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Synthesis and reactivity of alkynyl(silylamido)uranium complexes

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Abstract

The metallacycle $[\{N(SiMe_3)_2\}_2\overline{UCH_2SiMe_2N}SiMe_3]$ reacts with terminal alkynes affording the stable silylamidouraniumalkynyl complexes $[\{NSiMe_3)_2\}_3U{-}C{\equiv}CR]$. Propanone inserted into the U–C bond to give the alkoxides $[\{NSiMe_3)_2\}_3U{-}O{-}C(Me_2)C{\equiv}CR]$, and after subsequent hydrolysis, the corresponding acetylenic alcohols were obtained in high yields.

Keywords: Uranium; Silylamido complexes; Alkynyl complexes; Insertion reactions

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Tris(hexamethyldisilylamido)methyluranium $[\{N(SiMe_3)_2\}_3UMe]$ **1** [1] has been described as thermally stable, but all attempts to isolate the homologous alkyl- or aryl-silylamidouranium: $[\{N(SiMe_3)_2\}_3UR]$ have failed. All these thermally unstable compounds give the metallacycle $[\{N(SiMe_3)_2\}_2\overline{UCH_2SiMe_2N}SiMe_3]$ **2** [2–4] by an intramolecular γ-elimination reaction. Both **1** and **2** have been widely used as reagents for organic synthesis [5–10].

In this paper, we report the synthesis and some reactions of a new class of stable silylamidouranium complexes with a strong uranium–carbon bond, the alkynyltris(hexamethyldisilylamido)uranium $[\{N(SiMe_3)_2\}_3U{-}C{\equiv}CR]$ **3**.

Ring opening of the uranium metallacycle **2** with acidic hydrogen compounds is well known [7,11–13] and we have found that **2** dissolved in pentane reacts with terminal aliphatic alkynes to give the corresponding alkynyl complexes **3a–3e** isolated after usual workup in 70–90% yield as orange-brown powders (95–98% pure by NMR spectroscopy).

$$\mathbf{2} + HC{\equiv}CR \rightarrow \left[\{N(SiMe_3)_2\}_3U{-}C{\equiv}CR\right]$$

3a–3e

a $R = (CH_2)_2CH_3$; **b**: $R = (CH_2)_3CH_3$;

c: $R = (CH_2)_4CH_3$;

d: $R = (CH_2)_5CH_3$; **e**: $R = C(CH_3)_3$.

These complexes were unambiguously identified by NMR analysis and chemical reactions. They are thermally stable, remaining unchanged after heating under reflux for 12 hours in benzene, and do not react with dihydrogen or carbon monoxide (atmospheric pressure, benzene solution, 20–80°C). However, they are able to coordinate isonitriles and to insert non-hindered ketones.

This high thermal stability can be rationalized in terms of a strong uranium–carbon bond with double-bond character. This latter is consistent with IR and NMR data. The IR stretching frequencies of the C≡C bonds at ca. 2077 cm^{-1} are significantly lower than those recorded for the free alkynes and slightly lower than those for the alkynyluranium complexes $[(C_5H_5)_3UC{\equiv}CR]$ ($R = H$ or C_6H_5) In these last compounds, the U–C–C angle is very close to 180° [14]. In the ^1H NMR spectra of compounds **3a–3d** (Table 1), the signals of the γ-methylene protons appear at very high fields (ca. -50 ppm) and the other alkynyl protons are also shielded. This can be compared with the chemical shifts of the corresponding γ-methylene and δ-methyl protons in $[(C_5H_5)_3U(CH_2)_3CH_3]$, -20.4 and -11.5 ppm, respectively [15]. It seems obvious that contact contributions dominate the considerable paramagnetic shifts observed for the linear alkynyls complexes. These important contact contributions suggest electron-transfer from the uranium atom through a U–C linkage with considerable double bond character [16]. Such a uranium–carbon double bond was first established by Gilge et al. [17].

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Table 1
Selected ^{1}H NMR data for alkynyluranium compounds (C_6D_6, 25°C)

	a	**b**	**c**	**d**
3: γ-CH_2	−49.95	−50.0	−49.95	−49.85
3: δ-CH_2	−18.2	−18.3	−18.3	−18.2
4: γ-CH_2	−33.6	−33.5	−35.2	−36.4
4: δ-CH_2	−10.8	−11.1	−11.65	−12.15
5: γ-CH_2	−0.90	−2.40	−0.86	−0.90
5: δ-CH_2	−0.60	−0.91	−0.55	−0.60
5: $C(CH_3)_2$	−0.36	−0.38	−0.43	−0.45

It was impossible to insert carbon monoxide or *t*-butyl isocyanide into these bonds, whereas the uranium–alkyl bonds in **1** and **2** react easily under the same conditions [2,9]. However, it was reported that the alkylidene complexes $[(C_5H_5)_3U = CHPR_3]$ react readily with carbon monoxide or nitriles by insertion [17,18]. The reaction of *t*-butylisocyanide with **3a–3d** led to the adducts $[\{N(SiMe_3)_2\}_3U{-}C{\equiv}CR\ (C{\equiv}NCMe_3)]$ **4a–4d**. After hydrolysis, the isonitrile was recovered unchanged. The solution IR spectrum of **4a**, showed a significant increase of $\nu(C{\equiv}N)$ (2182 cm^{-1} vs. 2134 cm^{-1} for free isonitrile) and a slight decrease of $\nu(C{\equiv}C)$ (2074 vs. 2077 cm^{-1} for **3a**). This behaviour of isonitrile-organoactinide adducts has been well established [19]. The ^{1}HNMR spectra of these complexes show a strong deshielding of the γ- and δ-methylene protons (ca. 15 and 10 ppm, respectively, Table 1).

When a stoichiometric amount of propanone was added to benzene solutions of complexes **3a–3d**, quantitative insertion reactions occured within 4 h affording the uranium alkoxides **5a–5d** (under the same conditions, the sterically hindered 2,2,4,4-tetramethylpentan-3-one does not react).

$$3 + Me_2C = O \rightarrow \left[\{N(SiMe_3)_2\}_3U{-}OC(Me_2)C{\equiv}CR\right]$$

5a–5d

The ^{1}H NMR spectra of these complexes show signals for the alkynyl protons almost unshifted from the diamagnetic region (−2.4–+0.8 ppm). Therefore these protons are strongly deshielded (ca. 48 ppm for γ-CH_2 protons). At the same time the $C(CH_3)_2$ signal is moderately shielded (ca. 3 ppm), as reported previously for complexes $[\{N(SiMe_3)_2\}_3U{-}OC(R_2)Me]$ [8]. After hydrolysis with aqueous HCl, the corresponding α-acetylenic alcohols were isolated in high yields (> 90% by GPC) and identified by comparison with authentic samples.

$$5 + H_3O^+ \rightarrow HOC(Me_2)C{\equiv}CR + [U]$$

This reaction established unambiguously the formation of the uranium alkoxides, the insertion of the ketone into the U–C bond and the structure of the starting materials **3**. The coordination of the carbonyl group to the uranium, which brings about a decrease in the uranium–carbon double-bond character, would be followed by the migration of the alkynyl group on to the strong electrophilic carbonyl center. Such a migration of the moderately nucleophilic alkynyl group did not occur in the less electrophilic atom of the isonitrile adduct.

The production of acetylenic alcohols from alkynes is a new example of the use of the uranium metallacycle **2** as a versatile reagent for organic synthesis. The reaction of functionalized alkynes with **2**, and the addition of the intermediate alkynyl complexes to ketones and aldehydes is now under investigation.

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