Journal of Organometallic Chemistry, 369 (1989) 245–251
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09864

The thermal and photochemical degenerate "walk" of (η^5-cyclopentadienyl)cobalt along η^4-bound 1,3,5-hexatriene

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(Received November 14th, 1988)

Abstract

This study reports that [η^4-1,2 : 3,4-(*trans*-6,6-dideuterio-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt undergoes facile thermal and photochemical degenerate interconversion with its 1,1-dideuterio regioisomer. The thermal process follows a first-order equilibrium kinetic expression. The Arrhenius activation parameters for the thermally-induced haptotropic rearrangement were determined: $E_a = 25.6 \pm 1.2$ kcal mol^{-1} and log $A = 12.5 \pm 0.6$.

Introduction

For the past several decades, the interaction of alkenes with metal centers has been a major focal point in catalyst research. A fundamental understanding of the nature and magnitude of these interactions is central to the development of a number of industrially important oligomerization and polymerization processes involving conjugated dienes [1]. In particular, catalyst systems containing η^4-complexed 1,3-dienes are commonly observed to undergo initial changes in coordination of the metal center, in order to allow subsequent reaction [2]. Efforts in this area have been oriented towards the detection and analysis of the elementary steps necessary to induce haptotropic changes.

Related to this process is the translational movement of metal atoms along extended π-systems. Such intramolecular migrations (the 'walk" or "slide" reaction) have been the subject of several reports on stereochemically non-rigid or "fluxional" molecules. A few comprehensive reviews in this area have been published [3]. With some exceptions [1,4,5], essentially all of the research has dealt with either metal-bound cyclic polyenes or anionic π-systems [6]. This paper describes the title

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transformation (eq. 1) and its associated kinetic parameters, made observable by regiospecific deuterium labelling.

Experimental

General procedure: Unless otherwise noted, materials were obtained from commercial supplies and used without further purification. Ether and THF were purified by stirring over sodium benzophenone ketyl followed by distillation under a nitrogen atmosphere. The reaction solutions were deoxygenated by either of two methods: (i) by bubbling nitrogen through the liquid for several hours (or until an approx. 10% decrease in solvent volume was observed) or, (ii) by subjecting the liquid to several freeze-evacuation-thaw cycles on a vacuum line [7]. All cobalt containing compounds were added to solutions that had been deoxygenated previously. The infrared absorption spectra were measured on a Perkin–Elmer infrared spectrometer model 681 and calibrated with a polystyrene standard. Proton NMR spectra were recorded on a Varian EM-390, UCB-180 or a UCB-250 spectrometer. The carbon NMR spectra were acquired on a UCB-250 spectrometer. The UCB-250 uses a Nicolet 1180 data system and has a Cryo Magnet Systems 5.7-Tesla magnet. All chemical shifts are reported in parts per million downfield of internal tetramethylsilane (Me_4Si). Mass spectral data were collected on an AEI-MS-12 (low resolution) or Du Pont CEC 21-110B (high resolution) instrument by the Mass Spectral Service at the University of California, Berkeley. Elemental analyses were carried out by the Microanalytical Laboratory.

Preparation of [η^4-1,2 : 3,4-(trans-2,4-pentadienal)](η^5-cyclopentadienyl)cobalt (2)

Compound **2** was prepared from $CpCo(CO)_2$ (1.8 g, 10 mmol) and *trans*-2,4-pentadienal [8] (0.7 g, 9.1 mmol) by irradiation at −30 °C in a deoxygenated THF solution (275 ml). A 250 watt pyrex Hanovia photoreactor was used for irradiation. The solvent was removed by vacuum transfer and the resulting purple residue purified by column chromatography on neutral alumina (Act III; 5% ether/pentane). The yield of **2** was 1.36 g (73%) as a viscous purple oil. The spectral data collected for **2** is as follows: IR (neat): 3110 (m), 3050 (m), 3000 (m), 2715 (m), 1670 (vs), 1455 (s), 812 (m) cm^{-1}; HRMS calc. $C_{10}H_{11}OCo$: 206.0140; found 206.0135; mass spectrum (70 eV) m/e (relative intensity) 206 (M^+, 47.2), 178 (46.9), 124 (100.0), 82 (15.5), 59 (41.6); ^{1}H NMR (250 MHz, C_6D_6) δ 9.25 (d, J 6.0 Hz, 1H, H(CHO)), 5.47 (dd, J 8.0, 4.6 Hz, 1H, H(3)), 4.70 (ddd, J 9.6, 6.6, 4.6 Hz, 1H,H(2)), 4.49 (s, 5H, H(Cp)), 1.98 (d, J 6.6 Hz, 1H, *E*-H(1)), 0.53 (dd, J 8.0, 6.0 Hz, 1H, *Z*-H(4)), 0.24 (d, J 9.6 Hz, 1H, *Z*-H(1)); ^{13}C NMR (63.07 MHz, C_6D_6) δ 196.64 (C(CHO)), 80.26 (C(3)), 79.49 (C(2)), 79.26 (C(Cp)), 47.40 (C(4)), 33.84 (C(1)).

Preparation of [η^4-1,2 : 3,4-(trans-6,6-dideuterio-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt (1a)

To a cold, deoxygenated ether solution (30 ml, −78 °C) were added $[(C_6H_5)_3PCD_3]^+I^-$ (1.26 g, 3.1 mmol) and butyllithium (15%/hexane, 2.25 ml, 3.5 mmol). The mixture was warmed to 0 °C and allowed to stir for 1 h. To the resulting deep orange solution was added [η^4-2,4-(*trans*-2,4-pentadienal)](η^5-cyclopentadienyl)cobalt (**2**; 0.74 g, 3.59 mmol). The mixture was stirred for 1 h at room temperature and then purified by column chromatography on deoxygenated neutral alumina (Act II, pentane), to give **1a** 0.447 g (70%) as a red oil. Further elution with 25% ether/pentane gave recovered **2** (0.089 g, 12%) and [η^4-1,3-(*trans*-1,3-nonadien-5-ol)](η^5-cyclopentadienyl)cobalt (0.047 g, 5%).

Spectral characteristics of 1a: IR (neat): 3090 (m), 3035 (m), 2985 (m), 2310 (m), 1575 (vs), 1428 (s), 1405 (s), 1190 (s), 1102 (m), 1005 (m), 988 (m), 795 (m), 700 (w) cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 206(M^+, 36.2), 205(15.3), 204(20.4), 203(12.7), 138(17.1), 124(100.0), 98(15.6), 81(21.7), 59(45.3); ^1H NMR (250 MHz, C_6D_6): δ 5.63 (bd, J 9.4 Hz, 1H, H(5)), 4.96 (ddd, J 8.2, 4.5, 0.9 Hz, 1H, H(3)), 4.82 (ddd, J 9.1, 6.4, 4.5 Hz, 1H, H(2)), 4.58 (s, 5H, H(Cp)), 1.88 (d, J 6.4 Hz, 1H, *E*-H(1)), 1.13 (dd, J 9.4, 8.2 Hz, 1H, *Z*-H(4)), −0.05 (d, J 9.1 Hz, 1H, *Z*-H(1)); ^{13}C NMR (63.07 MHz, C_6D_6): δ 144.36 (C(5)), 109.53 (C(6)), 80.86 (C(Cp)), 79.84 (C(3)), 76.63 (C(2)), 51.53 (C(4)), 31.24 (C(1)).

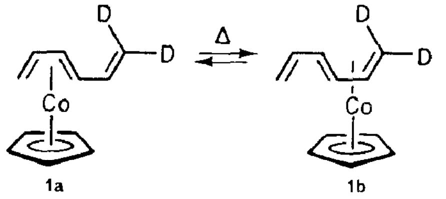
Spectral characterisation of [η^4-1,3-(trans-1,3-nonadien-5-ol)](η^5-cyclo-pentadienyl)cobalt. Mass spectrum (70 eV) m/e (relative intensity) 264(M^+, 59.7), 244(19.4), 189(23.3), 137(19.8), 124(75.4), 85(51.7), 81(78.6), 67(100.0), 59(32.8); chemical ionization (CH_4) m/e (relative intensity) 264(M^+, 63.1), 247(100.0), 207(9.9), 165(14.0), 143(49.0), 125(32.3); ^1H NMR (250 MHz, C_6D_6) δ 5.14 (dd, J 9.1, 4.3 Hz, 1H), 4.88 (ddd, J 9.8, 6.7, 4.3 Hz, 1H), 4.64 (s, 5H), 3.40 (m, 1H), 1.82 (d, J 6.7 Hz, 1H), 1.78–1.35 (bm, 5H), 1.02 (dd, J 9.8, 4.9 Hz, 3H), 0.37 (dd, J 9.1, 5.7 Hz, 1H), −0.23 (d, J 9.88 Hz, 1H).

Solution phase thermolysis procedure

The thermal equilibration of **1a** with **1b** was carried-out using the following experimental procedure. Using standard syringe techniques, the pyrolysis samples were prepared by dissolving 8.2 mg (38.8 μmol) of **1a** in deoxygenated benzene-d_6 (5.6 ml). To this solution was added 6 μl of dioxane as an internal standard. The resulting reaction medium ($[\mathbf{1a}]_0 = 6.93 \times 10^{-3}$ M) was partitioned equally among four 5 mm precision-bore medium-walled NMR tubes which were subsequently sealed. The pyrolyses were carried-out in a 180 MHz ^1H NMR spectrometer which allowed for the continuous monitoring of the extent of reaction. The reaction was followed by measuring the relative decrease in the *Z*-H(1) proton resonance (δ −0.05) versus the *Z*-H(4) absorption (δ 1.13). The *Z*-H(4) proton signal can be used as the internal standard since its concentration remains constant throughout the reaction; the *Z*-H(4) proton is chemically shifted equivalent in both compound **1a** and **1b**. The NMR probe was thermally equilibrated at the set-temperature before the introduction of the NMR tube containing the reaction mixture. Probe temperatures were calibrated by using the temperature dependence of the difference in chemical shifts between the ^1H resonance of the methylene and hydroxyl groups of ethylene glycol [9]. Each sample was placed in the probe and allowed to thermally equilibrate (5 min) before data acquisition commenced. The samples were analyzed at the following temperatures: 36, 44, 54, and 62° C. The spectral data were acquired at 15 min intervals throughout a total of two to three half-lives.

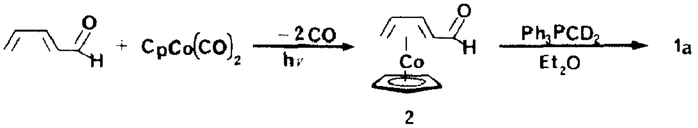
Results and discussion

In connection with a research project concerned with the potential electrocyclization of acyclic metal-bound polyene moieties, if became necessary to ascertain to what extent a bound (η^5-cyclopentadienyl)cobalt fragment would mimic the migratory behavior of (tricarbonyl)iron in linear polyene isomerizations [4,5]. In particular, the polyene "walk" or "slide' equilibration reaction of [η^4-1,2 : 3,4-(*trans*-6,6-dideuterio-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt (**1a**) with its complementary 1,1-dideuterio regioisomer (**1b**) was examined (eq. 1). Compound **1a** was chosen for study since the use of deuterium labelling would impart a minimum amount of steric and electronic perturbation on the conjugated π-system during the intended transformation.



(1)

The regiospecific preparation of the **1a** was accomplished via a modified Wittig reaction of $(C_6H_5)_3P{=}CD_2$ with [η^4-2,3 : 4,5-(*trans*-2,4-pentadien-1-al)](η^5-cyclopentadienyl)cobalt (**2**; eq. 2). Due to the large chemical shift difference between the olefinic protons of metal-bound and uncomplexed π-systems, the desired rearrangement could be monitored readily by ^{1}H NMR; the *E*-H(1) (δ 1.88) and *Z*-H(1) (δ −0.05) proton resonances are shifted to substantially higher field compared to those of the *E*-H(6) (δ 5.08) and *Z*-H(6) (δ 5.25) proton signals.



(2)

Thermolysis samples were prepared as dilute benzene-d_6 solutions ($[\mathbf{1a}]_0 = 6.93 \times 10^{-3}$ *M*) in order to minimize the occurrence of competing bimolecular reactions. No dimeric materials were observed to be formed under our reaction conditions (36–62° C). Previously, structure **1** has been observed to undergo the irreversible production of dimeric complexes at higher temperatures and concentrations [10]; the conversion of **1** to form dimeric products at 125° C, was as follows: $[\mathbf{1}]_0 = 0.385$ *M* 75% conversion in 1 h and $[\mathbf{1}]_0 = 0.075$ *M* 40% conversion in 2 h.

Indeed, on heating, the facile isomerization of **1a** to **1b** was observed. The equilibration reaction was found to follow a first-order rate expression over the time period measured. Using the integral form of the rate expression for the unimolecular equilibration between two isomers, straight line plots were obtained; the following k_{obs} values were determined (Table 1). An Arrhenius analysis of the data in Table 1 yielded a straight line plot (correlation coefficient = 0.9989) generating an $E_a = 25.6 \pm 1.2$ kcal mol^{-1} and $\log A = 12.5 \pm 0.6$. Thus at 25° C, the kinetic analysis of these data yield a $\Delta H^\ddagger$ 25.0 kcal mol^{-1} and a $\Delta S^\ddagger$ −3.3 e.u.

The data indicate the thermally induced CpCo "walk" process to be 5 to 8 kcal mol^{-1} more facile than that of the corresponding isolobal tricarbonyliron systems ($E_a = 31 \pm 2$ kcal mol^{-1}). This observation is consistent with a stronger binding of the triene ligand to the metal fragment of iron than to the cobalt system. The lower activation energy for CpCo might then reflect a diminished orbital interaction between its degenerate e_1 set and the triene moiety (due to a smaller diene-cobalt overlap) relative to that of the corresponding 2e orbitals on the $Fe(CO)_3$ fragment

Table 1

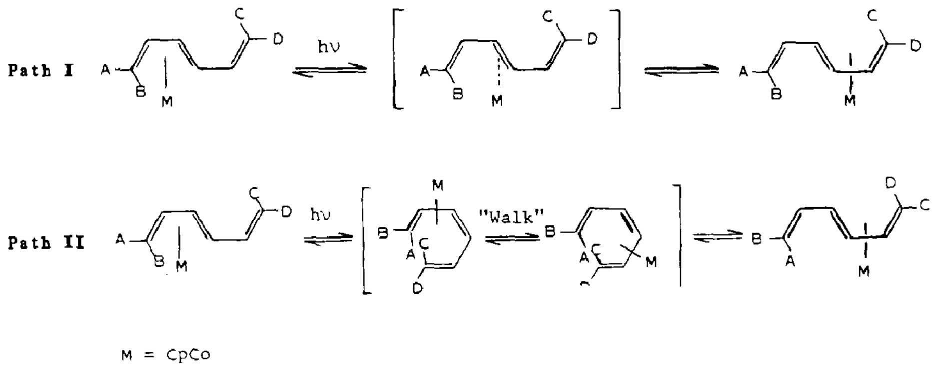
First-order rate constants for the equilibration of **1a** with **1b**

Run	$[\mathbf{1a}]_0$ (M)	Temperature (K)	k_{obs} (s^{-1})
1	6.93×10^{-3}	309.2 ± 0.3	$2.59\ (\pm 0.13) \times 10^{-6}$
2	6.93×10^{-3}	317.2 ± 0.3	$7.85\ (\pm 0.32) \times 10^{-6}$
3	6.93×10^{-3}	327.2 ± 0.3	$2.36\ (\pm 0.12) \times 10^{-5}$
4	6.93×10^{-3}	335.2 ± 0.3	$6.97\ (\pm 0.34) \times 10^{-5}$

[3a,c,11]. The net effect is a more facile η^4-η^2 haptotropic rearrangement for the cobalt system. Further experimental support for this idea is provided by comparison of the MO-energy levels for the two types of metal fragments as measured by photoelectron spectroscopy [12], and from the electrochemical work of Geiger [13].

For comparative purposes, the photochemical analog of this valence tautomerization was examined. Low temperature solution irradiation of **1a** (12 mg, 0.7 ml toluene-d_8, −96 °C) for 2 h using 410 nm light (1.8 watt krypton-ion laser), gave essentially complete equilibration of **1a** with **1b**. No *cis-trans* isomerization of the hexatriene moiety was observed to occur during the irradiation process; it has been demonstrated for (η^4-butadiene)cyclopentadienylcobalt complexes, that both haptotropic rearrangement (path I; scheme 1) and envelope inversion (path II) can occur during irradiation with 410 nm light [14]. Without specifically labelling each end of the hexatriene moiety, one can not determine which pathway is operative during the photochemically-induced isomerization. Neither degradation of material nor any side reaction was detectable under these conditions. Thus, the equilibration of **1a** with **1b** is demonstrated to be quite a facile photochemically induced transformation.

The thermal isomerization of **1a** suffers none of the mechanistic ambiguity inherent in its photochemically induced rearrangement (path I versus path II). No thermally induced envelope inversion process has been reported for the Group VIII metals. Our attempts to detect such a pathway with a number of specifically labeled (η^4-diene)CpCo complexes proved fruitless. For example, spectroscopic examination of the reaction solutions containing the η^5-CpCo complex of 1,4-*cis,cis*-dideuteriobutadiene during pyrolysis indicated no deuteroisomerization at temperatures below 140 °C; as the reaction temperatures were increased (175–195 °C), gradual



Scheme 1

decomposition of the complex was observed with concomitant stereorandomization of the ligand [14]. Sterically encumbered, electron-withdrawing substituents such as the phenyl group, electronically comparable to the vinyl group, do not facilitate an inversion process. When (η^4-1,-*Z*-phenylbutadiene)cyclopentadienylcobalt was pyrolyzed in solution, only slow isomerization to the *E*-isomer was observed (10 h; 150 °C) [14b].

In summary, the acyclic polyene "walk" process for (η^5-cyclopentadienyl)cobalt is shown to be induced both photochemically and thermally under mild conditions. Furthermore, the thermal transformation for the (η^5-cyclopentadienyl)cobalt system is found to be more facile than for its isolobal tricarbonyliron fragment. Thus, chemical processes which require activation via an initial coordination change at the metal center (e.g η^4-η^2), may proceed more efficiently with CpCo catalysts than with the corresponding $Fe(CO)_3$ systems.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract DE-AC03-76SF00098.

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