J. Am. Chem. Soc. **1984**, *106*, 3484–3491

primarily 1-pentene. Polymerization or extended oligomerization does not occur in any of these reactions because the product olefins are less reactive than their precursors toward the dirhenium center, presumably for steric reasons.

We are currently exploring the chemistry of various phosphine-substituted (μ-hydrido)(μ-alkenyl)dirhenium carbonyl compounds, to vary the steric and electronic characteristics of the catalyst and to address the problem of catalyst decomposition. We are also investigating other polynuclear metal systems with respect to similar catalytic activity.

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Registry No. I, 82621-42-9; I-d_4, 88035-65-8; IIa, 82638-69-5; IIb, 88082-36-4; IIIa, 82621-39-4; IIIb, 88082-37-5; IIIc, 82621-43-0; IV, 89958-85-0; V, 90026-98-5; *cis*-V, 89958-86-1; $Re_2(CO)_{10}$, 14285-68-8; C_2H_4, 74-85-1; C_2D_4, 683-73-8; (μ-H)(μ-*trans*-CH=CHPh)$Re_2(CO)_8$, 86244-50-0; ^{13}CO, 1641-69-6; PPh_3, 603-35-0; $HRe(CO)_4(PPh_3)$, 25838-69-1; Re, 7440-15-5; *trans*-4-methyl-2-pentene, 674-76-0; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; 1-pentene, 109-67-1; *cis*-2-butene, 118-03-6; *trans*-2-butene, 624-64-6; 2-hexene, 592-43-8; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8; methyl vinyl ether, 107-25-5; 1-hexene, 592-41-6; butene, 25167-67-3; styrene, 100-42-5; 1-butene, 106-98-9; propylene, 115-07-1.

Organoactinide Carbonylation and Carboxylation Chemistry. Structural, Electronic, Bond Energy, and Photochemical Effects on Migratory Insertion in the Tris(cyclopentadienyl)thorium Hydrocarbyl Series

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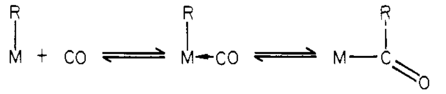
Abstract: This contribution reports a synthetic and kinetic study of CO migratory insertion for the series of thorium hydrocarbyls $Th(\eta^5\text{-}C_5H_5)_3R$, R = *i*-$C_3H_7$, *sec*-$C_4H_9$, neo-$C_5H_{11}$, *n*-$C_4H_9$, $CH_2Si(CH_3)_3$, CH_3, and $CH_2C_6H_5$. Under the conditions employed, the reaction was found to be first order in $Th(C_5H_5)_3R$ and first order in CO. In the above order, the relative rates of migratory insertion were found to be 42:18:1.3:1.0:0.02:0.01:<0.01. In the case of R = CH_3, *i*-C_3H_7, *n*-C_4H_9, neo-C_5H_{11}, and *sec*-C_4H_9, carbene-like (by spectroscopic and chemical properties) η^2-acyl insertion products, $Th(C_5H_5)_3(\eta^2\text{-COR})$, could be isolated and characterized. In the case of R = *i*-C_3H_7 and $CH_2Si(CH_3)_3$, enolate rearrangement products were isolated and characterized. The relative rates of CO insertion reflect both steric and electronic effects; there is a significant correlation with experimentally determined Th–R bond disruption enthalpies. For $Th(C_5H_5)_3CH_2Si(CH_3)_3$, it was also found that the rate of migratory CO insertion could be significantly accelerated by photolysis. However, secondary reactions of the insertion product are also observed. A comparative study of CO_2 migratory insertion to yield bidentate carboxylates revealed that carboxylation is significantly slower than carbonylation (a factor of 50 for $Th(C_5H_5)_3CH_3$; a factor of 10^5 for $Th(C_5H_5)_3(i\text{-}C_3H_7)$) and that for the above two compounds sensitivity of the rate to the nature of R is considerably altered vis-à-vis CO migratory insertion.

The migratory insertion of carbon monoxide into metal–carbon bonds to yield metal acyls (eq 1) is an extremely important transformation in stoichiometric and catalytic organotransition-metal chemistry.[1] Mechanistically, the process is now reasonably well understood (at least for middle and late transition metals), and factors such as the dependence of rate on the identity of R have been investigated in some detail.[1,2] Of late, it has become evident that organoactinides[3] display an unusual, distinctively nonclassical carbonylation chemistry, which differs from middle and late transition-metal complexes in a number of surprising ways.[4] In view of these dissimilarities, it would be of great interest to investigate migratory insertion reactivity patterns in a structurally well-defined and chemically well-characterized, homologous series of 5f hydrocarbyls.



$$\overset{R}{\underset{}{\overset{|}{M}}} + CO \rightleftharpoons \overset{R}{\overset{|}{M}}\leftarrow CO \rightleftharpoons M-\overset{R}{\overset{|}{C}}{\diagdown}O \qquad (1)$$

In the present contribution, we report such an investigation of migratory insertion reactivity for the tris(cyclopentadienyl)thorium hydrocarbyls Cp_3ThR (A) Cp = η^5-C_5H_5; a preliminary account was communicated several years ago.[5] This particular series has

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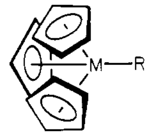

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been selected for a number of reasons. In terms of practicality, there is sufficient coordinative saturation to render rate measurements by conventional means feasible (i.e., the reaction rates are not extremely fast). In terms of information content, the Cp_3ThR series offers the widest range of R functionalities of any thermally stable class of actinide hydrocarbyls.[3,6] Furthermore, recently acquired thermochemical Th–R bond disruption enthalpy data[7] offer a unique opportunity to probe bond strength/insertion reactivity relationships. In addition, the well-established tendency of Cp_3ThR compounds to react in a less coordinatively saturated manner upon photoexcitation (e.g., photoinduced β-hydride elimination[8]) suggests a means, which will be explored herein, to photochemically accelerate migratory CO insertion. Lastly, organoactinides are also known to undergo facile migratory insertion of carbon dioxide[9] (eq 2).[10] In the present contribution, we relate

(2)

the first comparative study of relative CO vs. CO_2 insertion reactivities for any d- or f-element hydrocarbyl series.

Experimental Section

Materials and Methods. All operations involving organothorium compounds 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 Corp.). Argon (Matheson, prepurified), dinitrogen (Matheson, prepurified), and carbon monoxide (Matheson, CP) were purified by passage through sequential columns of MnO (supported on vermiculite)[11] and activated Davison 4-A molecular sieves. ^{13}C-Enriched carbon monoxide (90%, Stohler Isotopes) was used as received without further purification. Carbon dioxide (Matheson, Coleman Instrument) was purified by passage through sequential columns of MnO on vermiculite and activated Davison 3A molecular sieves. Diethyl ether, heptane, pentane, tetrahydrofuran, and toluene (previously distilled from Na/K/benzophenone) were condensed and stored in vacuo in bulbs on the vacuum line. Acetic acid (Mallinckrodt, Analytical Reagent) was dried over triacetyl borate[12] and distilled in vacuo immediately prior to use. Isobutyric acid (Aldrich) was dried over freshly activated and degassed Davison 4A molecular sieves. The reagent Cp_3ThCl was prepared by the literature procedure.[13a]

Analytical Methods. Proton and carbon NMR spectra were recorded on either a Perkin-Elmer R-20B (CW, 60 MHz), a JEOL FX-90Q (FT, 90 MHz), or a JEOL FX-270 (FT, 270 MHz) spectrometer. Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer using either Nujol or Fluorolube mulls sandwiched between KBr plates in an o-ring-sealed, air-tight holder.

Solution infrared spectral studies were carried out in previously described anaerobic NaCl solution cells.[13b] The solutions (in some cases previously saturated with CO on the vacuum line) were loaded into the cells by syringe. For low-temperature spectroscopy, the anaerobic sample cell was held in a windowed Styrofam container within the closed, nitrogen-purged sample compartment of the spectrometer. Temperature control was effected by passing a stream of gaseous nitrogen through a 77 K heat exchanger and then into the Styrofoam container. Temperatures were measured with a pentane thermometer placed adjacent to the cell. Ample time for equilibration was allowed at each new temperature.

Elemental analyses were performed by Dornis and Kolbe Mikroanalytisches Laboratorium, Mülheim, West Germany.

Synthesis of Cp_3ThR Complexes. The Cp_3ThR complexes (**1a**, R = CH_3; **1b**, R = i-C_3H_7; **1c**, R = n-C_4H_9; **1d**, R = *neo*-C_5H_{11}) were prepared and purified as previously described.[6,8b]

$Cp_3ThCH_2C_6H_5$ (1e). Following the procedure of Bruno et al. for the preparation of $Cp_3U(sec\text{-}C_4H_9)$,[8b] 1.00 g (2.20 mmol) of Cp_3ThCl and 0.40 g (2.4 mmol) of $LiCH_2C_6H_5{\cdot}THF$ were dissolved in 75 mL of toluene at −78 °C. The mixture was allowed to slowly warm to 10 °C over a period of 3 h and then filtered, and the solvent was removed in vacuo. The crude brown product was allowed to stand at room temperature for 24 h and then redissolved in 50 mL of toluene. The resulting solution was filtered and the volume concentrated to ca. 10 mL. Pentane (ca. 10 mL) was distilled onto the toluene solution, and this mixture was slowly cooled to −78 °C, yielding 0.70 g (62%) of a colorless, microcrystalline solid. ^1H NMR (C_6D_6): δ 7.30 (5 H, m), 5.91 (15 H, s), 2.50 (2 H, s). Anal. Calcd for $C_{22}H_{22}Th$: C, 50.97; H, 4.28. Found: C, 50.93; H, 4.37.

$Cp_3Th(sec\text{-}C_4H_9)$ (1f). Following the above procedure for the preparation of $Cp_3ThCH_2C_6H_5$, 2.25 g (4.6 mmol) of Cp_3ThCl was dissolved in 75 mL of toluene, and this mixture was cooled to −78 °C. To this solution was added 7.2 mL of commerical *sec*-butyllithium in cyclohexane (1.25 M, 9.0 mmol). The resulting solution was allowed to slowly warm to 10 °C over a period of 3 h and then worked up as above. Recrystallization from ca. 10 mL of toluene and 5 mL of pentane (−78 °C) yielded 1.22 g (52%) of colorless, microcrystalline solid. ^1H NMR (C_6D_6): δ 5.90 (15 H, s), 2.21 (1 H, m), 1.85 (3 H, d), 1.55 (1 H, m), 1.26 (3 H, m), 0.84 (1 H, m). Anal. Calcd for $C_{19}H_{24}Th$: C, 47.11; H, 4.96. Found: C, 47.04; H, 4.93.

$Cp_3ThCH_2Si(CH_3)_3$ (1g). Following a procedure similar to that of the *sec*-butyl analogue, 1.0 g (2.2 mmol) of Cp_3ThCl was dissolved in 60 mL of toluene and the mixture was cooled to −78 °C. To this solution 0.23 g (2.5 mmol) of $LiCH_2Si(CH_3)_3$ was added, and the resulting mixture was allowed to slowly warm to room temperature over a 4-h period. At that point, the reaction mixture was filtered and the filtrate volume reduced to ca. 10 mL. Heptane (ca. 5 mL) was condensed onto this toluene solution, and the mixture then slowly cooled to −78 °C, giving a colorless microcrystalline solid (yield 46%). ^1H NMR (C_6D_6): δ 5.95 (15 H, s), 0.38 (9 H, s), 0.16 (2 H, s). Anal. Calcd for $C_{19}H_{26}ThSi$: C, 44.36; H, 5.06. Found: C, 44.35; H, 5.04.

Carbonylation Chemistry. Isolation of products. Typical reactions were carried out in a foil-wrapped 50-mL flask with ca. 0.20 g of Cp_3ThR compound dissolved in 15 mL of toluene. Carbon monoxide (700–720 torr in an enclosed total volume of ca. 400 mL) was then introduced at room temperature. The uptake of carbon monoxide was monitored by a mercury-filled manometer. If no CO uptake was detected within 12 h at room temperature (as was the case with **1a**, **1e**, and **1g**), the reaction was warmed to 50 °C. After the Cp_3ThR compound had completely reacted, the carbon monoxide was removed in vacuo and the reaction mixture filtered. At this point, the solvent was evaporated and the resulting solid pumped on in vacuo for 2 h. The products were then purified and characterized as described below.

Cp_3ThCH_3 + CO. Carbonylation of compound **1a** yields product **2a**, a light orange solid in ca. 30% yield (by ^1H NMR) obtained from the filtrate of a toluene/pentane (1:1) 0 °C crystallization of the solid product. ^1H NMR (C_6D_6): δ 6.07 (15 H, s), 2.10 (3 H, s). IR (mull): 1490 (m) cm^{-1}. Compound **2a** was not stable under the conditions of the carbonylation process and could not be completely separated from all of the reaction side products.

$Cp_3Th(i\text{-}C_3H_7)$ + CO. Carbonylation of complex **1b** yields **2b**, a yellow solid in 80–95% isolated yield as the sole, initial reaction product. ^1H NMR (C_6D_6): δ 6.09 (15 H, s), 2.76 (1 H, m), 1.16 (6 H, d). IR (mull): 1475 (s), 1442 (s), 1360 (m), 1198 (w), 1127 (2), 1010 (s), 975 (m), 770 (vs) cm^{-1}. Anal. Calcd for $C_{19}H_{22}ThO$: C, 45.78; H, 4.46. Found: C, 45.77; H, 4.57. When the reaction is performed by using ^{13}C-enriched CO, **2b*** is obtained. The infrared spectrum of **2b*** is nearly identical with that of **2b**, except that the ν_{CO} transition in **2b** at 1476 cm^{-1} shifts to 1437 cm^{-1} in **2b***. ^{13}C NMR (C_6D_6): δ 352.8. Complex **2b** is

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not indefinitely stable at room temperature in solution. After 2 months, **2b** in a toluene solution under argon (in the dark) is converted to **3b**, a light tan solid in 50–60% (isolated) yield. ^1H NMR (C_6D_6): δ 6.55 (1 H, m), 6.15 (15 H, s), 1.84 (3 H, s), 1.71 (3 H, s). IR (mull): 1658 (m), 1440 (m), 1222 (w), 1192 (s), 1010 (m), 775 (vs), 668 (m), 445 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{22}ThO$: C, 45.78; H, 4.46. Found: C, 45.75; H, 4.55. Similarly, **2b*** is converted to **3b*** under identical conditions. The infrared spectrum of **3b*** differs from that of **3b** in that the absorbances at 1658 and 1191 cm^{-1} in **3b** are displaced to 1634 (m) and 1171 (s) cm^{-1}, respectively.

$Cp_3Th(n\text{-}C_4H_9)$ + CO. Compound **1c** reacts to form **2c**, a yellow solid, in 50% yield (via NMR) as the initial and primary product. ^1H NMR (C_6D_6): δ 6.09 (15 H, s), 2.65 (2 H, t), 1.74 (2 H, m), 1.33 (2 H, m), 0.92 (3 H, t). IR (mull): 1482 (m), 1440 (s), 1180 (w), 1006 (s), 767 (vs) cm^{-1}. When the reaction is carried out with ^{13}C-enriched carbon monoxide, compound **2c*** is produced. The IR spectral properties of **2c*** differ from those of **2c** only in that the ν_{CO} band at 1482 cm^{-1} in **2c** is displaced to a region under the ligand 1440 cm^{-1} transition, resulting in detectable broadening. ^{13}C NMR (C_6D_6): δ 353.6. As was the case with **2a**, **2c** could not be completely freed from reaction side products.

$Cp_3Th(neo\text{-}C_5H_{11})$ + CO. Carbonylation of compound **1d** yields **2d**, a yellow-orange solid in 75–85% (isolated) yield as the sole, initial reaction product. ^1H NMR (C_6D_6): δ 6.10 (15 H, s), 2.58 (2 H, s), 1.12 (9 H, s). IR (mull): 1492 (m), 1442 (m), 1363 (m), 1200 (w), 1011 (s), 774 (vs) cm^{-1}. When the carbonylation reaction is performed utilizing ^{13}C-enriched CO, compound **2d*** is obtained. The infrared spectrum of **2d*** is quite similar to that of **2d**, except the ν_{CO} mode at 1492 cm^{-1} disappears. ^{13}C NMR (C_6D_6): δ 356.7. Anal. Calcd for $C_{21}H_{26}ThO$: C, 47.90; H, 4.99. Found: C, 48.00; H, 5.03.

$Cp_3ThCH_2C_6H_5$ + CO. No reaction was observed at temperatures as high as 50 °C over a period of 3 days.

$Cp_3Th(sec\text{-}C_4H_9)$ + CO. Carbonylation of **1f** yields product **2f**, a yellow solid, in 75–90% isolated yield as the sole reaction product. ^1H NMR (C_6D_6): δ 6.10 (15 H, s), 2.41 (1 H, m), 1.92 (1 H, m) 1.44 (1 H, m), 1.10 (3 H, d), 0.92 (3 H, t). IR (mull): 1495 (m), 1440 (m), 1368 (m), 1182 (w), 1010 (s), 772 (vs) cm^{-1}. Anal. Calcd for $C_{20}H_{24}ThO$: C, 46.88; H, 4.69. Found: C, 47.00; H, 4.80.

$Cp_3ThCH_2Si(CH_3)_3$ + CO. Carbonylation of complex **1g** yields complex **3g**, a light tan solid, in 50–70% isolated yield as the sole reaction product. ^1H NMR (C_6D_6): δ 6.21 (15 H, s), 4.87 (1 H, s), 4.45 (1 H, s), 0.24 (9 H, s). IR (mull): 1567 (m), 1432 (m), 1355 (m), 1237 (m), 1200 (s), 1004 (m, sh), 992 (s), 837 (m, br), 770 (vs), 430 (m) cm^{-1}. Anal. Calcd for $C_{20}H_{26}ThOSi$: C, 44.36; H, 4.47. Found: C, 44.34; H, 4.63.

Cp_3ThR + CO Reaction Stoichiometry by Toepler Pump. The equivalents of carbon monoxide consumed in the carbonylation reaction per equivalent of Cp_3ThR complex were measured for **1b** and **1f**. In a typical experiment, a 25-mL foil-wrapped flask was charged with 20–100 mg of Cp_3ThR compound (weighed by difference). The flask was attached to a calibrated gas addition bulb, which was then attached to the high-vacuum line. Toluene (10 mL) was condensed into the flask, and the stopcock leading to the flask was closed. After residual solvent vapor was removed from the gas addition bulb, carbon monoxide (100–720 torr) was introduced. The addition bulb-to-vacuum line stopcock was then closed and the gas introduced into the flask containing the toluene solution of organometallic. Upon completion of the reaction (**1b**, 23 h; **1f**, 12 h), the flask was cooled to −78 °C. The gases were passed through a series of two dry ice/acetone traps and collected in a calibrated volume via Toepler pump. The pressure was measured and the amount of unreacted CO then determined. In the case of **1b**, 0.020 g of complex (0.042 mmol) was reacted at 24.0 °C with 72.2 torr of CO (bulb volume = 51.3 mL, 0.200 mmol), and the amount of gas collected was 147.8 torr in a 20.2-mL volume. Proton NMR analysis of product mixture showed only **2b** present after reaction. In the case of **1f**, 0.088 g of complex (0.18 mmol) was reacted at 21.6 °C with 704.5 torr of CO (bulb volume = 54.6 mL, 2.08 mmol), and the amount of gas collected was 251.0 torr in a 137.6-mL volume.

Cp_3ThR + CO Reaction Kinetics. The NMR kinetics vessel utilized to study the reaction of the Cp_3ThR complexes (**1a**, **1b**, **1c**, **1d**, **1f**, and **1g**) with carbon monoxide has been described elsewhere.[4g] The vessel consists of a 10-mm thin-walled NMR tube, attached to a 500-mL round-bottom flask, fitted with a Kontes valve to vacuum line adapter and a greaseless solvent-seal joint with cap. In a typical kinetics experiment, ca. 25 mg of the complex was transferred into the vessel in the glovebox, and a small stirring bar (capable of stirring horizontally in the NMR tube) was introduced. The vessel was then placed on the high-vacuum line and ca. 2.5 mL of deuterated benzene (predried over Na/K and degassed) was condensed into the NMR tube portion of the apparatus. After the complex had completely dissolved, the NMR tube portion of the reaction vessel (which contained the actinide solution) was placed in a 0 °C bath and the vessel was charged with the desired amount of carbon monoxide (45–720 torr). The vessel was removed from the vacuum line and the solution was then allowed to warm to room temperature. At this point, the small stir bar was lifted from the NMR tube by means of an external magnet and was placed in the holding chamber blown onto the flask portion of the reaction vessel. The NMR tube was then placed in the probe of the JEOL FX-90Q spectrometer, which had been pretuned for a nonspinning sample and the probe temperature preadjusted to the desired temperature. After the ^1H NMR spectrum was obtained, the vessel was quickly removed from the probe, the stir bar was reintroduced into the solution, and the NMR tube portion of the vessel was immersed in a water bath maintained at the desired temperature (±0.2 °C) with a Haake-FS regulating bath. The bath was wrapped in aluminum foil and the vessel draped in black cloth to exclude room light. The stirring rate was adjusted so that the reaction solution reached a vortex. Control experiments established that the kinetic results were not sensitive to stirring rate in this agitation regime. At appropriate time intervals, the kinetics vessel was removed from the water bath, the stir bar returned to its holding chamber, and the NMR tube placed in the spectrometer probe to collect further data.

All Cp_3ThR + CO reactions were monitored for a minimum of 3 half-lives. The kinetics were followed by measuring the disappearance of Cp_3ThR. Two methods were utilized to do this. First, for all five complexes investigated, the decrease in the area of the Cp resonance (A_t) standardized to the area of the residual C_6D_5H signal in the reaction solvent was followed over time. A slight overlap between the Cp resonances of the starting material and the Cp resonances of the product occurs, so these two resonances were deconvoluted via computer (Hewlett-Packard Series 1000 and interfaced graphics terminal) simulation of the spectrum, using an assumed Lorenztian line shape for the Cp peaks. An alternative method was also used in the study of the carbonylation of **1b**. In this procedure, the decrease in area of the methyl resonances on the isopropyl group (standardized as in the first method), A_t', was followed over time. There was good agreement between the two methods. In all cases, plots of ln A_t (or ln A_t') vs. time were fit by standard linear regression techniques to obtain the rate constants, k_{obsd}, quoted herein. Standard deviations were derived from the fitting procedure.

Photochemical Reactions of Cp_3ThR Compounds with CO. $Cp_3ThCH_2Si(CH_3)_3$ + CO. A solution of 25 mg (0.050 mmol) of **1g** in 2.5-mL of benzene-d_6 was placed in the kinetics reaction vessel under 670 torr of CO. The NMR tube portion of the apparatus, containing the solution of **1g**, was immersed in a room-temperature water bath ca. 10 cm from a Hanovia 679A36 450-W medium-pressure mercury lamp.[14] With vigorous stirring, the reaction solution was irradiated (using a Pyrex filter) until all of the starting material had reacted (as determined by ^1H NMR). At that point, the reaction solution was removed from the vessel by syringe, filtered, and characterized by ^1H NMR and infrared spectroscopy. The major component (ca. 20% by ^1H NMR) was determined to be **3g**, the sole product of the thermal carbonylation (vide supra). A second set of ^1H NMR resonances at δ 6.07, 2.73, and 0.25 (ca. 15% yield) and an infrared absorbance at 1493 (m) cm^{-1} could be assigned to a type-**2** compound (**2g**). This could not be completely separated from the reaction mixture by fractional crystallization.[15]

Photolysis of $Cp_3ThCH_2Si(CH_3)_3$. By a procedure identical with that for the photolysis of **1g** in the presence of CO, the experiment was repeated under argon, in place of CO, and irradiation was performed for 52 h. A green precipitate, identified by infrared spectroscopy as Cp_3Th,[8a] was produced, and the ^1H NMR spectrum of the reaction solution indicated that ca. 25% decomposition of **1g** had occurred with the concurrent production of tetramethylsilane.

Photolysis of 3g. By use of a method identical with that for the photolysis of **1g**, a solution of **3g** (30 mg) in benzene-d_6 (2.6 mL) under a carbon monoxide atmosphere was photolyzed for 34 h, approximately 3 times longer than the time required for the complete photochemical reaction of **1g** with CO. The ^1H NMR spectrum of the solution revealed that <10% of **3g** had reacted.

Photolysis of 2d. By use of a method similar to that above, a solution of **2d** (20 mg) in benzene-d_6 (0.4 mL) was loaded into a 5-mm thin-walled NMR tube, which was then sealed under argon. The tube was submerged in a room-temperature water bath and photolysis was performed as above, with irradiation for 19 h. The ^1H NMR spectrum of the solution at this point is extremely complex, and **2d** is ca. 70% consumed (by ^1H NMR analysis).[16]

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(14) Major output (W) at 254 (5.8), 265 (4.0), 297 (4.3), 303 (7.2), 313 (13.2), 366 (25.6), and 405 nm (11.0). Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 112.

(15) Other ^1H NMR resonances of the product mixture (C_6D_6): δ 6.60, 6.43, 6.37, 6.33, 6.27, 6.24, 6.11, 0.46, 0.28, 0.00.

Cp_3ThR + CO. Variable-Temperature Infrared Studies. In a typical experiment, a freshly prepared CO-saturated toluene-d_8 solution of **1a** (ca. 2.5 × 10^{-2} M) was syringed into the septum-capped cavity cell (1-mm pathlength). The cell was placed in the Styrofoam container and the temperature of the solution controlled by varying the flow rate of gaseous nitrogen into the container. Control experiments, with a nitrogen-saturated toluene-d_8 solution of **1a** under identical conditions, were also performed.

Reactions of 1a and 1b with CO_2. In these studies, a Griffin-Worden pressure vessel, fitted with a pressure gauge, was employed.[17] The vessel was loaded with 0.20 g of complex and attached to the high-vacuum line, and toluene (ca. 15 mL) was condensed in. Then the vesseel was charged with CO_2 (ca. 5-8 atm), wrapped in aluminum foil, placed in a 55 °C oil bath for 4 days, and stirred vigorously. At this point, the solution was allowed to cool to room temperature, and the CO_2 removed. The product solution was then transferred to a filtration apparatus, and the vessel was rinsed with 20 mL of fresh toluene, the washings being subsequently combined with the reaction solution. This solution was then filtered, and the filtrate evaporated to dryness. The reaction products were analyzed by ^1H NMR and infrared spectroscopy: **1a** produces **4a** in an isolated yield of 60-80% and **1b** produces **4b** in a yield of 12-20% (determined by ^1H NMR analysis).[18]

Also, competition experiments between **1a** and **1b** for CO_2 were performed by repeating the above procedure, except with equimolar amounts of both **1a** and **1b** present. After 8 days of reaction, the toluene-soluble fraction of the reaction mixture was analyzed by ^1H NMR to determine the relative amounts of **1a** and **1b** remaining. This was accomplished by comparing the areas of the methyl resonance of **1a** to the methyl resonances (from the isopropyl group) of **1b**.

Synthesis of $Cp_3ThO_2CCH_3$ (4a). To 225 mg (0.49 mmol) of Cp_3ThCH_3 dissolved in 40 mL of diethyl ether at -78 °C was added dropwise with vigorous stirring over a 4-h period 25 μL (0.44 mmol) of anhydrous acetic acid in 25 mL of diethyl ether. After being stirred for 12 more h at -78 °C, the reaction mixture was allowed to warm to -10 °C over a 3-h period. At this point, the solvent was removed in vacuo, yielding a white solid which was washed twice with 10 mL of toluene and dried under vacuum (yield 80-90%). IR (mull): 1520 (vs), 1445 (s), 1418 (s), 1010 (s), 782 (vs), 628 (m), 480 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{18}ThO_2$: C, 41.98; H, 3.68. Found (from acetic acid route) C, 42.26; H, 3.26; (from CO_2 insertion route) C, 42.19; H, 3.22. Compound **4a** is insoluble in hydrocarbon and ethereal solvents and decomposes in dimethyl sulfoxide and chlorinated hydrocarbons.

Synthesis of $Cp_3ThO_2C(\textit{i}\text{-}C_3H_7)$ (4b). By a method identical with that of the preparation of **4a**, isobutyric acid (35 μL, 0.38 mmol) was reacted with Cp_3ThMe (200 mg, 0.43 mmol), producing a toluene-soluble, white solid (yield 50-60%). ^1H NMR (C_6D_6): δ 6.09 (15 H, s), 2.48 (1 H, m), 1.15 (6, H, d). 1R (mull): 1515 (vs), 1445 (s), 1425 (s), 1285 (m), 1015 (m), 780 (s), 645 (m) cm^{-1}. Anal. Calcd for $C_{19}H_{22}ThO_2$: C, 44.36; H, 4.28. Found: C, 44.43; H, 4.20.

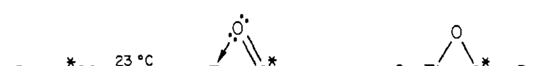
Results

Synthesis of Tris(cyclopentadienyl)thorium Hydrocarbyls. The thorium alkyl compounds for this study were prepared via the route of eq 3,

$$Cp_3ThCl + RLi \rightarrow Cp_3ThR + LiCl \qquad (3)$$

1a, R = CH_3
1b, R = $\textit{i}\text{-}C_3H_7$
1c, R = $\textit{n}\text{-}C_4H_9$
1d, R = neo-C_5H_{11}
1e, R = $CH_2C_6H_5$
1f, R = $\textit{sec}\text{-}C_4H_9$
1g, R = $CH_2Si(CH_3)_3$

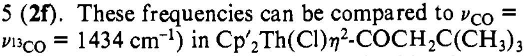
$Th(C_5H_5)_3R$ Carbonylation Chemistry. The reactivity of the above Cp_3ThR compounds with respect to migratory CO insertion is a rather sensitive function of R group. For R = $\textit{i}\text{-}C_3H_7$, $\textit{sec}\text{-}C_4H_9$, neo-$C_5H_{11}$, and $\textit{n}\text{-}C_4H_9$, migratory insertion is complete at room temperature, 1 atm of CO pressure, within 1.5, 5, 50, and 70 h, respectively (eq 4) (see the following section for detailed kinetic data). Products **2b**, **2c**, **2d**, and **2f** were characterized by standard techniques. Infrared spectra reveal characteristic low-energy C–O stretching frequencies typical of actinide dihaptoacyls,[3,4] i.e., ν_{CO} = 1476 cm^{-1} ($\nu_{^{13}CO}$ = 1437 cm^{-1}) (**2b**), ν_{CO} = 1482 ($\nu_{^{13}CO} \approx 1440$) (**2c**), ν_{CO} = 1492 ($\nu_{^{13}CO} < 1492$) (**2d**), ν_{CO} = 1495 (**2f**). These frequencies can be compared to ν_{CO} = 1469 cm^{-1} ($\nu_{^{13}CO}$ = 1434 cm^{-1}) in $Cp'_2Th(Cl)\eta^2\text{-}COCH_2C(CH_3)_3$ (Cp′ = $\eta^5\text{-}(CH_3)_5C_5$), which has been characterized by single-crystal X-ray diffraction.[4a,c] The ^{13}C NMR spectra of **2b**, **2c**, andd **2d** also reveal the characteristic low-field resonance position of inserted ^{13}CO in a η^2-acyl, i.e., δ 352.8, 353.6, and 356.7, respectively. These compare favorably to that in $Cp'_2Th(Cl)\eta^2\text{-}^{13}COCH_2C(CH_3)_3$, δ 360.2.[4a,c] Toepler pump experiments with **1b** and **1f** also established that, to within experimental error, the stoichiometry of carbonylation is that depicted in eq 4.[19]



(4)

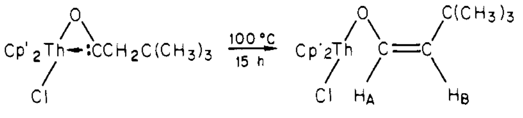
2b, R = $\textit{i}\text{-}C_3H_7$; **2b***, *C = ^{13}C
2c, R = $\textit{n}\text{-}C_4H_9$; **2c***, *C = ^{13}C
2d, R = neo-C_5H_{11}; **2d***, *C = ^{13}C
2f, R = $\textit{sec}\text{-}C_4H_9$

Dihaptoacyl **2b** is not indefinitely stable at room temperature. Rather, in solution or in the solid state, it slowly (over the course of weeks) undergoes isomerization to enolate **3b** (eq 5). The structure of **3b** is assigned on the basis of elemental analysis, the olefinic resonance at δ 6.54 and nonequivalent methyl signals in the ^1H NMR, and the $\nu_{C=C}$ stretch in the infrared at 1658 cm^{-1}, which is displaced to 1634 cm^{-1} in **3b***. This rearrangement process is consistent with the carbene-like character of actinide η^2-acyls.[3,4,20] The related complex $Cp'_2Th(Cl)\eta^2\text{-}COCH_2C(CH_3)_3$ undergoes a similar, unimolecular rearrangement process to produce enolate **4** (eq 6).[4a,c,i] Moreover, the spectroscopic characteristics of **4** (δ_{H_A} = 6.30, $\nu_{C=C}$ = 1628 cm^{-1}, $\nu_{^{13}C=C}$ = 1608 cm^{-1})[4a,c,21] are closely analogous to those of **3b**. Small olefinic ^1H NMR spectral features apparent after 2-3 half-lives in the carbonylation of **1c** are suggestive of minor rearrangement of **2c** under the reaction conditions to yield an enolate such as **5** or **6**.



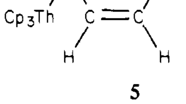
(5)

3b
3b*, *C = ^{13}C

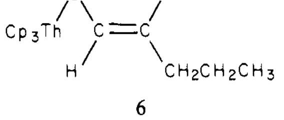


(6)

4



5



6

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(16) Resonances in the ^1H NMR spectrum other than those of **2d** (δ 6.07 (47 H)) are (with approximate integration) δ 6.66 (3 H), 6.60 (11 H), 6.56 (5 H), 6.49 (13 H), 6.42 (12 H), 6.39 (8 H), 6.35 (7 H), 6.33 (30 H), 6.27 (14 H), 6.20 (6 H), 6.17 (20 H), 6.16 (20 H) 6.15 (13 H), 5.04 (1 H), 2.68 (4 H), 2.36 (11 H), 1.41 (11 H), 1.33 (9 H), 1.20 (18 H), 1.18 (19 H), 1.09 (9 H), 0.95 (7 H), 0.93 (15 H), 0.90 (18 H), 0.89 (8 H), 0.84 (57 H), 0.28 (3 H).

(17) We observed no reaction of the type-**1** complexes with carbon dioxide at room temperature and pressures of 1 atm over a 1-month period.

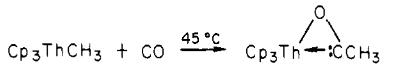
(18) The only species present in the product mixture are **1a**, **1b** and **4a**,**4b**, respectively.

(19) 0.93 (9), and 1.17 (12) equiv of CO for **1b** and **1f**, respectively.

(20) (a) Jones, W. M. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 97-119. (b) Moss, R. A.; Jones, M., Jr. In "Reactive Intermediates"; Jones, M., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1981; Vol. 2, pp 96-100. (c) Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Hones, M., Jr.; Levin, R. H.; Sohn, M. B.; In "Carbenes"; Jones, J., Jr., Moss, R. A., Eds.; Wiley-Interscience: New York, 1973; Vol. I, p 128. (d) Moss, R. A. In ref 20c, p 280. (e) Wentrup, C. *Top. Curr. Chem.* **1976**, *62*, 173.

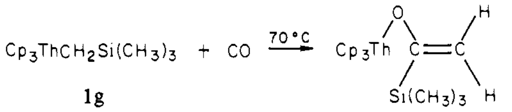
(21) (a) Fagan, P. J. Ph.D. Thesis, Northwestern University, 1981. (b) Fagan, P. J.; Maatta, E. A.; Manriquez, J. M.; Moloy, K. G.; Day, V. W.; Marks, T. J., manuscript in preparation.

In contrast to the isopropyl, *n*-butyl, neopentyl, and *sec*-butyl complexes, the carbonylation of **1a** and **1g** requires heating to achieve conveniently measurable rates at 1 atm of CO pressure. At 45 °C, **1a** initially yields **2a**, which is formulated as an η^2-acyl (eq 7) on the basis of infrared (ν_{CO} = 1482 cm^{-1}) and ^{1}H NMR data (δ 6.07 (15 H), 2.10 (3 H)). However, additional olefinic resonances are detectable in the ^{1}H NMR after ca. 1 half-life, and it is possible that **2a** undergoes hydrogen atom rearrangement analogous to **2b** (eq 5). It did not prove possible to isolate the rearrangement product in a pure state by fractional crystallization. However, a transition observed in the infrared of the crude product at 1670 cm^{-1} is consistent with an enolate formulation (vide supra). In the absence of light, there is no detectable reaction between **1g** and CO at room temperature. However, at 70 °C carbonylation is complete within 4 days to yield product **3g** (eq 8), which is formulated as an enolate on the basis of infrared spectroscopy ($\nu_{C=C}$ = 1567 cm^{-1}) and ^{1}H NMR (olefinic resonances at δ 4.45 and 4.87 $J < 1$ Hz). This type of product has been identified in closely analogous bis(pentamethylcyclopentadienyl) chemistry and has been connected with the facile rearrangement of an intermediate acyl (eq 9). Enolate **7** exhibits $\nu_{C=C}$ = 1576 cm^{-1} ($\nu_{^{13}C=C}$ = 1538 cm^{-1}) and ^{1}H NMR olefinic resonances of the proper intensities at δ 4.54 and 4.88 (singlets). The greater migratory aptitude of a third-row element such as silicon over that of hydrogen is well documented in carbene chemistry.[20a,c,22] In the case of eq 8, compounds **1g** and **3g** are the only species observed by ^{1}H NMR during the course of the reaction at 70 °C. From these results and those in eq 9, it is inferred that the rate-limiting step in eq 8 is CO activation and that subsequent rearrangement of the resulting acyl **2g** to **3g** is comparatively rapid under these conditions.



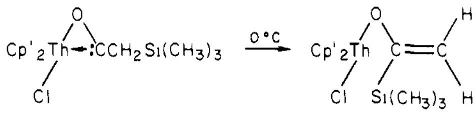
$$\mathrm{Cp_3ThCH_3 + CO \xrightarrow{45\,°C} Cp_3Th\overset{O}{\leftarrow:}CCH_3} \qquad (7)$$

1a 2a



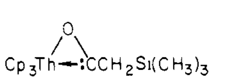
$$\mathrm{Cp_3ThCH_2Si(CH_3)_3 + CO \xrightarrow{70\,°C} Cp_3Th{-}O{-}C(Si(CH_3)_3){=}CH_2} \qquad (8)$$

1g 3g



$$\mathrm{Cp'_2Th(Cl)\overset{O}{\leftarrow:}CCH_2Si(CH_3)_3 \xrightarrow{0\,°C} Cp'_2Th(Cl){-}O{-}C(Si(CH_3)_3){=}CH_2} \qquad (9)$$

7



$$\mathrm{Cp_3Th\overset{O}{\leftarrow:}CCH_2Si(CH_3)_3}$$

2g

The benzyl compound **1e** is the least reactive of the thorium hydrocarbyls investigated. At 50 °C, 1 atm of CO, negligible carbonylation is observed after 3 days. At higher temperatures, the ^{1}H NMR of the reaction mixture evidences a great multiplicity of resonances, suggesting that insertion is accompanied by a number of other chemical transformations.

$Th(C_5H_5)_3R$ Carbonylation Kinetics. Once the nature of the Cp_3ThR carbonylation chemistry had been established, a detailed examination of reaction velocities was carried out by ^{1}H NMR. The rate of disappearance of Cp_3ThR resonances was monitored at various CO pressures under conditions which were pseudo first order in CO. In all cases, plots of ln A_t vs. time were linear over at least 3 half-lives. Some representative data for $Cp_3ThCH_2C(CH_3)_3$ are shown in Figure 1. Fitting of these plots by standard linear-regression techniques yields observed reaction rate constants, k_{obsd}, which are compiled in Table I. It was also found that the magnitude of k_{obsd} was linearly dependent upon the CO pressure (Figure 2). Assuming that Henry's law is obeyed, these observations are consistent with the rate law shown in eq 10 where k_{obsd} = k[CO]. Table I also shows derived k values. From these data, it can be seen that the variation of migratory CO insertion with R functionality follows the ordering isopropyl > *sec*-butyl ≫ neopentyl > *n*-butyl ≫ $CH_2Si(CH_3)_3$ > methyl > benzyl. The

$$\text{rate} = k_{obsd}[Cp_3ThR] = k[Cp_3ThR][CO] \qquad (10)$$

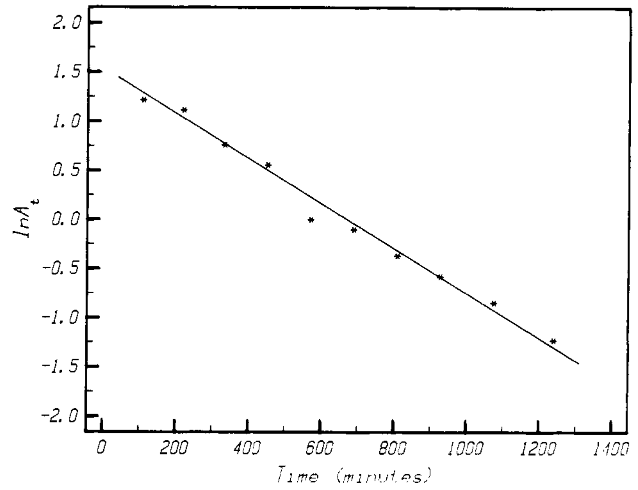


Figure 1. Kinetic plot for carbonylation (disappearance) of $Th(C_5H_5)_3CH_2C(CH_3)_3$ at 23 °C and 680 torr CO.

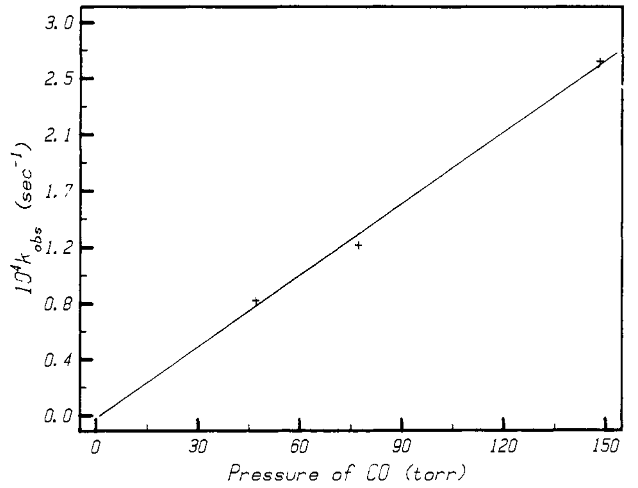


Figure 2. Dependence of the observed rate constant for the carbonylation of $Th(C_5H_5)_3(i\text{-}C_3H_7)$ on CO pressure.

Table I. Kinetic Data for Cp_3ThR Migratory CO Insertion[a]

compd	T, °C	P_{CO}, torr	10^5k_{obsd},[b] s^{-1}	10^5k, s^{-1} atm^{-1}
$Cp_3Th(i\text{-}C_3H_7)$	23	47	8.8 (1.0)[c]	130 (10)
		77	11 (2)	
		77	13 (2)[c]	
		82	14 (2)[d]	
		148	26 (3)[c]	
$Cp_3Th(sec\text{-}C_4H_9)$	23	44	3.2 (9)	55 (15)
$Cp_3Th(neo\text{-}C_5H_{11})$	23	680	3.5 (5)	3.9 (6)
$Cp_3Th(n\text{-}C_4H_9)$	23	690	2.6 (3)	2.9 (3)
$Cp_3ThCH_2Si(CH_3)_3$	45	690	0.23 (4)	0.25 (4)
Cp_3ThCH_3	45	700	0.12 (2)	0.13 (2)

[a] All rates are the average of at least two separate trials. [b] Error limits are 95% confidence interval. [c] Obtained by using A_t' in place of A_t. [d] Using 70% of normal spinning rate during the reaction.

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(22) (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; Chapter 12. (b) Robson, J. H.; Shechter, H. *J. Am. Chem. Soc.* **1967**, *89*, 7112.

dispersion in these rates with alkyl group is significant. For example, there is a 10^3-fold decrease in rate on proceeding from R = isopropyl to R = methyl.

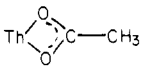
Photoassisted Migratory CO Insertion. Migratory insertion of CO was also found to occur under conditions of photochemical excitation. Experiments with $Cp_3ThCH_2Si(CH_3)_3$, which is not susceptible to photoinduced β-hydride elimination,[8] revealed that the photochemical insertion is not as clean as the thermal reaction, but that insertion/rearrangement product **3g** is initially formed more rapidly (20% yield in 11 h for the photochemical reaction vs. no detectable reaction (<5%) for the thermal reaction in the same time period). Also present in the ^1H NMR spectrum of the photochemical reaction mixture are singlets (δ 6.07 (15 H), 2.73 (2 H), 0.25 (10 H)) reasonably assignable to acyl complex **2g**. The infrared spectrum of the crude product exhibits a transition at 1493 cm^{-1}, also in accord with this assignment (ν_{CO}).

In several control experiments, it was found that photolysis of $Cp_3ThCH_2Si(CH_3)_3$ solutions under argon produced only traces (ca. 6%) of $ThCp_3$ and $Si(CH_3)_4$ under conditions where photoassisted CO insertion was complete. It was also found that a solution of enolate **3g** was photochemically inert under an atmosphere of CO. However, photolysis of acyl-**2d** under an argon atmosphere resulted in 70% decomposition after 19 h. The ^1H NMR spectrum of the reaction solution is extremely complex, indicating a multitude of products. From these results, we conclude that photoassisted migratory insertion indeed occurs and that the multiple products are likely due to secondary photochemistry of the initial acyl insertion product.

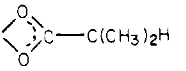
$Th(C_5H_5)_3R$ Carboxylation Chemistry. The thorium alkyls **1a** and **1b** were also found to react with carbon dioxide to yield carboxylate insertion products (eq 11). The CO_2 migratory

$$Cp_3ThR + CO_2 \xrightarrow[\text{4 days}]{\text{5–8 atm, 55 °C}} \begin{array}{l} Cp_3ThO_2CR \\ \textbf{4a},\ R = CH_3 \\ \textbf{4b},\ R = i\text{-}C_3H_7 \end{array} \qquad (11)$$

insertion process is found to be significantly slower than that for CO. In addition, the sensitivity of insertion rate to R is considerably different than for CO. Using published solubility data for CO_2[23] and making the reasonable assumption that eq 11 follows the same type of rate law as eq 4, we estimate that for Cp_3ThCH_3, $k(CO) \approx 50k(CO_2)$, while for $Cp_3Th(i\text{-}C_3H_7)$, $k(CO) \approx 10^5k(CO_2)$. Thus for carbonylation, $Cp_3Th(i\text{-}C_3H_7)$ is 4200 times more reactive than Cp_3ThCH_3, and conversely for carboxylation, $Cp_3Th(i\text{-}C_3H_7)$ is approximately one-quarter as reactive as Cp_3ThCH_3. The carboxylation ligation in **4a** and **4b** has been



4a

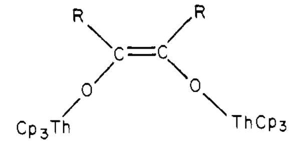


4b

tentatively assigned by using standard vibrational spectroscopic criteria.[24] From these correlations based upon the energy dispersion of the intense carboxylate C–O stretching transitions, **4a** and **4b** both appear to have symmetrical coordination, i.e., $\Delta(``\nu_{C=O}" - ``\nu_{C-O}")^{24} \approx 100$ cm^{-1}.

Discussion

As found in the bis(pentamethylcyclopentadienyl) actinide hydrocarbyl series,[3,4] the products of Cp_3ThR migratory insertion are η^2-acyls (**2**). As judged by ν_{CO} and ^{13}C NMR data, the acyl-to-metal bonding is rather similar to that in the former series. In that case ($R = CH_3$), migratory insertion to produce a η^2-acyl is estimated to be exothermic by ca. 15 kcal/mol.[7a] The validity of a carbene-like bonding description in the present dihaptoacyls (eq 4) is supported by the hydrogen atom and $Si(CH_3)_3$ migration patterns observed. Interestingly, however, and possibly as a consequence of greater steric demands, the formation of enediolates (**8**)[3,4] was not observed upon Cp_3ThR carbonylation.



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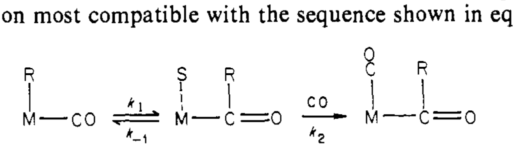
The majority of the transition-metal hydrocarbyl systems investigated to date exhibit a kinetic rate law for CO migratory insertion most compatible with the sequence shown in eq 12,[1,2]



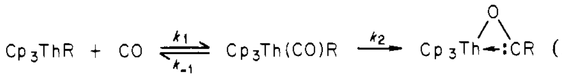
$$\overset{R}{\overset{|}{M}}—CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{S}{\overset{\vdots}{M}}—\overset{R}{\overset{|}{C}}=O \xrightarrow[k_2]{CO} \overset{\overset{O}{C}}{\overset{|}{M}}—\overset{R}{\overset{|}{C}}=O \qquad (12)$$

in which there is evidence in certain cases, for solvent (S) assistance or an η^2-acyl. Where investigated, there is retention of stereochemical configuration at the migrating α-carbon atom.[1,26,27] Application of the steady-state approximation to eq 12 yields the expression shown in eq 13, where rates can become independent

$$\text{rate} = \frac{k_1k_2[M(R)CO][CO]}{k_{-1} + k_2[CO]} \qquad (13)$$

of [CO] (or attacking nucleophile L) at high $P_{CO}([L])$. Although it has not always proven possible to obtain k_1 values accurately, the general pattern which has emerged for the d-element systems is that migratory insertion is accelerated when R is electron releasing and/or sterically demanding—there is not universal agreement on the relative importance of electronic and steric effects, nor has the influence of metal–ligand bond energy been addressed. For $CpFe(CO)_2R$ systems in Me_2SO,[2k] the insertion rate (k_1) as a function of R is $CH[Si(CH_3)_3]_2 \gg$ neopentyl > *sec*-butyl > isopropyl > $CH_2Si(CH_3)_3$ > *n*-butyl > CH_3; $k_1(i\text{-}C_3H_7) \approx 200\ k_1(CH_3)$; k_1 (neopentyl) $\approx 600\ k_1(CH_3)$. Benzylic transition-metal complexes are generally of low reactivity.[1,2]

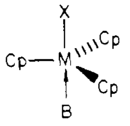
The present organoactinide systems present a somewhat different mechanistic situation than above in that the reactant is not a carbonyl complex. Equation 14 presents a reasonable scenario



(14)

9

for migratory insertion. Importantly, the kinetic data do not, a priori, differentiate between the case where k_1 is rate limiting and where k_2 is rate limiting. For either CO coordination being a rapid preequilibrium or the slow step, velocity will be proportional to $[Cp_3ThR][CO]$. Species **9** is a Th(IV) (f^0) carbonyl, for which there is no precedent.[3] However, stoichiometrically analogous, pseudo-trigonal-bipyramidal organoactinides of the type $M(\eta^5\text{-}C_5H_5)_3X\cdot B$ (**10**)[28] and $M(\eta^5\text{-}C_5H_5)_3X_2^-$ (**11**)[29] are well documented



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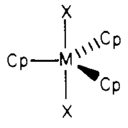

11

(e.g., $UCp_3(NCS)\cdot NCCH_3$,[28] $UCp_3(NCS)_2^{-\,29b}$). Furthermore,

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(23) Gjaldbaek, J. C.; Andersen, E. K. *Acta Chem. Scand.* **1954**, *8*, 1398.

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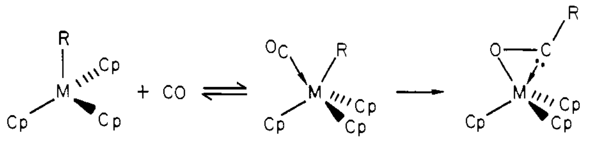
Table II. Alkyl Group Parameters Relevant to Cp_3ThR Migratory Insertion

	i-C_3H_7	s-C_4H_9	neo-C_5H_{11}	n-C_4H_9	$CH_2Si(CH_3)_3$	CH_3	$CH_2C_6H_5$
Taft σ^* [a]	−0.19	−0.21	−0.165	−0.13	−0.26	0	+0.215
Taft E_s [b]	−1.71	−2.34	−2.98	−1.63	−2.87	−1.24	−1.61
Hancock E_s^c [b]	−2.32		−3.29	−1.94		−1.24	
Charton ν [c]	0.76	1.02	1.34	0.68		0.52	
θ, [d] deg	106	106	113	95	114	84	97
D(Th–R) [e]	77.1 (2.7)		77.9 (3.0)		86.1 (3.6)	82.7 (1.1)	77.8 (2.1)
relative rate of Cp_3ThR carbonylation	42	18	1.3	1	0.02	0.01	<0.01

[e] Gas-phase Th–R bond disruption enthalpy in kcal/mol. All values are for the Cp_3ThR series (ref 7b). Numbers in parentheses represent two standard deviations. [b] Reference 43. [c] Reference 44. [d] Tolman cone angle. Calculated by the procedure described in ref 45. [e] Gas-phase Th–R bond disruption enthalpy in kcal/mol. All values are for the Cp_3ThR series (ref 7b). Numbers in parentheses represent two standard deviations.

one d^0 (Zr(IV)) carbonyl has been observed in a low-temperature solution infrared study[30] (having an admittedly adventitious CO coordination environment), and trivalent actinide carbonyls have been identified in cryogenic matrices.[31] To better define the stability of species **9**, low-temperature infrared spectroscopic studies (see Experimental Section for details) were undertaken on CO and ^{13}CO-saturated toluene-d_8 solutions of Cp_3ThCH_3. No evidence for a carbonyl was evident in the 1900–2400-cm^{-1} C–O stretching region down to −65 °C, and using published data on ν_{CO} extinction coefficients,[32] we estimate that $K = k_1/k_{-1} <$ 10 M^{-1} at −65 °C. Efforts to observe analogous adducts with isocyanides were thwarted by what appeared to be rapid migratory insertion.[33] Needless to say, a pseudorotation-like rearrangement of the coordination sphere would be required to effect migratory insertion in a structure such as **10**. Alternatively, the CO molecule might initially bind adjacent to the hydrocarbyl group (**12**, eq 15) in analogy to the expansion of the coordination sphere represented by $Cp_3M(\eta^1\text{-allyl}) \rightleftharpoons Cp_3M(\eta^3\text{-allyl})$[3b,6,34] or $Cp_3M(\eta^1\text{-X}) \rightarrow Cp_3M(\eta^5\text{-Cp})$.[3b,35]



(15)

12

The sensitivity of migratory CO insertion rates to the nature of the migrating hydrocarbyl group has been a topic of considerable discussion for the transition-metal systems investigated to date.[1,2] Efforts have been made to correlate rates with both electronic and steric factors, while explicit analyses in light of extensive metal–hydrocarbyl bond disruption enthalpy data have been largely unavailable.[36] To the extent that Taft polar substituent constants[37] measure functional group electron-donating tendency,[38] it can be seen in Table II that there is a rough qualitative correlation between relative Cp_3ThR insertion rate and hydrocarbyl group σ^*. The more electron-releasing substituents generally undergo more rapid insertion, while the less electron-releasing substituents (benzyl being the most striking example) undergo insertion less readily. This type of trend has been observed before[1,2] and could be viewed as being consistent with intramolecular nucleophilic attack on coordinated, positively polarized CO being rate limiting. Such a trend is also evident in theoretical studies on $RMn(CO)_5$ systems,[39] and seems less plausible for the case where k_1 is rate limiting.

Any assessment of R group steric factors in Cp_3ThR carbonylation must begin by recognizing that diffraction studies[3,35] show that actinide Cp_3MR molecules are rather congested (although further expansion of the coordination sphere can occur—vide supra) as does a dynamic NMR study of restricted rotation about the U–$CH(CH_3)_2$ bond in $Cp_3U(i\text{-}C_3H_7)$ ($E_a \approx 10$ kcal/mol).[34] Quantitative estimates of steric effects in the present case are complicated by what appears to be a considerable flexibility in the actinide–hydrocarbyl bonding. Thus, U–C(α)–C(β) (C(α) formally sp^3 hybridized) angles as large as ca. 130° have been reported in Cp_3UR compounds,[3,35,40] while a Th–C(α)–C(β) angle of 160° is found in the case of highly congested $Th[(CH_3)_5C_5]_2[CH_2C(CH_3)_3]_2$.[41] An extensive series of cobalt hydrocarbyls also evidences large, sterically induced distortions.[42] Thus, steric relationships in the Cp_3ThR series may not conform to orderings operative in less flexible hydrocarbon frameworks. In Table II are compared the relative rates of migratory insertion to some commonly employed measures of steric influence, i.e., Taft E_s,[37,43] Hancock E_s^c,[43] Charton ν,[43,44] and Tolman[45] cone angle parameters. Although no strictly 1:1 correlations are evident, it is apparent that migratory insertion is generally most rapid for sterically demanding hydrocarbyl groups. This general trend has also been noted in kinetic investigations of d-block systems and in R vs. R′ competition studies with $Cp_2Zr(R)R'$ complexes.[2h,46] The present result suggests that, whatever the structure of the transition state, energetic factors other than minimization of direct

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(30) $Zr[(CH_3)_5C_5]_2H_2 \cdot CO$: Marsella, J. A.; Curtis, C. J.; Bercaw, J. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 7244.

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(36) (a) Connor[36b] has noted that the resistance of $Mn(CO)_5CF_3$ to carbonylation vis-à-vis $Mn(CO_5)CH_3$ is in accord with bond energy orderings. (b) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Saied, N. I.; Suradi, S.; Carson, R.; Takhin, G. A.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166.

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(38) This relationship remains controversial. See ref 37 and Charton, M. *J. Am. Chem. Soc.* **1977**, *99*, 5687 and references therein.

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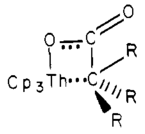
CO-alkyl steric interactions dominate the kinetics.

In a more quantitative and relevant fashion than various tabulated parameters, experimentally determined[7] Th–R bond disruption enthalpies (D(Th–R))[47] should embody many of the electronic and steric characteristics important for understanding the Cp_3ThR carbonylation process. Indeed, reference to Table II indicates that, for the data available and R = a simple hydrocarbyl group, there is an approximate correlation of migratory insertion rate with the "weakness" of the Th–R bond. The marked deviation for R = benzyl appears to reflect characteristics evident in the σ^* parameters: much different electronic properties in either the ground or transition state.

A pronounced increase in migratory insertion rate was observed upon photochemical excitation of a $Cp_3ThCH_2Si(CH_3)_3$ + CO reaction mixture. To our knowledge, this observation represents one of the very few examples of photoinduced migratory CO insertion,[48] although the reverse transformation is well documented.[49] No effort was made to optimize the efficiency of this process (i.e., by increasing the CO pressure), and secondary photoreactions of the product were observed. In other work,[8] we have demonstrated that photoexcitation of Cp_3ThR and Cp_3UR molecules (R containing a β-hydrogen atom) results in efficient β-hydrogen elimination. It was postulated that weakening of actinide–η^5-C_5H_5 bonding (e.g., via ligand-to-metal charge transfer) results in decreased coordinative saturation of the metal center, promoting β-hydride elimination. In the present case, photoexcitation might create a highly reactive, coordinatively unsaturated Th(η^3-C_5H_5), Th(η^1-C_5H_5), or Cp_2ThR[8,50,51] species which would rapidly scavenge dissolved CO.

This study also represents the first comparative study of CO vs. CO_2 migratory insertion rates into a d- or f-metal hydrocarbyl bond. It is found that CO_2 insertion rates are not as rapid as CO insertion rates and surprisingly are depressed by steric bulk in the hydrocarbyl functionality. Furthermore, neither the greater electron-releasing tendency of R nor the relatively low D(Th–R) in $Cp_3Th(i\text{-}C_3H_7)$ results in a rate enhancement over Cp_3ThCH_3 CO_2 insertion. This kinetic ordering suggests a much greater steric sensitivity for Th–R carboxylation, as illustrated in the plausible transition state **13**.



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Registry No. **1a**, 80410-05-5; **1b**, 58920-13-1; **1c**, 54067-92-4; **1d**, 58920-14-2; **1e**, 89746-40-7; **1f**, 89789-14-0; **1g**, 89746-39-4; **2a**, 89746-41-8; **2b**, 89746-42-9; **2b***, 89746-43-0; **2c**, 89746-45-2; **2c***, 89746-46-3; **2d**, 89773-12-6; **2d***, 89746-47-4; **2f**, 89746-48-5; **2g**, 89746-50-9; **3b**, 89746-44-1; **3b***, 89746-53-2; **3g**, 89746-49-6; **4a**, 89746-51-0; **4b**, 89746-52-1.

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(51) Photolysis of mixtures of $Th(C_5H_5)_3CH_2C_6H_5$ and $Th(C_5D_5)_3CH_2$-C_6H_5 under CO gives insertion products (enolates by ^1H NMR) with extensive scrambling of C_5H_5 and C_5D_5 rings as detected by detected by mass spectrometry (Mintz, E. A.; Marks, T. J., unpublished results).