

early-transition-metal thiolates.⁹ Our finding provides useful information relevant to the mechanism of industrially important hydrosulfurization processes promoted by, e.g., commercial Co-Mo/Al₂O₃ catalysts.¹⁰ The mechanism of reaction 1 and reactivity of **2b,c** are under investigation.

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Supplementary Material Available: Positional and thermal parameters, bond distances, and bond angles for **2b** (5 pages). Ordering information is given on any current masthead page.

(9) (a) Cp₂Nb(BH₄) was found to react with *t*-BuSH yielding (Cp₂Nb)₂(μ-S)₂ presumably via a thiolate-bridged intermediate (Cp₂Nb)₂(μ-S-*t*-Bu)₂ and subsequent loss of the *t*-Bu group: Skripkin, Yu. V.; Eremenko, I. L.; Pasyanski, A. A.; Struchkov, Yu. T.; Shklover, V. E. *J. Organomet. Chem.* **1984**, *267*, 285-292. (b) It has been known that the hydrocarbon linkage of the dithiolate ligands in, e.g., (CpMo)₂(S₂)₂ undergoes an exchange reaction with alkenes and alkynes: DuBois, M. R.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245-5252. (c) Interestingly, reaction of K₂[ReCl₆] with excess of ethane-1,2-dithiolate in methanol produces [ReS(SCH₂CH₂S)₂]⁻: Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chim. Acta* **1982**, *65*, L225-L226.

(10) For example, see: Mitchell, P. C. H. "Catalysis"; Kemball, C., Ed.; The Chemical Society: London, 1977; Vol. 1.

First Photochemical Envelope Isomerization of a Late-Transition-Metal 1,3-Butadiene Complex: A Triple Stereochemical Labeling Experiment

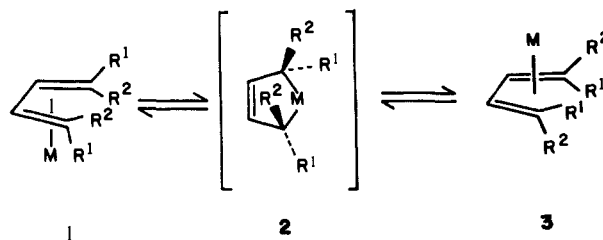
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Several reports have appeared¹ concerning a fundamentally new thermal isomerization reaction of early-transition-metal η⁴-butadiene complexes in which exo and endo substituents at C-1 and/or C-4 exchange positions (e.g., **1** ⇌ **3**, Scheme I). A common intermediate that has been proposed in these transformations is the metallacyclopent-3-ene **2** characteristic of a so-called "envelope flip" process. However, mechanistic evidence for this rare species has been scarce and stepwise pathways, such as those

Scheme I



involving (perhaps concerted) reversible butadiene-cyclobutene closures² and others,³ have not been ruled out. We report here the first photochemical isomerization of this type, the first to be observed for a late transition metal (e.g., cobalt), and a stereochemical experiment clearly linking simultaneous double exo-endo exchange with a switch of the metal from one π face of the ligand to the other (inversion at the metal) as required by Scheme I.

Our experiment took its motivation from the observation that while the η⁵-CpCo complex of 1,4-*cis,cis*-dideuteriobutadiene (**1**) (M = CpCo, R¹ = H, R² = D) underwent stereorandomization at temperatures above 140 °C, irradiation at -96 °C with a krypton ion laser (406, 413, 415 nm) led to rapid and stereospecific equilibration with (η⁴-1,4-*trans,trans*-dideuteriobutadiene)cyclopentadienylcobalt (**3**) (M = CpCo, R¹ = H, R² = D), none of the *cis,trans* isomer being detectable.^{3,4} The stereochemistry of both reactions was ascertained by oxidative demetalation (Fe³⁺), which was shown to be stereospecific, and Raman analysis of the free ligand.⁵ While this experiment was consistent with an envelope flip, which necessitates such a double exchange, the unique feature of inversion with respect to the ligand π system had to be proven by an additional experiment. For this purpose, we chose to prepare the two diastereomers **4** and **5** bearing three stereochemical labels. Scheme I requires diastereoisomerization with concomitant deuterioisomerization, e.g., **4** ⇌ **6** and **5** ⇌ **7**, whereas any pathway involving retention at the metal would lead to equilibrations **4** ⇌ **7** and **5** ⇌ **6**.

The required chiral and stereospecifically labeled ligand was made as shown in Scheme II. The crucial features of the sequence are benzylation of 1-(trimethylsilyl)butyne⁶ via its anion,⁷ regio- and stereoselective hydrosilylation-deuteriodesilylation,⁸ stereospecific bromination⁹ of a 2-deuterio-1-alkyl-1-silylethene, stereospecific palladium-catalyzed coupling¹⁰ of a deuterated vinyl bromide with *trans*-1-(tributylstannyl)-2-(trimethylsilyl)ethene,¹¹ and the stereospecific deuteriodesilylation of a 1,3-diene to give the target structure.¹² Its stereochemistry was unambiguously confirmed by complexation to cobalt [CpCo(CH₂=CH₂)₂],¹³ pentane, 25°C, 4h) to give **4** and **5** (1:1, 75%, the stereochemical

(2) See: Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, 15. Grimme, W.; Köser, H. G. *J. Am. Chem. Soc.* **1981**, *103*, 5919 and the references therein.

(3) A topologically similar but thermal and catalytic isomerization effected by Ni⁰ has been postulated to proceed through η³-allyl intermediates: Graham, C. R.; Stephenson, L. M. *J. Am. Chem. Soc.* **1977**, *99*, 7098.

(4) King, J. A., Jr. Ph.D. Thesis, UC Berkeley, 1983. The ligand was prepared as in: Stephenson, L. M.; Gemmer, R. V.; Current, S. P. *J. Org. Chem.* **1977**, *42*, 212.

(5) Stephenson, L. M.; Gemmer, R. V.; Brauman, J. I. *J. Am. Chem. Soc.* **1972**, *94*, 8620.

(6) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

(7) Rajagopalan, S.; Zweifel, G. *Synthesis* **1984**, 111.

(8) Hurdlik, P. F.; Schwartz, R. H.; Hogan, J. C. *J. Org. Chem.* **1979**, *44*, 155.

(9) Miller, R. B.; McGarvey, G. *Synth. Commun.* **1977**, *7*, 475. For a review, see: Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

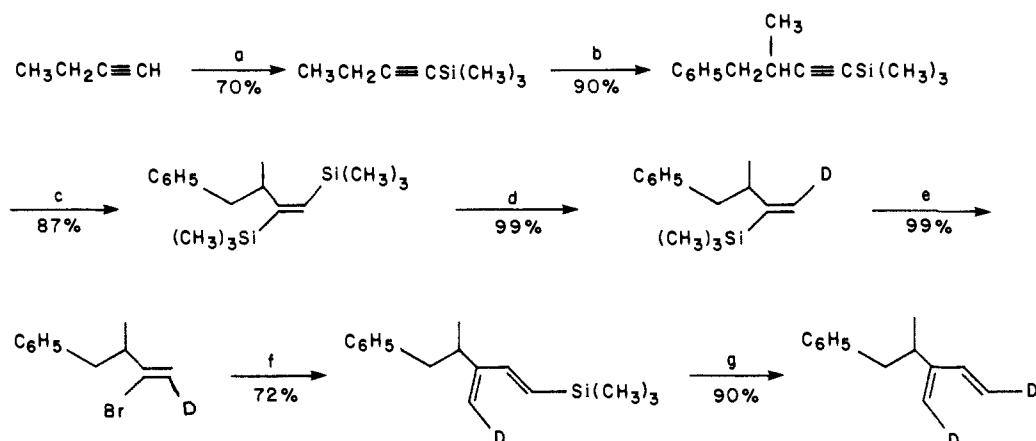
(10) In analogy to: Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630. Professor Stille has kindly informed us about work in his group concerned with the analogous coupling of vinyl iodides: Labadie, S. S. Ph.D. Thesis, Colorado State University, 1983.

(11) After: Cunico, R. F.; Clayton, F. J. *J. Org. Chem.* **1976**, *41*, 1480; but modified by using AIBN as initiator (**2d**) to avoid contamination by the *cis* isomer.

(12) All new compounds gave satisfactory analytical and/or spectral data.

(13) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 716; *Angew. Chem. Suppl.* **1983**, 1005.

(1) (a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858; *Ann. N.Y. Acad. Sci.* **1977**, *295*, 186. (b) Yasuda, H.; Tatsumi; Nakamura, A. *Acc. Chem. Res.* **1985**, *18*, 120 and the references therein. (c) Benn, R.; Schroth, G. *J. Organomet. Chem.* **1982**, *228*, 71. (d) Erker, G.; Engel, K.; Krüger, C.; Tsay, Y.-H.; Samuel, E.; Vogel, P., *Z. Naturforsch., B* **1985**, *40b*, 150.

Scheme II^a

^a (a) (1) CH_3MgBr , THF, 25 °C, 10 h; (2) $(\text{CH}_3)_3\text{SiCl}$, 25 °C, 4 h; (b) (1) $(\text{CH}_3)_3\text{SiCl}$, THF, -70 °C, 5 h; (2) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{C}\equiv\text{CH}$, -50 °C, 45 min; (c) (1) H_2PtCl_6 , $\text{CH}_2\text{Cl}_2/\text{SiH}_4$, 25 °C, 12 h, 60 °C, 2 h; (2) CH_3MgBr , ether, 25 °C, 18 h, Δ , 5 h; (d) CF_3COOD , CH_2Cl_2 , 25 °C, 1 h; (e) (1) Br_2 , CH_2Cl_2 , -78 °C, 20 min; (2) CH_3ONa , CH_3OH , CH_2Cl_2 , -10 to -25 °C, 3 h; (f) *trans*-1-(tributylstannyl)-2-(trimethylsilyl)ethene, $\text{Pd}[\text{P}(\text{C}_6\text{H}_5)_3]_4$, THF, Δ , 40 h; (g) CF_3COOD , CH_2Cl_2 , -10 to -5 °C, 1 h.

Table I. ¹H NMR (300 MHz, C_6D_6) Chemical Shifts of Complexes 4–7 in δ and J (Hz)

	4	5	6	7
H^1	1.76 (br s)	1.84 (br s, 1 H)	-0.57 (br s)	-0.46 (br s)
H^2	4.81 (br d, $J = 8.6$)	4.73 (br d, $J = 8.6$)	same as 5	same as 4
H^3	-0.31 (d, $J = 8.6$)	-0.34 (d, $J = 8.6$)	1.67 (d, $J = 7.5$)	1.76 (d, $J = 7.5$)
H^4	2.70 (dd, $J = 9.0, 22.0$)	2.65 (dd, $J = 12.6, 20.1$)	same as 5	same as 4
$\text{H}^{4'}$	3.18 (dd, $J = 3.9, 9.0$)	2.95 (dd, $J = 4.7, 12.6$)	same as 5	same as 4
H^5	2.65 (m)	2.43 (m)	same as 5	same as 4
CH_3	1.05 (d, $J = 6.3$)	1.33 (d, $J = 7.1$)	same as 5	same as 4
Cp	4.62 (s)	4.65 (s)	same as 5	same as 4

assignment with respect to the metal center is arbitrary), partially separable by HPLC (alumina) and exhibiting highly diagnostic chemical shifts for the complexed diene hydrogens (Table I).¹⁴

Irradiation (GE-ELH, 300 W, two lamps, 6 h, or krypton ion laser, 2 W, 30 min) of a 1:5 mixture of 4 and 5 in C_6D_6 gave complete diastereoisomerization (e.g., 4 \rightleftharpoons 6; 5 \rightleftharpoons 7; 1:1) as evidenced by the equilibration of the peaks for 4 and 5 to equal intensity, except for H^1 and H^3 for which new peaks emerged characteristic of 6 and 7 in a 1:5 ratio. Concomitant with their appearance, the intensity of the peaks for H^1 and H^3 of 4 and 5 decreased by 50%. Because $J_{\text{trans}} \sim J_{\text{cis}}$ in these complexes,¹⁴ the resonances for H_2 only broaden ($J_{\text{trans}} = 8.6$ Hz, $J_{\text{cis}} = 7.5$ Hz, Table I). The results clearly show that isotopomerization occurs synchronous with diastereoisomerization and without ligand crossover.

We believe that this experiment provides the so far most conclusive evidence for the occurrence of the envelope inversion mechanism in the fluxional behavior of η^4 -diene complexes. The

utility of stoichiometric thermal intermediates of the type 2 in synthetic organic chemistry^{1b,15} has been demonstrated, and our examples suggest that it may be catalytically exploitable in the extensive photochemistry of metal dienes.¹⁶

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Supplementary Material Available: Spectral data of all new compounds reported (2 pages). Ordering information is given on any current masthead page.

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