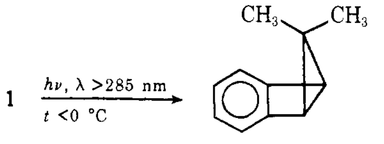
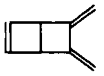


7

(3 H), 1.06 (3 H), and 2.54 (2 H) and a pair of symmetrical multiplets at δ 6.62 (2 H) and 6.82 (2 H). The singlet bridgehead proton absorption (δ 2.54) was at almost the exact chemical shift which would be predicted for this molecule considering the chemical shifts of the benzylic protons of benzocyclobutene (δ 3.14),[10] the allylic protons of cyclobutene (δ 2.54),[11] and the bridgehead protons of bicyclo[2.1.0]pent-2-ene (δ 2.0).[12] On the other hand, the bridgehead protons of the Dewar-*o*-xylylene species **8** are at δ 3.73.[13] This, plus the



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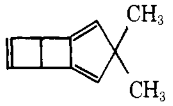

9

fact that **8** is relatively stable thermally, makes the alternative photoproduct structure **9** highly unlikely. The ready thermal reconversion of the photoproduct to isoindene **1** taken together with the simplicity of the NMR spectrum makes dimeric structures highly improbable. Hence, the benzobicyclo[2.1.0]-pent-2-ene structure can be invoked with confidence.

Note Added in Proof. Recently, evidence for intermediacy of unsubstituted isoindene in a photobisdecarbonylation reaction has been reported. It is apparently stable to a 1,5-hydrogen shift at −50 °C, but only dimers and trapping products were isolated: R. N. Warrener, R. A. Russell, and T. S. Lee, *Tetrahedron Lett.*, 49 (1977).

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Photochemical Synthesis of Low-Valent Organothorium Complexes. Evidence for Photoinduced β-Hydride Elimination

Sir:

An important chemical property of transition metal organometallic compounds is the widespread existence of multiple formal oxidation states for the metal ions and the general tendency of these ions to readily shuttle between oxidation states.[1] The situation is not so clear for organothorium and organouranium complexes, and by far the great bulk of known compounds contain the actinide ion in the +4 oxidation state.[2] The only low-valent (<IV) complexes of these metals reported to date are several uranium(III) complexes[3] and the deep violet $(C_5H_5)_3Th$.[4] The latter compound, prepared by reduction of $(C_5H_5)_3ThCl$, is especially noteworthy because few thorium(III) complexes of any type are known,[5,6] and because there is great current interest in the low oxidation state organometallics of the isoelectronic Ti, Zr, and Hf.[7] For these reasons we have initiated a study of new synthetic routes to low-valent organoactinides, and of the chemical and physicochemical properties of such species. In this communication we report an efficient, high-yield photochemical synthesis of two new thorium(III) complexes and some surprising observations on how $(C_5H_5)_3ThR$ photochemistry differs from the thermal chemistry.

It is known that $(\eta^5\text{-}C_5H_5)_3ThR$ compounds (e.g., R = *i*-propyl) thermolyze cleanly in toluene at 170 °C according to eq 1.[8]

$$2(C_5H_5)_3Th(i\text{-}C_3H_7) \xrightarrow[\Delta]{} \underset{\mathbf{1}}{[(C_5H_5)_2Th(C_5H_4)]_2} + 2C_3H_8 \quad (1)$$

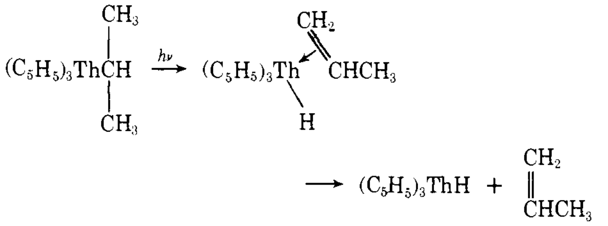
Essentially no β-hydride elimination[9] is observed, but rather hydrogen is intramolecularly abstracted from a cyclopentadienyl ring to quantitatively yield propane and the $\eta^5{:}\eta^1$-cyclopentadienylthorium(IV) complex **1**.[10] In marked contrast, we find that irradiation (Hanovia 679A36 medium pressure mercury lamp) of benzene solutions (0.10–0.30 M) of $(C_5H_5)_3Th(i\text{-}C_3H_7)$ in quartz at 5 °C produces (within 1–2 h) a ≥ 92% yield of the highly air-sensitive, dark green microcrystalline complex **2a** as well as comparable quantities[11] of propane (53%) and propene (47%)

$$(C_5H_4R)_3Th(i\text{-}C_3H_7) \xrightarrow{h\nu} \underset{\mathbf{2}}{(C_5H_4R)_3Th} + \text{propane} + \text{propene} \quad (2)$$

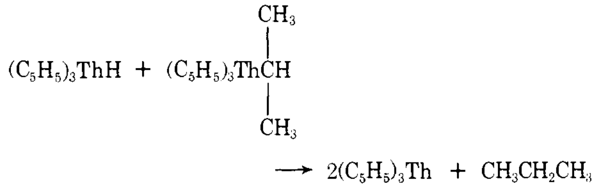
2a, R = H
2b, R = CH_3

In a similar manner, the methylated analogue, **2b**, can be prepared. Though different in properties from the above-mentioned violet species,[4] the data at hand lead us to also formulate **2a** as $(C_5H_5)_3Th$. Anal. Calcd for $C_{15}H_{15}Th$: C, 42.12; H, 3.54. Found: C, 42.26; H, 3.77. The infrared spectrum (Nujol mull) of **2a** exhibits the characteristically simple pattern[8,12,13] of an η^5-C_5H_5 unit (as in the triscyclopentadienyl lanthanides[14]): 1261 w, 1065 w, 1008 m, 832 w, sh, 800 s, sh, 700 vs, 670 m, sh cm^{-1}. The laser Raman spectrum of **2a** (spinning sample, 5145 Å Ar^+ excitation) is also similar to the lanthanide triscyclopentadienyls[16] and other[8,12,17] η^5-C_5H_5 complexes: 1870 vw, 1866 vw, 1854 w, 1436 vw, 1136 w, 1121 s, 1068 vw, 1007 vw, 900 vw, 893 vw, 885 w, 840 s, 806 vw, 790 vw, 780 w, 615 w, 254 s, 234 s, 157 s cm^{-1}. No evidence for a metal hydride or any other non-η^5-C_5H_5 species is observed in these spectra or in those of the $(C_5D_5)_3Th$ analogue. The mass spectrum of **2a** exhibits a strong peak at $(C_5H_5)_3Th^+$; ions as high as $[(C_5H_5)_3Th]_2{}^+$,[18] which fragment by loss of C_5H_5, C_2H_2,[19] or C_3H_3[19] are also observed. Methanolysis of **2a** produces cyclopentadiene in greater than 95% yield. The methylated complex **2b** has chemical and spectral properties consistent with $(C_5H_4CH_3)_3Th$. Neither **2a** nor **2b** is sufficiently soluble for NMR studies. The room temperature magnetic susceptibility of **2a** is in accord with a Th(III) ($5f^1$) formulation (in a site of low symmetry[22]): $\chi_M = 1845 \times 10^{-6}$ cgs, $\mu_{eff}^{298} = 2.10\ \mu_B$. The electronic spectrum (Nujol mull) exhibits broad maxima at 16 000, 21 000, and 23 600 cm^{-1}. As yet neither **2a** nor **2b** has been obtained as crystals suitable for diffraction studies. Whether association (dimerization or greater) via partial bridging of the cyclopentadienyl rings between metal ions occurs in the solid as in the triscyclopentadienyllanthanides[23,2c] (taken to be evidence for appreciable ionic character in the metal-ligand bonding[23a,2c]) remains to be determined.

The presence of nearly comparable quantities of propene and propane as $(C_5H_5)_3Th(i\text{-}C_3H_7)$ photolysis products differs significantly from the thermolysis findings.[8] The most reasonable interpretation of this result is the photoinduced β-hydride elimination[9] sequence shown in eq 3 and 4. There is



$$(C_5H_5)_3Th\underset{CH_3}{\overset{CH_3}{C}}H \xrightarrow{h\nu} (C_5H_5)_3Th(H)(CH_2{=}CHCH_3) \longrightarrow (C_5H_5)_3ThH + \overset{CH_2}{\underset{CHCH_3}{\|}} \qquad (3)$$



$$(C_5H_5)_3ThH + (C_5H_5)_3Th\underset{CH_3}{\overset{CH_3}{C}}H \longrightarrow 2(C_5H_5)_3Th + CH_3CH_2CH_3 \qquad (4)$$

considerable evidence for thermally induced intra- and intermolecular analogues of this multistep process.[9,24] The nature and yields of the organic products are incompatible with predominant formation via isopropyl radical disproportionation since the disproportionation to combination ratio for this radical in solution is ca. 1.2.[25] Furthermore, photolysis of a frozen benzene solution of $(C_5H_5)_3Th(i\text{-}C_3H_7)$ yields, upon thawing, 74% propene and 26%[11] propane. This is consistent with the expectation that olefin yield will be increased by favoring reaction 3 at the expense of 4. We also find by ^1H NMR that concurrent isomerization to the *n*-propyl compound occurs to a small (ca. 5%) but nonnegligible extent. Readdition of olefin to the metal hydride (which could lead to isomerization) is observed in many,[9,24b,26] but not all[27] systems undergoing β-hydride elimination. Further support for the proposed mechanism of eq 3 and 4 as well as information on less important, competing processes is provided by studies of $(C_5D_5)_3Th(i\text{-}C_3H_7)$ (97% D) photochemistry in C_6H_6 and C_6D_6. We find that only ca. 4% of the propane formed arises from solvent hydrogen abstraction (possibly via isopropyl radicals) and only ca. 4% arises from photochemical promotion of the thermal (ring hydrogen abstraction[8]) reaction.[28] Since the propene formed contains $\leq 1\%$ D, the propane-d_1 does not arise from cyclopentadienyl-isopropyl deuterium exchange prior to rupture of the Th-C σ bond. Preliminary studies on $(C_5H_5)_3Th(n\text{-}Bu)$ indicate similar photochemical behavior.

In addition to providing a facile route to low-valent thorium organometallics, this work represents the first example to date where photoexcitation induces β-hydride elimination in an organometallic system which thermally resists it.[29,30] The change in reaction pathway most likely reflects photochemical weakening of the η^5-C_5H_5 ligand attachment[31] (e.g., promotion to an η^3-C_5H_5 or η^1-C_5H_5 excited state) and subsequent reduction of the thorium ion coordinative saturation.[2a] The generality of this photochemical process and its importance in generating other new low-valent organometallics and hydrides is under continuing investigation.

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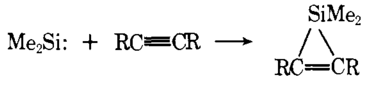
Photochemical Generation of Silacyclopropene[1]

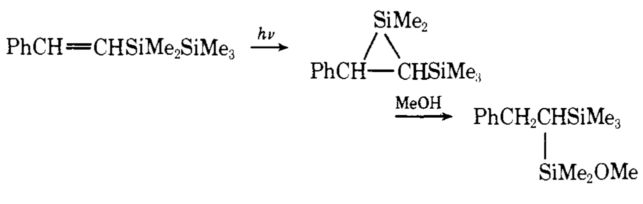
Sir:

Isolation of the first silacyclopropene, 1,1-dimethyl-2,3-diphenyl-1-silacycloprop-2-ene, from the addition of the dimethylsilylene to diphenylacetylene was claimed by Volpin and co-workers in 1962,[2] although the product was demonstrated to be the dimer later.[3] Very recently, Conlin and Gaspar[4a] and Seyferth, Annarelli, and Vick[4b] have reported that the addition of dimethylsilylene to acetylene really resulted in the formation of silacyclopropene.



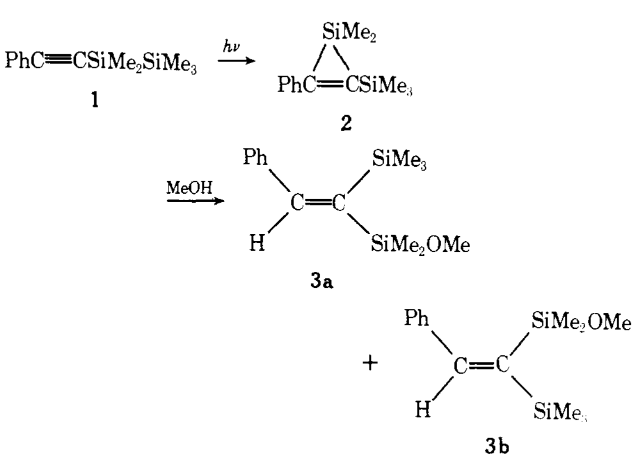
R = Me[4a]
R = Me$_3$Si[4b]

In a recent paper,[5] we demonstrated that photolysis of styrylpentamethyldisilane gave silacyclopropane which afforded 1-trimethylsilyl-1-methoxydimethylsilyl-2-phenylethane upon methanolysis.



As a logical consequence, we have examined the photolysis of (pentamethyldisilanyl)phenylacetylene (**1**) which led to an entirely new route to silacyclopropene. We have also studied a variety of reactions of the photochemically generated silacyclopropene, which open a fascinating new field in organosilicon chemistry.

Irradiation of a methanol solution of **1**[6] in a quartz tube for 1.5 h with a 450-W high-pressure mercury arc lamp[7] afforded a mixture of **3a** and **3b** in 50–90% yield.[8] Both **3a** and **3b** gave 1,1-bis(trimethylsilyl)-2-phenylethylene by treatment with methylmagnesium bromide.



The ratio of each isomer was in favor of **3a** at the early stage of the reaction, but approached 1:1 after prolonged irradiation. Independent irradiation of each isomer gave the same 1:1 isomeric mixture.

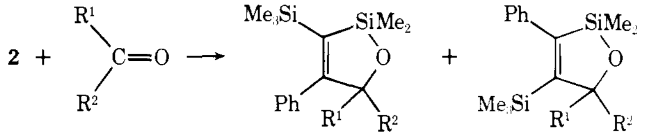
The structure of **3a** is consistent with the intermediacy of 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacycloprop-2-ene (**2**),[4,9] and **2** can be prepared as a fairly thermally stable compound in solution. Irradiation of **1** (0.3 mmol) in benzene (0.3 mL) in a quartz tube afforded a solution containing ca. 75% of **2**. The proton NMR spectrum of the solution displays two sharp singlets of SiMe at δ 0.32 and 0.39 in ratio of peak areas 3:2 in addition to Si–Me signals of **1** at δ 0.29 and 0.40 (ca. 13%). The solution also contains ca. 12% of (trimethylsilyl)phenylacetylene (**4**), the SiMe signal of which appears at δ 0.39.[10] Addition of methanol to the solution destroys **2** within a minute to give **3a** quantitatively.[11]

Although quite reactive toward air and moisture, **2** is thermally stable and unchanged by irradiation through a Pyrex filter. However, **2** gave **4** quantitatively upon irradiation through quartz; the ejected dimethylsilylene was trapped by diethylmethylsilane to give 1,1,2-trimethyl-2,2-diethyldisilane (**5**).

$$\mathbf{2} \xrightarrow{h\nu} \underset{\mathbf{4}}{\mathrm{PhC{\equiv}CSiMe_3}} + :\mathrm{SiMe_3} + \xrightarrow{\mathrm{Et_2MeSiH}} \underset{\mathbf{5}}{\mathrm{Et_2MeSiSiMe_2H}}$$

Irradiation of **1** (0.4 mmol) in a mixture of methanol (2 mL) and diethylmethylsilane (2 mL) gave only **3a** and **3b** in 44.0% yield with a trace of **5**. The thermal and photochemical behavior of silacyclopropene contrast interestingly to those of silacyclopropanes,[12] which are photochemically stable but thermally unstable, ejecting silylenes.[13]

We report in this paper two spectacular examples of reactions of **2**. The reaction of **2** with ketones gave products with the general structure 1-sila-2-oxacyclopent-4-ene, but reactivities are quite different depending on the structure of ketones. Aliphatic ketones such as acetone and cyclohexanone gave a mixture of **6** and **7** only upon irradiation (with a high-pressure Hg arc lamp for 0.5 h). No dark reaction occurred for **2** with these ketones.



6 **7**

a, R^1 = R^2 = CH$_3$
b, R^1 = R^2 = -(CH$_2$)$_5$-
c, R^1 = R^2 = Ph

The yield of **6** and **7** was 30–60% and the ratio of **6** to **7** varied from 6/1 to 2/1.[14] In contrast to aliphatic ketones,