

## 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  $\text{RLi}$  ( $\text{R} = \text{Me, Bu}^n$ ) to give the alkyl compounds  $\text{cp}_3\text{URLi}$  (**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  $\text{U}^{\text{IV}}$  complexes.<sup>1-3</sup> 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  $\pi$  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**) ( $\text{cp} = \eta\text{-C}_5\text{H}_5$ ).<sup>5</sup>

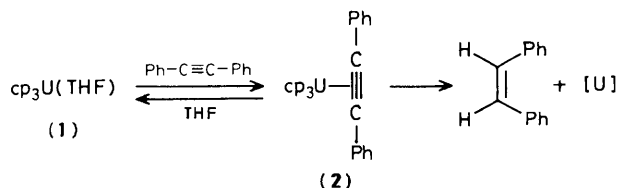
Addition of diphenylacetylene (0.20 mmol) to a solution of (**1**) (0.065 mmol) in THF (5 ml) led to an equilibrium between (**1**) and the alkyne complex  $\text{cp}_3\text{U}(\text{Ph-C}\equiv\text{C-Ph})$  (**2**) [(**1**):(**2**) = 9:1] which was characterized by n.m.r. spectroscopy.‡

† Deceased.

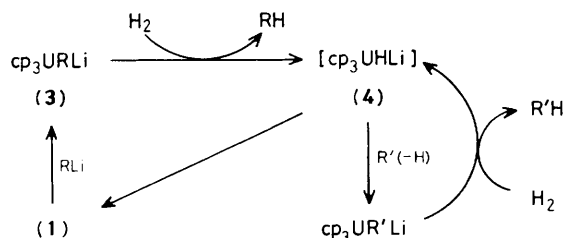
‡ (**2**):  $\delta$  ( $^1\text{H}$ , 60 MHz, 30°C,  $[\text{D}_8]\text{THF}$ ) -14.97 (15H, s, cp), 8.52 (2H, t,  $J$  7.5 Hz, *p*-H), 13.29 (4H, t,  $J$  7.5 Hz, *m*-H), 17.65 (4H, d,  $J$  7.5 Hz, *o*-H);  $\delta$  ( $^{13}\text{C}$ , 75 MHz, 30°C, THF) 241.13 (cp), 124.26, 89.92, and 86.68 (*p*-, *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  $\text{cp}_3\text{UR}$  yielding  $\text{RH}$ ,<sup>6</sup> and is classical in titanocene chemistry.<sup>7</sup>

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, Bu<sup>n</sup>; R' = Bu<sup>n</sup>, n-C<sub>5</sub>H<sub>11</sub>.

was proposed as an intermediate in the cyclisation of diphenylacetylene into an uranatetraphenylcyclopentadiene compound.<sup>2</sup>

We found that (1) can be a precursor for the synthesis of alkyluranium(III) complexes, which are very rare.<sup>2,3</sup> Reaction of (1) with 1 equiv. of RLi (R = Me, Bu<sup>n</sup>) led immediately to the quantitative formation of the complexes cp<sub>3</sub>URLi (3).<sup>3</sup> In contrast with the inertness of the cp<sub>3</sub>UR compounds,<sup>8</sup> (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 H<sub>2</sub>). Hydrogenolysis of cp<sub>3</sub>UMeLi in the presence of pent-1-ene [(3) : H<sub>2</sub> : alkene 0.1 : 2 : 6] gave after 15 h the pentyl derivative cp<sub>3</sub>U–n-C<sub>5</sub>H<sub>11</sub>Li 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 D<sub>2</sub> instead of H<sub>2</sub> led to cp<sub>3</sub>U–CH<sub>2</sub>CHDC<sub>3</sub>H<sub>7</sub>Li. 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 intermediate<sup>9</sup> (4). This mechanism is similar to that proposed for the

hydrogenation of alkenes catalysed by [(η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>MH]<sub>n</sub> compounds (M = Nd, U); in this latter case, the corresponding uncongested alkyl derivatives (η-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>MR were not observed.<sup>10</sup>

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