3440 *Inorg. Chem.* **1996,** *35,* 3440−3441

Thermal Transformation of *cis*- and *trans*-$[\{Mo(CO)_3H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_3(SiMe_2)_2C_5H_3\}]$ into $[\{Mo(CO)_3\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4(SiMe_2SiMe_2)\text{-}C_5H_4\}]$(*Mo*−*Mo*) Promoted by Hydride Migration

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Received January 27, 1995

Introduction

We recently reported[1] the stereoselective synthesis of *cis*- and *trans*-$[\{Mo(CO)_3H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_3(SiMe_2)_2C_5H_3\}]$ (**1**) and were interested in studying the attainable pathways, if any, for the interconversion between both isomers. Here we report the results of the thermal transformations observed when solutions of *cis*- and *trans*-**1** were heated to 90 °C leading to $[\{Mo(CO)_3\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4(SiMe_2SiMe_2)C_5H_4\}]$ (**2**). The preparation of **2** by reaction of $(C_5H_5SiMe_2SiMe_2C_5H_5)$ with $Mo(CO)_6$ has been previously reported.[2]

Experimental Section

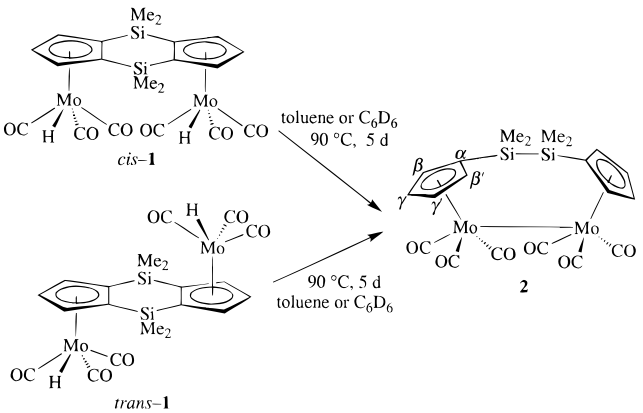
All manipulations were carried out under argon. Toluene and hexane were dried and distilled from sodium. The ^{1}H and ^{13}C NMR spectra were recorded at 499.83 and 125.71 MHz, respectively, on a Varian Unity 500 spectrometer; chemical shifts, in ppm, are positive downfield relative to external $SiMe_4$. Complexes *cis*- and *trans*-**1** were prepared according to ref 1. Complex *trans*-**1**-d_1 was obtained as *trans*-**1** but in THF-d_8 using acetic acid-d_1 for the preparation.

Preparation of 2. A solution of *cis*-**1** or *trans*-**1** (0.78 g, 1.3 mmol) in toluene (15 mL) is stirred and heated at 90 °C for 5 days in an ampule sealed *in vacuo*. The color of the solution changes from pale yellow to red. After filtration, the solution is evaporated to dryness to give a microcrystalline red solid, which was washed with hexane (10 mL), dried *in vacuo*, and characterized as **2** (0.70 g, 90%, mp 179−180 °C). Anal. Calcd for $C_{20}H_{20}O_6Si_2Mo_2$: C, 39.7; H, 3.3. Found: C, 40.2; H, 3.4. MS: *m/e* 604 (M^+). IR (THF): ν(CO) 2000 s, 1928 s, 1897 s. ^{1}H NMR (C_6D_6): δ 5.00 (AA′ part of an AA′BB′ spin system, 1 H, C_5H_4, H_β), 4.68 (BB′ part of an AA′BB′ spin system, 1 H, C_5H_4, H_γ), 0.63 (s, 3 H, Si*Me*$_2$). H_β and H_γ were assigned by a NOE difference experiment with saturation of the Me_2Si ^{1}H resonance (NOE effect for $H_\beta \approx 4\%$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 230.2 (s, *C*O *trans* to metal−metal bond), 226.5 (s, *C*O *cis* to metal−metal bond), 110.6 (s, C_5H_4, C_α), 96.5 (s, C_5H_4, C_β; from ^{13}C, ^1J(C−H) = 177 Hz), 94.1 (s, C_5H_4, C_γ; from ^{13}C, ^1J(C−H) = 176 Hz), 7.8 (s, Si*Me*$_2$; from ^{13}C, ^1J(C−H) = 121 Hz). C_β and C_γ were assigned by selective irradiation of H_β and H_γ resonances.

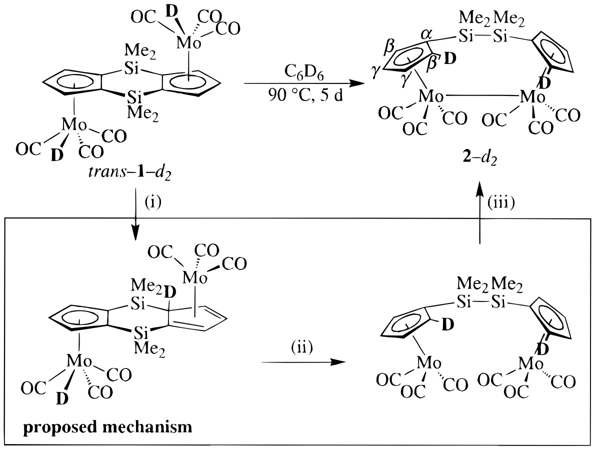
Results and Discussion

Initial experiments were carried out in sealed tubes by heating gradually C_6D_6 solutions of *cis*- and *trans*-**1**, and the reactions were monitored by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of *cis*-**1** shows two singlets at −0.02 and 0.46 ppm (Me_2Si), one singlet at −4.94 ppm (Mo−H), and two groups of resonances at 4.78 and 5.02 ppm (A and BB′ parts of the Cp ABB′ spin system) and remains unchanged at temperatures below 90 °C. At this temperature (Scheme 1), all the resonances due to *cis*-**1** decrease, while resonances due to a new complex **2** appear as one singlet at 0.63 ppm (Me_2Si) and two groups of resonances at 4.68 and 5.00 ppm (AA′ and BB′ parts of the Cp AA′BB′ spin system). The overall transformation proceeds quite slowly and requires 5 days at 90 °C to be completed. Complex *trans*-**1** is also transformed into **2** by a similar procedure, without significant differences in time or temperature. Complex **2** was isolated in 90% yield when the above reaction was carried out at a preparative level and has been completely characterized.

Scheme 1



Scheme 2



The formation of **2** from either *cis*-**1** or *trans*-**1** implies formally the rupture of two Si−C bonds, one from each cyclopentadienyl group, and the formation of two C−H bonds one Si−Si bond, and one Mo−Mo bond. It is well-known[3] that some hydride complexes of the type $[CpMo(CO)_3H]$ (Cp = η^5-C_5H_5, η^5-C_5Me_5, etc.) decompose to give the dimer $[CpMo(CO)_3]_2$(*Mo*−*Mo*) and H_2 when treated thermally. However reductive elimination of H_2 and formation of $[\{Mo(CO)_3\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_3(SiMe_2)_2C_5H_3\}]$(*Mo*−*Mo*)[4] was not observed for complex **1**.

Labeling studies provided more information on this reaction. When deuterated *trans*-**1**-d_2 (Scheme 2) is thermally decomposed in C_6D_6, the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the solid obtained (**2**-d_2) are analogous to those of **2** except for the cyclopentadienyl resonances. The relative intensity of the ring proton resonances observed in the ^{1}H NMR spectrum at 5.00

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S0020-1669(95)00091-7 CCC: $12.00

(H_β) and 4.68 (H_γ) ppm is 1:1 for **2** but 1:2 for **2**-d_2, in agreement with a structure for **2**-d_2 in which the deuterium atoms are located in β positions (Scheme 2). In the $^{13}C\{^1H\}$ NMR spectrum, the resonance found in **2** at 96.5 ppm (C_β) appears in **2**-d_2 as a group of resonances assigned to the deuterated ($^1J(CD) \approx 25$ Hz) and undeuterated β-carbons.

The partial mechanism proposed in Scheme 2 can account for the experimental observations. According to this mechanism, the formation of the metal−metal bond (step iii) is proposed to be subsequent to the ring transformation (steps i and ii), and therefore no significant difference is observed between the transformation of *cis*-**1** and *trans*-**1**. The first step (i) is the migration of one hydrogen from the metal to one of the silicon-bonded carbons of the cyclopentadienyl ring, in agreement with the location of the deuterium in the β position in **2**-d_2. This first step is similar to other metal-to-ring migrations reported in the literature[5] and implies the formation of a species with one 18e and one 16e Mo center. The C−Si bond breaking and Si−Si bond coupling could be induced by the metal-to-ring migration of the second deuterium (step ii). Step ii implies the formation of a 17e complex and could occur in a concerted way with step iii, in which the 18e are attained, lowering the activation energy of the process. Probably, metal-to-ring hydrogen transfer and C−Si bond breaking are also involved in ring desilylation reactions of monobridged C_5H_4-$SiMe_2C_5H_4$ complexes through the formation of the hydride $[\{Mo(CO)_3H\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4SiMe_2C_5H_4\}]$ proposed as an intermediate.[6]

Conclusion

In this paper, we have shown that hydrogen metal-to-ring migration is another process to take into account to explain the thermal behavior of some cyclopentadienylmetal hydride complexes. In fact, ^1H and ^{13}C NMR studies prove that thermal activation of deuterated *cis*- and *trans*-$[\{Mo(CO)_3H\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_3(SiMe_2)_2C_5H_3)]$ (**1**) occurs only *via* metal-to-ring migration giving $[\{Mo(CO)_3\}_2\{\mu\text{-}\eta^5{:}\eta^5\text{-}C_5H_4(SiMe_2SiMe_2)C_5H_4\}]$ (**2**).

Acknowledgment. We gratefully acknowledge financial support from the Comisión Asesora de Investigación Científica y Técnica (ref no. PB92-0178-C).

IC950091E

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