

(C₅Me₅)₂UCl·tetrahydrofuran. Oxidative-addition and Related Reactions

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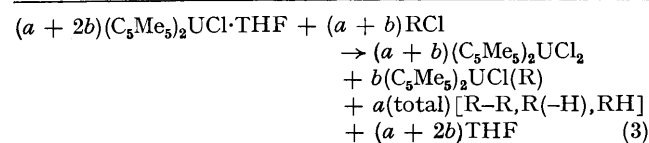
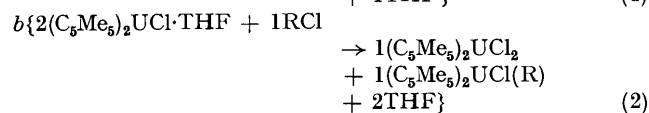
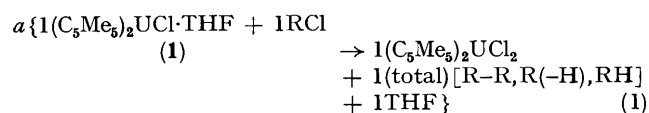
Summary The first examples of organoactinide oxidative-addition of alkyl halides are reported, reactions which proceed at unprecedented rates; the results presented include the stoichiometries of these reactions, the new

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 $\pm 10\%$, 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 organoactinide 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, λ_{max} 740 nm, benzene solutions of (**1**) react immediately upon mixing with $PhCH_2Cl$, Me_3CCH_2Cl , Me_3CCl , 1-adamantyl chloride, Bu^nCl , $CH_2CH_2CHCH_2Cl$, $CH_2=CHCH_2CH_2Cl$, 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 $R\cdot$ intermediate was observed. The observed stoichiometries, equation 3, can be considered as arising from a plus b ratios, respectively, of parallel reactions, equations 1 and 2.



For example the stoichiometry observed for $PhCH_2Cl$ [*i.e.* the $(a+2b)/(a+b)$ ratio] (equation 3) was 1.0/1 with

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

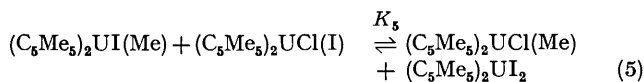
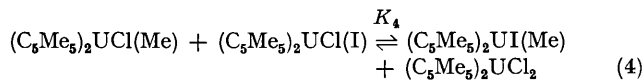
‡ L.w. $_{1/2}$ = line width at half height.

§ 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: $(C_5Me_5)_2UMe_2 + (C_5Me_5)_2UCl_2 \rightleftharpoons 2(C_5Me_5)_2UCl(Me)$.

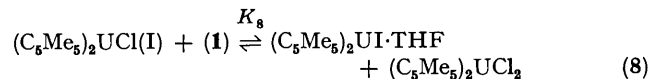
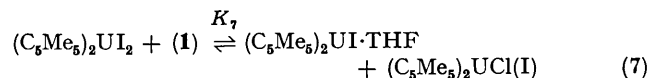
1 mol of $(C_5Me_5)_2UCl_2$, no $(C_5Me_5)_2UCl(CH_2Ph)$ (δ 9.45), and 0.48 mol of $PhCH_2CH_2Ph$ observed by 1H n.m.r. spectroscopy for each mol of $PhCH_2Cl$ consumed. For Bu^tCl oxidative-addition, 1 mol of $(C_5Me_5)_2UCl_2$, 0.12 mol of Me_3C-CMe_3 , 0.42 mol of $Me_2C=CH_2$, and 0.42 mol of Me_3CH were observed in a 1.0/1 stoichiometry reaction.⁴ For RCl with less bulky alkyls or which correspond to less stable $R\cdot$, the observed stoichiometries approach the limiting 2.0/1 stoichiometry reaction of equation 2, a stoichiometry characteristic of atom abstractors like⁵ $Co(CN)_5^{3-}$; $2Co^{II} + 1RX \rightarrow 1R-Co^{III} + 1X-Co^{III}$. 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 equilibrium⁶ $\overline{CH_2CH_2CHCH_2} \rightleftharpoons \cdot CH_2CH_2CH=CH_2$, 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 [$3(C_5Me_5)_2UCl_2 + 2BI_3 \rightarrow 3(C_5Me_5)_2UI_2 + 2BICl_3$], 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 $K_4 = 1.3 \pm 0.1$, $K_5 = 0.11 \pm 0.01$, $K_6 = K_4 \times K_5 = 0.15 \pm 0.01$ (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 $K_4 = 0.49 \pm 0.05$, $K_5 = 0.36 \pm 0.04$, and $K_6 = 0.18 \pm 0.02$, respectively, at 39 °C in benzene. A similar set of halide redistribution equilibria are known for Cp_2MX_2 ($M = Ti, Zr, Hf$).⁷



A second type of exchange reaction was discovered during the oxidative-addition of MeI, PhCH₂I, or I₂ in the presence of an excess of (1). The sequential addition of (1) to the products of the I₂ reaction confirmed that the new species was (C₅Me₅)₂UI·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).



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

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¹ J. P. Collman and L. S. Hegedus, 'Principles and Applications of Organotransition Metal Chemistry,' University Science Books, Mill Valley, California, 1980, ch. 4.

² Further details will be published elsewhere: R. G. Finke, D. A. Schiraldi, and Y. Hirose, *J. Am. Chem. Soc.*, 1981, in the press.

³ (a) J. M. Manriquez, P. J. Fagan, and T. J. Marks, *J. Am. Chem. Soc.*, 1978, **100**, 3939; (b) J. M. Manriquez, P. J. Fagan, T. J. Marks, S. H. Vollmer, C. S. Day, and V. W. Day, *ibid.*, 1979, **101**, 5075 {pure (C₅Me₅)₂UCl·THF was obtained by THF addition to [(C₅Me₅)₂UCl]₃ prepared from (C₅Me₅)₂UCl(Me) and H₂. Na(Hg) reduction of (C₅Me₅)₂UCl₂ gives (C₅Me₅)₂UCl₂·Na⁺ rather than the desired product}; (c) P. J. Fagan, J. M. Manriquez, and T. J. Marks in 'Organometallics of the F-Elements,' eds. T. J. Marks and R. D. Fischer, D. Reidel Publishing Co., Dordrecht, 1979.

⁴ Known $k(\text{disproportionation})/k(\text{combination})$ values for Me₃C· and Bu[•] are 7.2 and 0.14, respectively: R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, 1970, **92**, 4395.

⁵ J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, 1965, **87**, 5361; J. Kwiatek, and J. K. Seyler, *J. Organomet. Chem.*, 1965, **3**, 421.

⁶ P. J. Krusic, P. J. Fagan, and J. San Filippo, Jr., *J. Am. Chem. Soc.*, 1977, **99**, 250; A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, and A. K. Serelis, *ibid.*, 1980, **102**, 1734.

⁷ P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spalding, and R. C. Srivastava, *J. Chem. Soc. A*, 1969, 2106. Here $K_{eq} = 0.24 \pm 0.03$ for $2Cp_2TiCl(Br) \rightleftharpoons Cp_2TiCl_2 + Cp_2TiBr_2$ at 38 °C in THF, equal to the statistical value for random redistribution, $K_{eq} = (1/2)^2 = 0.25$.