

periments demonstrated that these quenchers do not quench fluorescence from photoexcited fluorenone under the reaction conditions. Thus, the observed chemiluminescence quenching in polymers must be due to interception of  $^1\text{O}_2$ .

$$I_{\text{CL}}^0/I_{\text{CL}} = 1 + [P_Q/(C_P + PC_A)]C_Q \quad (6)$$

Since our experimental method is novel and potentially subject to unsuspected artifacts, we seek independent confirmation that our conclusions are tenable. With the assumption that the diffusivities of  $^1\text{O}_2$  and  $^3\text{O}_2$  are similar, we may evaluate the lifetime,  $\tau$ , of singlet oxygen from the equation  $l = \sqrt{3D\tau}$ , where  $D$  is the diffusion coefficient of  $^3\text{O}_2$ . Taking our experimental values of  $l$  and literature values of  $D$ , we calculate  $\tau(^1\text{O}_2)$  is  $135 \times 10^{-6}$  and  $430 \times 10^{-6}$  s in PS and PMMA, respectively. These values fall in the range of literature values<sup>8</sup> reported for the lifetime of  $^1\text{O}_2$  in fluid solutions:  $10 \times 10^{-6}$  to  $1000 \times 10^{-6}$  s. Furthermore, our values of ( $\sim 500$ – $600$  Å) are comparable with those found<sup>9</sup> for the average diffusional distance of  $^1\text{O}_2$  in stearate monomolecular films ( $\sim 500$  Å). The ratio of quenching constants for Rylex and Cyasorb derived from the ratio of slopes in Figure 3 is  $\sim 7$  ( $6.7 \times 10^4$  vs.  $9.4 \times 10^3$ ). The ratio of rate constants for these quenchers in fluid solution is  $\sim 30$  ( $5 \times 10^9$  vs.  $1.6 \times 10^8$ ).<sup>7</sup> This difference is attributable to a "leveling" effect of the polymer medium on relative quenching rates.<sup>10</sup>

The conformity of our data and conclusions with those derived from three completely independent sources of measurement is substantial support for the validity of the proposed mechanism. The measurement of relative quenching constants for  $^1\text{O}_2$  in polymers now is relatively straightforward matter. It will be of interest to study quenching effectiveness of "physical" and "chemical" quenchers of  $^1\text{O}_2$  in polymers and to compare these results with those obtained from liquid-phase experiments. Such investigations are now in progress and will be reported in due course.

**Acknowledgment.** The authors thank the Air Force Office of Scientific Research and the National Science Foundation for their generous support of this research.

## References and Notes

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- (5) The  $l$  is the value of the end to end distances of random walks in  $n$  hops, according to  $l = a \times n^{1/2}$ , when  $a$  is the average separation distance between nearest neighbor monomers and is taken to be 5.5 Å for PS.
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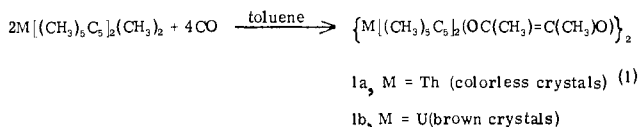
## Bis(pentamethylcyclopentadienyl)actinide Alkyls: Facile Activation of Carbon Monoxide, Carbon-Carbon Double Bond Formation, and the Production of Unusual Oxygen-Bonded Migratory Insertion Products

Sir:

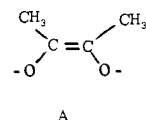
As part of our investigation of the relationship of organoactinide<sup>1</sup> electronic configuration and ligation pattern to chemical reactivity,<sup>2</sup> we recently reported thermally stable bis(pentamethylcyclopentadienyl)thorium and -uranium dialkyls<sup>3</sup> and their rapid hydrogenolysis to give bis(pentamethylcyclopentadienyl)actinide dihydrides.<sup>3,4</sup> The enhanced reactivity of the organoactinides over analogous titanium and zirconium compounds was noted.

Recently, there has been considerable interest in the reactions of early transition metal organometallics with carbon monoxide since the products,<sup>5,6</sup> which are frequently not classical<sup>7</sup> metal acyls, may be representations of intermediates in the catalytic reduction of  $\text{CO}$ .<sup>5b,8,9</sup> Carbonylation chemistry of organoactinides would clearly be of interest, and we report here the very facile activation of  $\text{CO}$  by bis(pentamethylcyclopentadienyl)thorium and -uranium alkyls (the first example of migratory insertion involving actinide-carbon  $\sigma$  bonds), the unusual molecular structure of the  $\text{Th}[(\text{CH}_3)_5\text{C}_5]_2(\text{CH}_3)_2$  dicarbonylation product, and some structure-sensitivity observations on the  $\text{CO}$  incorporation process.

In toluene solution at  $-80$   $^\circ\text{C}$ ,  $\text{Th}[(\text{CH}_3)_5\text{C}_5]_2(\text{CH}_3)_2$ <sup>3</sup> and  $\text{U}[(\text{CH}_3)_5\text{C}_5]_2(\text{CH}_3)_2$ <sup>3</sup> take up 2.0 equiv of carbon monoxide ( $<1$  atm) within 1 h (eq 1). Warming to room temperature

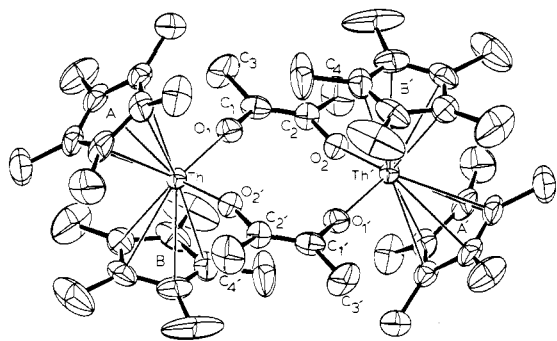


produces **1** in quantitative yield. The insertion products were recrystallized from toluene and characterized by standard analytical techniques;<sup>10</sup> cryoscopic molecular measurements reveal them to be dimeric.<sup>10</sup> Infrared transitions at 1655 ( $\nu_{\text{C}=\text{C}}$ ), 1252 and 1220 ( $\nu_{\text{C}=\text{O}}$ )  $\text{cm}^{-1}$  as well as a single nonring methyl signal in the  $^1\text{H}$  NMR spectrum are suggestive of a 2-butene-2,3-diolate fragment (A). This ligand was proposed



for the monomeric product of the slower (requiring 24 h at 75  $^\circ\text{C}$ ) dicarbonylation of  $\text{Zr}[(\text{CH}_3)_5\text{C}_5]_2(\text{CH}_3)_2$ .<sup>5a</sup>

Single crystals of **1a**, obtained by cooling of a hot toluene solution, are monoclinic, space group  $P2_1/n$  (an alternate

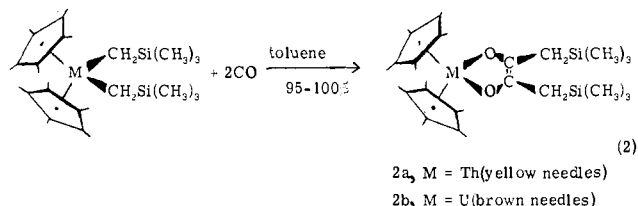


**Figure 1.** ORTEP drawing of the nonhydrogen atoms for  $[\text{Th}(\eta^5\text{-C}_5(\text{CH}_3)_5)_2(\mu\text{-O}_2\text{C}(\text{CH}_3)_2)]_2$  molecule, **1a**. All atoms are represented by thermal vibrational ellipsoids drawn to encompass 50% of the electron density. Atoms of a given type labeled with a prime (') are related to those labeled without, by the crystallographic inversion center midway between the two thorium atoms. The crystallographically independent pentamethylcyclopentadienyl ligands are labeled A and B, respectively.

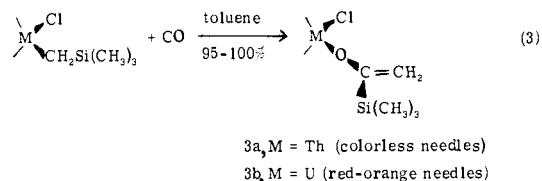
setting of  $P2_1/c\text{-}C_{2h}^5(14)$  with  $a = 11.819(2) \text{ \AA}$ ,  $b = 13.661(3) \text{ \AA}$ ,  $c = 15.658(2) \text{ \AA}$ ,  $\beta = 107.08(1)^\circ$ , and  $Z = 2$  (dimeric species). Three-dimensional diffraction data (a total of 8296 independent reflections having  $2\theta$  ( $\text{Mo K}\alpha$ )  $< 63.7^\circ$ ) were collected on a computer-controlled Syntex PI autodiffractometer using graphite-monochromated  $\text{Mo K}\alpha$  radiation and full ( $1^\circ$  wide)  $\omega$  scans. The structural parameters have been refined to convergence ( $R = 0.035$  for 2402 independent reflections having  $2\theta$  ( $\text{Mo K}\alpha$ )  $< 43^\circ$  and  $I > 3\sigma(I)$ ) in cycles of unit-weighted full-matrix least-squares refinement which used anisotropic thermal parameters for all nonhydrogen atoms.<sup>11</sup> Crystals of **1a** are composed of centrosymmetric dimers (Figure 1) in which each thorium(IV) ion adopts the familiar, pseudotetrahedral "bent sandwich"  $\text{M}(\eta^5\text{-C}_5\text{H}_5)_2\text{X}_2$  configuration.<sup>12</sup> The X groups are oxygen atoms of bridging 2-butene-2,3-diolate ligands, which constitute the organic portion of the ten-atom, two-thorium metallocycle. The structure of **1a** closely approximates  $C_{2h}$  symmetry with the two thorium atoms, and the center of gravity ( $C_{PA}$ ,  $C_{PB}$ ,  $C_{PA'}$ , or  $C_{PB'}$ ), as well as one carbon atom with its methyl substituent from each  $(\text{CH}_3)_5\text{C}_5$  ring, being coplanar to within  $0.04 \text{ \AA}$ . This least-squares mean plane intersects those of the (essentially) planar bridging ligands in dihedral angles of  $90.5^\circ$ .

Bond lengths and angles for selected chemically distinct bonds in **1a**, averaged according to approximate  $C_{2h}$  symmetry, are as follows: Th–C, 2.845 (13, 28, 66, 10),<sup>13</sup> Th–O, 2.154 (8, 2, 2, 2), C–O, 1.37 (2, 1, 1, 2),  $\text{C}_1\text{--C}_2$ , 1.33 (2),  $\text{C}_1\text{--C}_3$ , 1.51 (2, 0, 0, 2); (cyclopentadienyl ring) C–C, 1.42 (2, 3, 9, 10), ( $C_p$  ring to methyl) C–C, 1.52 (2, 2, 4, 10)  $\text{Å}$ ;  $C_{PA}\text{Th}C_{PB}$ ,  $129.5^\circ$ ,  $\text{O}_1\text{ThO}_2'$ ,  $99.8(3)$ ,  $\text{CpThO}$ ,  $106.0(-, 12, 15, 4)$ ,  $\text{ThO}_1\text{C}_1$ ,  $163.6(8, 11, 11, 2)$ ,<sup>13</sup>  $\text{O}_1\text{C}_1\text{C}_2$ ,  $122(1, 2, 2, 2)$ ,  $\text{O}_1\text{C}_1\text{C}_3$ ,  $115(1, 1, 1, 2)$ ,  $\text{C}_3\text{C}_1\text{C}_2$ ,  $125(1, 2, 2, 2)^\circ$ . The Th–Th' separation is  $5.407(1) \text{ \AA}$ . Atoms  $\text{O}_1$ ,  $\text{O}_2$ ,  $\text{C}_1$ , and  $\text{C}_2$  of the bridging ligands are coplanar to within  $0.01 \text{ \AA}$  while the methyl carbon atoms ( $\text{C}_3$  and  $\text{C}_4$ ) are displaced by  $0.09$  and  $0.11 \text{ \AA}$  on opposite sides of the four-atom mean plane. The eight nonmetallic atoms of the ten-atom metallocycle are coplanar to within  $0.01 \text{ \AA}$ ; Th and Th' are displaced by  $0.59 \text{ \AA}$  on opposite sides of this eight-atom mean plane to give a "chair" conformation for the metallocycle. Values of  $1.33(2)$  and  $1.37(2, 1, 1, 2) \text{ \AA}$  for the  $\text{C}_1\text{--C}_2$  and  $\text{C}_1\text{--O}_1$  bonds of **1a** are typical C=C and alcoholic C–O bond lengths, respectively.<sup>14</sup>

The nature of the carbonylation products can be modified to a significant degree by variation of the actinide substituents. Thus, for  $\text{M}[(\text{CH}_3)_5\text{C}_5]_2[\text{CH}_2\text{Si}(\text{CH}_3)_2]_2$  ( $\text{M} = \text{Th}, \text{U}$ ),<sup>15</sup> the bulky trimethylsilylmethyl groups lead to monomeric products (eq 2). These insertion products were characterized by the standard methods.<sup>16</sup> In contrast to the above CO coupling results, carbonylation of the monoalkyl  $\text{M}[(\text{CH}_3)_5\text{C}_5]_2(\text{Cl})\text{-}$

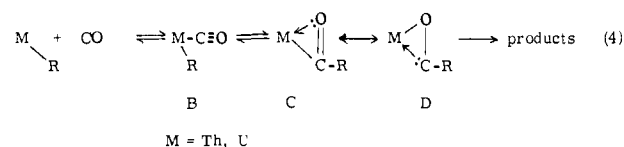


$\text{CH}_2\text{Si}(\text{CH}_3)_2$  complexes<sup>17</sup> leads to trimethylsilyl migration (eq 3). Products **3a** and **3b** were characterized by the standard



methods and by parallel studies of the products prepared from  $^{13}\text{CO}$ .<sup>18</sup>

A plausible scheme for the observed CO activation and product formation is presented in eq 4. Although there is



precedent for actinide carbonyl complexes (**B**) in cryogenic matrices ( $\text{U}(\text{CO})_n$ ,  $n = 1\text{--}6$ ),<sup>19</sup> the present results provide the first evidence for such species in organoactinide reaction chemistry. Dihapto acyl coordination (**C**, **D**) is known for titanium and zirconium biscyclopentadienyls<sup>5a,6a-c</sup> and appears to reflect, among other factors, the affinity which early transition metals and actinides in relatively high oxidation states exhibit for oxygen-containing ligands.<sup>20,21</sup> Such considerations also serve to explain the carbenoid character of the acyl chemistry. Alkoxy carbenes are generally nucleophilic in character and dimerization to form olefins is frequently competitive with insertion into C–H bonds or addition to olefins.<sup>22</sup> The 1,2 trimethylsilyl shift of eq 3 is additional support for the carbene-like reactivity of such insertion products.<sup>23</sup>

This work further underscores the parallels in organoactinide and early transition metal chemistry, with a major difference being the enhanced reactivity of the organoactinides. Migratory CO insertion occurs readily in the present coordinatively unsaturated actinide systems and the tendency of the resulting species to subsequently react as O-bonded carbenoids is a significant feature of the chemistry. The possibility that such reaction patterns may be relevant to mechanistic discussions of carbon monoxide reduction, especially with actinide oxide catalysts,<sup>9a,b,24</sup> is under scrutiny.

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- (10) The thorium compound, **1a**, displays infrared absorptions (Nujol mull) characteristic of an  $\eta^5\text{-}(\text{C}_6\text{H}_5)_5\text{C}_5$  ligand<sup>9</sup> at 1019 and 799  $\text{cm}^{-1}$ , as well as bands at 1655, 1252, and 1220  $\text{cm}^{-1}$ . <sup>1</sup>H NMR signals ( $\text{C}_6\text{D}_6$ ) are observed at  $\delta$  2.19 (30 H, s) and 2.03 (6 H, s). Anal. Calcd for  $\text{C}_{48}\text{H}_{72}\text{Th}_2\text{O}_4$ : C, 48.98; H, 6.17; mol wt, 1177 g/mol. Found: C, 49.84; H, 6.20; mol wt, 1210  $\pm$  10% g/mol (cryoscopic in benzene). The uranium derivative, **1b**, exhibits an identical infrared spectrum. Isotropically shifted singlets are observed in the <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ) at  $\delta$  0.22 (30 H) and 1.08 (6 H). Anal. Calcd for  $\text{C}_{48}\text{H}_{72}\text{U}_2\text{O}_4$ : C, 48.48; H, 6.02; mol wt, 1189 g/mol. Found: C, 48.56; H, 6.13; mol wt, 1167  $\pm$  10% g/mol (cryoscopic in benzene).
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- (14) "Tables of Interatomic Distances and Configurations in Molecules and Ions; *Chem. Soc., Spec. Publ.* **1965**, No. 18, M665.
- (15) The bis(pentamethylcyclopentadienyl)uranium and -thorium bis(trimethylsilylmethyl) derivatives were prepared with trimethylsilylmethylolithium using the procedure employed for the dimethyls.<sup>3</sup> The air-sensitive products were recrystallized from pentane. Anal. Calcd for  $\text{C}_{28}\text{H}_{52}\text{USi}_2$ : C, 49.25; H, 7.67; mol wt, 683 g/mol. Found: C, 48.96; H, 7.46; mol wt, 688  $\pm$  10% g/mol (cryoscopic in benzene). The infrared spectrum (Nujol mull) exhibits absorptions at 1252, 1241, 1018, 897, 820, 736, and 705  $\text{cm}^{-1}$ . The <sup>1</sup>H NMR spectrum exhibits isotropically shifted singlets at  $\delta$  5.04 (30 H), –89 (4 H), and –6.14 (18 H). Anal. Calcd for  $\text{C}_{28}\text{H}_{52}\text{ThSi}_2$ : C, 49.68; H, 7.74; mol wt, 677 g/mol. Found: C, 49.57; H, 7.71; mol wt, 645  $\pm$  10% g/mol (cryoscopic in benzene). The infrared spectrum is identical with that of the uranium derivative. The <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ) spectrum exhibits sharp singlets at  $\delta$  1.98 (30 H), –0.43 (4 H), and 0.31 (18 H).
- (16) For **2a**, the infrared spectrum (Nujol mull) displays bands at 1632, 1250, 1240, 1192, 1110, 1020, 956, 842, and 800  $\text{cm}^{-1}$ ; the <sup>1</sup>H NMR spectrum ( $\text{C}_6\text{D}_6$ ) exhibits singlets at  $\delta$  1.96 (30 H), 1.77 (4 H), and 0.31 (18 H). Anal. Calcd for  $\text{C}_{30}\text{H}_{52}\text{ThO}_2\text{Si}_2$ : C, 49.16; H, 7.15; mol wt, 733 g/mol. Found: C, 49.20; H, 7.19; mol wt, 781  $\pm$  10% g/mol (cryoscopic in benzene). The infrared spectrum of **2b** is identical with that of **2a**. The <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ) exhibits isotropically shifted singlets at  $\delta$  1.89 (30 H), –8.72 (4 H), and –2.58 (18 H). Anal. Calcd for  $\text{C}_{30}\text{H}_{52}\text{UO}_2\text{Si}_2$ : C, 48.75; H, 7.09; mol wt, 739. Found: C, 48.67; H, 7.14; mol wt, 769  $\pm$  10% g/mol (cryoscopic in benzene).
- (17) Prepared from the corresponding dialkyls and dichlorides using the procedure of ref 3. Anal. Calcd for  $\text{C}_{24}\text{H}_4\text{ThSiCl}$ : C, 46.11; H, 6.61; Cl, 5.67 mol wt, 625 g/mol. Found: C, 46.16; H, 6.56; Cl, 6.40; mol wt, 660  $\pm$  10% g/mol (cryoscopic in benzene). The infrared spectrum (Nujol mull) exhibits absorptions at 1249, 1238, 1018, 892, 865, 850, 820, and 720  $\text{cm}^{-1}$ . The <sup>1</sup>H NMR spectrum ( $\text{C}_6\text{D}_6$ ) displays sharp singlets at  $\delta$  2.04 (30 H), 0.24 (2 H), and 0.45 (9 H). Anal. Calcd for  $\text{C}_{24}\text{H}_4\text{USiCl}$ : C, 45.67; H, 6.55; Cl, 5.62; mol wt, 631 g/mol. Found: C, 45.59; H, 6.59; Cl, 5.70; mol wt, 634  $\pm$  10% g/mol (cryoscopic in benzene). The infrared spectrum is identical with that of the thorium derivative; the <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ) exhibits isotropically shifted singlets at  $\delta$  9.48 (30 H), –124 (2 H), and –11.52 (9 H).
- (18) The infrared spectrum of **3a** (Nujol mull) shows bands at 3075,  $\nu_{\text{C}=\text{C}}$  1576, 1253, 1243,  $\nu_{\text{CO}}$  1198, 1015, 1000, 842, 828, 752, and 685  $\text{cm}^{-1}$ ; the <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ) exhibits signals at  $\delta$  2.01 (30 H, s), 0.24 (9 H, s), 4.54 (1 H, s), and 4.88 (1 H, s). In the compound prepared from <sup>13</sup>CO,  $\nu_{\text{C}=\text{C}}$  and  $\nu_{\text{CO}}$  shift to 1536 and 1168  $\text{cm}^{-1}$ , respectively; the latter three <sup>1</sup>H NMR signals become doublets with  $J_{\text{H}^{13}\text{C}} = 2.0, 9.6,$  and 6.6 Hz, respectively. Anal. Calcd for  $\text{C}_{25}\text{H}_4\text{ThSiClO}$ : C, 45.97; H, 6.33; Cl, 5.43; mol wt, 653 g/mol. Found: C, 45.89; H, 6.26; Cl, 5.39; mol wt, 690  $\pm$  10% g/mol (cryoscopic in benzene). The infrared spectral data of **3b** are identical with those of **3a**. The <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ ) displays isotropically shifted signals at  $\delta$  5.51 (30 H, s), –1.67 (9 H, s), 7.46 (1 H, s), and –11.08 (1 H, s). In the compound prepared from <sup>13</sup>CO, the latter three signals become doublets with  $J_{\text{H}^{13}\text{C}} = 2.0, 9.6,$  and 6.6 Hz, respectively. Anal. Calcd for  $\text{C}_{25}\text{H}_4\text{USiClO}$ : C,
- 45.55; H, 6.27; Cl, 5.38; mol wt, 659 g/mol. Found: C, 45.37; H, 6.27; Cl, 5.75; mol wt, 623  $\pm$  10% g/mol (cryoscopic in benzene).
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## Novel Photochemical Addition Reactions of Iminium Salts. Electron Transfer Initiated Additions of Olefins to 2-Phenyl-1-pyrrolinium Perchlorate

Sir:

We recently described a novel photocyclization reaction involving the conversion of *N*-allyliminium salts to pyrrolidines.<sup>1</sup> In order to gain more information about the mechanistic details of this process and to probe its generality, we have initiated a more broadly targeted study of the photochemical behavior of iminium salt-olefin systems. We report here the results of our preliminary efforts using a simple iminium salt, 2-phenyl-1-pyrrolinium perchlorate (**1**), and a series of olefins of varying electron-donating ability.

Irradiations<sup>2</sup> of methanolic solutions of **1** (14 mM) containing isobutylene, cyclohexene, methyl  $\beta,\beta$ -dimethylacrylate, or 1,3-butadiene (1 M) gave after neutralization and chromatographic separation the pyrrolidine ethers and olefins shown in Chart I. Triplet-sensitized irradiations of **1** in the presence of isobutylene using benzophenone, acetone, or xanthone failed to promote formation of the ether **2**. Triplet energy transfer from  $\text{Ph}_2\text{CO}$  to **1** is occurring under these conditions since **1** quenches both photoreduction and oxetane-forming processes. Structural assignments<sup>4</sup> to the photoproducts were made using characteristic spectroscopic properties<sup>5</sup> and, in selected cases, by independent synthesis. Interestingly, pyrrolizidine **11**,<sup>4</sup> prepared by reduction ( $\text{LiAlH}_4$ ) of the thermodynamic epimer of **6**, was derived

