

Alkyne- and Alkyl-tris(cyclopentadienyl) Complexes of Uranium(III)

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Treatment of $\text{cp}_3\text{U}(\text{THF})$ (**1**) ($\text{cp} = \eta\text{-C}_5\text{H}_5$, THF = tetrahydrofuran) with diphenylacetylene affords the alkyne complex $\text{cp}_3\text{U}(\text{Ph-C}\equiv\text{C-Ph})$; (**1**) reacts with RLi ($\text{R} = \text{Me, Bu}^n$) to give the alkyl compounds cp_3URLi (**3**); hydrogenolysis of (**3**) in the presence of a terminal alkene $\text{R}'(-\text{H})$ leads to the formation of $\text{cp}_3\text{UR}'\text{Li}$.

Organometallic compounds of uranium(III) are not common and are generally synthesized by reduction of U^{IV} complexes.¹⁻³ A series of tris(cyclopentadienyl)uranium derivatives $(\text{C}_5\text{H}_4\text{R})_3\text{UL}^4$ were isolated from the corresponding THF complex (THF = tetrahydrofuran); the purported π donor character of the trivalent uranium metallocenes was shown by synthesis of the carbon monoxide complex $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UCO}^4$ which is stable under an atmosphere of CO. Here we report that alkyne and alkyl complexes of uranium(III) can be obtained from $\text{cp}_3\text{U}(\text{THF})$ (**1**) ($\text{cp} = \eta\text{-C}_5\text{H}_5$).⁵

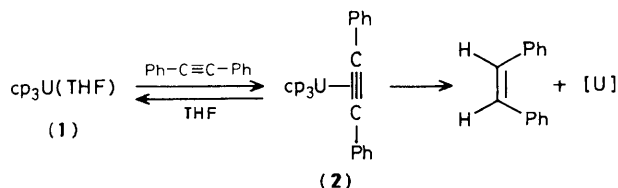
Addition of diphenylacetylene (0.20 mmol) to a solution of (**1**) (0.065 mmol) in THF (5 ml) led to an equilibrium between (**1**) and the alkyne complex $\text{cp}_3\text{U}(\text{Ph-C}\equiv\text{C-Ph})$ (**2**) [(**1**):(**2**) = 9:1] which was characterized by n.m.r. spectroscopy.[‡]

[†] Deceased.

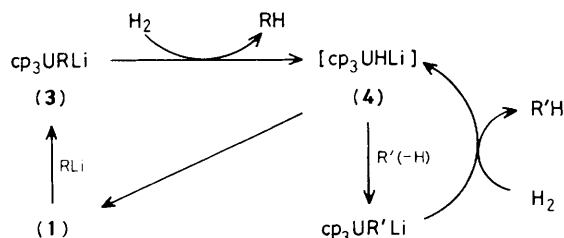
[‡] (**2**): δ (^1H , 60 MHz, 30°C, $[\text{C}_6\text{D}_6]\text{THF}$) -14.97 (15H, s, cp), 8.52 (2H, t, J 7.5 Hz, *p*-H), 13.29 (4H, t, J 7.5 Hz, *m*-H), 17.65 (4H, d, J 7.5 Hz, *o*-H); δ (^{13}C , 75 MHz, 30°C, THF) 241.13 (cp), 124.26, 89.92, and 86.68 (*p*-, *m*-, and *o*-C).

Almost total conversion of (**1**) was observed by using a large excess of diphenylacetylene (>50 equiv.); however, (**2**) could not be obtained pure as it gave progressively *cis*-stilbene (0.3 equiv. after 3 h; n.m.r. and g.c.-mass spectral analysis) and a not yet identified uranium species (Scheme 1). Labelling experiments indicated that the solvent was not involved in this hydrogen transfer reaction; intramolecular abstraction of hydrogen from a cp ring was noted in thermolysis of the alkyl-uranium(IV) complexes cp_3UR yielding RH ,⁶ and is classical in titanocene chemistry.⁷

Even though it is unstable, (**2**) represents the first f-element alkyne complex which is directly observed; such a complex



Scheme 1



Scheme 2. R = Me, Buⁿ; R' = Buⁿ, n-C₅H₁₁.

was proposed as an intermediate in the cyclisation of diphenylacetylene into an uranatetraphenylcyclopentadiene compound.²

We found that (1) can be a precursor for the synthesis of alkyluranium(III) complexes, which are very rare.^{2,3} Reaction of (1) with 1 equiv. of RLi (R = Me, Buⁿ) led immediately to the quantitative formation of the complexes cp₃URLi (3).³ In contrast with the inertness of the cp₃UR compounds,⁸ (3) reacted in THF, with hydrogen or deuterium to give (1) (97% by n.m.r. spectroscopy) and RH(D) (by mass spectral analysis) under mild conditions (20 °C, 10 h, 1 atm H₂). Hydrogenolysis of cp₃UMeLi in the presence of pent-1-ene [(3) : H₂ : alkene 0.1 : 2 : 6] gave after 15 h the pentyl derivative cp₃U–n-C₅H₁₁Li in quantitative yield (by n.m.r. spectroscopy) whereas a third of the pentene was hydrogenated into n-pentane (g.c. analysis). The same experiment under D₂ instead of H₂ led to cp₃U–CH₂CHDC₃H₇Li. Substitution of the R group in compounds (3) could be achieved only with terminal alkenes. The results are in agreement with the catalytic cycle shown in Scheme 2 in which the key step is the insertion of alkene into the U–H bond of the intermediate⁹ (4). This mechanism is similar to that proposed for the

hydrogenation of alkenes catalysed by [(η-C₅Me₅)₂MH]_n compounds (M = Nd, U); in this latter case, the corresponding uncongested alkyl derivatives (η-C₅Me₅)₂MR were not observed.¹⁰

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