
- [2] a) J. L. Kiplinger, T. G. Richmond, C. E. Osterberg, *Chem. Rev.* **1994**, *94*, 373; b) J. Burdeniuc, B. Jedlicka, R. H. Crabtree, *Chem. Ber.* **1997**, *130*, 145; c) T. G. Richmond, *Topics in Organometallic Chemistry, Vol. 3*, Springer, New York, **1999**, p. 243.
- [3] a) X. M. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1994**, *116*, 10015; b) T. Wondimagegn, Z. T. Xu, K. Vanka, T. Ziegler, *Organometallics* **2004**, *23*, 3847; c) T. J. Woodman, M. Thornton-Pett, M. Bochmann, *Chem. Commun.* **2001**, 329; d) V. Amo, R. Andres, E. de Jesús, F. J. de la Mata, J. C. Flores, R. Gómez, M. P. Gómez-Sal, J. F. C. Turner, *Organometallics* **2005**, *24*, 2331; e) R. Gómez, P. Gómez-Sal, P. A. del Real, P. Royo, *J. Organomet. Chem.* **1999**, 588, 22.
- [4] a) T. Wondimagegn, K. Vanka, Z. T. Xu, T. Ziegler, *Organometallics* **2004**, *23*, 2651; b) T. Wondimagegn, Z. T. Xu, K. Vanka, T. Ziegler, *Organometallics* **2005**, *24*, 2076.
- [5] a) J. Cano, P. Royo, M. Lanfranchi, M. A. Pellinghelli, A. Tiripicchio, *Angew. Chem.* **2001**, *113*, 2563; *Angew. Chem. Int. Ed.* **2001**, *40*, 2495; b) J. Cano, P. Royo, H. Jacobsen, O. Blacque, H. Berke, E. Herdtweck, *Eur. J. Inorg. Chem.* **2003**, 2463; c) M. Sudupe, J. Cano, P. Royo, E. Herdtweck, *Eur. J. Inorg. Chem.* **2004**, 3074; d) J. Cano, M. Sudupe, P. Royo, M. E. G. Mosquera, *Organometallics* **2005**, *24*, 2424.
- [6] J. Z. Jin, D. R. Wilson, E. Y. X. Chen, *Chem. Commun.* **2002**, 708.
- [7] a) V. C. Gibson, M. J. Humphries, K. P. Tellmann, D. F. Wass, A. J. P. White, D. J. Williams, *Chem. Commun.* **2001**, 2252; b) T. M. Kooistra, Q. Knijnenburg, J. M. M. Smits, A. D. Horton, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2001**, *113*, 4855; *Angew. Chem. Int. Ed.* **2001**, *40*, 4719; c) W. Steffen, T. Blömker, N. Kleigrew, G. Kehr, R. Fröhlich, G. Erker, *Chem. Commun.* **2004**, 1188; d) N. Kleigrew, W. Steffen, T. Blömker, G. Kehr, R. Fröhlich, B. Wibbeling, G. Erker, J. C. Wasilke, G. Wu, G. C. Bazan, *J. Am. Chem. Soc.* **2005**, *127*, 13955.
- [8] **2**: ¹H NMR (300 MHz, C₆D₆): δ = 0.21, 0.33 (2s, 2 × 6H, SiMe₂), 0.94 (s, 18H, NtBu), not observed (BCH₃), 6.31 (m, 1H, C₅H₃), 6.48 ppm (m, 2H, C₅H₃). ¹³C NMR (75 MHz, C₆D₆): δ = 1.5 (2 × SiMe₂), 34.8 (NCMe₃), 58.6 (NCMe₃), 127.5 (3 × C₅H₃), 136.5 ppm (4 × C₆F₅). ¹⁹F NMR (280 MHz, C₆D₆): δ = 132.1 (m, 2F, *o*-C₆F₅), 163.6 (m, 1F, *p*-C₆F₅), 167.2 ppm (m, 2F, *m*-C₆F₅). Elemental analysis (%) calcd: C 49.65, H 3.97, N 2.76; found: C 50.51, H 3.71, N 3.35.
- [9] H. Hatop, H. W. Roesky, T. Labahn, A. Fischer, H. G. Schmidt, M. Noltemeyer, *Organometallics* **2000**, *19*, 937.
- [10] **3**: ¹H NMR (300 MHz, C₆D₆): δ = 0.53, 0.61 (2s, 2 × 6H, SiMe₂), 1.31 (s, 18H, NtBu), 6.69 (m, 1H, C₅H₃), 6.88 ppm (m, 2H, C₅H₃). ¹³C NMR (75 MHz, C₆D₆): δ = 2.4, 5.1 (2 × SiMe₂), 36.4 (NCMe₃), 56.7 (NCMe₃), 120.7, 124.1, 127.7 ppm (3 × C₅H₃). ¹⁹F NMR (280 MHz, C₆D₆): δ = -24.9 ppm. Elemental analysis (%) calcd: C 47.28, H 7.70, N 6.49; found: C 47.90, H 7.11, N 6.36.
- [11] **4**: ¹H NMR (300 MHz, C₆D₆): δ = 0.45, 0.53 (2s, 2 × 6H, SiMe₂), 1.25 (s, 18H, NtBu), 6.37 (m, 1H, C₅H₃), 6.69 ppm (m, 2H, C₅H₃). ¹³C NMR (75 MHz, C₆D₆): δ = 1.9, 2.5 (2 × SiMe₂), 35.5 (NCMe₃), 57.2 (NCMe₃), 116.9, 124.4, 125.0 (3 × C₅H₃), 135.8, 139.1, 147.9, 150.1 ppm (4 × C₆F₅). ¹⁹F NMR (280 MHz, C₆D₆): δ = 109.1 (m, 2F, *o*-C₆F₅), 155.9 (m, 1F, *p*-C₆F₅), 162.4 ppm (m, 2F, *m*-C₆F₅). Elemental analysis (%) calcd: C 47.64, H 5.74, N 4.83; found: C 47.92, H 5.27, N 4.63.
- [12] a) V. Taberero, C. Maestre, G. Jiménez, T. Cuenca, C. R. de Arellano, *Organometallics* **2006**, *25*, 1723; b) K. Phomphrai, A. E. Fenwick, S. Sharma, P. E. Fanwick, J. M. Caruthers, W. N. Delgass, M. M. Abu-Omar, I. P. Rothwell, *Organometallics* **2006**, *25*, 214.
- [13] S. Dagorne, I. A. Guzei, M. P. Coles, R. F. Jordan, *J. Am. Chem. Soc.* **2000**, *122*, 274.
- [14] L. Jia, X. M. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 842.
- [15] P. Arndt, U. Jäger-Fiedler, M. Klahn, W. Baumann, A. Spannenberg, V. V. Burlakov, U. Rosenthal, *Angew. Chem.* **2006**, *118*, 4301; *Angew. Chem. Int. Ed.* **2006**, *45*, 4195; ebthi = 1,2-ethylene-1,1'-bis(η⁵-tetrahydroindenyl).
- [16] S. Döring, G. Erker, R. Fröhlich, O. Meyer, K. Bergander, *Organometallics* **1998**, *17*, 2183.
- [17] CCDC-613558 (**4**), CCDC-613223 (**5**), and CCDC-613224 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [18] **6**: ¹H NMR (300 MHz, C₆D₆): δ = 1.47 ppm (s, BMe); ¹³C NMR (75 MHz, C₆D₆): δ = 29.2 ppm (BMe); ¹⁹F NMR (280 MHz, C₆D₆): δ = 124.5, 128.4, 131.8, 162.5, 165.8 ppm (3 × C₆F₅, 2 × C₆F₄).