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## Preliminary Communication

# Reactivity of U–H and U–C bonds in electron poor cyclopentadienyluranium complexes: electronic effects

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### Abstract

The organouranium complexes $[(C_5H_4PPh_2)_3UX]$ (X = Cl, (**1a**) X = Me (**1b**); X = H (**1c**)) react with $BH_3 \cdot SMe_2$. **1a** affords the stable $[(C_5H_4PPh_2 \cdot BH_3)_3UCl]$ (**2a**). Both **1b** and **1c** give finally $[(C_5H_4PPh_2 \cdot BH_3)_3UBH_4]$ (**3**). The transient $[(C_5H_4PPh_2 \cdot BH_3)_3UMe]$ (**2b**) is observed. **2a** and **3** may easily be reduced to $[(C_5H_4PPh_2 \cdot BH_3)_3U]$ (**4**).

*Key words:* Uranium; Cyclopentadienyl; Electron deficiency; Electronic effects; Synthesis

The organometallic chemistry of cyclopentadienyluranium compounds has been developed from electron-rich cyclopentadienyl complexes [1] whereas the chemistry of electron-poor cyclopentadienyluranium complexes containing the heterodifunctional bridging ligand $C_5H_4PPh_2$ has scarcely been investigated. The coordination of d metals to phosphorus strongly enhances the electron-withdrawing power of bridging ligands, as illustrated by the variations in the $U^{III}/U^{IV}$ redox potential from $[(C_5H_5)_3UCl]$, −1.29 V, to $[Mo(CO)_4][(C_5H_4PPh_2)_3UCl]$, −0.99 V [2]. The same effect can also be obtained by replacing the d metal by a simple Lewis acid such as borane.

To determine how this modifies the reactivity of both U–H and U–C bonds, preliminary experiments were made using borane adducts of phosphidocyclopentadienyl complexes instead of uranium heterobimetallic compounds and the syntheses of $[(C_5H_4PPh_2 \cdot BH_3)_3UR]$ ($R = CH_3$ (**1b**); R = H (**1c**)) were investigated.

Two ways were used (Scheme 1) to synthesize these complexes from the previously reported $[(C_5H_4PPh_2)_3UCl]$ (**1a**) [2]. (i) addition of borane to **1a** and subsequent reaction of the intermediate borane adduct **2a** with $Na[HBEt_3]$ or LiMe; (ii) addition of 3 equivalents of borane to the methyl derivative **1b** or to the known hydride **1c**.

Borane insertion into the U–H bond [1] and to a lesser extent into the U–C bond [3] occurs readily. To avoid this reaction, path (i) seemed more appropriate. It has been established that borane complexation to phosphorus atoms of bis(diphenylphosphidocyclopentadienyl)uranium complexes is complete within a few minutes at room temperature and such adducts are very stable. After 10 days at 70°C with an excess of triethylamine, decomplexation of $BH_3$ is not complete [4].

The borane adduct **2a** was isolated as a microcrystalline orange powder. Treatment of **2a** with the stoichiometric amount of LiMe or $Na[HBEt_3]$ did not give **2b** or **2c**. The reaction was monitored by NMR spectroscopy ($C_6D_6$, 25°C) and showed the immediate formation of the single borohydride **3** identified by comparison with an authentic sample obtained from **2a** and $Tl[BH_4]$ [4].

The alternative route (ii) to **2b** or **2c** was investigated on the NMR scale. The corresponding methyl derivative **1b** or the hydride **1c** [2] were synthesized from **1a**. After the addition of 3 equivalents of $BH_3 \cdot SMe_2$, **1c** was immediately converted into **3**, whereas **1b** led to the expected **2b** which was observed by NMR spectroscopy ($C_6D_6$) for more than 1 h and was converted into **3** overnight (Scheme 2).

In both cases, only **3** was observed as final soluble product, and yields were estimated by NMR spectroscopy to be about 70%, very close to the expected yield (75%). In all cases, the formation of **3** implies the formation of byproducts containing fewer than three

$$\begin{tikzcd}
\underset{(\mathbf{1a})}{[(C_5H_4PPh_2)_3UCl]} \arrow[r, "BH_3", "i"'] \arrow[d, "R^-", "ii"'] & \underset{(\mathbf{2a})}{[(C_5H_4PPh_2 \cdot BH_3)_3UCl]} \arrow[d, "R^-"] \\
\underset{(\mathbf{1b},\ \mathbf{1c})}{[(C_5H_4PPH_2)_3UR]} \arrow[r, "BH_3"] & \underset{(\mathbf{2b},\ \mathbf{2c})}{[(C_5H_4PPh_2 \cdot BH_3)_3UR]}
\end{tikzcd}$$

Scheme 1.

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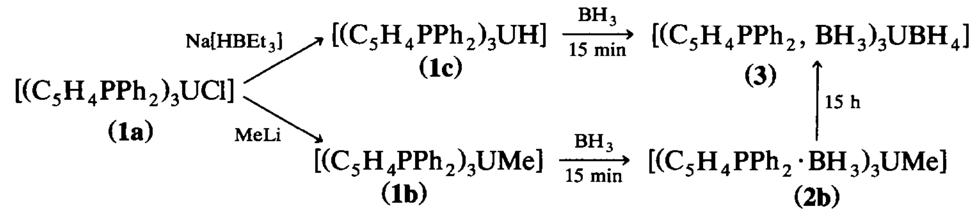
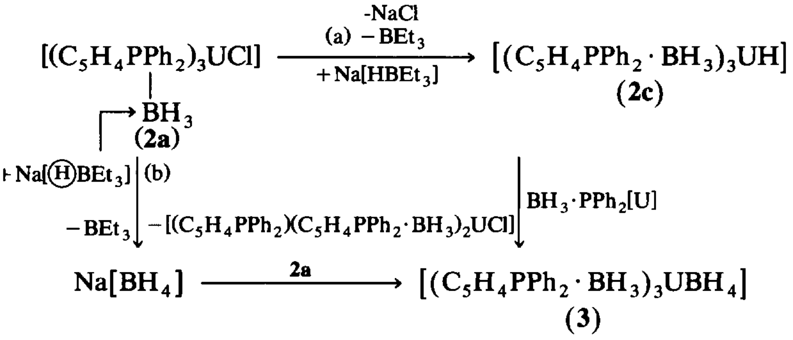
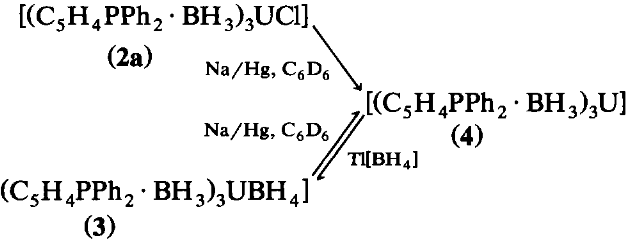


Scheme 2.



Scheme 3.

molecules of borane per uranium. Such complexes were not detected in the reaction mixtures but might be insoluble. The borane insertion which allows the formation of **3** from **2b** without further addition of reagent may involve an intermolecular or intramolecular borane migration followed by ligand exchange. The hydride **2c** has not been detected, but this compound is a likely intermediate in the formation of **3** from **2a** (Scheme 3, path (a)). This reaction is very fast and even if an alternative reaction (Scheme 3, path (b)) involving the initial formation of $Na[BH_4]$ occurs the displacement of a $Cl^-$ by $BH_4^-$ is known to require some hours in THF [5] and is ineffective in toluene. In toluene the displacement requires $Tl[BH_4]$ [6]. It is also noteworthy that the reaction of $[(C_5H_4SiMe_3)_3UH]$ with the $PPh_3 \cdot BH_3$, similar to the second step of path (a), requires 4 h in refluxing THF [7]. The failure to isolate **2b** and **2c** illustrates the great importance of electronic effects in uranium organometallic chemistry and these preliminary experiments suggest that in related uranium heterobimetallic compounds both U–H and U–C bonds should show enhanced reactivity towards insertion reactions.



Scheme 4.

Table 1
$^1$H and $^{31}$P NMR data of the new complexes **1b**, **2a**, **2b**, **3** and **4** (those of previously reported **1a** and **1c** are cited for comparison)

| Complex | δ (ppm) | | | | |
|---|---|---|---|---|---|
| | $^1$H NMR | | | | $^{31}$P NMR |
| | $C_5H_4$ | | $BH_3$ | Me, H or $BH_4$ | |
| **1a** | +7.90 | −6.30 | | | −130 |
| **1b** | +3.20 | −3.20 | | −125.2 | −152 |
| **1c** | +23.48 | −12.66 | | +305.5 | −179 |
| **2a** | +4.50 | −4.57 | −8.70 | | −67 |
| **2b** | −9.80 | −29.30 | −5.00 | −152.0 | −64.5 |
| **3** | +4.80 | −11.54 | −4.50 | −27.7 | −63 |
| **4** | +2.03 | −20.50 | −31.30 | | −323 |

As a consequence of the electron-withdrawing power of the $PPh_2 \cdot BH_3$ group, **2a** and **3** were very easily reduced by sodium amalgam in toluene affording the neutral complex **4** isolated as a tan powder. **4** was readily oxidized to **3** after addition of a stoichiometric amount of $Tl[BH_4]$ [8] (Scheme 4).

NMR data are summarized in Table 1. Aromatic proton resonances are omitted for clarity but they are found in the range δ = 6–8 ppm

## Acknowledgments

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