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Carbon Monoxide Activation by Organoactinides. Catalytic Hydrogenation of Inserted CO

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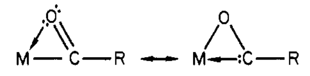
Organoactinide compounds provide an unusual opportunity to assess the chemical consequences of carbon monoxide activation in an environment of high oxophilicity and kinetic lability. In an investigation of the properties of the carbene-like η^2-acyl migratory insertion products (A, B),[1] we have explored their reactivity with



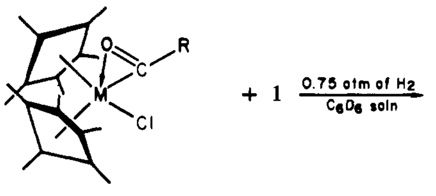
A B

M = Th, U

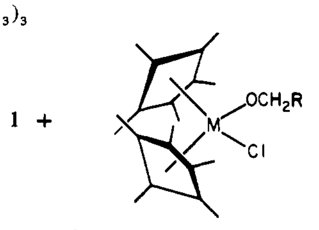
R = hydrocarbyl functionality

respect to metal hydrides. We report here that homogeneous hydrogenation of the η^2-acyls to the corresponding alkoxide derivatives [$M(\eta^2\text{-COR}) \rightarrow M{-}OCH_2R$] can be readily effected at room temperature and less than 1 atm of H_2 pressure by using the hydride $(Th[(CH_3)_5C_5]_2H_2)_2$ (**1**)[2] as a catalyst.

The η^2-acyl **2a** reacts with H_2 at 0.75 atm according to eq (1)



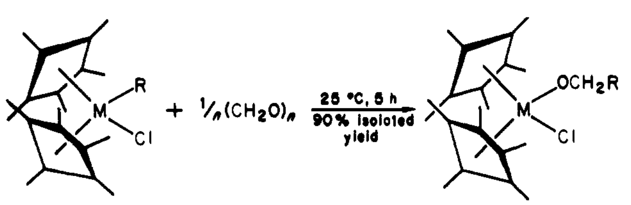
2a, M = U; R = C_6H_5
b, M = Th; R = $CH_2C(CH_3)_3$



(1)

3a, M = U; R = C_6H_5
b, M = Th; R = $CH_2C(CH_3)_3$

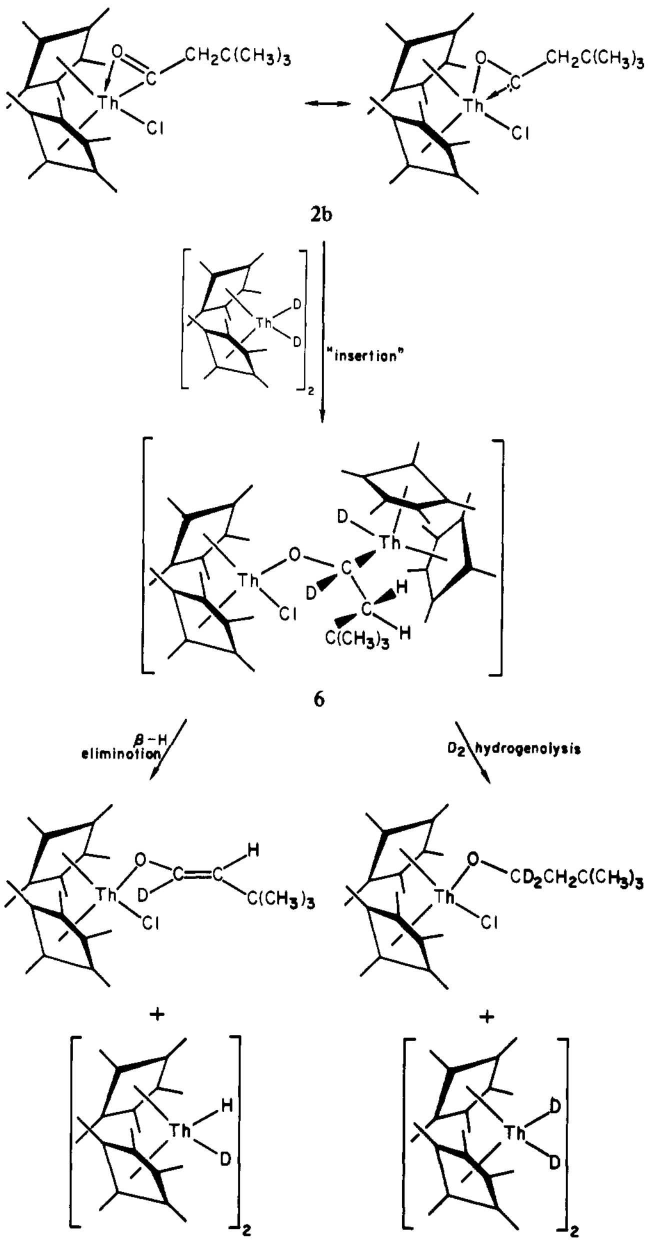
to yield the corresponding alkoxide **3a**. Compound **2b** undergoes an analogous catalytic hydrogenation (eq 1) under these conditions; however, a competing and informative catalytic side reaction (vide infra) is also observed. For [**1**] = 5.8×10^{-4} M and [**2a**] = 3.1×10^{-3} M, the initial hydrogenation turnover frequency (N_t) per ThH_2 moiety at 35 °C is 0.9 h^{-1}, while for [**1**] = 1.3×10^{-3} M and [**2b**] = 9.0×10^{-3} M, N_t = 4.8 h^{-1}. Upon completion of these reactions, compound **1** can be recovered quantitatively. In a preparative-scale reaction, the **1**/**2a** system was run for 50 turnovers with negligible degradation of the catalyst. The alkoxide reduction products were characterized by standard techniques.[3a] Furthermore, authentic samples could be prepared by reacting the appropriate $M[(CH_3)_5C_5]_2Cl_2$ compounds with $NaOCH_2R$ in ethereal solvents or, preferentially (and more interestingly), via the facile reaction of the hydrocarbyl precursors with a stoichiometric quantity of paraformaldehyde in toluene (eq 2).[4]



3a,b

(2)

Scheme I



Mechanistic information on the hydrogenation reaction is provided by deuterium labeling studies as well as by the elucidation of the aforementioned side reaction, which is exclusive in the absence of H_2. When compounds **2a** and **2b** are treated with

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[1] (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393-5396. (b) Fagan, P. J.; Maatta, E. A.; Marks, T. J. *ACS Symp. Ser.*, in press.

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[3] (a) All new compounds gave satisfactory elemental analyses and ^1H NMR and infrared spectra. (b) No H-D exchange involving $(CH_3)_5C_5$ hydrogen atoms is detected under the conditions of this reaction. It does, however, occur at higher temperatures.[3c] (c) Fagan, P. J.; Maatta, E. A.; Manriquez, J. M.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.*, in press.

[4] This appears to be a general reaction pattern for f-element hydrocarbyls: Maatta, E. A.; Mintz, E. A.; Marks, T. J., unpublished results.

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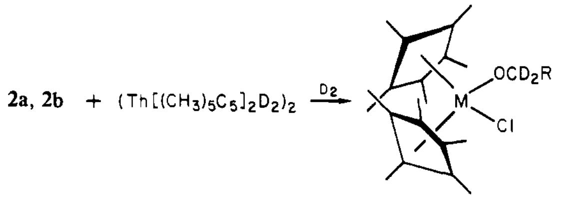
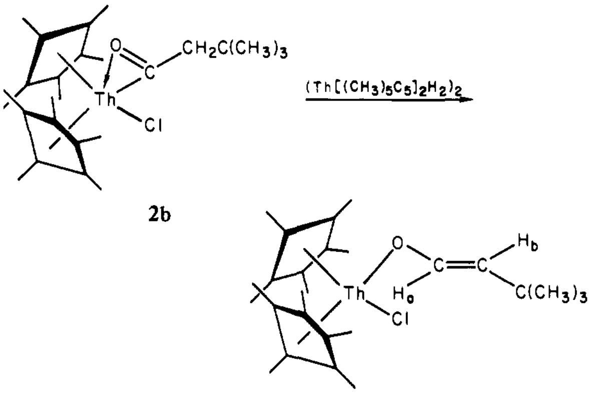
$(Th[(CH_3)_5C_5]_2D_2)_2$ (**4**)[2a] under an atmosphere of D_2, the alkoxide products are deuterated exclusively (≳90% by NMR spectroscopy) in the α position (eq 3).[3b] When no H_2 is present, **1** catalyzes the isomerization of **2b** to quantitatively yield the *trans*-enolate **5** (eq 4) with $N_t \approx 3$ h^{-1} when [**1**] = 2.5×10^{-3} M and [**2b**] = 4.6×10^{-3} M. Under the conditions of eq 1 (0.75 atm of H_2), the isomerization thus competes significantly with **2b** → **3b**. The trans stereochemistry of **5** (≳95% isomeric purity) was established by ^1H NMR spectroscopy ($^3J_{H_a-H_b}$ = 12.0 Hz vs. 7.2 Hz in the cis isomer[1]). When $(Th[(CH_3)_5C_5]_2D_2)_2$ (**4**) is used as the catalyst in eq 4, compound **5** is obtained, selectively deuterated (≳90% by ^1H NMR) in the H_a position (eq 5).[3b,6] The ^1H NMR spectrum reveals the conversion of 1.0 ± 0.1 proton per molecule of **2b** to a thorium hydride $[(Th[(CH_3)_5C_5]_2D_xH_{2-x})_2]$. Although compound **1** is a homogeneous olefin hydrogenation catalyst[3c,5] and slowly converts **5** to **3b**, the rate is far too slow ($N_t \sim 0.01$ h^{-1}) to explain the formation of **3b** under the reaction conditions.

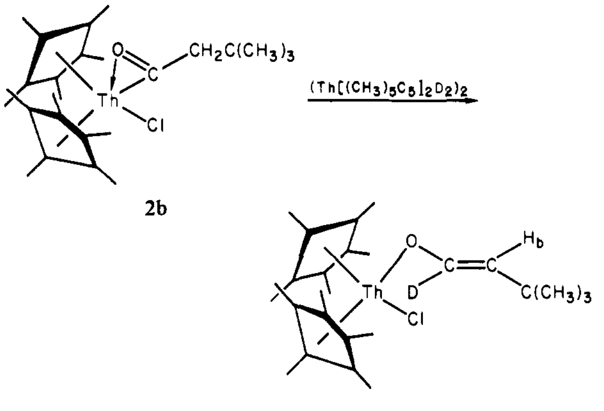


(3)



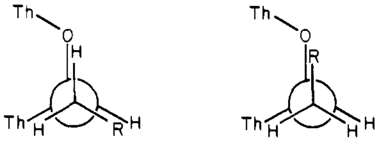
(4)

5



(5)

Mechanistically, we interpret the above observations for **2b** and **4** in terms of Scheme I. Although the overall catalytic pathways shown are, to our knowledge, unique, there is considerable precedent for many of the individual steps. Thus, the "oxycarbenoid" character of actinide[1,7] (and early transition metal[8]) η^2-acyls is amply documented by structural, spectral, and reactivity data. The crucial step is our scheme invokes the formal insertion of the carbenoid acyl carbon atom into a Th–D (or Th–H) bond to yield the key intermediate **6**. The formal insertion of free or metal-bound carbenes into transition metal- and metalloid-to-hydride bonds has considerable precedent.[9] In addition, several transition-metal complexes analogous to **6** have been recently isolated.[10] Interestingly, we find that actinide η^2-carbamoyls $[M(\eta^2\text{-}CONR_2)]$[11] do not undergo hydride-catalyzed hydrogenation or isomerization, consistent with the diminished carbenoid character of these species. Following the insertion process, intermediate **6** is not unexpectedly[2c,3c,12] unstable with respect to β-H elimination, and Th–H extrusion yields an enolate. The particular trans stereochemistry obtained is readily understandable in terms of the sterically most favorable conformer C (rather than D).



C D

Configuration C represents the eclipsed conformer which minimizes the repulsion between the bulky $Th[(CH_3)_5C_5]_2$ and $C(CH_3)_3$ groups (as verified by inspection of crystallographically derived scale models). Elimination of the favorably[13] eclipsed Th–H moiety from C thus yields the observed *trans*-enolate product.[14] In the presence of D_2 (or H_2), intermediate **6** can be intercepted, suffering the well-documented[2,12a] and facile Th–C σ bond hydrogenolysis reaction to yield an alkoxide and to concurrently regenerate the catalyst. An analogous scheme can be generated for **2a**; however, the lack of a suitable hydrogen atom precludes the isomerization process, and only hydrogenation occurs (eq 1).

This work underscores the oxycarbenoid character of organoactinide η^2-acyls and demonstrates that the carbene-like reactivity can be exploited catalytically to bring about carbon-centered, homometallic hydrogenation and rearrangement processes. Our results establish that for certain coordination environments, the utilization of CO and H_2 in a carbonylation–hydrogenation sequence can be effected under remarkably mild conditions of temperature and pressure and that this sequence provides a true

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(6) In this reaction, protio forms of the thorium catalyst are much more efficient rearrangement catalysts than their deuterio counterparts. Thus, to obtain the α-d_1 enolate in strict isotopic purity, a predominance (ca. 12-fold molar excess) of scrupulously pure $(Th[(CH_3)_5C_5]_2D_2)_2$ must be present in order to circumvent the avidity of the $(Th[(CH_3)_5C_5]_2HD)_2$ coproduct. Although we have not yet quantified it, a substantial kinetic isotope effect is indicated.

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(14) It seems unlikely to us that this product arises from Cl^-–H^- exchange to form a hydridoacyl which rearranges to a thorium(II) η^2-aldehyde,[8] suffers β-hydride elimination, and then undergoes Cl^-–H^- exchange again. We find such ligand exchange reactions for thorium to be slow on the time scale of this reaction,[3c] and the Th(II) oxidation state far less accessible than that of zirconium.[5,12]

"formladehyde equivalent". Needless to say, these observations convey attractive mechanistic suggestions for certain types of CO reduction catalysis.[15,16]

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High-Resolution NMR Spectra in Inhomogeneous Magnetic Fields: Application of Total Spin Coherence Transfer Echoes

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The homogeneity of the static magnetic field is the most common limitation on the resolution of NMR spectra, and a variety of spin echo techniques have been devised to extract high-resolution information from inhomogeneously broadened samples.[1-9] In this communication, we demonstrate a novel method for recording high-resolution spectra which, for a coupled spin system, gives transitions at the same frequencies and resolution as would be seen with an absolutely homogeneous field. The method uses multiple quantum coherence transfer echoes[5] and is applicable to both single quantum and multiple quantum spectra of coupled systems consisting of one or more spin species in liquids, liquid crystals, or solids. Unlike previous methods, it is not restricted by the relative size of the shift differences and the spin-spin couplings;[4,7,8] it does not require two-dimensional projections to obtain high resolution;[5,9] and it does not increase the number of transitions nor alter their positions.[6]

As an illustrative example, Figure 1 shows single quantum proton spectra of a nonspinning 10-mm sample of acetaldehyde partially oriented in a nematic liquid crystal. Figure 1a is the normal single-pulse Fourier transform spectrum and shows the inhomogeneity of the magnetic field to be greater than 1 ppm. Figure 1b is the total spin coherence transfer echo spectrum and gives line widths of ~4 Hz (~0.02 ppm). The line positions are governed by both direct and indirect spin-spin couplings and a chemical shift difference, and the spectral simulation in Figure 1c shows that all are preserved. The line widths obtained are independent of magnetic field homogeneity in the limit of negligible diffusion.[1,2]

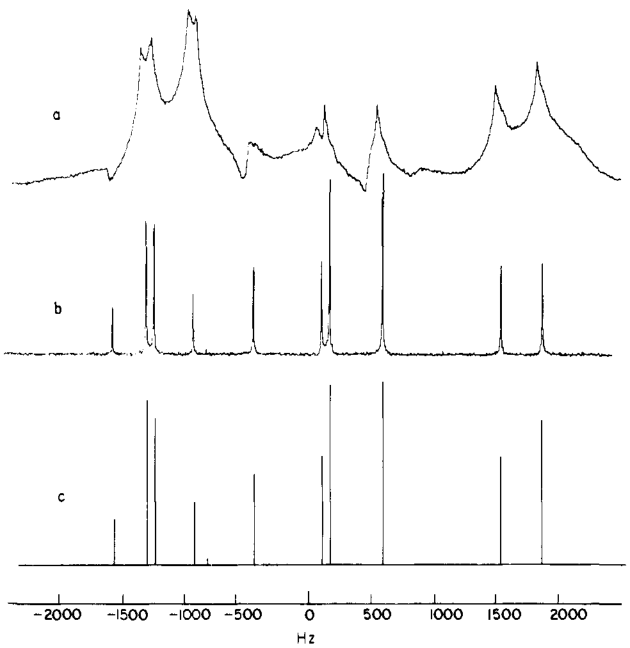

Figure 1. Removal of inhomogeneous broadening by total spin coherence transfer echo spectroscopy. (a) Single quantum Fourier transform proton spectrum of acetaldehyde in a nematic liquid crystal was taken in an inhomogeneous field and then (b) with the pulse sequence of Figure 2. The simulation of this AB_3 system is shown in (c) with parameters $J_{AB} = 2.8$ Hz, $\nu_{AB} = 1360.9$ Hz, $D_{AB} = -179.0$ Hz, $D_{BB} = 458.6$ Hz. The lines of E symmetry are absent, because they do not correlate with the total spin transition.

Figure 2. General sequence to use total spin coherence transfer echoes to produce multiple quantum spectra without inhomogeneous broadening. U is a preparation sequence for N-quantum (total spin) coherence. This evolves for a time nt_1/N at which time a pulse or sequence of pulses W transfers the total spin coherence to other n-quantum coherence. At time t_1 echoes are observed through transfer by V to single quantum coherence. Fourier transformation with respect to t_1 gives a homogeneous n-quantum spectrum. For the spectrum in Figure 1b, U was the sequence $(\pi/2)$-$(\tau/2)$-π-$(\tau/2)$-$(\pi/2)$, W was a $\pi/2$ pulse, V was omitted, $N = 4$ and $n = 1$. The $\pi/2$ time was 4.5 μs.

To understand the essence of the technique, consider a system of N coupled proton spins. The idea is to exploit the properties of the unique N-quantum coherence, the *total spin coherence*, which connects the extreme eigenstates of the coupled spin system. In the resonant rotating frame (defined so that the sum of the chemical shifts is zero), this coherence evolves only under the inhomogeneous Zeeman term and independently of chemical shift differences and spin-spin couplings. By having the spins evolve for a period in this N-quantum coherence and then in any other n-quantum coherence, the inhomogeneous term can be completely removed from the n-quantum spectrum.

Figure 2 is a general schematic diagram of pulse sequences for total spin coherence transfer echo spectroscopy. The total spin coherence is prepared by a propagator U acting on the equilibrium density operator. Evolution proceeds in the inhomogeneous field for a time nt_1/N where $n = \Delta M$ (difference in Zeeman quantum numbers) is the order of the coherence we wish to observe. At this time a coherence transfer to the lines of order n takes place under the action of the homogeneous propagator W, and evolution proceeds for the time t_1, at the frequencies of interest. At the end of t_1 only that part of the coherence which spent period nt_1/N as $\pm N$ quantum coherence and period t_1 as $\mp n$ quantum coherence has amplitude independent of magnet inhomogeneity. The only modulation of the amplitude of this echo is due to the internal

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