following p2 and, as a result, does not provide information about the lifetime of the emitting species. This emission spectrum compares well with those reported for TPM• in frozen solutions at 90 K[30] and at 77 K[11] and therefore represents the first such measurement for TPM• in room temperature solution.

Preliminary results of time-resolved absorption experiments, obtained for TPM• generated from *tert*-butyl triphenylperacetate, which utilized the two sets of pulse sequences described for TPMCl revealed that the spectral evolution of this system is analogous to that recorded for TPM• generated from TPMCl. These results indicate that the presence of Cl• is not necessary for the generation of the 440-nm band.

Our current tentative assignment of the species responsible for the 440-nm absorption band observed at early times after 355-nm excitation of TPM• is a $D_n \leftarrow D_1$ transition of TPM•. A firm assignment awaits the results of experiments that are in progress. Among these experiments is the measurement of the emission lifetime associated with the spectrum depicted in Figure 2, so that a comparison can be made with the decay time of the 440-nm absorption band. Also underway are attempts to probe the behavior of TPM•–Cl• pairs in solvents that react less rapidly with Cl•.

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Gas-Phase Reactions of Bis(η^5-cyclopentadienyl)methylzirconium(1+) with Dihydrogen, Ethylene, and Propylene

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Electron deficient d^0 transition-metal and d^0f^n lanthanide complexes have shown a wide range of reactivities including the catalysis of alkene polymerization[1-6] and the metatheses of both saturated and unsaturated hydrocarbons.[7,8] The synthetic utility of these reactions has generated considerable interest in this area of C–C bond-forming and C–H bond-activating processes. Our interest in directly comparing solution-phase and gas-phase reactions at metal centers[9] led us to investigate the ion/molecule reactions of a cationic d^0 zirconium(IV) alkyl complex, $[Cp_2ZrCH_3]^+$ (**1**; Cp = cyclopentadienyl), which has also been studied in solution by Jordan and co-workers.[4] To our knowledge this is the first direct comparison of an isolated cationic homogeneous mononuclear ethylene polymerization catalyst to its gas-phase analogue.

We applied Fourier transform ion cyclotron resonance mass spectrometry[10] to study the gas-phase reactions of $[Cp_2ZrCH_3]^+$. Electron impact (11 eV) on $Cp_2Zr(CH_3)_2$ ($P \approx 10^{-8}$–10^{-7} Torr) yields predominantly $[Cp_2ZrCH_3]^+$ and $[Cp_2Zr]^+$. A RF pulse is used to eject $[Cp_2Zr]^+$ from the ICR cell, thereby isolating $[Cp_2ZrCH_3]^+$ for ion/molecule reaction studies with substrates ($P \approx 10^{-6}$ Torr). Collision-induced dissociation[11,12] (CID) experiments on **1** show the loss of CH_3, strongly implying a metal–methyl structure. Binuclear zirconium ion formation limits the study of ion/molecule reactions to those with rate constants in the 3×10^9–5×10^{11} $M^{-1}\,s^{-1}$ (2×10^{-12}–8×10^{-10} $cm^3\,s^{-1} \approx k_{collision}$)[13] range. No evidence was found for the involvement of the Cp rings in the reactions examined; therefore, the transformations below are assumed to retain the Cp_2Zr unit.

Reaction of **1** with D_2 is observed with formation of a deuteride complex exclusively, proceeding at ~375 K with a second-order rate constant $k = 3.7 \times 10^9$ $M^{-1}\,s^{-1}$ (6.1×10^{-12} $cm^3\,s^{-1}$, efficiency = $k/k_{collision} \approx 0.006$) (eq 1). This result is consistent with a

$$[Cp_2ZrCH_3]^+ + D_2 \rightarrow [Cp_2ZrD]^+ + CH_3D \qquad (1)$$

four-membered transition state used to describe the metathesis reactions of other d^0f^n metal complexes.[6,7,14] The reverse of eq 1 is not observed, and, unlike the bond strengths determined in the gas phase for most bare metal–methyl and metal–hydride ions,[15] eq 1 indicates $D[Cp_2Zr–CH_3]^+ < D[Cp_2Zr–H]^+$. Clearly, addition of ligands to the zirconium ion leads to a gas-phase bond strength order typical for condensed-phase-ligated transition-metal complexes.[16]

Jordan et al.[4] have observed ethylene polymerization by $[Cp_2ZrCH_3(THF)]^+$ in CH_2Cl_2 solution, but polymerization of ethylene by the solvent-free ion **1** is not observed in the gas phase. Instead, interaction of ethylene with **1** is followed by an intramolecular decomposition of the apparent insertion product, producing a metal–allyl complex, $[Cp_2ZrC_3H_5]^+$ (**2**), and H_2 (eq 2).

$$Cp_2ZrCH_3^+ + C_2H_4 \rightarrow Cp_2ZrC_3H_5^{\bullet +} + H_2 \qquad (2)$$

Reactions of **1** with ethylene and propylene follow the stoichiometry $\mathbf{1} + C_nH_m \rightarrow [Cp_2ZrC_{n+1}H_{m+1}]^+ + H_2$. CID experiments performed on **2** are consistent with allyl formation, as fragments corresponding only to the loss of one and two molecules of H_2 as well as C_3H_5 are produced. The absence of further reaction of **2** with ethylene is also consistent with an η^3-allyl structure. Ballard and co-workers[21] reported the absence of activity toward polymerization of ethylene for the closely related complex $Cp_2ZrCl(C_3H_5)$.

Reaction of **1** with ethylene does not produce $[Cp_2ZrH]^+$; thus, β-hydride abstraction followed by alkene elimination[1,17] is not observed in the gas phase. Insufficient information is available on the polymer formed in the Jordan system to determine the significance of reaction 2 in the solution polymerization of ethylene by **1**.[18]

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(1) Borr, J. *Ziegler–Natta Catalysts and Polymerizations*; Academic: New York, 1979.

(2) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

(3) (a) Soto, J.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4479. (b) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377.

(4) Jordan, R. F.; Chandrasekhar, S. B.; Willet, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410.

(5) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.

(6) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(7) (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1.

(8) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491.

(9) (a) Richardson, D. E.; Christ, C. S.; Sharpe, P.; Eyler, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3894. (b) Richardson, D. E.; Christ, C. S.; Sharpe, P.; Eyler, J. R. *Organometallics* **1987**, *6*, 1819.

(10) For recent reviews of the Fourier transform ion cyclotron resonance technique, see: (a) Baykut, G.; Eyler, J. R. *Trends Anal. Chem.* **1986**, *5*, 44. (b) Marshall, A. G. *Acc. Chem. Res.* **1985**, *18*, 316. (c) Wanczek, K. P. *Int. J. Mass. Spec. Ion. Proc.* **1984**, *60*, 11. (d) Gross, M. L.; Rempel, D. C. *Science (Washington, D.C.)* **1984**, *226*, 261.

(11) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736.

(12) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.

(13) $k_{collision}$ is the Langevin collision rate constant. See, e.g.: Su, T.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Vol. I, p 84.

(14) Jordan, R. F.; Chandrasekhar, S. B.; Dasher, W. E.; Rheingold, A. L. *Organmetallics* **1987**, *6*, 1041.

(15) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627.

(16) (a) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415. (b) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (c) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79.

(17) Tait, P. J. T. In *Coordination Polymerization*; Chien, J. C. W., Ed.; Academic Press: New York, 1975; p 155.

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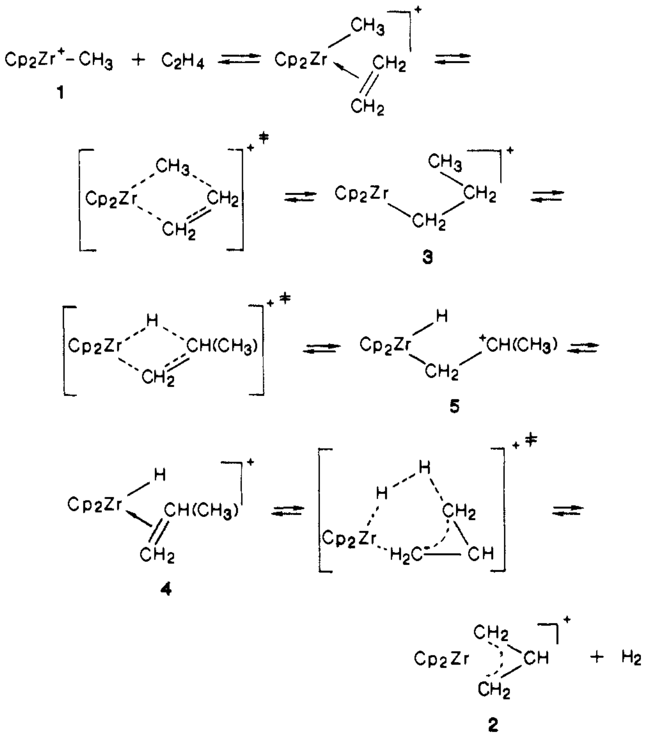
Scheme I



An investigation of mechanistic aspects of the ethylene reaction by using C_2D_4 shows a significant amount of hydrogen–deuterium scrambling, eliminating 11% D_2, 74% HD, and 15% H_2, which is somewhat different from the statistical distribution of 28.6% D_2, 57.1% HD, and 14.3% H_2. A similar experiment with $[Cl_2TiCH_3]^+$ and C_2D_4 was performed by Uppal et al.,[19] and, in contrast to our result, at least 85% HD is lost. Reaction of $[Cp_2ZrD]^+$ with propylene produces a degree of scrambling very close to the statistical distribution of 28.6% HD to 71.4% H_2 loss (eq 3).

$$\mathrm{Cp_2ZrD^+ + C_3H_6} \to \begin{cases} \mathrm{Cp_2ZrC_3H_5^+ + HD} & (23\%) \\ \mathrm{Cp_2ZrC_3H_4D^+ + H_2} & (77\%) \end{cases} \qquad (3)$$

A possible mechanism for the reaction of **1** with ethylene to produce **2** is given in Scheme I. Scrambling probably occurs during interconversion of the insertion product **3** and the hydride intermediate **4** possibly via successive hydride shifts along the three-carbon framework of intermediate **5**.

Lack of thermochemical data for the zirconium–carbon and zirconium–allyl bond energies prevents the complete determination of the enthalpies of the proposed insertion reactions and insertion/elimination processes. However, an indication of the relative exothermicities of the insertion reactions is given by the enthalpies for the general reaction $^\bullet CH_3 + C_nH_m \to {}^\bullet C_{n+1}H_{m+3}$ ($\Delta H^{0\prime}$).[20] When applied to the reactions of **1** with ethylene and propylene, $\Delta H^{0\prime}$ values are −23.5 and −24.1 kcal mol^{-1}, respectively. The net exothermicity is reduced when H_2 is eliminated, e.g., $^\bullet CH_3 + C_2H_4 \to {}^\bullet C_3H_5 + H_2$ ($\Delta H^0 = -4.6$ kcal mol^{-1}), but this is compensated by the expected stability of the zirconium–allyl product.

Our observations suggest that intermediates of polymerization and metathesis reactions also occur in the solvent-free reactions of an electron deficient d^0 transition-metal complex ion. Complexes formed following elimination of H_2 from these chemically activated[22] gas-phase intermediates are possible products of chain termination in the polymerization of alkenes by solvated d^0f^n metal catalysts. In addition, the formation of allyl species in solution and the possible role of this process in introducing unsaturation into polymers warrants further investigation.

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(18) Jordan, R. F., private communication.

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

(20) Values for $\Delta H^{0\prime}$ are calculated from published experimental values or are derived from group additivities (Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279. O'Neal, H. E.; Benson, S. W. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II.

(21) Ballard, D. G. H.; Jones, E.; Medinger, T.; Pioli, A. J. P *Die Makromolekulare Chemie* **1971**, *148*, 175.

(22) (a) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: New York, 1972. (b) Forst, N. *Theory of Unimolecular Reactions*; Academic: New York, 1973.

Palladium-Catalyzed Coupling of Vinyl Epoxides with Organostannanes

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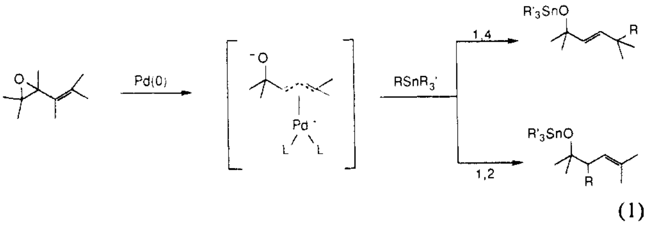
The palladium-catalyzed alkylation of vinyl epoxides by soft nucleophiles derived from carbon acids is both regioselective (1,4-addition) and stereospecific, with alkylation occurring at the π-allyl face opposite to that bonded to palladium.[1,2] The mild, neutral reaction conditions are ideally suited for the synthesis of a variety of organic compounds.[3] Because 1,3-dienemonoepoxides readily undergo oxidative addition to palladium(0), they should also catalytically couple with organostannanes (eq 1), allowing alkylation by the variety of organic groups available with the tin reagents.[4]



(1)

Indeed this reaction takes place with a weakly ligated palladium catalyst, $(CH_3CN)_2PdCl_2$,[5] in a polar solvent such as DMF at ambient temperature to give good yields of coupled product (Table

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[1] For a survey of π-allyl Pd complexes and reactivity patterns, see: (a) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (b) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, W. E., Eds.; Pergamon Press: New York, 1982; Vol. 8, p 799.

[2] (a) Trost, B. M.; Molander, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 5969. (b) Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575.

[3] (a) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1981**, *103*, 5972. (b) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6112; **1983**, *105*, 5940. (c) Kabat, M. M.; Wicha, J. *J. Chem. Soc., Chem. Commun.* **1983**, 985. (d) Takahashi, T.; Ootake, A.; Tsuji, J. *Tetrahedron* **1985**, *41*, 5747. (e) Trost, B. M.; Angle, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 6123. (f) Deardorff, D. R.; Myles, D. C.; MacFerrin, K. D. *Tetrahedron Lett.* **1985**, *26*, 5615. (g) Trost, B. M.; Scanlan, T. S. *Tetrahedron Lett.* **1986**, *27*, 4141. (h) Tsuda, T.; Tokai, M.; Ishida, T.; Saegusa, T. *J. Org. Chem.* **1986**, *51*, 5216. (i) Deardorff, D. R.; Shambayati, S.; Linde, R. G.; Dunn, M. M. *J. Org. Chem.* **1988**, *53*, 189. (j) Trost, B. M.; Kuo, G.-H.; Benneche, T. *J. Am. Chem. Soc.* **1988**, *110*, 621.

[4] (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.

[5] This catalyst was prepared by a procedure analogous to that for the benzonitrile complex: Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216.

0002-7863/88/1510-4039$01.50/0