experiments revealed the correlation among the labeled carbons (Figure 1) and the reasonable values of coupling constants (data not shown). The indirect incorporation of [2-^{13}C]acetate can be reasonably explained by the multiple passages of [2-^{13}C]acetate through the Krebs cycle followed by the methyl malonate–propionate shunt via succinate. For the first cycle, only C-3 of propionate derived from succinate would be labeled. However, for the second cycle, C-1, C-2, and C-3 of propionate derived from succinate should be labeled in the enrichment ratio of 0.5:0.5:1. This ratio would reach 1:1:1 by the multiple passages (Scheme I). From the above results, it has been concluded that cationomycin is biosynthesized from 8 mol of acetate, 9 mol of propionate, and 2 mol of methionine methyl as shown in Scheme II.

In order to study in more detail the biosynthetic pathway of cationomycin, appropriately labeled preformed side chain acids were used for the feeding experiments. However, both [OCH_3-^{13}C]-4-methoxy-6-methylsalicylate[13] and [CH_3-^{3}H]orsellinate[14] were not incorporated at all. It appears that the preformed acids are not activated in vivo.

Registry No. Cationomycin, 80394-65-6; acetic acid, 64-19-7; propionic acid, 79-09-4.

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[13] The compound was prepared from orsellinic acid ([methyl-^{13}C]methyl iodide (90% enriched), KOH/Me_2SO, 30 min at room temperature). Satisfactory analytical data have been obtained for the compound.

[14] Labeled by Tritium Labelling Services of Amersham International Limited, Buckinghamshire, England HP7 9LL. The specific activity was 0.408 Ci/mol.

Thermochemically Based Strategies for C–H Activation on Saturated Hydrocarbon Molecules. Ring-Opening Reactions of a Thoracyclobutane with Tetramethylsilane and Methane

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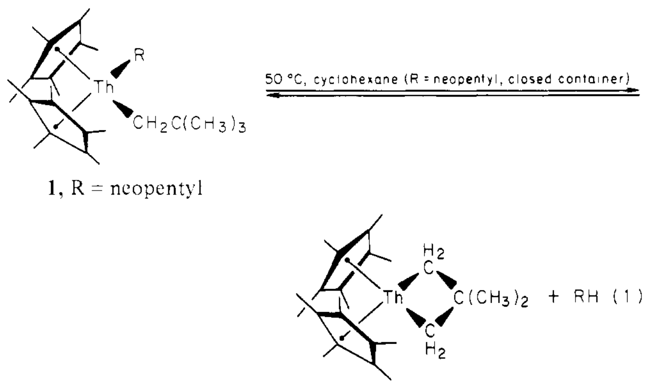
Devising effective strategies for the selective, metal-mediated, homogeneous activation of C–H bonds on exogenous saturated hydrocarbon molecules currently represents a great challenge.[1,2] Transition-metal systems involving oxidative addition/reductive elimination sequences have received the greatest attention,[1-3] although recent results with a trivalent organolanthanide[4] suggest "heterolytic" C–H activation pathways may also be widely applicable. We recently reported an actinide-centered cyclometalation reaction in which extrusion of a saturated hydrocarbon molecule occurs (eq 1, R = neopentyl) to yield thoracyclobutane 2.[5] Thermochemical data[6] (D(Th–R))[7] indicate that unfavorable nonbonded interactions[5b,8] and/or intrinsically weak Th–neopentyl bonds in **1** partly compensate for the nonnegligible metallacyclic ring strain energy in **2** (ca. 15 kcal/mol[6]). As a consequence, the endothermicity of eq 1 (ca. +7 kcal/mol) is sufficiently small for R = neopentyl to be outweighed by entropic ($T\Delta S$)[9,10] factors; thus, $\Delta G < 0$. These observations raise the fascinating question as to whether, for judiciously selected D(Th–R) and D(R–H), eq 1 can be rendered sufficiently endothermic (eq 2)[11] that $\Delta G >$

$$\Delta H_1 \approx D(\mathrm{Th{-}R}) + D(\mathrm{neopentyl{-}H}) - D(\mathrm{Th{-}CH_2(\mathbf{2})}) - D(\mathrm{R{-}H}) \quad (2)$$

0, i.e., that complex **2** will stoichiometrically activate saturated hydrocarbons.[12] Taking tetramethylsilane and methane as examples, we confirm this hypothesis and report that these substrates are readily activated by a tetravalent actinide complex according to the reverse of eq 1.



1, R = neopentyl

2

Complex **2** was synthesized and purified as described previously.[5a] Due to the extreme sensitivity of the subject compounds, reactions were carried out in sealed NMR tubes under scrupulously anaerobic and anhydrous conditions in the dark. From steric considerations and since D(Th–secondary alkyl) is likely to be less than D(Th–primary alkyl),[6,13a] cyclohexane-d_{12} was chosen as the solvent.[13b] The reaction of **2** with tetramethylsilane, as monitored by 270-MHz ^{1}H NMR, is shown in Figure 1. Disappearance of signals due to **2** is accompanied by the appearance of a new thorium complex, **3**, formulated as shown in eq 3 on the basis of ^{1}H and ^{13}C NMR as well as comparison with an authentic sample.[14a,b] The very high solubility of **3** has so far limited isolated

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[5] (a) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357–7360; (b) *J. Organomet. Chem.* **1983**, *150*, 237–246. (c) Bruno, J. W.; Smith, G. M.; Marks, T. J., manuscript in preparation.

[6] (a) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824–6832. (b) Sonnenberger, D. C.; Marks, T. J. Morss, L. R., submitted for publication.

[7] D = Bond disruption enthalpy, as defined in: Pilcher, G.; Skinner, H. A. In "The Chemistry of the Metal–Carbon Bond"; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; pp 43–90.

[8] Bruno, J. W.; Smith, G. M.; Day, V. W.; Marks, T. J.; Schultz, A. J., manuscript in preparation. The neutron diffraction derived molecular structure of **1** reveals even more severa $Cp'\cdots R$ and $R\cdots R$ nonbonded interactions than in $Cp'_2Th[CH_2Si(CH_3)_3]_2$.[5b]

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[11] D(Th–CH_2(**2**)) in eq 2 refers to the metallocycle-opening bond disruption enthalpy in **2**.

[12] Complex **2** has previously been shown to activate arenes[5a]—usually[1-3] a far less demanding transformation.

[13] (a) For example, Cp'_2Th isopropyl compounds rapidly and quantitatively isomerize to the *n*-propyl analogues.[13c] (b) Thermolysis of **2** in cyclohexane-d_{12} and subsequent GC/MS analysis of the hydrolysis products gives no evidence of C–D activation.[13c] (c) Bruno, J. W. Ph.D. Thesis, Northwestern University, Evanstown, IL, 1982.

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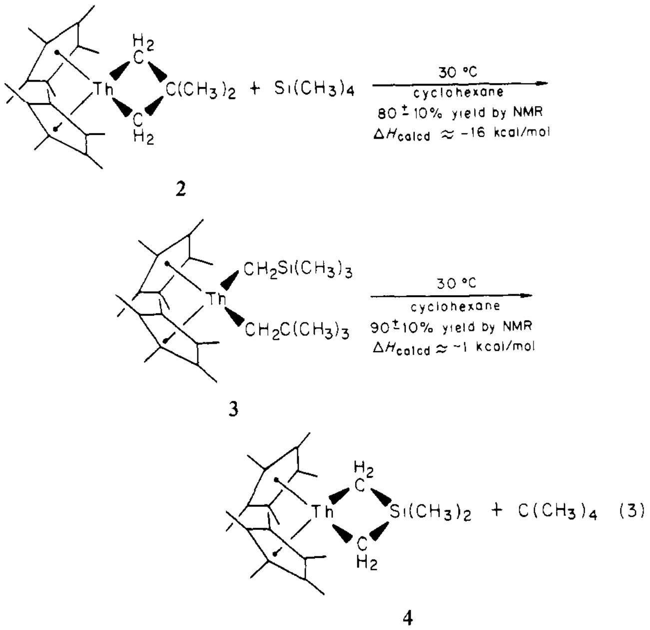
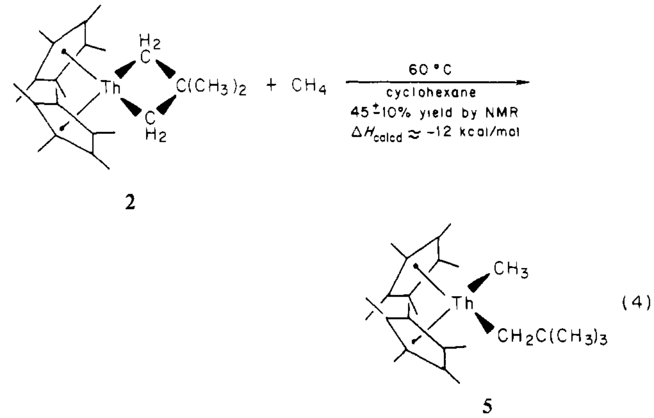


yields of pure (>95%) material to ca. 10% for 100-mg scale reactions. Solution reaction enthalpies, estimated from literature $D(\mathrm{Th{-}R})$[6] and $D(\mathrm{R{-}H})$[15] values, are also given in eq 3. Interestingly, Figure 1 reveals that upon continued heating, **3** disappears and a third complex, the known[5a] metallacycle **4**, is the resulting product.[14c] Entropic factors are likely of thermodynamic and kinetic[2b,10] importance in the second reaction.

Figure 2 illustrates the reaction of **2** with methane as monitored by 270-MHz ^{1}H NMR. The spectral changes are interpreted in terms of eq 4, where **5** is assigned on the basis ^{1}H and ^{13}C NMR data as well as comparison with an authentic sample.[16] The high solubility of **5** has so far precluded isolation of crystalline samples (>90% pure) in yields of more than ca. 10% for 300-mg scale



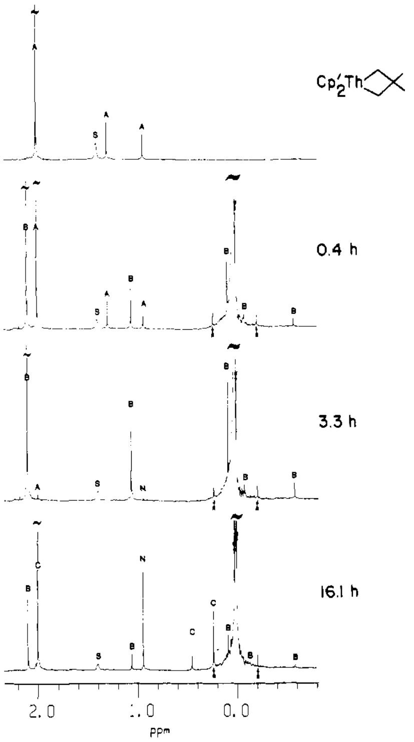


Figure 1. Proton NMR spectra (FT, 270 MHz) of the reaction of $\mathrm{Cp'_2ThCH_2C(CH_3)_2CH_2}$ (**2**, ca. 0.1 M) with $\mathrm{Me_4Si}$ (ca. 2 M) in $\mathrm{C_6D_{12}}$ at 30 °C for the first 3.3 h then at 60 °C. S = solvent, N = neopentane, A = $\mathrm{Cp'_2ThCH_2C(CH_3)_2CH_2}$,[14a] B = $\mathrm{Cp'_2Th[CH_2C(CH_3)_3][CH_2Si(CH_3)_3]}$ (**3**),[14b] C = $\mathrm{Cp'_2ThCH_2Si(CH_3)_2CH_2}$ (**4**),[14c] and arrows indicate ^{13}C and ^{29}Si satellites of $\mathrm{Me_4Si}$. The low-field ^{29}Si satellite has been truncated in the 0.4 and 3.3 h spectra.

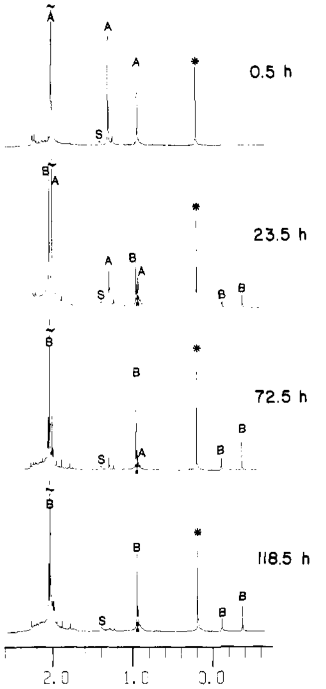


Figure 2. Proton NMR spectra (FT, 270 MHz) of the reaction of $\mathrm{Cp'_2ThCH_2C(CH_3)_2CH_2}$ (**2**, ca. 0.2 M) with $\mathrm{CH_4}$ (ca. 10 atm, ca. 0.2 M in solution) in $\mathrm{C_6D_{12}}$ at 60 °C. S = solvent, A = $\mathrm{Cp'_2ThCH_2C(CH_3)_2CH_2}$,[14a] B = $\mathrm{Cp'_2Th[CH_2C(CH_3)_3]CH_3}$ (**5**),[16] * = $\mathrm{CH_4}$, and arrow indicates neopentane.

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[14] (a) Complex **2**: ^{1}H NMR ($\mathrm{C_6D_{12}}$, 90 MHz) δ 1.98 (30 H, s), 1.27 (6 H, s), 0.91 (4 H, s). (b) Complex **3** was prepared from $\mathrm{Cp'_2Th(Cl)CH_2Si(CH_3)_3}$[14d] and $\mathrm{LiCH_2C(CH_3)_3}$ in ether (68% yield).[14e] ^{1}H NMR ($\mathrm{C_6D_{12}}$, 90 MHz) δ 2.10 (30 H, s), 1.04 (9 H, s), 0.08 (9 H, s), −0.08 (2 H, s), −0.58 (2 H, s); ^{13}C NMR ($\mathrm{C_6D_{12}}$, 67.80 MHz) δ 123.7 (s), 110.4 (t, J_{CH} = 99.9 Hz), 74.2 (t, J_{CH} = 99.9 Hz), 39.1 (s), 36.6 (q, J_{CH} = 122 Hz), 12.1 (q, J_{CH} = 126 Hz), 4.9 (q, J_{CH} = 117 Hz); IR (Nujol mull, cm^{-1}) 2800 sh, 2770 sh, 2720 sh, 1354 s, 1310 w, 1280 w, 1250 s, 1240 s, 1225 sh, 1205 m, 1060 w, 1020 m, 990 w, 925 sh, 890 s, 840 s, 815 sh, 740 s, 715 s, 670 m, 565 m, 505 m, 440 sh, 410 sh. Anal. Calcd for $\mathrm{C_{29}H_{52}SiTh}$: C, 52.71; H, 7.93. Found: C, 52.60; H, 7.26. (c) Complex **4**: ^{1}H NMR ($\mathrm{C_6D_{12}}$, 90 MHz) δ 1.98 (30 H, s), 0.43 (4 H, s), 0.22 (6 H, s). (d) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667. (e) Smith, G. M.; Marks, T. J., manuscript in preparation.

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[16] Prepared from $\mathrm{Cp'_2Th(Cl)CH_2C(CH_3)_3}$[14d] and $\mathrm{LiCH_3}$ in pentane/ether (28% yield). ^{1}H NMR ($\mathrm{C_6D_{12}}$, 270 MHz) δ 2.01 (30 H, s), 0.94 (9 H, s), −0.12 (2 H, s), −0.38 (3 H, s); ^{13}C NMR ($\mathrm{C_6D_6}$, 67.80 MHz) δ 123.2 (s), 101.7 (t, J_{CH} = 103.6 Hz), 71.7 (q, J_{CH} = 111.8 Hz), 37.2 (s), 36.9 (q, J_{CH} = 124.7 Hz), 11.7 (q, J_{CH} = 125.9 Hz); IR (Nujol mull, 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 $\mathrm{C_{26}H_{42}Th}$: C, 53.23; H, 7.22. Found: C, 53.23; H, 7.44.

reactions. Extraneous signals in the η^5-$(CH_3)_5C_5$ region indicate that competing thermolysis of **2**,[17a] which likely involves ring methyl metalation,[4b,13c,17b] is also operative. Interestingly, the reaction of **2** with CD_4 is significantly slower than with CH_4 and a preliminary analysis yields a kinetic isotope effect of 6 ± 2.[18] This result argues that H_3C–H bond breaking is the rate-limiting step in methane activation. That hydrolysis of the CD_4 reaction product produces pentamethylcyclopentadiene with <3% $H(CH_3)_4(CH_2D)C_5$ by GC/MS indicates that CD_4 attack on a ring-metalated species is not a major reaction pathway. That the neopentane produced upon hydrolysis contains ca. 3 ± 1% neopentane-d_2[19] suggests that eq 4 may be reversible.

These results demonstrate that it is possible to design isolable organoactinides of sufficiently high energy content that the stoichiometric (as opposed to catalytic) activation (with some selectivity) of saturated hydrocarbon molecules becomes thermodynamically favorable. Moreover and perhaps most fascinating, such activations are kinetically rather facile.

Acknowledgment. We thank the National Science Foundation (Grants CHE-8009060 and CHE-8306255) for generous support of this research. We thank G. M. Smith for sharing data on $Cp'_2Th[CH_2C(CH_3)_3][CH_2Si(CH_3)_3]$ and Dr. P. L. Watson for information in advance of publication.

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[17] (a) Verified by independent thermolysis of **2** in C_6D_{12}. (b) For example, thermolysis of **2** in C_6D_{12} followed by D_2O quenching results in appreciable quantities of $D(CH_3)_4(CH_2D)C_5$.[13c]

[18] A highly accurate measurement is precluded by the considerably greater participation of the side reactions under these conditions.

[19] In addition to the expected neopentane-d_1, substantial quantities of neopentane-d_0 are also detected. Such a result is expected from the competing thermolysis of **2**, which produces a ring-metalated neopentyl compound.[13c,17]

Synthesis of a Stable Cyclopropene Fused by a Six-Membered Ring. A Novel Approach from Fused Thiirene Sulfoxide

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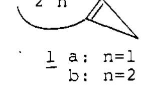
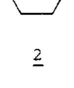
Received December 21, 1983

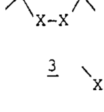
Considerable attention has recently been focused on strained bicyclic alkenes, especially the [*n*.1.0]bicyclic system **1** (*n* = 1–4).[1]



1 a: n=1
b: n=2
c: n=3
d: n=4



2



3

Although olefins should have a planar structure unless geometrical constraints[2a,b] are present or the appropriate symmetry[2c] is lacking, Wagnar[3a] and Pople[3b] have shown by ab initio calculations that all bicyclic alkenes **1** should have nonplanar structures. Considerably efforts have been directed toward the preparation of bicyclic alkenes.[1,4] Evidence for intermediacy of bicyclo[4.1.0]alkene[5] **1d**[6,7] as well as **1a**,[8] **1b**,[9] and **1c**,[7] produced by dehydrohalogenation and dehalogenation of the corresponding halides, was presented as trapped Diels–Alder adducts by Gassman[6] and Wiberg.[7] The dimethyl derivative **2** was spectroscopically identified below −35 °C by Closs and Boll.[10] However, experimental structural studies have never been reported for **1** owing to their instability.

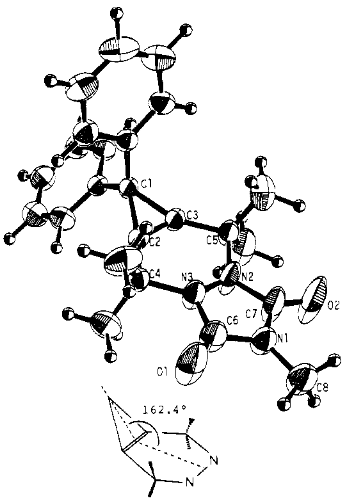
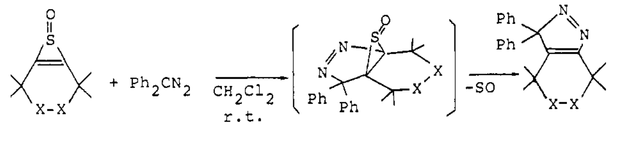


Figure 1. ORTEP drawing of the molecular structure of bicyclo[4.1.0]hex-1(6)-ene **8**. Bond lengths (Å): C_1–C_2 1.521, C_1–C_3 1.526, C_2–C_3 1.286, C_2–C_4 1.491, C_3–C_5 1.478. Bond angles (°): C_2–C_1–C_3 49.92, C_1–C_2–C_3 64.82, C_1–C_3–C_2 65.26, C_2–C_3–C_5 130.23, C_3–C_2–C_4 129.16.

We wish to report an attractive route to a thermally stable bicyclo[4.1.0]hept-1(6)-ene derivative via [2 + 3] cycloaddition of fused thiirene sulfoxide **3** with diphenyldiazomethane and its X-ray crystal analysis.

Fused thiirene sulfoxide **3**, recently prepared in our laboratory, was shown to be quite reactive.[11] It was treated with a 5-fold amount of diphenyldiazomethane in CH_2Cl_2 at room temperature. After standing for several hours, 3*H*-pyrazole **5** (54%)[12,13] was obtained by chromatographic purification.



3 4 5

Photolysis (≥365 nm)[14] of **5** in benzene at room temperature

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[12] Spectral and elemental analysis data of **5**: mp 142.0–143.0 °C from hexane–benzene; ^1H NMR δ ($CDCl_3$) 1.34 (s, 6 H), 2.08 (s, 6 H), 3.10 (s, 3 H), 7.64–7.35 (m, 10 H); ^{13}C NMR δ ($CDCl_3$) 157.4, 153.7, 153.4, 150.2, 133.3, 129.0, 128.3, 107.2, 62.4, 59.1, 25.1, 25.0, 23.6; UV (nm, hexane) λ_{max} 356 (ϵ 203) (N=N); MS, *m/e* 415 (M^+). Anal. Calcd for $C_{25}H_{25}N_5O_2$: C, 69.40; H, 6.02; N, 16.87. Found: C, 69.22; H, 6.15; N, 16.79.

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