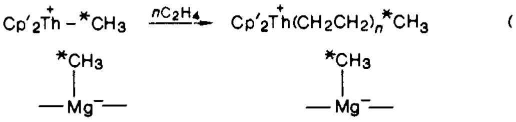
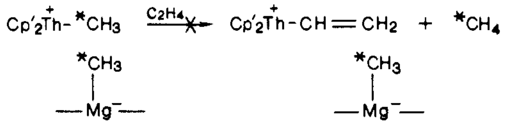
Bloch decay, and variable contact time experiments[2,17] indicate that the surface thorium complexes are relatively immobile. From data for other systems,[2,5] we assign the small, unreactive (vide infra) Th–CH_3 shoulder at δ 55 to a $Cp'_2Th(CH_3)O$– species, presumably formed in protonolysis by surface 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



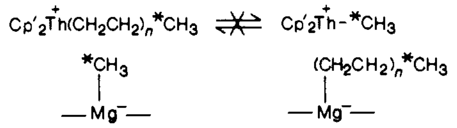
$$\begin{array}{ccc} \mathrm{Cp'_2\overset{+}{Th}-{}^*CH_3} & \xrightarrow{n\mathrm{C_2H_4}} & \mathrm{Cp'_2\overset{+}{Th}(CH_2CH_2)_n{}^*CH_3} \\ \mathrm{{}^*CH_3} & & \mathrm{{}^*CH_3} \\ | & & | \\ \mathrm{-Mg^{-}-} & & \mathrm{-Mg^{-}-} \end{array} \quad (1)$$

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)



$$\begin{array}{ccc} \mathrm{Cp'_2\overset{+}{Th}-{}^*CH_3} & \xrightarrow{\mathrm{C_2H_4}}\!\!\!\!\!\!\times\;\; & \mathrm{Cp'_2\overset{+}{Th}-CH{=}CH_2 + {}^*CH_4} \\ \mathrm{{}^*CH_3} & & \mathrm{{}^*CH_3} \\ | & & | \\ \mathrm{-Mg^{-}-} & & \mathrm{-Mg^{-}-} \end{array} \quad (2)$$

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



$$\begin{array}{ccc} \mathrm{Cp'_2\overset{+}{Th}(CH_2CH_2)_n{}^*CH_3} & \cancel{\rightleftharpoons} & \mathrm{Cp'_2\overset{+}{Th}-{}^*CH_3} \\ \mathrm{{}^*CH_3} & & \mathrm{(CH_2CH_2)_n{}^*CH_3} \\ | & & | \\ \mathrm{-Mg^{-}-} & & \mathrm{-Mg^{-}-} \end{array} \quad (3)$$

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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[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.; Pērez, 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]

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[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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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.

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[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.

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

Scheme I

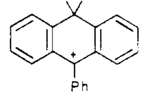
$$\begin{array}{lrr}
 & \Delta G^{\circ} & \\
A^{\ddagger} \rightleftharpoons A^{2+} + e^- & FE_1^{\circ} & (1) \\
A^{\bullet}\text{-}Nu^+ + e^- \rightleftharpoons A^{\bullet}\text{-}Nu^+ & -FE_2^{\circ} & (2) \\
\hline
A^{2+} + Nu \rightleftharpoons A^{+}\text{-}Nu^+ & -RT\ln K(DC) & (3) \\
A^{\bullet}\text{-}Nu^+ \rightleftharpoons A^{\ddagger} + Nu & RT\ln K(CR) & (4) \\
\hline
\log K(DC) - \log K(CR) = F(E_1^{\circ} - E_2^{\circ})/2.30RT & & (5)
\end{array}$$

Table I. Electrode Potential and Equilibrium Data for Reactions of the Cation Radical and Dication of 9,10-Diphenylanthracene

	X in DPA$^+$-X^b	
quantity	CF_3COO	HO
$E_1^0 - E_2^0$/mV^a	1130	1230
log K(DC) - log K(CR)	19	21

[a] Difference in reversible potentials estimated from cyclic voltammetry data in ref 11. [b] See structure below:

DPA$^+$-X =



DPA$^{\bullet}$-Nu$^+$, the cation radical/nucleophile adduct formed in eq 4, but E^{rev} can be estimated with an accuracy of about 0.1 V giving rise to a maximum error in log K(DC) - log K(CR) of 2 units or less.

Pertinent electrode potential data for the application of the thermodynamic cycle for the equilibria of cation radicals and dications of 9,10-disubstituted anthracenes with a number of nucleophiles were published some time ago.[11] Data for 9,10-diphenylanthracene dications in dichloromethane–trifluoroacetic acid reacting with trifluoroacetic acid and water as nucleophiles are summarized in Table I. The analysis resulted in log K(DC)-log K(CR) of 19 and 21 for the two nucleophiles. The rate constant for the reaction of DPA^{2+} in acetonitrile at 273 K was determined by derivative cyclic voltammetry (DCV)[12] to be 900 s^{-1}, corresponding to $k(DC) = 9 \times 10^4$ M^{-1} s^{-1} for the reaction with water ([H_2O] = 10 mM). The rate constant for the reaction of DPA$^{\bullet+}$ with water under similar conditions has been reported to be equal to 0.083 M^{-1} s^{-1}.[13] In dichloromethane (273 K) second-order rate constants of 0.035 and 1.25×10^5 M^{-1} s^{-1} were obtained by DCV for the reactions of DPA$^{\bullet+}$ and DPA^{2+}, respectively, with methanol.

The intrinsic reactivity of cation radicals as compared to the more reactive dications and carbenium ions has been assessed to be unusually low.[3,4] On the basis of our relative equilibrium constants, $K(DC)/K(CR) = 10^{20}$, we predict that the dication should react faster than the cation radical with nucleophiles. The relative rate constants observed, $k(DC)/k(CR) = 10^6$, are in the expected direction but very much smaller than the equilibrium constant ratio. Since Ritchie has found that rate and equilibrium constants for the reactions of carbenium ions with nucleophiles do not correlate,[14] it is not justified to conclude that it is the dications rather than the cation radicals that react unusually slowly. A possible reason for the fact that our rate and equilibrium constants do not correlate is that rate–equilibrium relationships break down when K becomes too far removed from unity.[15] Our data do suggest that it is not justified to conclude that cation radicals react unusually slowly when compared to the reactions of the corresponding dications. A change from a singly charged ion to a doubly charged ion is a very big perturbation and is expected to have a large effect on reactivity.

Table II. Acidity Constants of Triarylmethanes and the Corresponding Cation Radicals and Dications

triarylamine	pK_{HA}^{a}	p$K_{HA^{\bullet+}}$^{b}	p$K_{HA^{2+}}$^{c}
p-methoxyphenyldiphenylmethane	32.5	−19	−57 (−60)
triphenylmethane	31.5	−24	−72 (−76)

[a] In dimethylsulfoxide, from ref 16. [b] Estimated from cyclic voltammetry data by using the procedure in ref 9. Oxidation potentials of carbanions were those reported in ref 16. [c] Application of the thermodynamic cycle in Scheme I; values in parentheses include a 200-mV kinetic shift correction for the oxidation potential of the triarylmethane cation radicals in dichloromethane

A variation of the thermodynamic cycle (Scheme I) can be applied to show the super acid properties of dications containing acidic hydrogen. Data for triarylmethanes (HA) are summarized in Table II. The pK_{HA} are those reported by Breslow,[16] and the p$K_{HA^{\bullet+}}$ were estimated by the method developed by Bordwell.[9] The most interesting feature of the data is the very large negative p$K_{HA^{2+}}$ values estimated (Table II) for the dications of p-methoxyphenyldiphenylmethane (−56) and triphenylmethane (−76).

The application of the thermodynamic cycle (Scheme I) has provided the first equilibrium data for the reactions of the highly reactive organic dications. The rate constants reported here are the first to be measured for the reactions of aromatic hydrocarbon dications. The pK_a value estimated for triphenylmethane dication is of the order of 50 units more negative than any previously reported values.

Acknowledgment. We gratefully acknowledge helpful comments by Professor John I. Brauman. The work was supported by a grant from the Norwegian Research Council for Science and the Humanities.

Registry No. DPa^{2+}, 70470-09-6; DPA$^{\bullet+}$, 34480-04-1; DPA$^+$-OC(O)CF_3, 112460-82-9; DPA$^+$-OH, 112460-83-0; H_2O, 7732-18-5; CF_3CO_2H, 76-05-1; p-$MeOC_6H_4CHPh_2$, 13865-56-0; p-$MeOC_6H_4CHPh_2^{\bullet+}$, 112481-57-9; p-$MeOC_6H_4CHPh_2^{2+}$, 112460-84-1; Ph_3CH, 519-73-3; $Ph_3CH^{\bullet+}$, 88424-77-5; Ph_3CH^{2+}, 112460-85-2.

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(17) The values of pK_{HA} and p$K_{HA^{\bullet+}}$ refer to DMSO as solvent while p$K_{HA^{2+}}$ − p$K_{HA^{\bullet+}}$ obtained by using eq 5 refer to CH_2Cl_2. The p$K_{HA^{2+}}$ in Table II assume that $E_{ox}^{\circ}(Ar_3CH) - E_{red}^{\circ}(Ar_3C^+)$ are the same in CH_2Cl_2 as in DMSO, within the limits of error (±100 mV) of the method.

Intermediacy of Paramagnetic Metal-Hydrocarbyl Species in Organometallic Reactions. Detection and Characterization of a Novel Paramagnetic Iron(II)-Benzyl Compound in the Coupling of Benzyl Halides[1]

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Paramagnetic metal–hydrocarbyl species have been postulated as intermediates in several organometallic reaction sequences.[3] In the preponderance of these reactions the paramagnetic intermediate has been detected by ESR spectroscopy. In other cases

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(2) Alfred P. Sloan Research Fellow, 1984–1988.

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