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The thermally-induced prototropic isomerization of η^4-1,3-, η^4-1,4-, η^4-1,5-dialkenes complexed to (η^5-cyclopentadienyl)cobalt

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Abstract

This study reports a series of facile, thermally-induced, prototropic isomerizations of η^4-1,4- and η^4-1,5-dienes of (η^5-cyclopentadienyl)cobalt to their corresponding η^4-1,3-complexes. The data indicate the *E*-isomers to be thermodynamically favored over the *Z*-isomers. Furthermore, in the case of η^4-hexadiene complexes, the η^4-2,4-*EE*-isomer is observed to be thermodynamically preferred relative to either the η^4-2,4-*E*,*Z*- or η^4-1,3-*E*-isomers.

1. Introduction

Organometallic diene complexes have been known for more than sixty years [1]. Research into the interaction of organometallic complexes with dienes has spawned a variety of commercially important processes [2]; catalytic olefin isomerization has been a central focus in much of this commercial chemistry.

In bound polyene systems, a variety of transition metals promote the thermal *cis* ↔ *trans* ($Z \leftrightarrow E$) isomerization in addition to olefin migratory reactions [2a,b,3]. In the latter case, double bond migrations generally proceed by either of two principal mechanisms: addition-eliminations [4] and 1,3-hydrogen (prototropic) shifts [2c,5]. These mechanisms are distinguishable via deuterium labeling experiments. In non-hydride metal diene complexes, 1,3-hydrogen shifts are the more common mode of isomerization. These metal-mediated rearrangements can be induced photochemically as well as thermally [6].

With acyclic diene hydrocarbons, metal-induced rearrangement results in predominantly internal, conjugated products [3]; these internal dienes tend to form the *E*,*E*-isomers. On isomerization, the more substituted diene isomers are generally the more favored.

Much of our work has focused on the metal-mediated interactions of the cyclopentadienylcobalt moiety with polyunsaturated systems [7]. In the course of preparing a variety of cobalt diene substrates for photochemical study, we had occasion to examine their thermochemistry, as well [7b]. This work details the thermally-induced prototropic isomerization of a number of aliphatic η^4-1,3-, η^4-1,4-, and η^4-1,5-dialkenes complexed to (η^5-cyclopentadienyl)cobalt.

2. Experimental details

2.1. General procedure

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. In all the synthetic preparations which start with $CpCo(CO)_2$, yields are based relative to $CpCo(CO)_2$. 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 approximately 10% decrease in sol-

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vent volume was observed) or, (ii) by subjecting the liquid to several freeze–evacuation–thaw cycles on a vacuum line [8]. All cobalt containing compounds were added to solutions that had been deoxygenated previously. The infrared adsorption spectra were measured on a Perkin-Elmer infrared spectrometer model 681 and calibrated using a polyethylene standard. Proton NMR spectra were acquired 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 system uses a Nicolet 1180 data system and a Cyro Magnet Systems 5.7-Tesla magnet. All chemical shift data are reported in parts per million relative to an internal tetramethylsilane (Me_4Si) standard. The photochemical work was performed using either a 4 watt Spectra Physics Model 171-01 Kr^+ ion (350 and 413 nm) or Ar^+ ion (514.5 nm) continuous wavelength (CW) laser; both were obtained from the San Francisco Laser Center. 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.

2.2. Preparation of [η^4-1,2:4,5-(1,4-pentadiene)](η^5-cyclopentadienyl)cobalt (1)

Compound **1** was prepared from 1,4-pentadiene (1.50 g, 22 mmol) and $CpCo(CO)_2$ (0.44 g, 2.4 mmol) by irradiation at −30°C in a deoxygenated THF solution (250 ml). A 250 watt Pyrex Hanovia photoreactor was used for irradiation. After 8 h, the solvent was removed by vacuum transfer and the resulting red oil purified by HPLC [9]. Three compounds eluted: i) **1** (0.065 g; 14% yield), ii) **2**-*E* (0.156 g; 34%), and iii) **2**-*Z* (0.012 g; 3%). The product characterizations follow: **1** orange oil; IR (neat) 2960m, 2920m, 2875m, 1420m, 1340s, 1258m, 1020m, 800m cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 192 (M^+, 26.8), 189(12.2), 124(100), 117(10.6), 68(82.5), 59(68.3); ^1H NMR (250 MHz, C_6D_6) δ 4.49 (s, 5H), 2.90 (m, 3H), 1.68 (d, $J = 6.8$ Hz, 2H), 1.24 (m, 1H), 0.45 (d, $J = 10.7$ Hz, 2H); ^{13}C NMR (63.07 MHz, C_6D_6) δ 81.23, 68.03, 45.60, 35.77. **2**-*E* red oil; mass spectrum (70 eV) *m/e* (relative intensity) 192 (M^+, 21.7), 189(5.4), 124(100), 59(10.5); ^1H NMR (250 MHz, C_6D_6) δ 5.15 (dddd, $J = 9.9$, 7.3, 4.4, 0.6 Hz, 1H), 4.85 (ddd, $J = 7.8$, 4.4, 2.1 Hz, 1H), 4.65 (s, 5H), 2.69 (ddq, $J = 7.3$, 7.2, 0.6 Hz, 1H), 1.90 (ddd, $J = 7.8$, 2.1, 0.7 Hz, 1H), 0.88 (dd, $J = 9.9$, 7.0 Hz, 1H), 0.70 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (63.07 MHz, C_6D_6) δ 82.60, 78.33, 73.48, 40.81, 25.36, 8.90. **2**-*Z* red oil; IR (neat) 3095m, 2980m, 2910m, 1450s, 1110m, 800m cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 192 (M^+, 32.7), 189(8.5), 124(100), 59(10.4); ^1H NMR (250 MHz, C_6D_6) δ 4.91 (ddd, $J = 9.7$, 6.7, 4.5 Hz, 1H), 4.75 (dd, $J = 9.7$, 4.5 Hz, 1H), 4.62 (s, 5H), 1.74 (dd, $J = 6.7$, 0.8 Hz, 1H), 1.04 (d, $J = 6.3$ Hz, 1H), 0.42 (dq, $J = 9.7$, 6.3 Hz, 1H), −0.32 (dd, $J = 9.8$, 0.8 Hz, 1H); ^{13}C NMR (63.07 MHz, C_6D_6) δ 80.74, 79.34, 74.57, 46.07, 29.66, 20.30.

2.3. Solution phase thermolysis of 1

Compound **1** (0.030 g; 0.16 mmol) and dioxane (0.5 μl) were dissolved into d_6-benzene (1.2 ml) and the resulting clear orange solution sealed in a 5 mm precision-bore NMR tube. The sample was heated at 50°C. The conversion of **1** to **2**-*E* (79.4%) and **2**-*Z* (20.6%) was observed to be complete within 1 h. On extended heating (24 h), the integrated ^1H NMR ratio of **2**-*E* to **2**-*Z* was observed to be invariant with time; no degradation of material was detectable—by ^1H NMR—under these conditions.

2.4. Solution phase thermolytic conversion of 2-Z to 2-E

A deoxygenated d_6-benzene solution (0.82 ml) of **2**-*Z* (0.015 g; 0.080 mmol) was sealed into a 5 mm precision-bore NMR tube. The NMR tube was immersed in an oil bath and heated at 100°C; the oil bath had been thermally equilibrated at 100°C prior to the addition of the reaction sample. Quantitative conversion of **2**-*Z* to **2**-*E* was observed to be complete within 48 h.

2.5. Preparation of [η^4-1,2:5,6-(1,5-hexadiene)](η^5-cyclopentadienyl)cobalt (3)

Compound **3** was prepared from 1,5-hexadiene (1.56 g; 19 mmol) and $CpCo(CO)_2$ (0.864 g; 4.8 mmol) by irradiation at −30°C in deoxygenated THF (275 ml) for 12 h. A 250 watt Pyrex Hanovia photoreactor was used for the irradiation. The solvent was removed by rotary evaporation. Purification of the red-orange residue by HPLC [9] gave **3** (0.474 g, 48% yield) as an orange-red oil: mass spectrum (70 eV) *m/e* (relative intensity) 206 (M^+, 78.2), 189(38.7), 138(18.7), 124(94.7), 98(26.7), 67(100), 59(68.4); HRMS calc. $C_{11}H_{15}Co$: 206.0506; found: 206.0501; ^1H NMR (250 MHz, C_6D_6) δ 4.41 (s, 5H), 3.88 (m, 2H), 2.37 (d, $J = 8.1$ Hz, 2H), 2.28 (m, 2H), 1.24 (m, 2H), 1.14(d, $J = 11.9$ Hz, 2H); ^{13}C NMR (63.07 MHz, C_6D_6) δ 83.33, 62.45, 38.98, 32.58; Anal. calc. $C_{11}H_{15}Co$: C, 64.08; H, 7.33. Found: C, 64.33; H, 7.55%.

2.6. Solution phase thermolysis of 3

The thermolysis solution was prepared by dissolving **3** (0.025 g; 0.12 mmol) in deoxygenated d_8-toluene (0.75 ml), transferring the solution into a 5 mm precision-bore NMR tube, and the NMR tube subsequently sealed. The reaction could be monitored by ^1H NMR using dioxane (2 μl) as an internal standard. When the sample was heated at 60°C, the conversion of **3** to **4**-*Z,E* (40%) and **4**-*E,E* (60%) was complete within 15 h. Repetition of this thermolysis experiment at 100°C, indicated complete conversion of **3** to **4**-*Z,E* (29.6%), **4**-*E,E* (66.7%), and **5** (3.7%) within 4 h.

2.7. Preparation of [η^4-2,3 : 4,5-(E,E-2,4-hexadiene)](η^5-cyclopentadienyl)cobalt (4-E,E)

Compound **4**-*E,E* was prepared via the photo-complexation of $CpCo(CO)_2$ (0.35 g; 1.9 mmol) with *E,E*-2,4-hexadiene (0.32 g; 3.9 mmol) in THF (275 ml) for 12 h. The solvent was removed by rotary evaporation and the resulting residue purified by column chromatography on Act. II alumina (pentane). The yield of **4**-*E,E* was 0.358 g (89%) as a red-purple oil: IR (CCl_4) 3040m, 2980m, 2965m, 1420s, 1010m, 990m cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 206 (M^+, 21.6), 189(6.5), 164(2.5), 138(8.9), 124(100.0), 59(15.6); ^{1}H NMR (250 MHz, C_6D_6) δ 4.66 (d, $J = 7.1$ Hz, 2H), 4.59 (s, 5H), 1.05 (d, $J = 6.4$ Hz, 6H), 0.33 (dq, $J = 7.1$, 6.4, 2H); ^{13}C NMR (63.07 MHz, C_6D_6) δ 79.89, 77.59, 45.19, 20.23; Anal. calc. $C_{11}H_{15}Co$: C, 64.08; H, 7.33. Found: C, 64.55; H, 7.30%.

2.8. Preparation of [η^4-2,3 : 4,5-(E,Z-2,4-hexadiene)](η^5-cyclopentadienyl)cobalt (4-E,Z)

Compound **4**-*E,Z* was prepared by solution phase pyrolysis of **3** (0.036 g; 0.18 mmol) in benzene (2 ml) at 50°C for 4 h. The desired product was isolated as a red viscous oil (0.011 g; 31% yield) using HPLC [9]: mass spectrum (70 eV) *m/e* (relative intensity) 206 (M^+, 20.3), 189(5.0), 138(9.0), 124(100.0), 59(15.0); ^{1}H NMR (250 MHz, C_6D_6) δ 4.89 (dd, $J = 7.4$, 5.0 Hz, 1H), 4.75 (dd, $J = 6.6$, 5.0 Hz, 1H), 4.61 (s, 5H), 2.58 (dq, $J = 6.9$, 6.6 Hz, 1H), 1.56 (dq, $J = 7.4$, 6.3 Hz, 1H), 1.09 (d, $J = 6.3$ Hz, 3H), 0.71 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (63.0 MHz, C_6H_6) δ 85.83, 79.89, 76.38, 44.99, 29.44, 21.17, 14.60; Anal. calc. for $C_{11}H_{15}Co$: C, 64.08; H, 7.33. Found: C, 64.66; H, 7.39%.

2.9. Preparation of [η^4-1,2:3,4-(E-1,3-hexadiene)](η^5-cyclopentadienyl)cobalt (5)

$CpCo(CO)_2$ (1.02 g, 5.6 mmol) and *E*-1,3-hexadiene (0.509 g, 6.2 mmol) were irradiated in deoxygenated THF (250 ml) using a Pyrex Hanovia photoreactor. After 12 h, the solvent was removed by rotary evaporation yielding **5** (1.10 g, 95%) as a pure (by ^{1}H NMR) red oil: IR (neat) 3095m, 3020m, 2960m, 2860m, 1450s, 1200s, 1105m, 1008m, 992m, 795m cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 206 (M^+, 39.3), 189(8.1), 164(3.0), 138(8.2), 124(100.0), 67(15.5), 59(45.4); ^{1}H NMR (250 MHz, C_6D_6) δ 4.92 (ddd, $J = 9.9$, 6.7, 4.9 Hz, 1H), 4.78 (dd, $J = 8.9$, 4.9 Hz, 1H), 4.65 (s, 5H), 1.76 (d, $J = 6.7$ Hz, 1H), 1.41 (m, 1H), 1.14 (m, 1H), 1.03 (t, $J = 7.1$ Hz, 3H), 0.37 (m, 1H), -0.32 (d, $J = 9.9$ Hz, 1H); ^{13}C NMR (63.07 MHz, C_6D_6) δ 80.8, 79.4, 75.2, 46.1, 29.7, 32.3, 23.2; Anal. calc. for $C_{11}H_{15}Co$: C, 64.08; H, 7.33. Found: C, 64.15; H, 7.28%.

2.10. Solution phase pyrolysis of 5

A deoxygenated d_6-benzene solution (0.78 ml) of **5** (0.036 g; 0.18 mmol) was heated at 150°C. After a total reaction time of 16.5 h, the starting material had been converted to **4**-*E,E*, quantitatively. A repetition of the preceding experiment at 100°C indicated no rearrangement of **5** after heating for 24 h.

2.11. Solution phase thermolysis of 4-E,Z

A deoxygenated d_6-benzene solution (0.85 ml) of **4**-*E,Z* (0.008 g, 0.034 mmol) and cyclohexane (0.5 μl) was heated at 100°C for 30 h in a 5 mm precision-bore NMR tube. Under these conditions, **4**-*E,Z* was observed to undergo quantitative conversion to **4**-*E,E* (reaction followed by ^{1}H NMR).

2.12. Photochemically-induced isomerization of 2-Z to 2-E

A deoxygenated d_8-toluene solution (0.95 ml) of **2**-*Z* (0.012 g; 0.064 mmol) sealed in a 5 mm precision-bore NMR tube, was irradiated (2.4 watt Ar^+ ion laser; 514.5 nm) at low temperature (−96°C). The reaction mixture was monitored at 30 min intervals using ^{1}H NMR spectroscopy. The conversion of **2**-*Z* to **2**-*E* was determined to be 80% complete within 3 h.

Repetition of the preceding experiment, using 413 nm irradiation (1.4 watt Kr^+ ion laser), produced complete conversion of **2**-*Z* to **2**-*E* in under 2 h.

2.13. Preparation of [η^4-1,2:3,4-(E/Z-1-phenyl-1,3-butadiene)](η^5-cyclopentadienyl)cobalt (6-E and 6-Z)

A deoxygenated acetonitrile solution (270 ml) of $CpCo(CO)_2$ (0.80 g, 4.4 mmol) and an *E/Z*-mixture (66:34, respectively) of 1-phenyl-1,3-butadiene (0.636 g, 4.9 mmol) were irradiated at room temperature. A 250 watt water-cooled, Pyrex Hanovia photoreactor was used for irradiation. The progress of the reaction was monitored by following the disappearance of $CpCo(CO)_2$ using HPLC [9]. When the reaction was 75% complete, the solvent was removed by rotary evaporation. The resulting oily red residue was purified by column chromatography (Act. III alumina; pentane eluent). The dark red band which eluted was purified further (HPLC [7]) to give: i) **6**-*E* (0.638 g; 57%) as a deep red oil which solidified on standing and ii) **6**-*Z* (0.134 g; 12%) as an orange oil. The product characterizations follow: **6**-*E* mp 68–69°C (from CH_3CN);

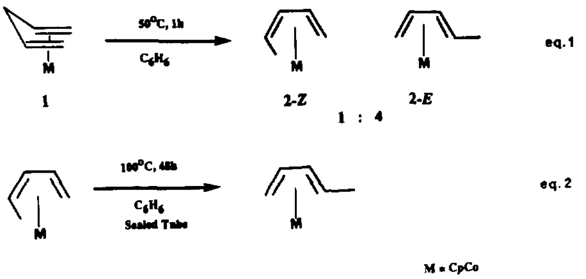
IR(neat) 3038m, 3008m, 2995m, 1595m, 1492m, 1480m, 1440m, 1420s, 1408m, 1108m, 1009s, 898m, 811m, 804m, 760s, 690m cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 254 (M$^+$, 95.6), 239(18.3), 189(21.5), 187(23.4), 130(70.7), 129(76.4), 124(100.0), 115(44.4), 59(36.6); HRMS Calc. $C_{15}H_{15}Co$: 254.0506; found: 254.0500; UV (hexane) λ_{max} 268 (log ϵ = 4.08), 282(4.06), 300(3.54), 357(3.03) nm; ^{1}H NMR (250 MHz, C_6D_6) δ 7.3 (m, 5H), 5.50 (dddd, J = 8.8, 4.4, 1.0, 0.9 Hz, 1H), 5.03 (dddd, J = 9.2, 6.7, 4.4, 0.8 Hz, 1H), 4.52 (s, 5H), 1.98 (ddd, J = 6.7, 1.6, 0.9 Hz, 1H), 1.31 (dd, J = 8.8, 0.8 Hz, 1H), 0.11 (ddd, J = 9.2, 1.6, 1.0 Hz, 1H); ^{13}C NMR (63.07 MHz, C_6D_6) δ 145.36, 127.82, 125.23, 123.59, 80.14, 77.15, 75.43, 49.50, 30.45. Anal. calc. $C_{15}H_{15}Co$: C, 69.43; H, 6.24. Found: C, 69.56; H, 6.07%. **6**-*Z* IR(neat) 2960m, 2920m, 2850m, 1592m, 1258s, 800m, 748s, 695m cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 254 (M$^+$, 100.0), 239(19.3), 189(20.5), 187(26.9), 130(84.9), 129(93.4), 124(98.3), 115(52.5), 59(35.9); HRMS Calc. $C_{15}H_{15}Co$: 254.0506; found: 254.0502; UV (hexane) 271 (log ϵ = 4.12), 278 (4.14), 347 (2.68), 410 (sh, 2.20) nm: ^{1}H NMR (250 MHz, C_6D_6) δ 7.08 (m, 3H), 6.93 (m, 2H), 5.05 (ddd, J = 9.5, 6.6, 3.8 Hz, 1H), 4.79 (dd, J = 7.6, 3.8 Hz, 1H), 4.62 (s, 5H), 4.24 (d, J = 6.6 Hz, 1H), 2.19 (d, J = 7.6 Hz, 1H), 0.23 (d, J = 9.5 Hz, 1H); ^{13}C NMR (63.07 MHz, C_6D_6) δ 142.08, 136.27, 128.45, 123.08, 83.18, 79.48, 74.54, 47.40, 37.25; Anal. calc. for $C_{15}H_{15}Co$: C, 69.43; H, 6.24. Found: C, 69.48; H, 6.19%.

2.14. Solution phase thermolytic conversion of 6-Z to 6-E

A deoxygenated d_6-benzene solution (1.2 ml) of **6**-*Z* (0.026 g; 0.102 mmol) and cyclohexane (2 μl) was heated in a sealed 5 mm precision-bore NMR tube at 150°C. Quantitative conversion (^{1}H NMR) of **6**-*Z* to **6**-*E* was observed to occur within 10 h; no detectable rearrangement was observed to have occurred in 24 h, when the experiment was repeated at 100°C. **6**-*E* was observed to be stable in solution up to approximately 210°C, whereupon slow decomposition to unidentifiable materials took place.

3. Results and discussion

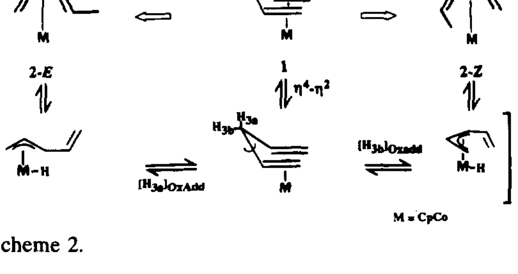
When [η^4-1,2 : 4,5-(pentadienyl)](η^5-cyclopentadienyl)cobalt (**1**) is heated at 50°C in deoxygenated benzene, complete rearrangement to **2**-*E* and **2**-*Z* is observed (Scheme 1; eqn. (1)). The isomerization of **1** produces a 4 : 1 (**2**-*E* : **2**-*Z*) distribution of the two complexes; at 50°C, the observed ratio is invariant on heating for an additional 3 h. At 100°C, **2**-*Z* is found to slowly isomerize to **2**-*E* (eqn. (2)). The conversion of **2**-*Z* to **2**-*E* is quantitative under these conditions. Neither reaction (Scheme 1) gave any indication of degradation during the course of their pyrolysis.



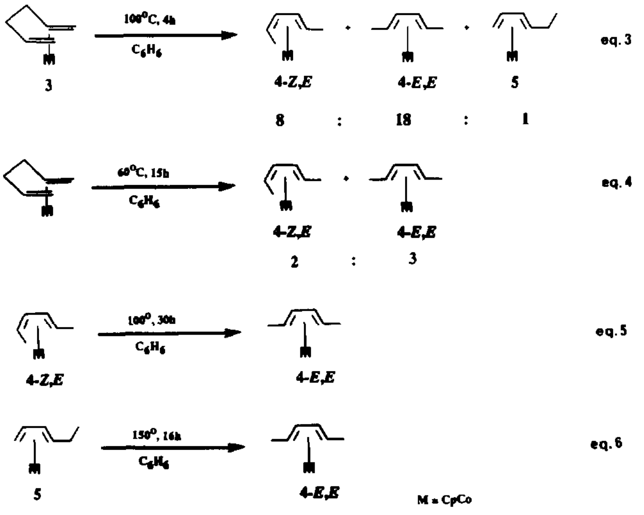
Scheme 1.

The slow, irreversible conversion of **2**-*Z* into **2**-*E*, indicates that the initial rearrangement of **1** produces a kinetic distribution. The facility with which **1** isomerizes to its conjugated isomers is consistent with a traditional prototropic rearrangement [2c,3d]. The high selectivity for the production of **2**-*E* over 2-*Z*, is indicative of a competitive rotation of an allyl group in an η^2-intermediate relative to hydrogen abstraction (Scheme 2); without competitive bond rotation, upon a change-in-hapticity (η^4–η^2), the more proximal allyl hydrogen (H_{3b}) should be preferentially abstracted and the **2**-*Z* isomer should predominate. The final η^4-pentadienyl complex (**2**-*E*) is stable in deoxygenated solution up to 200°C.

For comparative purposes, the low temperature photochemically-induced rearrangement of **2**-*Z* to **2**-*E* was briefly examined, as well. When a toluene solution of **2**-*Z* was irradiated at −96°C at 413 nm (Kr$^+$ ion laser), conversion to **2**-*E* was complete within 2 h. Repetition of the same experiment using 514.5 nm light (Ar$^+$ ion laser), produced a much slower rate of conversion. In this later case, the reaction was only 80% complete after 3 h. The more rapid rate of reaction induced by the shorter wavelength light—at the same power setting—may merely indicate a higher quantum efficiency for initiating the change-in-hapticity prior to the prototropic rearrangement. More probably, the 413 nm light is sufficient to induce a photochemical "envelope flip" isomerization [7b]. Neither photochemical reaction indicated the presence of degradation or the 1,4-isomer.



Scheme 2.

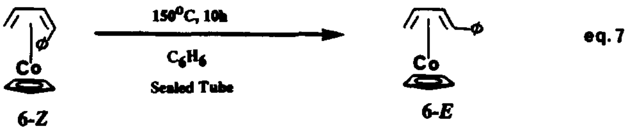


Scheme 3.

The extension of the thermal chemistry to the next higher diene homolog produces similar results. When $[\eta^4$-1,2 : 5,6-(1,5-hexadiene)$](\eta^5$-cyclopentadienyl)cobalt (**3**) is heated at 100°C in deoxygenated benzene, the internal, conjugated **4**-*E*,*E* isomer is produced to a greater extent than the other possible isomers (**4**-*Z*,*E* and **5**; Scheme 3; eqn. (3)). It is interesting to note that at 60°C, no **5** is observable by ^{1}H NMR and the ratio of **4**-*E*,*E* to **4**-*Z*,*E* decreases to 3 : 2 (from 9 : 4; eqn. (4)); the lower reaction temperature appears to enhance the selectivity for formation of the less stable isomer. The rearrangement of both the **4**-*Z*,*E* and the **5** is extremely slow at 100°C. The transformation of pure **4**-*Z*,*E* takes roughly 30 h under these conditions (eqn. (5)). Compound **5** shows no tendency to rearrange at 100°C by ^{1}H NMR. At 150°C, the rearrangement of **5** to **4**-*E*,*E* is still quite slow (eqn. (6)), the reaction going to completion in 16 h; no other products besides **4**-*E*,*E* were detectable during the course of the isomerization. These data indicate that initial rearrangement of **3** at 100°C produces a kinetic distribution of isomeric complexes. The fact that *all* the isomers eventually rearrange to the **4**-*E*,*E* isomer indicates it to be the thermodynamic sink in this system.

The relative thermodynamic stability of acyclic CpCo[diene] complexes is indicated to be conjugated > non-conjugated, internal olefins > terminal olefins, and *E*-configuration > *Z*-configuration. The preference between the geometric *E versus Z* isomers may be the result of simple steric compression from a 1,4-transannular methyl–hydrogen interaction in the *Z* complexes. The coplanar *syn* geometry of the 1,3-CpCo[diene] complexes forces this interaction; such an interaction would explain the absence of the **4**-*Z*,*Z* whose methyl groups would be forced into a space which would be less than the sum of their van der Waals radii [10*]. The electronic (bonding) preference of the conjugated over non-conjugated and internal over terminal olefins appears to follow the trend of the uncomplexed ligands in terms of their relative stability.

As a test the effect of the 1,4-transannular interaction on the relative stability of the diene complexes, **6**-*Z* was prepared [11*]. The constraint of having a phenyl group in the *Z*-geometry should destabilize its complex relative to the *E*-isomer. Compound **6**-*Z* was observed to be quite thermally stable in solution (eqn. (7)). Complete conversion of **6**-*Z* to **6**-*E* took 10 h at 150°C. The formation of **6**-*E* proved irreversible. The slow rate of isomerization of the *Z*-isomer may be due to the lack of a simple prototropic pathway being available for the isomeric interconversion; a thermal "envelope flip" mechanism appears unlikely, as well [7b]. The *E*-isomer was found to be stable in solution to 210°C, whereupon a slow degradation took place.



In summary, a number of acyclic CpCo[diene] complexes was studied thermolytically in deoxygenated solution. The most thermodynamically stable isomers were indicated to be the *E*-isomers of the internal, conjugated complexes. The facility with which the non-conjugated CpCo[diene] complexes rearrange to their conjugated analogs, is consistent with a traditional prototropic isomerization mechanism [2c].

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References and notes

1 H. Reihlen, A. Gruhl, G. Von Hessling and O. Pfregle, *Liebigs Ann. Chem.*, *482* (1930) 161.

2 (a) Y. Qian, G. Li, Y. He, W. Chen, B. Li and S. Chen, *J. Mol. Catal.*, *60* (1990) 19; (b) H. Lehmkuhl and Y.-L. Tsien, *Chem. Ber.*, *116* (1983) 2437; (c) G.W. Parshall and S.D. Ittel, *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes, Second Edition*, Wiley-Interscience, New York, 1992, pp. 10–161; (d) H. Yamamoto, H. Yasuda, K. Tatsumi, K. Lee, A. Nakamura, J. Chen, Y. Kai and N. Kasai, *Organometallics*, *8* (1989) 105; (e) A.T. Aguayo, J.M.

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* Reference number with asterisk indicates a note in the list of references.

Arandes, M. Olazar and J. Bilbao, *Ind. Eng. Chem. Res., 29* (1990) 1172.

3 (a) A. Nakamura, *J. Organomet. Chem., 400* (1990) 35; (b) G. Erker, C. Krüger and G. Müller, *Adv. Organomet. Chem., 24* (1985) 1; (c) H. Yasuda and A. Nakamura, *Angew. Chem. Int. Ed. Engl., 26* (1987) 723; (d) J. Rodriguez, P. Brun and B. Waegell, *Bull. Soc. Chim. France, 6* (1989) 799; (e) M.D. Fryzuk, W.E. Piers, S.J. Rettig, F.W.B. Einstein, T. Jones and T.A. Albright, *J. Am. Chem. Soc., 111* (1989) 5709; (f) C.W. Ong, W.T. Liou and W.S. Hwang, *J. Organomet. Chem., 384* (1990) 133; (g) C. Ebert, T. Gianferrara, M. Graziani, J. Kašpar, P. Linda and A. Trovarelli, *J. Catal., 124* (1990) 4331; (h) J. Kašpar, M. Graziani, A. Trovarelli and G. Dolcetti, *J. Mol. Catal., 55* (1989) 229; (i) N. Satyanarayana and M. Periasamy, *J. Organomet. Chem., 319* (1987) 113; (j) D. Ma, Y. Yu and X. Lu, *J. Org. Chem., 54* (1989) 1105; (k) J. Heveling, *J. Mol. Catal., 58* (1990) 1; (l) D.N. Cox, T. Lumini and R. Roulet, *J. Organomet. Chem., 438* (1992) 195; (m) E. Melendez, A.M. Arif, A.L. Rheingold and R.D. Ernst, *J. Am. Chem. Soc., 110* (1988) 8703; (n) B. Buchmann, U. Piantini, W. von Philipsborn and A. Salzer, *Helv. Chim. Acta, 70* (1987) 1487, and references therein.

4 (a) W. Hendrix and J.L. van Rosenberg, *J. Am. Chem. Soc., 98* (1976) 4850; (b) C.a. Tolman, *J. Am. Chem. Soc., 94* (1972) 2994; (c) D. Bingham, D.E. Webster, and P.B. Wells, *J. Chem. Soc., Dalton Trans.*, (1974) 1514; (d) D. Bingham, D.E. Webster and P.B. Wells, *J. Chem. Soc., Dalton Trans.*, (1974) 1519; (e) H.-F. Klein, R. Hammer, J. Gross and U. Schubert, *Angew. Chem. Int. Ed. Engl., 19* (1980) 809; (f) M. Brookhart and D.M. Lincoln, *J. Am. Chem. Soc., 110* (1988) 8719; (g) M.L.H. Green, A. Sella and L.-L. Wong, *Organometallics, 11* (1992) 2650.

5 D. Bingham, B. Hudson, D. Webster and P.B. Wells, *J. Chem. Soc., Dalton Trans.*, (1974) 1521.

6 (a) R.G. Salomon, *Tetrahedron, 143* (1982) 485; (b) C.G. Kreiter, *Adv. Organomet. Chem., 26* (1986) 297; (c) Y.L. Chow, H. Li and M.S. Yang, *J. Chem. Soc., Perkin Trans., 2* (1990) 17; (d) Y. Inoue, N. Yamasaki, A. Tai, Y. Daino, T. Yamada and T. Hakushi, *J. Chem. Soc., Perkin Trans., 2* (1990) 1389.

7 (a) J.A. King Jr. and K.P.C. Vollhardt, *J. Organomet. Chem., 369* (1989) 245; (b) B. Eaton, J.A. King Jr. and K.P.C. Vollhardt, *J. Am. Chem. Soc., 108* (1986) 1359; (c) J.A. King Jr. and K.P.C. Vollhardt, *Organometallics, 2* (1983) 684; J.A. King Jr. and K.P.C. Vollhardt, *J. Am. Chem. Soc., 105* (1983) 4846.

8 D.F. Shriver and M.A. Drezdzon, *The Manipulation of Air-Sensitive Compounds, 2nd edition*, Wiley-Interscience, New York, 1986.

9 J.M. Huggins, J.A. King Jr., K.P.C. Vollhardt and M.J. Winter, *J. Organomet. Chem., 208* (1981) 73.

10 Organometallic catalysts which initiate olefin isomerization but are not bound to the product often do produce the *Z,Z*-isomers in diene systems. See for example, the titanocene systems [2a,b], also: L. Shusen and Q. Yanlong, *J. Mol. Sci., 5* (1987) 73.

11 The more sterically encumbered *Z*-1-t-butyl-1,3-butadiene produced no CpCo complex under our standard method of synthesis.