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Comments on Reactions of Oxide Derivatives of Uranium with Hexachloropropene to give UCl<sub>4</sub>

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#### **Experimental**

#### General

Manipulations to prepare UCl<sub>4</sub> were carried out using Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. <sup>13</sup>C NMR spectra were recorded on Bruker 300 or AV400 spectrometers operating at 75.4 or 155.54 MHz, respectively; chemical shifts are quoted in ppm and are relative to SiMe<sub>4</sub>. FTIR spectra were recorded on a Bruker Tensor 27 spectrometer. Hexachloropropene was used as supplied. The hexachloropropene recycling is conducted under air, and no special measures need to be taken other than performing the distillation in a well-ventilated fumehood.

### Synthesis of 2

A solution of **1** (0.30 g, 0.84 mmol) and Ph<sub>3</sub>P (0.22 g, 0.84 mmol) in toluene was heated to reflux overnight. Upon cooling to -30 °C **2** formed as large colourless crystals and Ph<sub>3</sub>PCl<sub>2</sub> remained in solution. Yield of **2**: 0.19 g, 80%. NMR spectroscopic data match those previously reported.<sup>1</sup>

<sup>13</sup>C{<sup>1</sup>H} NMR (155 MHz, CDCl<sub>3</sub>) for **2**: δ 135.6, 132.0, 131.6, 118.6 ppm. FTIR *v* (cm<sup>-1</sup>) for **2**: 1637, 1601 (s, C=C), 1208 (s, C-Cl), 1166, 934, 798, 659, 657 (s, C-Cl).

# Synthesis of C<sub>6</sub>Br<sub>6</sub>

Compound 1 (0.10 g, 0.28 mmol) was dissolved in neat  $Br_2$  (5 ml, 98 mmol) and stirred for 1 week. Red crystals were observed to form which were isolated, washed with cold DCM and dried *in vacuo*. Yield of C<sub>6</sub>Br<sub>6</sub>: 0.14 g, 91%. NMR data are consistent with an authentic sample.<sup>1,2 13</sup>C{<sup>1</sup>H} NMR (155 MHz, CDCl<sub>3</sub>) for C<sub>6</sub>Br<sub>6</sub>:  $\delta$  128.4 ppm.



Scheme S1. Proposed mechanism for the conversion of 1 to C<sub>6</sub>Br<sub>6</sub>.

A proposed mechanism (Scheme S1) for this unusual ring expansion and halide substitution involves the formation of a bromonium ion at the exocyclic alkene position, followed by an 1,2-

alkyl shift to form a carbocationic 6-membered ring. Nucleophilic attack of a Br<sup>-</sup> ion on a Cl atom at the position next to the carbocation (with concomitant elimination of volatile ClBr) would form a cyclohexadiene derivative, which can subsequently react to form a new bromonium ion. This then eliminates BrCl as before. Iterative repetition of this process eventually leads to the removal of all of the chlorine atoms and an elimination event which forms  $C_6Br_6$ .

## References

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