# $(C_5Me_5)_2UCl\cdot$tetrahydrofuran. Oxidative-addition and Related Reactions

By Richard G. Finke,* Yoshiki Hirose, and Glen Gaughan
(*Department of Chemistry, University of Oregon, Eugene, Oregon* 97403)

*Summary* The first examples of organoactinide oxidative-addition of alkyl halides are reported, reactions which proceed at unprecedented rates; the results presented include the stoicheiometries of these reactions, the new complexes $(C_5Me_5)_2UX_2$, $(C_5Me_5)_2UX(Y)$, and $(C_5Me_5)_2UY(R)$ (X,Y = Br, I), the series of halide exchange equilibria by which these new complexes are formed, determination of the appropriate equilibrium constants to ± 10%, independent syntheses for these new complexes, and evidence for a previously unknown type of $U^{III}$ to $U^{IV}$ redox–halide exchange equilibrium and its equilibrium constant.

The class of reactions known as oxidative-additions occupies a position of fundamental importance in organo-transition metal chemistry.[1] Herein we report the first alkyl halide oxidative-additions in organo*actinide* chemistry, reactions which proceed at rates unprecedented in organo-transition metal chemistry.[2]

Samples of green, formally $U^{III}$, $(C_5Me_5)_2UCl{\cdot}THF$, (**1**) (THF = tetrahydrofuran), used in this work were prepared by the published procedure.[3] Freshly prepared (**1**) is analytically pure, is monomeric in benzene by cryoscopy, is quite $O_2$-sensitive, and exhibits an $E_{1/2}$ $(U^{IV}/U^{III})$ at *ca.* −1·3 V *vs.* saturated calomel electrode by cyclic voltammetry (Pt, MeCN, 0·1 M $Bu_4NPF_6$).

Green, $\lambda_{max}$ 740 nm, benzene solutions of (**1**) react immediately upon mixing with $PhCH_2Cl$, $Me_3CCH_2Cl$, $Me_3CCl$, 1-adamantyl chloride, $Bu^nCl$, $\overline{CH_2CH_2CH}CH_2Cl$, $CH_2{=}CHCH_2CH_2Cl$, MeI, MeBr, $PhCH_2I$, and $I_2$. Although $H_2$ fails to react (1 atm, 1 h, 25 °C, by $^1H$ n.m.r. spectroscopy), PhCl reacts with $t_{1/2}$ *ca.* 3 min [PhCl and (**1**) each 0·06 M] for the usual green to red colour change. Using 100 MHz $^1H$ n.m.r. spectroscopy,† the loss of RX and loss of (**1**) (δ −4·2, $C_5Me_5$, l.w.$_{1/2}$ = 125 Hz‡) were observed with the appearance of red $(C_5Me_5)_2UCl_2$ (δ 12·7, l.w.$_{1/2}$ = 66 Hz), red to black[3b] $(C_5Me_5)_2UCl(R)$ (δ 7·7—10, l.w.$_{1/2}$ = 6 Hz), and the appearance of organic dimers (R–R), olefins [R(–H)], and alkanes (RH) characteristic of an R· intermediate was observed. The observed stoicheiometries, equation 3, can be considered as arising from *a* plus *b* ratios, respectively, of parallel reactions, equations 1 and 2.

$$\begin{aligned} a\{1(C_5Me_5)_2UCl{\cdot}THF + 1RCl \\ (\mathbf{1})\qquad\qquad & \rightarrow 1(C_5Me_5)_2UCl_2 \\ & + 1(\text{total})[R\text{–}R,R(\text{–}H),RH] \\ & + 1THF\} \qquad (1) \end{aligned}$$

$$\begin{aligned} b\{2(C_5Me_5)_2UCl{\cdot}THF + 1RCl \\ & \rightarrow 1(C_5Me_5)_2UCl_2 \\ & + 1(C_5Me_5)_2UCl(R) \\ & + 2THF\} \qquad (2) \end{aligned}$$

$$\begin{aligned} (a + 2b)(C_5Me_5)_2UCl{\cdot}THF + (a + b)RCl \\ & \rightarrow (a + b)(C_5Me_5)_2UCl_2 \\ & + b(C_5Me_5)_2UCl(R) \\ & + a(\text{total})[R\text{–}R,R(\text{–}H),RH] \\ & + (a + 2b)THF \qquad (3) \end{aligned}$$

For example the stoicheiometry observed for $PhCH_2Cl$ [*i.e.* the $(a+2b)/(a+b)$ ratio] (equation 3) was 1·0/1 with 1 mol of $(C_5Me_5)_2UCl_2$, no $(C_5Me_5)_2UCl(CH_2Ph)$ (δ 9·45), and 0·48 mol of $PhCH_2CH_2Ph$ observed by $^1H$ n.m.r. spectroscopy for each mol of $PhCH_2Cl$ consumed. For $Bu^tCl$ oxidative-addition, 1 mol of $(C_5Me_5)_2UCl_2$, 0·12 mol of $Me_3C{-}CMe_3$, 0·42 mol of $Me_2C{=}CH_2$, and 0·42 mol of $Me_3CH$ were observed in a 1·0/1 stoicheiometry reaction.[4] For RCl with less bulky alkyls or which correspond to less stable R·, the observed stoicheiometries approach the limiting 2·0/1 stoicheiometry reaction of equation 2, a stoicheiometry characteristic of atom abstractors like[5] $Co(CN)_5{}^{3-}$; $2Co^{II} + 1RX \rightarrow 1R\text{–}Co^{III} + 1X\text{–}Co^{III}$. In the case of $Bu^nCl$, 1·55 mol of (**1**) were consumed for each mol of $Bu^nCl$, with 0·55 mol of $(C_5Me_5)_2UCl(Bu^n)$ [δ 7·75 (s, 30H, $C_5Me_5$), −9·35 (t, *J* 7 Hz, 3H, $CH_3$), −17·6 (br s, 2H, $CH_2$), −30·1 (br s, 2H, $CH_2$), and −90·8 (br s, 2H, $CH_2$)] and 0·25 mol of the dimer, octane,[4] present, by $^1H$ n.m.r. spectroscopy. Both cyclopropylmethyl chloride and 4-chlorobut-1-ene gave *ca.* 30% of $(C_5Me_5)_2UCl(CH_2CH_2CH{=}CH_2)$ (δ 8·50, $C_5Me_5$) initially, thereby providing good evidence for the equilibrium[6] $\overline{CH_2CH_2CH}CH_2{\cdot} \rightleftharpoons {\cdot}CH_2CH_2CH{=}CH_2$, and thus the intermediacy of radicals in these oxidative-addition reactions.

The oxidative-addition of alkyl iodides or bromides is interesting in that products containing all the possible halide combinations are observed. For example, MeI oxidative-addition shows 2 mol of (**1**) consumed for each mol of MeI with 0·31 mol of $(C_5Me_5)_2UCl_2$ (δ 12·7), 0·25 mol of $(C_5Me_5)_2UCl(I)$ (δ 14·7), 0·03 mol of $(C_5Me_5)_2UI_2$ (δ 16·8), 0·19 mol of $(C_5Me_5)_2UCl(Me)$ (δ 8·75), and 0·22 mol of $(C_5Me_5)_2UI(Me)$ (δ 10·40) as products. The $^1H$ n.m.r. product assignments are supported by independent syntheses using $BI_3$ $[3(C_5Me_5)_2UCl_2 + 2BI_3 \rightarrow 3(C_5Me_5)_2UI_2 + 2BCl_3]$, using $I_2$ + (**1**), and by the internal consistency of the $^1H$ n.m.r. chemical shifts. In all cases so far, the observed chemical shifts are to smaller δ values in the order (downfield) I>Br>Cl (upfield) for the complexes $(C_5Me_5)_2UX(Y)$, $(C_5Me_5)_2UX(R)$, and $(C_5Me_5)_2UX_2$ (X,Y = I, Br, Cl).§ These additional organouranium products containing all the possible halide combinations are, in all probability, due to the reasonably facile halogen and/or alkyl exchange or redistribution equilibria,¶ equations 4, 5, and 6 with $K_4 = 1{\cdot}3 \pm 0{\cdot}1$, $K_5 = 0{\cdot}11 \pm 0{\cdot}01$, $K_6 = K_4 \times K_5 = 0{\cdot}15 \pm 0{\cdot}01$ (at 39 °C in benzene) subsequent to the initial oxidative-addition reaction. The presence of these equilibria was confirmed and their equilibrium constants were measured by the addition of $(C_5Me_5)_2UCl_2$ to the (**1**)-plus-MeI product mixture. The new position of the equilibria, as monitored by $^1H$ n.m.r. spectroscopy, was established in quantitative accordance with equations 4, 5, and 6, their equilibrium constants, and the law of mass action. For MeBr addition, the bromide equilibria corresponding to equation 4, 5, and 6 have $K_4 = 0{\cdot}49 \pm 0{\cdot}05$, $K_5 = 0{\cdot}36 \pm 0{\cdot}04$, and $K_6 = 0{\cdot}18 \pm 0{\cdot}02$, respectively, at 39 °C in benzene. A similar set of halide redistribution equilibria are known for $Cp_2MX_2$ (M = Ti, Zr, Hf).[7]

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† Unless stated otherwise, all chemical shift values are δ ($Me_4Si$) in $C_6D_6$ at 39 °C, and are temperature-dependent.

‡ L.w.$_{1/2}$ = line width at half height.

§ A similar situation occurs in Ti and Zr chemistry (ref. 7).

¶ The $^1H$ n.m.r. slow exchange limit is observed, however, at 39 °C. Marks has found (ref. 3a), consistent with what we observe, that the following equilibrium exists and lies predominantly to the right: $(C_5Me_5)_2UMe_2 + (C_5Me_5)_2UCl_2 \rightleftharpoons 2(C_5Me_5)_2UCl(Me)$.

$$(C_5Me_5)_2UCl(Me) + (C_5Me_5)_2UCl(I) \overset{K_4}{\rightleftharpoons} (C_5Me_5)_2UI(Me) + (C_5Me_5)_2UCl_2 \qquad (4)$$

$$(C_5Me_5)_2UI(Me) + (C_5Me_5)_2UCl(I) \overset{K_5}{\rightleftharpoons} (C_5Me_5)_2UCl(Me) + (C_5Me_5)_2UI_2 \qquad (5)$$

$$2(C_5Me_5)_2UCl(I) \overset{K_6}{\rightleftharpoons} (C_5Me_5)_2UCl_2 + (C_5Me_5)_2UI_2 \qquad (6)$$

A second type of exchange reaction was discovered during the oxidative-addition of MeI, $PhCH_2I$, or $I_2$ in the presence of an excess of (**1**). The sequential addition of (**1**) to the products of the $I_2$ reaction confirmed that the new species was $(C_5Me_5)_2UI\cdot THF$ ($\delta$ − 1·1, $l.w._{1/2}$ = 62 Hz) and that it was formed by the $U^{III}$, $U^{IV}$ redox–halide exchange equilibria, equations 7 and 8, with $K_7 = 20 \pm 2$ and $K_8 = 19 \pm 2$ (39 °C in benzene).

$$(C_5Me_5)_2UI_2 + (\mathbf{1}) \overset{K_7}{\rightleftharpoons} (C_5Me_5)_2UI\cdot THF + (C_5Me_5)_2UCl(I) \qquad (7)$$

$$(C_5Me_5)_2UCl(I) + (\mathbf{1}) \overset{K_8}{\rightleftharpoons} (C_5Me_5)_2UI\cdot THF + (C_5Me_5)_2UCl_2 \qquad (8)$$

An initial mechanistic study of these facile oxidative–addition reactions has also been completed.[2]

Financial support through an N.S.F. grant and a grant from Chevron Research is gratefully acknowledged.

(*Received, 4th November* 1980; *Com.* 1186.)

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