polarized RMgX. So, contrary to the suggestion made by Lawler and Livant,[2] trace impurities native to our magnesium do not effectuate CIDNP due to reactions 5–8 and therefore are not equivalent to added $FeCl_2$.

Results, similar to those mentioned above, were obtained for other alkyl bromides and iodides and also in di-*n*-butyl ether. The solvent dependence of CIDNP is opposite for uncatalyzed metal–halogen exchange and Grignard formation: in the first case it is observed in strongly basic THF only,[2] in the latter it increases with decreasing solvent basicity.[1c]

A second point which we want to discuss in relation to the sequence 5–8 is the influence of the concentration of preformed Grignard reagent (R′MgY) on the intensity of CIDNP in the newly formed Grignard reagent; both from reaction 5 and reaction 8 (a SH2 type reaction on magnesium) it is to be expected that polarization would increase with increasing concentration of preformed R′MgY. No such increase was observed in a series of experiments in which 0.5 M isobutyl bromide was treated with magnesium in the presence of ethylmagnesium bromide (0, 0.3, 0.7, 1, 1.5, and 2 M) in THF. On the contrary a decrease in the intensity of CIDNP was observed in the newly formed Grignard reagent which can be attributed to both increasing viscosity of the reaction medium as well as the decreasing amount of uncoordinated solvent present.

The results of these experiments exclude SH2 type reactions on magnesium. This is in agreement with the results of an experiment where polarized radicals were created photochemically in the presence of ethylmagnesium bromide;[5] in this case also no SH2 type reaction was observed. Under similar conditions SH2 reactions have been reported for other metal centers.[6] Therefore, the question arises if not processes other than eq 8 are responsible for the incorporation of polarized radicals into the Grignard compound even in the metal–halogen exchange reaction.

However, it might be argued that the SH2 reaction is inefficient under ordinary Wurtz-type reaction conditions but exceptionally efficient under Grignard formation conditions, because in the latter case relatively high concentrations of monosolvated and unpolymerized Grignard species, i.e., RMgX·ether, might be present. It is conceivable that this species would be more susceptible to radical attack both for electronic and especially for steric reasons. Although there are no experimental data to exclude this possibility there is no need for it either, in order to explain the experimental data obtained for the Grignard formation reaction.[1,7]

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(3) All Grignard reagents were prepared from magnesium crystals (Specpure from Johnson and Matthey, Chemicals Ltd., London) with the following impurities: Si 3 ppm, Fe 2 ppm, Cu 1 ppm, Mn 1 ppm, Al, Ca, and Pb <1 ppm.

(4) Except for methyl iodide which gave fast reactions; cf. L. I. Zhakharkin, O. Yu. Okhlobystin, and K. A. Bilevitch, *J. Organomet. Chem.*, **2**, 309 (1964).

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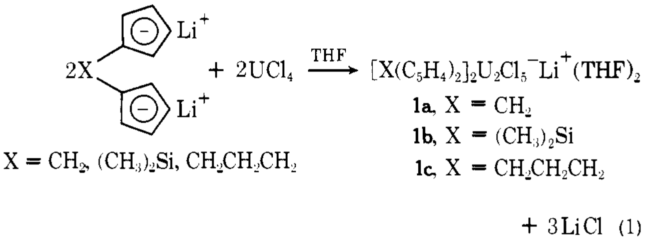
Ring-Bridged Biscyclopentadienyluranium(IV) Halides

Sir:

The pronounced differences in chemical properties of $(\eta^5\text{-}C_5H_5)_3UR$ and UR_4 systems suggest that coordinative saturation is a key factor controlling many reaction patterns of organoactinides.[1] The above two systems represent extremes in this respect, and precursors intermediate in coordinative saturation might be expected to have a far more flexible and elaborate chemistry. The instability with respect to ligand redistribution of plausible[2] starting materials such as $(\eta^5\text{-}C_5H_5)_2UCl_2$[3] has seriously impeded testing of the above hypotheses. We report here an effective synthetic approach to a series of highly stable biscyclopentadienyluranium(IV) halide systems, the unusual molecular structure of one such derivative, and some initial observations on the chemistry.

Anionic biscyclopentadienides[4] containing a variable bridging group react with uranium tetrachloride in tetrahydrofuran (−78°) to yield, after extractive workup (Soxhlet extraction with pentane), dark-red air-sensitive crystalline materials (eq 1).



The new compounds have been characterized by elemental analysis as well as vibrational, ^1H NMR, and mass spectroscopy.[5] Crystals of **1a** were grown from toluene/pentane at −20° and are orthorhombic, space group $P2_12_12_1$-D_2^4 (No. 19) with $a = 11.510\,(3)$ Å, $b = 15.357\,(4)$ Å, $c = 19.036\,(5)$ Å, and $Z = 4$. Three-dimensional diffraction data were collected on a Syntex $P\bar{1}$ autodiffractometer with slow θ–2θ scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. The structure was solved using the heavy-atom technique and the resulting structural parameters have been refined to convergence ($R = 0.060$ for 1731 independent reflections having $2\theta_{\text{MoK}\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$) in cycles of empirically weighted least-squares refinement which employed anisotropic thermal parameters for all uranium and chlorine atoms and isotropic thermal parameters for all remaining nonhydrogen atoms. Although the combination of very "heavy" atoms, a noncentrosymmetric space group, and crystals with only marginally acceptable diffractive properties prevented a highly precise structure determination, it was possible by optimizing the data collection procedures (slow scan rates and long background counts) with monochromated radiation to obtain data of sufficient quality to allow a qualitative and semiquantitative description of the structure. Efforts are presently underway to grow higher quality crystals.

The solid state structure of **1a** consists of discrete, neutrally charged trinuclear units (Figure 1). Each uranium(IV) is bonded to one terminal chlorine, three bridging chlorines, and

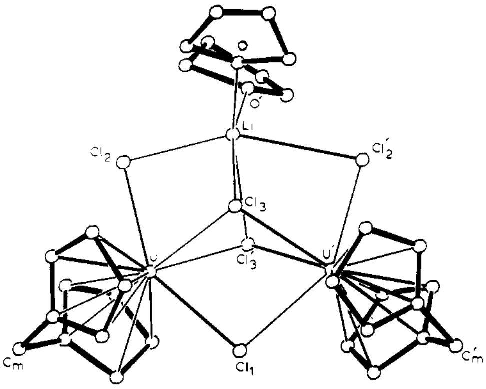


Figure 1. Perspective drawing (adapted from an ORTEP plot) of the $[LiU_2Cl_5(CH_2(C_5H_4)_2)_2(OC_4H_8)_2]$ molecule. All atoms are represented by small circles which are in no way representative of their true thermal motion. Atoms of a given type labeled with and without a prime (′) are related to each other by the pseudo-C_2 axis which passes through Cl_1, the midpoint of the U···U′ vector and the Li ion.

to one chelating biscyclopentadienyl moiety. Although the molecule possesses no rigorous crystallographic symmetry, it approximates rather closely C_{2v} site symmetry with the idealized C_2 axis passing through Cl_1, the midpoint of the U···U′ vector, and the Li^+ ion. A triple halogen bridge has not previously been observed for an organoactinide; it apparently reflects, in the present case, the common propensity for actinide (IV) organometallics to attain formal ten coordination[6] (assuming η^5-C_5H_4X units occupy three coordination positions). Intramolecular bond lengths of interest, averaged according to the approximate C_{2v} molecular symmetry, are: U–Cl_1, 2.82 (1, 1, 1)[7] Å; U–Cl_3, 2.84 (1, 1, 1) Å; U–Cl_2, 2.68 (1, 1, 1) Å; U–C(cyclopentadienyl), 2.72 (5, 3, 12) Å; cyclopentadienyl C–C, 1.43 (7, 5, 17) Å; and C_m–C(cyclopentadienyl), 1.57 (8, 2, 5) Å. These parameters are in agreement with those for other chloro(cyclopentadienyl)uranium(IV) structures.[6b,8] Similarly averaged intramolecular bond angles of interest are:[7] Cl_1UCl_3, 73.3 (3, 3, 4)°;[7] Cl_2UCl_3, 79.1 (4, 6, 12)°; Cl_3UCl_3, 68.9 (3, 2, 2)°; Cl_1UCl_2, 146.3 (4, 3, 3)°; UCl_1U, 95.4 (3)°; UCl_2Li, 88 (2, 1, 1)°; UCl_3Li, 88 (2, 3, 5)°; UCl_3U, 94.3 (3, 2, 2)°; and CC_mC, 100 (5, 1, 1)°.

The sixfold coordination geometry about the lithium is approximately octahedral and is uncommon except in complex metal oxides and in LiCl.[9] The average Li–Cl distance in the present case is 2.74 (9, 15, 29) Å, which is somewhat longer than in LiCl (2.57 Å)[10] or solvated LiCl structures (2.33–2.42 Å);[11] from these data it is not clear to what extent the lithium ion is holding the unusual structure together, or whether it is simply sequestered by the organoactinide. The Li–O distance to the two tetrahydrofurans, 2.06 (10, 10, 10) Å, is comparable within experimental error to values in similar four-coordinate compounds.[11]

The isotropically shifted ^1H NMR spectra of **1** indicate that the unsymmetrical solid state structure persists in benzene-d_6 solution. As an example, for **1a** ring proton resonances occur at −70.5, −59.3, +62.8, and +76.1 ppm vs. C_6D_5H (+35 °C), while the methylene protons on C_m appear as an AB pair at +16.2 and +16.8 ppm. The THF resonances occur at +7.1 and +10.1 ppm and therefore are also shifted by the paramagnetism. Incremental addition of THF evidences rapid exchange of free and coordinated THF. In pure THF the spectrum collapses to a more symmetrical pattern indicating, along with an altered electronic spectrum, cleavage of the dimer. All of the new compounds exhibit high thermal stability and appear to be indefinitely stable in solution at room temperature.

Initial chemical results indicate that **1** can serve as a source of $X(C_5H_4)_2UCl_2$.[12] Lewis bases cleave the dimer to yield air-stable, crystalline adducts $X(C_5H_4)_2UCl_2{\cdot}B$, B = 2,2′-bipyridyl, 1,10-phenanthroline. Reaction of **1** with $NaBH_4$ produces volatile tetrahydroborate derivatives $X(C_5H_4)_2U(BH_4)_2$; vibrational spectra indicate tridentate[13] BH_4^- ligation. Treatment with $X(C_5H_4)_2{}^{2-}$ yields the homoleptic organometallics $[X(C_5H_4)_2]_2U$. Lithium reagents yield dark red alkyl complexes. The *n*-butyl complex of **1a** decomposes below room temperature to form, as volatile organic products, only *n*-butane (60%) and 1-butene (40%). The neopentyl derivative is somewhat more thermally stable, but decomposes at room temperature to yield exclusively neopentane. Thus, in accord with other U(IV) alkyl systems,[1] reductive elimination[14] to yield the dimer of the alkyl moiety is not observed. Rather, β-hydride elimination occurs where possible;[14a,b,15] otherwise hydrogen is abstracted by the alkyl group.[1,14a,b] Interestingly, the more coordinatively saturated $X(C_5H_4)_2UCl_2{\cdot}B$ complexes appear to form dialkyl derivatives with considerably greater thermal stability.[16]

These results demonstrate that it is possible to stabilize biscyclopentadienyluranium(IV) halides by joining the rings, and that these compounds offer a facile entry to much new chemistry. Suitable variation of the ring bridges and coordinated Lewis bases also offers the possibility of sequentially manipulating coordinative saturation. The instability of $(C_5H_5)_2UCl_2$ appears to reflect deviation from a preferred organouranium(IV) coordination number.

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(17) Camille and Henry Dreyfus Teacher–Scholar.

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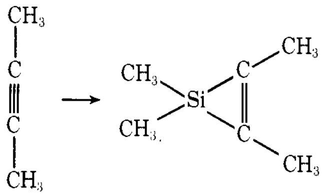
Tetramethylsilacyclopropene

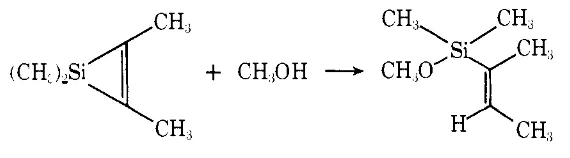
Sir:

In his recent review of the chemistry of silacyclopropanes,[1] Seyferth noted the many attempts which preceded his first successful synthesis of 1972.[2] There are no recorded failures in the synthesis of silacyclopro*penes*, for, with the notable exception discussed below, the idea that a silacyclopropene might prove to be stable did not dawn on the chemical world until Seyferth uncovered the unexpected stability of the saturated compound.



We wish to report that tetramethyl-1-silacycloprop-2-ene has been obtained as the addition product of dimethylsilylene $(CH_3)_2Si$: and 2-butyne, and is stable for many weeks at room temperature in the absence of air. Gas-phase flow-pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane at 600 °C and pressures below 100 μ were employed to generate dimethylsilylene[3] in the presence of a tenfold excess of 2-butyne.[4] Absolute yields of ca. 50% were obtained as determined by the methanolysis described below.

Trap-to-trap distillation of the reaction mixture provided solutions containing 10–20% of the silacyclopropene in dimethoxydimethylsilane together with ca. 5% of other compounds.[5] The proton NMR spectrum of such a solution displays two sharp singlets at δ 0.15 and 1.96 in ratio of peak areas 1:1, and the mass spectrum, obtained by combined gas chromatography-mass spectroscopy indicates a parent peak at *m/e* 112 and base peak at *m/e* 97, thus eliminating all alternative structures except $(CH_3)_2C{=}C{=}Si(CH_3)_2$. This latter structure is not consistent with the evidence afforded by methanolysis of the compound, which proceeds in ca. 80% yield to give *cis*-1,2-dimethylvinyldimethylmethoxysilane:[6]



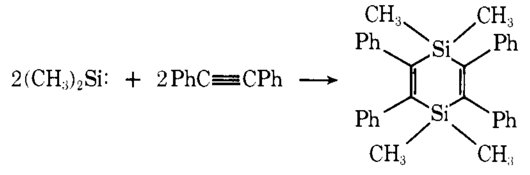
The stereochemistry of this reaction was established by independent synthesis of the cis and trans isomers[7] and the demonstration that the stereoisomers could be distinguished by proton NMR spectroscopy. Use of methanol-OD proved that hydroxyl hydrogen is the source of the vinyl hydrogen in the methanolysis product.

The ^{13}C NMR spectrum of product mixtures has also been obtained. The lone resonance whose ^{13}C chemical shift is 152 ppm downfield from tetramethylsilane and which remains a singlet in the absence of proton spin decoupling is assigned to the ring carbons and provides strong evidence for the cyclic structure. The *C*-methyl and *Si*-methyl ^{13}C resonances are found at 11.9 and −2.4 ppm downfield from Me_4Si with proton coupling constants 125 ± 2 and 120 ± 2 Hz, respectively.

While tetramethylsilacyclopropene is quite stable in the absence of air and moisture, exposure to the laboratory atmosphere initiates an exothermic reaction which destroys the compound within a minute. When a solution containing 20% of the silacyclopropene was heated at 75 °C for 3 h, no diminution of the characteristic NMR signals was observed. When the temperature was raised to 105° the silacyclopropene was destroyed within an hour. The NMR spectrum indicated only polymeric product and no observable 2-butyne. Thus the mode of thermal decomposition of tetramethylsilacyclopropene in dimethoxydimethylsilane solution is *not* the extrusion of dimethylsilylene observed by Seyferth for hexamethylsilacyclopropane.[8]

There is much indirect evidence for the addition of silylene to carbon–carbon multiple bonds forming three-membered silicon-containing rings.[9,10] We believe, however, that this is the first report of the direct detection by spectroscopic means and the chromatographic separation of the primary silylene adduct.[1]

The addition of silylenes to acetylenes has had a checkered history. The claim of Volpin and co-workers to have isolated 1,1-dimethyl-2,3-diphenyl-1-silacycloprop-2-ene from the addition of the dimethylsilylene to diphenylacetylene[11] was soon refuted by the demonstration that the product isolated was dimeric:[12]



While the proposal that silacyclopropene intermediates may intervene in the formation of disilacyclohexadienes from the reactions of silylenes and acetylene has been widely discussed,[13] this suggestion has recently been revived[14] to account for the formation of a disilacyclobutene as an isolable product. However, the demonstration by Barton and Kilgour that disilacyclobutenes can act as precursors to disilacyclohexadienes[15] and our recent finding that dimethylsilylene can undergo dimerization[5b,16] suggest that silacyclopropenes may play no role in the formation of disilacyclohexadienes, if the alternative reaction, Scheme I discussed by Barton[15] proves to be correct.

Since the reactions leading to the formation of disilacyclohexadienes are generally carried out as static pyrolyses of the silylene precursors in the liquid phase at temperatures above 150°, conditions under which the lifetime of tetramethylsilacyclopropene is short, the suggestion that the disilacyclobutene arises from silylene addition to a silacyclopropene seems no more likely than the silylene dimerization followed by cycloaddition pictured above.

Nevertheless, evidence has been presented for the formation of silacyclopropenes as fleeting intermediates in the addition of silylenes to acetylenes. The silylacetylenes formed from