Actinacyclobutanes. Implementation of Thermochemically Based Strategies for the Ring-Opening Stoichiometric C–H Functionalization of Saturated and Olefinic Hydrocarbons

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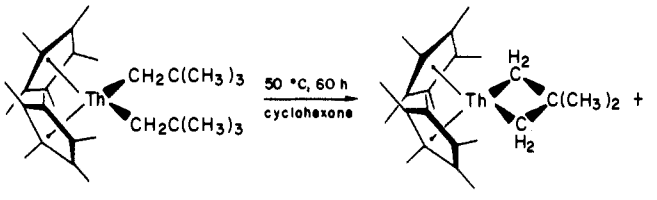
Abstract: The strained thoracyclobutane $Cp'_2\overline{ThCH_2C(CH_3)_2CH_2}$ (**1**, $Cp' = \eta^5$-$(CH_3)_5C_5$) undergoes facile ring-opening C–H activation reactions with saturated hydrocarbons and related molecules, RH, to yield complexes of the type $Cp'_2Th(R)$-$[CH_2C(CH_3)_3]$. All new complexes have been characterized by standard spectroscopic/analytical methodology. Approximate relative rates of the R–H functionalization are $Sn(CH_3)_4 \gtrsim Si(CH_3)_4 >$ cyclopropane $\approx P(CH_3)_3 >$ benzene $> CH_4 \gtrsim C_2H_6 \gg$ cyclohexane. For $Si(CH_3)_4$, the reaction obeys the rate law $v = k[\mathbf{1}][Si(CH_3)_4]$ with $k = 7.0\ (5) \times 10^{-5}\ M^{-1}\ s^{-1}$ at −10 °C. In the case of $Si(CH_3)_4$, $Sn(CH_3)_4$, and $P(CH_3)_3$, further reaction (cyclometalation) after ring opening affords the heteroatom-substituted metallacycles $Cp'_2\overline{ThCH_2Si(CH_3)_2CH_2}$, $Cp'_2\overline{ThCH_2Sn(CH_3)_2CH_2}$, and $Cp'_2\overline{ThCH_2P(CH_3)CH_2}$. NMR data indicate that the metallacyclic ring of the latter complex is probably not planar and that the phosphorus lone pair does not interact with the thorium ion. In the case of cyclopropane and benzene, a follow-up C–H activation reaction leads to the corresponding Cp'_2ThR_2 complexes and neopentane. The CH_4/CD_4 activation process by **1** exhibits a substantial kinetic isotope effect, $k_H/k_D = 6\ (2)$ at 60 °C, and the deuterium distribution in the products gives no evidence of significant Cp′ methyl group involvement in the methane functionalization. The ethane reaction with **1** does not lead to a stable ethyl complex, but rather thorium hydride products are detected (suggesting follow-up β-hydride elimination). There is no evidence of a reaction between **1** and cyclohexane. The reaction of **1** with propylene and ethylene does not involve C–H activation, but rather insertion of the C=C double bond into the Th–C σ bond occurs to yield the metallacyclohexanes $Cp'_2\overline{ThCH_2C(CH_3)_2CH_2CH(CH_3)CH_2}$ and $Cp'_2\overline{ThCH_2C(CH_3)_2CH_2CH_2CH_2}$, respectively. The courses of most of the transformations reported herein can be readily understood on the basis of Th–ligand and R–H bond disruption enthalpy data. Mechanistically, a heterolytic "four-center" pathway appears to be the most viable description of the Th(IV)-centered C–H activation process.

The central position that metallacyclic compounds[1] occupy in contemporary organometallic chemistry derives both from the rich stoichiometric and homogeneous catalytic chemistry[2] that they are known to exhibit as well as from the possibility that such species may be involved in a host of other important catalytic transformations.[1,3,4] Our interest in actinide metallacyclic compounds[5] originated in the observation that thoracyclobutanes are cleanly formed in intramolecular γ-C–H activation processes involving saturated hydrocarbon ligands (e.g., eq 1).[6] That α-C–H



1 $C(CH_3)_4$ (1)

$\Delta H^{\ddagger} = 21.2\ (8)$ kcal/mol
$\Delta S^{\ddagger} = -16\ (2)$ eu

activation does not occur to yield an alkylidene[7] and that the observed cyclometalation is unlikely to involve conventional oxidative addition/reductive elimination sequences[8,9] stands in marked contrast to results for many transition-metal d^0 and d^8 systems, respectively. Thermochemical studies[10] indicate that eq 1 is entropically driven ($\Delta H \approx +7$ kcal/mol; $T\Delta S \approx +12$ kcal/mol) and that thoracyclobutanes such as **1** have a rather high enthalpy content (ring strain).

In designing new chemical transformations which would exploit the enthalpy content of thoracyclobutanes, two questions came to mind. The first concerned whether variants of eq 1 might be devised in which the cyclometalation equilibrium lies to the left, i.e., reactions in which compound **1** could stoichiometrically effect C–H activation[11,12] on an exogenous saturated hydrocarbon

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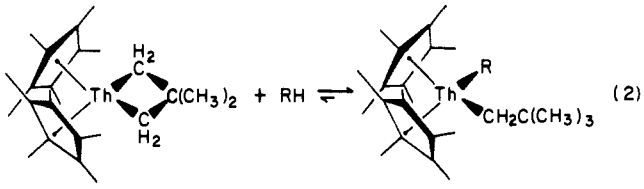
molecule (eq 2) (apparently less-demanding C–H activation of arenes by **1** had already been demonstrated[6a]). The second



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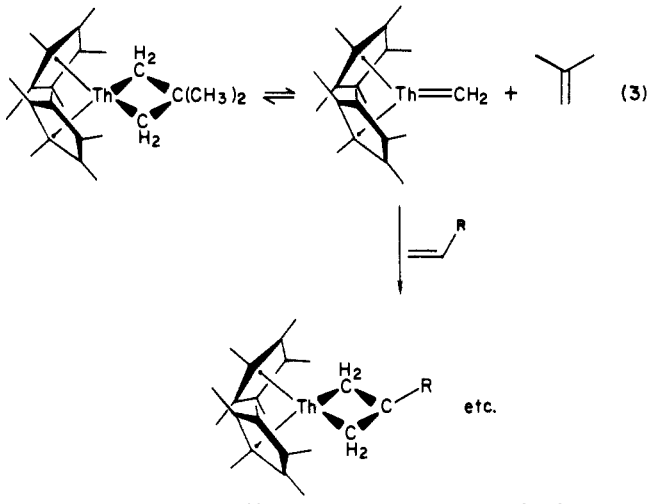
question concerned the accessibility from **1** of a thorium alkylidene which might, for example, be discerned via olefin exchange/metathesis activity (eq 3).[2,13] Such alkylidene species not sta-



(3)

bilized by a heteroatom[14] are completely unknown for f-element ions.

With the above two questions as the focal point, we present here a discussion of our synthetic/mechanistic studies involving saturated hydrocarbon and olefin functionalization by the thoracyclobutane **1**. It will be seen that the route of eq 2 not only represents a viable strategy for the rational activation of saturated hydrocarbon molecules with some selectivity[15] but also a new route to methylene-bridged binuclear organometallic compounds. It will also be seen that the olefin chemistry of **1** involves neither eq 3 nor C–H activation. However, the chemistry which does occur as well as the hydrocarbon activation chemistry can be predicted surprisingly well on the basis of recently acquired Cp'_2ThR_2 thermochemical data.[10]

Experimental Section

Physical and Analytical Methods. Proton and carbon NMR spectra were recorded on either a JEOL FX-270 (FT, 270 MHz, ^{13}C 67.80 MHz), a JEOL FX-90Q (FT, 90 MHz), or a Varian EM-390 (CW, 90 MHz) spectrometer. Chemical shifts are reported relative to internal TMS. Integration for reaction yields and kinetic studies was performed by photocopying expanded spectra, followed by cutting and weighing. Residual $C_6D_{11}H$ in the cyclohexane-d_{12} was used as an internal standard. Yields in NMR reactions are the average of two or more experiments. Phosphorus NMR spectra were recorded on a JEOL FX-270 (FT, ^{31}P 109.16 MHz) spectrometer. Shifts are reported relative to external 85% H_3PO_4 (values downfield from the external H_3PO_4 are positive in sign). Infrared spectra were obtained on Nujol mulls sandwiched between KBr plates in an o-ring sealed air-tight holder on a Perkin-Elmer 599B or 283 infrared spectrophotometer and were calibrated with polystyrene film. GC/MS spectra were recorded with a Hewlett-Packard GC(HP-5985A) MS (5840A) with a Hewlett-Packard (HP-2113B) 21 MX E series computer using 15- or 70-eV ionizing voltage. Deuterium analysis followed procedures described elsewhere.[6]

Elemental analyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany.

Materials and Methods. Air-sensitive compounds were handled with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line, in Schlenk-type glassware interfaced to a high-vacuum (10^{-5} torr) system or in a Vacuum Atmospheres glovebox with an efficient recirculator. Argon (Matheson, prepurified), dinitrogen (Liquid Air Corp., high purity), methane (Matheson, UHP), CD_4 (MSD Isotopes, 99% D), cyclopropane (Matheson, CP), ethane (Matheson, research purity), ethylene (Matheson, CP), and propylene (Matheson, CP) were purified by passage through sequential columns of MnO and Davison 4-Å molecular sieves.[16]

Diethyl ether (Et_2O), heptane, and pentane were distilled from Na/K/benzophenone under dinitrogen and were condensed and stored in vacuo in bulbs containing a small amount of $[Ti(Cp)_2Cl]_2ZnCl_2$ as an oxygen indicator.[17] Cyclohexane was dried over Na/K alloy and stored in vacuo over Na/K. Deuterated solvents were dried over Na/K alloy and transferred in vacuo before use. The D_2O (Bio-Rad Laboratories, 99.87%), 2,2,4-trimethylpentane (99+%, Aldrich), and 2,2-dimethylpentane (99+%, Aldrich) were used without further purification.

Tetramethylsilane (Aldrich) and trimethylphosphine (Strem Chemical) were dried over Na/K and transferred in vacuo before use. Tetramethyltin (99+%, Aldrich) was dried over freshly activated Davison 4-Å activated molecular sieves. Cyclopropyllithium[18] was prepared by metalation of the alkyl chloride with lithium wire. The lithium reagent, $LiCH_2P(CH_3)_2$, was prepared by the reaction of $P(CH_3)_3$ with *n*-BuLi.[19] Solutions of commercial methyllithium (as a complex with lithium bromide in Et_2O) (Aldrich) and allyllithium in Et_2O (Alfa) were used without further purification.

The complexes Cp'_2ThCl_2,[20] $Cp'_2Th(Cl)[CH_2C(CH_3)_3]$,[21,22] and $Cp'_2\overline{ThCH_2C(CH_3)_2CH_2}$ (**1**)[6b] were prepared by the literature methods.

Gas pressures for NMR tube reactions were determined by using a mercury manometer and a 13.874-mL calibrated gas bulb, with a vacuum line adaptor. High-pressure NMR reactions were carried out in sealed 5-mm Pyrex tubes.

$Cp'_2Th(CH_3)[CH_2C(CH_3)_3]$ (2). A 30-mL reaction flask was charged with 0.62 g (1.01 mmol) of $Cp'_2Th(Cl)[CH_2C(CH_3)_3]$ and 0.16 g (1.42 mmol) of MeLi·LiBr. Diethyl ether, 15 mL, was condensed onto the solids and the reaction stirred at room temperature for 3 h. The solvent was next removed from the mixture in vacuo and the resulting brown solid extracted with pentane (2 × 15 mL) to give a yellow–orange filtrate. The volume of the filtrate was then reduced to 5 mL and the solution slowly cooled to −78 °C. The resulting pale-yellow solid was collected by filtration and recrystallized from pentane: yield, 0.17 g, 28%; ^1H NMR (C_6D_{12}, 270 MHz) δ −0.38 (s, 3 H), −0.12 (s, 2 H), 0.94 (s, 9 H), 2.01 (s, 30 H); ^{13}C NMR (C_6D_6, 67.80 mHz) δ 123.2 (s), 101.7 (t, J_{C-H} = 103.6 Hz), 71.7 (q, J_{C-H} = 111.8 Hz), 37.2 (s), 36.9 (q, J_{C-H} = 124.7 Hz), 11.7 (q, J_{C-H} = 125.9 Hz); IR (Nujol, cm^{-1}) 1353 s, 1261 w, 1226 m, 1205 s, 1107 s, 1063 w, 1021 s, 988 m, 951 w, 921 w, 903 w, 802 m, 740 s, 731 sh, 663 w, 588 m, 502 m, 470 w.

Anal. Calcd. for $C_{26}H_{42}Th$: C, 53.23; H, 7.22. Found: C, 53.23; H, 7.44.

Reaction of $Cp'_2\overline{ThCH_2C(CH_3)_2CH_2}$ with CH_4. A 5-mm Pyrex tube,

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sealed at one end, was charged with $Cp'_2ThCH_2C(CH_3)_2CH_2$, 0.015 g (0.026 mmol). Cyclohexane-d_{12}, 0.17 mL, and methane (0.446 mmol, about 10 atm of pressure) were then condensed into the tube at −196 °C. The tube was next sealed with a torch and wrapped with aluminum foil. After it was allowed to warm to room temperature, the tube was placed in a 60 °C constant temperature bath. The progress of the reaction was monitored by 270-MHz ^1H NMR.

Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ + CD_4. This reaction was carried out in the same manner as the methane reaction above using 0.015 g (0.026 mmol) of $Cp'_2ThCH_2(CH_3)_2CH_2$ and CD_4 (0.446 mmol). When the reaction was complete, the tube was taken into the glovebox, cracked open, and the contents transferred to a small, two-necked flask. Water, 10 μL, was syringed into the flask under argon flush. The volatiles were then vacuum-transferred to another flask and a GC/MS recorded.

Isolation of $Cp'_2Th(CH_3)[CH_2C(CH_3)_3]$ (2) from the Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with CH_4. A Griffin–Worden pressure vessel equipped with a magnetic stirring bar was charged with 0.33 g (0.58 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$, and the vessel was then connected to the vacuum line. Cyclohexane, 20 mL, and methane, enough to pressurize the vessel to 85 psi (5.8 atm), were condensed into the vessel at −196 °C. The valve on the vessel was then closed, and the reaction vessel was allowed to warm to room temperature. Next, it was wrapped with aluminum foil and kept in a 60 °C constant temperature bath with magnetic stirring for 2 days. In the glovebox, the reaction solution was then transferred to a 30-mL reaction flask. The reaction tube was rinsed with heptane (3 × 1 mL), and the washings were added to the reaction solution. The solvent was then removed in vacuo, 2 mL of heptane was condensed into the flask, and the solution was cooled to −78 °C over a period of 1 h. The resulting pale-yellow precipitate was collected by filtration at −78 °C and was identified as $Cp'_2Th(CH_3)[CH_2C(CH_3)_3]$ by ^1H NMR; yield, 0.08 g, 24%.

Thermolysis of $Cp'_2ThCH_2C(CH_3)_2CH_2$. A 5-mm Pyrex tube, sealed at one end, was charged with 0.015 g (0.026 mmol) of $Cp'_2ThCH_2C(CH_3)CH_2$, and 0.2 mL of C_6D_{12} was condensed into the tube. Next, argon (0.450 mmol ≈ 10 atm) was condensed into the tube at −196 °C and the tube sealed. The tube was wrapped with aluminum foil and placed in a 60 °C constant temperature bath. The course of the thermolysis was monitored by 270-MHz ^1H NMR.

$Cp'_2Th(CHCH_2CH_2)_2$ (3). A 30-mL reaction flask was charged with 1.00 g (1.74 mmol) of Cp'_2ThCl_2 and 0.78 g (5.78 mmol) of cyclopropyllithium·lithium bromide. Diethyl ether was condensed onto the solids at −78 °C, and then the reaction mixture was warmed to room temperature and stirred for 3 h. The Et_2O was next removed in vacuo to give an orange solid. The solid was extracted with 20 mL of pentane and the mixture filtered. The volume of the filtrate was then reduced to 10 mL in vacuo and slowly cooled to −78 °C. The resulting cream solid was collected by filtration at −78 °C. Recrystallization from pentane followed by recrystallization from Et_2O yielded a colorless, microcrystalline solid; yield, 0.52 g, 51%; ^1H NMR (C_6D_6, 270 MHz) δ −0.64 (m, 2 H), 0.17 (m, 4 H), 0.95 (m, 4 H), 2.01 (s, 30 H); ^1H NMR (C_6D_{12}, 270 MHz) δ −0.72 (m, 2 H), −0.03 (m, 4 H), 0.78 (m, 4 H), 2.04 (s, 30 H); ^{13}C NMR (C_6D_{12}, 67.80 MHz) δ 123.47 (s), 70.33 (d, J_{C-H} = 128.3 Hz), 11.54 (q, J_{C-H} = 125.8 Hz), 8.59 (t, J_{C-H} = 157.6 Hz); IR (Nujol, cm^{-1}) 1260 w, 1170 m, 1100 w, 1009 s, 864 s, 806 m, 781 w, 586 w.

Anal. Calcd for $C_{26}H_{40}Th$: C, 53.42; H, 6.89. Found: C, 53.08; H, 7.03.

Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with Cyclopropane. A 5-mm Pyrex tube sealed at one end was charged with 0.020 g (0.035 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$ and the tube attached to a vacuum adaptor. Cyclohexane-d_{12}, 0.3 mL, and cyclopropane (0.437 mmol) were condensed into the tube at −196 °C and the tube sealed. The tube was wrapped with aluminum foil and was allowed to warm to room temperature. Next, the tube was placed in a 60 °C constant temperature bath, and the ensuing reaction was monitored by 270-MHz ^1H NMR. When the reaction was complete, the tube was taken into the glovebox, cracked open, and the contents transferred to a small two-necked flask. Under an argon flush, 10 μL of D_2O was added by syringe and the resulting mixture stirred. A GC/MS was then recorded.

Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with Ethane. A 5-mm Pyrex tube, sealed at one end, was charged with 0.015 g (0.026 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$. Cyclohexane-d_{12}, 0.2 mL, and ethane (0.456 mmol) were condensed into the tube at −196 °C. The tube was sealed and wrapped with aluminum foil. It was then allowed to warm to room temperature and immersed in a 60 °C constant temperature bath. The subsequent reaction was followed by 270-MHz ^1H NMR.

Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with TMS. A 5-mm NMR tube was charged with 0.015 g (0.026 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$. Cyclohexane-d_{12}, 0.3 mL, and TMS, 0.07 mL (0.51 mmol), were condensed into the tube at −196 °C. The tube was sealed and wrapped with aluminum foil. The reaction mixture was then warmed to 30 °C and immediately placed in the 30 °C probe of the NMR spectrometer. The progress of the reaction was monitored by 270-MHz ^1H NMR. When starting material was no longer visible in the ^1H NMR spectrum, the tube was placed in a 60 °C constant-temperature bath, and ^1H NMR monitoring was continued.

Isolation of $Cp'_2Th[CH_2Si(CH_3)_3][CH_2C(CH_3)_3]$ (4) from the Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with TMS. A 5-mL reaction flask was charged with 0.11 g (0.19 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$. Cyclohexane, 2 mL, was condensed in and the reaction stirred until all solids dissolved. Next, tetramethylsilane, 1 mL (7.3 mmol), was condensed in and the reaction mixture stirred at 30 °C for 4 h. The solvent was removed in vacuo and the resulting solid recrystallized from heptane; yield, 0.01 g, 8%; ^1H NMR (C_6D_{12}, 90 MHz) δ −0.58, (s, 2 H), −0.08 (s, 2 H), 0.08 (s, 9 H), 1.04 (s, 9 H), 2.10 (s, 30 H).

Kinetics of the Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with TMS. A 5-mm NMR tube was charged with 0.015 g (0.026 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$ and the tube attached to a vacuum line adaptor. Cyclohexane-d_{12} and TMS were then condensed into the tube to give the desired TMS concentration and a total volume of 0.34 ± 0.01 mL. The extent of reaction was subsequently monitored at −10 °C with the 270-MHz ^1H NMR spectrometer.

Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with $Sn(CH_3)_4$. A 5-mm NMR tube was charged with 0.015 g (0.026 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$ and the tube attached to a vacuum line adaptor. Cyclohexane-d_{12}, 0.5 mL, and $Sn(CH_3)_4$ (0.175 mmol) were condensed into the tube at −196 °C, and the tube was sealed. The reaction mixture was then warmed to room temperature and placed immediately in the probe of the NMR spectrometer. The reaction was allowed to proceed at room temperature until no more starting material was observed by 270-MHz ^1H NMR. The sample tube was then placed in a 60 °C constant-temperature bath, and further reaction was monitored by ^1H NMR.

After the reaction was complete, the NMR tube was taken into the glovebox, broken open, and the contents transferred to a flask. The solvent was removed in vacuo and 0.5 mL of pentane condensed onto the solid. Under an argon flush, D_2O, 10 μL, was syringed into the flask. After stirring, the volatiles were vacuum-transferred to another flask in vacuo, and a GC/MS was recorded.

$Cp'_2ThCH_2Sn(CH_3)_2CH_2$ (8): ^1H NMR (C_6D_{12}, 270 MHz) δ 0.32 (s, 6 H), 0.88 (s, 4 H), 1.94 (s, 30 H); ^{13}C NMR (C_6D_{12}, 67.80 Hz) δ 122.52 (s), 66.15 (t, J_{C-H} = 121.8 Hz), 11.43 (q, J_{C-H} = 125.2 Hz), −11.15 (q, J_{C-H} = 127.5 Hz).

Isolation of $Cp'_2Th[CH_2Sn(CH_3)_3][CH_2C(CH_3)_3]$ (7). A 30-mL flask was charged with 0.30 g (0.52 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$. Cyclohexane, 15 mL, and $Sn(CH_3)_4$, 0.5 mL (3.61 mmol), were condensed into the flask. The reaction was stirred for 4 h at room temperature and the solvent removed in vacuo to give an orange solid. Pentane, 10 mL, was condensed onto the solid and the resulting solution filtered. The solution volume was then reduced to 5 mL, the solution slowly cooled to −78 °C, and the resulting solid collected by filtration at −78 °C. Recrystallization from Et_2O afforded a colorless solid; yield, 0.05 g, 13%; ^1H NMR (C_6D_6, 270 MHz) δ −0.24 (s, 2 H, $^2J_{SnCH}$ = 44.2 Hz), 0.13 (s, 2 H), 0.36 (s, 9 H, $^2J_{SnCH}$ = 24.0 Hz), 1.24 (s, 9 H), 1.99 (s, 30 H); ^1H NMR (C_6D_{12}, 270 MHz) δ −0.44 (s, 2 H), −0.02 (s, 2 H), 0.13 (s, 9 H), 1.00 (s, 9 H), 2.05 (s, 30 H); ^{13}C NMR (C_6D_{12}, 67.80 MHz) δ 123.84 (s), 103.36 (t, J_{C-H} = 103.6 Hz), 77.66 (t, J_{C-H} = 104.5 Hz), 36.99 (s), 36.88 (q, J_{C-H} = 126.5 Hz), 12.13 (q, J_{C-H} = 125.9 Hz), −4.18 (q, J_{C-H} = 127.2 Hz); IR (Nujol, cm^{-1}) 1353 m, 1260 w, 1228 w, 1204 w, 1181 w, 1088 br, w, 1020 m, 850 w, 800 w, 756 m, 601 s, 512 s, 505 sh, 469 w.

Anal. Calcd for $C_{29}H_{52}SnTh$: C, 46.35; H, 6.97. Found: C, 46.94; H, 7.29.

$Cp'_2ThCH_2P(CH_3)CH_2$ (9). The complex $Cp'_2Th(Cl)[CH_2C(CH_3)_3]$, 0.66 g (1.09 mmol), and $LiCH_2P(CH_3)_2$, 0.09 g (1.14 mmol), were combined in a 30-mL reaction flask. Diethyl ether, 15 mL, was condensed onto the solids and the reaction mixture stirred at room temperature for 5.5 h. During this time, the color changed from pale yellow to lemon yellow. Next, the solvent was removed in vacuo, and the solids were dried for 2 h. Recrystallization of the crude product from pentane gave a bright-yellow microcrystalline solid; yield, 0.27 g, 43%; ^1H NMR

(C_6D_{12}, 270 MHz) δ 0.97 (d of d, 2 H, $^2J_{HCH}$ = 12.0, $^2J_{PCH}$ = 4.0 Hz), 1.10 (d, 3 H, $^2J_{PCH}$ = 5.9 Hz), 1.63 (d of d, 2 H, $^2J_{HCH}$ = 12.1, $^2J_{PCH}$ = 29.0 Hz), 1.90 (s, 15 H), 1.99 (s, 15 H); ^{13}C NMR (C_6D_{12}, 67.80 Hz) δ 123.33 (s), 122.54 (s), 76.44 (t of d, J_{C-H} = 128.3, J_{C-P} = 44.0 Hz), 19.63 (q of d, J_{C-H} = 126.5, J_{C-P} = 31.2 Hz), 11.81 (q, J_{C-H} = 124.2 Hz), 11.18 (q, J_{C-H} = 127.7 Hz); ^{31}P NMR (C_6D_{12}, 109.16 MHz) δ −117.7 (t of m); IR (Nujol, cm^{-1}): 1369 m, 1095 v br, w, 1020 m, 950 m, 855 s, 809 s, 690 s, 582 s, 508 m, 412 w.

Anal. Calcd for $C_{23}H_{37}PTh$: C, 47.91; H, 6.47; P, 5.37. Found: C, 47.43; H, 6.48; P, 5.01.

Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with $P(CH_3)_3$. A 5-mm NMR tube was charged with 0.020 g (0.035 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$ and the tube attached to a vacuum line adaptor. Cyclohexane-d_{12}, 0.3 mL, and $P(CH_3)_3$, 0.025 g (0.35 mmol), were condensed into the tube at −196 °C. The tube was next sealed and wrapped with aluminum foil. The tube was allowed to warm to room temperature and then placed in a 60 °C constant temperature bath. The ensuing reaction was monitored by 270-MHz ^{1}H NMR.

$Cp'_2Th[CH_2P(CH_3)_2]_2$ (10). A 30-mL flask was charged with 0.50 g (0.87 mmol) of Cp'_2ThCl_2 and 0.16 g (1.95 mmol) of $LiCH_2P(CH_3)_2$. Diethyl ether, 15 mL, was condensed into the flask at −78 °C and the reaction warmed to room temperature. After the reaction mixture had stirred for 2 h, the solvent was removed in vacuo. The solids were then extracted with 15 mL of pentane and filtered. The filtrate volume was then reduced to 5 mL and the solution cooled slowly to −78 °C. The resulting pale-yellow precipitate was collected by filtration at −78 °C; yield, 0.29 g, 51%; ^{1}H NMR (C_6D_{12}, 270 MHz) δ 0.07 (s, 4 H), 1.12 (s, 12 H), 2.02 (s, 30 H); ^{13}C NMR (C_6D_{12}, 67.80 MHz) δ 123.19 (s), 68.88 (t of t, J_{C-H} = 118.2, J_{C-P} = 44.0 Hz), 18.62 (q of m, J_{C-H} = 127.1 Hz), 12.02 (q, J_{C-H} = 125.9 Hz); ^{31}P NMR (C_6D_{12}, 109.16 MHz) δ −48.0; IR (Nujol, cm^{-1}) 1414 w, 1404 w, 1315 m, 1270 w, 1253 w, 1155 br, w, 1018 m, 931 s, 880 w, 860 w, 822 w, 798 w, 740 w, 721 s, 688 m.

Anal. Calcd for $C_{26}H_{46}P_2Th$: C, 47.79; H, 7.10; P, 9.49. Found: C, 47.28; H, 7.28; P, 9.68.

$Cp'_2ThCH_2P(CH_3)CH_2$ from Thermolysis of $Cp'_2Th[CH_2P(CH_3)_2]_2$. An 5-mm NMR tube was charged with 0.02 g (0.03 mmol) of $Cp'_2Th[CH_2P(CH_3)_2]_2$. Cyclohexane-d_{12}, 0.5 mL, was condensed into the tube and the tube sealed. After the solution had warmed to room temperature, the tube was wrapped with aluminum foil and was placed in a 60 °C constant-temperature bath. The subsequent reaction was monitored by 270-MHz ^{1}H NMR.

Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with Propylene. A 5-mm Pyrex tube, sealed at one end, was charged with 0.015 g (0.026 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$. Cyclohexane-d_{12}, 0.4 mL, and propylene (0.450 mmol, about 10 atm) were condensed into the tube at −196 °C. Next, the tube was sealed, allowed to warm to room temperature, and allowed to stand an additional 2 h after shaking. The 270-MHz ^{1}H NMR spectrometer was then used to monitor the reaction.

Isolation of $Cp'_2ThCH_2C(CH_3)_2CH_2CH(CH_3)CH_2$ (11). A Griffen–Worden pressure vessel equipped with a magnetic stirring bar was charged with 0.35 g (0.61 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$. The vessel was then connected to the vacuum line. Cyclohexane, 35 mL, and propylene, enough to pressurize the vessel to 42 psi (2.8 atm), were condensed into the vessel at −196 °C. The valve on the vessel was then closed, and the vessel was wrapped with aluminum foil. The reaction solution was allowed to warm to room temperature and stirring was initiated. After 1 h, the color of the solution changed from orange to pale yellow. After stirring an additional 12 h, the pressure was released and the solution transferred in the glovebox to a 30-mL flask. The solvent was then removed in vacuo, and 10 mL of heptane was condensed into the flask. Slow cooling to −78 °C and filtration at −78 °C yielded a pale-yellow, microcrystalline solid. Recrystallization from heptane resulted in a colorless solid; yield, 0.11 g, 29%; ^{1}H NMR (C_6D_6, 270 MHz) δ −0.01 (d, 1 H, $^2J_{HCH}$ = 14.2 Hz), 0.29 (d, 1 H, $^2J_{HCH}$ = 12.2 Hz), 0.42 (d of d, 1 H, $^2J_{HCH}$ = 14.0, $^4J_{HCCCH}$ = 2.1 Hz), 0.71 (t, 1 H, $^2J_{HCH} \approx {}^3J_{HCCH} \approx$ 13.0 Hz), 0.82–1.10 (m, 3 H), 1.20 (s, 3 H), 1.27 (s, 3 H), 1.55 (d, 3 H, $^3J_{HCCH}$ = 5.9 Hz), 1.95 (s, 15 H), 1.99 (s, 15 H); ^{1}H NMR (C_6D_{12}, 270 MHz) δ −0.20 (d, 1 H, $^2J_{HCH}$ = 14.2 Hz), 0.09 (d, 1 H, $^2J_{HCH}$ = 12.2 Hz), 0.24 (d of d, 1 H, $^2J_{HCH}$ = 14.0, $^4J_{HCCCH}$ = 2.1 Hz) 0.49 (t, 1 H, $^2J_{HCH} \simeq {}^3J_{HCCH} \simeq$ 13.0 Hz), 0.84 (m, 3 H), 0.97 (s, 3 H), 0.98 (s, 3 H), 1.32 (d, 3 H, $^3J_{HCCH}$ = 5.9 Hz), 2.00 (s, 15 H), 2.02 (s, 15 H); ^{13}C NMR (C_6D_{12}, 67.80 MHz) δ 122.75 (s), 122.22 (s), 85.52 (t, J_{C-H} = 123.6 Hz), 82.68 (t, J_{C-H} = 115.5 Hz), 53.47 (t, J_{C-H} = 128.3 Hz), 39.04 (q, J_{C-H} = 126.5 Hz), 37.58 (s), 32.42 (q, J_{C-H} = 127.4 Hz), 29.72 (q, J_{C-H} = 126.5 Hz), 27.56 (d, J_{C-H} = 106.3 Hz), 11.43 (q, J_{C-H} = 125.9 Hz), 11.93 (q, J_{C-H} = 125.9 Hz); IR (Nujol cm^{-1}) 1260 s, 1170 w, 1153 sh, 1098 br, m, 1020 s, 889 w, 801 s, 720 m, 500 w.

Anal. Calcd for $C_{28}H_{46}Th$: C, 54.71; H, 7.54. Found: C, 54.35; H, 7.56.

$Cp'_2Th(C_3H_5)[CH_2C(CH_3)_3]$ (12). Allylithium, 2.1 mL (0.80 mmol) as a 0.38 M solution in Et_2O, was syringed into a two-necked 30-mL reaction flask under an argon flush and the solvent removed in vacuo. A solid addition tube was charged with 0.47 g (0.77 mmol) of $Cp'_2Th(Cl)[CH_2C(CH_3)_3]$ and the tube attached to the reaction flask. In vacuo at −78 °C, 20 mL of Et_2O was condensed into the flask and the $Cp'_2Th(Cl)[CH_2C(CH_3)_3]$ added to the resulting solution. The reaction mixture was stirred at −78 °C for 15 min and then allowed to warm to room temperature. After 4 h, the solvent was removed in vacuo and the residual solids dried under high vacuum for 1 h. Pentane, 15 mL, was condensed onto the solids and the mixture filtered. The solids on the frit were next washed with pentane (3 × 5 mL) via Soxhlet extraction and the washings combined with the yellow filtrate. The filtrate volume was reduced in vacuo to 5 mL and the solution slowly cooled to −78 °C. The resulting pale-yellow microcrystalline product was collected by filtration at −78 °C; yield, 0.15 g, 31.0%; ^{1}H NMR (C_6D_{12}, 270 MHz) δ 0.61 (s, 2 H), 1.02 (s, 9 H), 1.97 (s, 30 H), 2.73 (d, 4 H), 5.37 (m, 1 H); IR (Nujol, cm^{-1}) 1566 w, 1510 w, 1353 w, 1349 w, 1250 w, 1270 m, 1043 w, 1020 m, 1000 m, 900 w, 810 s, 745 w, 722 m.

Anal. Calcd for $C_{28}H_{46}Th$: C, 54.71; H, 7.54. Found: C, 53.86; H, 7.15.

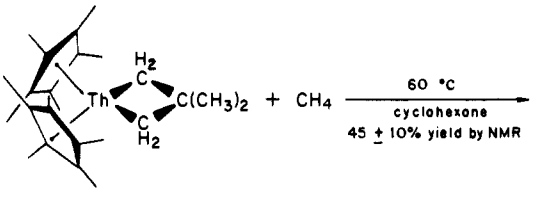
$Cp'_2Th(C_3H_5)[CH_2C(CH_3)_3]$ Thermolysis under Propylene. A 5-mm Pyrex tube, sealed at one end, was charged with 0.020 g (0.032 mmol) of $Cp'_2Th(C_3H_5)[CH_2C(CH_3)_3]$. The tube was attached to an adaptor with a calibrated gas bulb, and 0.30 mL of C_6D_{12} and propylene (0.453 mmol) were condensed into the tube at −196 °C. The tube was then sealed and allowed to warm to room temperature. After shaking, the reaction mixture was allowed to stand at room temperature for 2 h and an ^{1}H NMR spectrum recorded on the 270-MHz NMR spectrometer. The tube was then immersed in a 60 °C constant temperature bath and the reaction progress monitored by ^{1}H NMR.

Reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ with Ethylene. A 5-mm Pyrex tube sealed at one end was charged with 0.015 g (0.026 mmol) of $Cp'_2ThCH_2C(CH_3)_2CH_2$. Cyclohexane-d_{12}, 0.3 mL, and ethylene (0.436 mmol) were condensed into the tube at −196 °C, and the tube was sealed. The tube was wrapped with aluminum foil, and the reaction mixture was allowed to warm to room temperature. The extent of reaction was then monitored by 270-MHz ^{1}H NMR. The spectral data reported below were recorded after 6-h reaction time.

$Cp'_2ThCH_2C(CH_3)_2CH_2CH_2CH_2$: ^{1}H NMR ($C_6D_{12}$, 270 MHz) δ 0.02 (s, 2 H), 0.23 (m, 4 H), 0.79 (t, 2 H), 0.93 (s, 6 H), 2.00 (s, 30 H); ^{13}C NMR (C_6D_{12}, 67.80 MHz) δ 122.57, 79.71, 73.36, 44.96, 35.67, 31.67, 20.16, 11.81.

Results

Reactions of 1 with Saturated Hydrocarbons. At concentrations in the tenth molar range, the reaction of thoracyclobutane **1** with methane can be conveniently monitored by ^{1}H NMR spectroscopy at 60 °C (eq 4, Figure 1). The identity of methylneopentyl



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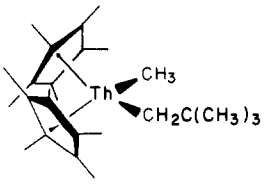


2 (4)

complex **2** is established on the basis of ^{1}H and ^{13}C NMR data as well as by comparison to an authentic sample prepared from $Cp'_2Th(Cl)][CH_2C(CH_3)_3]$ and CH_3Li (see Experimental Section for details). By NMR, the yield of **2** in this process is estimated to be 45 ± 10%. The other products of this reaction are oily

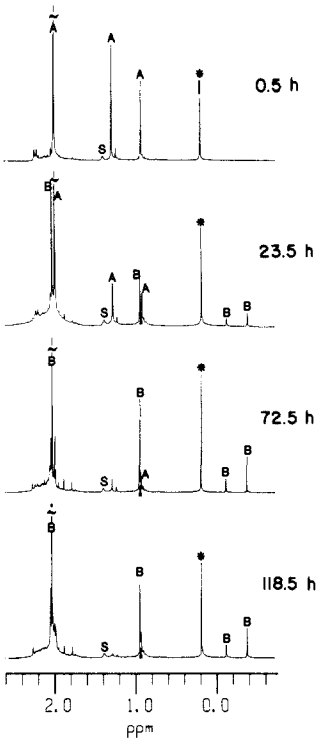
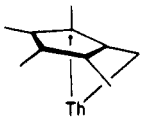


Figure 1. Proton NMR spectra (FT, 270 MHz) of the reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ (**1**, ca. 0.2 M) with CH_4 (ca. 10 atm, ca. 0.2 M in solution) in cyclohexane-d_{12} at 60 °C. S = solvent, A = $Cp'_2ThCH_2C(CH_3)_2CH_2$, B = $Cp'_2Th(CH_3)[CH_2C(CH_3)_3]$ (**2**), * = CH_4, an arrow indicates neopentane.

materials that arise from the independent thermolyses of **1** and **2** (verified by appropriate control experiments) and are indicated in the ^1H NMR by broad, extraneous features in the Cp′ region as well as by the presence of neopentane. Previous work[6a,23a] has shown that the thermolysis chemistry of **1** does not involve cyclohexane solvent attack (no neopentane-d_n, $n \neq 0$, is formed in C_6D_{12}; no cyclohexyl functionalities are incorporated in the thermolysis product), nor does this material, when prepared in C_6D_{12}, contain large amounts of ring-metalated species (e.g., A)



A

(addition of D_2O yields pentamethylcyclopentadiene which is ca. 90% d_1 and only ca. 10% d_2[23a]). Under the same reaction conditions, no $Cp'_2Th(CH_3)_2$ is detected in the reaction of **1** with methane. When eq 4 is carried out on a preparative (300 mg) scale, compound **2** can be isolated from cold pentane as a microcrystalline solid in ca. 24% yield. This relatively low yield of isolated material is due to the high solubility of **2** in hydrocarbon solvents.

The reaction of **1** with CD_4 was also studied under the conditions employed in eq 4. Assuming the rate of thermolysis of **1** is independent of added methane, then the reaction of **1** with CH_4/CD_4 exhibits an approximate kinetic isotope effect (k_H/k_D) at 60 °C of 6 ± 2. Hydrolysis (H_2O) of the reaction product of **1** and CD_4 in C_6D_{12} yields, by GC/MS, pentamethylcyclopentadiene (≤1% d_1) and a mixture of neopentane-d_1 (ca. 97%) and neopentane-d_2 (ca. 3% as $C(CH_3)_2(CH_2D)_2$ or $C(CH_3)_3CHD_2$). Clearly little deuterium is transferred from CD_4 to the Cp′ ligand.

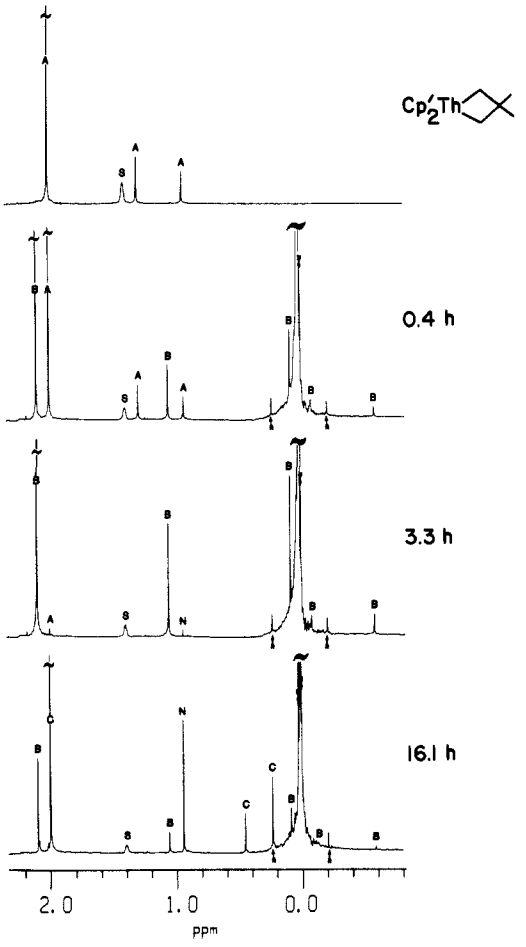
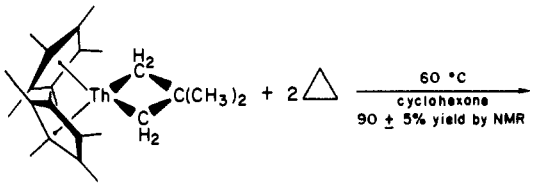


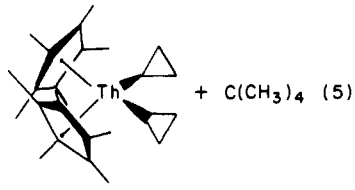
Figure 2. Proton NMR spectra (FT, 270 MHz) of the reaction of $Cp'_2ThCH_2C(CH_3)_2CH_2$ (**1**, ca. 0.1 M) with TMS (ca. 2 M) in cyclohexane-d_{12} at 30 °C for the first 3.3 h and then at 60 °C. S = solvent, N = neopentane, A = $Cp'_2ThCH_2C(CH_3)_2CH_2$ (**1**), B = $Cp'_2Th[CH_2C(CH_3)_3][CH_2Si(CH_3)_3]$ (**4**), C = $Cp'_2ThCH_2Si(CH_3)_2CH_2$ (**5**), and arrows indicate the ^{13}C and ^{29}Si satellites of $Si(CH_3)_4$.

The reaction of **1** with ethane was studied under approximately the same concentrations as the **1** + CH_4 reaction above and at 60 °C. Qualitatively, the reaction appears to be somewhat slower than eq 4, and there is no evidence by 270-MHz ^1H NMR for the formation of a $ThCH_2CH_3$ functionality[10a,20] during the course of the reaction. Rather, the predominant pathway appears to be the thermolysis of **1**. In addition, several weak Th–H signals[20,21] are observed in the δ 13–19 region; however, ethylene is not evident. Thus, if the hydrides are formed via the β-hydride elimination of one or more transitory $Th-CH_2CH_3$ intermediates (usually an endothermic[10] but sometimes kinetically facile[20,23b,c] reaction for this type of thorium complex), the ethylene must be consumed in some follow-up process (plausibly reaction with **1**—vide infra). This reaction was not investigated further.

The reaction of **1** with cyclopropane is very rapid at 60 °C in cyclohexane, and under the conditions of eq 4, displacement of the metallacyclic fragment is complete in less than 4.5 h (eq 5). Significant quantities of an intermediate such as $Cp'_2Th(CHCH_2CH_2)[CH_2C(CH_3)_3]$ are not evident in the 270-MHz ^1H NMR. The identity of the bis(cyclopropyl) complex **3** is established on the basis of ^1H and ^{13}C NMR spectroscopy as well as by comparison with an authentic sample prepared from Cp'_2ThCl_2 and cyclopropyllithium (see Experimental Section for details). In the ^1H NMR spectrum of **3**,[24] the doublets at δ 0.78

(23) (a) Bruno, J. W. Ph.D. Thesis, Northwestern University, Evanston, June 1983. (b) For example, the reaction of Cp'_2ThCl_2 with 2 equiv of isopropyllithium at low temperatures results in $Cp'_2Th(n\text{-propyl})_2$ in essentially quantitative yield.[23a] A plausible mechanism for this process is a β-hydride elimination–addition sequence. (c) Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576–3578.





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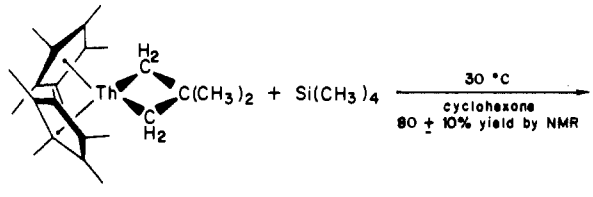
and −0.03 and the multiplet at −0.72 ppm are readily assigned to the cyclopropyl ligands. The ^{13}C NMR resonance at 70.33 ppm is assigned to the carbon atom of the cyclopropyl moiety bound directly to the thorium ion. The other cyclopropyl carbon atoms resonate at δ 8.59. Resonances at 123.47 and 11.54 ppm are assigned to the carbon atoms of the Cp′ ligands. GC/MS analysis of the volatiles from the deuterolysis (D_2O) of the reaction mixture reveals, in addition to Cp′D and cyclopropane-d_1, traces of neopentane-d_1.

Reactions of 1 with $Si(CH_3)_4$, $Sn(CH_3)_4$, and $P(CH_3)_3$. The ring-opening reaction of thoracyclobutane **1** with a 10–20-fold excess of TMS is rapid in C_6D_{12} at 30 °C (eq 6, Figure 2). The identity of complex **4** is established on the basis of ^1H and ^{13}C NMR spectroscopy as well as by comparison with an authentic sample.[6] An NMR kinetic study of the reaction of **1** with TMS



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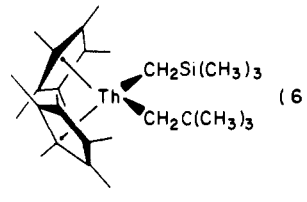


4

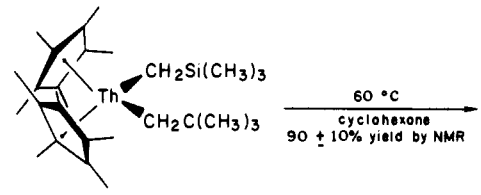
was carried out by monitoring the decay of the Cp′ resonance of **1** as a function of TMS concentration under conditions which were pseudo-first-order in TMS. The data (Figure 3) indicate the reaction to be first-order in metallacycle and first-order in TMS (eq 7) with $k = 7.0 \pm 0.5 \times 10^{-5}$ M^{-1} s^{-1} at −10 °C. On a

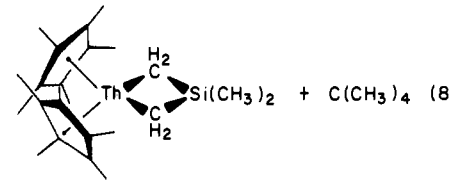
$$\frac{d[\mathbf{1}]}{dt} = -k[\mathbf{1}][\mathrm{TMS}] \qquad (7)$$

preparative scale (ca. 100 mg), complex **4** can be isolated from the reaction in ca. 8% yield. Higher isolated yields of **4** via crystallization from hydrocarbon solvents have been precluded by the very high solubility of this compound.

If the reaction in eq 6 is continued or the temperature raised, complex **4** undergoes cyclometalation to form known metallacycle **5** (eq 8). The mechanistic details of this reaction (intramolecular γ-C–H activation) are discussed elsewhere.[6b] In the presence of the present 10–20-fold excess of TMS at 60 °C, it is also found that the equilibrium between compound **5** and the ring-opened bis[(trimethylsilyl)methyl] complex **6** can be displaced partly to the right, in accord with the thermochemical results[10a] (eq 9).

(24) See paragraph at end of paper regarding supplementary material.





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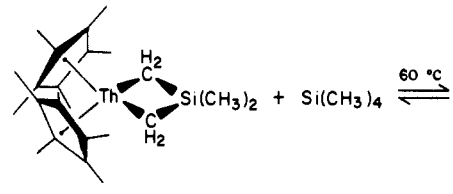

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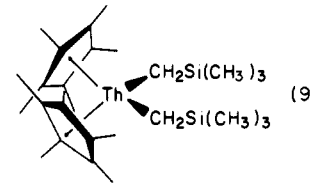
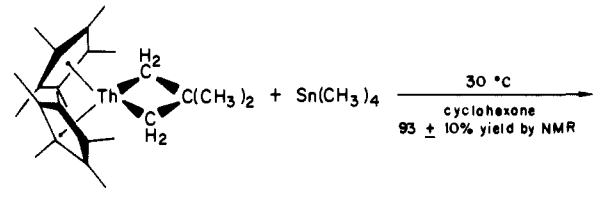
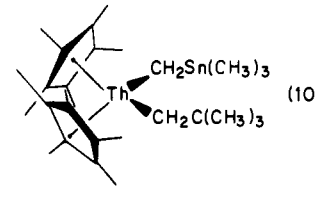


6

At room temperature, thoracyclobutane **1** undergoes a rapid ring-opening reaction with a 7-fold excess of tetramethylstannane that is complete within 2.2 h (eq 10). Complex **7** can be isolated





7

in a 13% yield (due to the high solubility) from a 300-mg scale reaction and can be characterized by standard analytical and spectroscopic techniques (see Experimental Section for details). The ^1H NMR spectrum of **7** in C_6D_6[24] displays parameters similar to those of transition-metal $MCH_2Sn(CH_3)_3$ complexes prepared by conventional procedures.[25a–c] The methyl hydrogen atoms of the neopentyl moiety resonate at δ 1.24, while the methyl resonance of the $Sn(CH_3)_3$ group occurs at δ 0.36 ($^2J_{SnCH}$ = 24.0 Hz). The resonances at δ −0.13 and δ −0.24 ($^2J_{SnCH}$ = 44.2 Hz) are assigned to the methylene hydrogen atoms of the neopentyl group and the $-CH_2Sn(CH_3)_3$ ligand, respectively. In the ^{13}C NMR spectrum,

(25) (a) Jeffrey, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1593–1605. (b) Truelock, M. M. D. Phil. Thesis, University of Sussex, 1975. (c) Collier, M. R.; Lappert, M. F.; Truelock, M. M. *J. Organomet. Chem.* **1970**, *25*, C36–C39. (d) Chambers, D. B.; Glockling, F.; Weston, M. *J. Chem. Soc. A* **1967**, 1759–1769. (e) Chambers, D. B.; Glockling, F.; Light, J. R. C. *Q. Rev. Chem. Soc.* **1968**, *22*, 317–337.

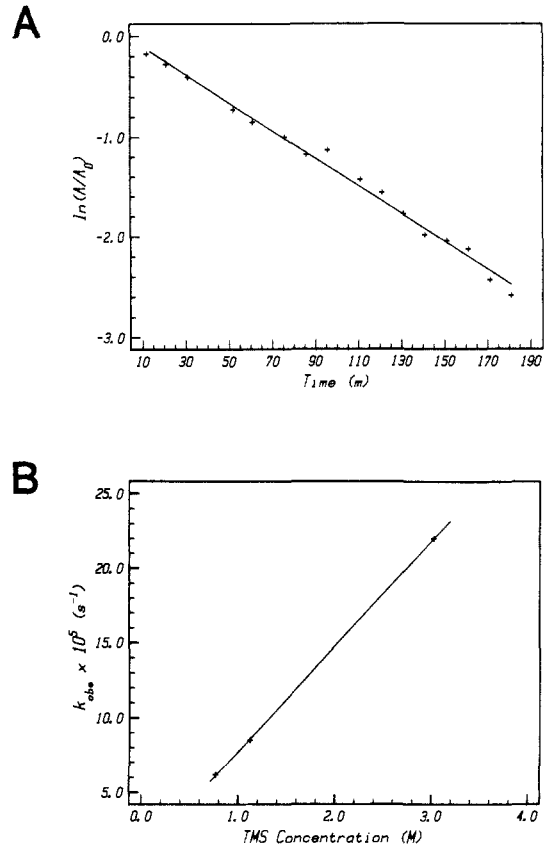


Figure 3. (A) Plot of ln $[A/A_0]$ vs. time (min) for the reaction of $Cp'_2\overline{ThCH_2C(CH_3)_2CH_2}$ (**1**) with TMS (0.772 M). A_0 = the total area of the Cp′ resonances. A = the area of the Cp′ resonance of **1**. (B) Plot of $k_{obsd} \times 10^5$ (s^{-1}) vs. TMS concentration (M) for the reaction of $Cp'_2\overline{ThCH_2C(CH_3)_2CH_2}$ (**1**) with TMS.

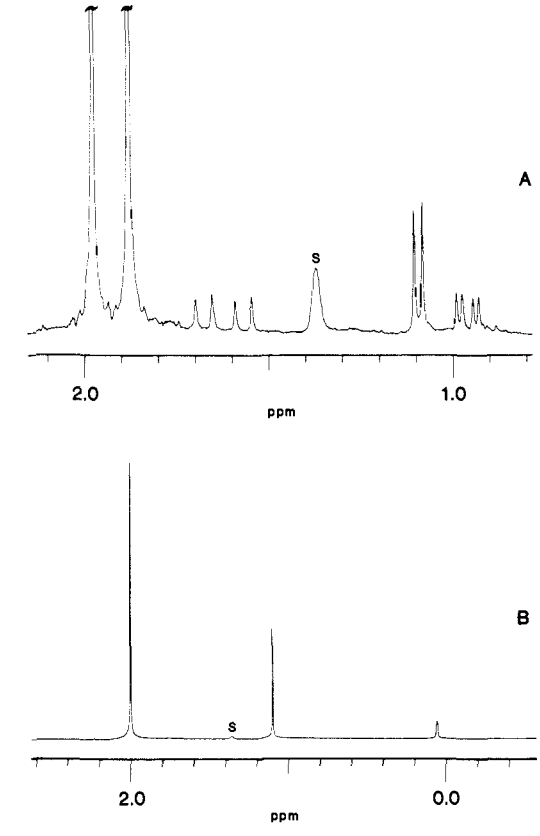
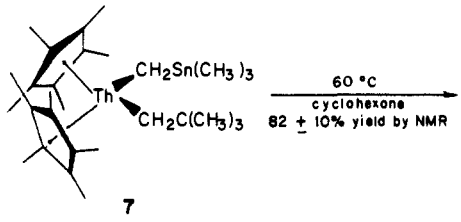


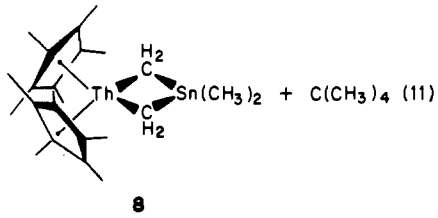
Figure 4. (A) Proton NMR spectrum (FT, 270 MHz) of $Cp'_2\overline{ThCH_2P(CH_3)CH_2}$ (**9**) in C_6D_{12}. S = solvent. (B) Proton NMR spectrum (FT, 270 MHz) of $Cp'_2Th[CH_2P(CH_3)_2]_2$ (**10**) in C_6D_{12}. S = solvent.

resonances at δ 123.84 and 12.13 are assigned to the Cp′ ring carbon atoms and Cp′ ring methyl atoms, respectively. The resonances at δ 103.36 and 77.66 are assigned to the two kinds of methylene carbon atoms. The resonances at δ 36.99 and 36.88 are due to the quaternary carbon and the methyl carbon atoms of the neopentyl ligand, respectively. The methyl carbon atoms attached directly to the tin atom resonate at δ −4.18. Deuterolysis of **7** followed by GC/MS yields pentamethylcyclopentadiene-d_1, neopentane-d_1, and $Sn(CH_3)_3CH_2D$ (readily assigned by comparison to a spectrum of $Sn(CH_3)_4$).[25d,c]

Thermolysis of complex **7** effects cyclometalation to the thoracyclobutane **8** in high yield (eq 11). The structure of **8** follows from the close congruence of NMR spectral parameters with those of compounds **1** and **5**. Thus, the ^1H resonance at δ 0.32 is



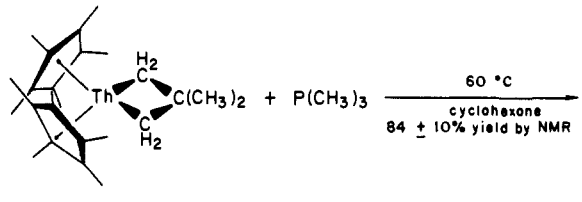
7

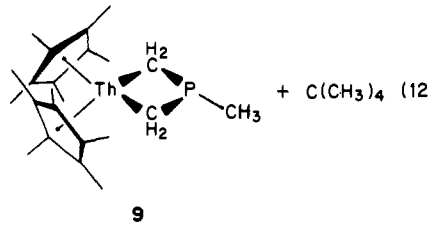


8

assigned to $SnCH_3$ protons and the resonance at δ 0.98 to $ThCH_2Sn$ protons. The resonance at δ 1.94 is ascribed to the methyl protons of the Cp′ ligands. The resonances in the ^{13}C NMR spectrum at δ 122.52 and 11.43 are assigned to the Cp′ ring carbon atoms and the Cp′ methyl carbon atoms, respectively. The methylene carbon atoms resonate at δ 66.15 and the methyl carbon atoms at δ −11.15. Furthermore, deuterolysis of the reaction mixture of eq 10 followed by GC/MS analysis indicates the presence of pentamethylcyclopentadiene-d_1, $Sn(CH_3)_2(CH_2D)_2$, and also traces of $Sn(CH_3)_3(CH_2D)$.

At 60 °C, complex **1** reacts rapidly with a 10-fold excess of trimethylphosphine to yield thoracyclobutane **9** (eq 12). No intermediate ring-opened species are detected by ^1H NMR. The

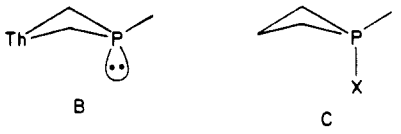




9

constitution and overall symmetry of compound **9** follow straightforwardly from the NMR data (Figure 4A). In the ^1H NMR, the $P-CH_3$ signal is located at δ 1.10, while the magnetically nonequivalent Cp′ (δ 1.90 and 1.99) and methylene (δ 0.97, $^2J_{PCH}$ = 4.0 Hz; δ 1.63, $^2J_{PCH}$ = 29.0 Hz) resonances reflect the disposition and conformational mobility of the phosphorus lone pair (inversion is slow on the NMR time scale at room temperature as expected[26]) as well as that of the four-membered metallocyclic

ring which is probably slightly puckered (B). Typical puckering



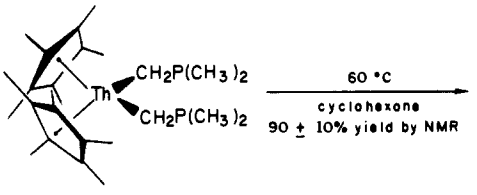
B C

angles in the phosphetane systems studied to date (C, -X = $-R^+$, = O) are in the range 16.7–34.9°.[27a,b] Karplus-like relationships between $^2J_{PCH}$ and dihedral angles in phosphines[27c,d] indicate that phosphorus lone pair–methylene C–H dihedral angles in **9** are probably near 0° and 100°, not exceptional for phosphetanes and related compounds.[27] In addition, the ^{31}P chemical shift in **9** (−117.7 ppm) is in accord with constricted valence angles about phosphorus[28] and negligible coordination to a metal ion.[28] Importantly, there is no evidence for a special conformation resulting from an interaction between the thorium ion and the phosphorus lone pair. The proton-coupled ^{31}P spectrum of **9** exhibits a triplet of multiplets due to coupling to the methyl and two types of methylene protons.

An authentic sample of **9** can also be prepared as shown in eq 13, with cyclometalation of the presumed intermediate $Cp'_2Th[CH_2C(CH_3)_3][CH_2P(CH_3)_2]$ apparently being quite rapid. The

$$Cp'_2Th(Cl)[CH_2C(CH_3)_3] + LiCH_2P(CH_3)_2 \xrightarrow[\text{room temperature}]{\text{ether}} 9 + C(CH_3)_4 + LiCl \quad (13)$$

sample of **9** prepared via this route was also characterized by elemental analysis and mass spectrometry. A third route to metallacycle **9** is by the thermolysis of $Cp'_2Th[CH_2P(CH_3)_2]_2$ (**10**, eq 14), prepared in turn from Cp'_2ThCl_2 and 2 equiv of $LiCH_2P(CH_3)_2$ (see Experimental Section for details). Complex **10** was characterized by standard methodology; the ^1H NMR spectrum is presented in Figure 4B. Spectral parameters are rather similar to those for other $MCH_2P(CH_3)_2$ complexes, including the small values of $^2J_{P\text{-}C\text{-}H}$.[29] There is no evidence from δ ^{31}P of phosphorus coordination to the thorium center.[28,29]



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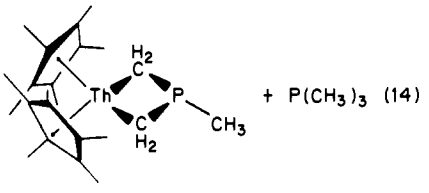
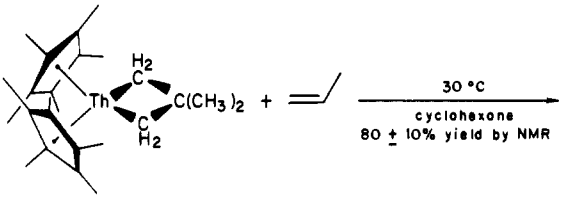
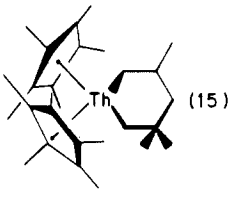


+ $P(CH_3)_3$ (14)

9

Reactions of 1 with Alkenes. Thoracyclobutane **1** reacts with propylene at room temperature according to eq 15; on a preparative scale, product **11** can be isolated in 29% yield. When eq 15 is monitored by ^1H NMR, there is no evidence for significant quantities of a new thoracyclobutane, as might arise through eq 3. The composition and structure of thoracyclohexane **11** follows



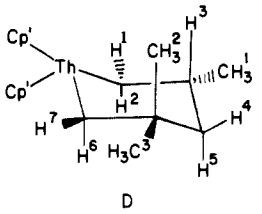


(15)

11

from elemental analysis, mass spectrometry, deuterolysis experiments, and $^1H/^{13}C$ NMR, aided by off-resonance and homonuclear decoupling experiments. Thus, the mass spectrum of **11** (15 eV) exhibits a parent ion at m/e 613 which corresponds to the loss of a hydrogen atom from the molecular ion. Deuterolysis of **11** followed by GC/MS analysis of the volatile organic products reveals the presence of pentamethylcyclopentadiene-d_1 and 2,2,4-trimethylpentane-d_2. The mass spectrum of the latter material is readily interpreted on the basis of the spectrum of an authentic sample of 2,2,4-trimethylpentane. In addition, hydrolysis (H_2O) of **11** yields 2,2,4-trimethylpentane.

NMR spectroscopic data (see Experimental Section for a complete compilation) are in best accord with structure D as the predominant conformation for complex **11**. Thus, the ^{13}C NMR



D

spectrum reveals magnetically nonequivalent Cp′ ligands with methyl signals at δ 11.93 and 11.43 and ring carbon signals at δ 122.75 and 122.22. Resonances at δ 85.52 and 82.68 are readily assigned[6,20] to the Th–CH_2 functionalities and the resonance at δ 53.47 to the remaining macrocyclic CH_2 group. The ^{13}C spectrum also reveals macrocyclic quaternary and tertiary carbon atoms at δ 37.58 and 27.56, respectively. Three methyl signals

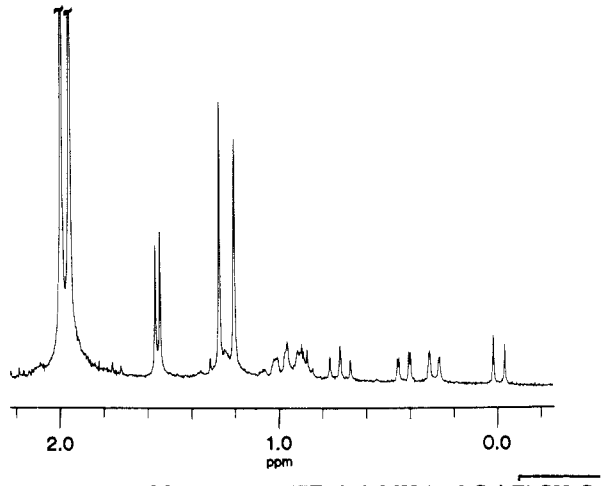


Figure 5. Proton NMR spectrum (FT, 270 MHz) of $Cp'_2ThCH_2C(CH_3)_2CH_2CH(CH_3)CH_2$ (**11**) in C_6D_6.

(26) (a) Smith, D. J. H. In "Comprehensive Organic Chemistry"; Sutherland, J. O., Ed.; Pergamon Press: Oxford, 1979; Vol. 2, pp 1127–1146. (b) Cremer, S. E.; Chorvat, R. J. *J. Org. Chem.* **1967**, *32*, 4066–4070.

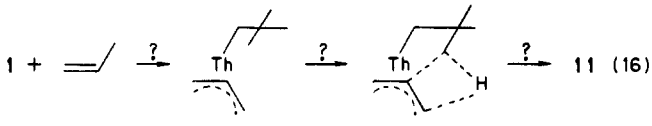
(27) (a) Haque, M.; Horne, W.; Cremer, S. E.; Kremer, P. W.; Kafarski, P. K. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1138–1142 and references therein. (b) Fitzgerald, A.; Campbell, J. A.; Smith, G. D.; Caughlan, C. N. *J. Org. Chem.* **1978**, *43*, 3513–3517 and references therein. (c) Albrand, J. P.; Gagnaire, D.; Martin, J.; Robert, J. B. *Bull. Soc. Chim. Fr.* **1969**, 40–48. (d) Albrand, J. P.; Gagnaire, D.; Robert, J. B. *Chem. Commun.* **1968**, 1469–1470.

(28) (a) Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog.* **1979**, *16*. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 319–321. (c) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Harper and Row: London, 1976; Chapter 3.1.

(29) (a) Karsch, H. H.; Schmidbaur, H. *Z. Naturforsch., B* **1977**, *32b*, 762–767. (b) Karsch, H. H.; Müller, G.; Krüger, C. *J. Organometal. Chem.* **1984**, *273*, 195–212. (c) Schore, N. R.; Young, S. J.; Olmstead, M. M.; Hofmann, P. *Organometallics* **1983**, *2*, 1769–1780. (d) Hofmann, P.; Stauffert, P.; Schore, N. E. *Chem. Ber.* **1982**, *115*, 2153–2174.

are observed at δ 39.04, 32.42, and 29.72. The ^{1}H NMR spectrum of **11** (Figure 5) is consistent with a metallacycle conformation[30] having two equatorial and one axial methyl group. Thus, resonances at δ -0.01 (doublet, $^2J_{HCH}$ = 14.2 Hz) and 0.42 (doublet of doublets, $^2J_{HCH}$ = 14.0, $^4J_{HCCCH}$ = 2.1 Hz) are assigned to protons 7 and 6, respectively. The 14.0-Hz coupling is typical of geminal interactions in cyclohexane rings,[31] while the 2.1-Hz coupling is reasonably ascribed to a long-range interaction with proton 4 or 5.[31] A proton signal at δ 0.71 is assigned to proton 2, with the apparent triplet multiplicity arising from near equivalence of geminal ($^2J_{HCH}$ ~ 13 Hz) and axial–axial vicinal ($^3J_{HCCH}$ ≈ 13 Hz) coupling constants. While the latter parameter is typical in magnitude of a cyclohexane axial–axial vicinal interaction, it is incompatible with the 0–5-Hz coupling characteristic of vicinal axial–equatorial and equatorial–equatorial interactions.[31] In accord with this reasoning, the doublet at δ 0.29 (J = 12.2 Hz) can be assigned to proton 1. Protons 3, 4, and 5 are assigned to a group of overlapping multiplets between δ 0.82 and 1.10. Singlets at δ 1.20 and 1.27 are assigned to the set of methyl groups 2 and 3, while the doublet at δ 1.55 ($^3J_{HCCH}$ = 5.9 Hz) is assigned to methyl group 1. The magnetically nonequivalent Cp′ ligands are associated with methyl signals at δ 1.95 and 1.99. Compound **11** is not sufficiently stable in cyclohexane-d_{12} at room temperature to permit supplementary 2D ^{13}C,^{1}H correlated NMR experiments.

To probe whether eq 15 might proceed via ring-opening C–H activation of propylene to form an allyl (there is precedent for allylic C–H activation in Cp'_2LnR chemistry, Ln = lanthanide[32]) followed by a second C–H activation (eq 16) to form a metal-



lacycle (analogues of this process are known[33]), an allyl neopentyl complex (**12**) was synthesized (eq 17). Complex **12** was characterized by standard techniques. At room temperature, the ^{1}H

$$Cp'_2Th(Cl)[CH_2C(CH_3)_3] + LiC_3H_5 \xrightarrow{\text{ether}} \underset{\mathbf{12}}{Cp'_2Th(C_3H_5)[CH_2C(CH_3)_3]} + LiCl \quad (17)$$

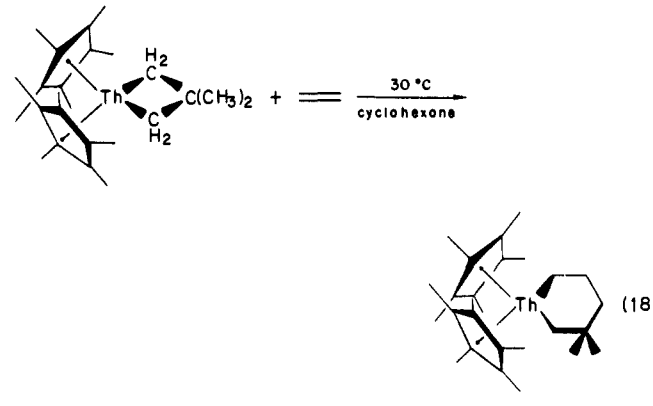
NMR spectrum of **12** exhibits magnetically equivalent Cp′ ligands and the A_4X pattern of a dynamic allyl (δ 2.73 (4 H), 5.37 (1 H), J = 12.2 Hz).[32b,34] Cooling the sample to −85 °C leads to collapse (270 MHz) of the A_4 doublet and the appearance of broad resonances at δ 4.16 and 2.31 (additional signals may be present but are severely overlapped with the Cp′ resonance). Although some broadening of the Cp′ resonance is also observed, it is not possible on the basis of the low-temperature NMR information to unambiguously distinguish η^1- from η^3-allyl instantaneous ligation. In support of η^3 ligation is the 1566-cm^{-1} band observed in the infrared spectrum of **12**[32b,35] and the abundance of well-characterized $Cp'_2Th(X)(Y)(Z)$ molecular structures.[36] In regard to the possibility of eq 16, it is important to note that complex **12** exhibits high thermal stability and, at room temperature, gives no evidence (by NMR) in neat C_6D_{12} or with added propylene for rearrangement to metallacycle **11**. The same observation obtains at 60 °C.

Table I. Estimated Values of $\Delta H°$ and $\Delta G°_{298}$ (kcal/mol) for the Ring-Opening C–H Activation by **1** of Various Substrates (RH)[a]

R	$\Delta H°_{calcd}$[b]	$\Delta G°_{298,calcd}$
CH_3	−13	−1
CH_2CH_3	−13	−1
C_6H_5	−20	−8
$CH_2Si(CH_3)_3$	−22	−10
$CHCH_2CH_2$	−23	−11

[a] [**1**], [RH] = 0.1 M. [b] For eq 2. Estimated uncertainty, ±4 kcal/mol.

The reaction of thoracyclobutane **1** with ethylene proceeds initially as shown in eq 18 to yield a metallacycle (**13**) which is considerably less thermally stable than **11**. The structure of



13

thoracyclohexane **13** is assigned on the basis of ^{1}H and ^{13}C NMR data as well as deuterolysis–GC/MS experiments. The ^{1}H NMR spectrum of **13** exhibits magnetically equivalent Cp′ ligands, magnetically equivalent metallacycle methyl substituents, and two sets of magnetically equivalent $ThCH_2$ protons (a singlet at δ 0.02 and a triplet at δ 0.79). These results are most reasonably interpreted in terms of an instantaneous metallacyclic structure similar to **D**. In the case of **13** but not **11**, rapid MC_5 ring inversion will be degenerate and will bring about a time-averaged molecular mirror plane.

Addition of D_2O to the **1** + ethylene reaction mixture (eq 18) after 1 h followed by GC/MS reveals Cp′D and 2,2-dimethylpentane-d_2 ($C_7H_{14}D_2$). With H_2O as the reagent, the MS of the latter fraction is identical with that of an authentic sample of 2,2-dimethylpentane. At longer reaction times, the mixture of volatiles from deuterolysis becomes very complex and includes products which appear to arise from β-hydride elimination of one metallacyclic $ThCH_2CH_2$ linkage ($C_7H_{13}D$), ethylene insertion into **13** followed by β-hydride elimination ($C_9H_{17}D$), and higher olefins associable with additional ethylene insertion/β-hydride elimination events as well as ethylene oligomerization.

No reaction is observed between **1** and isobutylene over the course of 4 h at room temperature. Heating the reaction mixture

(30) To our knowledge, diffraction structural data are not available for any d- or f-block metallacyclohexane containing only aliphatic carbon atoms in the metallacycle. Perhaps the closest structurally characterized example is $Cp_2ZrCH_2Si(CH_3)_2CH_2CH_2O$,[30a] which possesses a distorted boat metallacycle conformation. Other recent preparative work on transition-metal metallacyclohexanes is referenced below[30b-d] or elsewhere in this section.[8a,60a] (a) Tikkanen, W. R.; Petersen, J. L. *Organometallics* **1984**, *3*, 1651–1655. (b) Diversi, P.; Ingrosso, G.; Lucherini, A.; Porzio, W.; Zocchi, M. *Inorg. Chem.* **1980**, *19*, 3590–3597. (c) Bezman, S. A.; Bird, P. H.; Fraser, A. R.; Osborn, J. A. *Inorg. Chem.* **1980**, *19*, 3755–3763. (d) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418–7420.

(31) (a) Lambert, J. B.; Schurvell, H. F.; Verbit, E. L.; Cooks, R. G.; Stout, G. H. "Organic Structural Analysis"; Macmillan Publishing Co., Inc.: New York, 1976; Chapter 4. (b) Thomas, W. A. *Ann. Rev. NMR Spectrosc.* **1968**, *1*, 61–82. (c) Segre, A.; Musher, J. I. *J. Am. Chem. Soc.* **1967**, *89*, 706–707.

(32) (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(33) A two-step pathway for the thermal cyclometalation of $Cp'_2Th[CH_2Si(CD_3)_3]_2$ involves ring metalation to form a transitory $Cp'[\eta^6\text{-}(CH_3)_4C_5CH_2]ThCH_2Si(CD_3)_3$ species which in turn undergoes cyclometalation to yield $Cp'[\eta^5\text{-}(CH_3)_4(CH_2D)C_5]Th(CH_2)(CD_2)Si(CD_3)_2$.[6b]

(34) (a) Faller, J. W.; Adams, M. A. *J. Organometal. Chem.* **1979**, *170*, 71–80 and references therein. (b) Hoffmann, E. G.; Kallweit, R.; Schroth, G.; Seevogel, K.; Stempfle, W.; Wilke, G. *J. Organometal. Chem.* **1975**, *97*, 183–202 and references therein.

(35) (a) Maslowsky, E., Jr. "Vibrational Spectra of Organometallic Compounds"; Wiley: New York, 1977; pp 263–276. (b) An analogous transition is observed at 1535 cm^{-1} in $Cp'_2Nd(\eta^3\text{-}C_3H_5)$.[32b]

(36) (a) Moloy, K. G.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.*, in press. (b) Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1983**, *105*, 5696–5698. (c) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–5396.

to 60 °C results only in the apparent thermolysis of **1**.

Discussion

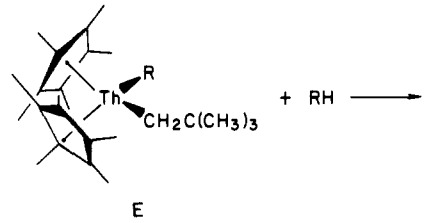
Alkane and $M(CH_3)_n$ Activation. Thermodynamics. A primary objective of this investigation was to determine whether eq 2 could be harnessed to effect the stoichiometric functionalization of saturated hydrocarbon molecules. Of crucial importance in such a strategy are the thermodynamic and kinetic constraints under which such transformations must take place.

In regard to reaction thermodynamics, the enthalpy of eq 2 can be approximately expressed as in eq 19, where D values are experimental bond disruption enthalpies.[10] Taking D(Th-R) to be

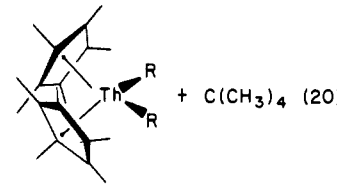
$$\Delta H°_{eq\,2} \approx D(\text{Th–CH}_2(\mathbf{1})) + D(\text{R–H}) - D(\text{Th–R}) - D(\text{Thneopentyl–H}) \quad (19)$$

the experimental D value in the corresponding Cp'_2ThR_2 compound,[10,37] D(Thneopentyl-H) the D(C-H) value in neopentane,[38] D(Th–CH_2(**1**))[37] from thermochemical studies of **1**,[10a] and D(R–H) from the literature,[38] the enthalpy change in eq 2 can be estimated for a variety of substrate molecules (Table I). Since both D(Thneopentyl-H) and D(Th–CH_2(**1**)) are constant, the exothermicity of eq 19 will be a delicate balance between the "strength" of the Th–C bond being made and of the C–H bond being broken. It is evident from Table I that all the reactions reported above for which D(Th–R) and D(R–H) data exist are predicted to be exothermic. However, whether or not such reactions are actually exergonic ($\Delta G° < 0$) must also reflect entropy changes, a major component of which will be associated with two molecules becoming one molecule. Although $\Delta S°$ values have not been measured for any of these reactions (such studies are in progress), a reasonable tentative estimate of the rotational and translational contribution to $T\Delta S°$ under the present reaction conditions is ca. −12 kcal/mol.[39] This information is incorporated in Table I, and it can be seen that while the activations of cyclopropane, TMS, and benzene are quite favorable, ring-opening methane and ethane functionalizations are estimated to be close to thermoneutral. In the case of the solvent cyclohexane, which is essentially unreactive toward **1**, D(C–H) = 95.5 ± 1 kcal/mol,[38] which is lower than the corresponding values for methane (105.1 ± 0.2 kcal/mol)[38] and in ethane (98.2 ± 1 kcal/mol).[38] Nevertheless, it is likely that the bulk of the cyclohexyl ligand and the congestion of the Cp'_2ThR_2 coordination environment[6b,36] result in a low D(Th–cyclohexyl).[10b] Hence, there are plausible thermodynamic reasons (as well as kinetic—vide infra) why cyclohexane is not attacked by complex **1**.

While eq 19 describes the initial ring-opening C–H activation process (eq 2), it is important to note that two additional types of C–H functionalization reactions are also observed. For cyclopropane and benzene,[6a] the ultimate reaction products with metallacycle **1** are the bis(cyclopropyl) and diphenyl derivatives, which may be formed via a ring-opened intermediate (E, eq 20). In the case of the benzene reaction, the rate law is known to be first-order in **1** and first-order in benzene.[6a,23] While the entropy change in eq 20 is probably small (two molecules → two molecules), the ring strain in **1** is no longer available to drive C–H activation. However, the Th–neopentyl bond is relatively "weak" in crowded $Cp'_2Th[CH_2C(CH_3)_3]_2$[6b] ($D \sim 72$ kcal/mol)[10a] and is likely to be comparably weak or weaker in E for the sterically demanding R = cyclopropyl and phenyl ligands. Using the D-(Th–$CH_2C(CH_3)_3$) value of $Cp'_2Th[CH_2C(CH_3)_3]_2$ and tabulated values for D(Th–R)[10], D(R–H),[38] and D(neopentyl–H),[38] we estimate that $\Delta H°_{eq\,20} \approx -10$ and −6 kcal/mol for R = cyclopropyl and phenyl, respectively. Thus, the second C–H activation process of eq 20 is accounted for thermodynamically.[40] Interestingly,



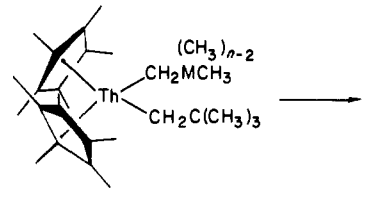
E

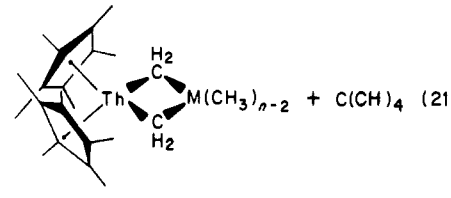


R = cyclopropyl, phenyl

for R = CH_3, it is estimated by the same procedure that $\Delta H°_{eq\,20} \sim -4$ kcal/mol. That $Cp'_2Th(CH_3)_2$ is not observed as a product in eq 4 may reflect the constraint that the second metalation is, within experimental error, thermoneutral and/or that the rate of the second step is very slow for methane (i.e., not competitive with thermal decomposition).

This work also identifies a number of new examples of C–H functionalization on exogeneous $M(CH_3)_n$ molecules. Precedent exists for intermolecular TMS metalation;[41] however, most reports of $P(CH_3)_3$ activation have dealt with complexes of this ligand.[42-44] As for the aforementioned hydrocarbons, C–H activation following eq 2 is also observed. However, in this case, the process involves cyclometalation (eq 21). In addition to the transposition of the





relatively "weak" Th–$CH_2C(CH_3)_3$ bond for a "stronger" (this has been verified for M = Si[10a]) Th–$CH_2M(CH_3)_{n-1}$ bond, eq 21 should enjoy a substantial entropic contribution to the driving force. For M = Si, n = 4, the $\Delta H°$ for eq 21 is estimated to be ca. −2 kcal/mol. If $T\Delta S° \approx 12$ kcal/mol,[39] eq 21 should lie far to the right, as observed. It should also be apparent that the eq 2, eq 21 reaction sequence offers a unique synthetic route to a

(37) For $Cp'_2Th(\overline{CHCH_2CH_2})_2$, D(Th–R) is 88.8 (5.3) kcal/mol in the gas phase and 88.0 (5.0) kcal/mol in toluene solution (Sonnenberger, D. C.; Marks, T. J., unpublished results).

(38) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(39) (a) Page, M. I. In "The Chemistry of Enzyme Action"; Page, M. I., Ed.; Elsevier: New York, 1984; pp 1–54. (b) Page, M. I.; Jencks, W. P. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 1678–1683.

(40) Mechanistic details of this second C–H activation process have not yet been elucidated and are presently under investigation. It is conceivable that species such as $Cp'_2Th(C_6H_5)CH_2C(CH_3)_3$ undergo neopentane elimination to yield a benzyne-like complex, which is then subject to arene attack. This mechanism is in accord with isotopic labeling results[6a,23a] and $Cp'_2Th(C_6H_5)_2$/arene metathesis chemistry.[20]

(41) (a) Green, M. L. H.; Berry, M.; Couldwell, C.; Prout, K. *Nouv. J. Chim.* **1977**, *1*, 187–188. (b) Lappert, M. F.; Engelhardt, L. M.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1982**, 1323–1324. (c) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276–277.

(42) (a) Grigoryan, E. A. *Russ. Chem. Rev.* **1984**, *53*, 210–220. (b) Ratke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272–3273. (c) Karsch, H. H.; Klein, H.-F.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637–638. (d) Karsh, H. H.; Klein, H.-F.; Schmidbaur, H. *Chem. Ber.* **1977**, *110*, 2200–2212. (e) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, *843*–855.

(43) Klein, H.-F.; Wenninger, J.; Schubert, U. *Z. Naturforsch., B* **1979**, *34b*, 1391–1397.

(44) (a) Mainz, V. V.; Andersen, R. A. *Organometallics* **1984**, *3*, 675–678. (b) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*, C60–C64. (c) Graimann, C. E.; Green, M. L. H. *J. Organomet. Chem.* **1984**, *275*, C12–C14. (d) Gibson, V. C.; Grebenik, P. D.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1101–1102.

variety of new binuclear methylene-bridged organometallic complexes.[45] Such chemistry is presently under investigation.

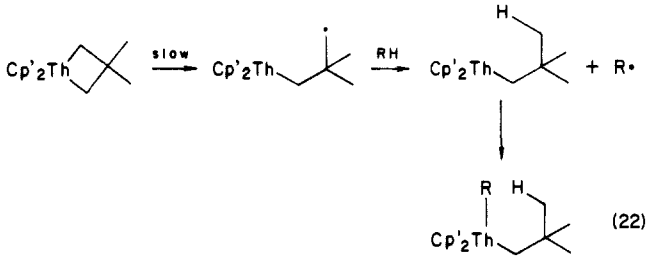
The question also arises as to whether thoracyclobutane **1** is unique, or whether other Cp'_2ThR_2 complexes can support C–H activation processes. Affirmative cases include degenerate arene metathesis by $Cp'_2Th(C_6H_5)_2$, which proceeds via a benzyne-like species,[20] and the reaction of $Cp'_2Th[CH_2C(CH_3)_3]_2$ with benzene to form $Cp'_2Th(C_6H_5)_2$, which takes place via initial cyclometalation[6] to form **1**.[6a,23a] In the contrasting case of $Cp'_2ThCH_2Si(CH_3)_2CH_2$, it was shown[10a] that the large D(Th–CH_2) values thermodynamically preclude certain ring-opening processes (e.g., reaction with benzene). In regard to simple, relatively unhindered alkyls, negligible reaction is detected between $Cp'_2Th(CD_3)_2$ and CH_4 ($\Delta H°_{calcd} = 0$ kcal/mol) or $Cp'_2Th(CH_3)_2$ and cyclopropane ($\Delta H°_{calcd} \sim -6$ kcal/mol for the first CH_4 elimination) at concentrations comparable to those in Figure 1 over the course of 1 week at 80 °C.[45] From these results, it thus appears that compound **1** is rather unusual for a $Cp'_2Th(alkyl)_2$ complex. The enhanced (thermodynamic, kinetic) proclivity for C–H functionalization reasonably resides both in the strained nature of the thoracyclobutane bonding as well as in the reduced steric hindrance offered an incoming hydrocarbon molecule.

Alkane and $M(CH_3)_n$ Activation. Rates and Mechanism. Although full, quantitative kinetic data for all reactions reported herein are not available, it is possible to make an approximate ordering of relative C–H reactivities toward thoracyclobutane **1**.

$$Sn(CH_3)_4 \gtrsim Si(CH_3)_4 > \text{cyclopropane} \approx P(CH_3)_3 > \text{benzene} > CH_4 \gtrsim C_2H_6 \gg \text{cyclohexane}$$

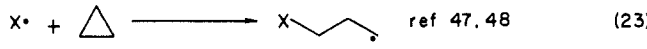
Where investigated, the reaction (eq 2) is found to be first-order in complex **1** and first-order in RH. In the case of CH_4/CD_4, a substantial kinetic isotope effect (6 ± 2) is observed, indicating considerable C–H bond scission in the rate-determining step of the reaction.

In regard to the mechanism of the ring-opening C–H activation, it is possible to straightforwardly discount the importance of several pathways. Thus, any sort of oxidative addition/reductive elimination sequence[8,9,12] involving formal Th(IV) ⇌ Th(VI) shuttling appears to be energetically[46] unreasonable. Likewise, a free radical process as in eq 22 seems unlikely from a number of standpoints.

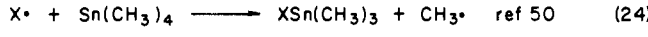


(22)

As written, such a pathway is inconsistent with the rate law for the TMS and benzene reactions as well as the kinetic isotope effect for the methane reaction (vide supra). In addition, the relatively clean character of the cyclopropane and $Sn(CH_3)_4$ activation reactions seems inconsistent with free radical chemistry, since fragmentation of the relatively weak C–C/Sn–C bonds (eq 23 and 24) is frequently observed in radical processes involving these substrates.[47-50] The absence of solvent involvement in any of the

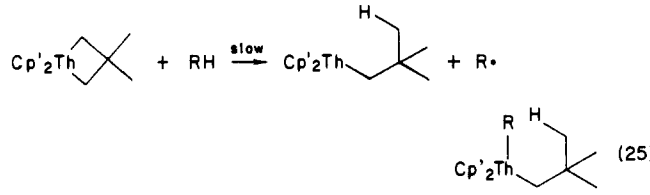


(23)



(24)

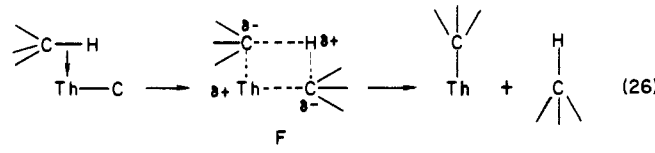
ring-opening chemistry and the lack of an obvious correlation between reaction rate and D(R–H) also argues against free-radical processes. Lastly, the activation energies likely associated with the present ring-opening C–H activation reactions appear to be incompatible (judging from the mild reaction conditions required) with processes involving the *complete* homolysis of a Th–C bond with $D \approx 65$ kcal/mol.[51] Expressed another way, the energy required[46] to reduce Th(IV) to Th(III) in a complete homolysis uncompensated by any other process appears to be incompatible with the activation energetics of the present transformations. A variant of eq 22 (eq 25) eliminates objections based upon the observed rate law and kinetic isotope effect; however, the activation



(25)

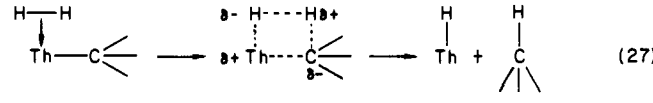
energetics of the homolysis, the lack of solvent involvement, the lack of cyclopropane/$Sn(CH_3)_4$ fragmentation, and the lack of correlation between rate and D(R–H) still present problems for a free-radical mechanism. While a tightly "caged" R· radical may eliminate several of these objections, invoking Th–R and C–H bond making in concert with R–H bond scission reduces the mechanism, in essence, to a concerted process.

A concerted, four-center heterolytic C–H activation pathway (eq 26) is compatible with the high electrophilicity of the Th(IV) ion and the pronounced polarity of the actinide-to-carbon σ bonding.[20,46,52] We as well as others have previously invoked such



(26)

a mechanism for intramolecular and intermolecular C–H activation at f-element centers.[6,15,32a] An analogous heterolytic pathway has also been invoked for metal–carbon bond hydrogenolysis in early transition-metal and f-element complexes (eq 27).[20,32b,52,53] That substitution of a π-donating alkoxide ligand



(27)

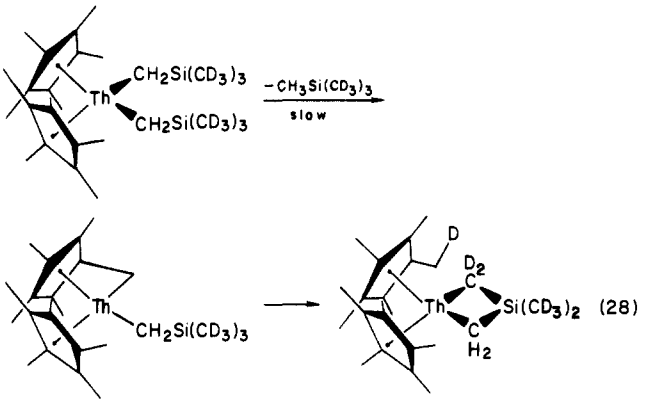
(OR) greatly depresses the rate of Th–CH_3 hydrogenolysis in $Cp'_2Th(OR)CH_3$ vs. $Cp'_2Th(CH_3)_2$[20,45] and that Cp'_2LnR (Ln = lanthanide) hydrogenolysis rates increase with decreasing Ln(III) effective ionic radius[53a] are both in accord with the electrophilicity required at M for such processes.

The rate of eq 2 for various RH molecules must necessarily reflect the stringent steric constraints imposed by the rather

(45) Fendrick, C. M.; Lin, Z.; Marks, T. J., unpublished results.
(46) Marks, T. J. *Prog. Inorg. Chem.* **1979**, *25*, 223–333.
(47) (a) Poutsma, M. L. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, pp 144–145, 178–181. (b) Huysen, W. A. "Free Radical Chain Reactions"; Wiley: New York, 1970; Chapter 4. (c) Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; Chapter 12.
(48) (a) Anpo, M.; Chatgilialoglu, C.; Ingold, K. U. *J. Org. Chem.* **1983**, *48*, 4104–4106. (b) Maynes, G. G.; Applequist, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 856–861. (c) Incremona, J. H.; Upton, C. J. *J. Am. Chem. Soc.* **1972**, *94*, 301–303.
(49) In the presence of strong metal electrophiles (e.g., Tl(III), Hg(II)), cyclopropane rings also undergo opening: Matteson, D. S. "Organometallic Reaction Mechanisms"; Academic Press: New York, 1974; pp 182–187.
(50) (a) Davies, A. G. *Adv. Chem. Ser.* **1976**, *157*, 26–40. (b) Davies, A. G.; Roberts, B. P.; Smith, J. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2221–2224. (c) Bouē, S.; Gielen, M.; Nasielski, J. *J. Organomet. Chem.* **1967**, *9*, 461–479. (d) The degree of fragmentation depends strongly on the identity of X.
(51) Conversely, activation energy arguments have been employed to estimate D(M–C) values: Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238–244 and references therein.
(52) (a) Marks, T. J.; Day, V. W. In "Fundamental and Technological Aspects of Organo-f-Element Chemistry"; Marks, T. J.; Fragalā, I. L., Eds.; Reidel: Dordrecht, 1985, pp 115–157. (b) Marks, T. J.; Ernst, R. D. In "Comprehensive Organometallic Chemistry"; Wilkinson, G. W., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Chapter 21. (c) Marks, T. J. *Science (Washington, D.C.)* **1982**, *217*, 989–997.
(53) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8111. (b) Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1–61. (c) Gell, K. I.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 3246–3248.

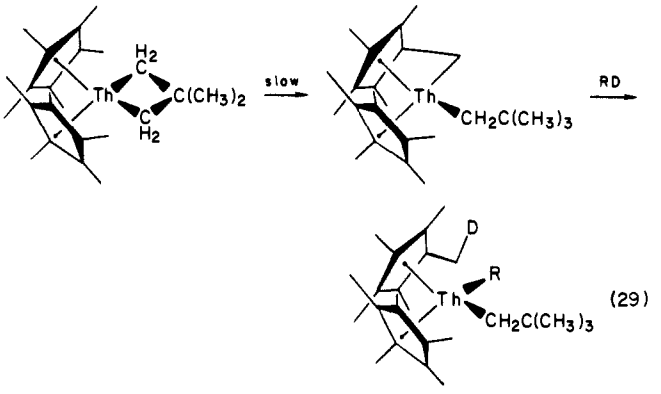
crowded Cp'_2ThR_2 coordination sphere[6,36,52] (especially in a transition state such as F[6b]) as well as the electronic demands of the C–H activation process. In regard to steric effects, the alkane trend $CH_4 \gtrsim C_2H_6 \gg C_6H_{12}$ is readily rationalized. However, the rapidity of the TMS, $Sn(CH_3)_4$, and cyclopropane reactions suggests that factors other than steric are also important. The cyclopropane and benzene results argue that D(C–H) is not the deciding factor. In attempting to understand the nature of transition states such as F, it is instructive to examine an RH parameter which can be roughly correlated with electron richness (susceptibility to electrophilic attack)—PES-derived ionization potential[54,55] and one that can be correlated with proton donor strength in nonpolar media—gas-phase acidity.[56] The ionization potentials of the substrates under examination here increase in the order (in eV) $P(CH_3)_3$ (8.62)[55] < $Sn(CH_3)_4$ (8.85) < benzene (9.25) < $Si(CH_3)_4$ (9.42) < propylene (9.73) < cyclopropane (9.96) < ethylene (10.52) < ethane (11.49) < methane (12.99). To a degree, these data correlate with the enhanced reactivity of $M(CH_3)_4$, $P(CH_3)_3$, benzene, and cyclopropane vis-ã-vis methane and ethane. Available gas-phase proton acidity data[56] are somewhat more qualitative but decrease in the order propylene > benzene > H_2 > ethylene, cyclopropane, methane, cyclohexane. Gas-phase acidity data are not available for $Si(CH_3)_4$ and $Sn(CH_3)_4$; however, correlations involving organophosphorus and organosulfur compounds[56b] as well as a great deal of solution chemistry suggest enhanced $M(CH_3)_4$ acidity over that of $C(CH_3)_4$.[57] From this rather limited information, all that can be said is that the enhanced benzene and probably $M(CH_3)_4/P(CH_3)_3$ reactivity over that of alkanes in eq 2 can also be correlated with gas-phase proton acidity.

The possible involvement of Cp′ ligand methyl groups in the present C–H activation chemistry is an issue which must also be addressed. In the case of $Cp'_2Th[CH_2Si(CH_3)_3]_2$ and $Cp'_2Th[CH_2Si(CD_3)_3]_2$ cyclometalation,[6b] the major pathway involves intramolecular C–H activation. However, this process exhibits a substantial kinetic isotope ($k_H/k_D \approx 10$) effect, and in the case of the deuterated derivative, ca. 30% of the reaction occurs via initial ring metalation[32a,58] (eq 28) (good agreement between TMS-d and pentamethylcyclopentadiene-d yields were obtained).[6b]



(28)

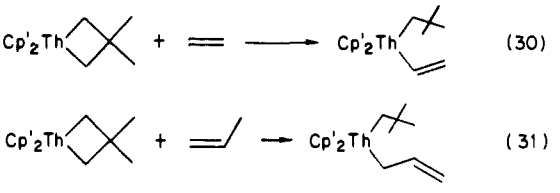
In the case of eq 2, an analogous scenario would require a unimolecular rate law and the delivery of one deuterium to the Cp′ ligand (eq 29). Such behavior is not compatible with the **1** +



(29)

TMS kinetic data nor with the CH_4/CD_4 nonzero kinetic isotope effect and product analysis results (one deuterium is incorporated in the formation of the neopentyl ligand and no pentamethylcyclopentadiene-d_1 is detected).[59] Thus, for the systems examined, ring participation in the C–H activation process appears to be minimal.

Olefin Activation. Although the aforementioned ionization potential and gas-phase acidity trends might predict a high reactivity of olefins for C–H activation, the reaction of **1** with ethylene and propylene takes an entirely different course: insertion[60] (eq 15 and 18). One explanation for this behavior lies in the reaction thermochemistry. If it is assumed that D(Th–vinyl) ≈ D(Th–C_6H_5)[10] and D(Th–allyl) ≈ D(Th–benzyl),[10] then ethylene and propylene C–H activations (eq 30 and 31) are predicted from literature D(C–H) values[38] to both be exothermic by ca. 25 kcal/mol. However, the insertion of ethylene into a



(30)
(31)

Th–C σ bond of **1** (eq 18) is estimated to be exothermic by ca. 36 kcal/mol. Clearly thermodynamics favors the insertion reaction. Nevertheless, C–H activation reactions have been reported for bulkier olefins in the case of scandium (propylene)[12h] and lutetium (isobutylene)[32a] alkyls. For nonbulky olefins such as ethylene, however, it appears that insertion is generally far more rapid than alkane activation. Thus, for Cp'_2LuCH_3 and closely related alkyls, the second-order rate constant for ethylene insertion exceeds 800 M^{-1} s^{-1} at 25 °C,[32b] while the rate constant for methane activation is reported to be 4.6×10^{-4} M^{-1} s^{-1} at 70 °C.[32a]

Although the present work does not represent an exhaustive investigation, it appears that alkylidene-related processes as in eq 3 are not competitive with olefin insertion rates. Whether this result indicates that Th(IV) alkylidenes are inaccessibly high-energy species when not stabilized by special environments[58a,b] remains unresolved.

Additional Mechanistic Comments. For the complexes under discussion, a plausible pathway for the above olefin insertion reaction (eq 32) bears an interesting analogy to the aforementioned reaction coordinates for C–H (eq 26) and H–H (eq 27) activation. In terms of orbital symmetry constraints, the MO explanation advanced by Lauher and Hoffmann[61] for facile olefin insertion

(54) (a) Turner, D. W. *Adv. Phys. Org. Chem.* **1966**, *4*, 31–71. (b) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; pp 449–456 and references therein.

(55) (a) Ikuta, S.; Kebarle, P.; Bancroft, G. M.; Chan, T.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 5899–5902 and references therein. (b) The lone pair of $P(CH_3)_3$ renders ionization potential–reactivity comparisons somewhat less straightforward.

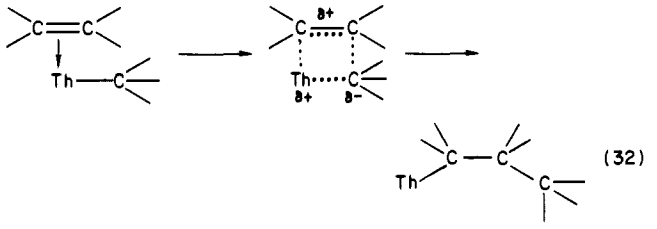
(56) (a) Pellerite, M. J.; Brauman, J. I. In "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1980; Part A, pp 55–96. (b) Streitwieser, A., Jr.; Juaristi, E.; Nebenzahl, L. L. Ibid., pp 322–381. (c) Bohme, D. K.; Lee-Ruff, E.; Young, L. B. *J. Am. Chem. Soc.* **1972**, *94*, 5153–5159. (d) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. F., Ed.; Academic Press: New York, 1979; Vol. 2, pp 87–121.

(57) (a) Armitage, D. A. In ref 52b, Chapter 9.1, pp 8–10. (b) Farah, D.; Karol, T. J.; Kuivila, H. G. *Organometallics* **1985**, *4*, 662–666 and references therein.

(58) (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.

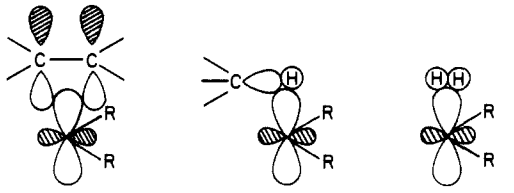
(59) A variant of eq 29 can be envisioned in which alkane activation rather than ring metalation is rate-determining. Nevertheless, delivery of a deuterium to the Cp′ ligand is expected.

(60) For some recent examples of the insertion of olefins into the metal–carbon linkages of metallacyclobutanes, see: (a) Binger, P.; Doyle, M. J.; Benn, R. *Chem. Ber.* **1983**, *116*, 1–10 and references therein. (b) Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461–486 and references therein.



(32)

in d^0 Cp_2MX_2 systems should be qualitatively applicable to C–H and H–H activation, with C–H and H–H a_1 and b_2 σ and σ^* orbitals replacing ethylene a_1 and b_2 π and π^* orbitals. Initial coordination to the a_1 LUMO[61,62] (G, H, and I) places the substrates in the appropriate spatial orientation for concerted M–C or M–H bond formation, M–R bond scission, and H–R bond formation.[63] More quantitative theoretical results on the hydrogenolysis process from Brintzinger (Zr)[64] and from Rabaâ, Saillard, and Hoffmann (lanthanides)[65] support this view. Although the role of 4f and 5f orbitals in such processes cannot yet be quantitatively assessed, a highly electrophilic metal center which would bind and positively polarize the substrate for nucleophilic attack by a proximate, negatively polarized ligand would appear to offer a major advantage in facilitating eq 26, 27, and 32. Optimizing the rates and selectivities of such processes will be the goal of future investigations.



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Registry No. 1, 83692-52-8; **2**, 94138-25-7; **3**, 99477-03-9; **4**, 99458-65-8; **7**, 99477-04-0; **8**, 99477-05-1; **9**, 99477-06-2; **10**, 99477-07-3; **11**, 99494-81-2; **12**, 99477-08-4; **13**, 99477-09-5; TMS, 75-76-3; $Cp'_2Th(Cl)[CH_2C(CH_3)_3]$, 74587-39-6; Cp'_2ThCl_2, 67506-88-1; CH_4, 74-82-8; $Sn(CH_3)_4$, 594-27-4; $LiCH_2P(CH_3)_2$, 64065-06-1; $P(CH_3)_3$, 594-09-2; LiC_3H_5, 3052-45-7; H_2, 1333-74-0; C, 7440-44-0; cyclopropyllithium, 3002-94-6; cyclopropane, 75-19-4; ethane, 74-84-0; propylene, 115-07-1; ethylene, 74-85-1.

Supplementary Material Available: ^{1}NMR of spectra of $Cp'_2Th(\overline{CHCH_2CH_2})_2$ (3) (Figure S-1) and $Cp'_2Th[CH_2C(CH_3)_3][CH_2Sn(CH_3)_3]$ (7) (Figure S-2) (2 pages). Ordering information given on any current masthead page.

(61) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

(62) (a) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragalà, I.; Ciliberto, E.; Coleman, A. W. *J. Electron Spectrosc. Rel. Phenom.* **1980**, *18*, 61–73. (b) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422–6433. (c) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433–6441. (d) Condorelli, G.; Fragalà, I.; Centineo, A.; Tondello, E. *J. Organomet. Chem.* **1975**, *87*, 311–315. (e) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *30*, 2290–2304 and references therein.

(63) An alternative picture could be drawn by using an unoccupied a_1 MO quantized between the two M–R bonds.

(64) Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337–344.

(65) Rabaâ, H.; Saillard, J.-Y.; Hoffmann, R., submitted for publication.

Electrically Conductive Metallomacrocyclic Assemblies. High-Resolution Solid-State NMR Spectroscopy as a Probe of Local Architecture and Electronic Structure in Phthalocyanine Molecular and Macromolecular "Metals"

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Abstract: This contribution reports a high-resolution solid-state ^{13}C CPMAS study of the low-dimensional phthalocyanine (Pc) conductors Ni(Pc)I, H_2(Pc)I, $\{[Si(Pc)O]I_{1.1}\}_n$, $\{[Si(Pc)O]X_y\}_n$ (X = BF_4, PF_6, SbF_6, $y \sim 0.35$), $\{[Ge(Pc)]I_{1.1}\}_n$, and Ni(Pc)X_z (X = BF_4, PF_6, SbF_6, $z \approx 0.33$), as well as of the precursors Ni(Pc), H_2(Pc), $[Si(Pc)O]_n$, and $[Ge(Pc)O]_n$. For the partially oxidized materials, large, locally resolved ^{13}C-conduction electron Knight shifts with dispersions as large as 400 ppm and multiplicities in accord with crystallographic site symmetries are observed. By using Ni(Pc)I selectively labeled with ^{13}C at the 1,1′ skeletal positions and with ^2H at the 4,4′ hydrogen atom positions, along with dipole dephasing techniques, it is possible to completely and unambiguously assign the CPMAS spectrum. From this information is obtained a map of the conduction electron hyperfine interaction about the carbon framework of the macrocycle. In Ni(Pc)I, the ratios of the 1,1′ to the 2,2′ ^{13}C spin–lattice relaxation times conform approximately to the Korringa relationship at room temperature. For the partially oxidized phthalocyanine series as a whole, a linear relationship is observed between the individual 1,1′ and 2,2′ ^{13}C Knight shifts and the corresponding Pauli-like magnetic susceptibilities.

As precursors for electrically conductive low-dimensional solids,[1] robust and chemically flexible phthalocyanines (A, M(Pc)) have proven to be extremely versatile.[2] The simple molecular compounds can be converted, using halogens[3,4] or a limited range of

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