process is not competitive with cyclometalation, and in this case there is no doubt that the intermolecular reaction product is thermodynamically favored ($\Delta H_{\text{calcd}} \sim -19$ kcal mol^{-1}).[15]

On a more general level, the present observations regarding the rather stringent spatial requirements of transition states such as G suggest that four-center, heterolytic types of processes offer a means to effect homogeneous C–H activation on saturated hydrocarbons with high intrinsic regioselectivity. Such an approach is presently under investigation.

Acknowledgment. We thank the National Science Foundation for support of this research at Northwestern University under grant CHE83-06255 and the Office of Basic Energy Sciences, Division of Materials Science, U.S. Department of Energy, for support of the neutron diffraction work at Argonne National Laboratory under contract W-31-109-Eng-38. We thank Dr. Paul Toscano for assistance in obtaining CP–MAS NMR spectra, Professor Victor Day for helpful discussions, and Dr. Doris Hung for GC–MS data.

Supplementary Material Available: A table of general temperature factor expressions (Table V) as well as a listing of observed and calculated structure factors from the final cycle of least-squares refinement for $Cp'_2Th(CH_2CMe_3)_2$; ^1H NMR spectra recorded during the course of the **6** → **7** thermolysis reaction (Figure S-1) and during the course of the **7** + Me_4Si reaction (Figure S-2) (20 pages). Ordering information is given on any current masthead page.

A Synthetic and Mechanistic Study of Oxycarbene-like Coupling Reaction Patterns of Actinide η^2-Acyl Complexes with Carbon Monoxide and Isocyanides

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Abstract: This contribution reports the synthesis and characterization of the ylide complexes $Cp'_2Th[OC(CH_2\text{-}t\text{-}Bu)C(PR_3)O](Cl)$ ($Cp' = \eta^5\text{-}C_5Me_5$; R = Me, Ph) formed by the carbonylation of $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**) in the presence of phosphines. Isotopic tracer studies with ^{13}CO indicate that the labeled carbon atom is incorporated regiospecifically at the ylide α-carbon atom position. The carbonylation of **1** to yield the enedionediolate $\{Cp'_2Th[OC(CH_2\text{-}t\text{-}Bu)CO](Cl)\}_2$ (**2**) or the ylide complexes was found to obey a second-order rate law where rate = $kP_{CO}[\mathbf{1}]$; $k = 1.50\ (5) \times 10^{-5}$ min^{-1} torr^{-1} for both carbonylations at 30.8 °C. The rate of formation of the ylide complexes was also found to be independent of solvent, phosphine concentration, and type of phosphine used. The carbonylation of **1** is therefore inferred to involve a rate-determining coupling of CO with the acyl to yield an intermediate ketene or ketene-like complex. The reaction of acyl **1** or $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2Ph)$ with a variety of isocyanides (RNC; R = t-Bu, C_6H_{11}, 2,6-$Me_2C_6H_3$) results in the formation of ketenimine complexes of the type $Cp'_2Th[OC(CH_2\text{-}t\text{-}Bu)CNR](Cl)$ and $Cp'_2Th[OC(CH_2Ph)CNR](Cl)$. Addition of a second equivalent of isocyanide yields simple adducts of the type $Cp'_2Th[OC(CH_2\text{-}t\text{-}Bu)CNR](CNR)(Cl)$ and $Cp'_2Th[OC(CH_2Ph)CNR](CNR)(Cl)$. These new complexes have been fully characterized by standard techniques and the ketenimine $Cp'_2Th(Cl)[OC(CH_2\text{-}t\text{-}Bu)(CN\text{-}2,6\text{-}Me_2C_6H_3)]$ by single-crystal X-ray diffraction. Under the appropriate conditions, the N-aryl complexes suffer secondary reactions in which the η^2-acyl ultimately undergoes coupling with 2 equiv of isocyanide to yield acetylindolate and acetylindoleninate derivatives. The η^2-acyl was also found to undergo coupling with 1 equiv of diphenylketene to yield the complex $Cp'_2Th[OC(CH_2\text{-}t\text{-}Bu)C(CPh_2)O](Cl)$. These coupling products have been fully characterized by conventional analytical and structural methodology. The mechanistic and reactivity results of this study are discussed in terms of the anchored Fischer carbene-like character of actinide η^2-acyls and the mechanism by which the carbonylation of **1** yields the enedionediolate **2**.

The bonding and reactivity properties of actinide,[1] lanthanide,[1a,2] and early transition element[1e,3-6] acyl complexes have recently been the subject of considerable attention. In particular, many of the spectroscopic, structural, and reactivity characteristics of these η^2-acyls are distinctive vis-à-vis those of middle and late transition elements and evidence unusual, perhaps catalytically significant,[1,7] modes of CO activation. To the extent that most metal–ligand bonding/reactivity descriptions are based upon formalisms and

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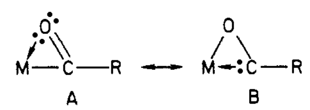
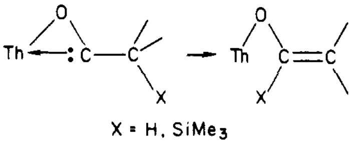
analogies, intriguing parallels between the properties of these η^2-acyls and those of Fischer "carbene" complexes[8] have been noted (A, B).[1,3a,9]



A B

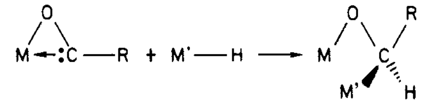
Spectroscopically, acyl carbon NMR chemical shift values in the δ 320–380 ppm range[10] are reminiscent of δ $^{13}C \approx 300$–400 ppm parameters observed for the "carbenoid" carbon in Fischer-type complexes (e.g., $M(CO)_5C(R)Y$, R = alkyl; Y = OR′, NR'_2, SR′; M = Cr, Mo, W).[8] Also in accord with resonance hybrid B is a diminution in the acyl C–O stretching frequencies of η^2-acyls. Thus, values for both f-element (1450–1490 cm^{-1}, assigned using ^{13}C substitution)[1] and early transition element (1530–1620 cm^{-1})[3-6] η^2-acyls are considerably lower in energy than those for typical nonconjugated η^1-acyls (1630–1680 cm^{-1}).[1d] The relatively small sensitivity of η^2-acyl stretching frequencies (for similar complexes) to relatively wide variations in the mass of M and R[7a,11] argues that kinematic effects are relatively constant and not the major source of the anomalously low vibrational frequencies. In regard to metrical information, meaningful bond distance comparisons suffer from a paucity of accurate structural data. Thus, while it is evident that for all η^2-acyl complexes the quantities $[r(M–O) - r(M–C(acyl)]$ and $\angle \overline{M–C(acyl)–O}$ fall with increasing metal oxophilicity,[1c,3,12] the trend in the key C–O distance parameter is more difficult to discern. For the most oxophilic metals, the reported values range from 1.18 (2) and 1.211 (8) Å in group 4[52] complexes[4] to 1.18 (3)[1e] and 1.30 (2) Å[13] for Th(IV). In comparison, typical C–O distances in Fischer MC(R)OR′ carbene complexes are in the 1.31–1.35 Å range,[8] while C–O distances average 1.42 Å in alkyl ethers, 1.34–1.37 Å in esters (single bond distances), or methyl allenyl ether, and 1.21 Å in aldehydes.[14]

By far, the most compelling argument for the "anchored" Fischer carbene description of actinide η^2-acyls derives from observations on chemical reactivity. For example, thorium η^2-acyls undergo carbene-like[15,16] intramolecular 1,2 rearrangements to enolates (eq 1).[1,17] Insertion of the acyl carbon atom into



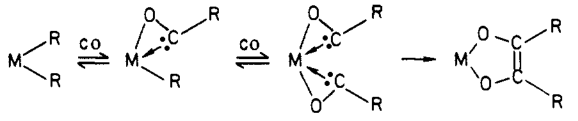
(1)

metal–hydrogen bonds (eq 2)[7b,c,18] and coupling reactions to



(2)

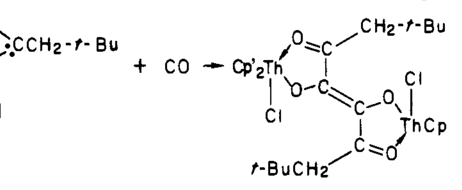
produce *cis*-enediolates (C, eq 3)[1,31,7b,18a,19] are also suggestive of carbenoid[15,16] character.



(3)

C

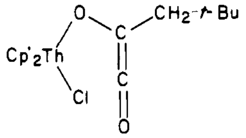
Perhaps the most elaborate and fascinating of the carbene-like actinide η^2-acyl reaction patterns is the carbonylation process which leads to dionediolate complexes in high yield (e.g., 2 in eq 4).[1e,20] Preliminary mechanistic studies[20] suggested that eq 4 proceeds



(4)

2

via a η^2-acyl-CO coupling reaction to yield a transitory, ketene-like species (e.g., 3). Analogous ketene-forming transformations are



3

known for both free[21] and complexed[22] carbenes. In the present

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(10) For example, $\delta(^{13}C)$ = 360.2 ppm in $Cp'_2Th(Cl)(\eta^2\text{-}^{13}COCH_2\text{-}t\text{-}Bu)$,[1d] 380.6 ppm in $Cp_2Lu(\eta^2\text{-}^{13}CO\text{-}t\text{-}Bu)$,[2a] and 318.7 ppm in $Cp_2Zr(Cl)(\eta^2\text{-}^{13}COCH_2\text{-}t\text{-}Bu)$.[3b]

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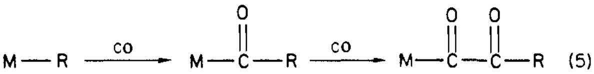
context, such chemistry represents further evidence for the carbene-like character of η^2-acyls, a new mode of CO oligomerization, and, to date, the only viable analogue to the oft-discussed but apparently thermodynamically unfavorable "double insertion" of carbon monoxide (eq 5).[23] In addition to this motivation,



$$M-R \xrightarrow{CO} M-\overset{\overset{\displaystyle O}{\|}}{C}-R \xrightarrow{CO} M-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-R \quad (5)$$

understanding η^2-acyl coupling processes is of direct relevance to the mechanism(s) of enediolate-forming reactions[19,24] and of indirect relevance to technologically significant transformations in which two (or more) CO molecules are reductively fused.[25]

In this contribution we present a full discussion of our synthetic/mechanistic studies relating to the carbene-like coupling reactions of actinide η^2-acyls and reaction pathways leading to species such as dionediolates (**2**). This presentation includes a kinetic/mechanistic/trapping study of the carbonylation of **1**, a new class of C=C bond-forming reactions between η^2-acyls and isocyanides (as models for CO reactions), and investigations focusing on possible interactions between η^2-acyls and species such as **3**, i.e., observation of a new type of coupling reaction between η^2-acyls and organic ketenes. For purposes of clarity, we allude briefly to the results of several single crystal diffraction studies. The full details of this structural work will be provided in a forthcoming contribution[26] devoted entirely to the comparative structural chemistry of organoactinide carbonylation products.

Experimental Section

Physical and Analytical Measurements. Proton, carbon, and phosphorus NMR spectra were recorded on either a Varian EM-390 (CW, 90 MHz), a JEOL FX-90Q (FT, 90 MHz), or a JEOL FX-270 (FT, 270 MHz) spectrometer. Chemical shifts are reported relative to internal tetramethylsilane (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 599B spectrophotometer with either Nujol mulls sandwiched between salt (KBr, NaCl) plates in an O-ring sealed air-tight holder or matched solution cells (KBr).

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

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, Vacuum Atmospheres glovebox. Argon (Matheson, prepurified) and carbon monoxide (Matheson, CP) were purified by passage through a supported MnO oxygen removal column[27] and a Davison 4A molecular sieve column. Enriched carbon monoxide (90%, ^{13}C, Stohler Isotopes) was used as received without further purification. All reaction solvents were distilled from Na/K/benzophenone under nitrogen and were condensed and stored in vacuo in bulbs on the vacuum line containing a small amount of $[Ti(\eta^5\text{-}C_5H_5)_2Cl]_2ZnCl_2$ as O_2/H_2O indicator.[28] Aromatic deuterated solvents were dried over Na/K alloy and vacuum transferred before use; $CDCl_3$ was dried over P_2O_5.

The complexes $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**) and $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2Ph)$ were prepared according to the literature procedures.[17a,29] The reagents trimethylphosphine (Strem), cyclohexyl isocyanide (Aldrich), and *tert*-butyl isocyanide (Strem) were freeze-pump-thaw degassed and then vacuum transferred onto freshly activated 4A molecular sieves before use. Triphenylphosphine (Aldrich) and 2,6-dimethylphenyl isocyanide (Fluka) were purified by sublimation. Diphenylketene[30] and *p*-tolyl isocyanide[31] were prepared according to the literature procedures and purified by distillation.

{$Cp'_2Th[OC(CH_2\text{-}t\text{-}Bu)CO](Cl)$}$_2$ (2a). A 25-mL round-bottom reaction flask equipped with a magnetic stir bar was charged with 0.90 g (1.41 mmol) of $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**). Toluene (12 mL) was condensed into the flask in vacuo, and CO (500 mmHg) was then introduced into the flask. After being stirred for 25 min at room temperature, the pale yellow solution had become deep violet in color. After 14.5 h, CO was removed in vacuo, and the toluene solution was filtered. Toluene was then removed in vacuo and pentane (6 mL) was condensed into the flask. The violet precipitate was isolated by filtration, washed with 1 mL of pentane, and dried in vacuo. The crude product (0.63 g) was recrystallized from toluene to yield ca. 0.3 g of deep-violet crystals.

^{1}H NMR (C_6D_6) δ 2.05 (30 H, s), 1.43 (9 H, s), and 3.57 (2 H, s); IR (Nujol mull) 1540 (s), 1347 (m), 1229 (s), 1100 (s), 1021 (m), 936 (s), 922 (w), and 800 (w) cm^{-1}. Anal. Calcd for $C_{54}H_{82}Cl_2O_4Th_2$: C, 48.76; H, 6.21; Cl, 5.34; mol wt, 1330 g/mol. Found: C, 48.76; H, 6.26; Cl, 5.85; mol wt (cryoscopic in benzene), 1260 ± 10% g/mol.

The complex {$Cp'_2Th[OC(CH_2\text{-}t\text{-}Bu)^{13}CO](Cl)$}$_2$ (**2b**) was prepared in an analogous manner from $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ and ^{13}CO.

^{1}H NMR (C_6D_6) δ 2.05 (30 H, s), 1.43 (9 H, s), and 3.57 (2 H, s); ^{13}C{^{1}H} NMR (C_6D_6) δ 158.6 (s); IR (Nujol mull) 1542 (s), 1348 (m), 1204 (s), 1095 (s), 1022 (m), 934 (w), 924 (w), and 800 (w) cm^{-1}.

The complex {$Cp'_2Th[O^{13}C(CH_2\text{-}t\text{-}Bu)CO](Cl)$}$_2$ (**2c**) was prepared from $Cp'_2Th(\eta^2\text{-}^{13}COCH_2\text{-}t\text{-}Bu)Cl$ and ^{12}CO.

^{1}H NMR (C_6D_6) δ 2.05 (30 H, s), 1.43 (9 H, s), and 3.57 (2 H, d, $^2J_{^{13}C\text{-}H}$ = 5.5 Hz); ^{13}C{^{1}H} NMR (C_6D_6) δ 216.8; IR (Nujol mull) 1512 (s), 1342 (m), 1229 (s), 1062 (s), 1022 (m), 934 (w), 924 (w), and 800 (w) cm^{-1}.

$Cp'_2\overline{Th[OC(CH_2\text{-}t\text{-}Bu)C(PPh_3)O}](Cl)$ (3a). $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**) (0.715 g, 1.12 mmol) and PPh_3 (0.31 g, 1.2 mmol) were placed in a 25-mL flask with a magnetic stir bar. The flask was evacuated and 10 mL of toluene was condensed in at −78 °C. The flask was backfilled with 600 mm of CO and the solution allowed to warm to room temperature. Gas uptake was monitored manometrically and continued over a period of 6–8 h. During this time the color of the solution changed from orange-yellow to bright lemon yellow. Upon stirring the solution overnight, a large amount of a bright yellow solid formed. After the suspension was cooled to −78 °C for 1 h, the yellow product was isolated by filtration and dried under vacuum. Yield: 0.93 g (1.00 mmol), 90%. Recrystallization of this complex may be carried out in a manner similar to the isolation procedure. ^{1}H NMR (C_6D_6, 90 MHz) δ 0.99 (s, 9 H), 1.62 (d, $^4J_{P\text{-}H}$ = 0.9 Hz, 2 H), 2.32 (s, 30 H), 6.9–7.2, 7.5–7.4 (m, 15 H); ^{13}P{^{1}H} (C_6D_6, 36 MHz) −1.8 ppm from 85% H_3PO_4; IR (Nujol) 3060 (w), 1633 (w), 1588 (w), 1513 (s), 1449 (s), 1420 (w), 1323 (s), 1308 (m), 1275 (s), 1249 (w), 1186 (w), 1165 (m), 1104 (s), 1019 (w), 998 (w), 905 (w), 875 (w), 777 (m), 751 (m), 745 (w), 724 (m), 714 (w), 695 (s), 612 (m), 562 (s), 541 (s), 528 (m), 502 (s), 427 (w) cm^{-1}. Anal. Calcd for $C_{45}H_{56}ClO_2PTh$: C, 58.28; H, 6.09; Cl, 3.82; P, 3.34. Found: C, 57.86; H, 5.90; Cl, 3.55; P, 3.17.

The complex $Cp'_2\overline{Th[OC(CH_2\text{-}t\text{-}Bu)^{13}C(PPh_3)O}](Cl)$ (**3b**) was prepared similarly with ^{13}CO. ^{13}C NMR (C_6D_6, 68 MHz) δ 117.8 (d, $^1J_{P\text{-}C}$ = 123 Hz).

$Cp'_2\overline{Th[OC(CH_2\text{-}t\text{-}Bu)C(PMe_3)O}](Cl)$ (4). $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**) (0.50 g, 0.78 mmol) was placed in a 25-mL reaction flask equipped with a magnetic stir bar. The flask was attached to a vacuum line and evacuated. Toluene (15 mL) and PMe_3 (0.13–0.15 mL, ca. 1.7 mmol) were condensed into the flask at −78 °C. The apparatus was next backfilled with 1 atm of CO and allowed to warm to room temperature with stirring. The color of the solution gradually began to fade and after 3 h a colorless, crystalline product began to precipitate. After 8 h, the volume of solvent was reduced by one-half and the suspension was slowly cooled to −78 °C. After an additional hour, the product was isolated by filtration and dried in vacuo. Yield 0.34 g (0.46 mmol), 59% (unoptimized); ^{1}H NMR (C_6D_6, 90 MHz) δ 0.91 (d, $^2J_{P\text{-}H}$ = 13.6 Hz, 9 H), 1.16 (s, 9 H), 1.87 (s, 2 H), 2.28 (s, 30 H); ^{31}P{^{1}H}

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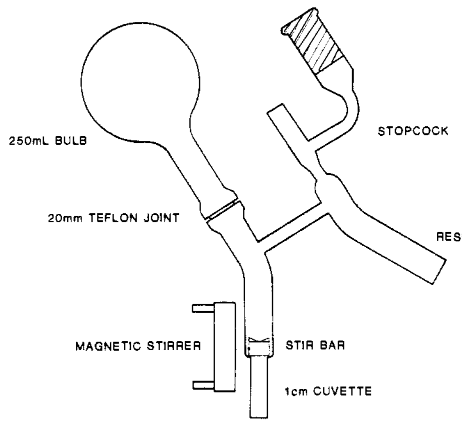


Figure 1. Quartz cuvette/gas bulb used for kinetic measurements when pseudo-first-order conditions in a reagent gas are required.

NMR (C_6D_6, 36 MHz) 2.30 ppm; IR (Nujol) 1550 (s), 1435 (m), 1360 (w), 1325 (s), 1304 (m), 1290 (w), 1276 (m), 1241 (w), 1169 (m), 1120 (m), 1068 (m), 1021 (m), 953 (s), 929 (w), 909 (w), 877 (m), 867 (m), 778 (m), 756 (w), 678 (m), 602 (m), 505 (s), 490 (s), 469 (w) cm^{-1}. Anal. Calcd for $C_{30}H_{50}ClO_2PTh$: C, 48.62; H, 6.80; Cl, 4.78; P, 4.18. Found: C, 49.66; H, 7.21; Cl, 4.93; P, 4.22.

Kinetic Studies. Method a. The rate of carbonylation of $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**) to complex 4 was determined spectrophotometrically by monitoring the disappearance of the band at 420 nm (ϵ = 1.4×10^2 cm^{-1} M^{-1}) due to the acyl. Complex 4 is colorless and hence does not absorb in this region. A large gas volume above the reaction solution and efficient mixing (refer to Figure 1) ensured pseudo-first-order conditions in CO for each determination, thus allowing a measurement of the reaction order in **1**.

In a typical experiment, 5–6 mL of a 7.066 mM stock solution of **1** in THF was added to the reservoir of the apparatus shown in Figure 1. The apparatus was next attached to the vacuum line and the solution was freeze–pump–thaw degassed three times. Trimethylphosphine (1.5–2.0 equiv), premeasured in a calibrated volume, was condensed into the reservoir at −78 °C. Next, the desired pressure of CO (determined with a U-tube manometer) was admitted to the device, while keeping the reaction solution at ca. 0 °C. The apparatus was then quickly backfilled with Ar such that the total pressure was ≥1 atm. The device was then tipped such that the solution flowed into the attached cuvette. The cell was then placed in a thermostated (30.8 ± 0.5 °C) compartment of a Perkin-Elmer 330 spectrophotometer which had been preprogrammed with the appropriate parameters required for the kinetic determination and was operated in the repetitive scan mode. An air-driven magnetic stirrer was placed next to the cell such that a disk-shaped, finned stir bar rotated freely and rapidly within the cell. The design of the apparatus allowed the solution level above the stir disk to undergo a vigorous vortexing action while at the same time the solution below the stir disk (and in the instrument light path) was stirred efficiently and without cavitation.

Carbonylation reactions were monitored for 3–4 half-lives. Plots of ln $(A_0 - A_\infty/A - A_\infty)$ vs. time and k_{obsd} vs. P_{CO} were found to be linear and were fit by standard linear regression techniques to obtain the second-order rate constant.

Method b. The rate of conversion of **1** to **2** or **3** was determined manometrically by monitoring the uptake of CO during the course of the reaction.

In a typical experiment, 10.0 mL of a 0.039 M solution of **1** in toluene was added to a reaction bulb fitted with a Teflon stopcock bearing a ground glass joint. The bulb was then attached to the vacuum line. The solution was freeze–pump–thaw degassed three times and then immersed in a thermostated bath held at 30.8 ± 0.5 °C. The apparatus was then backfilled with 592 torr of CO and the solution vigorously stirred. Pressure measurements were accomplished with a cathetometer and a U-tube manometer. Recordings were initiated 2–3 min after the start of the reaction to allow calibration. The total change in CO pressure was kept at ≤5% in order to approach pseudo-first-order conditions (using various portions of the vacuum line as ballast).

In a similar manner, 0.20 g (0.76 mmol) of PPh_3 was added to the stock solution and the rate of conversion of **1** to **3a** was determined at 592 torr of CO.

Plots of ln $(P_0 - P_\infty/P - P_\infty)$ vs. time were fit by standard linear regression techniques to obtain k_{obsd}.

$Cp'_2Th(Cl)[OC(CH_2\text{-}t\text{-}Bu)CN\text{-}t\text{-}Bu]$ (5). $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**, 0.50 g, 0.74 mmol) was placed in a 50-mL two-neck reaction flask fitted with a magnetic stir bar, Teflon stopcock, and a filtering device. The apparatus was evacuated and 20 mL of toluene was condensed in at −78 °C; the system was then backfilled with 1 atm of argon. Next, 0.45 mL of a 1.63 M solution of t-BuNC (0.74 mmol) in toluene was added via syringe through the stopcock under a flush of argon. The yellow solution was then allowed to warm to room temperature with stirring. After 3–4 h, no color changes were observed and the solvent was removed in vacuo to yield a yellow, gummy foam. All attempts (pentane, heptane, Et_2O) to obtain a crystalline product failed. ^1H NMR (C_6D_6, 270 MHz) δ 1.08 (s, 9 H), 1.30 (s, 9 H), 2.04 (d, $\Delta\delta$ = 0.002 ppm, 30 H), 2.78 (AB quartet, J = 13.5 Hz, $\Delta\delta$ = 0.17 ppm, 2 H); IR (Nujol) 1996 (s), 1210 (m), 1190 (s), 1138 (m), 1022 (m), 937 (w), 920 (w), 891 (w), 868 (w), 820 (w), 800 (w), 612 (w), 566 (w) cm^{-1}.

$Cp'_2Th(Cl)[OC(CH_2\text{-}t\text{-}Bu)CN(2,6\text{-}Me_2C_6H_3)]$ (8). $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (0.80 g, 1.3 mmol) and $2,6\text{-}Me_2C_6H_3NC$ (0.17 g, 1.30 mmol) were combined in a 25-mL reaction flask equipped with a magnetic stir bar. The flask was evacuated and 10 mL of toluene was condensed in at −78 °C. The flask was then backfilled with Ar and the solution was allowed to warm to room temperature. After 1 h the solution had turned slightly more orange. The solution was filtered and the solvent removed in vacuo in yield a gummy foam. After several pentane addition/removal cycles a bright yellow microcrystalline material was obtained which was isolated by filtration from cold (−78 °C) pentane. Yield 0.57 g (0.74 mmol), 59%; ^1H NMR (C_6D_6, 90 MHz) δ 1.13 (s, 9 H), 2.03 (s, 30 H), 2.28 (s, 2 H), 2.44 (s, 6 H), 7.1–6.9 (m, 3 H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 10.9 (q, J_{CH} = 126 Hz, Cp′ ring methyl), 18.7 (q, J_{CH} = 127 Hz, aromatic methyl), 30.0 (q, J_{CH} = 126 Hz, $C(CH_3)_3$), 32.3 (s, $C(CH_3)_3$), 47.0 (t, J_{CH} = 127 Hz, CH_2), 110.3 (s, $C{=}C{=}N$), 124.7 (d, J_{CH} = 159 Hz, para), 126.4 (s, Cp′ ring), 128.3 (d, J_{CH} = 159 Hz, meta), 128.4 (s, ortho), 143.5 (s, ipso), 216.8 (s, $C{=}C{=}N$); IR (Nujol) 2004 (s), 1593 (w), 1468 (s), 1363 (m), 1312 (m), 1279 (w), 1217 (s), 1164 (s), 1130 (m), 1088 (w), 1032 (m), 936 (w), 915 (m), 892 (m), 868 (m), 782 (w), 769 (m), 739 (m), 682 (w), 578 (w), 563 (w), 533 (w), 497 (w), 460 (w) cm^{-1}. Anal. Calcd for $C_{35}H_{50}ClNOTh$: C, 54.72; H, 6.56; N, 1.82; Cl, 4.61. Found: C, 54.89; H, 6.83; N, 1.90; Cl, 4.87.

$Cp'_2Th(Cl)[OC(CH_2R)CNR'](CNR')$ (9, R = R′ = t-Bu; 10, R = Ph, R′ = t-Bu; 11, R = t-Bu, R′ = C_6H_{11}). In a typical experiment, 0.8 mmol of the appropriate acyl complex ($Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**) or $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2Ph)$) was placed in a two-neck 25-mL reaction flask fitted with a magnetic stir bar, a Teflon stopcock/gas inlet, and a filter frit. The flask was then attached to the vacuum line and evacuated. Next, 15–20 mL of toluene was condensed in at −78 °C, and the flask was backfilled with Ar. Then, ≥2 equiv of the desired isocyanide (t-BuNC or $C_6H_{11}NC$) was added via syringe through the stopcock under a flush of Ar. The solution was then allowed to warm to room temperature with stirring. After 1 h, a small but noticeable change in color from yellow to yellow-orange had occurred, and the solvent was removed under vacuum (these reactions were judged to be complete and quantitative within 30 min as determined by ^1H NMR). The resulting oils were dried in vacuo for several hours. After several heptane addition/removal cycles, tractable solids were obtained which were isolated by cold (−78 °C) filtration, and the resulting products were dried under vacuum. Isolated yields varied from 50 to 70%.

For **9**: ^1H NMR (C_6D_6, 270 MHz) δ 0.82 (s, 9 H), 1.06 (s, 9 H), 1.28 (s, 9 H), 2.06 (s, 30 H), 2.39 (AB quartet, J = 15.5 Hz, $\Delta\delta$ = 0.18 ppm, 2 H); IR (Nujol) 2188 (s), 1984 (s), 1601 (m), 1460 (s), 1312 (m), 1275 (m), 1240 (m), 1210 (m), 1190 (s), 1138 (s), 1031 (w), 935 (w), 929 (m), 889 (w), 877 (m), 849 (w), 829 (w), 800 (w), 717 (w), 698 (w), 645 (w), 610 (w), 572 (m), 533 (w), 458 (m) cm^{-1}. Anal. Calcd for $C_{36}H_{59}ClN_2OTh$: C, 53.82; H, 7.40; N, 3.49; Cl, 4.41. Found: C, 53.76; H, 6.68; N, 3.70; Cl, 4.66.

For **10**: ^1H NMR (C_6D_6, 270 MHz) δ 0.72 (s, 9 H), 0.96 (s, 9 H), 1.92 (d, $\Delta\delta$ = 0.013 ppm, 30 H), 3.58 (AB quartet, J = 14.7 Hz, $\Delta\delta$ = 0.089 ppm, 2 H), 7.0 (m, 5 H); IR (Nujol) 2190 (m), 2002 (s), 1603 (m), 1496 (m), 1454 (m), 1361 (m), 1265 (w), 1231 (w), 1209 (m), 1183 (s), 1062 (w), 1023 (w), 935 (w), 890 (m), 842 (w), 803 (w), 752 (m), 702 (m), 682 (w), 610 (w), 591 (w), 547 (w) cm^{-1}. Anal. Calcd for $C_{38}H_{55}ClN_2OTh$: C, 51.73; H, 6.73; N, 3.40; Cl, 4.31. Found: C, 52.36; H, 7.08; N, 3.36; Cl, 4.19.

For **11**: ^1H NMR (C_6D_6, 60 MHz) δ 0.7–2.5 (br m, 24 H), 1.18 (s, 9 H), 2.13 (s, 30 H); IR (Nujol) 2195 (s), 1998 (s), 1592 (w), 1395 (w), 1359 (s), 1330 (w), 1205 (s), 1162 (s), 1127 (w), 1020 (m), 960 (m), 920 (w), 904 (m), 890 (m), 863 (w), 849 (w), 814 (w), 773 (w), 706 (m), 611 (w), 555 (w), 522 (w) cm^{-1}. Anal. Calcd for $C_{40}H_{63}ClN_2OTh$: C, 56.16; H, 7.42; N, 3.27; Cl, 4.14. Found: C, 55.86; H, 7.05; N, 3.57; Cl, 4.66.

Spectroscopic Characterization of $Cp'_2Th(Cl)[OC(CH_2\text{-}t\text{-}Bu)CN(2,6\text{-}Me_2C_6H_3)](CN\text{-}2,6\text{-}Me_2C_6H_3)$ (12). In the glovebox, 15 mg (0.022 mmol) of $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**) and ca. 9 mg (0.069 mmol) of $2,6\text{-}Me_2C_6H_3NC$ were combined in 1 mL of toluene. The solution was

Table I. Infrared, ^{1}H NMR, and ^{13}C NMR Spectral Data for the Complex $\{Cp'_2Th[OC(CH_2\text{-}t\text{-}Bu)CO](Cl)\}_2$ (**2**)

complex	^{1}H NMR^a η^5-$C_5(CH_3)_5$	^{1}H NMR^a -$C(CH_3)_3$	^{1}H NMR^a CH_2	IR (cm^{-1})^{b,c} $\nu_{C=O}$	IR (cm^{-1})^{b,c} ν_{C-O}	^{13}C NMR^a $^{13}C\{^1H\}^a$
$\{Cp'_2ThOC[OC(CH_2\text{-}t\text{-}Bu)CO(Cl)]\}_2$ (**2a**)	2.05 (s)	1.43 (s)	3.57 (s)	1540	1229	
$\{Cp'_2Th[OC(CH_2\text{-}t\text{-}Bu)^{13}CO](Cl)\}_2$ (**2b**)	2.05 (s)	1.43 (s)	3.57 (s)	1542	1204	158.6 (s)
$\{Cp'_2Th[O^{13}C(CH_2\text{-}t\text{-}Bu)CO](Cl)\}_2$ (**2c**)	2.05 (s)	1.43 (s)	3.57 (d) ($^2J_{^{13}C\text{-}H}$ = 5.5 Hz)	1512	1229	216.8 (s)

[a] Recorded in C_6D_6 solution; reported in ppm from Me_4Si. [b] Nujol mull. [c] As expected, $\nu_{C=C}$ is not observed in the infrared spectrum since the molecule has an inversion center.

transferred to an IR solution cell which was then removed from the glovebox. Infrared analysis showed bands at 2000 and 2153 cm^{-1} attributable to the ν_{CCN} and ν_{CN} absorptions of the title complex. Unreacted isocyanide was also observed with ν_{CN} = 2109 cm^{-1}, in agreement with the literature.[31]

In a separate experiment, 60 mg (0.078 mmol) of $Cp'_2Th(Cl)[OC(CH_2\text{-}t\text{-}Bu)CN(2,6\text{-}Me_2C_6H_3)]$ (**8**) and 11 mg (0.084 mmol) of 2,6-$Me_2C_6H_3NC$ were dissolved in 0.5 mL of C_6D_6. After 45 min, the ^{1}H NMR spectrum was recorded which showed that complete conversion to **12** had occurred. ^{1}H NMR (90 MHz) 1.23 (s, 9 H), 2.09 (s, 30 H), 2.20 (s, 6 H), 2.46 (s, 6 H), 2.52 (s, 2 H), 6.6–7.1 (m, 6 H). Heating the sample at 85 °C (≤1 h) results in complete loss of **12** and formation of **13** in ca. 95% yield.

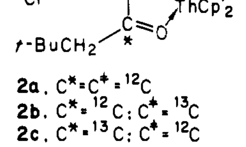
$Cp'_2Th(Cl)(C_{27}H_{29}N_2O)$ (13). $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (0.61 g, 0.91 mmol) and 2,6-$Me_2C_6H_3NC$ (0.26 g, 2.0 mmol) were combined in a 25-mL reaction flask equipped with a magnetic stir bar. After the flask and its contents were cooled to −78 °C, the apparatus was evacuated and then 15 mL of toluene was condensed in. The flask was backfilled with 1 atm of Ar and the yellow solution was allowed to warm to room temperature with stirring. After 30 min at 25 °C, the color of the solution had turned to yellow-orange and the formation of **12** was judged to be complete. The flask was then immersed in a 80 °C oil bath such that the oil level was coincident with the solution level. After 3.5 h of heating, the solution had turned yellow-red in color and the flask was removed from the oil bath. The toluene was then removed under vacuum to yield a reddish foam. Pentane (10 mL) was condensed into the flask, resulting in the formation of an orange powder. The suspension was cooled to −78 °C for 1 h to precipitate more product, which was then isolated by filtration and dried in vacuo. This complex may be recrystallized from pentane or heptane to yield orange crystals. Yield 0.51 g (0.55 mmol), 60%; ^{1}H NMR (C_6D_6, 270 MHz) δ 1.04 (s, 3 H), 1.32 (s, 9 H), 2.12 (s, 15 H), 2.15 (s, 3 H), 2.21 (s, 15 H), 2.22 (s, 3 H), 2.33 (d, J = 0.9 Hz, 3 H), 4.47 and 2.36 (AX pair, J = 12.5 Hz, 2 H), 5.44 (dd, J = 5.5, 9.0 Hz, 1 H), 5.58 (m, 1 H), 5.92 (dd, J = 9.0, 0.5 Hz, 1 H), 7.0 (m, 3 H); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 176.6 (s), 171.2 (s), 165.8 (s), 148.0 (s), 132.2 (d, J = 171 Hz), 130.3 (d, J = 161 Hz), 129.8 (s), 129.39 (s), 128.0 (d, J = 171 Hz), 127.5 (d, J = 151 Hz), 126.5 (s), 125.9 (d, diastereotopic Cp′ ring carbon atoms, Δδ = 0.07 ppm), 125.7 (s), 124.0 (d, J = 164 Hz), 122.4 (d, J = 161 Hz), 59.6 (s), 46.2 (t, J = 127 Hz, CH_2), 32.4 (s, $C(CH_3)_3$), 30.9 (q, J = 125 Hz, $C(CH_3)_3$), 23.3 (q, J = 133 Hz), 21.8 (q, J = 127 Hz), 20.1 (q, J = 129 Hz), 19.5 (q, J = 125 Hz), 12.0 (dq, diastereotopic Cp′ methyl carbon atoms, Δδ = 0.09 ppm, J = 127 Hz); IR (Nujol/NaCl) 1646 (m), 1624 (w), 1598 (w), 1576 (s), 1338 (s), 1277 (m), 1259 (m), 1209 (w), 1198 (w), 1152 (m), 1138 (w), 1090 (w), 1020 (m), 964 (m), 927 (m), 883 (w), 868 (w), 835 (w), 810 (w), 771 (w), 753 (m), 721 (m), 724 (w), 708 (w) cm^{-1}. Anal. Calcd for $C_{44}H_{59}ClN_2OTh$: C, 58.76; H, 6.61; N, 3.11; Cl, 3.94. Found: C, 58.37; H, 6.76; N, 3.44; Cl, 4.64.

$Cp'_2Th(Cl)(C_{22}H_{24}N_2O)$ (14). $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (0.49 g, 0.77 mmol) and toluene (10 mL) were placed in a 25-mL two-neck reaction flask fitted with a filter frit, magnetic stir bar, and a Teflon vacuum valve/gas inlet. The resulting yellow solution was cooled to −78 °C and 0.195 mL of *p*-tolNC (1.6 mmol) was added via syringe through the gas inlet under a flush of argon. The solution was then allowed to warm to room temperature with stirring. After 5 min, the yellow solution began to turn red in color, and after 15 min, red needles began to precipitate. After 2 h, the volume of toluene was reduced by one-half and the solution was slowly cooled to −78 °C to precipitate more product. The product was then isolated in the form of brilliant red needles by filtration, washed with 1–2 mL of toluene, and dried in vacuo. Yield: 0.26 g (0.30 mmol), 39%. An additional 0.15 g of product was obtained from the mother liquor (using 1:1 heptane/toluene) to give a total yield of 0.41 g (0.47 mmol), 61%. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.25 (s, 9 H), 2.01 (s, 30 H), 2.25 (s, 3 H), 2.25 (s, 3 H), 2.29 (s, 30 H), 3.18 (s, 2 H), 5.72 (br s, 1 H), 6.85 (AA′XX′ pseudo quartet, 4 H), 7.08 (d, J = 2.0 Hz, 1 H), 8.52 (d, J = 8.9 Hz, 1 H); ^{1}H NMR (C_6D_6, 270 MHz) δ 6.78 (AA′XX′ pseudo quartet, 4 H), 7.06 (dd, J = 1.5, 9.1 Hz, 1 H), 9.17 (d, J = 9.1 Hz, 1 H); ^{13}C NMR (C_6D_6, 67.8 MHz) δ 199.0 (s), 150.7 (s), 144.3 (s), 143.4 (s), 133.3 (s), 131.6 (d, J = 159 Hz), 130.2 (d, J = 152 Hz), 129.9 (s), 129.1 (s), 127.3 (s), 125.9 (s, Cp′ ring carbons), 121.2 (d, J = 164 Hz), 120.3 (d, J = 161 Hz), 115.5 (d, J = 157 Hz), 50.1 (t, J = 125 Hz, CH_2), 33.5 (s, $C(CH_3)_3$), 30.9 (q, J = 129 Hz, $C(CH_3)_3$), 21.3 (q, J = 127 Hz), 20.5 (q, 129 Hz), 12.1 (q, J = 126 Hz, Cp′ methyl carbons); IR (Nujol) 3373 (m), 1620 (w), 1524 (s), 1481 (s), 1366 (w), 1348 (w), 1317 (w), 1280 (s), 1245 (m), 1231 (w), 1195 (w), 1159 (m), 1125 (w), 1076 (w), 1027 (w), 966 (w), 867 (w), 843 (w), 806 (m), 759 (w), 727 (w), 696 (w), 645 (w), 611 (w) cm^{-1}. For reasons unknown to us, we have been unable to obtain consistent elemental analyses for samples of this complex having comparable purity (by NMR). Herein we report the results of two separate analyses. Anal. Calcd for $C_{42}H_{55}ClN_2OTh$: C, 57.89; H, 6.36; N, 3.21; Cl, 4.07. Found: C, 54.63, 58.22; H, 5.93, 7.81; N, 1.99, 3.57; Cl, 4.89, 4.60.

$Cp'_2Th[OC(CPh_2)C(CH_2\text{-}t\text{-}Bu)O](Cl)$ (15). In a 25-mL reaction flask equipped with a magnetic stir bar was combined 15 mL of toluene, 0.50 g (0.78 mmol) of $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$, and 0.14 mL (0.80 mmol) of diphenylketene under an argon atmosphere. The flask was immersed in a 55 °C oil bath such that the oil level was coincident with the solution level. After the reaction solution was stirred at this temperature for 13 h, the flask was removed from the oil bath. A color change from yellow to bright red-orange was noted. The solution was next filtered and solvent removed in vacuo to yield a gummy semisolid. After several heptane addition/removal cycles a tractable, orange powder was obtained. After the sample was cooled to −78 °C for 1 h in order to precipitate more product, the material was isolated by filtration. The complex was washed with 2 mL of cold heptane and dried in vacuo. Yield: 0.40 g (0.48 mmol), 62%. Recrystallization of this complex may be accomplished from cold heptane or pentane, resulting in the formation of orange blocks of the title compound. ^{1}H NMR (C_6D_6, 90 MHz) δ 0.87 (s, 9 H), 1.89 (s, 2 H), 2.12 (s, 30 H), 7.5–7.1 (m, 10 H); IR (Nujol) 3060 (w), 1573 (s), 1494 (w), 1365 (m), 1260 (s), 1223 (m), 1154 (w), 1117 (w), 1072 (w), 1029 (w), 952 (w), 763 (m), 744 (w), 703 (m), 676 (w), 635 (w), 612 (w), 520 (w) cm^{-1}. Anal. Calcd for $C_{40}H_{51}ClO_2Th$: C, 57.79; H, 6.18; Cl, 4.26. Found: C, 57.55; H, 6.18; Cl, 4.59.

Results

η^2-Acyl–CO Coupling. When a pale-yellow toluene solution of $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2\text{-}t\text{-}Bu)$ (**1**) is stirred under CO (≤1 atm) at room temperature, the color of the solution gradually becomes wine-red. After 25 min, the solution is deep violet, and CO uptake continues for 6–8 h. Subsequent workup affords a violet, crystalline product (**2**) in 30–40% isolated yield. Parallel experiments in NMR tubes indicate that the overall yield of **2** is approximately 90%. The molecular structure of **2** has been determined by single-crystal X-ray diffraction[20] and the result is recounted in Figure 2A. Importantly, the metrical parameters are in reasonable accord with the valence bond picture of structure **2**. Assignment of the NMR and infrared spectral parameters for **2** is considerably aided by the synthesis of ^{13}C-labeled derivatives. Infrared, ^{1}H,



2a, $C^* = C^\# = {}^{12}C$
2b, $C^* = {}^{12}C$; $C^\# = {}^{13}C$
2c, $C^* = {}^{13}C$; $C^\# = {}^{12}C$

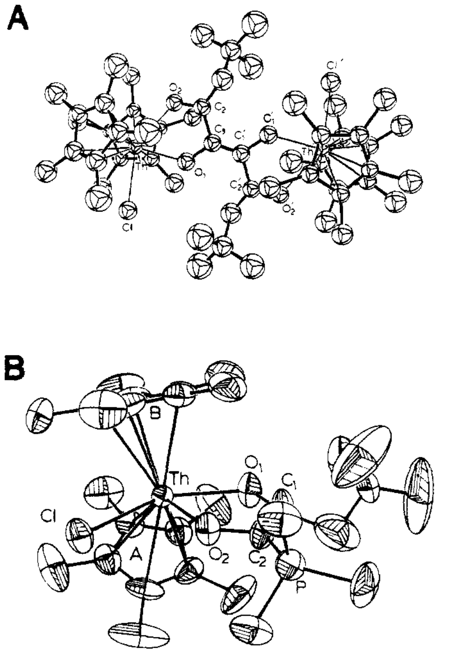
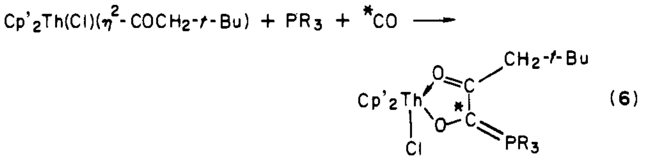


Figure 2. (A) One of the two crystallographically independent {Cp'$_2$Th[OC(CH$_2$-*t*-Bu)CO](Cl)}$_2$ molecules (**2**). Both molecules have crystallographic inversion centers. Atoms of a given type labeled with a prime are related to those without a prime by the crystallographic inversion center midway between the two thorium atoms. Important bond lengths and angles are the following: Th–Cl, 2.690 (6, 9, 9, 2) Å; Th–C(cyclopentadienyl), 2.82 (2, 3, 5, 20) Å; Th–O$_a$, 2.53 (1, 2, 2, 2) Å; Th–O$_b$, 2.27 (1, 2, 2, 2) Å; C$_a$–O$_a$, 1.26 (2, 3, 3, 2)°; C$_a$C$_1$, 1.51 (2, 3, 3, 2) Å; C$_b$–O$_b$, 1.34 (2, 1, 1, 2) Å; C$_a$–C$_b$, 1.52 (3, 3, 9, 12) Å; C$_b$–C$_b$', 1.35 (4, 2, 2, 2) Å; C$_g$–Th–C$_g$, 134.9 (–, 12, 12, 2)°; O$_a$–Th–O$_b$, 52.7 (5, 4, 4, 2)°. Reprinted with permission from ref 17a. Copyright 1978 American Chemical Society. (B) Perspective ORTEP drawing of the non-hydrogen atoms in Cp'$_2$Th[OC(CH$_2$-*t*-Bu)C(PMe$_3$)O](Cl) (4). All atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. Important bond lengths (Å) and angles (deg) for chemically distinct groups of atoms are the following: Th–O$_1$ = 2.340 (9), Th–O$_2$ = 2.256 (8), Th–Cl = 2.753 (4), C$_1$–O$_1$ = 1.33 (2), C$_2$–O$_2$ = 1.35 (2), C$_1$–C$_2$ = 1.36 (2), C$_2$–P = 1.73 (1), P–C(methyl) = 1.79 (2, 1, 2, 3), O$_1$–Th–O$_2$ = 67.4 (3)°, O$_2$–Th–Cl = 78.3 (2)°, C$_1$–O$_1$–Th = 119.2 (9)°, C$_2$–O$_2$–Th = 120.197)°, (ring center of gravity)–Th–(ring center of gravity) = 133.6°. The Th, P, and neopentylmethylene carbon atoms are displaced from the O$_1$C$_1$C$_2$O$_2$ least-squares mean plane by +0.22, –0.11, and +0.652 Å, respectively. Reprinted with permission from ref 20. Copyright 1983 American Chemical Society.

and ^{13}C NMR assignments are set out in Table I. The ^{13}C labeling experiments also establish that the acyl–CO unit in **2** does not scramble with the second equivalent of added CO, but rather the incorporation is regiospecific.

η^2-Acyl–CO Coupling Reactions in the Presence of Phosphines. The reaction of Cp'$_2$Th(Cl)(η^2-COCH$_2$-*t*-Bu) (**1**) with carbon monoxide in the presence of either trimethyl- or triphenylphosphine results in the formation of the ylide complexes **3** and **4**, respectively, in high yield (eq 6). In each case the reaction is found to proceed



3a, R = Ph; *C = ^{12}C
3b, R = Ph; *C = ^{13}C
4 R = Me

cleanly (when monitored by NMR spectroscopy) and quantitatively (≥95%) within 5–6 h at room temperature and ca. 1 atm of CO. The ^{31}P chemical shifts of **3** and **4** appear at –1.8 and 2.30 ppm, respectively, and compare favorably with literature values for analogous ylides.[32] Also, **3b** exhibits a phosphorus–carbon coupling constant (δ *C = 117.8 ppm) of 123 Hz, indicative of a conjugated, ylide-like phosphorus–carbon bond.[32a] The ^{1}H NMR and infrared spectra as well as analytical data are also in accord with the proposed structures (see Experimental Section for details). Further verification has been provided by a single-crystal diffraction study[20] of **4** (Figure 2B). What appear to be single bond C–O contacts (1.33 (2) and 1.36 (2) Å)[14] and a double bond C$_1$–C$_2$ contact (1.36 (2) Å)[14,33] suggest an important contribution from resonance hybrid **F**.

Kinetic Studies of the Carbonylation of Cp'$_2$Th(Cl)(η^2-COCH$_2$-*t*-Bu) (1). The rate of conversion of the η^2-acyl **1** to

Table II. Rate Constants for the Coupling of Cp'$_2$Th(Cl)(η^2-COCH$_2$-*t*-Bu) (**1**) with CO at 30.8 °C

reaction	k_{obsd} ($\times 10^{-3}$ min^{-1})^c	P_{CO} (torr)
1 → **2**^{a}	9.44	592
1 → **3**^{a}	9.48	592
1 → 4	1.76	89
	4.61	310
	9.89	606
	12.03	831

^{a}Measured in toluene solution. ^{b}Measured in THF solution. ^{c}The estimated error in these values is 5%.

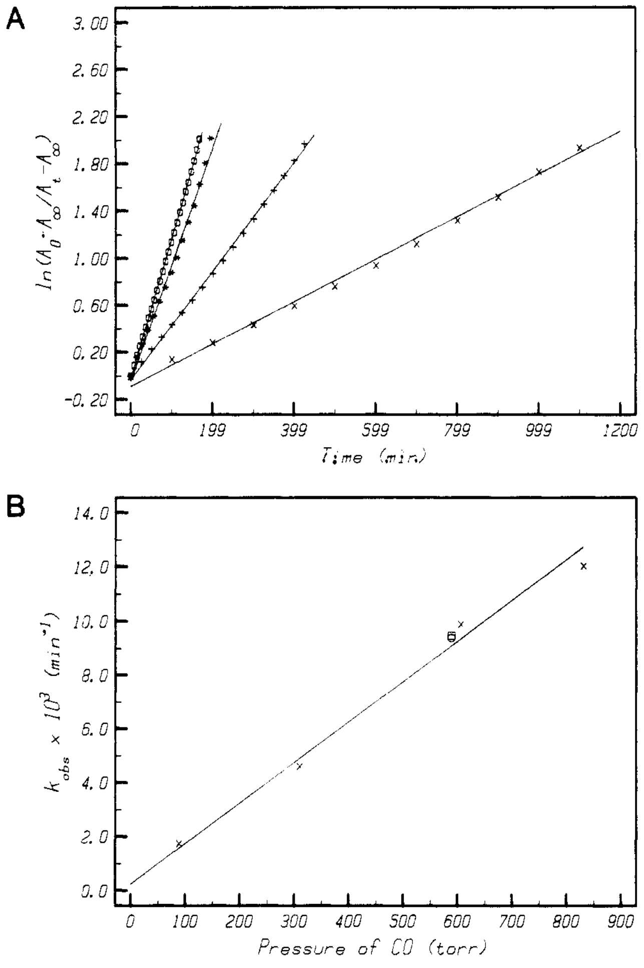


Figure 3. (A) Kinetic plots for the reaction of **1** with CO in the presence of excess PMe$_3$ at various CO pressures: □, 831 torr; *, 606 torr; +, 310 torr; ×, 89 torr. (B) Dependence of the observed rate constant on CO pressure: ×, **1** + excess PMe$_3$ → **4** in THF; □, **1** + excess PPh$_3$ → **3** in toluene; ○, **1** → **2** in toluene.

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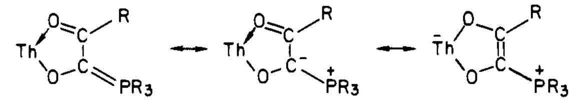
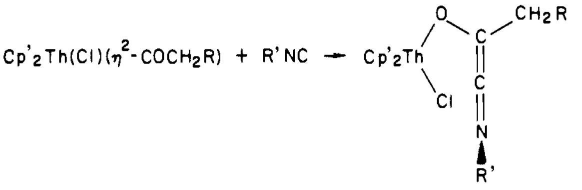


D **E** **F**

complexes **2**, **3**, or **4** was determined either spectrophotometrically by monitoring the disappearance of the band at 420 nm due to **1** or by gas uptake measurements (refer to the Experimental Section for details). Kinetic data are given in Table II and first-order plots are shown in Figure 3. At a given pressure of CO the rate of **1** → **4** was found to be first order in acyl over 3–4 half-lives. Furthermore, plots of k_{obsd} vs. P_{CO} were found to be linear with a zero intercept, indicating a first-order dependence on CO ($P_{\text{CO}} \propto$ [CO], assuming Henry's law is obeyed[34]). The rates of conversion of **1** to **2** or to **3** were found to be indistinguishable under equivalent conditions of CO pressure and temperature thereby implying a zero-order dependence on phosphine concentration. Also, because the observed (i.e., pseudo-first-order) rate constants for the conversion of **1** to **2** or to **3** were found to fall precisely on the line derived from the plot of k_{obsd} vs. P_{CO} for the reaction **1** → **4**, the carbonylation of **1** is also deduced to be independent of the solvent (THF vs. toluene) and of the phosphine used (PPh_3 vs. PMe_3). As a final check, no reaction was observed between complex **2** and triphenylphosphine, ruling out a possible cleavage of the dimer by phosphine to yield complexes **3** and **4**. Thus, the rate law for each carbonylation reaction is found to obey eq 7, where k = 1.50 (5) × 10^{-5} min^{-1} torr^{-1} at 30.8 ± 0.5 °C.

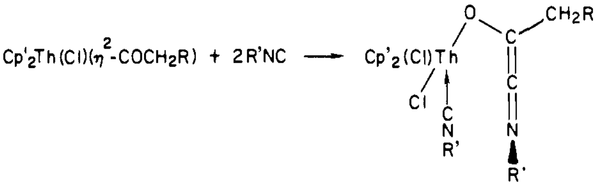
$$\text{rate} = k^1[\mathbf{1}][\text{CO}] = kP_{\text{CO}}[\mathbf{1}] \qquad (7)$$

η^2-Acyl–Isocyanide Coupling. Synthesis and Characterization of Ketenimine Complexes. Treatment of **1** or $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2Ph)$ with isocyanides affords the ketenimine complexes **5–8** (eq 8). With 2 equiv of isocyanide, the simple adducts **9–12** are obtained (eq 9). Both reactions proceed quantitatively within 30 min at room temperature as determined by ¹H NMR spectroscopy. Complexes **5–7**, however, were isolated as gummy oils or foams which were exceedingly difficult to manipulate. The isocyanide adducts **9–11** were isolated as solid, tractable powders, albeit with some difficulty. Consequently, complexes **5–7** were generally converted to the adducts for detailed characterization. In contrast, complex **8** was readily isolable as a yellow, crystalline solid, thus allowing a full structural characterization of this species (vide infra). Conversely, however, the isocyanide adduct **12** could not be isolated from the reaction solution. Upon workup, this compound was converted into a new complex (**13**), the structure and properties of which will be discussed below. Nevertheless, the reaction of η^2-acyl **1** with 2 equiv of $2,6\text{-}Me_2C_6H_3NC$ was found to first produce **12** quantitatively as determined by in situ ¹H NMR and infrared measurements, thus allowing partial characterization of this complex (vide infra). Organic ketenimines bearing nonaromatic groups are almost invariably isolated as viscous oils whereas those bearing aromatic groups tend to be crystalline solids at room temperature;[35] the complexes presented herein appear to follow this trend.



(8)

5, R = *t*-Bu, R' = *t*-Bu
6, R = Ph, R' = *t*-Bu
7, R = *t*-Bu, R' = C_6H_{11}
8, R = *t*-Bu, R' = $2,6\text{-}Me_2C_6H_3$

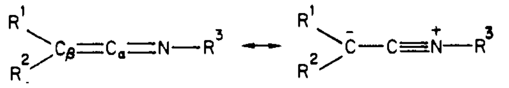


(9)

9, R = *t*-Bu, R' = *t*-Bu
10, R = Ph, R' = *t*-Bu
11, R = *t*-Bu, R' = C_6H_{11}
12, R = *t*-Bu, R' = $2,6\text{-}Me_2C_6H_3$

The new ketenimine complexes were readily characterized by infrared and ¹H NMR spectroscopy. Thus, complexes **5–8** and **9–12** exhibit a strong transition in the infrared spectrum at ca. 2000 cm^{-1}, attributable to a ketenimine CCN vibration.[35] In addition to this band, complexes **9–12** display a band due to coordinated isocyanide approximately 30 cm^{-1} higher in energy than that of the free ligand. This shift toward higher frequency is consistent with coordination to an electron-deficient metal center.[36] The unperturbed, high-energy position of the ketenimine ν_{CCN} vibration as well as the insensitivity of this band to additional isocyanide ligation rule out coordination of the ketenimine to the metal via the nitrogen lone pair or the π system. Both σ- and π-coordinated ketenimines of this latter type exhibit stretcthing frequencies assigned to ν_{CCN} at 1700–1450 cm^{-1}.[37] The ¹H NMR spectra of the present complexes are also in accord with the above structural assignment. Due to the asymmetric nature of the ketenimine ligand, the methylene and pentamethylcyclopentadienyl protons appear as diastereotopic pairs in the ¹H NMR spectra. Complex **8** proved to be somewhat anomalous and was found to exhibit sharp singlets in the ¹H NMR spectrum (25 °C) for both the Cp' and methylene protons. At low temperatures, however, the Cp' resonance was found to broaden and eventually (T_c ~ −77 °C) separate into two distinct resonances in a 1:1 ratio. The $\Delta G^{\ddagger}$ for this dynamic process is estimated[38] to be 9.6 (5) kcal/mol at the coalescence temperature. Unfortunately, the downfield Cp' resonance obscures the methylene region and the diagnostic AB pattern expected for these protons cannot be identified.

The free energy barrier to nitrogen inversion (racemization) in most organic ketenimines lies in the range of ca. 7–15 kcal/moi.[35,39] In these cases, the barrier to inversion of sp² nitrogen is attributed to contributions from resonance hybrid **H** in the transition state. As this picture predicts, electron-withdrawing groups attached to C_β lower the barrier to racemization.[35,39] In



G **H**

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[33] C–C = 1.501 (5) Å (CH_3CHO); C–C = 1.534 (5) Å (C_2H_6), 1.337 (5) Å (C_2H_4); C–P = 1.841 (5) Å ($P(CH_3)_3$).[14b]

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[39] (a) Jochims, J. C.; Herzberger, S.; Gambke, B.; Anet, F. A. L. *Tetrahedron Lett.* **1977**, 2255–2258. (b) Firl, J.; Runge, W.; Hartmann, W.; Utikal, H.-P. *Chem. Lett.* **1975**, 51–54. (c) Reilly, J. L.; Krow, G. R.; Ramey, K. C. *J. Org. Chem.* **1972**, *37*, 2364–2366. (d) Krow, G. R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 435–528. (e) Anet, F. A. L.; Jochims, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 5524–5525.

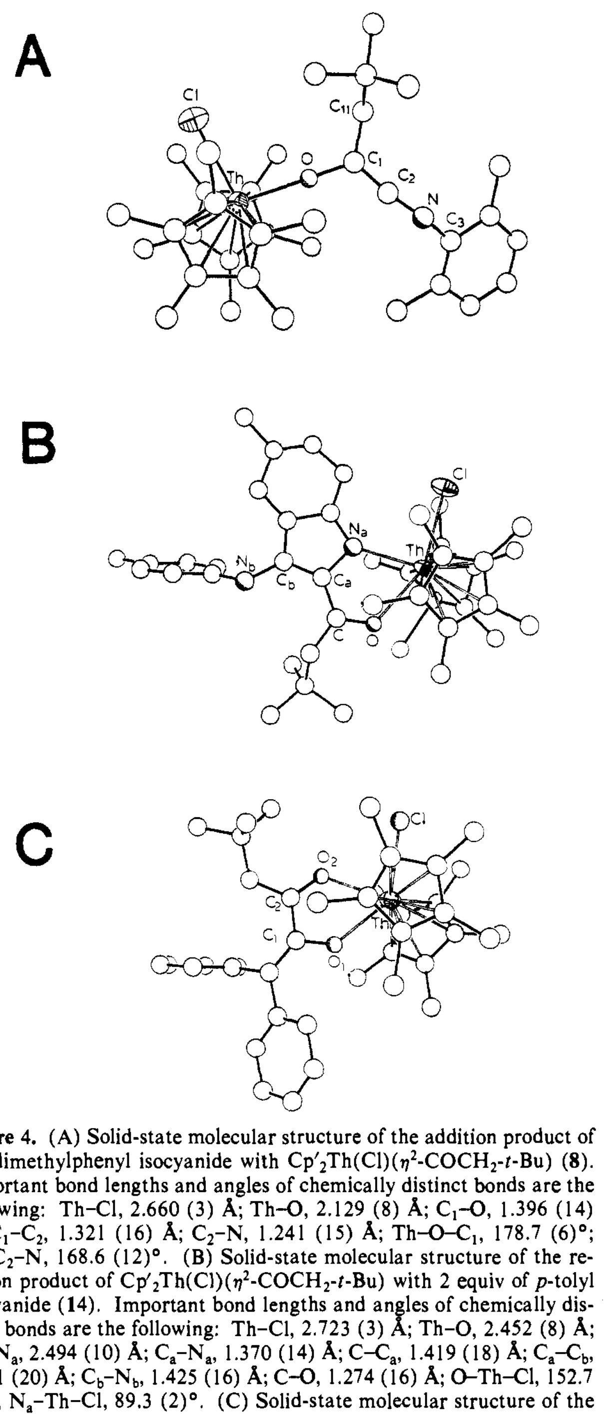
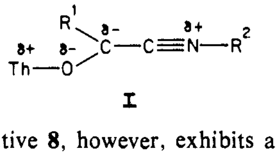


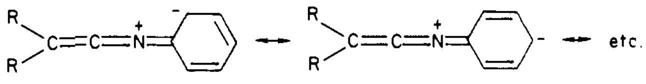
Figure 4. (A) Solid-state molecular structure of the addition product of 2,6-dimethylphenyl isocyanide with Cp$'_2$Th(Cl)(η^2-COCH$_2$-*t*-Bu) (**8**). Important bond lengths and angles of chemically distinct bonds are the following: Th–Cl, 2.660 (3) Å; Th–O, 2.129 (8) Å; C_1–O, 1.396 (14) Å; C_1–C_2, 1.321 (16) Å; C_2–N, 1.241 (15) Å; Th–O–C_1, 178.7 (6)°; C_1–C_2–N, 168.6 (12)°. (B) Solid-state molecular structure of the reaction product of Cp$'_2$Th(Cl)(η^2-COCH$_2$-*t*-Bu) with 2 equiv of *p*-tolyl isocyanide (**14**). Important bond lengths and angles of chemically distinct bonds are the following: Th–Cl, 2.723 (3) Å; Th–O, 2.452 (8) Å; Th–N_a, 2.494 (10) Å; C_a–N_a, 1.370 (14) Å; C–C_a, 1.419 (18) Å; C_a–C_b, 1.411 (20) Å; C_b–N_b, 1.425 (16) Å; C–O, 1.274 (16) Å; O–Th–Cl, 152.7 (2)°; N_a–Th–Cl, 89.3 (2)°. (C) Solid-state molecular structure of the coupling product of Cp$'_2$Th(Cl)(η^2-COCH$_2$-*t*-Bu) and diphenylketene (**15**). Important bond lengths of chemically distinct bonds are the following: Th–Cl, 2.690 (2) Å; Th–O_1, 2.269 (6) Å; Th–O_2, 2.481 (6) Å; C_1–O_1, 1.345 (11) Å; C_2–O_2, 1.24 (12) Å; C_1–C_2, 1.504 (13) Å. Structures A–C are reprinted with permission from ref 1a. Copyright 1985 Reidel.

the present systems, the partial negative charge on oxygen would be expected to energetically disfavor an analogous hybrid such as **I**, resulting in an increased barrier to inversion. The stereochemical rigidity of derivatives **5**–**7** may thus be accounted for.

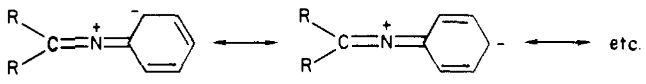


I

The *N*-aryl derivative **8**, however, exhibits a lower barrier to inversion than that of the *N*-alkyl analogues and more typical of ketenimines in general. Aryl substituents on nitrogen are known to lower the barrier to inversion in both ketenimines[39] and ketimines.[40] Contributing resonance structures such as **J** and **K** have been invoked to account for the lowered barrier. It is also known[40]



J



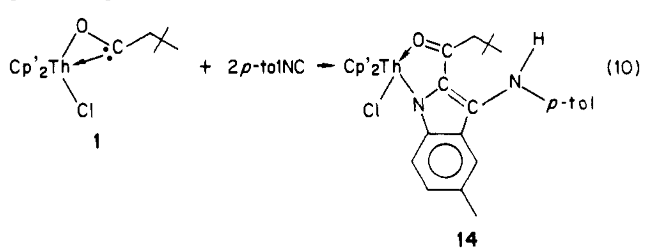
K

that *o*-alkyl substituents substantially reduce inversion barriers in *N*-aryl ketimines—an effect that is presumably steric in origin. Thus, the reduced barrier to racemization in complex **8** may be understood in terms of electronic and steric effects.

The ^{13}C NMR spectrum of complex **8** is also consistent with the assigned structure. In particular, the resonances of C_α and C_β (C_β=C_α=N) are found at δ 216.8 and 110.3, respectively. These values are at lower field than those typically observed (δ 189–196 for C_β, δ 37–78 for C_α) for simple organic ketenimines (i.e., those bearing alkyl and aryl substituents).[35,39b] However, the presence of a heteroatom substituent on the cumulene is expected to result in a downfield shift for these resonances, as is observed for $C_6H_{11}N{=}C{=}C(OCH_3)(CH_3)$, where δ C_α = 206.3 ppm and δ C_β = 110.7 ppm.[41,42] Final verification of the proposed structure of **8** has been provided by a single-crystal diffraction study.[1a,26] As already mentioned, full details will be provided in a forthcoming contribution devoted entirely to the comparative structural chemistry of organoactinide carbonylation products;[26] the overall result and several relevant metrical details are given in Figure 4A.

Multiple η^2-Acyl–Isocyanide Coupling Reactions. During our quest for crystalline actinide ketenimine complexes, we attempted to synthesize derivatives bearing aromatic groups since such substituents are known to impart crystallizability to organic ketenimines (vide supra).[35] Although ketenimine **8** was, in fact, isolated as a crystalline solid, the corresponding isocyanide adduct **12** was found to undergo a followup reaction to yield a new complex, **13**, and **12** could not be isolated in a pure state. Also, treatment of acyl compound **1** with greater than 2 equiv of *p*-tolyl isocyanide (*p*-tolNC) in toluene results in the formation of brilliant red needles of complex **14** within 15 min at room temperature. The infrared spectra of **13** and **14** do not exhibit features in the 2500–1700 cm^{-1} region characteristic of a ketenimine complex; however, a band assignable to an N–H stretching transition is observed in the spectrum of **14**.

The molecular structure of **14** has been determined by X-ray diffraction and will be discussed in detail elsewhere.[26] It suffices for the present to indicate that the diffraction analysis (Figure 4B) reveals the unusual coupling reaction shown in eq 10. The spectroscopic data (^{1}H and ^{13}C NMR, IR) obtained for the



(10)

complex are entirely consistent with the structure. First, the ^{1}H NMR spectrum exhibits two distinct aromatic methyl resonances in addition to Cp$'$, CH$_2$, and *t*-Bu signals in the proper intensity ratios. Also, a somewhat broad N–H resonance is observed at 5.72 ppm. Second, in the high-field (67.8 MHz) ^{13}C NMR spectrum, all 20 unique carbon atoms can be located; both the ^{13}C chemical shifts and spin multiplicities are consistent with the

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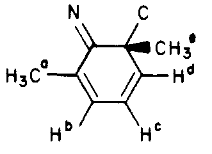
(40) McCarty, C. G. In "The Chemistry of the Carbon–Nitrogen Double Bond"; Patai, S., Ed.; Wiley-Interscience: New York, 1970; Chapter 9, pp 405–408.

Table III. ^{1}H NMR Spectral Assignments for the Diene Protons in $Cp'_2Th(Cl)(C_{27}H_{29}N_2O)$ (13)

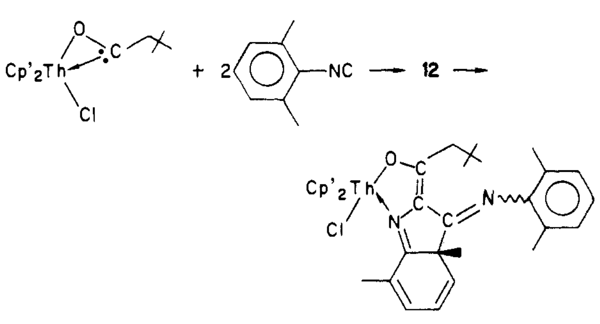


	H^a	H^b	H^c	H^d	H^e
δ	2.33 (d)	5.58 (m)	5.44 (dd)	5.92 (dd)	1.04 (s)

J_{ab} = 0.9 Hz J_{bc} = 5.5 Hz
J_{bd} = 0.5 Hz J_{cd} = 9.0 Hz

above structure. Finally, a sharp band in the infrared at 3373 cm^{-1} can be attributed to ν_{NH}.

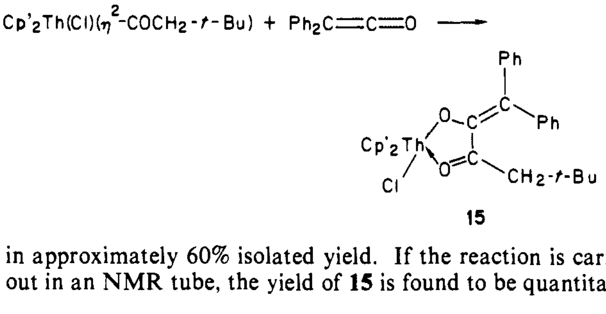
On the basis of the above structure determination and the following spectroscopic evidence, the final product (**13**) from the reaction of **1** with $2,6\text{-}Me_2C_6H_3NC$ is proposed to be as shown in eq 11. The ^{1}H NMR spectrum of **13** exhibits both diastereotopic Cp′ rings and methylene protons, consistent with the lack of mirror symmetry. The diene ring protons are readily located in the ^{1}H NMR spectrum at 5.4–6.0 ppm, and decoupling experiments are consistent with the ring fusion shown in eq 11 (see Table III for assignments). Also of interest in the ^{1}H NMR is the fact that four distinct methyl resonances (neglecting the *t*-Bu and Cp′ resonances) are observed, suggesting that hindered rotation about the nitrogen–$2,6\text{-}Me_2C_6H_3$ bond is occurring. Consequently, in addition to the two unique methyl groups on the fused ring, the aryl methyl protons are also magnetically inequivalent. This observation is further supported by the ^{13}C NMR spectrum where four distinct methyl carbon resonances (again, neglecting the Cp′ and *t*-Bu resonances) are observed at 23.3, 21.8, 20.1, and 19.5 ppm. Also, it can be seen that hindered rotation about the nitrogen–aryl bond renders not only the aryl methyl carbon atoms inequivalent but also every carbon atom within the aryl ring. Indeed, a total of 26 distinct carbon resonances (with the correct spin multiplicities) are observed in the 68-MHz ^{13}C spectrum, including the diastereotopic ring carbons (Δδ = 0.09 ppm for the Cp′ methyl carbons, Δδ = 0.07 ppm for the Cp′ ring carbons). These data, along with the structural characterization of **14**, are therefore entirely consistent with a structure such as **13**.



(11)

13

The Insertion of Diphenylketene into the Thorium–Carbon Bond of a η^2-Acyl Complex. Reaction of acyl complex **1** with diphenylketene proceeds as shown in eq 12. Orange crystals of the insertion product **15** may be obtained from hydrocarbon solvents in approximately 60% isolated yield. If the reaction is carried out in an NMR tube, the yield of **15** is found to be quantitative after several hours at 55 °C. The molecular structure of **15** follows straightforwardly from the ^{1}H NMR, infrared, and analytical data (see Experimental Section for details) and, as will be discussed in detail elsewhere,[26] has been confirmed by X-ray diffraction (Figure 4C). Structural parameters are in good agreement with the valence bond description of **15** shown above.

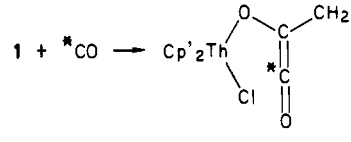


(12)

15

Discussion

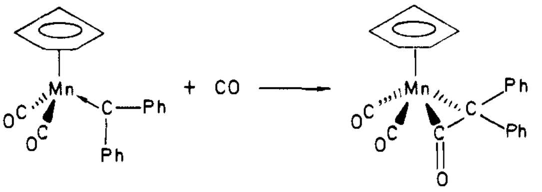
In the presence of less than 1 atm of CO, η^2-acyl complex **1** is found to undergo coupling with one molecule of carbon monoxide per thorium ion to form the enedionediolate complex **2**. Because the acyl is synthesized from $Cp'_2Th(Cl)(CH_2\text{-}t\text{-}Bu)$ and CO, the formation of this dimer represents the direct coupling of four carbon monoxide molecules in a linear array. To date, there is only one other example of this type of reaction in the literature.[2] If the present reaction is monitored by either ^{1}H NMR or infrared spectroscopy, no intermediates are detected. This result along with the results of the ^{13}C labeling study suggest that the initial step in the formation of **2** may involve a rate-determining coupling of the η^2-acyl with CO to yield a transitory ketene-like species (e.g., **3** in eq 13).[43] If the η^2-acyl precursor is viewed as having significant oxycarbene character (i.e., B) then this reaction may be understood in terms of a carbene-like coupling reaction with CO (eq 14). Coupling reactions of this type have been used in some cases to trap carbenes.[21] More importantly, there exist many examples in which transition-metal carbene and carbyne complexes have been shown to undergo coupling with CO to yield ketene complexes,[22] cf. eq 15[22d] and 16.[22f] In order to better understand the nature of this reaction, the following mechanistic study was carried out.



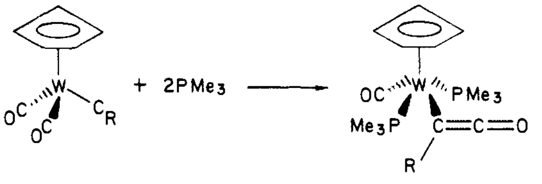
(13)

3

(14)



(15)



(16)

If in fact an intermediate ketene complex such as **3** is formed during the carbonylation of **1**, such a species may be susceptible to trapping reactions common to more classical ketenes. Typically, ketenes undergo nucleophilic attack at the α-carbon atom.[44a] They are usually trapped with reagents such as alcohols or primary and secondary amines, resulting in the formation of esters or amides,

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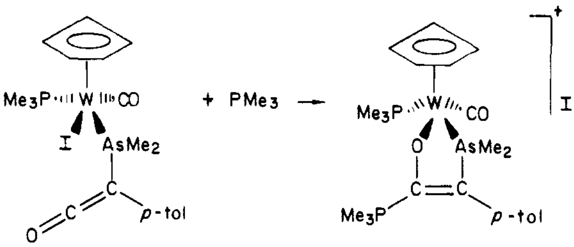
(41) Kreiter, C.; Aumann, R. *Chem. Ber.* **1978**, *111*, 1223–1227.

(42) Gill, D. S.; Baker, P. K.; Green, M.; Paddick, K. E.; Murray, M.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 986–988.

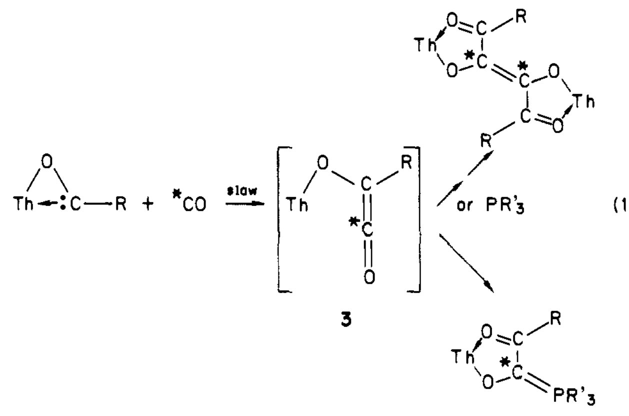
(43) While the kinetic data provide information on the stoichiometry of **3**, they do not, of course, indicate the structure. Some degree of interaction in **3** of the thorium center with either the carbon (*C) or oxygen atom (or both) of the added CO cannot be rigorously ruled out.

(44) (a) Black, P. In "The Chemistry of Ketenes, Allenes, and Related Compounds"; Patai, S., Ed.; Wiley-Interscience: New York, 1980; Chapter 9, pp 309–342. (b) Fagan, P. J., unpublished observations.

respectively. Since such traps are incompatible with the thorium η^2-acyl complex (and organoactinides in general) it was decided to employ phosphines, which are unreactive toward the η^2-acyl,[44b] as the nucleophilic trapping reagent. As shown in eq 6, this approach proved successful and the ylide complexes **3** and **4** are formed in quantitative yield as determined by ^{1}H NMR. This reaction is most plausibly the result of attack by phosphine at the ketene α-carbon with commensurate coordination of the ketene oxygen to thorium. Kreissl et al. have recently reported a similar reaction between an isolable ketene complex and trimethylphosphine as shown in eq 17.[45] The ^{13}C labeling studies for each (i.e., the dimerization and trapping) reaction are also compatible with the proposed reaction scheme. From these results it is deduced that the carbon atom of the added CO molecule is incorporated at the α-carbon position of the proposed ketene intermediate (eq 18).[43]



(17)

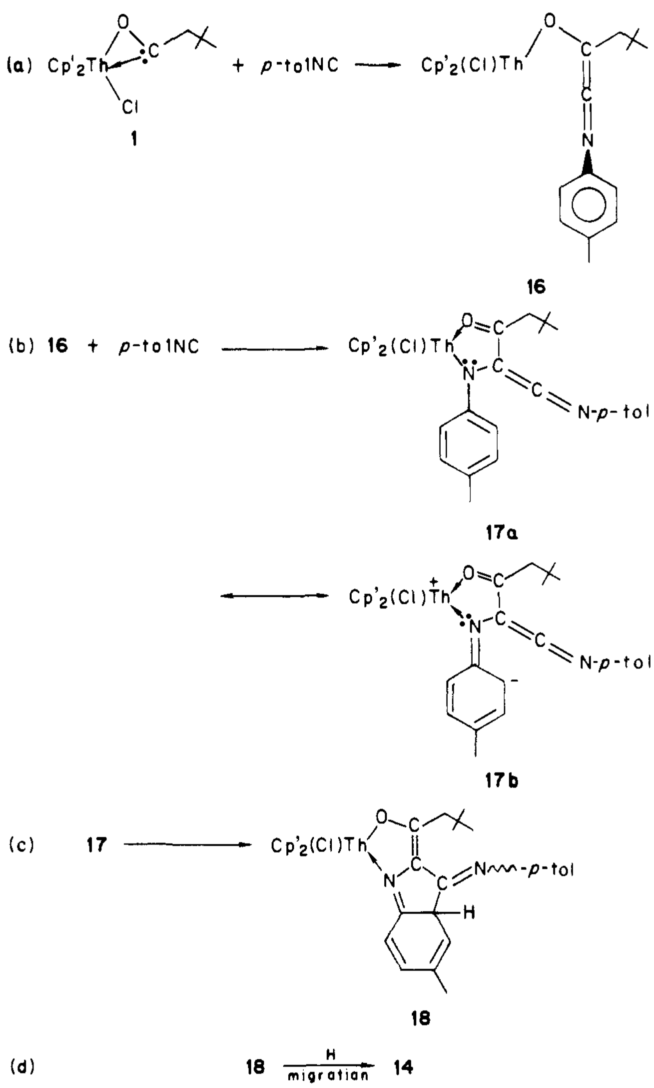


(18)

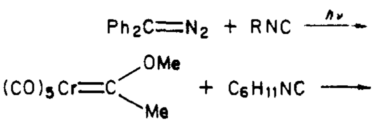
If in fact the phosphine is trapping a reactive intermediate common to both of these reactions and trapping occurs after the rate-determining step, then the kinetic behavior of each reaction should be identical. That is, if the rate-determining step involves coupling of CO with the η^2-acyl to yield a reactive ketene intermediate (or a species which exhibits the reactivity of or undergoes rearrangement to a ketene), then both reactions would be expected to exhibit a first-order dependence on both acyl and CO concentration as well as to proceed at the same rate under identical reaction conditions. The rates must also be independent of phosphine concentration and the type of phosphine used if this scenario is correct. As discussed above, a full kinetic study shows that these requirements are indeed fulfilled by the acyl carbonylation reactions. Kinetically, then, the formation of the dimer **2** and the ylides **3** and **4** is entirely compatible with the reaction sequence shown in eq 18.

To gather further evidence for the formation of ketenes from carbene-like η^2-acyls and CO, model reactions with the isoelectronic isocyanides were investigated. As described above and indicated in eq 7 and 8, the reaction of a variety of isocyanides with acyl complex **1** or with $Cp'_2Th(Cl)(\eta^2\text{-}COCH_2Ph)$ results in a coupling reaction to form ketenimine complexes **5–8** and **9–12**. The coupling of carbenes (free[39d,46] or metal bound[41]) with isocyanides to yield ketenimines has ample precedent (eq 19 and 20) and directly parallels the coupling of carbenes and CO to yield ketenes (free or complexed, eq 15 and 16). Thus, the synthesis of these ketenimine complexes appears to be a credible model for the CO/acyl coupling reaction.

Scheme I. Proposed Pathway for the Formation of Complex 14



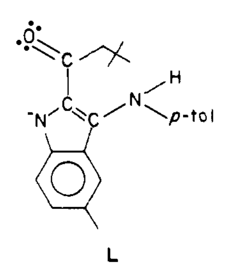
$$Ph_2C{=}N_2 + RNC \xrightarrow{h\nu} Ph_2C{=}C{=}NR \qquad (19)^{39d}$$



$$(CO)_5Cr{=}C(OMe)(Me) + C_6H_{11}NC \longrightarrow$$

$$(CO)_5Cr[(Me)(MeO)C{=}C{=}N(C_6H_{11})] \qquad (20)^{41}$$

While exploring the coupling reactions of isocyanides with the η^2-acyls, an interesting reaction was discovered involving aryl isocyanides. Treatment of **1** with 2 equiv of *p*-tolNC proceeds according to eq 9 to yield the coupling product **14** as brilliant red needles. As shown by X-ray diffraction (Figure 4B),[26] the acyl ligand has undergone coupling with two isocyanide molecules, resulting in the formation of a chelating acetylindolate ligand **L**. A possible mechanism for this reaction is depicted in Scheme I.



L

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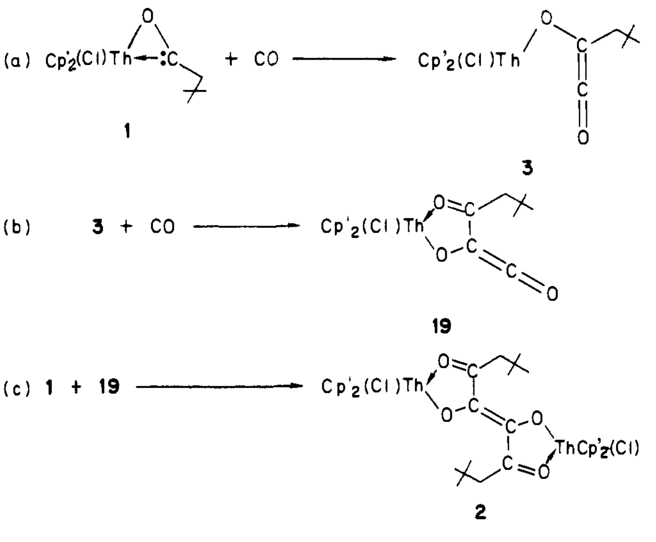
(45) Kreissl, F. R.; Wolfgruber, M.; Sieber, W. J. *Organometallics* **1983**, *2*, 1266–1267.

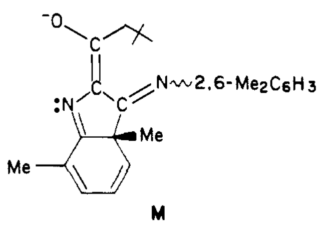
(46) (a) Takizawa, T.; Obata, N.; Suzuki, Y.; Yanagida, T. *Tetrahedron Lett.* **1969**, 3407–3410. (b) Muramatsu, M.; Obata, N.; Takizawa, T. *Tetrahedron Lett.* **1973**, 2133–2136. (c) Obata, N.; Mizuno, H.; Koitabashi, T.; Takizawa, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2287–2293.

Scheme II. Proposed Pathway for the Formation of $\{Cp_2Th[OC(CH_2\text{-}t\text{-}Bu)CO](Cl)\}_2$ (**2**)



step a we propose that the acyl complex undergoes coupling with 1 equiv of isocyanide to form the ketenimine **16**. This postulate is, of course, founded on chemistry presented above where analogous species were isolated and fully characterized. If ketenimine **16** is in fact formed, it would be expected that the cumulene α-carbon would be susceptible to nucleophilic attack. Ketenimines readily undergo such reactions with nucleophiles in the same manner as that discussed above for ketenes.[35] Also, there is ample evidence (vide supra) that the isoelectronic ketene complex **3** readily undergoes nucleophilic attack by phosphines. On the basis of this precedent and the nucleophilic nature of isocyanides, it is reasonable that, subsequent to the initial coupling reaction, ketenimine **16** would undergo a coupling reaction with a second equivalent of isocyanide to yield a new ketenimine complex, **17** (step b). The greater susceptibility of the *N*-aryl ketenimine complexes to nucleophilic attack vis-à-vis the *N*-alkyl analogues likely reflects the electron-withdrawing character of the aryl substituent in the former. To explain the ring fusion reaction, it should be recognized that a chelating arylamido ligand has been formed. This lends credibility to a resonance hybrid such as **17b** in which negative charge may be delocalized from the thorium-bound nitrogen atom onto the ortho (and para) positions of the aryl ring. Now, since both an electrophilic center (the ketenimine α-carbon atom) and a nucleophilic center (the ortho carbon atom) are held in close proximity, carbon–carbon bond formation (and ring fusion) may occur (step c). Finally, migration of the ortho hydrogen to nitrogen reforms the aromatic ring and yields the observed product (step d).

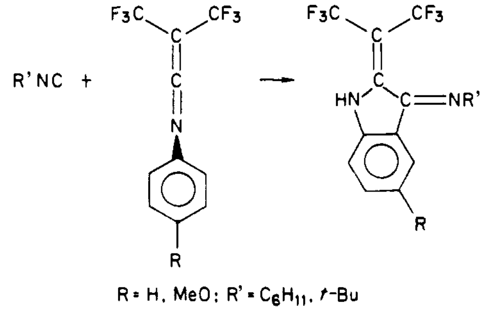
Reaction Scheme I also explains the formation of the product **13** from the reaction of η^2-acyl **1** with 2 equiv of $2,6\text{-}Me_2C_6H_3NC$. For this isocyanide, the initial coupling product, ketenimine complex **8**, is a stable, isolable compound. Addition of a second equivalent of $2,6\text{-}Me_2C_6H_3NC$ results in the initial formation of a simple isocyanide adduct (**12**), which then slowly undergoes conversion to a complex containing the chelating ligand **M**. The



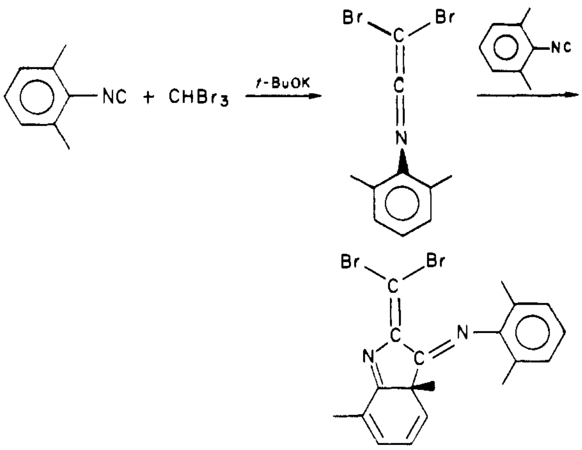
M

formation of this species is proposed to proceed through the same reaction pathways as that for **14**. The only difference in this example is that methyl is an inferior migrating group relative to hydrogen and consequently the reaction is halted at step c of Scheme I.

The coupling of aryl isocyanides with ketenimines to yield indole and indolenine derivatives has considerable precedent[46,47] and offers further support for the above proposals. Thus, the reactions shown in eq 21 and 22 exactly parallel the results presented herein.

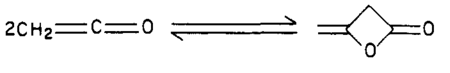


(21)[46]

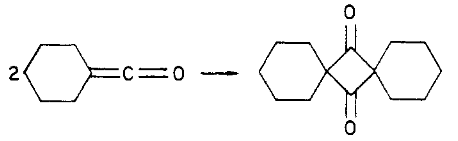


(22)[47]

It is now of interest to consider possible reaction pathways leading from the intermediate ketene complex **3** to the dimer **2**. Because the enedionediolate **2** is simply a dimer of the ketene **3**, it is attractive to consider this reaction in terms of a simple dimerization reaction. Although ketenes are known to undergo dimerization (cf. eq 23 and 24)[43] they are not known to form

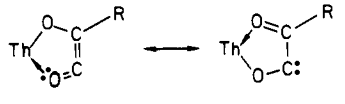


(23)



(24)

dimers in the manner observed for **2**.[48] One possible mechanism for a dimerization reaction, however, could involve initial coordination of the oxygen atom of the ketene to the very oxophilic thorium atom (**N**, **O**). Here a resonance hybrid such as **N** de-



N **O**

scribes the ketene α-carbon atom as carbene-like. Because many carbenes are known to undergo coupling to form olefins, dimerization of a species such as **O** could account for the formation of **2**. A carbene-like structure for the intermediate ketene would also account for the trapping reactions with trimethyl- and tri-

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(47) Del'-tsova, D. P.; Avetisyan, E. A.; Gambaryan, N. P.; Knunyants, I. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1973**, 355–358.

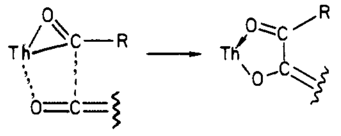
(48) Of course, it is impossible to predict if or how the presence of a thoroxy substituent on a ketene might alter the mode of dimerization.

phenylphosphine to yield the ylide complexes **3** and **4**.

A mechanism for enedionediolate formation involving the dimerization of species such as **N**, **O** suffers from two major deficiencies. First, the contributing hybrid **N** would appear, from the required distortion of the cumulene fragment, to be of prohibitively high energy content. Indeed, nitrogen lone-pair coordination to thorium is not observed in the isoelectronic ketenimine complexes **5–8** (vide supra).[49] Thus, in this picture, carbene structure **O** would be the major contributor to a bonding description. However, we find that the reaction of **1** with CO to produce **2** is neither diverted by nor impeded by the addition of olefins. Thus, in the presence of ca. 3 equiv of *trans*-PhHC=CHPh or in neat $Me_2C{=}CMe_2$, no cyclopropane formation is observed and only complex **2** is detected as the reaction product. This result appears to argue against an intermediate such as **O** to account for the dimerization reaction.[50]

A second plausible pathway for the formation of **2** is shown in Scheme II. First, the rate-determining reaction of acyl **1** with CO to yield a transient ketene (step a) has already been discussed in ample detail. The second step b involves nucleophilic attack by CO on the ketene α-carbon to yield the new ketene complex **19**. There is also ample support for this proposal. First, ylide complexes **3** and **4** are reasonably described as the nucleophilic interception products of such an intermediate (eq 6). Second, this type of coupling reaction directly parallels that proposed for the formation of **13** and **14** (Scheme I, step b). The reaction of isocyanides with ketenimines therefore provides a plausible model for the coupling of carbon monoxide with thorium-bound ketenes.

The final step of this sequence involves a reaction of the ketene **19** with starting acyl **1** to form the observed product (**2**, step c). In order to model this step of the sequence, the reaction between acyl **1** and diphenylketene was investigated. As described above, this reaction proceeds smoothly and quantitatively to form complex **15**. This reaction can be understood formally in terms of an insertion of a ketene into a actinide–carbon bond to yield an alkoxide (eq 25).[51] In the present example, the only difference is that a chelating alkoxide is formed. Therefore, justification



(25)

for the last step of this reaction sequence is provided.

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Registry No. 1, 99112-54-6; **2a**, 99147-69-0; **2b**, 99127-92-1; **2c**, 99127-93-2; **3a**, 99112-55-7; **3b**, 99112-56-8; 4, 99112-57-9; **5**, 99127-94-3; **6**, 99112-66-0; **7**, 99112-67-1; **8**, 99112-58-0; **9**, 99112-65-9; **10**, 99112-59-1; **11**, 99112-60-4; **12**, 99112-61-5; **13**, 99112-62-6; **14**, 99112-63-7; **15**, 99112-64-8; $Cp_2Th(\eta^2\text{-}^{13}COCH_2\text{-}t\text{-}Bu)Cl$, 99147-67-8; $Cp_2Th(Cl)(\eta^2\text{-}COCH_2Ph)$, 99147-68-9; PPh_3, 603-35-0; PMe_3, 594-09-2; *t*-BuNC, 7188-38-7; 2,6-$Me_2C_6H_3NC$, 2769-71-3; $C_6H_{11}NC$, 931-53-3; *p*-tolNC, 7175-47-5; CO, 630-08-0; ^{13}CO, 1641-69-6; diphenylketene, 525-06-4.

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(49) The substitution of the ketenimine nitrogen atom admittedly alters the steric aspects of the lone-pair coordination.

(50) It is difficult to predict the exact degree to which species such as **O** will conform to the behavior of typical heteroatom-substituted nucleophilic carbenes (e.g., $(MeO)_2C$:). Sufficient nucleophilic character results in preferential dimerization over addition to olefins. However, monoxycarbenes such as (PhO)(H)C: are readily trapped by simple olefins such as tetramethylethylene.[15b]

(51) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.

(52) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Studies on the Mechanism of Transition-Metal-Assisted Sodium Borohydride and Lithium Aluminum Hydride Reductions

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Abstract: Studies on the course of transition-metal-assisted $NaBH_4$ and $LiAlH_4$ reductions of (1) nitriles, (2) alkenes, and (3) alkyl halides are described. (1) The kinetics of benzonitrile (PhCN) reduction indicate that at high nitrile:catalyst ratios, the rate of reduction is independent of PhCN concentration. Furthermore, the rate of PhCN reduction exhibits a first-order dependence on $NaBH_4$ concentration, as measured over a fourfold range of BH_4^- concentrations and several half-lives of PhCN. Moreover, when PhCN was reduced with equimolar mixtures of $NaBH_4$ and $NaBD_4$, a significant primary kinetic isotope effect was observed. Rapid complexation of PhCN to the boride surface apparently activates the nitrile group toward rate-determining hydride addition from dissolved, uncoordinated $NaBH_4$. (2) The selective reduction of alkenes by $NaBH_4$–$CoCl_2$ is attributed to adventitious heterogeneous catalytic hydrogenation. (3) The combination of $LiAlH_4$ with $CoCl_2$ forms a black precipitate of cobalt aluminide (CoAl) which was isolated, analyzed by atomic absorption spectroscopy, and shown to play an essential catalytic role in the reduction of alkyl halides. Labeling experiments demonstrate stereochemical randomization by a heterogeneous process involving solvent as the hydrogen donor and $LiAlH_4$ as a co-reductant. A radical mechanism involving halide atom transfer or oxidative addition to the aluminide is proposed.

Since their discovery four decades ago in the laboratories of Professor H. I. Schlesinger,[1,2] both sodium borohydride ($NaBH_4$) and lithium aluminum hydride ($LiAlH_4$) have become the preeminent reducing agents of modern organic chemistry. All