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COMMUNICATIONS

Published on Web 06/29/2006

Unique σ-Bond Metathesis of Silylalkynes Promoted by an *ansa*-Dimethylsilyl and Oxo-Bridged Uranium Metallocene

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During the last two decades, the chemistry of electrophilic d^0/f^n lanthanide and actinide compounds has been the source of intense investigation and has reached a high level of sophistication.[1] The broad interest of these compounds originates from their unique structure−reactivity relationships and their remarkable performances in homogeneous catalysis.[2] However, organometallic complexes of the f-elements are known to be especially sensitive to moisture, and the decomposition products are generally the hydroxide and/or oxo-bridged derivatives.[3] The presence of metal−oxide bonds normally induces a reduced catalytic activity of the complexes in one hand, but outstanding catalytic performances can be expected if coordinative unsaturated complexes are obtained. In this contribution, we present the synthesis and characterization of an organoactinide complex containing the M−O−M motif and its unexpected catalytic reactivity, despite its high oxophilicity, in the σ-bond metathesis of silylalkynes. The observed structure−reactivity may serve as a model for oxide-supported heterogeneous organometallic catalysts or metal−oxide containing catalysts.[4]

The oxide-bridged dibutyl uranium complex (**3**) was prepared through the alkylation of $[\{[\eta 5\text{-}(C_5Me_4)_2SiMe_2]UCl\}_2(\mu\text{-}O)(\mu\text{-}Cl)\bullet Li\bullet 1/2DME]_2$ (**2**) (Figure 1) with 2 equiv of *n*-butyllithium following the reaction sequence shown in Scheme 1.[5] Although complex **3** was not obtained as single crystals, the two butyl groups were confirmed by its reaction with an excess amount of $PhSiH_3$ to produce *only* 2 equiv of the corresponding $PhSiH_2Bu$.

We were interested to compare the reactivity of complex **3**, in the hydrosilylation of alkynes, with that obtained by other *ansa*-organoactinides.[1,6] Hence, the reaction of TMSC≡CH with $PhSiH_3$ promoted by complex **3** produced TMSH, HC≡CH, and TMSC≡CTMS as the major products with only trace amounts of the alkene TMSCH=CHTMS. However, when complex **3** was reacted with TMSC≡CH in the absence of $PhSiH_3$, a disproportionation reaction took place selectively without the formation of enynes or dienynes, as obtained for other *ansa*-organoactinides (eq 1).[2]

$$2\ \mathrm{TMSC{\equiv}CH} \xrightleftharpoons[\mathrm{THF}]{\mathbf{3}} \mathrm{TMSC{\equiv}CTMS} + \mathrm{HC{\equiv}CH} \qquad (1)$$

Interestingly, the unexpected σ-bond silyl metathesis toward the cleavage and formation of Si−C motifs is rare. Silylalkynes are important synthons in organic chemistry[7] and have been prepared from metal salts of a terminal alkyne with a suitable silyl chloride compound,[8a] or via the metathesis and the cross-metathesis of silylalkynes with alkynes over KF/Al_2O_3 or KNH_2/Al_2O_3.[8b]

To study the scope of the σ-bond silyl metathesis, the cross-metathesis of different terminal alkynes with TMSC≡CH was investigated (eq 2), and the results as a function of time are summarized in Table 1. When the reaction of TMSC≡CH with

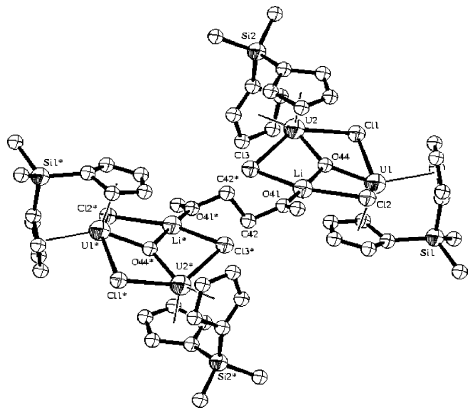
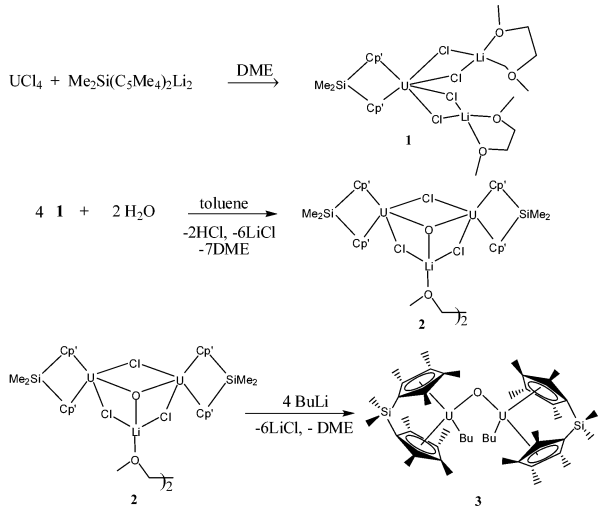


Figure 1. ORTEP plot of the molecular structure of complex $[\{[\eta^5\text{-}(C_5Me_4)_2SiMe_2]UCl\}_2(\mu\text{-}O)(\mu\text{-}Cl)Li\bullet O(CH_3)CH_2]_2$ (**2**) drawn at 50% probability level. Methyl groups at the Cp rings, hydrogen atoms, and DME crystal inclusion molecules were omitted for clarity.

Scheme 1. Synthetic Route toward Complex **3**



RC≡CH (R = ^{i}Pr, ^{t}Bu) was conducted at room temperature in THF, no product formation was observed, except for 2 equiv of butane. However, when the same reaction was carried out at refluxing THF (66 °C), a smooth reaction was observed. At a short period of time, TMSC≡CTMS was the major observed product. Nevertheless, following the reaction as a function of time shows that the TMSC≡CTMS product is consumed, while the amount of the cross-metathesis product TMSC≡CR is increased.

Since TMSC≡CTMS seems to be the important intermediate for the σ-bond silyl cross-metathesis reaction of TMSC≡CH with terminal alkynes, the reactions of TMSC≡CTMS with various alkynes, RC≡CH (R = ^{i}Pr, ^{t}Bu, ^{n}Bu, Ph, Me), were carried under the same reaction conditions, yielding the cross-metathesis products

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10.1021/ja063443x CCC: $33.50

Table 1. Data for The σ-Bond Silyl Cross-Metathesis of TMSC≡CH with RC≡CH Catalyzed by Complex **3** in Refluxing THF

run	R in RC≡CH	TMSC≡CH:RC≡CH	time (h)	TMSC≡CTMS (%)	TMSC≡CR (%)
1	^{i}Pr	1:4	20	14.1	40.2
			44	7.8	59.8
			64	6.2	68.5
			139	2.6	93.6
2	^{t}Bu	2:1	38	24.1	3.4
			61	28.6	3.7
			90	26.3	11.4

Table 2. Data for the Cross-Metathesis Reaction of TMSC≡CR′ with RC≡CH Catalyzed by Complex **3**

run	R in RC≡CH R′ in TMSC≡CR′	TMSC≡CR′ :RC≡CH	time (h)	TMSC≡CR (%)	TMSC≡CH (%)
1	R′ = TMS, R = ^{i}Pr	1.62:2.94	26	32.2	14.7
			66	45.9	12.0
2	R′ = TMS, R = ^{t}Bu	1.62:7.40	66	56.4	13.2
			90	62.4	12.1
3	R′ = TMS, R = ^{n}Bu	1.62:14.02	23	53.8	13.9
			45	74.6	12.7
			66	88.8	5.6
4	R′ = TMS, R = CH_3	1.62:7.79	44	100	0
5	R′ = TMS, R = Ph	1.62:9.23	4	61.2	19.4
			23	100	0
6	R′ = CH_3, R = ^{t}Bu	5.4:9.89	45	13.6	
			92	16.8	

TMSC≡CR, TMSC≡CH, and HC≡CH (eq 3). To obtain better conversions, we have found that the terminal alkynes must be in excess amounts compared to the amount of TMSC≡CTMS.

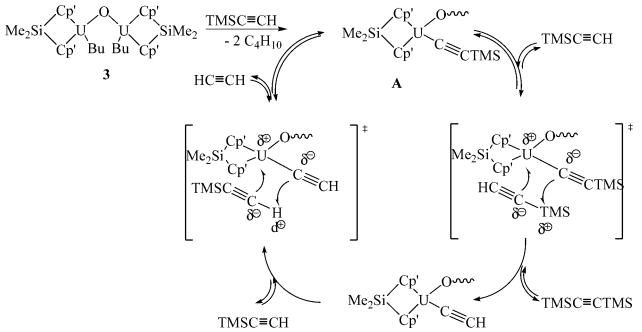
$$\text{TMSC}{\equiv}\text{CH} + \text{RC}{\equiv}\text{CH} \underset{\text{THF}}{\overset{\mathbf{3}}{\rightleftharpoons}} \text{TMSC}{\equiv}\text{CTMS} + \text{TMSC}{\equiv}\text{CR} + \text{HC}{\equiv}\text{CH} \quad (2)$$

$$\text{TMSC}{\equiv}\text{CTMS} + \text{RC}{\equiv}\text{CH} \underset{\text{THF}}{\overset{\mathbf{3}}{\rightleftharpoons}} \text{TMSC}{\equiv}\text{CH} + \text{TMSC}{\equiv}\text{CR} + \text{HC}{\equiv}\text{CH} \quad (3)$$

The data for the diverse cross-metathesis results are summarized in Table 2. The cross-metathesis of $CH_3C{\equiv}CH$ with TMSC≡CTMS yields selectively only the product TMSC≡CCH_3. Surprisingly, ^{n}-BuCH=CH_2 or $CH_3C{\equiv}CCH_3$ did not react with TMSC≡CTMS. These results implicate that, in the σ-bond metathesis reaction, the terminal hydrogen of the terminal alkyne is indispensable. It is important to point out that only a Si−C bond cleavage and a C−C bond formation are involved in the metatheses processes. This has also been confirmed by the fact that no metathesis reaction between the internal alkyne 2-butyne with a range of terminal alkynes is observed.

However, when the internal alkyne, TMSC≡CCH_3, was used as the starting material (source of TMS group) and reacted with ^{t}BuC≡CH, the cross-metathesis products ^{t}BuC≡CTMS and $CH_3C{\equiv}$CH were obtained, although the reaction progress was very slow. From the activity exhibited by the different alkynes used as a source of the TMS group, we have found that the reactivity toward the cross-metathesis reaction is as follows: TMSC≡CTMS > TMSC≡CCH_3. In addition, the reactivity of the terminal alkynes follows the order of the following: TMSC≡CH > PhC≡CH > $CH_3C{\equiv}$CH > ^{n}BuC≡CH > ^{t}BuC≡CH > ^{i}PrC≡CH.

Scheme 2. Plausible Mechanism for the Disproportionation of TMSC≡CH Promoted by Complex **3** (only a half molecule of the organometallic complex is presented for clarity)



A plausible mechanism for metathesis of a silylalkyne catalyzed by complex **3** is presented in the Scheme 2. The first step of the catalytic cycle involves the rapid reaction of the starting complex **3** with the silyl acetylene to form the corresponding uranium acetylide complex **A** and 2 equiv of butane. Complex **A** reacts in a four-centered transition state with an additional TMSC≡CH cleaving the Si−C bond, forming the internal alkyne, TMSC≡CTMS, and the corresponding U−C≡CH complex as presented in complex **B**. The consecutive protonolysis reaction of complex **B** with another molecule of TMSC≡CH regenerates complex **A** and forms the obtained acetylene HC≡CH. A similar mechanism can be depicted for the cross-metathesis of TMSC≡CR (R = H, TMS, CH_3) with terminal alkynes. In conclusion, we have shown a unique structure−reactivity relationship in an oxophilic *ansa*-organoactinide complex. The high coordinative unsaturation at the metal center was found to be the leading feature for higher reactivities serving to design better M−O−M catalytic heterogeneous chemistry.

Acknowledgment. This research was supported by the Israel Science Foundation, administrated by the Israel Academy of Science and Humanities under Contract 1069/05.

Supporting Information Available: Crystallographic data of complex **2**. Complete Experimental Section, including the synthesis and characterization of complex **3** and detailed procedures for the catalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA063443X