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Thermally and photochemically induced vinyl-hydrogen activation of [η^4-1,2 : 3,4-(*trans*-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt: regio- and stereospecific hydrogen migrations

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Abstract

[η^4-1,2 : 3,4-(*trans*-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt (**3**) undergoes dimerization to form a flyover carbene, **5**, with concomitant elimination of one equivalent of *trans*-1,3,5-hexatriene. Structure **5** thermally rearranges via a metal-mediated [1,5]-H shift to carbene **6**: $E_a = 29.1 \pm 0.4$ kcal mol^{-1}, log $A = 11.6 \pm 0.6$. The structures of **5** and **6** were confirmed by single crystal X-ray determination. Low temperature irradiation of **6** generates **13** which undergoes a thermally induced reversion to **6**: $E_a = 19.4 \pm 0.9$ kcal mol^{-1}, log $A = 10.0 \pm 1.3$. Deuterium labeling studies indicate the mechanisms involved in these C–H transformations are intramolecular, regio-, and stereospecific. The chemical study of this system is extended to include a variety of homologous CpCo(triene) complexes. A comparison between the triene approach to the formation of these flyover pentadienyl carbenes and direct carbene addition is described.

Key words: Cobalt; Photochemistry; Hydrogen migration; Bond activation; Thermochemistry; Metallocarbene

1. Introduction

The study of the chemical interactions of unsaturated hydrocarbons with metal centers has been a major focus in catalyst research for more than half a century [1]; this interest has been driven, in part, by the large natural abundance of several industrially important hydrocarbons (*e.g.* ethene, ethyne, propene, butadiene, *etc.*). Many of these metal-induced transformations have been demonstrated to involve the formation of metallocarbenoid species [2]. Such carbenoid species would be derived via C–H bond activation of the initial hydrocarbon [3].

During our work on CpCo bound polyolefin complexes, we wished to examine whether CpCo(η^4-trienes) would undergo ring closure to the corresponding CpCo(η^4-cyclohexadienes); uncomplexed 1,3,5-hexatrienes are known to readily undergo electrocyclic ring closure [4]. Rather, we report that the $(CpCo)_2$ moiety mediates an unprecedented series of intramolecular vinyl-hydrogen rearrangements starting from [η^4-1,2 : 3,4-(*trans*-1,3,5-hexatriene)](η^5-cyclopentadienyl)-cobalt (**3**). These rearrangements result in the formation of pentadienyl metallocarbenes. These metal-mediated carbene transformations can be induced both photochemically and thermally, and reveal stereospecificity for the hydrogen migrations. A preliminary communication has been published [5].

2. Experimental details

2.1. General procedure

Unless otherwise specified, materials were obtained from commercial suppliers 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 subjecting the liquid to several freeze-evacuation-thaw cycles with concomitant atmospheric purge-ex-

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change (*via* a vacuum/nitrogen line assembly); or (ii) by bubbling nitrogen through the liquid for several hours (or until an approx. 10% decrease in solvent volume was observed). All (η^5- cyclopentadienyl)cobalt containing compounds were added to solutions that had been rigorously deoxygenated prior to their use.

The column chromatographic separations were carried out using neutral alumina which had been deactivated to Activity III with water (5% w/w); the neutral alumina was either Alfa Products, activated neutral (CAMAG 95 + % Al_2O_3, 60 mesh) or Woelm N (Activity I, Al_2O_3). High performance liquid chromatography (HPLC) separations and analyses were carried out on a modified Altex/Beckmann Model 330 Isocratic liquid chromatographic system redesigned to handle air-sensitive materials [6]. Altex Ultrasphere-ODS reverse phase columns (10 mm × 25 cm) were used with either an Act. III neutral alumina or a silica supported C_{18} precolumn. The *cis* and *trans* isomers of 1,3,5-hexatriene were separated using preparative scale gas chromatography [7]; the separation was carried out using a Varian Aerograph Model 920 gas chromatograph containing a 6 m × 6 mm stainless steel column packed with 20% Apiezon N on Chromosorb W. All analytical G.C. work was performed on a Hewlett-Packard 5880 analytical gas chromatograph equipped with an HP 5880a mini-computer/integrator outfitted with a 30 m × 0.249 mm DB1, fused silica capillary column from J and W scientific.

Electronic spectra were recorded on either a Varian Cary 219 UV spectrometer or a Hewlett-Packard 8950 UV-visible spectrometer. 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. 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-T magnet. All chemical shift data are reported in parts per million downfield from an internal tetramethylsilane (Me_4Si) standard. Where necessary, the molecular configuration and the proton-proton coupling constants were verified using homonuclear decoupling techniques. Mass spectral data were collected on an AEI-MS-12 (low resolution) or Du Pont CEC 12-110B (high resolution) instrument by the Mass Spectral Service at the University of California, Berkeley. The elemental analyses were carried out by the Microanalytical Laboratory at the University of California, Berkeley.

The continuous wavelength (CW) lasers used in the low temperature photochemical work were either a Spectra Physics Model 171-01 4 W Kr^+ ion CW laser (350 and 413 nm) or the corresponding Coherent Radiation CR-4 4 W Ar^+ ion CW laser (488 and 514.5 nm). Both were obtained from the San Francisco Laser Center.

2.2. *X-Ray structure determinations*

The structures were determined at the University of California Chemistry Department X-Ray Crystallographic Facility (CHEXRAY). The preliminary unit cell and space group were determined from precession photographs. All crystal fragments studied were inserted into thin-wall glass capillaries which were then blown-out with dry N_2 and flame-sealed. All other operations were carried out on either of two Enraf-Nonius CAD-4 diffractometers, one controlled by a DEC PDP 8/a with a RK05 disk and the other by an DEC PDP 8/e with an RL01 disk. Both use Enraf-Nonius software as described in the *CAD-4 Operation Manual*, Enraf-Nonius, Delft, Nov. 1977, updated Jan. 1980. The diffractometers were outfitted with highly oriented graphite monochrometer ($2\Theta_m = 12.2°$) in perpendicular mode, assumed 50% perfect, using Mo Kα radiation (λ 0.71073 Å). Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Kα components of 24 reflections with 2Θ between 24° and 31°.

Crystal data **5**: $C_{16}H_{18}Co_2$, $M = 328.185$, air stable (from acetonitrile), crystal size 0.13 × 0.31 × 0.43 mm^3; a monoclinic Laue symmetry; space group $P2_1/n$ (non-standard setting of $P2_1/c$ (C^5_{2h}, No. 14)); $a = 5.9689(7)$ Å, $b = 26.434(5)$ Å, $c = 8.5044(14)$ Å, $\beta = 98.478(13)°$; $V = 1327.0(6)$ Å^3 at 25°C; $Z = 4$; $\mu_{calcd} = 25.7$ cm^{-1}; $d_{calcd} = 1.65$ g cm^{-3}; scan range $1.5° \leq 2\theta \leq 45°$.

A total of 1793 reflections were collected and reduced to structure factor amplitudes and their e.s.d.s. following our standard procedures [8*–10*]. Analysis of the intensities of several reflections near $\chi = 90°$, measured at 10° increments of rotation around the diffraction vector, showed a variation $I_{max}/I_{min} = 1.39$. The data were corrected for absorption using a Gaussian grid approximation and the measured crystal size and bounding planes. The maximum and minimum transmission factors were 0.733 and 0.476, respectively. Systematic absences were removed and equivalent data averaged to yield 1730 unique reflections of which 1559 had $F^2 > 3\sigma(F^2)$ and were used in least-squares refinement. The three-dimensional Patterson map was interpreted to yield the positions of the two cobalt atoms. A Fourier map phased on these positions yielded

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

the positions of all the remaining non-hydrogen atoms. Refinement of all non-hydrogen atom positions and anisotropic thermal parameters converged with residual [11*], $R = 4.28\%$ and $wR = 7.00\%$. A difference-Fourier map showed density near all positions at which hydrogens were expected. Positions for the hydrogens were then calculated based on idealized geometry and included in the structure factor calculations but not refined. Refinement continued to converge with residuals of $R = 0.0296$, $wR = 0.0458$, and GOF = 3.21 for 163 parameters refined against the 1559 reflections with $F_o^2 > 3\sigma(F_o^2)$. The R-value for all 1730 reflections was 3.78%.

The quantity minimized by the least-squares program was $\Sigma w \| F_u | - | F_c \|^2$, where w is the weight of a given reflection [11*]. The p-factor, used to reduce the weights of high intensity reflections was set at 0.02 throughout the refinement. Trends of the values of the residuals with respect to sin Θ/λ, $|F_o|$, parity and values of h, k, and l were normal. There was no evidence for secondary extinction. The largest peak on the final difference-Fourier had an electron density of 0.35 e $Å^{-3}$, and residual peaks were apparently uncorrelated with the structure. The analytical forms of the scattering factor tables were used [12] and all non-hydrogen scattering factors were corrected for the real and imaginary components of anomalous dispersion [13].

Positional and thermal parameters of the non-hydrogen atoms along with the positions of the hydrogen atoms and a tabulation of the values of F_o and F_c are available as supplementary material.

Crystal data for **6**: $C_{16}H_{18}Co_2$, $M = 328.185$, air stable (from acetonitrile), crystal size 0.16 × 0.26 × 0.30 mm^3; orthorhombic Laue symmetry; space group *Pbca* (No. 61); $a = 8.444(1)$ Å, $b = 13.270(3)$ Å, $c = 23.782(2)$ Å; $V = 2665(1)$ $Å^3$ at 25°C; $Z = 8$; $\mu_{calcd} = 25.6$ cm^{-1}, $d_{calcd} = 1.636$ g cm^{-3}; scan range = $3° \leq 2\theta \leq 45°$.

Preliminary precession photographs showed orthorhombic ($m\,m\,m$) Laue symmetry and systematic absences consistent with space group *Pbca*. Accurate cell dimensions and orientation matrix data were obtained in the preceding fashion. Inspection of the $h = 0$, $k = 0$, and $l = 0$ zones confirmed the systematic absences ($0kl$, $k \neq 2n$; $h0l$, $l \neq 2n$; $hk0$, $h \neq 2n$) noted in the precession photographs.

The 2029 measured intensities were reduced to structure factor amplitudes and their e.s.d.s. by correction for background, scan speed, and Lorentz and polarization effects [8*–10*]. Rejection of the systematic absences yielded 1732 unique data of which 1377, had values of $F^2 > 3\sigma(F^2)$ and were used in the refinement. An absorption correction ($\mu = 25.6$ cm^{-1}) was performed after partial refinement of the structure. The maximum and minimum transmission coefficients were 0.673 and 0.475, respectively.

The structure was solved by normal three-dimensional Patterson and Fourier techniques. The refinement of all non-hydrogen atoms positions and anisotropic thermal parameters converged with residuals $R = 4.74\%$ and $wR = 6.48\%$ [11]. Application of the absorption correction to the data dropped these residuals to $R = 0.0392$ and $wR = 0.0575$ and a difference Fourier map showed peaks near all expected hydrogen atom positions. Idealized hydrogen atom positions were calculated and hydrogens were included in the calculated of structure factors but not refined. After two cycles of least-squares refinement, another difference Fourier showed its largest peak near C_{12} in such a position as to show that the assumption of sp^2 hybridization for C_{12} was poor. All hydrogens were calculated; H_{12}, in particular, was calculated to lie half-way between the idealized sp^2 and sp^3 positions.

The final residuals for 163 variables refined against the 1377 data for which $F^2 > 3\sigma(F^2)$ were $R = 2.27\%$, $wR = 2.84\%$ and GOF = 1.76. The R-value for all 1732 data was 3.96%. The largest peak in the final difference Fourier map had an electron density of 0.19 e $Å^{-3}$ near C_9 and C_{10}. There was no indication of residual density near H_{12}.

The positional and thermal parameters of the non-hydrogen atoms along with the positions of the hydrogen atoms and a listing of the F_o and F_c are available as supplementary material.

Lists of crystal and data collection parameters have been deposited with the Cambridge Crystallographic Data Centre.

2.3. *Preparation of [η^4-1,2:3,4-(trans-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt (3)*

A deoxygenated THF solution (275 ml) of *trans*-1,3,5- hexatriene (0.861 g, 10.75 mmol) was loaded into a medium-pressure Hanovia photoreactor (450 W, Hg vapor lamp). While this reaction medium was being irradiated, a THF solution (10 ml) of $CpCo(CO)_2$ (2.218 g, 11.8 mmol) was added over an 8 h time period at 23°C. When the addition of the $CpCo(CO)_2$ was complete, the resulting dark red solution was irradiated for an additional 4 h to insure complete photo-complexation. The solvent was removed by rotary evaporation and the red-black oily residue purified by column chromatography. Elution with pentane furnished an initial red-brown oily fraction containing **3**,**5**,**6**,**7**, and **8**, followed by a red-purple fraction of $(CpCo)_2(CO)_3$ (49 mg, 2%) as an oil [14]. Subsequent elution with 30% ether/pentane resulted in the elution of $(CpCo)_3(CO)_2$ (90 mg, 5%) as a green black solid [14]. The first red-brown fraction could be purified further using reverse phase HPLC [6] giving (in order of elution): **7** (126 mg, 6% yield) as a brown-black crystalline solid, **3** (140 mg, 64%) as a red oil, **6** (39 mg, 2%) as a green-black crystalline prisms, **5** (232 mg, 12%) as a green-black crystalline solid, and **8** (43 mg, 2%) as a red oil.

[η^4-1,2:3,4-(trans-1,3,5-hexatriene)](η^5- cyclopentadienyl)-cobalt (**3**): IR (neat): 3143, 3100, 3055, 3023, 2980, 2020, 1995, 1642, 1440, 1255, 1182, 1142, 1088, 1040, 1024, 912, 835 cm^{-1}. Mass spectrum (70 eV): *m/e* (relative intensity) 204 (M$^+$, 28.4), 202 (25.2), 189 (18.2), 138 (3.9), 137 (16.0), 124 (100), 105 (11.0), 98 (11), 91 (17.7), 79 (93.7), 66 (47.5), 59 (28.4). UV (hexane, $\lambda_{max} = 282$ (log $\epsilon = 4.07$): 245 (4.02), 256 (4.0), 267 (4.04), 273 (4.02), 352 (3.35), 520 (2.49) nm. ^{1}H NMR (C_6D_6): δ 5.63 (ddd, $J = 15.8$, 9.4, 9.3 Hz, 1H); 5.25 (dd, $J = 15.8$, 2.1 Hz, 1H); 5.08 (dd, $J = 9.4$, 2.1 Hz, 1H); 4.96 (ddd, $J = 8.2$, 4.5, 0.9 Hz, 1H); 4.82 (ddd, $J = 9.1$, 6.4, 4.5 Hz, 1H); 4.58 (s, 5H); 1.88 (ddd, $J = 6.4$, 1.8, 0.9 Hz, 1H); 1.13 (ddd, $J = 9.3$, 8.2, 0.9 Hz, 1H); -0.05 (ddd, $J = 9.1$, 1.8, 0.9 Hz, 1H). ^{13}C NMR (C_6D_6): δ 143.4, 108.6, 79.9, 78.9, 75.7, 50.7, 30.4. Anal. Found: C, 64.66; H, 6.63. $C_{11}H_{13}Co$ Calcd.: C, 64.69; H, 6.42%.

Bis(η^5-cyclopentadienyl)-μ-[cis,cis-2,4-hexadienylidene-1(1,2,3-η^3) : 2(4,5-η^2)1κC^1 : 2κC^1]-dicobalt (Co–Co) (**5**): m.p. 145–146°C (CH_3CN; green-black prisms). IR (CCl_4): 3100, 3000, 2985, 2930, 2890, 1438, 1412, 1362, 1200, 1110, 1032, 995, 858, 850 cm^{-1}. Mass spectrum (70 eV): *m/e* (relative intensity). 328 (M$^+$, 22.8), 326 (31.8), 203 (81.6), 189 (100.0), 143 (13.7), 137 (14.2), 124 (56.3), 118 (26.2), 59 (33.3). UV (hexane, $\lambda_{max} = 256$(log $\epsilon = 3.90$)): 294 (sh, 3.86), 372 (sh, 3.79), 390 (sh, 3.60) nm. ^{1}H NMR (C_6D_6): δ 7.71 (dd, $J = 4.9$, 1.3 Hz, 1H, H_1); 4.72 (s, 10H); 4.56 (ddd, $J = 3.2$, 3.2, 1.3 Hz, 1H, H_3); 4.02 (ddd, $J = 4.9$, 3.2, 0.8 Hz, 1H, H_2); 3.56 (ddd, $J = 8.2$, 3.2, 0.8 Hz, 1H, H_4); 2.68 (dq, $J = 8.2$, 6.4 Hz, 1H, H_5); 0.94 (d, $J = 6.4$ Hz, 3H, H_{methyl}). ^{13}C NMR (C_6D_6): δ 207.7, 82.7, 79.8, 78.5, 66.2, 56.4, 50.3, 18.5. Anal. Found: C, 58.44; H, 5.50. $C_{16}H_{18}Co_2$. Calcd.: C, 58.53; H, 5.53%.

Bis(η^5-cyclopentadienyl)-μ-[1-methyl-cis-2,4-pentadienylidene-1(1,2,3-η^3) : 2(4,5-η^2)1κC^1 : 1κC^1]-dicobalt (Co–Co) (**6**): m.p. 104–106°C (CH_3CN; green-black crystals). IR (CCl_4): 3100, 3015, 2986, 2920, 2885, 2830, 1458, 1356, 1208, 1190, 1110, 1060, 1008, 997, 925, 830 cm^{-1}. Mass spectrum (70 eV): *m/e* (relative intensity) 328 (M$^+$, 33.5), 326 (54.1), 260 (11.0), 203 (99.6), 189 (100.0), 149 (10.8), 124 (32.0), 118 (16.3), 59 (9.7). UV (hexane, $\lambda_{max} = 277$ (log $\epsilon = 4.14$): 343 (sh, 3.66), 474 (sh, 3.29) nm. ^{1}H NMR (C_6D_6): δ 4.82 (dd, $J = 2.4$, 1.6 Hz, 1H, H_3); 4.80 (s, 5H); 4.65 (s, 5H); 3.34 (dddd, $J = 10.2$, 6.9, 1.6, 1.4 Hz, 1H, H_4); 3.24 (dd, $J = 2.4$, 1.4 Hz, 1H, H_2); 2.68 (s, 3H, H_{methyl}); 1.75 (dd, $J = 6.9$, 0.9 Hz, 1H, *E*-H_5); 0.08 (dd, $J = 10.2$, 0.9 Hz, 1H, *Z*-H_5). ^{13}C NMR (C_6D_6): δ 83.6, 79.3, 73.7, 53.1, 52.5, 32.9, 27.5 (the carbene carbon peak could not be located). Anal. Found: C, 58.18; H, 5.59. $C_{16}H_{18}Co_2$ Calcd.: C, 58.53; H, 5.53%.

(μ_2-η^4-syn-1,3,5-hexatriene)(μ_2-carbonyl)[(η^5-cyclopentadienyl)cobalt]$_2$(Co–Co) (**7**): m.p. 121–123°C (CH_3CN); on further heating, the melt was observed to resolidify yielding a second melting point of 200–205°C dec. IR (CCl_4): 3000, 2975, 1980, 1785, 1615, 1430, 1405, 1055, 888 cm^{-1}. Mass spectrum (70 eV): *m/e* (relative intensity) 356 (M$^+$, 4.9), 326 (18.1), 279 (17.3), 204 (68.8), 202 (64.1), 189 (79.9), 167 (38.1), 149 (52.2), 138 (18.1), 137 (58.1), 124 (67.1), 100 (26.6), 98 (60.6), 79 (77.3), 59 (100). ^{1}H NMR (C_6D_6): δ 5.51 (ddd, $J = 16.8$, 10.7, 8.9 Hz, 1H); 5.05 (dd, $J = 16.8$, 1.4 Hz, 1H); 4.87 (d, $J = 8.9$, 1.4 Hz, 1H); 4.83 (dd, $J = 10.3$, 7.1 Hz, 1H, 1H); 4.66 (ddd, $J = 11.8$, 8.2, 7.1 Hz, 1H); 4.66 (s, 5H); 4.64 (s, 5H); 1.91 (dd, $J = 8.2$, 1.7 Hz, 1H); 0.65 (dd, $J = 10.7$, 10.3 Hz, 1H); -0.73 (dd, $J = 11.8$, 1.7 Hz, 1H). ^{13}C NMR (C_6D_6): δ 143.94, 108.69, 86.37, 85.40, 50.24, 45.50, 44.10, 20.30. Anal. Found: C, 57.45; H, 5.24. $C_{17}H_{18}Co_2O$ calcd.: C, 57.30; H, 5.09%.

[(trans-1,3,5-hexatriene)-(η^5-cyclopentadienyl)cobalt]$_2$ (**8**): mass spectrum (70 eV): *m/e* (relative intensity) 408 (M$^+$, 1.12), 407 (1.58), 340 (17.9), 328 (16.1), 326 (25.4), 284 (58.8), 260 (13.9), 217 (29.7), 203 (100.0), 189 (97.4), 163 (10.6), 137 (34.2), 124 (85.6), 118 (22.4), 98 (13.8), 91 (39.2), 79 (18.5), 66 (31.9), 59 (64.2). ^{1}H NMR (C_6D_6): δ 6.18 (m, 1H); 6.0–5.7 (m, 2H); 5.64 (bd, $J = 10$ Hz, 1H); 5.36–5.25 (m, 1H); 5.23–5.03 (m, 2H); 4.97–4.84 (m, 1H); 4.68 (s, 5H); 4.67 (s, 5H); 3.08 (m, 1H); 2.65 (m, 1H); 2.15–1.12 (m, 2H); 0.98 (m, 1H); 0.67 (t, $J = 7.2$ Hz, 1H); 0.28 (t, $J = 7.7$ Hz, 1H); -0.28 (d, $J = 8.4$ Hz, 1H). Compound **8** was found to be *extremely* heat and air-sensitive and could not be characterized further.

2.4. Photochemical generation of bis(η^5-cyclopentadienyl)-μ-[cis,trans-2,4-hexadienylindene-1(1,2,3-η^3) : 2(4,5-η^2),1κC^1 : 2κC^1]-dicobalt (Co–Co) (13)

Compound **6** (18 mg, 0.0441 mmol) was dissolved in toluene-d_8 (0.8 ml) and then sealed in a 5-mm precision-bore pyrex NMR tube under mild vacuum; the sample was deoxygenated using a freeze-thaw procedure [15]. The sample was cooled to -96°C and irradiated for 1 h using 514.5 nm light to generate compound **13**. The relative quantity of **13** produced at this wavelength is observed to be **13**:**6** = 63:37; this **13**:**6** ratio was found to be time-invariant and is presumed to be a photostationary equilibrium. Compound **13** rapidly reverts to **6**, without degradation, on warming the sample to room temperature. ^{1}H NMR (toluene-d_8): δ 7.95 (dd, $J = 5.1$, 2.6 Hz, 1H, H_1); 4.60 (s, 5H); 4.58 (s, 5H); 4.58 (ddd, $J = 3.2$, 3.1, 2.6 Hz, 1H, H_3); 3.58 (ddd,

$J = 5.1, 3.1, 0.8$ Hz, 1H, H_2); 2.96 (ddd, $J = 8.7, 3.2, 0.8$ Hz, 1H, H_4); 1.15 (d, $J = 6.4$ Hz, 3H, H_{methyl}); 0.73 (dq, $J = 8.7, 6.4$ Hz, 1H, H_5). Due to its thermal sensitivity this compound was not isolated.

2.5. *Solution phase thermolysis of 5*

The thermolysis solutions were prepared by dissolving **5** in benzene-d_6 (0.6 ml) and sealing the deoxygenated solutions in 5-mm precision-bore NMR tubes. The samples were run at the following concentrations and temperatures: $[\mathbf{5}]_0 = 3.36 \times 10^{-3}$ M (81.0 ± 0.3°C), $[\mathbf{5}]_0 = 1.355 \times 10^{-2}$ M (100.0 ± 0.3°C), $[\mathbf{5}]_0 = 1.288 \times 10^{-2}$ M (115.0 ± 0.5°C), $[\mathbf{5}]_0 = 1.226 \times 10^{-2}$ M (150.0 ± 1.0°C). The samples were monitored periodically using ^1H NMR spectroscopy. A total of 15–20 data points were acquired on each sample. The reactions were followed for at least three half-lives by monitoring the relative decrease in the methyl doublet signal of **5** (δ 0.94) and the increase in the H_1-endo signal of **6** (δ 0.08) *vs.* an internal standard (1–2 μl of cyclohexane or dioxane). First-order plots of the data yielded straight lines with the following k_{obs} values: $k_{81} = 4.08\ (0.19) \times 10^{-7}\ s^{-1}$, $k_{100} = 3.02\ (0.14) \times 10^{-6}\ s^{-1}$, $k_{115} = 2.53\ (0.15) \times 10^{-5}\ s^{-1}$, $k_{150} = 3.13\ (0.21) \times 10^{-4}\ s^{-1}$. An Arrhenius plot of these data gave $E_a = 29.1 \pm 0.35$ kcal mol^{-1} and log $A = 11.6 \pm 0.6$ (correlation coefficient of $r = 0.9948$).

2.6. *Preparation of [η^4-2,3:4,5-(trans, trans-2,4-hexadienal)](η^5-cyclopentadienyl)cobalt*

A deoxygenated THF solution (275 ml) of *trans*, *trans*-2,4-hexadienal (1.50 g, 15.6 mmol) was loaded into a medium-pressure Hanovia photoreactor. To this reaction medium was added a THF solution (10 ml) of $CpCo(CO)_2$ (1.4 g, 7.8 mmol) at 23°C over a 10 h time period. When the addition was complete, the resulting solution was irradiated for an additional 5 h. The solvent was removed by rotary evaporation and the deep purple-red residue purified by column chromatography (pentane). A total of 1.41 g (82%) of the desired aldehyde complex was collected as a red-purple oil: IR (neat): 3100, 3000, 2955, 2900, 2848, 2705, 1665, 1450, 1165, 1132, 1115, 810 cm^{-1}. Mass spectrum (70 eV): m/e (relative intensity) 220 (M^+, 8.6), 189 (2.7), 124 (34.9), 96 (2.2), 81 (6.7), 72 (44.2), 71 (42.2), 59 (9.7), 42 (100). HRMS calcd. for ($M^+ - 16$) $C_{11}H_{13}Co$: 204.0308. Found: 204.0301. ^1H NMR (C_6D_6): δ 9.23 (d, $J = 6.1$ Hz, 1H); 5.39 (dd, $J = 8.2$, 4.6 Hz, 1H); 4.42 (m, 1H); 4.41 (s, 5H); 0.86 (m, 1H); 0.86 (s, 3H); 0.44 (dd, $J = 8.2$, 6.1 Hz, 1H). ^{13}C NMR (C_6D_6): δ 196.96, 82.23, 79.87, 76.94, 50.49, 46.88, 19.83. Anal. $C_{11}H_{13}CoO$ calcd.: C, 60.04; H, 5.95%. Found: C, 60.74; H, 6.50.

2.7. *Preparation of [η^4-1,2:3,4-(trans-1,3,5-heptatriene)](η^5-cyclopentadienyl)cobalt (**14a**) and [η^4-3,4:5,6-(trans-1,3,5-heptatriene)](η^5-cyclopentadienyl)cobalt (**14b**)*

To cold, deoxygenated THF (300 ml, −78°C) were added n-butyllithium (2.75 ml, 4.54 mmol; 1.65 M in hexane) and $[\Phi_3PCH_3]^+I^-$ (1.836 g, 4.54 mmol). The mixture was stirred for 2 h at −78°C. To the resulting orange colored solution was added [η^4-2,3:4,5-(*trans*-2,4-hexadienal)(η^5-cyclopentadienyl)cobalt (490 mg, 2.23 mmol) dissolved in THF (10 ml), dropwise over a 10 min time period. The solution was stirred at −78°C for 1 h then allowed to warm slowly to room temperature. After stirring at room temperature for 30 min, the solvent was removed by vacuum transfer. The resulting oil was purified by column chromatography (pentane). A red band eluted containing **14a,b** and Φ_3PO (approx. 500 mg total). This sample was purified further using reverse phase HPLC [6] to give a mixture of **14a** and **14b** (84:16, 266 mg, 55%) as a red oil.

Characterization of the mixture: IR (neat): 3050, 3005, 2999, 2952, 2920, 2850, 1645, 1618, 1440, 1418, 1380, 1202, 1158, 1108, 1008, 995, 970, 890, 804 cm^{-1}. mass spectrum (70 eV): m/e (relative intensity) 218 (M^+, 42.9) 216 (25.8), 203 (9.6), 189 (18.8), 151 (18.5), 124 (100), 98 (13.8), 94 (19.1), 91 (14.6), 79 (42.4), 77 (23.8), 66 (27.8), 65 (17.4), 59 (34.4). ^1H NMR (C_6D_6) of **14a**: δ 5.68 (dq, $J = 13.6$, 6.3 Hz, 1H); 5.48 (dd, $J = 13.6$, 8.6 Hz, 1H); 4.95 (m, 1H); 4.88 (m, 1H); 4.63 (s, 5H); 1.88 (dd, $J = 6.3$, 1.6 Hz, 1H); 1.51 (dd, $J = 6.3$, 1.8 Hz, 3H); 1.23 (dd, $J = 9.9$, 8.6 Hz, 1H); −0.08 (d, $J = 8.7$ Hz, 1H). ^1H NMR (C_6D_6) of **14b**: δ 5.68 (m, 1H); 5.26 (m, $J = 16.5$, 1.5 Hz, 1H); 5.07 (dd, $J = 9.7$, 1.5 Hz, 1H); 4.88 (m, 1H); 4.62 (m, 1H); 4.52 (s, 5H); 1.03 (d, $J = 5.8$ Hz, 3H); 1.00 (m, 1H); 0.62 (dq, $J = 9.6$, 5.8 Hz, 1H). Anal. Found: C, 65.82; H, 7.05. $C_{12}H_{15}Co$ calcd.: C, 66.06; H, 6.93%.

2.8. *Thermal rearrangement of **14a** and **b***

The regioisomeric mixture of **14a** and **14b** (5.0 mg, 0.0229 mmol) was dissolved in deoxygenated benzene-d_6 (0.7 ml) and then heated at 150°C for 18 h. The crude ^1H NMR indicated 5–6 sets of CpCo pairs were detectable of which three complexes were dominant; five to six compounds total with three major products. This solution was purified by HPLC, producing one brown-black fraction which contained **15** (68%), **16** (24%), and **17** (8%) as an inseparable mixture (3.2 mg, 64%); the ratio of products was determined from their relative ^1H NMR integrations.

Characterization of the purified pyrolysis mixture: mass spectrum (70 eV): m/e (relative intensity) 342 (M^+, 23.7); 340 (29.8); 217 (66.9); 215 (27.8); 189 (100.0); 149 (33.7); 124 (29.5); 94 (14.4); 93 (14.6); 91 (17.7); 84

(56.5); 79 (31.4); 77 (19.3); 66 (76.1); 59 (6.6); 57 (34.1). ^{1}H NMR of **15** (C_6D_6): δ 4.82 (m, 1H, H_3); 4.74 (s, 5H); 4.63 (s, 5H); 3.16 (m, 1H, H_2); 3.02 (dd, $J = 4.2$, 1.1 Hz, 1H, H_4); 2.98 (dq, $J = 7.4$, 7.3 Hz, 1H, H–CH_2); 2.60 (dq, $J = 7.4$, 7.3 Hz, 1H, H–CH_2); 1.41 (dd, $J = 6.8$, 0.8 Hz, 1H, H_5-exo); 0.92 (t, $J = 7.3$ Hz, 3H, H–CH_3); −0.40 (dd, $J = 10.1$, 0.8 Hz, 1H, H_5-endo). ^{1}H NMR of **16** (C_6D_6): δ 4.71 (s, 5H); 4.61 (s, 5H); 4.43 (m, 1H, H_3); 2.94 (bs, 1H, H_2); 2.88 (m, 1H, H_4); 2.54 (s, 3H, C_1–CH_3); 0.82 (d, $J = 6.2$ Hz, 3H, C_5–CH_3); 0.56 (m, 1H, H_5-endo). ^{1}H NMR of **17** (C_6D_6): δ 4.73 (m, 1H, H_3); 4.69 (s, 5H); 4.61 (s, 5H); 4.32 (m, 1H, H_2); 3.47 (m, 1H, H_4); 3.06 (m, 1H, H_5-exo); 2.38 (s, 3H, C_1–CH_3); 0.52 (d, $J = 5.9$ Hz, 3H, C_5–CH_3).

2.9. Solution phase thermochemical reversion of 13 to 6

The solution of **13** to be pyrolyzed was prepared by dissolving **6** (1.5 mg, 0.00457 mmol) in toluene-d_8 (0.56 ml). The resulting solution ($[\mathbf{6}]_0 = 8.17 \times 10^{-3}$ M) was sealed in a precision-bore 5-mm NMR tube under mild vacuum; the identical sample was used for all pyrolysis runs. The runs were carried out in an NMR spectrometer probe at the following temperatures: 18 ± 0.3, 28 ± 0.3, 41 ± 0.3 and 57 ± 0.3°C. Before each run, the sample was irradiated (514.5 nm) at −96°C until a **13**:**6** ratio of at least 55:45 was attained. The data were acquired at intervals (10, 15, or 25 min) such that 10–20 data points were collected before complete reversion to **6** occurred. The extent of reversion was followed by monitoring the relative rate of decrease in the methyl doublet absorption of **13** (δ 1.15) and the rate of increase of the methyl singlet of **6** (δ 2.68) *vs.* a cyclohexane standard. The data followed a first-order rate expression yielding straight line plots with the following k_{obs} values: $k_{18} = 2.65(0.16) \times 10^{-5}$ s^{-1}, $k_{28} = 5.36(0.26) \times 10^{-5}$ s^{-1}, $k_{41} = 1.80(0.14) \times 10^{-4}$ s^{-1}, $k_{57} = 1.64(0.22) \times 10^{-3}$ s^{-1}. An Arrhenius plot of these data yields $E_a = 20.2 \pm 0.9$ kcal mol^{-1} and log $A = 10.4 \pm 1.3$ (correlation coefficient $r = 0.984$).

2.10. Preparation of [η^4-1,2 : 3,4-(cis-1,3,5-hextriene)](η^5-cyclopentadienyl)cobalt (2)

cis-1,3,5-Hexatriene (62.5 mg, 0.780 mmol) [7] and $CpCo(CO)_2$ (93.6 mg, 0.520 mol) dissolved in deoxygenated toluene-d_8 (0.70 ml) were sealed in a 5-mm precision-bore NMR tube under mild vacuum. The sample was immersed in a cooling bath (−78°C) and then irradiated using an ORIEL lamp (Model 6285, 500 W, medium-pressure Hg lamp). To minimize the potential for photochemically induced side-reactions, the light was filtered using both a $CuSO_4/H_2O$ solution (for IR radiation) and a Corning Pyrex filter (Model 3389, 2 mm thick, 404 nm $\lambda_{\text{cut-off}}$). The reaction progress was monitored periodically using ^{1}H NMR spectroscopy. After approximately 36 h, the concentration of **2** reached a maximum (35% yield). Continued irradiation led to increasing amounts of its geometric isomer, [η^4-1,2 : 3,4-(*trans*-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt (**3**) at the expense of **2**. Irradiation at higher temperatures or the use of different light sources resulted in similar or diminished yields of the desired material. ^{1}H NMR spectrum (toluene-d_8) of **2**: δ 6.95 (ddd, $J = 11.1$, 10.3, 9.8 Hz, 1H, H_5); 5.79 (d, $J = 11.1$ Hz, 1H, Z-H_6); 5.18 (d, $J = 9.8$ Hz, 1H, E-H_6); 5.15 (m, 1H, H_3); 5.00 (m, 1H, H_2); 4.41 (s, 5H, H_{Cp}); 4.14 (ddd, $J = 10.3$, 8.0, 1.6 Hz, 1H, H_4); 2.65 (d, $J = 6.4$ Hz, 1H, E-H_1); 1.87 (d, $J = 8.6$ Hz, 1H, Z-H_1).

2.11. Preparation of [η^2-1,2-(cis-1,3,5-hexatriene)](PPh_3)(η^5-cyclopentadienyl)cobalt (4)

cis-1,3,5-hexatriene (15 mg, 0.172 mmol) [7] and $CpCo(PPh_3)_2$ (56 mg, 0.086 mmol) dissolved in deoxygenated benzene-d_6 (1.5 ml) were filtered through a packed glass-wool plug and then transferred into a 5-mm precision-bore NMR tube. The latter was sealed under a nitrogen atmosphere and examined using ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum revealed the presence of both complexed (δ 7.76 and 7.15) and uncomplexed (δ 7.48 and 7.15) PPh_3, free *cis*-1,3,5-hexatriene, and **4**. ^{1}H NMR (C_6D_6) of **4**: δ 7.05 (ddd, $J = 16.6$ 10.2, 9.8 Hz, 1H, H_5); 6.18 (dd, $J = 10.2$, 8.6 Hz, 1H, H_4); 5.45 (d, $J = 16.6$ Hz, 1H, Z-H_6); 5.42 (dd, $J = 9.6$, 8.6 Hz, 1H, H_3); 5.26 (d, $J = 9.8$ Hz, 1H, E-H_6); 4.50 (d, J(P–H) = 1.04 Hz, 5H, H_{Cp}); 2.63 (dddd, $J = 12.1$, 11.7(P–H), 9.6, 7.7 Hz, 1H, H_2); 2.52 (ddd, $J = 12.1$ 3.8(P–H), 0.9 Hz, 1H, Z-H_1); 1.34 (ddd, $J = 9.9$(P–H), 7.7, 0.9 Hz, 1H, E-H_1). When this solution was heated to 45°C, **4** was observed to cleanly produce a 1:1 mixture of [η^4-1,2:3,4-(*trans*-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt (**3**) and uncomplexed PPh_3 within a 3.5 h time period; no other species were detectable in solution.

2.12. Preparation of [η^4-1,2:9,10-(ortho-divinylbenzene)](η^5-cyclopentadienyl)cobalt (18)

$CpCo(CO)_2$ (277 mg, 154 mmol) and *o*-divinylbenzene (200 mg, 154 mmol) were dissolved in deoxygenated THF (275 ml) and irradiated in a medium-pressure Hanovia photoreactor at room temperature. After the photo-complexation was complete (~ 8 h), the solvent was removed by rotary evaporation yielding **18** (372 mg, 95%) as an orange-red liquid (> 98% pure by ^{1}H NMR analysis). The neat material crystallized on standing: m.p. 98–99°C. IR (KBr) 3058, 0340, 3010, 2970, 1572, 1486, 1448, 1408, 1353, 1180, 1018, 885, 810, 790, 743 cm^{-1}. Mass spectrum (70 eV): m/e (relative intensity) 254 (M^+, 49.5), 252(30.3), 189(7.7), 187(33.2), 130(75.4), 129(77.2), 128(81.0), 124(67.4), 115(70.9), 102(22.6), 98(15.4), 84(100), 59(47.4). ^1H NMR (C_6D_6): δ 7.1–6.98 (m, 4H); 4.38 (s, 5H); 4.24 (dd, J = 11.4, 8.8 Hz, 2H); 2.70 (d, J = 8.8 Hz, 2H); 1.38 (d, J = 11.4 Hz, 2H). ^{13}C NMR (C_6D_6): δ 147.05, 126.15, 124.26, 84.11, 59.63, 43.35. Anal. Found: C, 69.87; H, 5.88. $C_{15}H_{15}Co$ calcd.: C, 70.80; H, 5.95%.

2.13. Preparation of [η⁴-1,2:3,4-(trans-1-phenyl-1,3-butadiene)](η⁵-cyclopentadienyl)cobalt (20) and [η⁴-1,2:3,4-(cis-1-phenyl-1,3-butadiene)](η⁵-cyclopentadienyl)cobalt (19)

$CpCo(CO)_2$ (0.80 g, 4.4 mmol) and a *cis/trans* mixture (34:66) of 1-phenyl-1,3-butadiene (0.636 g, 4.9 mmol) were irradiated in acetonitrile (270 ml) using a medium-pressure Hanovia photoreactor; the photoreactor was immersed in an ice-water bath to maintain a solution temperature of *ca.* 23°C. The reaction progress was monitored using HPLC by following the disappearance of $CpCo(CO)_2$. When 75% of the latter had been consumed, irradiation was stopped, the solvent removed by rotary evaporation, and the resulting red oily residue purified using column chromatography (pentane eluent). A red band eluted and its components separated using reverse phase HPLC. This procedure yielded **19** (134 mg, 12%) as an orange oil and **20** (638 mg, 57%) as a deep red oil which solidified on standing.

Characterization of **19**: IR (neat): 2960, 2920, 2850, 1592, 1258, 800, 748, 695 cm^{-1}. Mass spectrum (70 eV): m/e (relative intensity) 254(M^+, 100); 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 Found $C_{15}H_{15}Co$: 254.0502. $C_{15}H_{15}Co$ calcd.: 254.0506. UV (hexane, λ_{max} = 278(log ϵ = 4.14)): 271 (4.12), 347 (2.68), 410 (2.20) nm. ^1H NMR (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 (C_6D_6): δ 142.08, 136.27, 128.45, 123.08, 83.18, 79.48, 74.54, 47.40, 37.25.

Characterization of **20**: m.p. 68–69°C (CH_3CN). IR (neat): 3038, 3008, 2995, 1595, 1492, 1480, 1440, 1420, 1408, 1108, 1009, 898, 811, 804, 760, 690 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), 115 (44.4), 59 (36.6). HRMS Found $C_{15}H_{15}Co$: 254.0500. $C_{15}H_{15}Co$ calcd.: 254.0506. UV (hexane, λ_{max} = 268(log ϵ = 4.08)): 282 (4.06), 300 (3.54), 357 (3.03) nm. ^1H NMR (C_6D_6): δ 7.30 (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 (C_6D_6): δ 145.36, 127.82, 125.23, 123.59, 80.14, 77.15, 75.43, 49.50, 30.45. Anal. Found: C, 69.56; H, 6.07. $C_{15}H_{15}Co$ calcd.: C, 69.43; H, 6.24%.

2.14. Solution phase thermolysis of cis- and trans-[η⁴-1,2:3,4-(1-phenyl-1,3-butadiene)](η⁵-cyclopentadienyl)cobalt (19 and 20)

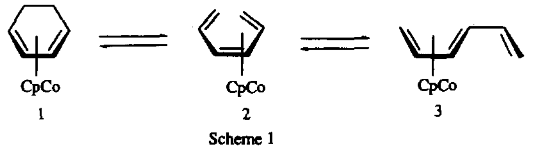
A deoxygenated benzene-d_6 solution (1.2 ml) of **20** (26 mg, 102 μmol) was sealed in a standard 5-mm precision-bore NMR tube and heated at 150°C by complete immersion in an oil bath. Periodic spectroscopic analysis revealed the quantitative conversion of **19**–**20** within 10 h; no rearrangement was observed when the identical experiment was performed at 100°C for 24 h. Compound **20** was found to be stable in solution up to approximately 210°C, whereupon gradual decomposition to unidentifiable (and intractable) materials took place.

2.15. Preparation of [η⁴-1,3-(trans-2-methyl-4-phenyl-1-oxo-1,3-butadiene)](η⁵-cyclopentadienyl)cobalt (22)

A THF solution (350 ml) containing $CpCo(CO)_2$ (1.20 g, 6.67 mmol) was irradiated at room temperature for 2 h using a Rayonet photoreactor (350 nm lamps); pre-generation of $Cp_2Co_2(CO)_3$ *in situ*. To the resulting purple-red solution was added the lithium salt of the tosyl hydrazone of *trans*-4-phenyl-3-buten-2-one (**21**; 0.534 g, 1.67 mmol). Irradiation was continued for another 16 h while the solution was purged with nitrogen. The solvent was removed by rotary evaporation to give a black-brown residue. The material was purified by column chromatography (pentane) to produce one red fraction containing impure **22**. Further purification by reverse phase HPLC gave **22** (186 mg, 40%) as orange needles: m.p. 152–153°C (CH_3CN). IR (CCl_4) 3030, 2960, 2920, 2858, 2360, 1769, 1485, 1377, 1113, 1030, 885, 868, 852, 695 cm^{-1}. Mass spectrum (70 eV) m/e (relative intensity) 282 (M^+, 25.6), 254 (58.8), 253 (53.0), 239 (68.8), 189 (8.2), 187 (22.7), 180 (22.1), 164 (12.7), 152 (23.0), 146 (14.6), 129 (29.6), 124 (100), 115 (21.7), 98 (22.1), 84 (64.1), 59 (65.2). ^1H NMR (C_6D_6) δ 7.13 (m, 5H); 5.70 (d, J = 8.6 Hz, 1H); 4.45 (s, 5H); 2.52 (d, J = 8.6 Hz, 1H); 1.41 (s, 3H). ^{13}C NMR (C_6D_6); δ 226.29, 143.41, 127.95, 126.84, 124.74, 88.31, 84.76, 48.84, 35.55, 12.26. Anal. Found: C, 67.45; H, 5.48. $C_{16}H_{15}CoO$ calcd.: C, 68.09; H, 5.36%.

3. Results and discussion

Our intended thrust was to study metal-mediated electrocyclic transformations on a CpCo template (Scheme 1); the classic comparative electrocyclic paradigm was to be the hexatriene–cyclohexadiene interconversion [4]. For this study, both the requisite CpCo complexes were prepared. The η⁴-1,2:3,4-(1,3-

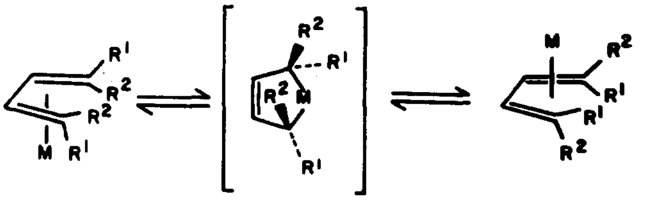


Scheme 1.

cyclohexadiene)](η^5-cyclopentadienyl)cobalt (**1**) was prepared via a previously published procedure [16]. Neither photochemical irradiation nor solution pyrolysis of **1** initiated electrocyclic ring opening of the complexed cyclohexadiene. These studies were terminated once decomposition of **1** became detectable.

The possibility that **1** represented a thermodynamic sink further necessitated the preparation and study of the *cis*-1,3,5-hexatriene complex. Unfortunately, our attempts to synthesize and isolate the pure η^4-1,2:3,4-(*cis*-1,3,5-hexatriene)CpCo complex **2** proved unsatisfactory; all attempts to isolate [η^4-1,2:3,4-(*cis*-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt (**2**) for complete characterization led to degradative decomplexation to the free ligand. The original approach to **2** was *via* a low-temperature (−78°C) photochemical complexation method. When stoichiometric amounts of pure *cis*-1,3,5-hexatriene and $CpCo(CO)_2$ were photolyzed in toluene-d_8, a small amount of **2** (30–85%) was observed. However, prolonged irradiation of this reaction mixture generated progressively more **3**. The amount of **3** formed appeared to increase over time at the expense of **2**; neither uncomplexed *cis*- nor *trans*-1,3,5-hexatriene was ever observed "free" in the reaction solution. The $\Delta^{3,4}$ *cis* → *trans* olefin isomerization of the hexatriene ligand of **2** in the formation **3**, is believed to occur through a photochemically induced "envelope" inversion process.

Such low temperature photochemical inversion processes, have been demonstrated for a series of related $CpCo(\eta^4\text{-butadiene})$ complexes [17].



Since a photo-complexation approach to **2** was hampered by its subsequent photochemically induced isomerization to **3**, an alternate route was employed. When *cis*-1,3,5-hexatriene was mixed stoichiometrically with $CpCo(PPh_3)_2$ (benzene-d_6; room temperature), the immediate, quantitative formation of [η^2-1,2-(*cis*-1,3,5-hexatriene)](PPh_3)(η^5-cyclopentadienyl)cobalt (**4**) was observed along with one equivalent of "free" PPh_3. Heating the solution containing **4** to 45°C, resulted in its gradual (3.5 h), quantitative conversion to **3**. The transient formation of **2** during **4**'s rearrangement to **3**, was never observed. Studies related to the direct thermolysis of **2** have been tabled until a more efficient synthesis can be developed.

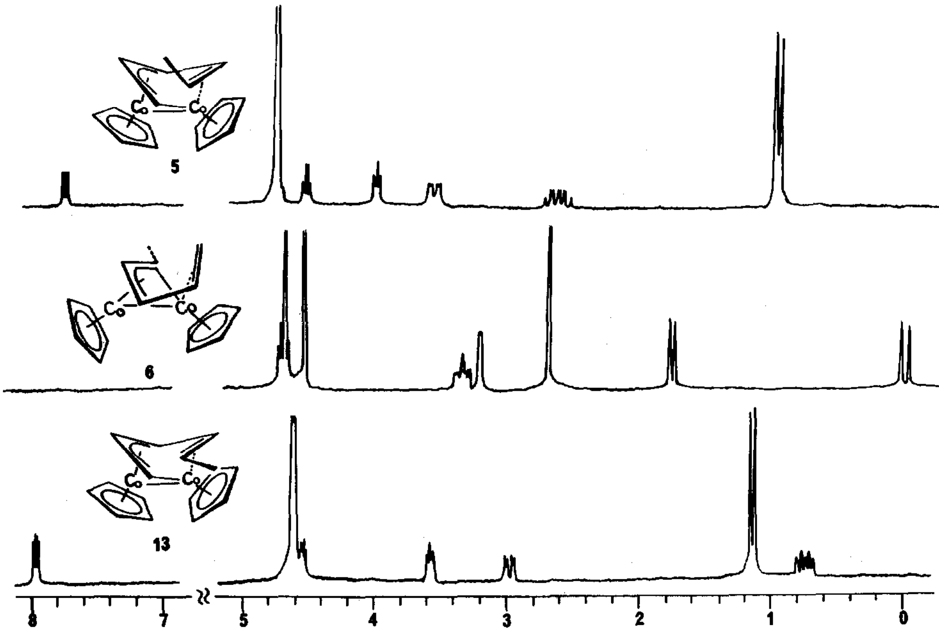


Fig. 1. ^{1}H NMR chemical shift comparison data of structures **5**, **6** and **13**.

Although undetectable, if compounds **2** and **3** were in equilibrium with each other, the metal-mediated electrocyclic rearrangement might still occur. The starting [η^4-1,2:3,4-(*trans*-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt (**3**) is conveniently prepared *via* the photo-complexation of *trans*-1,3,5-hexatriene with $CpCo(CO)_2$ in a 64% isolated yield. A number of secondary products are generated during the complexation reaction as well: **5** (12%), **6** (2%), [μ_2-η^4-syn-1,3,5-hexatriene]-(μ_2-carbonyl)[(η^5-cyclopentadienyl)-cobalt]$_2$(*Co–Co*) (**7**; 6%), the clusters $(CO)_3(CpCo)_2$ (2%) and $(CO)_2(CpCo)_3$ (5%) [14], and an extremely sensitive red oil having the composition of a dimer of **3** (**8**; 2%) [18]. The unique structure of these secondary cobalt complexes (*e.g.* **5** and **6**) indicated a series of novel prototropic rearrangement of the hexatriene moiety had occurred. The source of these unexpected complexes form the focus of this paper.

The configuration of **5** and **6** could be readily deduced from their respective NMR spectra (Fig. 1). In the ^1H NMR, **5** shows five distinct proton resonances, one high field methyl doublet (δ 0.94), and a singlet which corresponds to two superimposed Cp rings at δ 4.72; the two Cp rings are distinguishable by ^{13}C NMR occurring at 79.8 and 82.7 ppm. The carbene ^{13}C signal is observed at 207.7 ppm and exhibits a diagnostic dd pattern at δ 7.71 in its proton NMR spectrum. Compound **6** shows five distinct proton resonances, two distinct Cp signals in both its proton (4.80 ppm and 4.65 ppm) and carbon (δ 83.6 and δ 79.3) spectra, but no ^1H carbene resonance. The methyl signal of **6** (fig. 1) appears as a singlet at δ 2.68 and the terminal methylene resonances of the olefin are shifted to high field: $H_Z = \delta$ 0.08 and $H_E = \delta$ 1.75. The relative proton-proton configurations for both pentadienyl backbones were verified using standard $^1H\{^1H\}$ decoupling techniques.

Although, the NMR data could be used to deduce the backbone configurations of **5** and **6**, their actual appended conformation to the Cp–Co–Co–Cp moiety could not. As a result, the interrelationship of these pentadienyl carbene complexes and their respective conformations were confirmed by single crystal X-ray structure determination (Figs. 2 and 3). Both structures **5** and **6** consist of discrete molecules of $Co_2(C_5H_5)_2(C_6H_8)$. The shortest intermolecular contact between molecules of **5** is a distance of 3.67 Å between C_7 and C_1 of a molecule related by the n-glide. The shortest intermolecular contacts of **6**, between non-hydrogen atoms in the molecules, are 3.44 Å and 3.47 Å from C_{14} to C_9 and C_{10} of the molecule related by the b-glide at $-1/4$ in x. All other intermolecular contacts are greater than 3.65 Å. The Co–Co bond lengths for **5** and **6** are 2.494 Å and 2.478 Å, respectively.

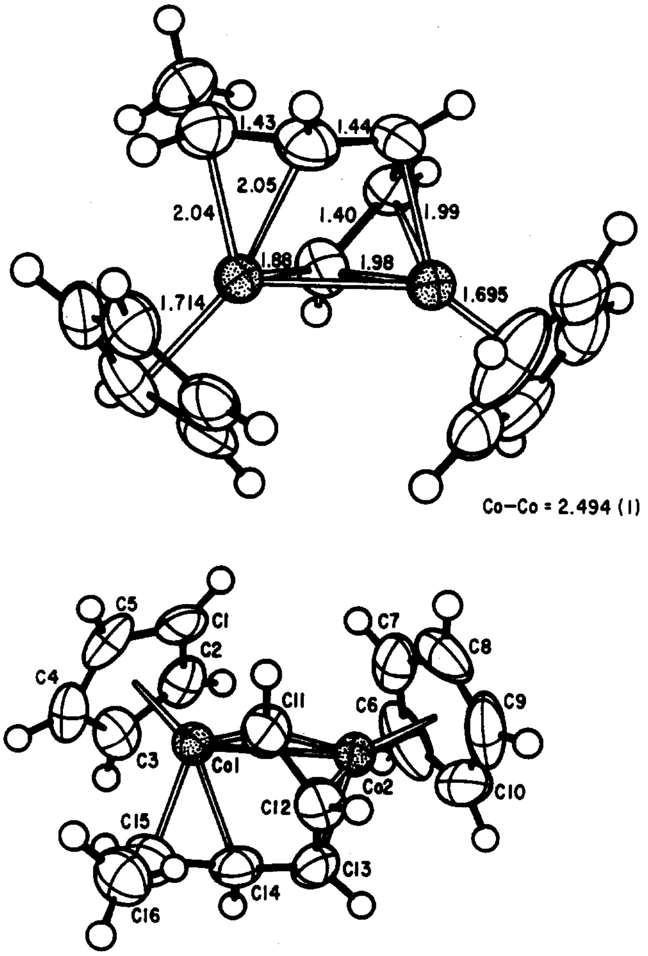


Fig. 2. The interrelationship of the pentadienyl carbene complexes and their respective confirmations.

The C_6H_8 moiety in each complex is completely bonded to the Cp–Co–Co–Cp portion. In **5** (Fig. 2), C_{11} is σ-bonded to Co_1 (1.884 Å) and shares in the allylic bonding to Co_2 of the C_{11}, C_{12}, C_{13} group, thus bridging the Co–Co_2 bond. Co_1 is also bonded to C_{14} (2.051 Å) and C_{15} (2.042 Å) in what can be considered formally as π-bonding of a double bond to the metal; this interaction appears very strong as evidenced by the extreme lengthening of the C_{14}–C_{15} double bond to 1.435 Å. The C_{14}–Co_2 distance is relatively short (2.555 Å) as well. The transannular pentadienyl ring distance, $C_{11} \leftrightarrow C_{15}$, is 2.838 Å. The interatomic distances are listed in Table 1.

In **6** (Fig. 3), C_{15} is σ-bonded to Co_1 and shares the π-allyl bonding to Co_2. Co_1 is π-bound to C_{11} (2.022 Å) and C_{12} (2.052 Å) as a double bond; the lengthening of this double bond (1.403 Å) is not as large as in **5**. The transannular ring distance ($C_{11} \leftrightarrow C_{15}$) in **6** is 2.773 Å. The distances between the cobalt centers and the centers of their corresponding Cp centroids are

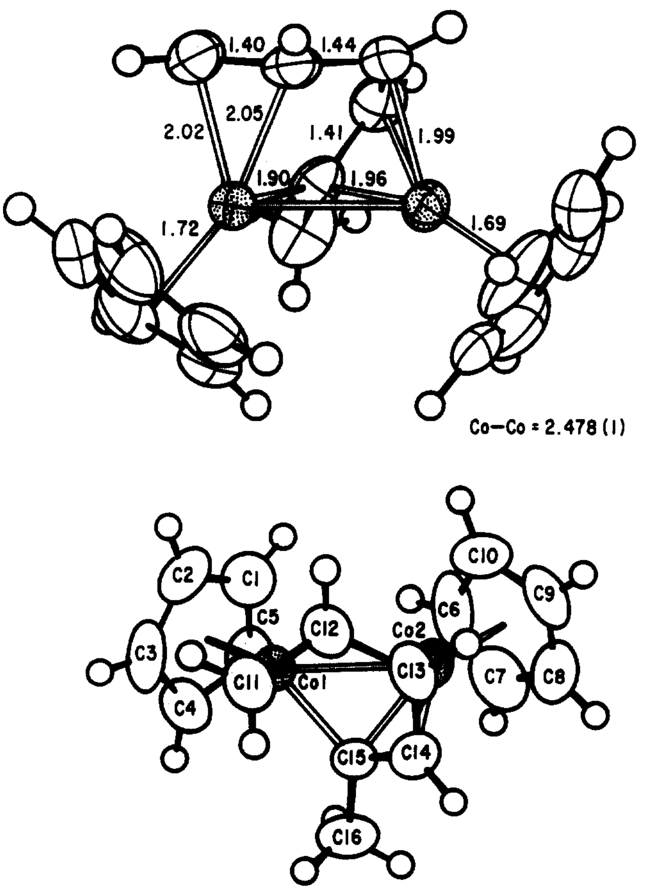


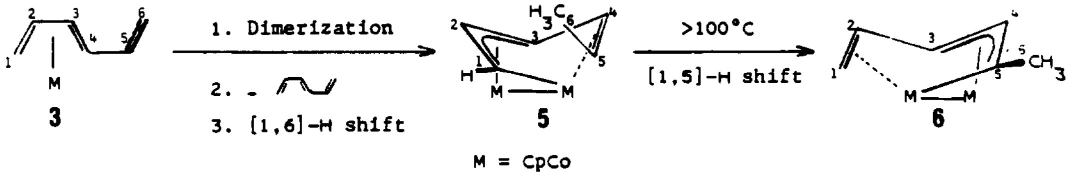
Fig. 3. The interrelationship of the pentadienyl carbene complexes and their respective confirmations.

nearly identical at 1.720 Å (Co_1–Cp) and 1.693 Å (Co_2–Cp). The interatomic distances are listed in Table 1.

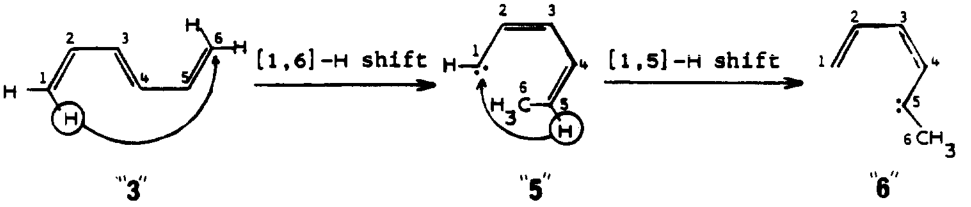
On heating, pure [η^4-1,2:3,4-(*trans*-1,3,5-hexatriene)](η^5-cyclopentadienyl)cobalt (**3**) undergoes a novel C–H skeletal rearrangement at modest temperatures (60–80°C, 12–24 h; Scheme 2). Compound **5** is formed quantitatively; no **1** was detectable. This transformation formally corresponds to a "CpCo" transfer reaction between two **3**s with the synchronous elimination of one equivalent of the *trans*-1,3,5-hexatriene ligand. The "flyover" carbene ligand of **5** derives from an intramolecular [1,6]-H transfer within the appended *trans*-1,3,5-hexatriene (Scheme 3). This thermally induced C–H activation of a CpCo bound hexatriene fragment, is in distinct contrast to the thermochemistry of the isostructural and isolobal CpRh [19] and $(CO)_3Fe$ [20] complexes. In these latter two systems, vinyl C–H activation has not been observed at any temperature; rather, simple thermally induced migration of the metal fragment along the ligand conjugated π-system is observed.

The structural rearrangement of the ligand during the [1,6]-H migration is quite remarkable (Scheme 3). The complexed *trans*-1,3,5-hexatriene undergoes a $\Delta^{3,4}$ geometric isomerization during the formation of the alkylidiene carbene; *i.e.* the central *trans* double bond ($\Delta^{3,4}$) is rotated 180° (**3**) into a cisoid form in **5**. The preparation of "flyover" carbene ligands similar to that of **5** (or **6**) is traditionally accomplished *via* the addition of allenes or acetylenes to metallo-carbenes [21]. The parent carbene ligand (*cis,cis*-pentadienylidene; *i.e.* no methyl substituent) has been prepared for the isolobal $Fe(CO)_3$ system by a metallo-carbene-acetylene method [21h,o].

The kinetic-rate expression for the thermolysis of **3**, was found to be concentration dependent. Under high



Scheme 2.



Scheme 3.

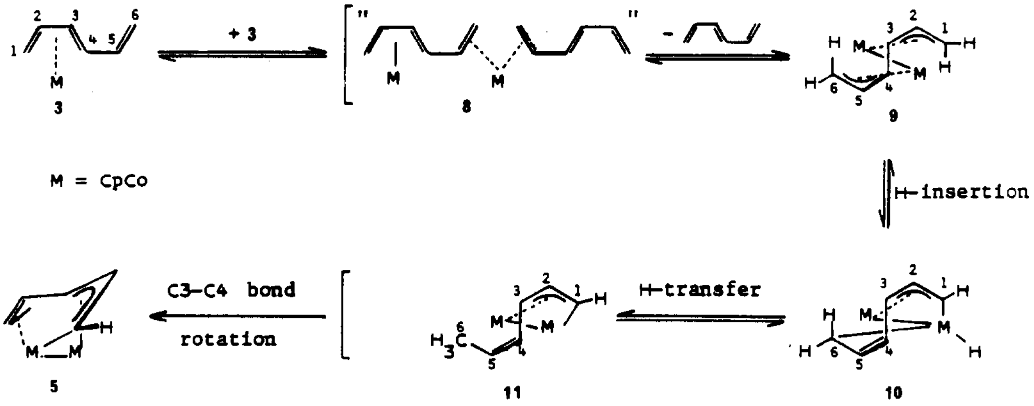
TABLE 1. Intramolecular bond distances (Å) of **5** and **6**

Compound **5**			Compound **6**		
Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co-1	Co-2	2.494(1)	Co-1	Co-2	2.478(1)
Co-1	C-1	2.069(2)	Co-1	C-1	2.094(3)
Co-1	C-2	2.096(2)	Co-1	C-2	2.113(3)
Co-1	C-3	2.102(2)	Co-1	C-3	2.089(3)
Co-1	C-4	2.089(2)	Co-1	C-4	2.084(3)
Co-1	C-5	2.082(2)	Co-1	C-5	2.060(3)
Co-2	C-6	2.046(3)	Co-2	C-6	2.051(3)
Co-2	C-7	2.051(3)	Co-2	C-7	2.071(3)
Co-2	C-8	2.081(3)	Co-2	C-8	2.059(3)
Co-2	C-9	2.059(3)	Co-2	C-9	2.063(3)
Co-2	C-10	2.046(3)	Co-2	C-10	2.048(3)
Co-1	Cp-1	1.714	Co-1	Cp-1	1.720
Co-2	Cp-2	1.695	Co-2	Cp-2	1.693
Co-1	C-11	1.884(2)	Co-1	C-11	2.022(3)
Co-1	C-14	2.051(2)	Co-1	C-12	2.052(2)
Co-1	C-15	2.042(3)	Co-1	C-15	1.906(3)
Co-2	C-11	1.986(3)	Co-2	C-13	1.995(3)
Co-2	C-12	1.966(2)	Co-2	C-14	1.953(3)
Co-2	C-13	1.990(2)	Co-2	C-15	1.960(3)
Co-2	C-14	2.555(3)	Co-2	C-12	2.636(3)
C-1	C-2	1.414(4)	C-1	C-2	1.369(5)
C-2	C-3	1.386(4)	C-2	C-3	1.407(5)
C-3	C-4	1.402(4)	C-3	C-4	1.380(5)
C-4	C-5	1.407(4)	C-4	C-5	1.411(4)
C-5	C-1	1.395(4)	C-5	C-1	1.392(5)
C-6	C-7	1.397(5)	C-6	C-7	1.360(5)
C-7	C-8	1.345(4)	C-7	C-8	1.362(5)
C-8	C-9	1.335(5)	C-8	C-9	1.345(5)
C-9	C-10	1.376(5)	C-9	C-10	1.410(5)
C-10	C-6	1.395(5)	C-10	C-6	1.410(5)
C-11	C-12	1.404(4)	C-11	C-12	1.403(4)
C-12	C-13	1.390(4)	C-12	C-13	1.445(4)
C-13	C-14	1.444(4)	C-13	C-14	1.410(4)
C-14	C-15	1.435(4)	C-14	C-15	1.406(4)
C-15	C-16	1.498(3)	C-15	C-16	1.508(4)
C-11	C-15	2.838(4)			

dilution conditions ($[\mathbf{3}]_o = 1.0 \times 10^{-3}$ M), the disappearance of **3** followed simple bimolecular kinetics. At higher concentrations (*e.g.* $[0.385\text{M}]_o$), the $-d[\mathbf{3}]_o/dt$ appeared to be pseudo first-order. The mechanistic implications of these concentration dependencies in the dimerization process of **3** to form **5** indicate: (i) the reaction may be encounter-limited under high dilution conditions; and (ii) the reaction appears to be dependent on a unimolecular (intramolecular) process at higher concentrations. The unimolecular process may involve a rate-determining change in hapticity (*i.e.* η^4-η^2 triene or η^5-η^3 Cp), to generate a reactive, coordinatively unsaturated metal species. This transient unsaturated species could then associate with any Lewis base it encounters (*e.g.* a vinyl group of second **3**). This latter process would allow for the facile transfer of an appended CpCo group from one ligand to another.

The effect of additives on the rate of reaction of **3** is consistent with a mechanism requiring an initial change in coordination at the metal center. The rate of the conversion of **3** to **5** is found to be inhibited by the addition of excess hexatriene. The influence of PPh_3 is consistent with this observation. When ten equivalents of PPh_3 are added to a thermolysis solution of **3** ($[\mathbf{3}]_o = 1.6 \times 10^{-2}$ M; 100°C), a substantial enhancement in both the rate of disappearance of **3** and formation of **5** is observed; using ^{1}H NMR, a small amount of $CpCo(PPh_3)_2$ ($\leq 4\%$) is observed to build up and then gradually disappear during the reaction. When 40 equivalents of PPh_3 are added under similar conditions ($[\mathbf{3}]_o) = 1.6 \times 10^{-2}$ M; 100°C), the disappearance of **3** is greatly accelerated and the $CpCo(PPh_3)_2$ is observed to form at a comparable rate with **5**. Free *trans*-1,3,5-hexatriene is observable in these reactions. The bisphosphine complex rapidly reaches a maximum solution concentration (42–44%); this complex is gradually consumed with the concomitant formation of **5**. Thus, an acceleration in the rate of formation of **5** with added phosphine, and its diminished rate of formation in the presence of excess hexatriene, indicate the loss of one equivalent of the complexed hexatriene to be a requisite to the formation of **5**.

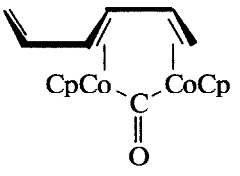
In order to gain a better understanding of the proton transfer process(es) involved in the vinyl C–H cleavage, a specifically labeled hexatriene complex was examined. Thermolysis of the complex **3**-6,6-d_2 [15] generated **5** deuterium-enriched at C_1 relative to C_6 ($k_H/k_D = 4.95 \pm 0.14$; 90°C) [22*]. Under the reaction conditions, **3**-6,6-d_2 was observed to be rapidly interconverting with its regio-isotopomer **3**,1,1-d_2 [15]. As a result, the measured isotope effect should reflect the inherent selectivity between the metal-mediated vinyl C–H and C–D activation energies for bond cleavage; *i.e.* its measured isotope value is not an artifact of the regioselective preparation of **3**-6,6d_2 [15]. By analogy to non-complexed organic systems, an isotope effect of this magnitude is indicative of a nearly linear transition-state for the [C_{vinyl}–H–metal] abstraction process (theoretical $k_H/k_D = 4.89$; 90°C) [23]. This analysis assumes the measured selectivity is a manifestation of the ΔE_a between C–H and C–D stretching modes; the activation energy difference between C–H and C–D bending modes, corresponding to a side-on addition of the metal, should exhibit much smaller isotope values. Suggs *et al.* have demonstrated that, in rhodium systems constrained to insert into C–H bonds in side-on



Scheme 4.

fashion, kinetic isotope effect magnitudes are substantially lower than the theoretical limit ($k_H/k_D = 3.4_{exp}$; 5.96_{theory}; 50°C) [24].

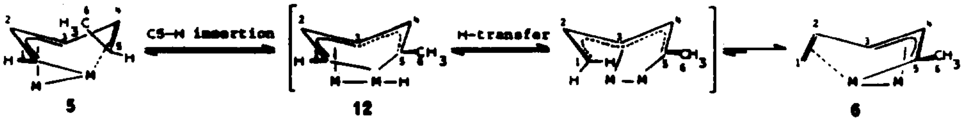
Compound 7 is the vinyl analog of the previously reported (μ-η^4-*syn*-1,3-butadiene)-(μ_2-carbonyl)[(η^5-cyclopentadienyl)cobalt]$_2$(*Co–Co*) complex [25]; the μ-carbonyl stretching frequency in the butadiene complex comes at $\nu(CO) = 1782$ cm^{-1} whereas in 7 at $\nu(CO) = 1785$ cm^{-1}. It presumably forms by the addition of CpCo(CO) to the initial photo-product 3. Compound 7 cleanly produces 6 on heating at 144°C (11 h, toluene-d_8). At lower reaction temperature (90°C), 7 is converted to 5; a small amount of 3 and $(CpCoCO)_2$ [26] are detectable under these latter conditions, as well. The preparation of 5 or 6 from 7 is mechanistically interesting. The thermally induced loss of CO from 7 would produce a coordinatively unsaturated intermediate having the exact elemental composition of 5 and 6. This result suggests a simple $(CpCo)_2$(hexatriene) complex as an intermediate in the formation of 5 from 3.



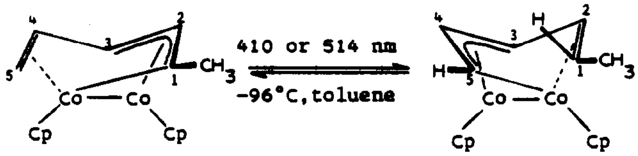
(7)

The suggested mechanism for the overall transformation of 3 to 5, consistent with the experimental observations, is shown in Scheme 4. Initially, 3 dimerizes to generate an intermediate mixed dinuclear complex, 8, which on loss of one equivalent of hexatriene, forms a transient bisallyl species, 9. Oxidative addition by either cobalt center in 9 (both are equivalent within the dinuclear bisallyl) into a proximal endo-vinyl-hydrogen bond (*e.g.* C_1) [27*], generates the structure 10. Transfer of the resulting metal-hydride to the unsaturated terminus of the π-allyl unit at C_5 (nucleophilic hydride addition), forms 11. Rotation about the C_3–C_4 bond transforms 11 into 5. Yamazaki et al. have isolated CpCo based metal–metal bonded bisallyl structures similar to 9, 10, and 11 [28]; these alkylidene complexes were prepared from the reaction of $CpCo(PPh_3)(RC \equiv CR)$ with diazo compounds. More recently, Wadepohl *et al.* have isolated $(CpCo)_2$(bisallyl) complexes similar to those of Yamazaki [29a]. These latter complexes were prepared by the reaction of $CpCo(C_2H_4)_2$ with η^4-1,2:3,4-(1,6-diphenyl-*trans*-1,3,5-hexatriene)CpCo; Adams and Wu have recently reported similar complexes derived from the addition of hexatrienes to ruthenium clusters [29b]. Thus, a structural precedent exists for each of the proposed intermediates.

Interestingly, continued heating of 5 results in its further rearrangement to 6. The rearrangement formally corresponds to a transannular, intramolecular [1,5]-H migration within the complexed "flyover" carbene moiety (Scheme 3). When solutions of 5 are heated above 80°C, quantitative rearrangement to 6



Scheme 5.



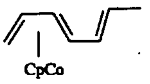
Scheme 6.

results; compound **6** is found to be thermally stable in solution up to 260°C. The thermal isomerization of **5** to **6** exhibits first-order kinetics ($E_a = 29.1 \pm 0.4$ kcal mol^{-1}, log $A = 11.6 \pm 0.6$). The stereochemistry of this formal [1,5]-H shift was probed using **5**-d_2 enriched in deuterium at C_1. The C_1 deuterium-labeled **5** indicated the C_5-proton to be transferred endo to the C_1-carbene. This observed stereospecific hydride transfer, is consistent with the following mechanism; an initial oxidative-addition of the bound cobalt center at C_5, generating a hydrido-cobalt intermediate **12**, which subsequently delivers the hydrogen to C_1 via reductive-elimination (Scheme 5). The thermodynamic preference of **6** relative to **5**, reflects the greater stability of a more substituted metallo-alkylidene carbene; this is consistent with what is observed for traditional organic carbenes. Neither **5** nor **6** exhibits any sensitivity towards air (O_2) in the solid state or in solution.

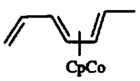
The photochemistry of **6** is also unique. When the alkylidene **6** is irradiated for 1 h at low temperature (514 nm argon ion laser; −96°C; toluene) **13** is generated (Scheme 6). This compound is the $\Delta^{4,5}$ geometric isomer of **5**. In contrast, **5** is photochemically inert under these reaction conditions. Structure **13** is formally the result of a photochemically induced [1,5]-hydrogen shift. The initial reaction solution reaches a photostationary ratio of 63 : 37 (**13** : **6**, respectively). The structure of **13** is readily discerned from its ^{1}H NMR spectrum (Fig. 1). Five distinct single proton resonances are observable between 0 and 8 ppm as are two nearly coincident Cp signals at δ 4.60 and δ 4.58. A high field methyl doublet comes at δ 1.15 which is coupled to the C_5-Z proton at δ 0.73 (dq). A diagnostic dd signal for the carbene proton of C_1 is observable at δ 7.95. The relative backbone configuration and ^{1}H-^{1}H coupling constants were determined by ^{1}H{^{1}H} decoupling methods. At higher temperature, **13** rapidly reverts to **6**. The reversion process is observed to follow a first-order kinetic rate expression ($E_a = 19.4 \pm 0.9$ kcal mol^{-1}; log $A = 10.0 \pm 1.3$). The facility with which **13** reverts to **6** rules out the intermediacy of **5** in the thermal reversion process.

The greater kinetic stability of complex **5** relative to **13** is interesting. It may be related to relative proximity of the **5**-C_{5E} *vs.* **13**-C_{5Z} vinyl hydrogen to the π-allyl bound cobalt center. An η^3-η^1 change-in-coordination, oxidative-addition into the C_5–H bond, and subsequent reductive elimination to C_1 would generate **6**. The smaller Arrhenius A-factor in the thermal isomerization of **13** to **6** relative to that of **5** to **6**, indicates a "tighter" transition-state in its rate-determining step. The added lengthening of the Co–Co bond which must take place in **5** (E-H_5) relative to **13** (Z-H_5), during the metal-mediated oxidative addition, may account for the observed difference in kinetic stability.

The study of the initial, thermally induced vinyl C–H activation chemistry of CpCo(hexatrienes) was extended to the next homolog [η^4-(1,3,5-heptatriene)](η^5-cyclopentadienyl)-cobalt (**14a,b**); this mixture will be rapidly equilibrating under our pyrolysis conditions [15]. Compound **14a,b** was selected since it was straightforward to prepare, homologous to **3**, and the anticipated [1,6]-hydrogen transfer process had the possibility of producing both symmetrical and unsymmetrical products. The distribution of products on pyrolysis would indicate the relative ease of addition between two types of C_{vinyl}–H bonds. Moreover, if the symmetrical isomer were produced, it might exhibit a degenerate [1,5]-hydride rearrangement (fluxionality) observable on the NMR timescale.

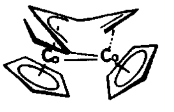


14a



14b

The mixture was prepared via the Wittig addition of Ph_3PCH_2 to [η^4-2,3 : 4,5-(*trans,trans*-2,4-hexadienal)](η^5-cyclopentadienyl)cobalt [30*]; the proton-proton coupling constants and configurational interrelationships were verified using standard ^{1}H{^{1}H} decoupling techniques. When **14a,b** (84 : 16, by ^{1}H NMR) was heated at 150°C for 18 h, a 64% isolated yield was obtained of a mixture of three isomers ($M^+ = 342$):**15** (68%), **16** (24%), and **17** (8%); these isomers were found to be inseparable by HPLC. The structures were distinguishable from their characteristic ^{1}H NMR spectra: (i) no signals were observed above 7.00 ppm implying no carbene proton was present (C_1–H range δ 7.7–8.2); (ii) **15** exhibits an ethyl group absorption (C_1–Et) and two C_5-hydrogens (H_5-exo δ 1.41; H_5-endo δ −0.40); (iii) **16** shows one singlet methyl resonance (δ 2.54; C_1–CH_3), one methyl doublet (δ 0.82; C_5–CH_3) and a diagnostic Z-H_5 proton resonance at δ 0.56; (iv) **17** exhibits one singlet methyl resonance (δ



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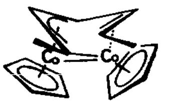

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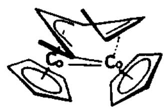


17

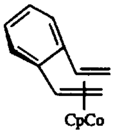
2.35; C_1–CH_3), one doublet methyl signal (δ 0.53; C_5–CH_3), and a E-H_5 proton at δ 1.89; three matched pairs of Cp resonances were cleanly observable as well. Furthermore, the relative backbone configurations were verified using $^1H\{^1H\}$ techniques.

Compounds **16** and **17** are $\Delta^{5,6}$ geometric isomers of one another. They bear the same relationship to one another as structure **13** does to structure **5**. Neither isomer was observed to undergo a facile, thermally induced [1,5] proton transfer (fluxionality) at room temperature on the ^1H NMR time scale.

The observed product distribution of **15**, **16**, and **17** is mechanistically important. It indicates the initial [1,6]-H transfer behaves similarly to the parent system (**3** → **5**). The predominance of structure **15** over **16** and **17** implies the initial oxidative addition of a cobalt center into a vinyl C–H bond prefers addition to the less substituted end of the appended triene. This process generates the ethyl substituent; the thermolysis conditions are sufficiently vigorous to convert the intermediate ethyl analog of **5** directly into **15**. The magnitude of this regio-preference is more than 2:1 (**15**:**16** plus **17**).

In apparent contrast to the greater kinetic stability of **5** *vs.* **13** in forming **6**, **16** predominates over **17** by approximately a 3:1 ratio. By the proposed mechanism (Scheme 2), **17** precedes the formation of **16**. The subsequent [1,5]-H transfer after the initial rearrangement generates **16** from **17** in the same fashion as **6** derives from **5**. However, unlike the parent system, the formation of a substituted alkylidene is no longer a thermodynamic driving force to distinguish between **16** and **17**. The observed ratio reflects the minor steric perturbational difference in energy between an endo- *vs.* an exo-cyclic methyl group in the alkylidene (**17** *vs.* **16**). The bonding data from **5** and **6** imply that **17** should be sterically less demanding than **16**; the longer Co–Co and transannular C_1–C_5 distances in **5** *vs.* **6** (2.494 Å *vs.* 2.478 Å and 2.838 Å *vs.* 2.773 Å) are consistent with this suggestion. Implicit in the formation of **15**, the reaction conditions are sufficient to allow the subsequent [1,5]-H conversion of **17** to **16** producing the observed larger amount of the latter. Compound **16** may also be equilibrating with **17** under these conditions. An insufficient number of variable temperature runs using **14a,b** were examined to determine if the observed ratio of products were representative of a thermodynamic distribution.

The extraordinary stability of these simple alkylidene complexes suggested that such carbene structures might be sufficiently robust to derive from polyene systems where one of the π-bonds originates within an arene ring *e.g.* **18**, **19**, and **20**. Such complexes have the possibility of disrupting the aromaticity of an arene ring and/or observing competitive, intramolecular aryl C–H *vs.* vinyl C–H activation. The CpCo moiety is known to form complexes readily with the π-system of vinyl arenes [29,31]. However, pyrolysis of these materials generated no identifiable carbene complexes. Thermolysis of **18** at 150°C gave only slow decomposition of the starting material to an intractable black material. When **19** was heated in solution at 150°C (10 h), quantitative *cis-trans* isomerization to **20** was observed; lower reaction temperatures only led to the more gradual formation of **20**. Compound **20** was found to be stable in solution up to roughly 210°C, at which point slow degradation to unidentifiable material occurred.



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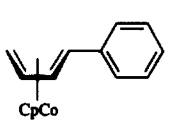

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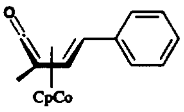
One final synthetic approach was tried as an entry into this class of metal–carbene complexes. The method involved the direct photochemical generation of a carbene in the presence of $CpCo(CO)_2$. The formation of bridging alkylidenes by similar methods has been observed for a number of transition metal complexes with diazoalkanes [32]. This approach would allow entry into dinuclear (Co–Co) alkylidene complexes which formally derive from precursors in the same family as **18**, **19** and **20**. For this reaction, two equivalents of $CpCo(CO)_2$ were added to a THF solution containing the lithium salt of the tosyl hydrazone of *trans*-4-phenyl-3-buten-2-one (**21**) at 35°C. Irradiation (350 nm) of the resulting solution for 12 h produced only a 40% isolated yield of an α,β-unsaturated ketene complex **22** (ν(CO) = 1769 cm^{-1}); both the CpCo complex and the isostructural, isolobal $Fe(CO)_3$ adduct of the ketene ligand have been characterized by single crystal X-ray analysis [33,34]. Structure **22** derives from the insertion of a carbonyl group into a mononuclear carbene. The remaining organometallic materials from our photocomplexation reaction were the small polynuclear species derived from $CpCo(CO)_2$ [14]. Variation of either the ratio of starting materials or the reaction times merely led to changes in the relative ratios of **22** and the $(CpCo)_x(CO)_y$ clusters. None of the desired μ-carbene was observed. Similar vinylketene complexes to **22** have been prepared previously for a few metal systems (*e.g.* Cr, Mo, Co, and Fe) [32,34,35].



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4. Summary and conclusions

The thermally induced rearrangement of the η^4-bound hexatriene ligand, **3**, to a dinuclear bound pentadienyl carbene **5**, is indicated to proceed *via* an initial transfer of a CpCo group onto **3** followed by a stereospecific metal mediated [1,6] hydrogen shift. Continued heating of **5** initiates an intramolecular [1,5] hydrogen migration which isomerizes **5** to **6**. The thermal chemistry can be extended to simple polyene homologues of **3**. The low temperature photochemically initiated rearrangements of **6**, stereospecifically generate the complementary $\Delta^{4,5}$ geometric isomer of **5**, structure **13**. A facile first-order rate of reversion of **13** to **6** is observed on warming it to room temperature.

The facility and efficiency with which the CpCo mediated hexatriene-alkylidienyl rearrangements take place is truly remarkable in comparison to similar iron and rhodium systems. The ease of formation of the pentadienyl carbenes under these conditions, proves to be a more effective synthetic entry into such complexes than do conventional methods of preparation.

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11 $R = (\Sigma \| F_o| - |F_c\|)/(\Sigma |F_o|)$, $wR = \{(\Sigma w(|F_o| - |F_c|)^2)/(\Sigma w F_o^2)\}^{1/2}$, $\mathrm{GOF} = \{(\Sigma w(|F_o| - |\mathrm{F}_c|)^2)/(n_o n_v)\}^{1/2}$ where n_o is the number of observations, n_v the number of variable parameters, and the weights w were given by $w = (4F_o^2)/(\sigma(F_o^2)$, $\sigma^2(F_o^2) = \{\sigma_o^2(F_o^2) + (\mathrm{p}F^2)^2\}$ where p is the factor used to lower the weight of intense – reflections.

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