The Insertion of Carbon Dioxide into Actinide Alkyl and Hydride Bonds*

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Abstract

This contribution reports on the insertion of CO_2 into actinide methyl and hydride bonds to yield acetate and formate complexes, respectively. Thus, addition of excess CO_2 to Cp'_2MMe_2 ($Cp' = \eta^5$-C_5Me_5, M = Th, U) results in the formation of $Cp'_2M(OAc)_2$ complexes in high yield. These new complexes, which could also be prepared from Cp'_2MCl_2 and 2 equiv. of NaOAc, were characterized by standard techniques. On the basis of infrared data and molecular weight measurements the bis(acetate) compounds are suggested to be monomeric with two bidentate acetate ligands, thus achieving a 10-coordinate geometry about the metal ion. The addition of only 1 equiv. of CO_2 to Cp'_2MMe_2 yields $Cp'_2MMe(OAc)$ complexes exclusively, suggesting that the formation of the bis(acetate) complexes proceeds sequentially. These complexes could also be prepared via metathesis of the corresponding Cp'_2MMeCl complexes with NaOAc. Although the reaction of CO_2 with $[Cp'_2Th(\mu\text{-}H)(H)]_2$ produces a variety of uncharacterizable products, $Cp'_2Th(O_2CH)(OCH\text{-}t\text{-}Bu)$ was formed upon treatment of $Cp'_2Th(H)(OCH\text{-}t\text{-}Bu)$ with CO_2.

Introduction

Recent work in our Laboratories has shown that alkyl and hydride complexes of the actinides display a markedly rich chemistry with carbon monoxide [1]. As a logical extension of this work, we have begun an investigation of the chemistry of these complexes with carbon dioxide, a reagent the fixation of which has been the subject of considerable recent interest [2]. Although the insertion of carbon dioxide into a metal–carbon or hydrogen bond to yield a carboxylate moiety (eqn. 1) is known for practically every d-transition and main group metal in the

$$M{-}R + CO_2 \longrightarrow M{-}O\overset{\overset{\displaystyle O}{\|}}{C}R \quad R = \text{alkyl, H} \qquad (1)$$

Periodic Table [3], the corresponding insertion chemistry of CO_2 into an f-element alkyl or hydride bond has attracted little attention†. However, recent work has shown that CO_2 (as well as COS and CS_2) will in fact insert into uranium–nitrogen bonds to yield carbamate complexes [5], suggesting that the analogous insertion into an actinide–alkyl bond should be possible. Consequently, in order to provide a base from which new f-element CO_2 chemistry might be derived, we have initially investigated the simple carboxylation chemistry of a series of actinide alkyl and hydride complexes. These results are described herein.

Experimental

Materials and Methods

All operations were performed with rigorous exclusion of oxygen and moisture in Schlenk-type glassware on a dual manifold Schlenk line or interfaced to a high vacuum (10^{-5} torr) system, or in a dinitrogen filled, recirculating glovebox (Vacuum Atmospheres Corporation). Argon (Matheson, prepurified) was purified by passage through sequential columns of MnO (supported on vermiculite) [6] and activated 4A molecular sieves. Carbon dioxide (Matheson, Coleman Instrument Grade) was purified by first condensing the gas from the gas cylinder into a trap at -196 °C. The trap was then evacuated until all traces of oxygen were removed and the liquid nitrogen dewar was replaced with a dry ice/acetone slush. The CO_2 was then allowed to expand into the vacuum line manifold. All solvents were distilled from Na/K/benzophenone and stored *in vacuo* in bulbs on the vacuum line. Each solvent bulb contained a small amount of $[Cp_2TiCl]_2ZnCl_2$ [7] as O_2/H_2O indicator. Deuterated solvents were stored over Na/K alloy and vacuum transferred before use. Cp'_2MCl_2 [8], Cp'_2MMe_2 [8], $Cp'_2M(Me)(Cl)$ [8] (M = Th, U), $Cp'_2Th(H)(OCH\text{-}t\text{-}Bu_2)$ [9], and $[Cp'_2Th(\mu\text{-}H)(H)]_2$ [9] were prepared according to the literature procedures.

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†Recent results in this Laboratory have shown that CO_2 will insert into the alkyl bonds of Cp_3ThR complexes, albeit sluggishly, see ref. 4.

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Analytical Methods

Proton NMR spectra were recorded on either Perkin–Elmer R-20B (CW, 60 MHz) or a JEOL FX-90Q (FT, 90 MHz) spectrometers. Infrared spectra were recorded on Perkin–Elmer 599 or 283 spectrometers using Nujol mulls sandwiched between KBr plates in an o-ring-sealed, air-tight holder.

Elemental analyses were performed by Dornis und Kolbe Mikroanalytisches Laboratorium, Mülheim, F.R.G.

$Cp'_2Th(OAc)_2$, 1

In a 25 ml flask was placed 0.29 g (0.54 mmol) Cp'_2ThMe_2. The flask was evacuated and 10 ml of toluene was condensed in at −78 °C, dissolving the complex. The flask was then backfilled with *ca.* 1 atm of CO_2. The solution was warmed to room temperature and stirred for 1 h. The toluene and excess CO_2 were next removed under vacuum to yield a colorless solid. Pentane (15 ml) was condensed into the flask and the colorless solution was filtered. The pentane was then carefully removed under vacuum until colorless crystals began to precipitate. The solution was then slowly cooled to −78 °C to precipitate more crystals which were isolated by filtration. Yield: 0.26 g (0.41 mmol), 76%. ^1H NMR (C_6D_6, 60 MHz): δ 1.85 (s, 6 H), 1.96 (s, 30 H). IR (Nujol, cm^{-1}): 1586 s, 1560 s, 1345 m, 1262 m, 1088 m, 1020 s, 937 w, 803 m, 720 w, 678 s, 642 m, 612 w, 533 w, 515. *Anal.* Calcd. for $C_{24}H_{36}ThO_4$: C, 46.45; H, 5.85; MW, 589 g/mol. Found: C, 46.50; H, 5.90; MW, 580 g/mol (cryoscopic in benzene).

This complex may also be prepared from Cp'_2ThCl_2 and NaOAc (2 equiv.) in THF. After 10–12 h stirring at room temperature, the solvent was removed under vacuum and the resulting colorless solid was worked up in the same manner (toluene/pentane) as above.

$Cp'_2U(OAc)_2$, 2

This complex was prepared as maroon crystals from Cp'_2UMe_2 or Cp'_2UCl_2 in the same manner as for $Cp'_2Th(OAc)_2$ above. ^1H NMR (C_6D_6, 60 MHz): δ 3.85 (s, 30 H), 12.49 (s, 6 H). IR (Nujol, cm^{-1}): 1540 s, 1060m, 1025 m, 940m, 803 w, 721 m, 677 s, 612 w. *Anal.* Calcd. for $C_{24}H_{36}UO_4$: C, 46.01; H, 5.79. Found: C, 46.08; H, 5.82.

$Cp'_2U(Me)(OAc)$, 3

Cp'_2UMe_2 (0.25 g, 0.46 mmol) was placed in a 25 ml flask which was then evacuated. Toluene (10 ml) was condensed in at −78 °C, dissolving all of the complex to give a red solution. Carbon dioxide (0.46 mmol), premeasured in a calibrated volume, was then condensed into the flask and the solution was allowed to warm to room temperature. After 1 h, no further color changes were observed and the solvent was removed *in vacuo*. The resulting maroon solid was slurried into pentane and isolated by filtration. Yield: 0.21 g (0.37 mmol), 80%. ^1H NMR (C_6D_6, 60 MHz): δ −16.0 (s, 3 H), 1.90 (s, 30 H), 75.0 (s, 3 H). IR (Nujol, cm^{-1}): 1520 s, 1110 m, 1021 m, 935 m, 803 w, 720 w, 678 s. *Anal.* Calcd. for $C_{23}H_{36}UO_2$: C, 47.42; 6.23. Found: C, 47.47; 6.25.

This complex may also be synthesized from Cp'_2UMeCl and NaOAc (1.0 equiv.) in THF. After 3–4 h stirring at room temperature, the solvent was removed under vacuum and the residue extracted with toluene. The complex was then isolated from pentane in the same manner as that described above.

$Cp'_2Th(Me)(OAc)$, 4

This colorless complex was prepared from Cp'_2ThMe_2 or $Cp'_2ThMeCl$ in the same manner as that for $Cp'_2U(Me)(OAc)$, above. ^1H NMR (C_6D_6, 60 MHz): δ 0.23 (s, 3 H), 1.74 (s, 3 H), 1.95 (s, 30 H). *Anal.* Calcd. for $C_{23}H_{36}ThO_2$: C, 47.91; H, 6.29. Found: C, 48.02; H, 6.34.

$Cp'_2Th(O_2CH)(OCH\text{-}t\text{-}Bu_2)$, 7

$Cp'_2Th(H)(OCH\text{-}t\text{-}Bu_2)$ (0.445 g, 0.688 mmol) was placed in a 50 ml reaction flask which was then evacuated. Toluene (10 ml) was condensed into the flask at −78 °C followed by 0.757 mmol of CO_2, premeasured in a calibrated volume. After 1 h at −78 °C, the colorless solution was allowed to warm to room temperature, and the solution was stirred overnight. The solvent was next removed under vacuum and the residue was analyzed by ^1H NMR (C_6D_6, 60 MHz). Resonances at δ 1.33 (s, 18 H), 2.05 (s, 30 H), 3.99 (s, 1 H), and 9.13 (s, 1 H) indicated the formation of the title complex. However, at least three additional resonances at δ 1.0, 2.1, and 2.2 were observed, albeit in low intensity. The yield of 7 at this point was estimated to be *ca.* 85%. Several attempts were made to purify the sample by recrystallization to no avail. An attempt was made to sublime the material (125 °C, 10^{-5} torr) in an effort to purify it. Only a very small amount of material sublimed; however, ^1H NMR analysis of the sublimed material showed that some of the impurities had been sublimed away from the desired product and the purity was raised to *ca.* 95%. IR (Nujol, cm^{-1}): 1553 s, 1390 m, 1368 s, 1356 m, 1319 m, 1162 w, 1049 m, 992 s, 960 m, 918 w, 802 m, 768 w, 723 w, 658 m. *Anal.* Calcd. for $C_{30}H_{50}ThO_3$: C, 52.16; H, 7.30. Found: C, 50.19; H, 7.67.

Results and Discussion

The insertion of CO_2 into actinide–methyl bonds of bis(pentamethylcyclopentadienyl) complexes proceeds rapidly and quantiatively (determined by ^1H NMR spectroscopy) at room temperatures as shown in eqn. (2) to yield the bis(acetate) complexes **1** and

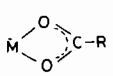
$$Cp'_2MMe_2 \xrightarrow{1\ atm\ CO_2} Cp'_2M(OAc)_2 \qquad (2)$$

1 M = Th **2** M = U

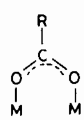
2. These complexes may be isolated in yields of 70–80% from cold pentane in crystalline form. Alternatively, authentic samples can be prepared by the metathesis reaction shown in eqn. (3). The

$$Cp'_2MCl_2 + 2NaOAc \longrightarrow Cp'_2M(OAc)_2 + 2NaCl \qquad (3)$$

new complexes were characterized by infrared and ^1H NMR spectroscopy and by elemental analysis. Unfortunately, single crystals of **2** did not prove suitable for an X-ray structure determination. On the basis of the infrared data ($\nu_{OCO} < 1590$ cm^{-1}) the acetate ligands are assigned bidentate (**A**) or bridging (**B**) ligation [10]*, thus achieving a comfortable 10-coordinate geometry about the metal.

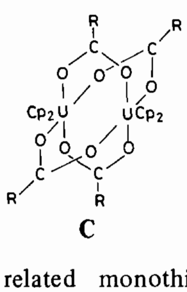


A



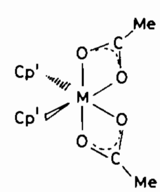
B

The related complexes with less sterically-demanding cyclopentadienyl ligands, $Cp_2U(O_2CR)_2$ ($Cp = \eta^5$-C_5H_5, R = Me, t-Bu, Ph), are also formally 10-coordinate and were shown to have the dimeric structure **C** where the carboxylate groups serve as bridging, rather than chelating moieties [11]. Curiously, the



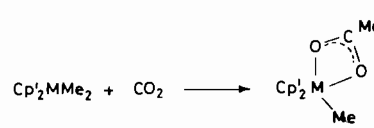
C

related monothiocarboxylate [5a], thiocarbamate [5a], and dithiocarbamate [5a] complexes were shown to be monomeric with bidentate ligands. Although $Cp_2U(OAc)_2$ is known to be dimeric, the infrared spectrum (in the carboxylate ν_{OCO} region) of this complex is virtually indistinguishable from that of monomeric $Cp_3Th(OAc)$, a compound with a bidentate acetate ligand [4]. Therefore, the infrared data alone cannot distinguish between a dimeric (bridging acetate ligands) or monomeric, bidentate acetate ligand. However, this ambiguity could be resolved by a cryoscopic molecular weight determination for **1**, which showed this complex to be monomeric in benzene. Hence, the bis(acetate) complexes described here are proposed to be structurally similar to the thiocarboxylate and carbamate compounds discussed above. Diffraction derived structures for similar monomeric, 10-coordinate $Cp'_2M(\eta^2$-$X)_2$ complexes are known [12] and based on this evidence a structure such as **D** is proposed for compounds **1** and **2**. Here the two acetate ligands are predicted to lie roughly in a plane perpendicular to the plane defined by the metal and the two ring centroids.



D

The formation of complexes **1** and **2** by addition of CO_2 to Cp'_2MMe_2 was also found to proceed sequentially. Thus, addition of one equivalent of CO_2 to the dimethyl complexes results in the formation of the monoacetate complexes **3** and **4** in high yield (eqn. 4). These new complexes may be crystallized from cold pentane and were characterized by stan-



(4)

3 M = U **4** M = Th

dard techniques (see Experimental Section for details). These complexes can also be prepared via the metathesis reaction shown in eqn. (5). On the basis of infrared data and solubility characteristics,

$$Cp'_2MMeCl + NaOAc \longrightarrow Cp'_2MMe(OAc) + NaCl \quad (5)$$

these species are postulated to be monomeric with chelating acetate ligands (*vide supra*). The metal ion is therefore believed to exhibit the familiar 9-coordinate geometry common to species of the type Cp'_2-$M(\eta^2$-X)(Y) [13].

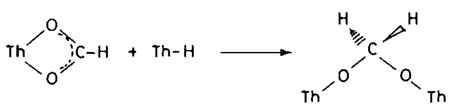
Once the insertion of CO_2 into actinide–alkyl bonds was demonstrated, it was of interest to explore the reactivity of the corresponding hydrides with this reagent. $[Cp'_2Th(\mu$-$H)(H)]_2$ was found to react instantly with CO_2 at –78 °C, yielding both soluble

*The energy difference between the asymmetric and symmetric OCO stretching frequencies has been used as a guide to the ligation of the carboxylate group [10a]. Hence, when $\Delta\nu(OCO) < 100$ cm^{-1}, a bidentate coordination mode is indicated. This criterion, however, has been criticized [10b, 11]. It is suggested that the appearance of a low energy (<*ca.* 1610 cm^{-1} for OAc) band assignable as the asymmetric OCO stretch is indicative of coordination by both carboxylate oxygen atoms [10b, 11].

and insoluble products. The infrared spectrum of either product exhibited bands in the region 1580–1330 cm^{-1}, suggesting that formate (-O_2CH) fragments [10] had indeed been formed, but little else could be concluded concerning the nature of the products of this reaction. ^1H NMR analysis of the benzene-soluble products showed a multiplicity of Cp$'$ resonances; clearly the reaction does not proceed cleanly. Toepler pump measurements indicated that the reaction stoichiometry is 1.5 CO_2/Th as shown in eqn. (6). Because no residual hydride signals

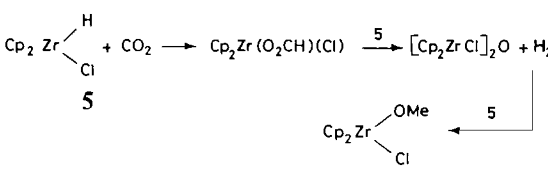
$$[Cp'_2Th(\mu\text{-}H)(H)]_2 + 3CO_2 \longrightarrow \text{products} \qquad (6)$$

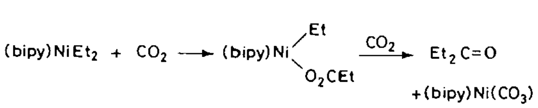
(10–20 ppm) were observed in the ^1H NMR spectrum, it is suggested that at least one secondary reaction pathway may involve attack of hydride on a coordinated formate ligand, resulting in the formation of a species such as **E** (eqn. (7)). The ^1H NMR


(7)

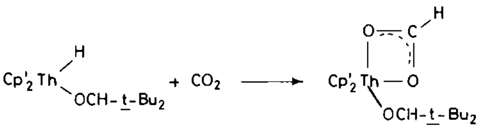
E

spectrum of the soluble product mixture also showed a singlet at δ 3.87 ppm which may be attributable to a species such as **E**. Furthermore, the presence of a strong band at 1105 cm^{-1} in the infrared spectrum is indicative of an alkoxide C–O stretch [10a]. This type of reaction finds some precedent, as shown in eqns. (8) [14] and (9) [15].


(8)


(9)

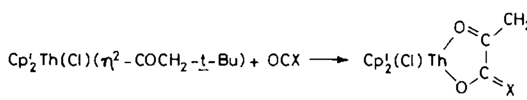
In order to avert secondary reactions such as that shown in eqn. (7) (*i.e.*, inter- or intramolecular hydride transfer) the reaction of CO_2 with Cp$'_2$-Th(H)(OCH-t-Bu_2) was investigated. As shown in eqn. (10), the hydride **6** reacts with one equivalent


(10)

6 **7**

of CO_2 to yield the formate complex **7**. This insertion reaction, however, does not proceed quantitatively and some secondary reaction products are formed. The yield of the formate, as determined by ^1H NMR spectroscopy, appears to be 85–90%. The impurities could not be removed by recrystallization techniques. Although sublimation yielded a somewhat purer product (as determined by ^1H NMR spectroscopy), unsatisfactory carbon and hydrogen analyses were obtained. Nevertheless, the formate could be readily characterized by infrared and ^1H NMR spectroscopy. Thus, the presence of a strong band in the infrared spectrum at 1553 cm^{-1} [8] and a singlet at δ 9.13 ppm in the ^1H NMR spectrum (along with Cp$'$ and OCH-t-Bu resonances in the proper intensity ratios) are indicative of a structure such as **7**.

The dihaptoacyl Cp$'_2$Th(Cl)(η^2-$COCH_2$-t-Bu) reacts rapidly with CO_2 at -78 °C to yield a host of products as determined by ^1H NMR spectroscopy. Unfortunately, no crystalline products could be isolated from the reaction mixture. However, the presence of a band at 1653 cm^{-1} (along with many others in the region 1600–1350 cm^{-1}) in the infrared spectrum of the resulting mixture suggests that a product such as **8** may have been produced. Precedent for this


(11)

8 X = O **9** X = CPh_2

type of reaction is provided by the analogous reaction with diphenylketene (which, of course, is isoelectronic with CO_2) to yield **9** [16] and may represent an example of CO/CO_2 coupling.

Acknowledgments

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