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Ziegler−Natta-like Olefin Oligomerization by Alkylzirconocene Cations in an Electrospray Ionization Tandem Mass Spectrometer

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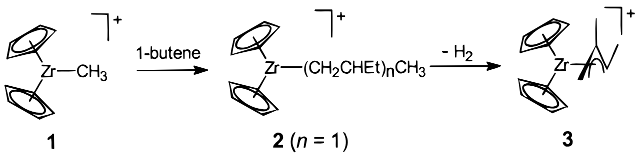
We report the direct observation of the addition of multiple olefinic units to isolated alkylzirconocene cations in the gas phase. The addition of 1-butene to the unsolvated cations occurs at a rate up to a few orders of magnitude slower than diffusion-controlled, which is still approximately 10^5 times faster than the corresponding solution-phase addition, for which the metallocene cation is part of an ion pair, often with one or more additional coordinating ligands (e.g., solvent). The observed gas-phase reaction corresponds to several propagation steps of a Ziegler−Natta polymerization,[1] which, while thoroughly investigated in solution with closely related homogeneous catalysts, has not been previously observed in mass spectrometric studies of isolated metallocene ions. The combination of electrospray ionization of known solution-phase catalysts and tandem mass spectrometry[2] opens new analytical, mechanistic, and even preparative possibilities.

The electrospray ionization[3,4] tandem mass spectrometric (ESI-MS/MS) experiment was performed in a modified Finnigan MAT TSQ-7000 mass spectrometer as described in our reports on gas-phase C−H activation[5] by $[CpIr(PMe_3)(CH_3)]^+$, oxo-transfer reactions[6] by $[O{=}Mn^V(salen)]^+$, olefin metathesis[7] by $[Cl_2Ru({=}CHPh)(Cy_2PCH_2CH_2NMe_3)]^+$, and reversible hydrogenation/dehydrogenation of olefins[8] by $[Rh(PMe_3)_2]^+$ ions. Stabile solutions of the tetrakis(pentafluorophenyl)borate salt of the methylzirconocene cation **1**, $[Cp_2ZrCH_3]^+$, suitable for electrospray, were prepared by treatment of a 10^{-3} M solution of $Cp_2Zr(CH_3)_2$ in acetonitrile with slightly less than 1 equiv of dimethylanilinium tetrakis(pentafluorophenyl)borate,[9] followed by 10-fold dilution with CH_2Cl_2. The solution was then electrosprayed with a "high" pressure, 10 mTorr of Ar, of thermalization gas in the first octopole region. The distribution and intensities of peaks in mass spectrum were extraordinarily sensitive to traces of water, oxygen, and other contaminants in the inlet system of the spectrometer. Electrospray of dilute CH_2Cl_2 solutions of $[Cp_2Zr(CH_3)(OTf)]^+$ was less successful due to difficulties in exclusion of traces of water and air during sample preparation and transfer. Traces of water invariably led to the appearance of large peaks consistent with oxygen-bridged binuclear complexes $[Cp_2Zr(L)O(L')ZrCp_2]^+$ with the additional ligands being methyl, acetonitrile, or triflate. Deuterium labeling of the original methylzirconocene triflate gave results consistent with the structures. Nevertheless, a dominant peak corresponding to ($\mathbf{1} + CH_3CN$) could be reproducibly observed. More severe desolvation conditions (higher tube lens potential) converted ($\mathbf{1} + CH_3CN$) to **1**, from which collision-induced dissociation (CID) in the second octopole gave loss of methyl. Use of 1-butene instead of Ar in the first octopole region and a tube lens potential set to produce **1** gave new peaks, prominent among which were the masses corresponding to **2** ($n = 1$) and **3**. The adduct **2** ($n = 1$) would be the product of insertion of the olefin into the Zr−C bond of **1**, while **3** would be the product arising from H_2 loss from **2**. Characterization of **2** by CID of the mass-selected ions in the second octopole gave the expected results. For **2** ($n = 1$), loss of H_2 was the predominant process when the gas pressure in the second octopole was low (below a few millitorr).



Mass selection of **2** ($n = 1$) in the first quadrupole and collision with more 1-butene (10 mTorr, near-zero collision energy) in the second octopole produced the daughter-ion mass spectrum shown in Figure 1. Although, as mentioned above, reactions in the first octopole gave complicated and variable distributions of products, presumably due to the multiplicity of species present, the reaction of mass-selected **2** ($n = 1$) in the second octopole was remarkably clean. Without doubt, addition of further units of the olefin has occurred, with **2** ($n = 1−3$) clearly visible and **2** ($n = 4$) present if the scale is magnified 10-fold. Reaction of **1** with isobutylene instead of 1-butene in the first octopole gives a prominent peak due to the addition product, with no accompanying loss of H_2 and only a small peak corresponding to CH_4 loss. Experiments with ethylene and propylene gave similar results, although H_2 loss from the analogue of **2** ($n = 1$) was more difficult to suppress. For ethylene, propylene, 1-butene, and isobutylene, a novel alkene dehydrogenation reaction could also be observed for **1**, but not for **2**.

The present results constitute the first observation of multiple olefin additions to a gas-phase metallocene cation that also performs Ziegler−Natta polymerization in solution.[10] While electrospray mass spectrometry has been used to study catalytic reactions,[11] reports in the literature have been limited to analysis of solutions which were catalytically active. The gas-phase ions themselves have been never shown to be competent as catalysts in those studies. Previous attempts to observe the Ziegler−Natta polymerization reaction in ICR experiments,[12] most notably by Richardson, Eyler, and co-workers,[13,14] invariably led to production of **3**. For the wide range of α-olefins investigated by Richardson and Eyler, the analogue of **3** (or a product derived from it) was the sole observed product of reaction of **1** with olefins bearing a *β*-hydrogen. In the case of other α-olefins lacking a *β*-hydrogen, e.g. isobutylene and α-methylstyrene, Richardson and Eyler report exclusive conversion to products coming from loss

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(1) A recent collection of reviews covers progress in the field: *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer: New York, 1995.

(2) For a recent monograph, see: *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, The Netherlands, 1996.

(3) The basic electrospray source for mass spectrometry is described by: Whitehouse, C. M.; Dreyer, R. N.; Yamashita, M.; Fenn, J. B. *Anal. Chem.* **1985**, *57*, 675.

(4) A complete monograph on the technique is: *Electrospray Ionization Mass Spectrometry*; Cole, R. D., Ed.; John Wiley: New York, 1997.

(5) Hinderling, C.; Plattner, D. A.; Chen, P. *Angew. Chem.* **1997**, *109*, 272. Hinderling, C.; Feichtinger, D.; Plattner, D. A.; Chen, P. *J. Am. Chem. Soc.* **1997**, *119*, 10793.

(6) Feichtinger, D.; Plattner, D. A. *Angew. Chem.* **1997**, *109*, 1796.

(7) Hinderling, C.; Adlhart, C.; Chen, P. *Angew. Chem.*, in press.

(8) Kim, Y. M.; Chen, P. Manuscript in preparation.

(9) Generous donation of a sample of dimethylanilinium tetrakis(pentafluorophenyl)borate by Dr. Marc O. Kristen, BASF, is gratefully acknowledged.

(10) There is one report of solution-phase polymerization of isobutylene by laser-vaporized metals, but the identity of the active species in solution is unclear: Vann, W.; Samy El-Shall, M. *J. Am. Chem. Soc.* **1993**, *115*, 4385.

(11) Dzhabieva, Z. M.; Kozlovskii, V. P.; Shul'ga, Yu. M.; Dodonov, A. F.; Belov, G. P. *Russ. Chem. Bull.* **1996**, *45*, 474. Saf, R.; Schitter, R.; Mirtl, C.; Stelzer, F.; Hummel, K. *Macromolecules* **1996**, *29*, 7651. Aliprantis, A. O.; Canary, J. W. *J. Am. Chem. Soc.* **1994**, *116*, 6985. Wilson, S. R.; Wu, Y. *Organometallics* **1993**, *12*, 1478. Alpin, R. T.; Baldwin, J. E.; Schofield, C. J.; Waley, S. G. *FEBS Lett.* **1990**, *277*, 212.

(12) Uppal, J. S.; Johnson, D. E.; Staley, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 508.

(13) Christ, C. S.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1988**, *110*, 4038. Christ, C. S.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 596. Alameddin, N. G.; Ryan, M. F.; Eyler, J. R.; Siedle, A. R.; Richardson, D. E. *Organometallics* **1995**, *14*, 5005.

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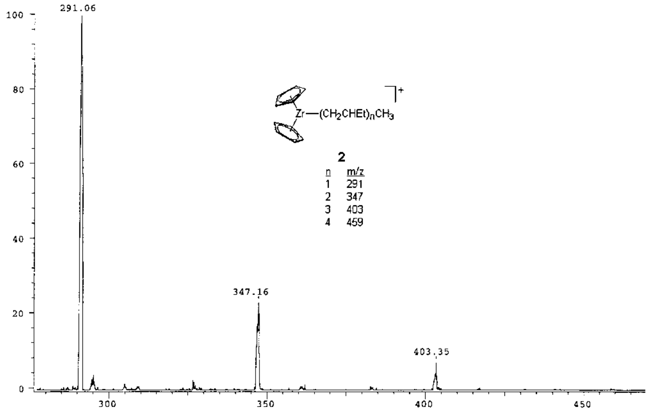

Figure 1. Daughter-ion spectrum taken by electrospray of $[Cp_2Zr\text{-}CH_3]^{+-}B(C_6F_5)_4$, in dilute CH_2Cl_2/CH_3CN solution, thermalization and reaction in octopole 1 with 1-butene, mass selection of $m/z = 291$ in quadrupole 1, further reaction with more 1-butene in octopole 2 under near-zero energy, multiple-collision conditions, and finally mass analysis in quadrupole 2. A small peak at $m/z = 459$ can be seen if the scale is enlarged. Addition of up to four units of 1-butene is evident, clearly showing that the Ziegler−Natta polymerization reaction proceeds in the mass spectrometer with completely unsolvated complexes. Note the absence of H_2 loss from the intermediate ions.

of CH_4. The H_2-loss and the CH_4-loss products, assumed to have π-allyl structures, are catalytically inactive in further Ziegler−Natta steps. Accordingly, addition of more than one unit of an olefin was not seen. On the other hand, reaction of olefins with laser-vaporized Ti^+ and Al^+ in high-pressure mass spectrometric experiments[15] gave multiple additions, frequently accompanied by extensive dehydrogenation. There are, however, no solution-phase analogues for these atomic cations or their reactions.

Richardson and Eyler attribute the difference between their results and the condensed-phase results to incomplete thermalization of the intermediate ions, e.g. **2**, in the very low-pressure environment of an ICR spectrometer cell. In the present results, the gas-phase reaction resembles that for the condensed phase. The complete absence of H_2 loss from **2** ($n > 1$) indicates that the increased density-of-states associated with the growing alkyl side chain sufficiently slows the H_2-loss reaction, allowing collisional stabilization of the adduct and/or further addition reactions in the present instrument, where higher pressures and shorter reaction times work against chemically activated reactions. The alkene dehydrogenation reaction, also a chemically activated reaction, is similarly quenched by higher pressure and longer chain lengths.

The most notable difference between the present gas-phase results and the analogous reaction in solution is the large rate acceleration. A kinetic study of the Cp_2ZrCl_2/MAO system in solution-phase olefin polymerization found $k_p = 168-1670\ M^{-1}\ s^{-1}$ at 70 °C with an absolute upper-bound of $k_p \leq 5000\ M^{-1}\ s^{-1}$ with 75−100% of the available zirconium available in a catalytically active form.[16] To estimate the second-order rate constant for addition of 1-butene to $[Cp_2ZrR]^+$ in the present work, ion mobility in the octopole collision cell at "high" pressure, i.e. tens of millitorr, was modeled using a Monte Carlo simulation assuming a Langevin cross section[17] for the collision rate in the presence of the radiofrequency field. The collision cell was found to behave similarly to an ion drift cell, with the incident ions undergoing (depending on conditions) up to 100 000 collisions with gas molecules before exit. The model was validated by measured ion residence times in the collision cell[18] and found to give excellent quantitative agreement. Comparing the measured product yield with the number of collisions gave a reaction probability per collision of about 10^{-3}, which means that the 1-butene addition to $[Cp_2ZrR]^+$ occurs with a second-order rate constant of $k \sim 10^8-10^9\ M^{-1}\ s^{-1}$ (at 70 °C), which is entirely consistent with a composite rate constant $k_{\mathbf{1} \rightarrow [\mathbf{2}\ (n=1)] \rightarrow \mathbf{3}} = (3.5 \pm 0.4) \times 10^8\ M^{-1}\ s^{-1}$ reported by Richardson et al.[14] The result is qualitatively reasonable on two grounds: (i) Lacking a counterion or any charge donation by even a weakly coordinating solvent molecule, and furthermore lacking any preequilibria to form the active species,[19] the isolated cations should be intrinsically more reactive. (ii) The electrostatic interaction,[20] either ion dipole or ion induced-dipole, which is screened out in solution, effectively lowers the activation energy of a bimolecular ion−molecule reaction by perhaps 10 kcal/mol relative to the same reaction in solution. Taken from another point of view, the high rate of olefin addition is completely normal for an ion−molecule reaction and therefore deserves no more than a passing comment. This argument, however, underestimates the potential presented by comparisons of the gas-phase and solution-phase results for closely related ions, especially when the solution-phase activation barrier is large enough so that it is not completely eliminated in the gas phase. Furthermore, one may venture to predict that the polymerization of a high pressure of an α-olefin (atmospheric pressure instead of the current ~ 10 mTorr) with an electrosprayed Ziegler−Natta catalyst may result in a product with a very narrow distribution of chain lengths due to "self-solvation" at a long enough chain length. An indication that this effect may already be operative for relatively short oligomers can be seen in the relative integrated peak intensities[21] of **2** ($n = 2-4$) in Figure 1. Kinetic modeling of the reaction of **2** ($n = 1$) with 1-butene as a series of consecutive reactions for a fixed total time finds that the rate constant drops off sharply, with $(k_{[\mathbf{2}\ (n=2) \rightarrow \mathbf{2}\ (n=3)]})/(k_{[\mathbf{2}\ (n=3) \rightarrow \mathbf{2}\ (n=4)]}) \gg 4$ measured reproducibly on independent runs. Whether the dropoff in rate is due to a nonspecific interaction with the growing chain, i.e. a continuum dielectric effect, or to specific intramolecular interactions such as the C−H agostic interactions currently believed to underlie stereoselection by chiral metallocene catalysts[22] is uncertain but will be the object of further work.

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[14] Richardson, D. E.; Alameddin, N. G.; Ryan, M. F.; Hayes, T.; Eyler, J. R.; Siedle, A. R. *J. Am. Chem. Soc.* **1996**, *118*, 11244.

[15] Guo, B. C.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 6152. Daly, G. M.; Samy El-Shall, M. *J. Phys. Chem.* **1994**, *98*, 696. Daly, G. M.; Samy El-Shall, M. *J. Phys. Chem.* **1995**, *99*, 5283. Bjarnason, A.; Ridge, D. P. *J. Phys. Chem.* **1996**, *100*, 15118.

[16] Chien, J. C. W.; Wang, B. P. *J. Polym. Sci., Part A* **1990**, *28*, 15.

[17] Comparisons of Langevin cross sections with those from better theory or from experiment indicate errors of perhaps a factor of 2 in σ: Su, T.; Bowers, M. T. In *Gas-Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 1, p 83.

[18] Simultaneous scanning of the quadrupoles before and after the octopole collision cell and measurement of ion loss as a function of delay between the two quadrupoles gives the residence time, which can be directly compared to the Monte Carlo model results. The measured residence times are on the order of several milliseconds for collision gas pressures on the order of several millitorr.

[19] The importance of counterions, solvent effects, and ion pairing has been discussed: Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1. Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634. Beck, S.; Prosenc, M. H.; Brintzinger, H. H.; Goretski, R.; Herfert, N.; Fink, G. *J. Mol. Catal. A* **1996**, *111*, 67.

[20] Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891. Olmstead, W. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 4219. Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715. Pellerite, M. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 5993. Sharma, S.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 19. Caldwell, G.; Magnera, T. F.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 959. McMahon, T. B.; Heinis, T.; Nicol, G.; Hovey, J. K.; Kebarle, P. *J. Am. Chem. Soc.* **1988**, *110*, 7591.

[21] The peak at $m/z = 291$, assigned as **2** ($n = 1$), was mass-selected in the first quadrupole. Any other species with the same mass would come through as well and add a nonreactive component to its intensity. Also, any nonthermal effects would be greatest for **2** ($n = 1$), so the comparison was done for only **2** ($n = 2-4$).

[22] Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. An alkyl chain long enough to easily provide a strong agostic interaction would contribute to a rate reduction by introducing an additional preequilibrium.