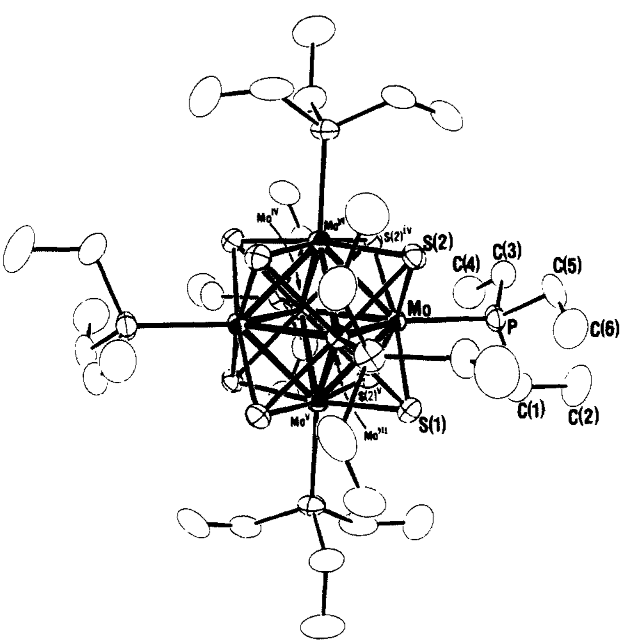

Figure 1. Structure with 50% probability ellipsoids and an atom-labeling scheme of $[Mo_6S_8(PEt_3)_6]$.

reaction of triethylphosphine on $Mo_3S_7Cl_4$.[9]

Thus the treatment of $[Mo_3S_4Cl_4(PEt_3)_4(MeOH)]$ (1.00 g, 0.94 mmol) with magnesium metal (0.06 g, 2.4 mmol) in THF (10.0 mL) at room temperature under argon for 24 h formed $[Mo_6S_8(PEt_3)_6]$ in 30% yield as a dark purple crystalline compound.[10] The complex was recrystallized from tetrahydrofuran, and the structure was determined by X-ray crystallography.[11] An ORTEP drawing of the molecule is illustrated in Figure 1. The result shows that the cluster has a regular octahedral core of six molybdenum atoms with eight face-bridging sulfur atoms and six triethylphosphines coordinated to each molybdenum. The Mo–Mo distances (2.664 and 2.662 Å, prependicular to and along the C_3 axis, respectively) are almost identical and shorter than those of the solid-state Mo_6S_8 (2.698 and 2.862 Å).[12]

The complex has 20 cluster valence electrons, and the formal oxidation state of the molybdenum atoms can be described as $Mo_2^{II}Mo_4^{III}$. However, it may be better to regard them as having an average oxidation state of 16/6 because of the equivalence of the Mo–Mo bond distances and the sharp peaks in the ^1H and ^{31}P NMR spectra suggesting the absence of unpaired electrons. In the Chevrel phase compounds, the relationship between the cluster valence electrons and the Mo–Mo bond distances has been established,[13] and the 20 e compounds exhibit the largest elongation along the C_3 axis of the trigonal antiprism. Although our cluster is a 20 e complex, the Mo–Mo bond distances are close to those of the solid-state Chevrel compounds with 24 cluster electrons.[14] It seems unlikely that the complex is more reduced and possesses either a hydrogen, carbon, or magnesium cation, because careful elemental analyses and ^1H and ^{13}C NMR spectra as well as the X-ray structure determination have not revealed the presence of an extra cation. The fact that the present complex displays a regular octahedral structure with relatively short Mo–Mo distances may be explained by the electron flow from basic triethylphosphines, lack of the intercluster interaction, or by the packing disorder due to the symmetrical nature of the cluster molecule.

The cyclic voltammetry and coulometry on a dichloromethane solution indicated reversible one-electron reduction and oxidation waves at −1.03 and +0.24 V, respectively.[15] The electronic spectrum of a benzene solution showed the bands at 289 nm (ϵ 31 000), 491 nm (ϵ 8100), 991 nm (ϵ 1200), and 1200 nm (ϵ 870). The analyses of these measurements together with the calculation of the energy levels for the present compound and for the more reduced clusters $[M_xMo_6X_8(PR_3)_6]$ which we are now trying to prepare will shed light on the above problem.

Acknowledgment. Support from the Ministry of Education, Science and Culture (Grant-in-Aid for Special Project Research no. 62115007) and the Iwatani Naoji Foundation's Research Grant are gratefully acknowledged. We thank Nippon Chemical Co. Ltd. for the gift of triethylphosphine.

Supplementary Material Available: Detailed crystal data and listings of atomic coordinates, thermal parameters, and bond distances and angles (6 pages); listings of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead pages.

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(8) (a) Adams, R. D.; Babin, J. E. *Inorg. Chem.* **1987**, *26*, 980. (b) Mertis, K.; Edwards, D. G.; Wilkinson, G.; Abdul Malik, K. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 705.

(9) Saito, T.; Yamamoto, N.; Yamagata, T.; Imoto, H. *Chem. Lett.* **1987**, 2025.

(10) Anal. Calcd for $C_{36}H_{90}Mo_6P_6S_8$: C, 28.06; H, 5.89; P, 12.1. Found: C, 28.06; H, 5.70; P, 11.9.

(11) Data collection with a Rigaku AFC-4 four-circle automated diffractometer and calculations were performed at the Crystallographic Research Center, Institute for Protein Research, Osaka University. Crystal data are as follows: space group $R\bar{3}$ with a = 17.460 (3) Å, c = 19.931 (6) Å, V = 5262 (2) Å^3, Z = 3. The structure was solved by using direct methods and Fourier synthesis. R = 0.039 and R_w = 0.043 for 1423 independent diffractions ($F > 6.0\sigma(F)$) with $2\theta < 60°$ (Mo Kα radiation). Selected bond distances (Å) and angles (deg) are as follows: Mo–Mo^{iii}, 2.664 (1); Mo–Mo^{iv}, 2.662 (1); Mo–S(1), 2.446 (2); Mo–S(2), 2.444 (3); Mo–P, 2.527 (3); Mo^{iii}–Mo–Mo^{iv}, 90.00; Mo^{iii}–Mo–Mo^{v}, 60.00; Mo^{iii}–Mo–Mo^{vi}, 59.98 (3); Mo^{iv}–Mo–Mo^{vi}, 60.05 (3); Mo^{iii}–Mo–S(1), 57.01 (4); Mo^{iii}–Mo–S(2), 56.84 (7); Mo^{iii}–Mo–P, 137.15 (8).

(12) Chevrel, R.; Sergent, M.; Prigent, J. *Mat. Res. Bull.* **1974**, *9*, 1487.

(13) Yvon, K. In *Current Topics in Material Science*; Kaldis, E., Ed.; North Holland: Amsterdam, 1979; Vol 3, p 53.

(14) Yvon, K. In *Superconductivity in Ternary Compounds I*; Fischer, O., Maple, M. B., Eds.; Springer Verlag: Berlin, 1982; p 87.

(15) The preliminary electrochemical measurements were carried out by Dr. K. Unoura of Yamagata University by using the thin-layer cyclic voltammetry and coulometry. Further study is being continued, and the details will be reported elsewhere.

$[(CH_3)_5C_5]_2Th(CH_3)_2$ Surface Chemistry and Catalysis. Direct NMR Spectroscopic Observation of Surface Alkylation and Ethylene Insertion/Polymerization on $MgCl_2$

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Received July 13, 1987

It is well-established that adsorption on inorganic surfaces can dramatically alter the reactivity of organometallic molecules;[1] however, the structural chemistry of the resulting adsorbates is frequently ill-defined. From CPMAS NMR studies of $Cp'_2Th(CH_3)_2$ ($Cp' = \eta^5\text{-}(CH_3)_5C_5$) on dehydroxylated γ-alumina (DA), we inferred the transfer of methyl groups to DA surface Lewis acid sites and the formation of less saturated "$Cp'_2Th(CH_3)^{+}$" species with cationic character.[2] Although model studies in solution support much of this chemical/spectroscopic hypothesis,[3-5] the small percentage ($\lesssim$4%) of $Cp'_2Th(CH_3)_2$/DA sites highly

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(1) (a) Xiaoding, X.; Boelhouwer, C.; Vonk, D.; Benecke, J. I.; Mol, J. C. *J. Mol. Catal.* **1986**, *36*, 47–66, and references therein. (b) Lamb, H. H.; Gates, B. C. *J. Am. Chem. Soc.* **1986**, *108*, 81–89, and references therein. (c) Hartley, F. R. *Supported Metal Complexes: A New Generation of Catalysts*; Reidel: Boston, 1985. (d) McDaniel, M. P. *Adv. Catal.* **1985**, *33*, 47–98. (e) Schwartz, J. *Acc. Chem. Res.* **1985**, *18*, 302–308. (f) Basset, J. M.; Choplin, A. *J. Mol. Catal.* **1983**, *21*, 95–108, and references therein. (g) Yermakov, Y. I. *J. Mol. Catal.* **1983**, *21*, 35–55, and references therein. (h) Yermakov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, 1981.

(2) (a) Toscano, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 653–659. (b) Toscano, P. J.; Marks, T. J. *Langmuir* **1986**, *2*, 820–823.

0002-7863/88/1510-1647$01.50/0

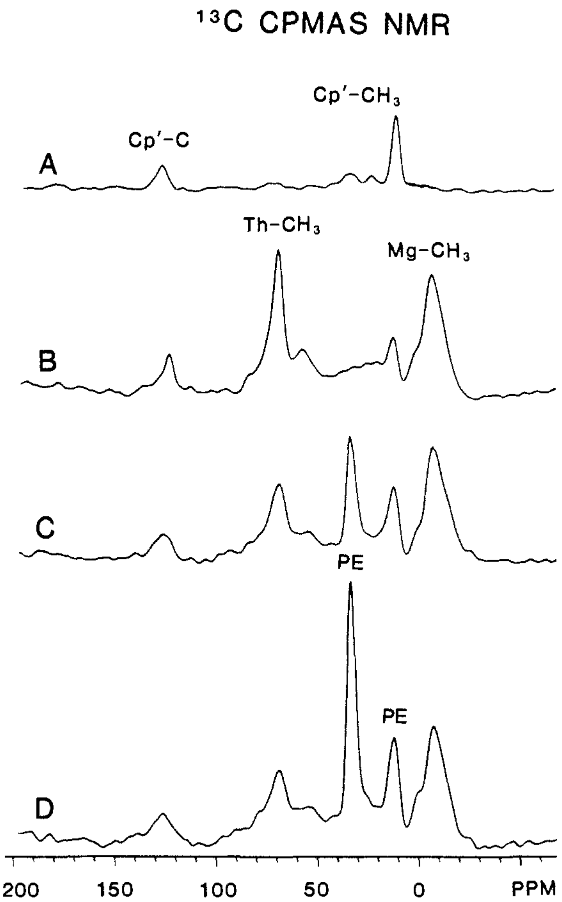


Figure 1. ^{13}C CPMAS solid-state NMR spectra (75.4 MHz, Varian VXR300 equipped with a Doty 7 mm solids probe, spinning rate = 4100 ± 100 Hz, repetition time = 5 s, contact time = 4.5 ms) of (A) $Cp'_2Th(CH_3)_2/MgCl_2$ (9900 scans), (B) $Cp'_2Th(^*CH_3)_2/MgCl_2$ (6050 scans), (C) $Cp'_2Th(^*CH_3)_2/MgCl_2$ + 5 equivalents of C_2H_4 (5700 scans), and (D) $Cp'_2Th(^*CH_3)_2/MgCl_2$ + 16 equiv of C_2H_4 (5900 scans): $^*C$ = 99% ^{13}C, PE = polyethylene. The Cp'–CH_3 and PE-CH_3 signals are coincident.

active for olefin hydrogenation and polymerization[6] renders the connection with catalysis necessarily indirect. We report here complementary studies with high surface area $MgCl_2$, the preferred support for "third generation" Ziegler–Natta catalysis,[7] which provide the first evidence for the catalytic importance of methyl/methide transfer on $MgCl_2$ and the first direct spectroscopic observation of the ethylene insertion/polymerization process on a supported catalyst.[8]

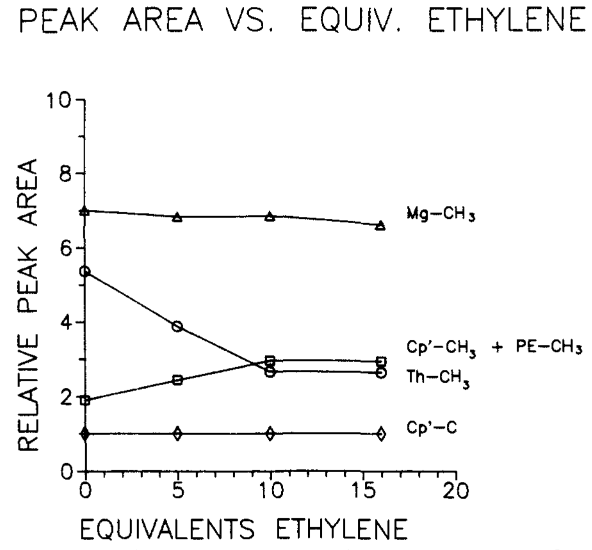
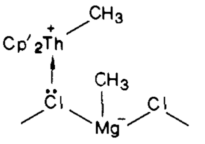


Figure 2. Relative NMR spectral peak areas exhibited by $Cp'_2Th(^*CH_3)_2/MgCl_2$ dosed with the indicated equivalents of ethylene: $^*C$ = 99% ^{13}C, PE = polyethylene.

Under anhydrous and anaerobic conditions, $MgCl_2$ (225–250 m^2/g by BET) was prepared[7e,9] from dibutylmagnesium and HCl. Isolation, drying, and stirring with $Cp'_2Th(CH_3)_2$ or $Cp'_2Th(^*CH_3)_2$ ($^*C$ = 99% ^{13}C) in pentane yields the ethylene polymerization catalysts[10] $Cp'_2Th(CH_3)_2/MgCl_2$ (**1**) and $Cp'_2Th(^*CH_3)_2/MgCl_2$ (**1***) as tan powders (ca. 0.25 Th/nm² coverage). CPMAS spectra (Figures 1A and B)[11] are readily assigned from isotopic labeling, dipolar dephasing,[2,12] and model compound data.[2,13] Resonances at δ 124 and 11 are attributed to Cp′–C and Cp'–CH_3 signals, respectively. Evidence for methyl transfer to the surface (e.g., I–III) is provided by the high field Mg–CH_3[14] resonance at δ −8.0. The low field resonance of approximately equal area at δ 69.0 is assigned to Th–CH_3 and is similar in field position to $Cp'_2Th(CH_3)_2$/DA (δ 71.0),[2] $Cp'_2Th(CH_3)(THF)_2{}^+BPh_4{}^-$ (δ 69.3),[3] and $Cp'_2Th(CH_3)^+BPh_4{}^-$ (δ 71.8).[3,15] Logical $MgCl_2$ methylation sites are exposed, coordinatively unsaturated Mg^{2+} centers on the (110) and (101) faces of the $CdCl_2$-type crystal structure.[16] Cessation of dipole decoupling,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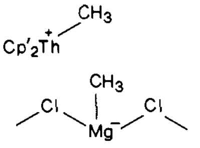
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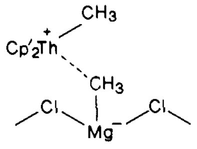
III

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[3] Lin, Z.; LeMarechal, J. F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127–4129.

[4] (a) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* **1986**, *108*, 7410–7411. (b) Jordan, R. F.; Dasher, W. E.; Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718–1719. (c) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610–1611. (d) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219–7221. (e) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 3377–3378.

[5] For isoelectronic Cp'_2MR systems, see: (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*, 203–219. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. (c) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091–8103. (d) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111–8118.

[6] (a) He, M.-Y.; Xiong, G.; Toscano, P. J.; Burwell, R. L., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 641–652. (b) He, M.-Y.; Burwell, R. L., Jr.; Marks, T. J. *Organometallics* **1983**, *2*, 566–569.

[7] (a) Barbè, P. C.; Cecchin, G.; Noristi, L. *Adv. Polym. Sci.* **1986**, *81*, 1–81. (b) Choi, K.-Y.; Ray, W. H. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1985**, *C25*, 1–56, 57–97. (c) Pino, P.; Rotzinger, B. *Macromol. Chem. Phys. Suppl.* **1984**, *7*, 41–61. (d) Karol, F. *J. Catal. Rev.-Sci. Eng.* **1984**, *26*, 557–595. (e) Goodall, B. L. In *Transition Metal Catalyzed Polymerizations*; Quirk, R. P., Ed.; Harwood Academic Publishers: New York, 1983; pp 355–378 and references therein.

[8] Reported in part at the 193rd ACS National Meeting, Denver, CO, April 5–10, 1987, Abstract INOR404.

[9] Kamienski, C. W. Ph.D. Thesis, University of Tennessee, 1967.

[10] Preliminary rate data (1 atm, 25 °C): 3.0 g/mmol min atm as a slurry in cyclohexane.

[11] Sample handling (recirculating glovebox) and data acquisition (O-ring-sealed rotors, N_2 spinning gas) were performed with rigorous exclusion of oxygen and moisture. Control experiments[2a] indicated negligible sample decomposition.

[12] (a) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6697–6704. (b) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854–5856.

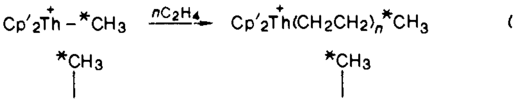
[13] Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40–56, and references therein.

[14] (a) Chisholm, M. H.; Godleski, S. *Prog. Inorg. Chem.* **1976**, *20*, 291–436. (b) Leibfritz, D.; Wagner, B. O.; Roberts, J. D. *Justus Liebigs Ann. Chem.* **1972**, *763*, 173–183. (c) $\delta(^{13}CH_3) = -10.8$ for solid CH_3MgBr (Toscano, P. J., unpublished results).

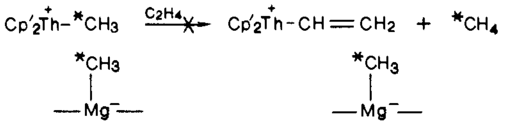
[15] $\delta(Cp'_2Th(^{13}CH_3)) \approx 70$ appears to be a necessary but not rigorously sufficient condition for a "cationic" structural assignment. While it excludes many conceivable structures (e.g., $Cp'_2Th(^{13}CH_3)O$–),[2,6] the observation of methyl transfer (to plausible surface sites) and catalytic activity[3,4] are equally persuasive. Thus, $\delta(Cp'_2Th(^{13}CH_3)_2) = 68.5$ and $\delta(Cp'_2Th(^{13}CH_3)Cl) = 67.6$, but neither complex is significantly active for ethylene polymerization in solution.

Bloch decay, and variable contact time experiments[2,17] indicate that the surface thorium complexes are relatively immobile. From data for other systems,[2,5] we assign the small, unreactive (vide infra) Th–CH_3 shoulder at δ 55 to a $Cp'_2Th(CH_3)O$– species, presumably formed in protonolysis by surface MgOH.[6] No other signals were observed between δ 470 and −90.[18]

Samples of **1*** were next dosed with measured quantities of ethylene (passed over MnO/SiO_2[6]) at 77 K and then slowly warmed to 300 K.[19] CPMAS spectra (Figure 1C,D) reveal growth of polyethylene resonances (PE–CH_2 expected at δ 33, PE–CH_3 at δ 10–15[20]), a substantial diminution in the Th–$^*CH_3$ signal, and negligible change in the Mg–$^*CH_3$ signal. No other signals are observed between δ 270 and −90.[18] These data can be analyzed in a quantitative fashion (Figure 2) by using the Cp′–C resonance as an internal integration standard. Spectra of **1*** and **1*** + 5 equiv of ethylene as a function of CP contact time (1, 3.5, 4, and 9 ms) indicate that, for constant chemical functionalities, this analysis based upon relative peak areas is not adversely affected by changes in CP dynamics.[18,21] Under these conditions, ethylene insertion occurs exclusively ($\gtrsim$90%) at the Th–CH_3 bond (eq 1), and approximately 50% of the Th sites are active versus $\lesssim$4% on DA[6,8] (an ordering reminiscent of support effects in Ti-based catalysts[7,16d,21-24]). That the diminution in Th–$^*CH_3$ does not arise from C–H activation processes (eq 2) is demonstrated by quantitative vacuum line/GC studies: evolved methane accounts for <2% of the Th sites. The lower reactivity of the $Cp'_2Th(CH_3)OMg$ center parallels other surface and solution reactivity observations for such species.[2b,6,26] From changes in Th–CH_3 signal area as a function of ethylene uptake, we also estimate that the average k(propagation)/k(initiation) ≈ 12 in the initial stages of the polymerization ($\leq$10 equiv of ethylene).[27]

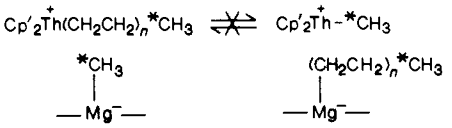


$$\begin{array}{c}\mathrm{Cp'_2\overset{+}{Th}-{}^{*}CH_3}\\ {}^{*}\mathrm{CH_3}\\ |\\ -\mathrm{Mg}^{-}-\end{array} \xrightarrow{n\mathrm{C_2H_4}} \begin{array}{c}\mathrm{Cp'_2\overset{+}{Th}(CH_2CH_2)_{\mathit{n}}{}^{*}CH_3}\\ {}^{*}\mathrm{CH_3}\\ |\\ -\mathrm{Mg}^{-}-\end{array} \qquad (1)$$



$$\begin{array}{c}\mathrm{Cp'_2\overset{+}{Th}-{}^{*}CH_3}\\ {}^{*}\mathrm{CH_3}\\ |\\ -\mathrm{Mg}^{-}-\end{array} \overset{\mathrm{C_2H_4}}{\nrightarrow} \begin{array}{c}\mathrm{Cp'_2\overset{+}{Th}-CH{=}CH_2}\\ {}^{*}\mathrm{CH_3}\\ |\\ -\mathrm{Mg}^{-}-\end{array} + {}^{*}\mathrm{CH_4} \qquad (2)$$

Finally, the time invariance of the spectra indicate that alkyl exchange processes (eq 3) are rather slow.



$$\begin{array}{c}\mathrm{Cp'_2\overset{+}{Th}(CH_2CH_2)_{\mathit{n}}{}^{*}CH_3}\\ {}^{*}\mathrm{CH_3}\\ |\\ -\mathrm{Mg}^{-}-\end{array} \not\rightleftharpoons \begin{array}{c}\mathrm{Cp'_2\overset{+}{Th}-{}^{*}CH_3}\\ \mathrm{(CH_2CH_2)_{\mathit{n}}{}^{*}CH_3}\\ |\\ -\mathrm{Mg}^{-}-\end{array} \qquad (3)$$

Acknowledgment. This research was supported by the DOE under contract DE-FG02-86ER13511. D.H. thanks Dow Chemical Co. for a fellowship. We thank Dr. P. J. Toscano for helpful discussions and R. Gillespie for assistance with the quantitative methane measurements.

Supplementary Material Available: Wide sweep width spectrum and diagrams showing the effect of varying CP contact time (3 pages). Ordering information is given on any current masthead page.

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(16) (a) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: New York, 1984; p 350. (b) Marigo, A.; Martorana, A.; Zannetti, R. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 65–68. (c) Bassi, I. W.; Polato, F.; Calcaterra, M.; Bart, J. C. J. *Z. Kristallogr.* **1982**, *159*, 297–302, and references therein. (d) Giannini, U. *Makromol. Chem. Suppl.* **1981**, *5*, 216–229.

(17) (a) Bronnimann, C. E.; Maciel, G. E. *J. Am. Chem. Soc.* **1986**, *108*, 7154–7159. (b) Schilling, F. C.; Bovey, F. A.; Tonelli, A. E.; Tseng, S.; Woodward, A. E. *Macromolecules* **1984**, *17*, 728–733. (c) Maciel, G. E.; Haw, J. F.; Chuang, I.-S.; Hawkins, B. L.; Early, T. A.; McKay, D. R.; Petrakis, L. *J. Am. Chem. Soc.* **1983**, *105*, 5529–5535. (d) Pfeifer, H.; Meiler, W.; Deininger, D. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 291–356. (e) Duncan, T. M.; Dybowski, C. *Surf. Sci. Rep.* **1981**, *1*, 157–250.

(18) See Supplementary Material for further details.

(19) Experiments were carried out on a high vacuum line with manometric monitoring of ethylene uptake, which begins and rapidly proceeds to completion above ca. −10 °C.

(20) VanderHart, D. L.; Përez, E. *Macromolecules* **1986**, *19*, 1902–1909, and references therein.

(21) The Th–$^*CH_3$ → PE–$^*CH_3$ transposition provides an internal check for *nonconstant* functionalities. While the relative intensities of both resonances become invariant at the same ethylene dosage (as expected, Figure 2), the lost Th–$^*CH_3$ intensity is not completely recovered in PE–$^*CH_3$, presumably due to the greater isotropic mobility of the polymer chain.[12,17,20]

(22) (a) Zakharov, V. A.; Bukatov, C. D.; Yermakov, Y. I. *Adv. Polym. Sci.* **1983**, *51*, 61–100. (b) Bukatov, C. D.; Shepelev, S. H.; Zakharov, V. A.; Sergeev, S. A.; Yermakov, Y. I. *Makromol. Chem.* **1982**, *183*, 2657–2665.

(23) Complementary experiments of dosing **1** with $^*CH_2{}^*CH_2$ are less informative due to the following: (1) Th–$^*CH_2/(^*CH_2{}^*CH_2)_n$ spectral dynamic range limitations; (2) a sizable, precedented[13] dispersion in δ-(Th$^*CH_2$–); and (3) ^{13}C–^{13}C scalar and dipolar coupling.[24]

(24) Menger, E. M.; Vega, S.; Griffin, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 2215–2218.

(25) In contrast, ~100% of the Th–CH_3 groups react with H_2 and CO (Hedden, D.; Marks, T. J., unpublished results).

(26) Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979–7985.

(27) Average k(propagation)/k(initiation) = (Y−X)/X where Y = μmol of ethylene absorbed and X = μmol of Th–$^*CH_3$ reacted.

Relative Affinities of Cation Radicals and Dications for Nucleophiles and the Super Acid Properties of Dications in Solution

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Received June 9, 1987
Revised Manuscript Received December 4, 1987

Although the chemistry of organic cation radicals has been under discussion for some time,[1-5] little is known about the reactions of the corresponding dications. In this communication a general method for the determination of the relative equilibrium constants for reactions 3 and 4 (Scheme I) is presented, and rate constants for the reactions of the dications are reported. The thermodynamic cycle[6] requires electrode potential data for reactions 1 and 2 in order to apply eq 5 which then gives the logarithmic difference in equilibrium constants.

Reversible electrode potentials for the oxidation of aromatic cation radicals to the corresponding dications (eq 1) can be measured in aprotic solvents when precautions are taken to remove nucleophilic impurities which rapidly react with the dications.[10] Electrode reactions (eq 2), the reductions of the dication/nucleophile adducts, have been characterized for reactions of 9,10-diarylanthracene (DPA) dications with water, methanol, and trifluoroacetic acid as nucleophiles in mixed solvent.[11] The peak potentials measured for reactions (eq 2) differ from the reversible values (E^{rev}) by the kinetic potential shift due to the reactions of

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(1) Parker, V. D. *Acc. Chem. Res.* **1984**, *17*, 143. Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55.

(2) Shine, H. J.; Murata, Y. *J. Am. Chem. Soc.* **1969**, *91*, 4584. Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368. Evans, J. F.; Blount, H. N. *J. Am. Chem. Soc.* **1978**, *100*, 419. Cheng, H. Y.; Sackett, P. H.; McCreery, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 962. Svanholm, U.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 101. Svanholm, U.; Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 997, 2942. Parker, V. D.; Eberson, L. *J. Am. Chem. Soc.* **1970**, *92*, 7488.

(3) Eberson, L.; Blum, Z.; Helgée, B.; Nyberg, K. *Tetrahedron* **1978**, *34*, 731.

(4) Pross, A. *J. Am. Chem. Soc.* **1986**, *108*, 3537.

(5) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1987**, *109*, 2521.

(6) Thermodynamic cycles have been invoked to obtain estimates of a number of different thermodynamic quantities including pK_a values for hydrocarbons[7] as well as pK_a values for cation radicals.[8,9]

(7) Jaun, B.; Schwartz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741 and references cited.

(8) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1980**, *60*, 2165.

(9) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473.

(10) Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 537.

(11) Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 4289.