These cycloadditions tend to be very clean processes yielding a single product. However, in the reaction of trimethylsilylacetylene, a second product was isolated in ca. 5–10% yield. Analysis of the IR (2168 cm^{-1}) and ^{13}C NMR spectra (three cyclopropane resonances at 16.6, 11.4, and 9.8 ppm) indicated that the structure was that represented by 7. Close examination of the spectrum of the crude reaction mixture revealed a similar adduct was produced in the reaction with *tert*-butylacetylene. No trace of these adducts was observed in the other acetylene cycloadditions. Insertion into the terminal C–H bond[12] appears to be a competitive reaction in those cases where a bulky group hinders coordination of the acetylene to the cobalt.[13] Two possible stereochemical outcomes (exo and endo) are possible for the acetylenyl group in adduct 7. In this instance it is impossible to distinguish between the two since the products are *enantiomers*. It is nevertheless of mechanistic significance. Experiments using a labeled norbornadiene will resolve the issue and are presently underway in our laboratories. We favor coordination to the endo face of the olefin since exo complexation cannot lead to formation of a cyclopropane ring.[14]

Deltacyclene has proven to be useful in the synthesis of highly strained unnatural products of theoretical interest.[15] More highly substituted deltacyclenes are now readily available. The results presented demonstrate a much broader scope of homo-Diels–Alder cycloadditions than was previously indicated.

Acknowledgment. This research was supported by the Natural Science and Engineering Research Council (NSERC) of Canada, the Bickell Foundation, and the University of Toronto. We thank Louise Edwards for preliminary experiments and Professor G. L. Lange for the use of valuable equipment. We also thank a reviewer for bringing ref 4i and 14 to our attention.

Supplementary Material Available: Details of the preparation and spectral data for all new compounds (8 pages). Ordering information is given on any current masthead page.

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[12] Insertion into terminal acetylenes is presumably one of the steps in carbonylation of terminal alkynes catalyzed by palladium salts: Tsuji, J.; Takahashi, M.; Takahashi, T. *Tetrahedron Lett.* **1980**, 849.

[13] Ethylene is known to react with norbornadiene to yield vinylnortricyclane (see ref 6). The mechanism in this reaction is proposed to proceed via a metallacycle which seems unlikely in the present case.

[14] Nickel catalyzes the vinylation of norbornene and norbornadiene to give the exo product. Bogdanovic, B.; Henc, B.; Losler, A.; Meister, B.; Pauling, H.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 954. However, no cyclopropane formation accompanies C–C bond formation.

[15] (a) von R. Schleyer, P.; Leone, R. E. *J. Am. Chem. Soc.* **1968**, *90*, 4164. (b) Coates, R. M.; Kirkpatrick, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 4883 and ref 5.

Mechanism of η¹-Pentadienyl Ligand Isomerization. First Structural Characterization of a 3-η¹-Pentadienyl-Metal Complex[1]

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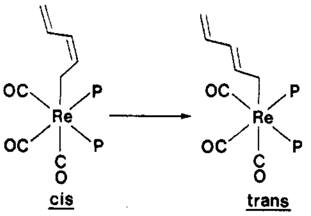
Received July 5, 1989

Summary: Treatment of (η^5-pentadienyl)Re(CO)$_3$ with 1 equiv of $Et_2PCH_2CH_2PEt_2$ (depe) produces (*cis*-η^1-pentadienyl)Re(CO)$_3$(depe) (**1**). Upon irradiation at 0 °C, **1** is converted to (3-η^1-pentadienyl)Re(CO)$_3$(depe) (**2**). This species rearranges thermally via a phosphine dissociation/association process to (*trans*-η^1-pentadienyl)Re(CO)$_3$(depe) (**3**). Compounds **1** and **2** have been structurally characterized.

Earlier, we reported cis → trans isomerization in the η^1-pentadienyl ligand of (η^1-pentadienyl)Re(CO)$_3$(PR$_3$)$_2$ (R = Me, Et) complexes.[2]



We now communicate new mechanistic information about this interesting ligand rearrangement, obtained from a study of the 1,2-bis(diethylphosphino)ethane (depe) system. Included in this report is an X-ray diffraction study of (3-η^1-pentadienyl)Re(CO)$_3$(depe), a key intermediate in the isomerization process. This represents the first structural characterization of a "3-η^1-pentadienyl" ligand, wherein the central carbon atom of the pentadienyl chain coordinates in a σ-fashion to the metal center.

Treatment of (η^5-pentadienyl)Re(CO)$_3$[3] with 1 equiv of 1,2-bis(diethylphosphino)ethane (depe) in diethyl ether leads to the formation of (*cis*-η^1-pentadienyl)Re(CO)$_3$(depe) (1).[4] The solid-state structure of 1, determined by X-ray crystallography, is shown in Figure 1.[5] The coordination geometry of 1 is octahedral with the three carbonyl ligands in a facial orientation. The *cis*-η^1-pentadienyl ligand exhibits an overall sickle shape with torsional angles of −0.5° and 178.0° for C1–C2–C3–C4 and C2–C3–C4–C5, respectively. The five pentadienyl carbon atoms are coplanar to within 0.02 Å, and the pentadienyl plane makes a dihedral angle of 29.7° with the complex's equatorial plane (Re/P1/P2/C11/C31).

Characteristic of the cis geometry about the internal double bond, C2–C3, is the relatively small coupling constant between H2 and H3 (11 Hz). A second distinguishing feature of the ^1H NMR spectrum of 1 is the downfield shift of H4's signal relative to that of H2 (δ 7.33 vs δ 6.42).

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[1] Pentadienyl-Metal-Phosphine Chemistry. 18. For the previous paper in this series, see: Bleeke, J. R.; Rauscher, D. J. *Organometallics* **1988**, *7*, 2328.

[2] Bleeke, J. R.; Rauscher, D. J.; Moore, D. A. *Organometallics* **1987**, *6*, 2614.

[3] Paz-Sandoval, M. A.; Powell, P. *J. Organomet. Chem.* **1981**, *219*, 81.

[4] **Synthesis of (*cis*-η^1-Pentadienyl)Re(CO)$_3$(Et$_2$PCH$_2$CH$_2$PEt$_2$) (1).** 1,2-Bis(diethylphosphino)ethane (depe) (0.12 g, 6.0×10^{-4} mol) was added to (η^5-pentadienyl)Re(CO)$_3$ (0.20 g, 6.0×10^{-4} mol) in 40 mL of diethyl ether, and the resulting solution was stirred for 4 days at room temperature. Solvent was then removed under vacuum. The residue was redissolved in diethyl ether and filtered through Celite. Slow evaporation of the diethyl ether solvent at room temperature yielded 0.12 g (37%) of pale yellow crystals. Anal. Calcd for $C_{18}H_{31}ReP_2O_3$: C, 39.77; H, 5.76. Found: C, 39.82; H, 5.62.

Spectroscopic Data for 1. ^1H NMR (benzene-d_6, 20 °C): δ 7.33 (d of t, J_{H-H5_a} = 17 Hz, J_{H-H5_s} = 11 Hz, 1, H4), 6.42 (q, J_{H-H} = 11 Hz, 1, H2), 5.82 (t, J_{H-H} = 11 Hz, 1, H3), 5.22 (d, J_{H-H4} = 17 Hz, 1, H5$_a$), 5.08 (d, J_{H-H4} = 11 Hz, 1, H5$_s$), 1.48 (m, 4, phosphine bridge CH$_2$'s), 1.38 (m, 2, H1's), 1.32 (m, 4, phosphine ethyl CH$_2$'s), 0.92 (m, 4, phosphine ethyl CH$_2$'s), 0.80 (m, 12, phosphine CH$_3$'s). $^{13}C\{^1H\}$ NMR (benzene-d_6, 20 °C): δ 148.6 (t, J_{C-P} = 4 Hz, C2), 134.4 (s, C4), 116.8 (s, C3), 110.6 (s, C5), 24.0 (m, phosphine bridge CH$_2$'s), 21.2 (d, J_{C-P} = 29 Hz, phosphine ethyl CH$_2$'s), 15.0 (d, J_{C-P} = 26 Hz, phosphine ethyl CH$_2$'s), 8.5 (s, phosphine CH$_3$'s), 7.9 (s, phosphine CH$_3$'s), −4.2 (t, J_{C-P} = 7 Hz, C1). $^{31}P\{^1H\}$ NMR (benzene-d_6, 20 °C): δ 27.4 (s). IR (toluene, 22 °C, selected peaks): 2002, 1928, 1885 cm^{-1} (s, C—O stretches); 1620 cm^{-1} (w, C═C stretch); 1040, 1030 cm^{-1} (m, P—C stretches). UV (acetonitrile, 22 °C): λ_{max} = 282 nm (ϵ = 6500).

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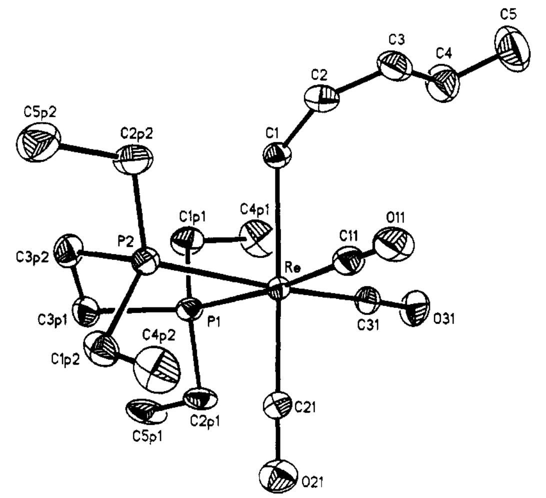

Figure 1. ORTEP drawing of (*cis*-η^1-pentadienyl)Re(CO)$_3$-($Et_2PCH_2CH_2PEt_2$) (**1**). Bond distances and angles: Re–P1, 2.429 (1) Å; Re–P2, 2.432 (1) Å; Re–C11, 1.945 (6) Å; Re–C21, 1.927 (5) Å; Re–C31, 1.944 (5) Å; Re–C1, 2.303 (5) Å; C1–C2, 1.475 (8) Å; C2–C3, 1.321 (8) Å; C3–C4, 1.45 (1) Å; C4–C5, 1.34 (1) Å; P1–Re–P2, 81.69 (5)°; P1–Re–C11, 173.6 (2)°; P1–Re–C21, 91.2 (2)°; P1–Re–C31, 91.6 (2)°; P1–Re–C1, 87.7 (2)°; P2–Re–C11, 92.7 (2)°; P2–Re–C21, 92.7 (1)°; P2–Re–C31, 171.5 (2)°; P2–Re–C1, 86.7 (1)°; C11–Re–C21, 92.1 (2)°; C11–Re–C31, 93.7 (2)°; C11–Re–C1, 88.9 (2)°; C21–Re–C31, 92.7 (2)°; C21–Re–C1, 178.8 (2)°; C31–Re–C1, 87.9 (2)°; Re–C1–C2, 113.2 (4)°; C1–C2–C3, 129.3 (6)°; C2–C3–C4, 125.0 (7)°; C3–C4–C5, 123.4 (9)°.

When **1** is stirred at room temperature in benzene under ambient light, it isomerizes slowly to the trans isomer (*trans*-η^1-pentadienyl)Re(CO)$_3$(depe) (**3**).[6] No intermediate species are observed by NMR. In the trans isomer, J_{H2-H3} = 14 Hz and the ^{1}H NMR signal for H4 overlaps with that for H2 (δ 6.72–6.58). Interestingly, when **1** is kept in the dark, the isomerization is shut down completely, indicating that the process has a photochemical step.

In an attempt to isolate the photoproduct of **1**, we irradiated it in diethyl ether solution at 0 °C, using a medium-pressure mercury-vapor lamp. After $^1/_2$ h, conversion to (3-η^1-pentadienyl)Re(CO)$_3$(depe) (**2**) was essentially complete.[7] However, the presence of a small amount of unreacted **1**, even after longer photolysis times, suggested that a photostationary state[8] was attained under these conditions.

Crystals of **2** were grown from diethyl ether and characterized by X-ray diffraction (Figure 2).[9] Once again, the three carbonyl ligands assume a facial arrangement. The 3-η^1-pentadienyl ligand has essentially a W shape with torsional angles of −134.3° and 130.2° for C1–C2–C3–C4 and C2–C3–C4–C5, respectively. The central carbon atom of the pentadienyl chain (C3) resides 0.84 Å out of the plane of the other four carbon atoms. In addition, one side of the 3-η^1-pentadienyl ligand (atoms C4 and C5) is pushed farther away from the complex's equatorial plane (Re/P1/P2/C22/C33) than the other side (C1 and C2), probably as a result of steric contacts between C4/C5 and ethyl groups on the depe ligand. Hence, C4 lies 0.35 Å farther from the equatorial plane than C2, while C5 resides 0.73 Å farther away than C1.

The ^{1}H NMR spectrum of **2** is quite simple, exhibiting just four pentadienyl signals: H2/H4, H1$_{anti}$/H5$_{anti}$, H1$_{syn}$/H5$_{syn}$, and H3. The H3 signal at δ 2.87 is diagnostic, since *cis*-η^1- and *trans*-η^1-pentadienyl ligands have no signals in this region.

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(5) Crystals of **1** are triclinic, space group $P\bar{1}$ (No. 2), with a = 10.097 (3) Å, b = 14.499 (8) Å, c = 8.779 (6) Å, α = 102.61 (3)°, β = 104.67 (4)°, γ = 110.95 (3)°, V = 1091 (2) Å^3, Z = 2, and d_{calcd} = 1.65 g/cm^3.

A pale gold crystal of dimensions 0.4 mm × 0.4 mm × 0.5 mm was grown from a saturated diethyl ether solution and sealed in a glass capillary under an inert atmosphere. X-ray diffraction data were collected at 22 °C on a Nicolet P3 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). A total of 5003 independent reflections with 4° < 2θ < 55° were collected by using the Wykoff scanning technique and a variable scan rate of 2–29°/min. All of the data reduction and structure refinement were done with a modified Enraf-Nonius structure determination package, SDPVAX (modified by B.A. Frenz and Assoc., Inc., College Station, TX), on a VAX 11/780 computer. The data were corrected for Lorentz and polarization effects, for linear decay (2.5%), and for absorption using ψ scans (μ = 58.00 cm^{-1}). Only the 4328 independent reflections with intensities greater than 3 times their estimated standard deviations were used in the least-squares refinements. A statistical weighting scheme to downweight intense reflections was used, introducing an experimental instability factor, ρ, in the calculation of $\sigma(|F_o|)$. The structure was solved by standard Fourier techniques following the location of the Re atom from a Patterson map. All non-hydrogens were refined anisotropically. Hydrogen atoms were found in the difference Fourier maps and given fixed isotropic thermal parameters for the structure factor calculations but were not refined. The convergence values of the agreement indices were R_F = 0.024 and R_{wF} = 0.034. The largest residual peak in the final difference Fourier map was 0.98 e/Å^3.

(6) **Synthesis of (*trans*-η^1-Pentadienyl)Re(CO)$_3$-($Et_2PCH_2CH_2PEt_2$) (3) from 1.** (*cis*-η^1-Pentadienyl)Re(CO)$_3$-($Et_2PCH_2CH_2PEt_2$) (**1**) (0.30 g, 5.5 × 10^{-4} mol) was dissolved in 50 mL of benzene and stirred at room temperature under ambient light for 2 weeks. The solvent was then removed under vacuum. The residue was treated with diethyl ether, and the resulting extract was filtered through Celite. Minimization of the solvent volume, followed by cooling to −30 °C, yielded 0.09 g (30%) of light yellow **3**. Anal. Calcd for $C_{18}H_{31}ReP_2O_3$: C, 39.77; H, 5.76. Found: C, 39.47; H, 5.61.

Spectroscopic Data for 3. ^{1}H NMR (benzene-d_6, 20 °C): δ 6.72–6.58 (m, 2, H2 and H4), 5.98 (d of d, J_{H-H} = 14, 11 Hz, 1, H3), 5.03 (d, J_{H-H4} = 17 Hz, 1, H5$_a$), 4.75 (d, J_{H-H4} = 10 Hz, 1, H5$_s$), 1.68–1.42 (m, 8, phosphine bridge and ethyl CH$_2$'s), 1.25 (m, 2, H1's), 1.20 (m, 4, phosphine ethyl CH$_2$'s), 0.92 (m, 12, phosphine CH$_3$'s). ^{13}C{^{1}H} NMR (benzene-d_6, 20 °C): δ 152.6 (t, J_{C-P} = 4 Hz, C2), 140.0 (s, C4), 119.0 (s, C3), 107.5 (s, C5), 23.4 (m, phosphine bridge CH$_2$'s), 21.4 (d, J_{C-P} = 29 Hz, phosphine ethyl CH$_2$'s), 15.0 (d, J_{C-P} = 27 Hz, phosphine ethyl CH$_2$'s), 8.6 (s, phosphine CH$_3$'s), 7.9 (s, phosphine CH$_3$'s), 0.4 (t, J_{C-P} = 7 Hz, C1). ^{31}P{^{1}H} NMR (benzene-d_6, 20 °C): δ 27.6 (s). IR (toluene, 22 °C, selected peaks): 2000, 1925, 1886 cm^{-1} (vs, C—O stretches); 1625 cm^{-1} (w, C═C stretch); 1030 cm^{-1} (w, P—C stretch). UV (acetonitrile, 22 °C): λ_{max} = 276 nm (ϵ = 7100).

(7) **Synthesis of (3-η^1-Pentadienyl)Re(CO)$_3$($Et_2PCH_2CH_2PEt_2$) (2).** In an inert atmosphere glovebox, (*cis*-η^1-pentadienyl)Re(CO)$_3$-($Et_2PCH_2CH_2PEt_2$) (**1**) (0.20 g, 3.7 × 10^{-4} mol) was dissolved in 15 mL of diethyl ether and transferred to a 50-mL Pyrex glass tube fitted with a vacuum stopcock. The sealed tube was removed from the glovebox, cooled to 0 °C in an ice bath, and irradiated for 30 min with a 450-W Conrad-Hanovia medium-pressure mercury-vapor lamp. The tube was then returned to the glovebox, where the solvent was removed under vacuum. The residue was dissolved in minimal diethyl ether, filtered through Celite, and cooled to −30 °C, producing 0.1 g (50%) of light yellow crystals of **2**. Anal. Calcd for $C_{18}H_{31}ReP_2O_3$: C, 39.77; H, 5.76. Found: C, 39.83; H, 5.72.

Spectroscopic Data for 2. ^{1}H NMR (benzene-d_6, 20 °C): δ 6.70 (d of t, $J_{H-H1/5_a}$ = 17 Hz, $J_{H-H1/5_s}$ = 10 Hz, 2, H2/4), 4.65 (d of d, $J_{H-H2/4}$ = 17 Hz, $J_{H-H1/5_s}$ = 2 Hz, 2, H1/5$_a$), 4.45 (d of d, $J_{H-H2/4}$ = 10 Hz, $J_{H-H1/5_a}$ = 2 Hz, 2, H1/5$_s$), 2.87 (m, 1, H3), 1.75, 1.42 (m's, 12, phosphine CH$_2$'s), 0.75 (m, 12, phosphine CH$_3$'s). ^{13}C{^{1}H} NMR (benzene-d_6, 20 °C): δ 152.8 (s, C2/4), 98.8 (s, C1/5), 26.9 (s, C3), 23.4 (m, phosphine bridge CH$_2$'s), 22.6 (d, J_{C-P} = 30 Hz, phosphine ethyl CH$_2$'s, 14.2 (d, J_{C-P} = 26 Hz, phosphine ethyl CH$_2$'s), 8.3, 8.1 (s's, phosphine CH$_3$'s). ^{31}P{^{1}H} NMR (benzene-d_6, 20 °C): δ 24.6 (s). IR (toluene, 22 °C, selected peaks): 2000, 1930, 1885 cm^{-1} (s, C—O stretches); 1625 cm^{-1} (w, C═C stretch); 1035 cm^{-1} (m, P—C stretch). UV (acetonitrile, 22 °C): λ_{max} = 272 nm (ϵ = 5000).

(8) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1976; pp 709–10.

(9) (a) Crystals of **2** are monoclinic, space group *Cc* (No. 9),[9b] with a = 18.404 (6) Å, b = 7.758 (3) Å, c = 16.457 (5) Å, β = 111.75 (2)°, V = 2183 (1) Å^3, Z = 4, and d_{calcd} = 1.65 g/cm^3. Data collection/reduction and structure solution/refinement followed the same procedure as outlined in ref 5: crystal color, pale yellow; crystal dimensions, 0.4 mm × 0.3 mm × 0.2 mm; 2147 independent reflections with 4° < 2θ < 50°; scan rate, 4–29°/min; linear decay correction, 56.3%; absorption correction, ψ scans, μ = 58.00 cm^{-1}; 1667 reflections with $I > 3\sigma(I)$; hydrogen atoms not included; R_F = 0.035, R_{wF} = 0.045; largest residual peak in difference Fourier = 0.82 e/Å^3. (b) The systematic absences were consistent with either space group *Cc* or space group *C*2/*c*. The unit cell volume indicated Z = 4, requiring that the molecule reside in a general position in *Cc* or on a special position (inversion center or 2-fold rotation axis) in *C*2/*c*. Since the expected molecular structure did not possess $\bar{1}$ or 2 symmetry, *Cc* was favored. In addition, N(*z*) statistics were consistent with an acentric space group. Successful structure refinement confirmed the choice of *Cc*.

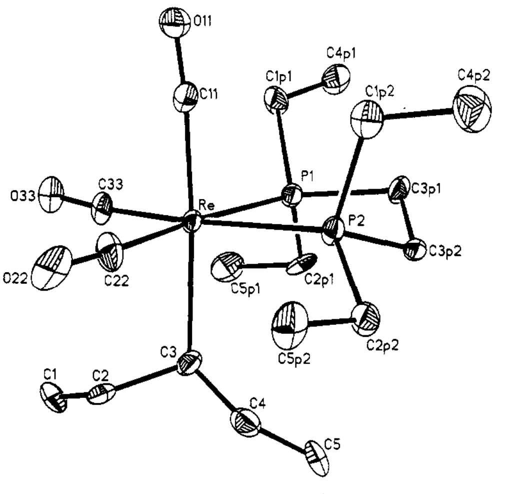
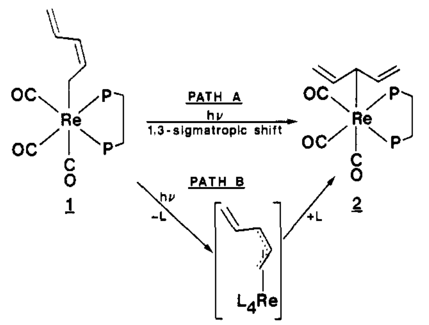


Figure 2. ORTEP drawing of (3-η^1-pentadienyl)Re(CO)$_3$(Et$_2$PCH$_2$CH$_2$PEt$_2$) (2). Bond distances and angles: Re–P1, 2.492 (4) Å; Re–P2, 2.449 (4) Å; Re–C11, 1.94 (2) Å; Re–C22, 1.91 (2) Å; Re–C33, 1.94 (1) Å; Re–C3, 2.35 (2) Å; C1–C2, 1.36 (3) Å; C2–C3, 1.46 (3) Å; C3–C4, 1.47 (2) Å; C4–C5, 1.32 (3) Å; P1–Re–P2, 80.4 (1)°; P1–Re–C11, 90.4 (5)°; P1–Re–C22, 176.2 (6)°; P1–Re–C33, 89.8 (5)°; P1–Re–C3, 88.6 (4)°; P2–Re–C11, 89.2 (5)°; P2–Re–C22, 97.6 (6)°; P2–Re–C33, 170.0 (6)°; P2–Re–C3, 96.8 (4)°; C11–Re–C22, 92.8 (8)°; C11–Re–C33, 89.3 (7)°; C11–Re–C3, 173.6 (6)°; C22–Re–C33, 92.4 (7)°; C22–Re–C3, 88.5 (8)°; C33–Re–C3, 84.4 (7)°; C1–C2–C3, 123 (2)°; Re–C3–C2, 108 (1)°; Re–C3–C4, 112 (1)°; C2–C3–C4, 109 (2)°; C3–C4–C5, 127 (2)°.

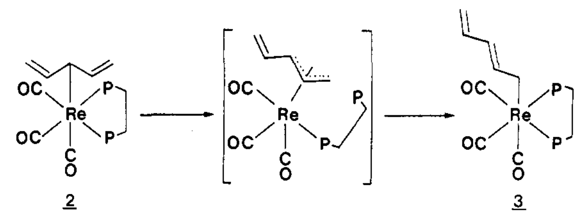
Scheme I



The mechanism of the photoconversion of 1 to 2 is still unclear. The two most likely possibilities are outlined in Scheme I. Pathway A involves a 1,3-sigmatropic shift with no ligand dissociation. Although photochemical 1,3-sigmatropic shifts involving transition metals have not been previously observed, thermal 1,5-sigmatropic shifts are quite common in organotransition-metal chemistry.[10] Hence, pathway A seems reasonable under the reaction conditions. However, ligand dissociation/association processes involving η^3-pentadienyl intermediates (pathway B) cannot be ruled out. Experiments designed to distinguish between these mechanistic possibilities (e.g., photolysis in the presence of labeled CO or phosphine) have proved inconclusive.

At room temperature, (3-η^1-pentadienyl)Re(CO)$_3$(depe) (2) isomerizes quite rapidly to the *trans*-η^1-pentadienyl isomer 3 *even in the absence of light.*[11] Hence, this second step in the overall conversion of 1 to 3 is thermal. Furthermore, it can be shut down by adding an excess of depe or PMe$_3$ to 2, strongly suggesting that the rearrangement of 2 to 3 involves phosphine loss, specifically the dissociation of one arm of the depe ligand (Scheme II).

Scheme II



In summary, we conclude that the conversion of the *cis*-η^1-pentadienyl ligand in 1 to its *trans*-η^1 isomer proceeds in two well-defined steps. The first step is photochemical and results in the formation of a 3-η^1-pentadienyl intermediate. The second step is thermal and proceeds via ligand dissociation/association. Further studies of these novel η^1-pentadienyl–rhenium complexes are in progress.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8520680) is gratefully acknowledged. Washington University's High Resolution NMR Service Facility was funded in part by National Institutes of Health Biomedical Research Support Instrument Grant 1 S10 RR02004 and by a gift from Monsanto Co.

Supplementary Material Available: Listings of final atomic coordinates, thermal parameters, bond lengths, bond angles, torsional angles, and significant least-squares planes including subtended dihedral angles for 1 and 2 (18 pages); listings of observed and calculated structure factor amplitudes for 1 and 2 (35 pages). Ordering information is given on any current masthead page.

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(10) Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 128–131.

(11) **Synthesis of (*trans*-η^1-Pentadienyl)Re(CO)$_3$(Et$_2$PCH$_2$CH$_2$PEt$_2$) (3) from 2.** (3-η^1-Pentadienyl)Re(CO)$_3$(Et$_2$PCH$_2$CH$_2$PEt$_2$) (2) (0.20 g, 3.7×10^{-4} mol) was dissolved in 30 mL of benzene and stirred at room temperature for 2 days. The solvent was then removed under vacuum. The residue was treated with diethyl ether, and the resulting extract was filtered through Celite. Cooling of the filtrate to −30 °C produced 0.14 g (70%) of 3. NMR spectra of 3 obtained by this method were identical with those of 3 obtained from 1 (see ref 6).

Photochemistry of Cyclopentadienyliron(II) Alkylborate Salts: Rapid Intra-Ion-Pair Electron Transfer Gives Alkyl Free Radicals

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Received July 5, 1989

Summary: Irradiation of tetrahydrofuran solutions of appropriate alkylborate [RB(Ph)$_3$]$^-$ salts of cyclopentadienyliron (II) arene cations [CpFeArH]$^+$ initiates an intra-ion-pair electron-transfer reaction to form a neutral 19-electron iron(I) species and a neutral boranyl radical [RBPh$_3$]$^\bullet$. Cleavage of the alkyl carbon–boron bond in the boranyl radical occurs more rapidly than does energy-wasting back electron transfer to regenerate the starting salt. The alkyl radical formed is detected by laser flash photolysis and by its characteristic chemical reactions in solution.

The electronically excited-state lifetimes of organometallic compounds in solution are typically very short. This fact often restricts reactions of these species to unimolecular ligand dissociations: Except at very high concentration of reagent, bimolecular reactions often cannot compete with the nonreactive, usually radiationless

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