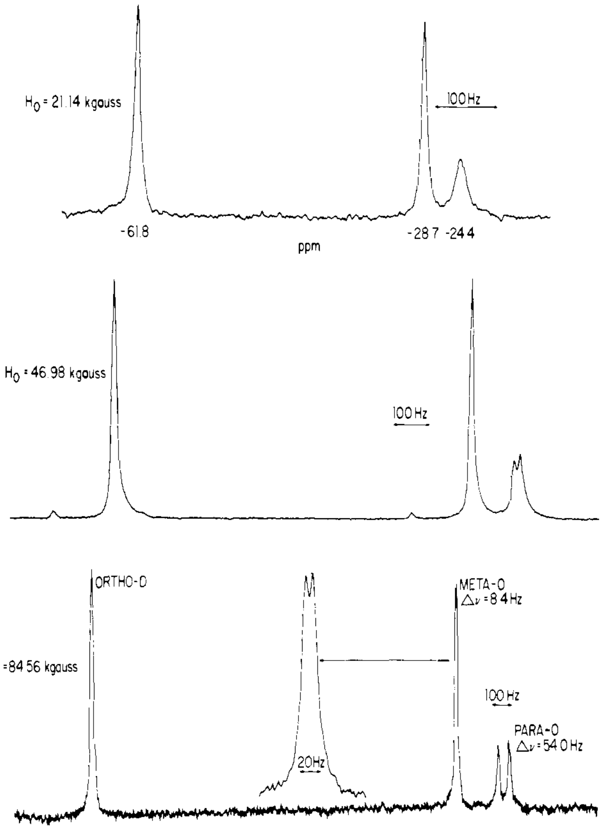

Figure 1. Field dependence of the ^2H NMR spectrum of a 0.08 M solution of Co(PTPB-d_5)$_2$ in chloroform at 295 K. HFX-90 spectrum (top), NT-200 spectrum (center), and WH-360 spectrum (bottom).

Measurement of the para-deuteron splitting in Co(PTPB-d_5)$_2$ ($\alpha = 0°$) yields the susceptibility anisotropy $[\chi_{zz} - (\chi_{xx} + \chi_{yy})/2] = \Delta\chi = 1.66 \times 10^{-26}$ cm^3 at 295 K.[7] Likewise, the splitting of the p-CD_3 resonance ($\alpha = 109.47°$) in Co(TTPB-d_7)$_2$ gives $\Delta\chi = 1.58 \times 10^{-26}$ cm^3. The small differences between these two independent results are explained by experimental uncertainties and by the assumed values for e^2qQ/h and α. Good agreement with the spin-isolation approach[8] ($\Delta\chi = 1.76 \times 10^{-26}$ cm^3) results; however, the quadrupolar method is less sensitive to molecular structure as there is no radial dependence.

Figure 2 verifies the quadratic field dependence of the ordering and illustrates the T^{-2} dependence resulting from a near T^{-1} dependence of $\Delta\chi$ and a further T^{-1} term in the order parameter. More precise data will define the temperature dependence of $\Delta\chi$.[9]

The above technique allows quick, accurate determination of the elements of **x** under NMR conditions, thus making unnecessary extrapolation from different phases, solvents, and temperatures. The method requires knowledge *only* of the angles of the C–D bonds to the magnetic axes; in molecules of C_{2v} symmetry or greater (where the inertial and magnetic axes are parallel), symmetry can define α and β. Unlike dipolar shifts, the splitting is independent of the distance from the paramagnetic center and is also independent of contact density. The technique is viable in cases where the assumption of isolated spin is inadequate and is applicable to molecules with nonmagnetic ground states where the ESR technique[2] fails.

All experimental restrictions hinge upon observation of an NMR spectrum with a quadrupolar splitting larger than the resonance line width. The many factors contributing to T_2 preclude a singular statement of the limitations. However, T_{1e} must be sufficiently rapid[1c] to produce a sharp (1–100 Hz) ^1H NMR spectrum, and the molecule must be small enough that rapid tumbling minimizes quadrupolar relaxation.[10]

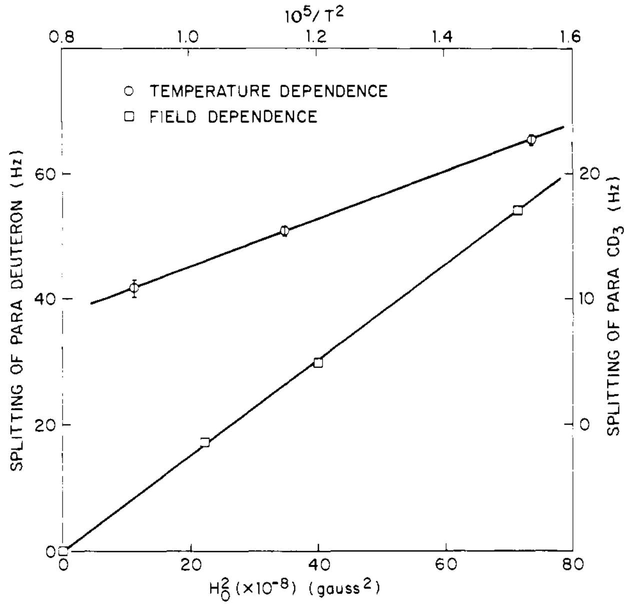

Figure 2. Field and temperature dependences of quadrupolar splitting. The field dependence uses the data of Figure 1 for Co(PTPB-d_5)$_2$. The temperature dependence of the p-CD_3 resonances in Co(TTPB-d_7)$_2$ in tetrahydrofuran is shown.

The technique is not universally applicable, but given the importance of **x** in the interpretation of dipolar NMR shifts, it can be applied to such traditional areas of paramagnetic NMR[1c] as transition metal complexes, lanthanide and actinide complexes, metallocenes, and biological systems.

Acknowledgments. The fine technical assistance of G. Watunya and I. R. Hartmann is gratefully acknowledged, and C. MacLean kindly provided copies of his work. Spectral data were obtained at the Middle Atlantic NMR facility (84.6 kG, NIH Grant RR542), Yale University (63.4 kG, J. W. Faller), and Nicolet Technology Corporation (47.0 kG, L. F. Johnson).

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[7] The quadrupole coupling constant in Co(PTPB-d_5)$_2$ was taken to be the same as in benzene-d_6 (185 ± 10 kHz) and that of $-CD_3$ in Co(TTPB-d_7)$_2$ the same as in toluene-d_3 (165 ± 10 kHz). See: Mantsch, H. M.; Saito, H.; Smith, I. C. P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 211–271.

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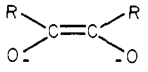
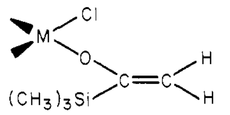
Carbon Monoxide Activation by f-Element Organometallics. An Unusually Distorted, Carbenelike Dihaptoacyl and CO Tetramerization

Sir:

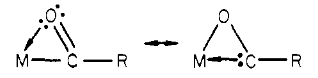
The search for new modes of CO reactivity has recently led to studies with early transition-metal[1-4] and actinide organometallics.[5,6] The latter offered us the possibility of elucidating CO activation patterns at molecular sites which might have characteristics similar to heterogeneous CO reduction sites[7] (high coordinative unsaturation and oxygen affinity)[7-9] and of drawing possible connections to the function of actinide oxide and actinide oxide supported CO reduction catalysts.[7,10] We recently reported that carbonylation of $M[\eta^5\text{-}(CH_3)_5C_5]_2R_2$ compounds (M = Th, U; R = alkyl functionality) results in rapid formation of enediolate (**A**) complexes while the analogous $M[(CH_3)_5C_5]_2[CH_2Si(CH_3)_3]Cl$ derivatives yield trimethylsilyl migration products, (**B**).[6b] In both cases, the intermediacy of a carbenelike dihaptoacyl (C,D) activated by the actinide coordination environment was proposed, but this species could not be isolated. We report now the isolation, characterization, and some of the unusual properties of such an organoactinide acyl. Included is an unprecedented carbonylation reaction in which CO insertion into a metal–carbon(acyl) bond occurs to produce, ultimately, a CO tetramer.



A



B



C D

Neopentyl bis(pentamethylcyclopentadienyl)thorium chloride (**1**) was prepared by reaction[11] of $Th[(CH_3)_5C_5]_2Cl_2$ with 1 equiv of neopentyllithium; it was characterized by standard methods.[12] In toluene solution, **1** quantitatively absorbs 1 equiv of CO (0.90 atm, eq 1) to yield insertion product **2** as pale yellow plates from pentane.[12] The C–O stretching frequency of **2a** (1469 cm^{-1}; 1434 cm^{-1} for **2b**) is substantially lower than that of typical, nonconjugated transition-metal dihaptoacyls (1505–1620 cm^{-1};[1,13] 1550 cm^{-1} for $Zr(C_5H_5)_2[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$,[1d] 1545 cm^{-1} for $Zr[(CH_3)_5C_5]_2(\eta^2\text{-}COCH_3)CH_3$[2b]), suggesting the greater importance of hybrid D. Furthermore, $\delta\,^{13}C$ for *C, 360.2 (C_6D_6), is quite low (cf. δ 318.7 for $Zr(C_5H_5)_2[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$[1f]) and in the region of carbene complexes.[14]

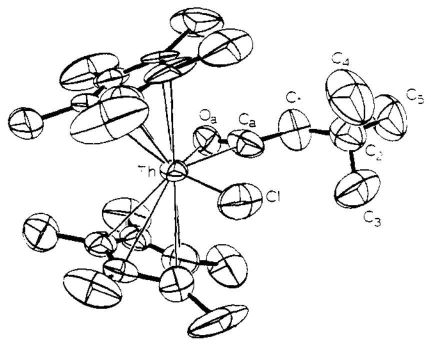


Figure 1. ORTEP drawing of the nonhydrogen atoms for the $Th[(CH_3)_5C_5]_2[\eta^2\text{-}COCH_2C(CH_3)_3]Cl$ molecule (**2**). All atoms are represented by thermal-vibration ellipsoids drawn to encompass 50% of the electron density. Important bond lengths and angles of chemically distinct bonds are the following: Th–Cl, 2.672 (6) Å;[15b] Th–O_a, 2.37 (2) Å; Th–C_a, 2.44 (2) Å; Th–C(cyclopentadienyl), 2.80 (2,2,3,10) Å; C_a–O_a, 1.18 (3) Å; C_a–C_1, 1.55 (3) Å; C_g–Th–C_g,[16] 137.5 (–)°; C_g–Th–Cl, 101.5 (–,5,5,2)°; C_g–Th–C_a, 106.4 (–,12,12,2)°; C_g–Th–O_a, 98.0 (–,10,10,2)°; Th–C_a–O_a, 73 (1)°; Th–C_a–C_1, 169 (2)°; and O_a–C_a–C_1, 118 (2)°.

The molecular structure of **2** (triclinic crystals from hot toluene) was determined by single-crystal X-ray diffraction techniques,[15a] and the thorium coordination geometry (Figure 1) is the familiar pseudotetrahedral $M[\eta^5\text{-}(CH_3)_5C_5]_2X_2$ arrangement where X = Cl and $\eta^2\text{-}COCH_2C(CH_3)_3$. Especially noteworthy is the dihaptoacyl ligation: Th–O is 0.07 Å shorter than Th–C(acyl) and

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(12) All new compounds gave expected spectral and analytical data; see supplementary material for details.

(13) (a) The effect of metal-atom mass on this internal coordinate change is small: $Zr(C_5H_5)_2(\eta^2\text{-}COCH_3)CH_3$, ν_{CO} = 1545 cm^{-1}; $Hf(C_5H_5)_2(\eta^2\text{-}COCH_3)CH_3$, ν_{CO} = 1550 cm^{-1}.[1c] (b) For $Zr(C_5H_5)_2(\eta^2\text{-}COCH[Si(CH_3)_3]_2)CH_3$,[1f] ν_{CO} is also rather low, 1470 cm^{-1}, suggesting that distortion of the dihaptoacyl may occur to relieve severe nonbonded repulsions.

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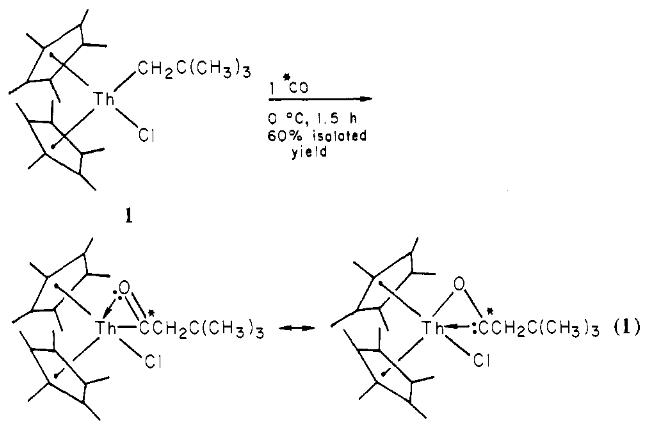
(15) (a) Single crystals of compounds **2** and **6** are triclinic, space group $P\bar{1}\text{-}C_i^1$ (No. 2). Compound **2**: a = 8.743 (2), b = 9.849 (3), c = 17.221 (6) Å; α = 89.83 (3), β = 108.50 (2), γ = 105.04 (2)°; Z = 2. Compound **6**: a = 10.625 (3), b = 18.453 (6), c = 19.391 (4) Å; α = 96.13 (2), β = 116.15 (2), γ = 113.01 (2)°; Z = 2 (dimeric units). Three-dimensional X-ray diffraction data were collected for those [6227 (**2**) and 16 246 (**6**)] independent reflections of both compounds having $2\theta_{Mo\ K\bar{\alpha}} < 58.7°$ by using graphite-monochromated Mo K$\bar{\alpha}$ radiation and full (1° wide) ω scans. The solid-state structures of both compounds were solved by using the "heavy-atom" technique. The resulting structural parameters have been refined to convergence [R(unweighted, based on F) = 0.058 for 2770 independent absorption-corrected reflections of **2** and R = 0.057 for 5124 independent absorption-corrected reflections of **6** having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > 3\,\sigma(I)$] by using unit-weighted full-matrix least-squares techniques with anisotropic thermal parameters for all nonhydrogen atoms of both compounds. Refinement is continuing for both compounds with those reflections having $2\theta_{MoK\bar{\alpha}} < 58.7°$. (b) The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

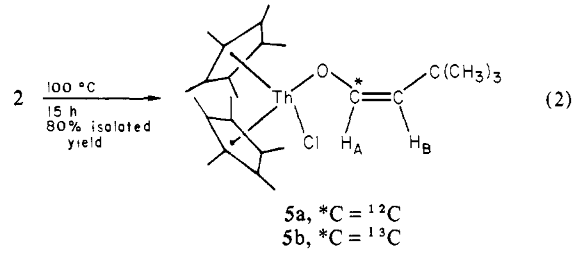


1

2a, *C = ^{12}C
2b, *C = ^{13}C

only slightly longer than the Th–O single-bond distance in the enediolate $\{Th[(CH_3)_5C_5]_2[\mu\text{-}O_2C_2(CH_3)_2]\}_2$ (2.150 (4) Å).[6b] In contrast, metal–oxygen(acyl) distances are significantly longer than metal–carbon(acyl) distances in the transition-metal dihaptoacyls studied to date: 2.19 (1) vs. 2.07 (2) Å in $Ti(C_5H_5)_2(\eta^2\text{-}COCH_3)Cl$ (**3**)[1b] and 2.290 (4) vs. 2.197 (6) Å in $Zr(C_5H_5)_2(\eta^2\text{-}COCH_3)CH_3$ (**4**).[1c,17] Furthermore, the metal–C–O angle in **2** [73 (1)°] is significantly smaller than in **3** or **4** [79.7 (6)° and 78.6 (4)°, respectively] while the metal–C_a–C_1 angle [169 (2)°] is larger [154.0 (16)° and 159.8 (5)°, respectively].[17] Interestingly, the orientation of the C_a–O_a vector in **2** (away from the X ligand) is in the *opposite direction* observed in **3** and **4**, but in the direction suggested by molecular orbital considerations for d-element derivatives.[18] Such conformational differences are inadequate to explain the distinctive spectral properties of **2**;[19] furthermore, the two conformations are essentially equal in free-energy content in the $M[(CH_3)_5C_5]_2[\eta^2\text{-}CON(CH_3)_2]Cl$ analogues, and $\Delta G^‡$ for their interconversion is ca. 10 kcal/mol.[6a]

Compound **2** undergoes two particularly interesting reactions. In toluene at 100 °C, it *does not* decarbonylate (**3** and **4** readily decarbonylate[1]) but smoothly rearranges via H migration to **5** (eq 2). The stereochemistry of compound **5** (colorless needles from pentane)[12] was established by NMR studies,[20] as was the integrity of the ^{13}C–O bond during the rearrangement.[12] Such a hydrogen atom migration is in accord with the proposed oxycarbene character of **2**.[21,22] In addition, **2** reacts irreversibly with excess CO (0.66 atm) in toluene to yield dark purple product **6** (eq 3), the molecularity of which, but few other structural details, could be established via standard methodology.[12] The molecular structure of **6** (triclinic crystals from toluene) was determined by



5a, *C = ^{12}C
5b, *C = ^{13}C

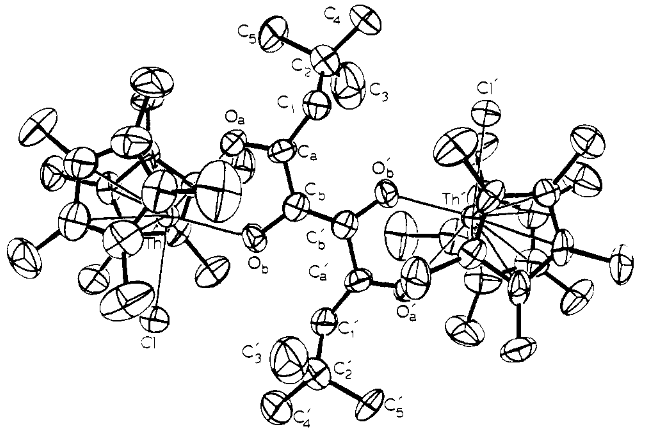
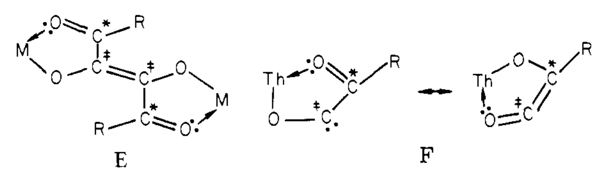


Figure 2. ORTEP drawing of the nonhydrogen atoms for one of the two crystallographically independent $\{Th[(CH_3)_5C_5]_2[\mu\text{-}CO(CH_2C(CH_3)_3)\text{-}CO]Cl\}_2$ molecules (**6**). Both molecules utilize crystallographic inversion centers. The stereochemistry of the second molecule differs from this one primarily in the orientation of the *tert*-butyl groups. All atoms are represented by thermal-vibration ellipsoids drawn to encompass 50% of the electron density. 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 for chemically distinct bonds are the following:[15b] 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,[16] 134.9 (–,12,12,2)°; C_g–Th–Cl, 98.7 (–,7,14,4)°; C_g–Th–O_a, 94.7 (–,16,19,4)°; C_g–Th–O_b, 111.8 (–,31,40,4)°; O_a–Th–O_b, 62.7 (5,4,4,2)°.

$$\underset{\mathbf{2}}{2Th[(CH_3)_5C_5]_2[{*}COCH_2C(CH_3)_3]Cl} \xrightarrow[\substack{25\ ^\circ C,\ 12h \\ 50\%\ \text{isolated yield}}]{{}^‡CO} \{Th[(CH_3)_5C_5]_2[{*}CO(CH_2C(CH_3)_3){}^‡CO](Cl)\}_2 \quad (3)$$

6a, *C = ‡C = ^{12}C
6b, *C = ^{13}C, ‡C = ^{12}C
6c, *C = ^{12}C, ‡C = ^{13}C

single-crystal diffraction techniques.[15a] It is seen (Figure 2) that a *coupling of four CO functionalities* has occurred to produce a centrosymmetric dimer with a unique, bridging enedione diolate ligand (E). This planar functionality occupies an XL position in the otherwise unexceptional (for actinide ions) $Th[\eta^5\text{-}(CH_3)_5C_5]_2X_2L$ coordination polyhedron.



E F

At present, the most plausible pathway from **2** to **6** appears to involve the addition of CO to the coordinated carbene to produce

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(16) C_g = center of gravity of the η^5-$(CH_3)_5C_5$ ring.

(17) (a) The disparity in $\{Mo(Cl)(CO)_2[P(CH_3)_3][\eta^2\text{-}COCH_2Si(CH_3)_3]\}_2$ is even greater: Mo–C = 2.023 (3) Å vs. Mo–O = 2.292 (2) Å; ∠Mo–C–O = 86.1 (2)°; ∠Mo–C–C_1 = 146.7 (3).[17b] (b) Carmona-Guzman, E.; Wilkinson, G.; Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1978**, 465–466. For still weaker ruthenium–oxygen interactions, see: Roper, W. R.; Taylor, G. E.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1979**, *182*, C46–C48.

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(19) (a) For $Zr(C_5H_5)_2[\eta^2\text{-}CO(p\text{-}C_6H_4CH_3)](p\text{-}C_6H_4CH_3)$, the conformer with the **2** orientation has ν_{CO} only 25 cm^{-1} lower and δ ^{13}CO only 1 ppm higher than the other conformer.[19b] (b) Erker, G.; Rosenfeldt, F. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 605–606.

(20) In **5a**, δH_A = 6.30, δH_B = 4.14, and J_{AB} = 7.2 Hz (C_6D_6); in **5b**, $J_{^{13}C\text{-}H_A}$ = 175 Hz, $J_{^{13}C\text{-}H_B} \approx$ 7.2 Hz (C_6D_6).[12] The thorium hydride-catalyzed rearrangement of **2** to an enolate complex yields an isomer of **5** with the opposite stereochemistry at the double bond: Maatta, E. A.; Marks, T. J., manuscript in preparation.

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a ketene,[23,24] possibly one involving metal coordination (F).[24] In regard to mechanism, it is important to note that NMR studies[12] of **6a**, **6b**, and **6c** indicate that *C and ‡C rigorously retain their respective identities in the homologation process (eq 3). Further mechanistic studies of actinide dihaptoacyl reactivity, including this new mode of CO activation and coupling, are in progress.

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Supplementary Material Available: Spectral and analytical data for **2a**,**b**, **5a**,**b**, and **6a–c** (2 pages). Ordering information is given on any current masthead page.

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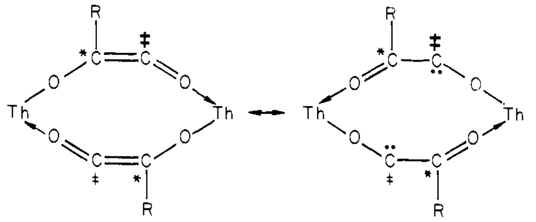

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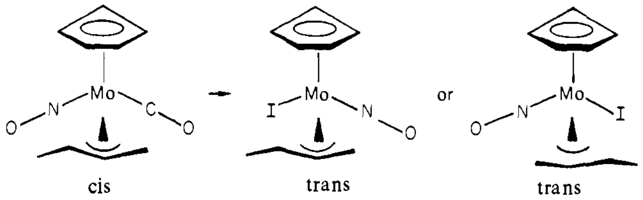
Retention of Configuration in Displacement of Carbonyl Ligands from Allyl(cyclopentadienyl)carbonylnitrosylmolybdenum Cations

Sir:

The observation that the electronic difference between NO and CO directs the stereoselective attack of nucleophiles on the allyl moiety in $(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_5)(NO)(CO)$ cations[1-3] suggested a more thorough investigation of the chirality, stability, and properties of the $(\eta^5\text{-}C_5H_5)Mo(NO)(X)$ fragment, where X = CO, I, $C_6H_5SO_3$, and CH_3CN. For synthetic purposes, particularly of asymmetric compounds, a method of directing the attack to the opposite terminus of the allyl or reversing the allyl coordination is desirable. Thus, we have explored carbonyl displacement reactions as a potential method of reversing the $(\eta^5\text{-}C_5H_5)Mo(NO)(X)$ configuration relative to a substituted allyl moiety.

We found that attack of halides on these cations resulted in displacement of the carbonyl rather than production of a coordinated allyl halide, as might have been anticipated on the basis of the chemistry found in the attack of softer nucleophiles, such as enamines. Examination of carbonyl displacement in the crotyl homologue, $(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_4H_7)(NO)(CO)$, indicated a stereospecific inversion of stereochemistry at either the molybdenum center of the allyl center;[4] however, the crystal structures of these racemic mixtures provided no means of distinguishing which center inverted.



Since the methyl group of the crotyl ligand might have had a directing effect on the stereochemical outcome of the reaction, the complex with deuterium cis to NO was prepared, $(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(CO)$,[5] and treated with iodide (eq 1).

$$\begin{aligned} &\textit{cis}\text{-}(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(CO)^+ \xrightarrow{I^-} \\ &\quad \textit{cis}\text{-}(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(I)\ (65\%) + \\ &\quad (35\%)\textit{trans}\text{-}(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(I) \end{aligned} \tag{1}$$

Analysis of the deuterium distribution suggested an ~90% retention of configuration of a given terminus relative to NO.[6] Furthermore, if one assumed the allyl moiety to retain its configuration, then the crotyl experiments suggested complete inversion of configuration at the molybdenum center whereas the allyl-*d* experiments suggested retention.

We have now prepared and resolved the neomenthylcyclopentadienyl complexes which allow us to establish unequivocally the stereochemistry of carbonyl displacement. Treatment of $(allyl)Mo(CO)_2(CH_3CN)_2Cl$[7] with the lithium salt of (+)-neomenthylcyclopentadiene[8] in THF produces the (neomenthyl-

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[5] Treatment of the allyl cation with $NaBD_3CN$ stereoselectively produces *cis*-$(\eta^5\text{-}C_5H_5)Mo(\eta^2\text{-}C_2H_3CH_2D)(NO)(CO)$. A 8:1 deuterium isotope effect, in addition to a 2:1 statistical preference for removal of H to D, produces *cis*-$[(\eta^5\text{-}C_5H_5)Mo(\eta^3\text{-}C_3H_4D)(NO)(CO)]PF_6$ in high yield.[3] The product contains predominantly the exo isomer (80%) with a *cis*-D to *trans*-D ratio of 85:15 by NMR.

[6] The iodide exists in solution as a rapidly equilibrating mixture of endo and exo isomers, the mechanism of which (π–σ–π) does not scramble the deuterium. The *endo-cis*-D/*endo-trans*-D ratio is 64:36. Consideration of the mode of isomer interconversion and the deuterium distribution in the cation implies that 100% retention would yield 71% *cis*-D iodide.[4]

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