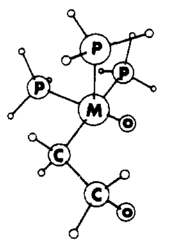

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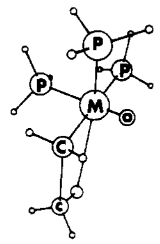

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at this time the possibility that aldehyde formation proceeds from this structure via an MOC_2H_4O– dangling and/or four-membered ring, intermediate. Such an intermediate would be consistent with the delayed formation of aldehyde in the Mo(VI) system:[11]

$$(O_2)(O)Mo(O_2C_2H_4) \nearrow (O_2)(O)MoO + C_2H_4O$$

$$(O_2)(O)Mo(O_2C_2H_4) \searrow (O_2)(O)Mo(OC_2H_4O) \rightarrow (O_2)(O)MoO + CH_3CHO$$

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Support from the National Science Foundation and from the Kansas State University Computing Center is also appreciated.

Appendix

The extended Hückel method, modified for the use of double exponent radial functions, was employed.[13] The starting structural parameters for $(H_3P)_3Rh(C_2H_4O_2)$ are as follows: Rh–P = 228 pm; P–H = 142 pm; Rh–C = 200 pm; C–C = 154 pm; C–O = 147 pm; O–O = 145 pm; Rh–O = 180 pm; all PRhP and PRhO angles = 90°; RhOC = 126°; OOC = 108°; OCC = 109°; CCRh = 115°; CRhO = 78.9°; HPRh = 109°; HCH = 109°. The P atoms are placed on the $+z$, $-x$, and $-y$ axes, Rh–O is along $+y$, and Rh–C approximately along $+x$.

Registry No. 2, 94324-89-7; 3, 94324-90-0.

(13) J. H. Ammeter, H.-B. Burgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, 100, 3686 (1978).

Photoinitiated Intramolecular Hydrogen Transfer from Rhenium Polyhydrides to C_8 Cyclopolyolefins

Michaeleen C. L. Trimarchi, Mark A. Green, John C. Huffman, and Kenneth G. Caulton*

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

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The phototransient ReH_5P_2 (P ≡ PMe_2Ph), formed by photolysis of ReH_5P_3, reacts with cyclooctatetraene to give first $(\eta^4\text{-}C_8H_{10})ReH_3P_2$ as a stereochemically rigid complex of cyclooctatriene. This undergoes a thermal reaction at 25 °C to give $(\eta^5\text{-}C_8H_{11})ReH_2P_2$, shown to be a 1–5-$\eta^5$-cyclooctadienyl complex by NMR spectroscopy and X-ray diffraction. This complex has a piano stool form with a *diag*-ReH_2P_2 unit forming the base. The two hydride ligands lie *in* a mirror plane of the open pentadienyl ligand, and these hydrides are thus inequivalent; the spectral data show that this complex is stereochemically rigid. Analogous η^4-diene complexes are made from 1,5-cyclooctadiene and ReH_5P_3 (photochemically) and from ReH_7P_2 (thermally). Deuterium labeling experiments (employing ReD_5P_3 and C_8H_8) reveal that the transfer of three hydrides from metal to ring in the production of $(\eta^5\text{-}C_8H_{11})ReH_2P_2$ is regiospecific (i.e., no scrambling) and is wholly endo, consistent with an intramolecular mechanism. Crystallographic data (at −160 °C): orthorhombic, *Pbca* with $Z = 8$ and $a = 12.391$ (4) Å, $b = 17.882$ (6) Å, and $c = 20.441$ (8) Å.

Introduction

Irradiation ($\lambda > 300$ nm) of $ReH_5(PMe_2Ph)_3$ expels PMe_2Ph to convert this relatively unreactive saturated complex into the highly reactive transient species ReH_5P_2 (P ≡ PMe_2Ph).[1] This species will catalytically hydrogenate 1-hexene, but not 2-hexene. We have shown this is caused by the formation of a complex of the internal olefin which resists internal transfer of hydrogen from rhenium to the bound internal olefin: in the case of cyclopentene (C_5H_8), we isolate $ReH_3P_3(C_5H_8)$.[2] The stoichiometry of this complex is not simply that of an adduct of cyclopentene and the phototransient ReH_5P_2 but involves instead return of photodissociated phosphine. In an effort to understand this, we have explored the reactions of ReH_5P_2 with other olefins, particularly polyolefins. We report here that this approach gives products that are in fact hydrogen redistribution products derived from adducts of the olefin with ReH_5P_2.

Experimental Section

Toluene, benzene, tetrahydrofuran, and diethyl ether were vacuum transferred from their solutions of sodium benzophenone ketyl. Hexane, pentane, and cyclohexane were vacuum distilled from sodium–potassium alloy. Benzene-d_6, toluene-d_8, and cyclohexane-d_{12} were dried over P_4O_{10} and vacuum distilled. Cyclooctatetraene was vacuum transferred at room temperature prior to use. Manipulations were performed in a N_2-filled Vacuum Atmospheres glovebox or on a Schlenk line equipped with a source of prepurified nitrogen.

Spectroscopy. Proton NMR spectra were recorded by using either a Varian T60 (at 35 °C), Varian HA-220 (at 16 °C), or Nicolet EM-360 (at 24 °C) spectrometer unless otherwise specified.

(1) Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* 1981, *103*, 695.
(2) Green, M. A.; Huffman, J. C.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. J. *J. Organomet. Chem.* 1981, *218*, C39.

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^{31}P NMR spectra were recorded at 40.5 MHz on a Varian XL-100-A spectrometer. ^{13}C spectra were recorded on the Nicolet EM-360. ^{2}H spectra were recorded by using the Varian HA-220 spectrometer. Proton and ^{13}C chemical shifts are reported relative to tetramethylsilane. Phosphorus chemical shifts are referenced to external H_3PO_4 (85%) with downfield shifts assigned positive values. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer.

Photolyses. Photolyses were conducted with a Hanovia 550-W medium-pressure mercury lamp housed in a water-cooled jacket made of Pyrex glass. The lamp jacket was suspended in a bath cooled by flowing cold tap water. Reaction vessels were Pyrex glass.

$ReH_5[P(CH_3)_2Ph]_3$. $ReH_5[P(CH_3)_2Ph]_3$ was synthesized by a literature procedure[3] with one modification: an aqueous perrhenic acid solution (50.08 wt % Re) was substituted for potassium perrhenate: ^1H NMR (C_6D_6, 16 °C) δ (ppm) −6.1 (q, J = 19 Hz, ReH), 1.66 (d, J = 7 Hz, PCH_3), 7.07 (m, *m*- and *p*-C_6H_5), 7.57 (br t, J = 7 Hz, *o*-C_6H_5); $^{31}P\{^1H\}$ NMR (C_6D_6 25 °C) δ (ppm) −16.5 (s); $^{31}P\{^1H\}$ NMR (toluene, −50 °C) δ (ppm) −13.0 (br s, 2 P), −21.9 (br s, 1 P).

$ReD_5(PMe_2Ph)_3$. To a solution of 2.65 g of $ReCl_3(PMe_2Ph)_3$ in 100 mL of dry THF was cautiously added 1.0 g of $LiAlD_4$ against a flow of N_2. The mixture was stirred at room temperature for 1 h and then refluxed for 0.5 h. After being cooled to room temperature, the reaction mixture was hydrolyzed by dropwise addition of a solution of 3 mL of D_2O in 50 mL of dry THF. When gas evolution ceased, the reaction mixture was pumped to dryness. The product was extracted from the gray residue into three 75-mL portions of hexane. When the hexane extract was reduced in volume, 0.65 g of product (white powder) was isolated by filtration. Further concentration of the hexane extracts gave an additional 0.75 g of $ReD_5(PMe_2Ph)_3$: ^1H NMR (C_6D_6), an ReH resonance was detected at 4% of the amplitude of the methyl resonance. This indicates 86% isotropic purity for $ReD_5(PMe_2Ph)_3$.

Photolysis of $ReH_5[P(CH_3)_2Ph]_3$ with Cyclooctatetraene. A solution of $ReH_5[P(CH_3)_2Ph]_3$ (0.25 g) and cyclooctatetraene (1 mL) in *n*-pentane (25 mL) was photolyzed for 90 min, during which time the solution turns from yellow to orange. The pentane was quickly removed in vacuo leaving a dark brown oil. The oil was dissolved in C_6D_6 and the ^1H and $^{31}P\{^1H\}$ spectra indicated the formation of $(\eta^4\text{-}C_8H_{10})ReH_3[P(CH_3)_2Ph]_2$ (due to the complexity of the 0–3 ppm region, not all of the ring hydrogens can be identified in the ^1H spectrum): ^1H NMR (C_6D_6) δ (ppm) −6.6 (t, J = 22 Hz, 2 H, ReH), −4.5 (t, J = 37 Hz, 1 H, ReH), 1.93 (d, J = 8 Hz, 6 H, PCH_3), 1.78 (d, J = 8 Hz, 6 H, PCH_3), 2.49 (br d, J = 7 Hz) of doublets (J = 3 Hz, 1 H), 3.10 (br t, J = 10 Hz, 1 H), 3.64 (br, 1 H), 5.96 (s, 1 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ (ppm) −18.0 and −20.2 (AB q, J_{PP} = 67 Hz, (the stronger central lines of the AB pattern each become quartets when selectively coupled to only the hydride protons)).

Upon standing overnight, either in solution or as an oil, both ^1H and $^{31}P\{^1H\}$ NMR spectra indicate the conversion of the intermediate $(\eta^4\text{-}C_8H_{10})ReH_3[P(CH_3)_2Ph]_2$ to the final product $(\eta^5\text{-}C_8H_{11})ReH_2[P(CH_3)_2Ph]_2$. Similar results (intermediate formation, followed by thermal conversion to final product) are observed when the reaction is run with cyclohexane, benzene, or hexane as the solvent. An oily sample (obtained above) of $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$ was dissolved in ethanol (30 mL), and the solution was filtered and then cooled to −196 °C. Upon thawing, the product precipitated as a golden yellow powder, which was filtered from the cold solution. A saturated solution of the powder was made in *n*-pentane and filtered through glass wool. The flask containing the solution was wrapped in a towel inside a Dewar, and slow cooling to −10 °C gave (after five days) $(\eta^5\text{-}C_8H_{11})ReH_2[P(CH_3)_2Ph]_2$ as yellow crystals: ^1H NMR (C_6D_6 (ring hydrogens are numbered according to the Results and drawing **2**)) δ (ppm) −13.4 (t (J_{PH} = 40 Hz) of doublets (J_{HH} = 10 Hz), 1 H, ReH, −3.82 (t (J_{PH} = 40 Hz) of doublets (J_{HH} = 10 Hz), 1 H, ReH), 0.94 (q J = 14 Hz) of br triplets (J = 2 Hz), 1 H, HG), 1.41 (d, J = 7 Hz, 6 H, PCH_3), 1.56 (d, J = 7 Hz, 7 H, PCH_3 and HF), 1.91 (t (J = 12 Hz) of br triplets (J = 2 Hz), 2 H, HE); 2.68 (br doublet (J = 12 Hz) of doublets (J = 3 Hz), 2 H, HD), 3.49 (m, 2 H, HC), 3.85 (br t, J = 7 Hz, 2 H, HB), 6.59 (t, J = 7 Hz, 1 H, HA), [$^1H\{^1H\}$ NMR experiments and the ^1H and ^2D NMR spectra of $(endo\text{-}D_3C_8H_8)ReD_2[P(CH_3)_2Ph]_2$ (vide infra) confirm the assignments of the C_8H_{11} proton resonances]; $^{31}P\{^1H\}$ NMR (C_6D_6) δ (ppm) −24.8 (s (triplet when selectively coupled to only the hydride protons)).

$(endo\text{-}D_3C_8H_8)ReD_2[P(CH_3)_2Ph]_2$. The deuterio analogue of $(\eta^5\text{-}C_8H_{11})ReH_2[P(CH_3)_2Ph]_2$ was prepared by using $ReD_5[P(CH_3)_2Ph]_3$ in pentane (and EtOD during workup) in the procedure described above: ^2H NMR (C_6H_6 at 33.7 MHz (ring H or D numbered according to drawing **2**)) δ (ppm) 1.9 (br s, HE), 1.6 (br s, HF), −3.6 (br t, J_{PD} = 6 Hz, ReD), −13.4 (br t, J_{PD} = 6 Hz, ReD); ^1H NMR (C_6D_6) δ (ppm) 0.91 (br s, 1 H, HG), 1.36 (d, J = 7 Hz, 6 H, PCH_3), 1.52 (d, J = 7 Hz, 6 H, PCH_3), 2.63 (br s, 2 H, HD), 3.47 (m, 2 H, HC), 3.85 (t, J = 7 Hz, 2 H, HB), 6.59 (t, J = 7 Hz, 1 H, HA).

$(\eta^4\text{-}1,5\text{-}COD)ReH_3(PMe_2Ph)_2$. Method 1. A solution of 1 g of $ReH_5(PMe_2Ph)_3$ and 6.5 mL of 1,5-cyclooctadiene in 100 mL of cyclohexane was photolyzed in a toroidal reactor[4] for 45 min. The solution was evaporated to dryness, leaving a dark yellow oil. The products were separated by chromatography on a *short* Florisil column. $ReH_3(PMe_2Ph)_2(\eta^4\text{-}1,5\text{-}COD)$ was eluted with toluene. $ReH_2(PMe_2Ph)_2(\eta^5\text{-}C_8H_{11})$, a minor product detectable by ^1H NMR prior to chromatography, subsequently eluted with THF. The toluene solution of $ReH_3(PMe_2Ph)_2(COD)$ was evaporated to dryness and the resulting oil triturated with ~2 mL of pentane, giving the product as a white air-stable powder. Note that $ReH_3(PMe_2Ph)_2(\eta^4\text{-}1,5\text{-}COD)$ decomposes if it is not quickly eluted from the Florisil column.

Method 2. A hexane solution (50 mL) of 1 g of $ReH_7(PMe_2Ph)_2$ and 5 mL of 1,5-cyclooctadiene was refluxed under N_2 for 4 h. A black precipitate was removed by filtration and the filtrate evaporated to dryness. The ^1H NMR spectrum of the resulting oil showed it to contain predominantly $ReH_3(PMe_2Ph)_2(1,5\text{-}COD)$ along with some $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$ and $Re_2H_8(PMe_2Ph)_5$.[1] The products were separated as in method 1.

A C_6D_6 solution of $ReH_3(PMe_2Ph)_2(\eta^4\text{-}1,5\text{-}COD)$ shows no sign of change (^1H NMR) over a period of 2 weeks at room temperature. Photolysis of $ReH_3(PMe_2Ph)_2(\eta^4\text{-}1,5\text{-}COD)$ for 1 h in C_6D_{12} similarly leads (by ^1H NMR) to no decomposition and *no* conversion to $ReH_2(PMe_2Ph)_2(\eta^5\text{-}C_8H_{11})$. NMR data for $(\eta^4\text{-}C_8H_{12})ReH_3(PMe_2Ph)_2$ in benzene-d_6: ^1H NMR (220 MHz) δ (ppm) 8.45 (4) (t, *o*-C_6H_5), 7.16 (m, *m*- and *p*-C_6H_5), 3.20 (4) (br s, vinyl H), 2.11 (4) (br q, J = 7 Hz, H_{endo} (or H_{exo})), 1.86 (16) (1:1:1 "virtual" triplet, J = 4 Hz, PCH_3 and H_{exo} (or H endo)), −4.73 (1) (br t, J = 35 Hz, ReH), −7.48 (2) (triplet of doublets, $J_{P\text{-}H}$ = 20 Hz, $J_{H\text{-}H}$ = 3 Hz, ReH); $^{31}P\{^1H\}$ NMR δ (ppm) −18.8 (s (quartet when selectively coupled to only the hydride protons)); $^{13}C\{^1H\}$ NMR (90 MHz) δ (ppm) 142.3 (t, $J_{P\text{-}C}$ = 20 Hz, ipso-C_6H_5), 130.0 (t, $J_{P\text{-}C}$ = 4.3 Hz, *o*-C_6H_5), 128.2 (s, *p*-C_6H_5), 127.9 (t, $J_{P\text{-}C}$ = 4.3 Hz, *m*-C_6H_5), 53.2 (t, $J_{P\text{-}C}$ = 2 Hz, vinyl C_8H_{12}), 28.2 (s, allyl C_8H_{12}), 21.5 (t, $J_{P\text{-}C}$ = 17 Hz, CH_3).

Crystallography. Elongated needles of $(C_8H_{11})ReH_2(PMe_2Ph)_2$ were grown by slow cooling from pentane. A crystal of appropriate size was obtained by cleaving the end of one such needle. Crystal data and parameters of the data collection are shown in Table I. Data were collected at −160 °C in the range 6° ≤ 2θ ≤ 45°, using methods which have been described,[4] and the structure was solved by direct methods (MULTAN 78) and refined (using the criterion $F > 3\sigma(F)$) by full-matrix least-squares methods. All hydrogen atoms were located in a difference Fourier phased on the non-hydrogen parameters, and these were included in the final cycles, which employed an absorption correction. A final difference Fourier was featureless except for one peak of density 1.35 e/Å^3 located 0.4 Å from Re; this peak probably arises from imperfections in the absorption correction.

The results of the X-ray study are shown in Tables II and III and Figures 1 and 2. Anisotropic U's, hydrogen positional and thermal parameters, and a table of observed and calculated structure factors are available as supplementary material. The phenyl ring C–C distances average to 1.383 Å, ranging from 1.347 (17) to 1.408 (19) Å. Phenyl ring carbons deviate by less than

(3) Douglas, P. G.; Shaw, B. L. *Inorg. Synth.* **1977**, *17*, 64.

(4) Huffman, J. D.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

(5) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

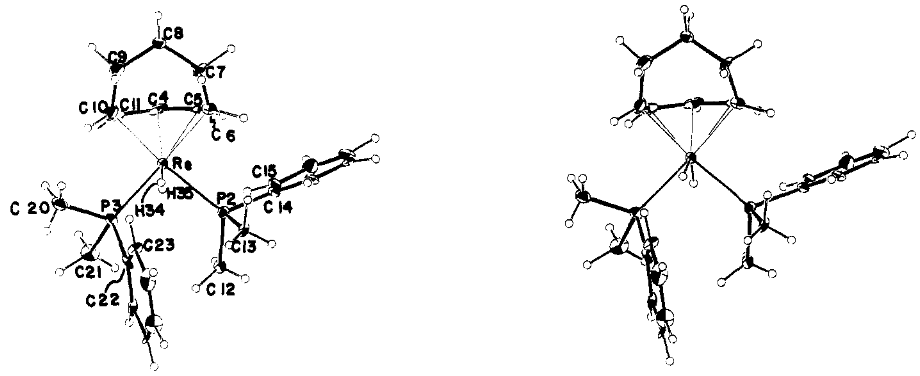


Figure 1. Stereo ORTEP drawing of (η^5-C_8H_{11})$ReH_2(PMe_2Ph)_2$, showing atom numbering.

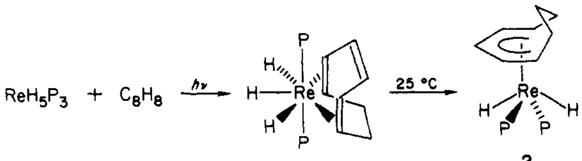
Table I. Crystal Data for (η^5-C_8H_{11})$ReH_2(PMe_2Ph)_2$

empirical formula	$ReP_2C_{24}H_{35}$
color	yellow
cryst dimens, mm	0.045 × 0.025 × 0.025
space group	*Pbca*
cell dimens at −160 °C; 38 reflctns)	
a, Å	12.391 (4)
b, Å	17.882 (6)
c, Å	20.441 (8)
molecules/cell	8
vol, Å^3	4529.32
D(calcd), g/cm^3	1.677
wavelength, Å	0.710 69
mol wt	571.7
linear abs coeff, cm^{-1}	55.8
no. of unique intensities	2971
no. with $F > 0.0$	2676
no. with $F > \sigma(F)$	2508
no. with $F > 2.33\sigma(F)$	2300
final residuals	
$R(F)$	0.0467
$R_w(F)$	0.0428
goodness of fit for the last cycle	1.338
max Δ/σ for last cycle	0.05

0.6σ from their least-squares plane; ring hydrogens deviate by less than 0.9σ from these planes and do so randomly to both sides of the plane. Carbon–hydrogen separations[5] in the phenyl rings average 0.95 Å (ranging from 0.75 to 1.06 Å) with a typical esd of 0.10 Å. Methyl group C–H separations average 0.96 Å (0.83–1.15 Å). Within the C_8H_{11} ring, C–H separations average 1.05 Å (0.92–1.14 Å). Methyl group H–C–H angles average 109.9° (98–123°). All methyl groups assume a staggered conformation about the P–C bonds. The H–C–H angles at C7, C8 and C9 are 98 (9)°, 95 (7)°, and 108 (8)°.

Results

Photolysis of $ReH_5[P(CH_3)_2Ph]_3$ and cyclooctatetraene in cyclohexane at 15 °C results in the formation of an η^4-diene complex (1), which, upon standing, converts to η^5-dienyl complex 2 (eq 1).



(1)

1 2

P=P(CH$_3$)$_2$Ph

The structure of the η^4-triene intermediate 1 is deduced from its ^{1}H and ^{31}P{^{1}H} spectra, which are detectable after 60–90 min of photolysis. The ^{31}P{^{1}H} spectrum consists of an AB quartet whose stronger lines each become quartets when the spectrum is selectively coupled to the hydride protons. Two broad triplets in a ratio of 2:1 are

Table II. Fractional Coordinates and Isotropic Thermal Parameters[a] for (η^5-C_8H_{11})$ReH_2(PMe_2Ph)_2$

	10^4x	10^4y	10^4z	$10B_{iso}$
Re(1)	1388.3 (4)	−1131.0 (2)	1648.2 (2)	9
P(2)	1030 (2)	−1932 (2)	2543 (2)	11
P(3)	1457 (3)	−2110 (2)	871 (1)	12
C(4)	2556 (10)	−151 (6)	1764 (7)	20
C(5)	1810 (9)	9849 (6)	2284 (5)	9
C(6)	632 (9)	9790 (6)	2247 (6)	13
C(7)	−54 (11)	401 (7)	1970 (6)	19
C(8)	433 (10)	843 (7)	1406 (6)	15
C(9)	525 (11)	368 (7)	794 (6)	22
C(10)	1266 (10)	−308 (7)	842 (6)	17
C(11)	2337 (10)	−286 (6)	1093 (6)	15
C(12)	1789 (10)	−2811 (7)	2623 (6)	14
C(13)	−346 (9)	−2288 (7)	2626 (6)	12
C(14)	1282 (10)	8465 (6)	3360 (6)	15
C(15)	2335 (10)	−1349 (6)	3542 (5)	14
C(16)	2569 (12)	−1027 (7)	4121 (6)	22
C(17)	1752 (12)	−836 (7)	4561 (6)	22
C(18)	680 (11)	8977 (6)	4400 (6)	17
C(19)	459 (11)	−1354 (6)	3806 (6)	16
C(20)	1125 (10)	−1885 (7)	20 (6)	18
C(21)	2739 (9)	7393 (7)	766 (6)	18
C(22)	487 (9)	−2882 (6)	975 (5)	11
C(23)	−579 (9)	−2717 (6)	915 (6)	11
C(24)	8677 (10)	6737 (8)	995 (6)	24
C(25)	8947 (10)	6004 (8)	1135 (6)	22
C(26)	13 (11)	−4173 (7)	1201 (5)	13
C(27)	798 (10)	−3620 (7)	1112 (5)	13
H(34)	985 (9)	348 (7)	358 (5)	16 (26)
H(35)	273 (7)	349 (5)	179 (4)	0 (20)

[a] Fractional coordinates are times 10^3 for hydrogen atoms. Isotropic values (Å^2) for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

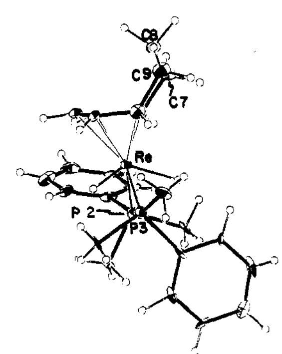


Figure 2. ORTEP drawing of (η^5-C_8H_{11})$ReH_2(PMe_2Ph)_2$, showing the orientation of the methylene groups in the cyclooctadienyl ring.

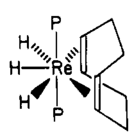
present in the hydride region of the ^{1}H NMR spectrum; the triplet pattern arises from nearly equivalent P–H coupling to the inequivalent phosphorus nuclei. The inequivalence of the phosphorus nuclei in 1 proves that the

Table III. Selected Bond Distances (Å) and Angles (deg) for $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$

Bond Distances					
Re-P(2)	2.366 (3)	Re-C(6)	2.256 (11)	C(6)-C(7)	1.496 (17)
Re-P(3)	2.365 (3)	Re-C(10)	2.215 (11)	C(7)-C(8)	1.521 (17)
Re-H(34)	1.75 (12)	Re-C(11)	2.226 (12)	C(8)-C(9)	1.516 (18)
Re-H(35)	1.32 (9)	C(4)-C(5)	1.409 (17)	C(9)-C(10)	1.521 (18)
Re-C(4)	2.285 (12)	C(4)-C(11)	1.420 (18)	C(10)-C(11)	1.424 (17)
Re-C(5)	2.243 (11)	C(5)-C(6)	1.465 (17)		
Bond Angles					
P(2)-Re-P(3)	94.5 (1)	P(3)-Re-H(35)	75 (4)	C(7)-C(8)-C(9)	111.3 (10)
H(34)-Re-H(35)	125 (6)	C(5)-C(4)-C(11)	127.1 (12)	C(8)-C(9)-C(10)	116.0 (11)
P(2)-Re-H(34)	78 (4)	C(4)-C(5)-C(6)	127.9 (11)	C(9)-C(10)-C(11)	124.2 (12)
P(2)-Re-H(35)	71 (4)	C(5)-C(6)-C(7)	122.2 (11)	C(4)-C(11)-C(10)	122.1 (12)
P(3)-Re-H(34)	64 (4)	C(6)-C(7)-C(8)	116.2 (11)		

C_8 carbons not bonded directly to rhenium are not all equivalent and thus establishes the presence of one uncoordinated olefinic linkage in this intermediate. This result also proves that the intermediate is stereochemically rigid at rhenium on the ^{31}P NMR time scale.

The identity of intermediate 1 is supported by corollary experiments using 1,5-cyclooctadiene (COD). When $ReH_5(PMe_2Ph)_3$ is photolyzed in cyclohexane in the presence of 1,5-COD, $(\eta^4\text{-}1,5\text{-COD})ReH_3(PMe_2Ph)_2$ is the major reaction product. The structure of $(\eta^4\text{-}1,5\text{-COD})ReH_3(PMe_2Ph)_2$ has been deduced from its ^1H, ^{13}C, and ^{31}P NMR spectra. The $^{31}P\{^1H\}$ spectrum is a singlet, indicating that the phosphorus nuclei occupy equivalent sites. The $^{13}C\{^1H\}$ NMR of the COD ligand shows only two resonances, confirming retention of the 1,5 isomer and indicating that this ring possesses two orthogonal mirror planes of symmetry. The phosphine methyl groups appear as a "virtual" triplet in both the $^{13}C\{^1H\}$ and ^1H NMR, indicating that the phosphorus nuclei are strongly coupled (i.e., transoid) and that the methyl groups on a given P are made equivalent by a molecular mirror plane of symmetry. Additionally, the ^1H NMR spectrum shows that three hydrides occupy two inequivalent sites in a ratio of 2:1, with both types of hydrides coupling to the two equivalent phosphine ligands. These data are best explained by the pentagonal-bipyramidal structure 3 in which the two



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phosphorus ligands occupy the axial sites. The structure is analogous to that of $ReH_3(PMe_2Ph)_3(\eta^2\text{-cyclopentene})$[2,6] with the additional olefin ligand replacing one equatorial phosphine. All evidence points to $(\eta^4\text{-}1,5\text{-COD})ReH_3(PMe_2Ph)_2$ being entirely analogous to $(\eta^4\text{-}C_8H_{10})ReH_3(PMe_2Ph)_2$, even to the point that the ^{31}P chemical shift of the former is the average of the two shifts seen in the latter.

Since it has been proposed that $ReH_7(PPh_3)_2$ reacts *thermally* by an initial dihydrogen elimination to give $ReH_5(PPh_3)_2$,[7] which is the oxidation level we have shown is reached upon photolysis of $ReH_5(PMe_2Ph)_3$, we sought an alternative synthesis of our bis(phosphine) 1,5-COD complex via *thermal* reaction with $ReH_7(PMe_2Ph)_2$. This does succeed, with reflux of $ReH_7(PMe_2Ph)_2$ and 1,5-cyclooctadiene in hexane (4 h), giving predominately $(1,5\text{-COD})ReH_3(PMe_2Ph)_2$.

Conversion of $(\eta^4\text{-}C_8H_{10})ReH_3(PMe_2Ph)_2$, **1**, as a neat oil or in hydrocarbon solvents, to $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$, **2**, is complete in less than 12 h at 25 °C. ^1H and ^{31}P NMR establish the existence of the ReH_2P_2 core in the final product **2**. Equivalent phosphorus nuclei give rise to a singlet in the $^{31}P\{^1H\}$ spectrum. The methyl groups on a given phosphine ligand appear as two doublets, so no mirror plane of symmetry passes through the P atoms. The hydride region of the ^1H NMR spectrum indicates two inequivalent sites in a ratio of 1:1, with each type of hydride split into a triplet due to coupling to the two equivalent phosphine ligands. Each triplet is split into doublets by coupling between the inequivalent hydride ligands. The two hydride resonances are separated by an exceptionally large amount (−13.4 and −3.82 ppm), indicating two distinctly different environments for the hydride sites.

Structural Study. An η^5-dienyl moiety coordinated to the ReH_2P_2 core is anticipated for **2**, since it yields an 18-valence electron count at rhenium. While this expectation is in agreement with the (rather complex) ^1H NMR spectrum of the C_8 hydrogens, it is simplest to first establish the pattern of carbon–carbon unsaturation in this ring using the crystallographic results, before describing the ^1H NMR spectrum. The X-ray study (Figure 1) shows the isolated material to have three methylene groups adjacent to one another, leaving a conjugated pentadienyl group for coordination to the metal. The "open" (terminal) ends of this pentadienyl system points toward one of the two hydride ligands, establishing the cycloolefin binding mode as the origin of the hydride inequivalence. Detection of this inequivalence by ^1H NMR of course requires a nonfluxional molecule, a point to which we shall return. The structural study establishes $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$ as having effective mirror symmetry, with a *diag*-ReH_2P_2 fragment. The bond lengths Re–P, Re–C, and C–C all exhibit (to within 3σ) noncrystallographic mirror symmetry, the idealized mirror plane passing through Re, C4, C8, and the refined hydride atoms H34 and H35.

The five metal-bound carbons are planar to within ±0.06 Å (or ±3σ). The metal lies 1.59 Å from this plane, while P(2) and P(3) are 3.16 and 3.19 Å from it. The C_8 ring takes up a scorpion-like conformation (Figure 2), with C(7) and C(9) 1.18 and 1.30 Å from the plane of the coordinated carbons; C(8) is 2.03 Å from this plane. Consistent with some previous pentadienyl structures,[8] the central carbon of the pentadienyl system (C(4) here) is farthest from the metal. The C⋯C distance between coordinated carbons averages 1.430 Å, longer than that in the phenyl rings (1.383 Å) but shorter than that (1.519 Å) for the bonds associated with the uncoordinated carbons C(7), C(8), and C(9). Interior angles within the C_8 ring average 126° for

(6) Muralidharan, S.; Ferraudi, G.; Green, M. A.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *244*, 47.
(7) Baudry, D.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1980**, 249.
(8) Baudry, D.; Ephritikhine, M.; Felkin, H.; Jeannin, Y.; Robert, F. *J. Organomet. Chem.* **1981**, *220*, C7.

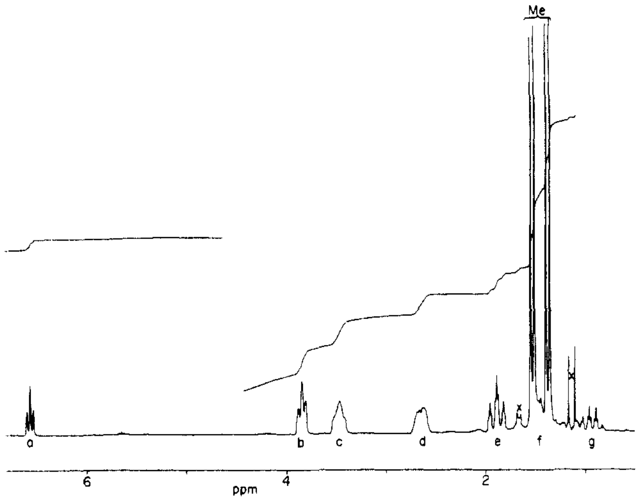
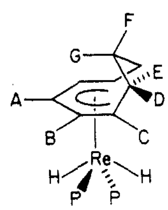


Figure 3. ^{1}H NMR spectrum (200 MHz in C_6D_6) of (η^5-C_8H_{11})$ReH_2(PMe_2Ph)_2$ in the region 0.5–6.9 ppm. "X" indicates impurity.

coordinated carbons and 114° for sp^3 carbons.

The two Re–P distances in (η^5-C_8H_{11})ReH_2P_2, 2.366 (3) Å are identical and are close to those determined in (η^5-C_6H_7)$ReH_2(PPh_3)_2$, 2.355 (5) Å.[8] The two Re–H distances in 2 differ by 0.43 Å; this difference, being 2.9σ (difference), is not statistically significant, in spite of the remarkable ^{1}H NMR spectroscopic disparity between the two hydrides. In (η^5-C_8H_{11})ReH_2P_2, the H–Re–H angle is 125° while the P–Re–P angle (determined by repulsions between the phosphine and the C_8 ring) is only 94.5°.

^{1}H NMR. The ring hydrogens in 2 occupy seven inequivalent sites (see 2); A, F, and G each have half the



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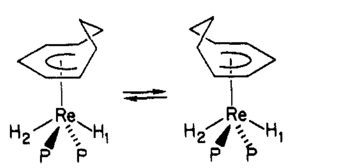
intensity of B, C, D, and E. Resonance a (Figure 3) is readily assigned to site A by its chemical shift, intensity, and triplet structure. The only other intensity 1 resonance *detected* is at 0.94 ppm. Selective homonuclear decoupling experiments allow the following assignment of chemical shifts to protons in **2**:

A 6.59 ppm
B 3.85 ppm (couples to 6.59 and 3.49 ppm)
C 3.49 ppm (couples to 3.85 ppm and weakly to 2.68 and 1.91 ppm)
D 2.68 ppm (couples to 3.49, 1.91, and 0.94 ppm)
E 1.91 ppm (couples to 3.49, 1.56, and 0.94 ppm)
G 0.94 ppm (couples to 2.68 and 1.91 ppm)

These assignments are based on chemical shift, residual splitting observed on selective homonuclear decoupling, and comparison of J values in different multiplets. A resonance for F can be detected flanking the upfield side of the δ 1.56 PMe doublet; however, its multiplicity, pattern, and response to homonuclear decoupling cannot be reliably assessed. The assignment of this to F and the δ 0.94 resonance to G (and not the reverse) follows because of the *two* large H/H coupling constants implicit in the (apparent) quartet of triplets observed at δ 0.94. This is actually a doublet of triplets of triplets, with a single-proton and a two-proton J(H–H) indistinguishable at a value of 14 Hz. One J value is the geminal J(G–F), and the second is a vicinal J(G–E); this latter J value is also evident in the E resonance. The reason that the vicinal coupling constant J(G–E) is so large is found in the crystal structure (Figures 1 and 2). The two crystallographically measured dihedral angles between G and E hydrogens are 159° and 158°. This is the region of the Karplus equation which gives vicinal coupling constants of 9–14 Hz, as we observe. Thus, the crystal structure, together with the Karplus equation, gives us an independent proof that the 0.94 ppm resonance must be due to hydrogen G, not F. Additional proof that a resonance at F is located under a PMe resonance is available from the following labeling experiment.

Regio- and Stereochemistry of the Hydrogenation. In order to establish the positions of the hydrogen attached to the C_8H_8 ring in the course of reaction 1, $ReD_5(PMe_2Ph)_3$ was irradiated with C_8H_8 in cyclohexane. Standard workup yields a product whose ^{2}H NMR spectrum shows (in addition to broad hydride triplets at −3.6 (J = 6 Hz) and −13.4 (J = 6 Hz) ppm) only two resonances: broad singlets at 1.6[9] and 1.9 ppm; the relative intensity of these four resonances was 1:1:1:2. This establishes that the ring hydrogenation is regiospecific in all of its steps and that label is not rapidly scrambled to other sp^2 carbons subsequent to the initial hydrogen transfer. That is, all deuteria transferred from Re to C are found on aliphatic carbons, and two aliphatic resonances (2.6 (D) and 0.9 (G) ppm) experience no deuteration. Finally, the proton chemical shift assignments discussed above permit the conclusion that the three transferred deuteria are all in ring positions endo to the metal, and thus an intramolecular mechanism is strongly indicated for all three transfers. The assignment of *endo*-D_3(η^5-$C_8H_8D_3$)$ReD_2(PMe_2Ph)_2$ stereochemistry to this product is corroborated by the ^{1}H NMR of this material. At 220 MHz, the 3.47 (C) ppm resonance shows better resolution (C now couples to fewer hydrogens), the 2.63 (D) ppm resonance has lost its larger (geminal) coupling to proton E, the 1.9 (E) and 1.6 (F) ppm resonances are absent, and the 0.94 (G) ppm resonance is now a single broadened resonance, due to the loss of ~14 Hz geminal (to F) and vicinal (to the E's) coupling. The vinylic resonances due to A and B are still sharp triplets.

Fluxionality. Given the unusual observation that (η^5-C_8H_{11})$ReH_2(PMe_2Ph)_2$ is stereochemically rigid (220 MHz, 16 °C), we sought evidence for the onset of possible fluxionality. Net rotation of the η^5-C_8H_{11} ring (eq 2) should



(2)

make the inequivalent hydrides equivalent and do the same to the diastereotopic methyl groups. In fact, by 75 °C (toluene-d_8), the methyl doublets broaden but the hydride resonances remain unchanged. At 93 °C, the methyl resonances are a broad singlet at δ 1.50, while the hydride resonances have broadened to the point where J_{H-H} coupling (10 Hz) is lost, but the triplet patterns ($J_{P-H} \approx 40$ Hz) are still resolved. This behavior is reversible; the original spectrum returns upon cooling the sample. Thus, at 93 °C, the rate of the degenerate rearrangement in eq 2 is on the order of 70 s^{-1}, which is still much too slow to

(9) This confirms that one hydrogen lies under the P–Me resonance, as deduced from the ^{1}H NMR spectrum.

show ^1H NMR averaging of hydride resonances separated by 2200 Hz.

Discussion

The work reported here shows that the polyolefin cyclooctatetraene has the capacity to trap the phototransient $ReH_5(PMe_2Ph)_2$ to give several hydrogen-transfer products, each of which is isomeric with simple adducts of the $ReH_5(PMe_2Ph)_2$ and C_8H_8. The formation of the η^4-diene intermediate from photogenerated ReH_5P_2 and C_8H_8 involves the transfer of two hydrogens from the metal to the coordinated olefin. Transfer of a third hydrogen to the cyclooctatriene ring in **1** yields final product **2**, the product of net transfer of three hydrogens from the phototransient ReH_5P_2 to C_8H_8. Coordinative saturation is maintained by forming one additional Re–C bond for every hydrogen transferred. The possibility that these Re-to-C hydrogen transfers are intramolecular is supported by deuterium label studies which show that all three transfers occur to the endo side of the bound C_8 ring.

Rhenium η^4-diene complexes analogous to **1** can be produced from transient $ReH_5(PMe_2Ph)_2$ (available either by photolysis of $ReH_5(PMe_2Ph)_3$ or by heating $ReH_7(PMe_2Ph)_2$) and 1,5-cyclooctadiene. The significant difference here is that the diene, once it is hydrogenated, is displaced by excess diene to give a trihydride complex lacking the hydrogenated fragment; metal–carbon bonds are broken when operating with diene substrates in a manner distinct from the case for cyclooctatetraene (eq 1). The results reported here also show a selectivity for the third hydrogen transfer (from **1** to **2**) to occur at a terminus of the polyolefin system, so as to maintain a conjugated π-olefin system in the product.

Both $(\eta^5\text{-}C_6H_7)ReH_2(PPh_3)_2$[8] and $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$ show remarkable differences for the chemical shifts of their two nonequivalent hydrides (−3 and −13 ppm). This effect is absent in compounds **1** and **3**. Each pentadienyl complex has a structure with one hydride "under" the open end of the pentadienyl π-cloud and the other hydride under the central carbon of the π-cloud. Since $(\eta^5\text{-}C_5H_5)ReH_2(PMe_2Ph)_2$, with no open end to its π-cloud, has only an upfield hydride chemical shift (−11.5 ppm),[2] we suggest that the −3 ppm chemical shift be associated with the hydrogen lying in the mirror plane at the open end of the pentadienyl π-system (H34 in Figure 1). Every π-orbital of the pentadienyl has either a node or a minimum in its electron density in this mirror plane, an effect perhaps responsible for the unusual chemical shift.

In contrast to $(\eta^5\text{-}C_8H_{11})ReH_2(PMe_2Ph)_2$, $(\eta^5\text{-}C_6H_7)ReH_2(PPh_3)_2$ is fluxional at 34 °C.[8] Upon cooling to −40 °C, two hydride environments are frozen out in $(\eta^5\text{-}C_6H_7)ReH_2(PPh_3)_2$; the hydride chemical shifts, δ −3.1 and −12.7, correspond closely to those reported here for the $\eta^5\text{-}C_8H_{11}$ complex. The larger ring analogue thus has the higher activation energy for ring rotation, a feature which appears to be due to the larger distance between the termini of the dienyl unit of the rings, coupled with the nodal properties of the open pentadienyl system.[10] $HZr(\eta^5\text{-}C_8H_{11})(Me_2PCH_2CH_2PMe_2)_2$ is similarly rigid.[11]

Stereochemical rigidity appears to be a characteristic, if unusual, property of several of the polyhydride rhenium complexes reported here, since $(\eta^4\text{-}C_8H_{10})ReH_3(PMe_2Ph)_2$ does not experience facile rotation of the cyclooctatriene moiety (to equivalence the two phosphorus nuclei), and both this and also $(\eta^4\text{-1,5-COD})ReH_3(PMe_2Ph)_2$ show no facile scrambling of the three hydride nuclei. Stereochemical rigidity among seven-coordinate complexes, and also among trihydride species, is uncommon.

Supplementary Material Available: Tables of observed and calculated structure factors, hydrogen positional and thermal parameters, and anisotropic thermal parameters (21 pages). Ordering information is given on any current masthead page.

(10) Albright, T. A.; Hoffmann, R.; Tse, Y.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812.
(11) Fischer, M. B.; James, E. J.; McNeese, T. J.; Nyburg, S. C.; Posin, B.; Wong-Ng, W.; Wreford, S. S. *J. Am. Chem. Soc.* **1980**, *102*, 4941.

Arene and Cyclohexadienyl Complexes as Intermediates in the Selective Catalytic Dehydrogenation of Cyclohexenes to Arenes

Robert H. Crabtree* and Charles P. Parnell

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06511

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A catalytic aromatization of cyclohexene to benzene is described by using $[IrH_2(Me_2CO)_2L_2]SbF_6$ (L = PPh_3) as catalyst in refluxing 1,2-$C_2H_4Cl_2$. *tert*-Butylethylene (tbe) acts as hydrogen acceptor; in the absence of tbe, 2 equiv of cyclohexane are formed per mole of benzene. A mechanism is suggested based on the isolation of the proposed intermediates $[Ir(\eta^5\text{-}C_6H_7)HL_2]SbF_6$ and $[Ir(\eta^6\text{-}C_6H_6)L_2]SbF_6$. Some reactions of these complexes are discussed.

Several methods are available for the homogeneous transition-metal-catalyzed aromatization of *cyclohexadienes*,[1] but there is no satisfactory method for the corresponding cyclohexenes. In view of the ability of $[IrH_2S_2L_2]A$ (**1**, S = Me_2CO, L = PPh_3, A = BF_4 or SbF_6) to stoichiometrically dehydrogenate alkenes and alkanes,[2] including, very recently, cyclohexane to benzene,[3] we wondered if this complex might catalyze the aromatization of cyclohexenes. This paper describes a successful ho-

(1) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153. Fu, P. P.; Harvey, R. G. *Ibid.* **1978**, *78*, 317.
(2) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.
(3) Burk, M. J.; Crabtree, R. H.; Parnell, C. P.; Uriarte, R. J. *Organometallics* **1984**, *3*, 816.

0276-7333/85/2304-0519$01.50/0