Migratory Insertion of Monoborane into the Uranium–Carbon σ-Bond of Tricyclopentadienyl(alkyl)uranium(IV) Complexes

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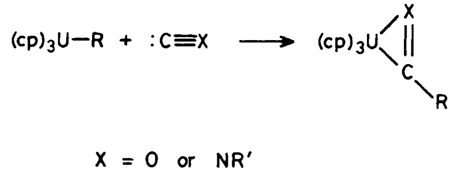
$U(cp)_3R$ (cp = η^5-cyclopentadienyl, R = Me or Et) reacts in toluene solution at room temperature with a number of appropriately labile adducts $L\cdot BH_3$ (L = BH_3, tetrahydrofuran or Me_2S) to give $U(cp)_3BH_4$ *via* the non-isolable, but spectroscopically well identified, primary insertion product $U(cp)_3(H_3BR)$; evidence of a corresponding, rather effective, insertion of the resulting BH_2R unit into U–C bonds is also apparent.

Recently, tricyclopentadienyluranium(IV) alkyls have been shown readily to insert *e.g.* carbon monoxide[1] and organic isocyanides,[2,3] respectively, into their U–C σ-bonds [reaction (1)]. Corresponding insertion reactions may be envisaged with a variety of other unsaturated molecules.[4] We now focus on monoborane, BH_3, as the first example of an unsaturated agent devoid of a double or triple bond. When clear solutions of $U(cp)_3R$ (R = Me or Et; cp = η^5-C_5H_5) in toluene are stirred at room temperature during 10—24 h, either under N_2 containing freshly generated B_2H_6[5] or in the presence of a large excess of $Me_2S\cdot BH_3$, the well known complex $U(cp)_3BH_4$[6] is finally obtained in almost quantitative yields, unambiguously identified by ^1H and ^{11}B n.m.r. spectroscopy (Table 2). However, work-up of the corresponding reaction mixtures† obtained either after notably shorter reaction times (reactant: B_2H_6), or by use of an excess of $U(cp)_3R$ relative to $Me_2S\cdot BH_3$, gave rise to samples the n.m.r. spectra of which indicated the presence of both $U(cp)_3BH_4$ and $U(cp)_3(H_3BR)$ (Table 1). Occasionally, also, resonances attributable to the starting compound $U(cp)_3R$ and/or to the hitherto unreported species $U(cp)_3(H_2BR_2)$ were detected (Table 2). The intermediate $U(cp)_3(H_3BEt)$ was clearly identified on the basis of its reported ^1H n.m.r. data.[7] Observations resulting from a systematic variation of the relevant reaction conditions lead to the generalization in Scheme 1.



(1)

X = O or NR′

Although an alternative reaction of *in situ*-generated H_2BR with $U(cp)_3R$ (formed in step v) cannot be fully excluded, approximately two equivalents of $Me_2S\cdot BH_3$ turn out to be necessary for the complete conversion of one $U(cp)_3R$ molecule into $U(cp)_3BH_4$. Steps ii—iv comprise the 'insertion' procedure.[8] Steps ii and iii bear some resemblance to the initial steps frequently suggested for alkene and alkyne hydroboration.[9] Step v may be considered as a slightly modified reversal of the successful preparation of $U(cp)_3(H_3BEt)$ from $U(cp)_3BH_4$ and BEt_3.[7]

Table 1. Composition of various mixtures after incomplete product formation (deduced from the integrals of the cp ^1H n.m.r. signals). R = Me unless otherwise stated; solvent: toluene.

Ratio of $U(cp)_3R$ to $L\cdot BH_3$[a]	Reaction time/h	$U(cp)_3R$ (%)	$U(cp)_3H_3BR$ (%)	$U(cp)_3BH_4$ (%)
1:1	1	8.5	33	58.5
1:1	2	4	40	56
1:1	24	4	37	59
3:4	20	—	20	80
2:3	22	—	15	85
1:2	68	—	—	100
2:3[b]	24	—	9	91
Excess[b,c]	2	—	25	75
Excess[b,c]	14	—	—	100

[a] L = SMe_2 unless otherwise stated. [b] R = Et. [c] L = BH_3.

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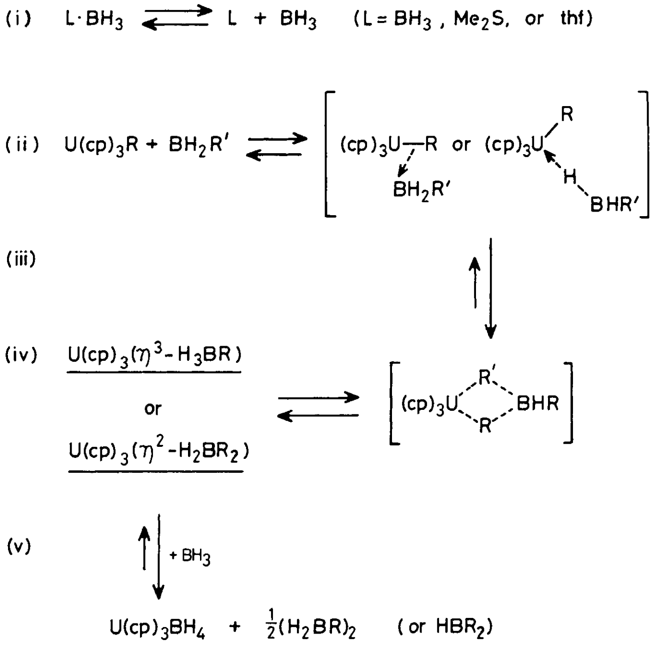
† Reactions were terminated by rapid solvent evaporation; the components of the solid mixture were subsequently identified by i.r. and ^1H and ^{11}B n.m.r. spectroscopy (C_6D_6).

Table 2. Characteristic n.m.r. data (^1H and ^{11}B) of various paramagnetic intermediates (positive sign corresponds to high-field shift).

Intermediate species		$^1H^a$			
	cp	BH_n	R		$^{11}B^b$
$U(cp)_3(H_3BMe)$	14.03 (s)	72.6 (br.q)	24.62 (s)		−96.7 (q)[e]
$U(cp)_3(H_3BEt)^c$	13.85 (s) [13.81 (s)]	73.6 (br.q) [73.6 (q)]	24.5 (s) [24.6 (q)]	17.8 (t) [17.97 (t)]	−86.76 (q)[e]
$U(cp)_3(H_2BMe_2)^d$	14.82 (s)				−37.05 (br.s)
$U(cp)_3(H_2BEt_2)^d$	14.23 (s)				

[a] C_6D_5H internal standard. [b] $BF_3 \cdot Et_2O$ external standard. [c] This work; values from ref. 7 in square brackets. [d] Other signals not assignable with certainty. [e] 1 : 2 : 2 : 1 quartet.



Scheme 1. Possible reaction steps leading from $U(cp)_3R$ and $L \cdot BH_3$ finally to $U(cp)_3BH_4$. R' = H or R; in square brackets: short-lived intermediates; underlined: observable intermediates.

BH_3-carriers, L, of Lewis basicity superior to those of Me_2S, BH_3, and tetrahydrofuran (thf)‡ (*e.g.* NEt_3, PPh_3, and pyridine) do not allow BH_3 attack of $U(cp)_3R$. Conversely, $U(cp)_3R$ reacts with AlR'_3[10] and BPh_3,[11] but not with the comparatively less acidic compound $B(OMe)_3$. Somewhat unexpectedly, $U(cp)_3Cl$ turns out to be unreactive towards both B_2H_6 and BPh_3.[10]

The recently described *dihapto*-acyl complexes $U(cp)_3(\eta^2\text{-}OCR)$[1] (R = Me and Et) react with $thf \cdot BH_3$ at room temperature in essentially the same way as their parent $U(cp)_3R$ systems. Corresponding behaviour was reported by Caulton and Marsella for the complex $Zr(cp)_2Me(\eta^2\text{-}COMe)$ even at 0 °C.[8a] As both the uranium and zirconium complexes are known to extrude CO reversibly above room temperature, the observed reaction with BH_3 might simply take place *via* $U(cp)_3R$ and $Zr(cp)_2Me_2$, respectively.§

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4 An insertion-like reaction of $(cp)_3UR$ with SO_2 has also been reported: L. Arnaudet, G. Folcher, and H. Marquet-Ellis, *J. Organomet. Chem.*, 1981, **214**, 215. Rapid insertion of ketones has also been observed: $U\text{–}R + O{=}CR_2' \rightarrow M\text{–}OCRR_2'$, T. J. Marks, NATO ASI on 'Fundamental and Technological Aspects of Organo-f-Element Chemistry,' Acquafredda di Maratea, Italy, Sept. 10—21, 1984 (Plenary lecture).

5 Prepared from solvent-free Bu_3SnCl and $NaBH_4$ at *ca.* 160 °C; see E. R. Birnbaum and P. H. Javora, *J. Organomet. Chem.*, 1967, **9**, 379.

6 *E.g.* R. v. Ammon, B. Kanellakopulos, and R. D. Fischer, *Chem. Phys. Lett.*, 1970, **4**, 553; T. J. Marks, W. J. Kennelly, J. R. Kolb, and L. A. Shimp, *Inorg. Chem.*, 1972, **11**, 2540.

7 T. J. Marks and J. R. Kolb, *J. Am. Chem. Soc.*, 1975, **97**, 27.

8 (a) The facile transformation of $Zr(cp)_2Me_2$ into $Zr(cp)_2(BH_4)_2$ by $BH_2 \cdot thf$ has also been termed an 'insertion' type reaction; see J. A. Marsella and K. G. Caulton, *J. Am. Chem. Soc.*, 1982, **104**, 2361. (b) Interestingly, compounds $BeMe_2$ and $AlMe_3$ have been reported to react with B_2H_6 to give $Be(BH_4)_2$ and $Al(BH_4)_3$, respectively, *via* various observable intermediates also involving the H_3BMe ligand: L. H. Long, *Adv. Inorg. Chem. Radiochem.*, 1973, **16**, 20.

9 See, *e.g.*, G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' Vol. 1, Methuen, London, 1967, p. 182. Initial attack on the metal by one hydrogen atom cannot fully be ruled out in view of the existence of a few complexes involving η^1-co-ordinated BH_4. See, *e.g.* C. Kutal, P. Grutsch, J. L. Atwood, and R. D. Roger, *Inorg. Chem.*, 1978, **17**, 3558; C. A. Ghilardi, S. Midolini, and A. Orlandini, *ibid.*, 1982, **21**, 4096.

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‡ The thf solution of $thf \cdot BH_3$ (Janssen Chimica) turned out to have suffered from 'ageing.' Thus, during the reaction with $U(cp)_3Me$, the ^1H n.m.r. spectrum of $U(cp)_3OBu^n$ was observed, whereas independent reaction of $U(cp)_3Me$ with B_2H_6 in toluene–thf did not give rise to this intermediate.

§ More detailed studies of the reaction of excess of $U(cp)_3(\eta^2\text{-}COR)$ with $Me_2S \cdot BH_3$ or B_2H_6 at low temperatures are underway.