Preparation, Dynamic Behavior, and C–H and C–C Cleavage Reactions of (η^4-C$_5$H$_6$)Re(PPh$_3$)$_2$H$_3$. Structures of (η^4-C$_5$H$_6$)Re(PPh$_3$)$_2$H$_3$, CpRe(PPh$_3$)$_2$H$_2$, and CpRe(PPh$_3$)H$_4$

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The complex (η^4-C$_5$H$_6$)Re(PPh$_3$)$_2$H$_3$ has been prepared by the reaction of Re(PPh$_3$)$_2$H$_7$ with cyclopentadiene at 25 °C and by photolysis of Re(PPh$_3$)$_3$H$_5$ in the presence of cyclopentadiene at 0 °C for short periods of time. Continued photolysis results in the formation of CpRe(PPh$_3$)H$_4$, whereas thermolysis at 60 °C produces CpRe(PPh$_3$)$_2$H$_2$, a hydrogen extrusion reaction that is catalyzed by Re(PPh$_3$)$_2$H$_7$. The structure of (η^4-C$_5$H$_6$)Re(PPh$_3$)$_2$H$_3$ is discussed. The low-temperature ^{1}H and ^{31}P NMR spectra are consistent with the complete lack of symmetry revealed in the X-ray structure. Variable-temperature ^{1}H NMR shows three distinct fluxional processes, one involving scrambling of the two equivalent hydrides with the third hydride ($\Delta G^\ddagger$ = 12.3 kcal/mol at T_c = 20 °C), a second involving exchange of the two inequivalent phosphines ($\Delta G^\ddagger$ = 12.1 kcal/mol at T_c = -15 °C), and one involving exchange of the endo-C$_5$H$_6$ hydrogen with the three hydride ligands ($\Delta G^\ddagger$ = 18.5 kcal/mol at T_c = 80 °C). Spin saturation transfer studies confirm the nature of the endo-hydrogen transfer. The dihydride CpRe(PPh$_3$)$_2$H$_2$ crystallizes in monoclinic space group *Pn* with Z = 2, d_{calcd} = 1.522 g/cm^3, and crystal parameters a = 10.185 (3) Å, b = 13.332 (3) Å, c = 13.766 (3) Å, and β = 92.58 (2)°. Convergence occurs with R = 0.0139, R_w = 0.0194, and GOF = 0.643. The two phosphines are trans with an angle of 108.5° at rhenium. Photolysis of (η^4-C$_5$H$_6$)Re(PPh$_3$)$_2$H$_3$ results in the ejection of PPh$_3$ and the formation of CpRe(PPh$_3$)H$_4$. The tetrahydride CpRe(PPh$_3$)H$_4$ crystallizes in triclinic space group *P*$\bar{1}$ with Z = 2, d_{calcd} 1.770 g/cm^3, and crystal parameters a = 9.784 (4) Å, b = 11.295 (4) Å, c = 9.053 (5) Å, α = 95.02 (4)°, β = 97.19 (4)°, and γ = 100.11 (4)°. Convergence occurs with R = 0.017, R_w = 0.027, and GOF = 1.19. The complexes CpRe(PAr$_3$)$_2$H$_2$ (Ar = Ph, 4-C$_6$H$_4$F, 4-C$_6$H$_4$Me, 4-C$_6$H$_4$OMe) can be prepared similarly. Methylcyclopentadiene is used to prepare *exo*- and *endo*-(η^4-C$_5$H$_5$Me)Re(PPh$_3$)$_2$H$_3$, which undergoes C–H and C–C cleavage reactions during the migration of the endo group to the metal. A discussion of the mechanism of the syntheses and dehydrogenation reactions is presented.

Introduction

Polyhydride complexes of transition metals make up an important class of compounds encompassing a wide variety of oxidation states and coordination numbers. Reductive elimination of dihydrogen is a convenient and often reversible method for generating vacant sites at the transition metal for chemical reaction. The variety of known polyhydrides and their derivative chemistry is an area of current interest, both in terms of their thermal and photochemical behavior.

Of all of the transition metals, rhenium is found to have one of the more diverse families of polyhydrides. The largest branch of these known complexes commonly contains phosphine ligands and spans oxidation states of rhenium from +7 to +1. Known monomeric species including Re(PR$_3$)$_2$H$_7$,[1] Re(PR$_3$)$_3$H$_5$,[2,3] Re(PR$_3$)$_4$H$_3$,[4-6] Re(PMe$_3$)$_5$H,[7,8] and [ReH$_9$]$^{2-}$.[9] Well-characterized dimeric compounds include Re$_2$(PMe$_2$Ph)$_5$H$_6$, Re$_2$(PMe$_2$Ph)$_4$H$_8$,[10] and {Re$_2$(PMe$_2$Ph)$_4$[P(OCH$_2$)$_3$CEt]$_2$}$^+$.[11] Preparation of the cyclopentadienyl derivatives CpRe(PPh$_3$)$_2$H$_2$[12] and CpRe(PPh$_3$)H$_4$[2] have also been reported in yields ranging from 15 to 60% using cyclopentadiene and a rhenium phosphine polyhydride.

After the discovery of ferrocene, a number of other cyclopentadienyl derivatives were synthesized from reactions of metals with cyclopentadiene. In several instances, evidence for the presence of the η^4-cyclopentadiene moiety has been presented although complexes of this type could only be isolated and structurally characterized in two cases, CpCo(η^4-C$_5$H$_5$Ph)[13] and CpRe(CH$_3$)$_2$(η^4-C$_5$H$_5$Me).[14]

In this paper, the preparation, isolation, and X-ray structure of the reactive intermediate (η^4-C$_5$H$_6$)Re(PPh$_3$)$_2$H$_3$ (1) is presented. The dynamic behavior of the hydrides in this molecule is discussed, as are the high yield thermal and photochemical reactions to produce the complexes CpRe(PPh$_3$)$_2$H$_2$ (2) and CpRe(PPh$_3$)H$_4$ (3) which were structurally characterized. An unusual rhenium-catalyzed reductive elimination of dihydrogen is also presented. Preliminary communications of this work have appeared.[15,16]

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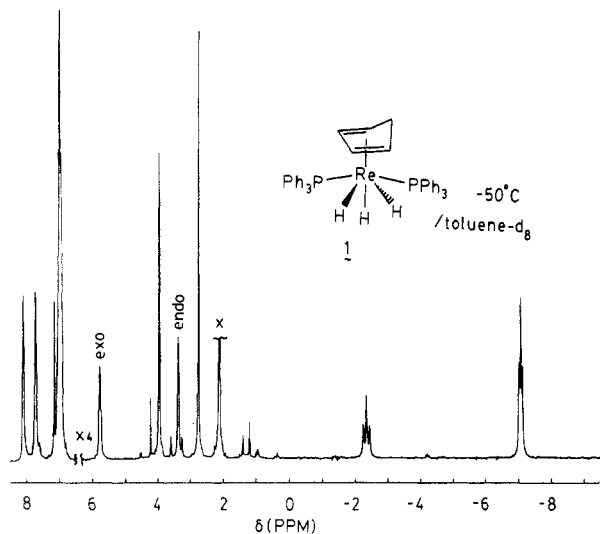
Figure 1. ^{1}H NMR spectrum of $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ (1) at -50 °C in toluene-d_8.

Figure 2. ORTEP drawing of $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ (1). Ellipsoids are shown at the 50% probability level. Hydrogens and phenyl carbons not attached to phosphorus have been omitted for clarity.

Results

A. Preparation of $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ (1). Lithium aluminum hydride reduction of the rhenium oxychloride $ReOCl_3(PPh_3)_2$ provides the thermally unstable complex $Re(PPh_3)_2H_7$, which reacts with cyclopentadiene in THF solution (1:4, v:v) upon standing at 25 °C for 24 h. Addition of ether produces white crystalline $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ (1) in 56% yield (eq 1). Alternatively,
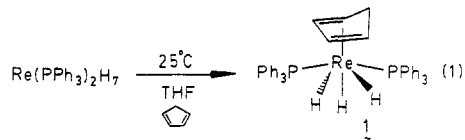
irradiation of a cyclopentadiene/THF solution (1:4) of $Re(PPh_3)_3H_5$ (1.5 M) at 0 °C for 15 min produces $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ in 23% yield upon precipitation with ether (eq 2).
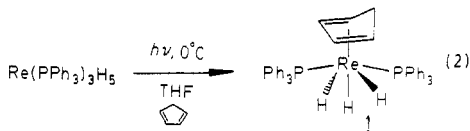
The ^{1}H NMR spectrum of 1 is fluxional at room temperature, as discussed below. At -50 °C in toluene-d_8 the ^{1}H NMR spectrum shows four peaks in a 1:2:1:2 ratio for an $\eta^4\text{-}C_5H_6$ group, two triplets in a 1:2 ratio for the hydride ligands, and a multiplet and two singlets in a 3:1:1 ratio for the phosphine meta plus para and ortho hydrogens, respectively (Figure 1). The ^{31}P NMR spectrum of 1 at -50 °C displays two distinct resonances at δ 35.03 (d, $J = 74$ Hz) and 33.75 (d, $J = 74$ Hz) indicating inequivalent phosphine ligands.

B. Structure of $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$. Recrystallization from THF/ether affords crystals of 1 that belong to the triclinic, acentric space group $P1$. Attempts to solve the structure in this space group gave only refinement to $R = 0.10$. Recrystallization of 1 from THF/hexane affords crystals in the space group $P2_1/n$, which was solved as previously described. The structure of 1 shown in Figure 2 displays several interesting features. The overall structure of the molecule can be described as a distorted pentagonal bipyramid in which the pentagonal plane contains the three hydride ligands and the two C_5H_6 double bonds. The axial phosphines form the P1-Re-P2 angle of 139.7°, the plane of which bisects the C_5H_6 group.
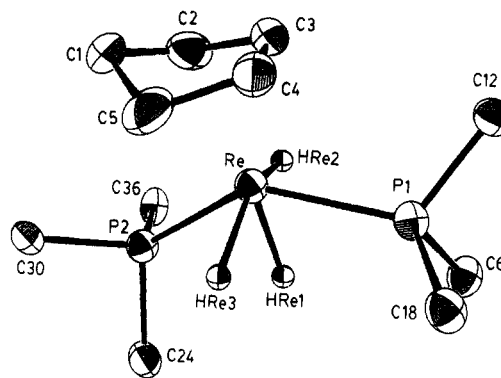
The centroid of the four olefinic C_5H_6 carbons lies directly opposite (176.6°) one of the rhenium bound hydride ligands. This unique hydride along with the remaining two hydrides lies in a plane bisecting the P1-Re-P2 angle, the latter forming an angle of 76 ± 2° relative to the unique equatorial hydride. The dihedral angle formed by the C1-C2-C5 and C2-C3-C4-C5 planes is 36.2°, compared with 36° in $(\eta^4\text{-}C_5H_5Ph)CoCp^{13}$ and 38° in $(\eta^4\text{-}C_5H_5Me)$-ReCpMe$_2$.^{14} The Re-H$_{endo}$ distance is 3.18 Å, indicating no interaction between the C_5H_6 hydrogen and the metal. An IR spectrum of the molecule shows two ν_{C-H} bands at 2755 and 3060 cm^{-1}.

The structures of two related molecules have been reported. The structure of $(\eta^4\text{-cyclohexadiene})Re(PPh_3)_2H_3$ was recently determined and found to possess a slightly larger P-Re-P bond angle of 142.5°.^{17} The CH$_2$-CH$_2$ bond distance was constrained to 1.54 Å to prevent refinement to an unreasonable value, and the hydride ligands could not be located. A pentagonal-bipyramid geometry with the diene and three hydride ligands in the pentagonal plane was also inferred for this molecule. The complex $Re[PPh(i\text{-}Pr)_2]_2(C_2H_4)_2H_3$ has also been prepared and found to exhibit spin saturation transfer exchange of the olefinic hydrogens with the hydrogen attached to the metal. Structural characterization shows a geometry similar to that of the other $(diene)Re(PR_3)_2H_3$ complexes with a P-Re-P bond angle of 137.7° and H-Re-H angles of 54° and 69°.^{18} Consequently, all of these complexes appear to have almost identical structures.

C. Dynamic Behavior of $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ (1). The ^{1}H NMR spectrum of 1 shows complicated temperature-dependent behavior that indicates the occurrence of several fluxional processes (Figures S1-S4). At -50 °C, the spectrum in toluene-d_8 shows separate resonances for phosphine, hydride, and cyclopentadiene groups as would be anticipated on the basis of the X-ray structure. The process observed to have the lowest barrier involves interchange of the two triphenylphosphine groups. Upon warming, coalescence of the ortho resonances of the phosphine phenyl groups is observed to occur at -15 °C. At this temperature, $\Delta\nu = 150$ Hz, which corresponds to a rate of interconversion of $\pi\Delta\nu/(2)^{1/2} = 333$ s^{-1}, or $\Delta G^{\ddagger} = 12.1$ kcal/mol.

The ^{31}P NMR spectra (162 MHz) also show this dynamic interchange of the phosphine groups. At -50 °C, two distinct resonances are observed at δ 35.03 (d, $J = 74$

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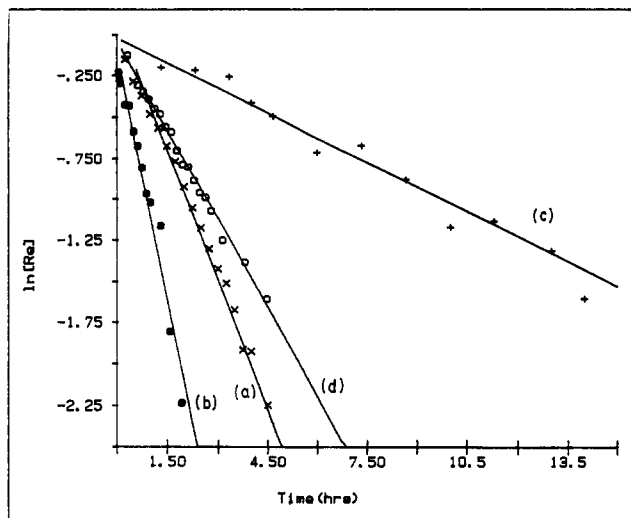
Figure 3. (a) Plot of ln % $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ vs. time in C_6D_6 at 60 °C (×). Least-squares linear fits are indicated. (b) With 20 mol % $Re(PPh_3)_2H_7$ added (●). (c) With 0.04 M added PPh_3 (+). (d) Under 580 mmH$_2$ (○).

Hz) and 33.75 (d, $J = 74$ Hz). Coalescence occurs upon warming to -30 °C with a rate of ~460 s^{-1} ($\Delta G^{\ddagger} \approx 11.2$ kcal/mol), producing a singlet resonance at δ 33.34 at 30 °C in approximate agreement with the proton data at slightly higher temperature. The difference in the values of $\Delta G^{\ddagger}$ can be attributed to the inaccuracy of determining the value of $\Delta\nu$ in the approximately first-order ^{31}P NMR spectrum rather than any real difference.

The next process that occurs involves interchange of the two types of hydride in the molecule. The distinct triplets observed at δ -7.087 (2 H) and -2.358 (1 H) in a 2:1 ratio are seen to coalesce at 20 °C to a broad singlet close to the weighted average of the two resonances (δ -5.67 (obsd vs.) -5.51 (calcd)). This process is calculated to occur with a rate of 4200 s^{-1} or $\Delta G^{\ddagger} = 12.3$ kcal/mol at 20 °C.

The last process to occur involves mutual exchange of the hydride ligands with the endo hydrogen of the C_5H_6 group and the equilibration of the exo hydrogen with the olefinic hydrogens. When the toluene solution of 1 is warmed to 60 °C, the coalesced singlet for the three (now equivalent) hydrides is seen to broaden and collapse as the four singlets for the C_5H_6 hydrogens broaden. At 80 °C, a new broad resonance begins to grow in at δ 3.57, but attainment of the limiting high-temperature spectrum is prevented due to the thermal dehydrogenation of 1 to form $CpRe(PPh_3)_2H_2$ (see section D, below).

Further evidence for the exchange of the endo-C_5H_6 hydrogen with the hydride ligands comes from a spin saturation transfer experiment at 40 °C. If the hydride resonance at δ -5.67 is irradiated, the resonance at δ 3.353 is observed to collapse. A similar collapse of the hydride signal is seen upon irradiation of the δ 3.353 resonance, indicating that the magnetization at one site is transferred to the other site at a rate approximately equal to the relaxation time T_1 (~1-5 s). The barrier for this transfer is approximately 18.5 kcal/mol and is clearly distinct from the process that equilibrates the phosphine and hydride ligands.

D. Thermal Reactions of $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ **(1).** Thermolysis of pure recrystallized 1 in C_6D_6 under a nitrogen atmosphere results in the first-order disappearance of the resonances for 1 and the appearance of resonances at δ -9.95 (t, $J = 40$ Hz, 2 H) and 4.27 (s, 5 H) as well as a phosphine multiplet attributable to the known complex $CpRe(PPh_3)_2H_2$ (2). A plot of ln [1] vs. time gives a fairly good straight line for which the slope at 60 °C is 1.5 × 10^{-4}

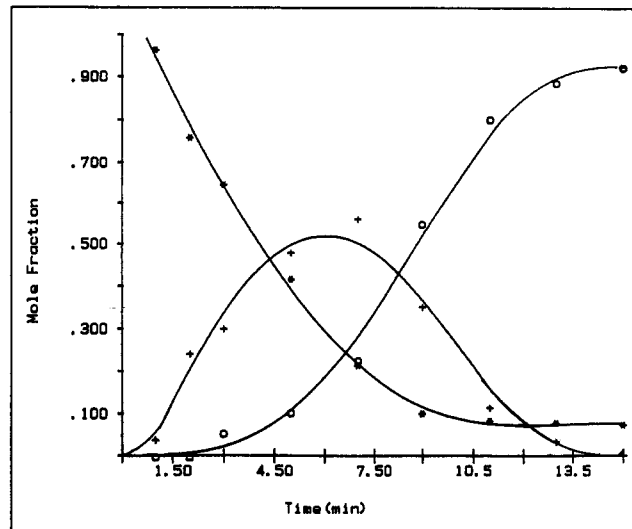**Figure 4.** Plot of mole fraction vs. time in the reaction of Re-$(PPh_3)_2H_7$ (*, 0.067 M) with cyclopentadiene (0.123 M) in THF-d_8 at 60 °C. $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ (+) and $CpRe(PPh_3)_2H_2$ (○) are the products.

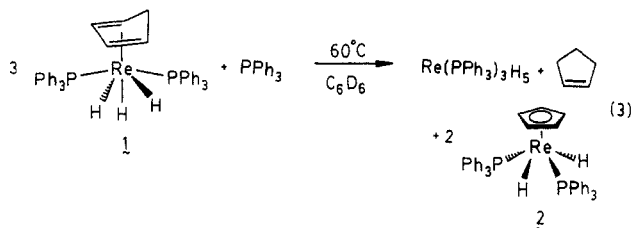s^{-1}, and hydrogen can be detected in the ^1H NMR spectrum (Figure 3a).

The rate of dehydrogenation of 1 corresponds to a half-life of approximately 100 min at 60 °C. Ephritikhine and Felkin reported the efficient formation of 2 by the reaction of $Re(PPh_3)_2H_7$ with 0.12 M cyclopentadiene in THF at 67 °C in only 15 min with complex 1 seen occasionally as a transient species.[19] The long half-life for dehydrogenation of 1 made it seem unlikely that it was an intermediate on the reaction pathway from $Re(PPh_3)_2H_7$ to 2 but rather that 1 was formed in a dead-end side reaction that occurred in the presence of large amount of cyclopentadiene. An examination of the reaction under the conditions reported by Ephritikhine and Felkin revealed that 1 was, in fact, an intermediate.

Reaction of a solution of $Re(PPh_3)_2H_7$ (0.067 M) with cyclopentadiene (0.123 M) in THF-d_8 in the probe of an NMR spectrometer heated to 60 °C showed the conversion of $Re(PPh_3)_2H_7$ and cyclopentadiene into 1 (48%) and cyclopentene after only 5 min. After 10 min, virtually all of the cyclopentadiene had been consumed while some of the $Re(PPh_3)_2H_7$ remained. In the next few min of reaction, however, all of complex 1 was converted into 2 plus dihydrogen (Figure 4). The dehydrogenation of 1 was being catalyzed under the reaction conditions employed by Ephritikhine and Felkin.

The loss of dihydrogen from 1 was found to be catalyzed by addition of small amounts of $Re(PPh_3)_2H_7$. The latter compound is known to lose hydrogen readily under the reaction conditions. Addition of 10 mol % heptahydride (0.008 M) to a benzene solution of purified 1 decreases the half-life for the dehydrogenation reaction from 100 to 20 min (Figure 3b), and addition of 1 equiv of $Re(PPh_3)_2H_7$ (0.04 M) decreases the half-life to approximately 7 min. None of the red dimer $Re_2H_8(PPh_3)_4$ is observed.[10]

The effects of added triphenylphosphine confirm the catalysis by a coordinatively unsaturated rhenium complex. Addition of triphenylphosphine greatly inhibits the conversion of 1 to 2 plus dihydrogen (Figure 3c). A solution of 1 containing 0.04 M PPh_3 (2 equiv) was found to slowly produce $Re(PPh_3)_3H_5$, cyclopentene, and 2 in a 1:1:2 ratio with a half-life of ~7 h at 60 °C (eq 3). Reaction under

(19) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1982**, *224*, 363-376.

$$3 \; Ph_3P{-}\overset{\Large\text{[cyclobutene]}}{\underset{\overset{|}{\underset{H}{H}}\;\overset{|}{H}}{Re}}{-}PPh_3 \; + \; PPh_3 \; \xrightarrow[C_6D_6]{60°C} \; Re(PPh_3)_3H_5 \; + \; \text{[cyclopentadiene]}$$

$$\mathbf{1}$$

$$+ \; 2 \; \overset{\Large\text{[Cp]}}{\underset{\overset{|}{\underset{H}{Ph_3P}}\overset{|}{\underset{PPh_3}{}}}{Re}}{\cdots}H \qquad (3)$$

$$\mathbf{2}$$

a hydrogen atmosphere has only a slight effect upon the rate of disappearance of **1** (Figure 3d), although **2** was now the major product observed with only a trace (<2%) of $Re(PPh_3)_2H_7$ and cyclopentene being formed.

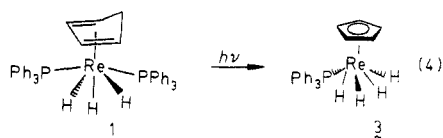Treatment of compound **1** with $P(C_6D_5)_3$ in benzene solution does not result in phosphine exchange, even after 35 days at 25 °C in the dark. Upon heating to 60 °C, cyclopentene, **2**, and pentahydride are observed. Since no free PPh_3 is seen, the pentahydride that is formed is formulated as $Re(PPh_3)_2[P(C_6D_5)_3]H_5$. Compound **1** also slowly reacts with a large excess of ethylene at 25 °C. The quantitative (NMR) formation of **2** and ethane is observed with a half-life of ~50 h.

Other $CpRe(PR_3)_2H_2$ complexes in which $R = p\text{-}C_6H_4F$, $p\text{-}C_6H_4Me$, and $p\text{-}C_6H_4OMe$ have been prepared in a similar fashion. The sequence involves preparation of the oxychlorides $Re(PR_3)_2OCl_3$ from perrhenic acid and phosphine followed by $LiAlH_4$ reduction to generate $Re(PR_3)_2H_7$. Treatment of the heptahydrides with an excess of cyclopentadiene in THF followed by gentle heating produces the dihydrides $CpRe(PR_3)_2H_2$ in high yield.

E. Structure of $CpRe(PPh_3)_2H_2$ (2). Colorless crystals of $CpRe(PPh_3)_2H_2$ suitable for X-ray examination were grown from benzene solution. Collection of one quadrant of data for a monoclinic cell with $4 \le 2\theta \le 47$ followed by Patterson map solution revealed the rhenium position 2.17 Å from a glide plane. Successful solution of the structure and refinement of the non-hydrogen atoms was carried out in space group Pn. A benzene molecule was also located in a crystal void. Hydrogens were placed in idealized locations on the Cp, phenyl, and benzene rings. A difference Fourier map was used to locate the two rhenium hydrides. Anisotropic refinement of the non-hydrogen atoms and isotropic refinement of the hydride ligands converged with $R = 0.0139$, $R_w = 0.0194$, and GOF = 0.643. Figure 5 shows an ORTEP plot of the molecule, Table II contains selected bond distances and angles, and Table III gives atomic coordinates.

The structure is that of a regular piano-stool molecule of the trans geometry with a P1–Re–P2 bond angle of 108.6°. The trans hydride ligands lie ~1.7 Å from the metal and are separated by an angle of 138°. The larger phosphine ligands are bent further from the Cp ring than the smaller hydrides.

F. Photochemical Reactions of $(\eta^4\text{-}C_5H_6)\text{Re-}(PPh_3)_2H_3$ (1). Photolysis (365 nm) of **1** in C_6H_6 solution at ~5 °C initially produces only $CpRe(PPh_3)H_4$ (**3**). Continued irradiation of the sample results in the conversion of $CpRe(PPh_3)H_4$ to $CpRe(PPh_3)_2H_2$ (eq 4). The

$$Ph_3P{-}\overset{\Large\text{[cyclobutene]}}{\underset{\overset{|}{\underset{H}{H}}\;\overset{|}{H}}{Re}}{-}PPh_3 \; \xrightarrow{h\nu} \; \overset{\Large\text{[Cp]}}{\underset{\overset{|}{\underset{H}{Ph_3P}}\overset{|}{\underset{H}{H}}}{Re}}{\cdots}H \qquad (4)$$

$$\mathbf{1} \qquad\qquad \mathbf{3}$$

complex $CpRe(PPh_3)H_4$ can be isolated as a white crystalline solid by addition of ether and displays a singlet at δ 4.291 (5 H) and a doublet at δ −7.954 (J = 19.0 Hz, 4 H) as well as multiplets for the phosphine phenyl groups at δ 7.700 (6 H) and 7.00 (9 H) in C_6D_6 solvent. Continued
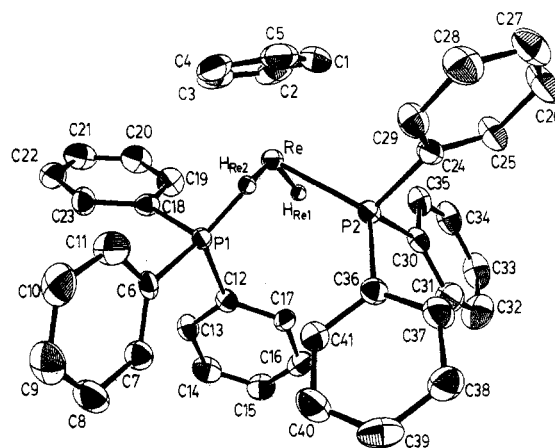

Figure 5. ORTEP drawing of $CpRe(PPh_3)_2H_2$. Ellipsoids are shown at the 50% probability level. Hydrogens attached to carbon have been omitted for clarity. Hydrides are located and refined.

Table I. Summary of Crystallographic Data[a]

	$CpRe(PPh_3)_2H_2\cdot$ C_6H_6	$CpRe(PPh_3)H_4$
	Crystal Parameters	
formula	$ReP_2C_{41}H_{37}$	$RePC_{23}H_{24}$
fw	777.90	517.62
cryst system	monoclinic	triclinic
space group	Pn	$P\bar{1}$
Z	2	2
a, Å	10.185 (3)	9.784 (4)
b, Å	13.332 (2)	11.295 (4)
c, Å	13.766 (3)	9.053 (5)
α, deg	90.0	95.02 (4)
β, deg	92.58 (2)	97.19 (4)
γ, deg	90.0	100.11 (4)
V, Å^3	1867 (1.3)	971.1 (1.5)
d_{calcd}, g/cm^3	1.363	1.77
Xtal dimens, mm	0.45 × 0.38 × 0.27	0.30 × 0.35 × 0.25
temp, °C	−41.5	25
	Measurement of Intensity Data	
diffractometer	Enraf-Nonius CAD4, κ geometry	
radiatn	Mo, 0.710 73 Å	
monochromator	graphite	
scan typ	$2\theta/\omega$	
scan rate, deg/min	2.8–20	
total bkgd time	scan time/2	
takeoff angle, deg	2.6	
scan range, deg—tan θ	0.65	0.65
2θ range, deg	4–47	4–50
data collected	$+h,+k,\pm l$	$+h,\pm k,\pm l$
no. of data collected	2935	3624
no. of unique data >3σ	2888	3390
no. of par varied	458	322
abs coeff, cm^{-1}	34.13	64.2
abs corr	empirical	empirical
range of trans. factors	0.897–0.999	0.917–0.999
systematic absences	$h0l, h + l$ odd	none
equiv data	none	$0kl = 0\bar{k}l$
agrmnt between equiv data		0.008
R	0.0139	0.0175
R_w	0.0194	0.0271
goodness of fit	0.643	1.189

[a] Scattering factors f, f', and f'' were taken from: Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

photolysis results in the disappearance of the $CpRe(PPh_3)H_4$, and photolysis without external cooling gives mostly $CpRe(PPh_3)_2H_2$.

G. Structure of $CpRe(PPh_3)H_4$ (3). Colorless crystals of $CpRe(PPh_3)H_4$ suitable for X-ray examination were grown from benzene solution. Initial cell parameters in-

Table II. Selected Distances (Å) and Angles (deg)

CpRe(PPh₃)₂H₂

Bond Distances

Re–P1	2.324 (1)	Re–HRe1	1.66 (6)
Re–P2	2.312 (1)	Re–HRe2	1.73 (9)
P1–C6	1.845 (5)	C1–C2	1.385 (13)
P1–C12	1.845 (5)	C2–C3	1.375 (11)
P1–C18	1.846 (5)	C3–C4	1.424 (10)
P2–C24	1.854 (6)	C4–C5	1.377 (10)
P2–C30	1.853 (5)	C1–C5	1.407 (13)
P2–C36	1.845 (6)		

Bond Angles

P1–Re–P2	108.62 (5)	P1–Re–HRe1	73 (2)
P1–Re–cen[a]	126.11 (4)	P1–Re–HRe2	82 (3)
P2–Re–cen[a]	125.26 (3)	P2–Re–HRe1	77 (2)
HRe1–Re–HRe2	138 (4)	P2–Re–HRe2	80 (3)

CpRe(PPh₃)H₄

Bond Distances

Re–P	2.346 (1)	C1–C2	1.396 (7)
P–C6	1.839 (3)	C2–C3	1.403 (7)
P–C12	1.837 (3)	C3–C4	1.406 (7)
P–C18	1.831 (3)	C4–C5	1.369 (8)
Re–H1a	1.62 (4)	C1–C5	1.425 (7)
Re–H1b	1.64 (4)		
Re–H1c	1.66 (5)		
Re–H1d	1.59 (4)		

Bond Angles

P–Re–cen[a]	122.70 (2)	cen–Re–H1c	107 (2)
P–Re–H1a	86 (1)	cen–Re–H1d	120 (2)
P–Re–H1b	61 (2)	H1a–Re–H1b	68 (2)
P–Re–H1c	130 (2)	H1a–Re–H1c	76 (2)
P–Re–H1d	83 (2)	H1a–Re–H1d	127 (2)
cen–Re–H1a	110 (1)	H1b–Re–H1c	70 (2)
cen–Re–H1b	176 (1)	H1b–Re–H1d	61 (2)
		H1c–Re–H1d	73 (2)

[a] cen is the Cp centroid.

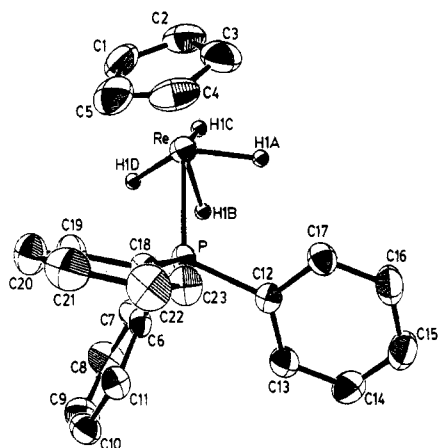**Figure 6.** ORTEP drawing of CpRe(PPh₃)H₄. Ellipsoids are shown at the 50% probability level. Hydrogens attached to carbon have been omitted for clarity. Hydrides are located and refined.

Table III. Fractional Atomic Coordinates for CpRe(PPh₃)₂H₂[a]

atom	x	y	z	B, Å²
Re	0.750	0.83826 (1)	0.750	1.743 (2)
P1	0.62976 (9)	0.88893 (6)	0.61114 (6)	1.65 (2)
P2	0.6826 (1)	0.67895 (7)	0.79157 (7)	1.76 (2)
C1	0.9340 (7)	0.8380 (3)	0.8483 (6)	4.9 (1)
C2	0.9667 (4)	0.8864 (4)	0.7637 (4)	4.4 (1)
C3	0.8905 (5)	0.9711 (3)	0.7525 3)	4.24 (9)
C4	0.8080 (5)	0.9763 (3)	0.8332 (4)	3.95 (9)
C5	0.8349 (5)	0.8940 (4)	0.8912 (3)	4.3 (1)
C6	0.4626 (3)	0.9384 (2)	0.6255 (3)	1.99 (6)
C7	0.3548 (4)	0.9095 (3)	0.5683 (3)	2.62 (7)
C8	0.2310 (4)	0.9493 (4)	0.5839 (4)	3.78 (9)
C9	0.2154 (4)	1.0204 (3)	0.6538 (4)	3.91 (9)
C10	0.3209 (5)	1.0491 (3)	0.7136 (4)	4.04 (9)
C11	0.4442 (4)	1.0067 (3)	0.6999 (3)	3.43 (9)
C12	0.6027 (3)	0.8059 (3)	0.5049 (2)	1.98 (6)
C13	0.5724 (5)	0.8444 (2)	0.4120 (3)	2.49 (9)
C14	0.5486 (4)	0.7790 (3)	0.3344 (3)	3.23 (8)
C15	0.5549 (5)	0.6772 (3)	0.3469 (3)	3.15 (9)
C16	0.5840 (4)	0.6393 (3)	0.4378 (3)	2.74 (8)
C17	0.6083 (4)	0.7023 (3)	0.5165 (2)	2.13 (7)
C18	0.7095 (4)	0.9931 (3)	0.5480 (3)	2.19 (7)
C19	0.8320 (4)	0.9743 (3)	0.5102 (3)	3.25 (8)
C20	0.8988 (5)	1.0492 (4)	0.4636 (3)	3.76 (9)
C21	0.8465 (6)	1.1433 (4)	0.4546 (4)	4.2 (1)
C22	0.7282 (7)	1.1639 (3)	0.4929 (5)	3.8 (1)
C23	0.6576 (4)	1.0906 (3)	0.5394 (3)	2.87 (8)
C24	0.7341 (4)	0.6457 (3)	0.9184 (3)	2.13 (7)
C25	0.8165 (4)	0.5658 (3)	0.9435 (3)	3.13 (8)
C26	0.8506 (5)	0.5455 (3)	1.0410 (3)	3.90 (9)
C27	0.8021 (5)	0.6048 (4)	1.1138 (3)	3.8 (1)
C28	0.7199 (5)	0.6833 (4)	1.0896 (3)	3.53 (9)
C29	0.6853 (4)	0.7035 (3)	0.9932 (3)	2.73 (7)
C30	0.7466 (4)	0.5710 (3)	0.7234 (2)	2.21 (7)
C31	0.6720 (5)	0.4908 (3)	0.6937 (3)	3.16 (8)
C32	0.7259 (5)	0.4146 (3)	0.6387 (3)	4.2 (1)
C33	0.8560 (5)	0.4165 (3)	0.6162 (3)	3.85 (9)
C34	0.9329 (5)	0.4960 (3)	0.6467 (3)	3.36 (8)
C35	0.8784 (4)	0.5735 (3)	0.6988 (3)	2.78 (7)
C36	0.5069 (4)	0.6464 (3)	0.7966 (3)	2.08 (7)
C37	0.4636 (4)	0.5694 (3)	0.8564 (3)	2.96 (8)
C38	0.3328 (4)	0.5458 (3)	0.8605 (3)	3.35 (8)
C39	0.2399 (4)	0.6003 (4)	0.8067 (3)	3.48 (9)
C40	0.2808 (4)	0.6771 (3)	0.7464 (5)	3.4 (1)
C41	0.4134 (4)	0.6982 (3)	0.7414 (3)	2.58 (7)
C42	0.610 (1)	0.3167 (5)	0.9900 (6)	7.1 (2)
C43	0.4787 (7)	0.3010 (5)	0.9663 (4)	5.5 (1)
C44	0.4442 (6)	0.2683 (5)	0.8756 (5)	5.9 (1)
C45	0.5386 (8)	0.2467 (6)	0.8135 (6)	8.2 (2)
C46	0.6697 (7)	0.2618 (5)	0.8427 (6)	7.5 (2)
C47	0.6976 (7)	0.2997 (6)	0.9262 (6)	7.1 (2)
HRE1	0.800 (4)	0.769 (3)	0.659 (3)	4 (1)*
HRE2	0.604 (6)	0.866 (4)	0.804 (4)	5 (1)*

[a] See footnote a in Table IV.

dicated a triclinic cell. Collection of one hemisphere of data with $4 \leq 2\theta \leq 50$ followed by Patterson map solution in space group P1̄ revealed a bent Cp–Re–PPh₃ structure. Hydrogens were placed in idealized locations on the Cp and phenyl rings. Following full refinement of all atoms, a difference Fourier map showed four of the top six peaks with intensities of 0.5–1.0 e/Å³ in the void near the rhenium. (The remaining two peaks were not within bonding distance to any atom.) Refinement of all atoms converged with $R = 0.017$, $R_w = 0.027$, and GOF = 1.19. Figure 6 shows an ORTEP drawing of the molecule, Table II gives selected distances and angles, and Table IV gives atomic coordinates.

The structure shows a bent Cp–Rh–P bond angle of 122.7°, with the rhenium, two hydrides (H1b and H1c), the Cp centroid, and the phosphorus lying in a plane. The remaining two hydrides (H1a and H1d) flank this plane, bending toward the smaller equatorial hydride H1b, and together with the rhenium and Cp centroid form a second plane that is at 89.9° to the first. The Cp centroid–Re–H1b angle is 176°. There are no short H–H distances that suggest the presence of a nonclassical dihydrogen complex.

H. C–C Cleavage in $(\eta^4\text{-}C_5H_5Me)Re(PPh_3)_2H_3$. In a reaction similar to that for the preparation of 1, Re(PPh₃)₂H₇ reacts with methylcyclopentadiene to give a solution whose ¹H NMR spectrum is consistent with the presence of two complexes, *exo-* and *endo-*$(\eta^4\text{-}C_5H_5Me)$Re(PPh₃)₂H₃, in a 20:1 ratio. The ¹H NMR spectrum of the mixture shows resonances for the major species at δ 7.906 (s, 12 H), 7.005 (m, 18 H), 3.808 (br s, 2 H), 3.129 (br s, 1 H), 2.763 (br s, 2 H), and 0.372 (d, J = 4.4 Hz, 3

Scheme I
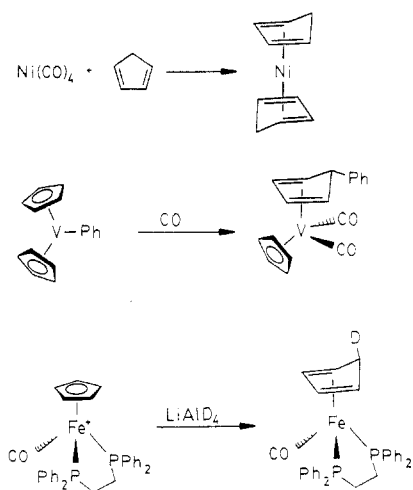
H), −5.7 (br, 2.5 H) assigned to the exo isomer and δ 7.982 (s, 12 H), 5.463 (br s, 1 H), 3.725 (br s, 2 H), 2.552 (br s, 2 H), and 0.198 (d, J = 5.8 Hz, 3 H) assigned to the endo isomer. The hydride resonance and the meta and para phenyl ring resonances of the endo-methyl complex are obscured by the resonances for the exo-methyl complex.

When this sample is heated to 110 °C for 45 min, a new product appears with ^{1}H NMR resonances at δ 7.665 (t, J = 7.6 Hz, 12 H), 6.955 (m, 18 H), 4.270 (s, 2 H), 3.969 (s, 2 H), 1.941 (s, 3 H), and −9.916 (t, J = 40.1 Hz, 2 H) consistent with the formation of $(C_5H_4Me)Re(PPh_3)_2H_2$. Free H_2 is also seen at δ 4.459. In addition, a second minor set of resonances for **2** and methane (δ 0.143) are observed (eq 5).
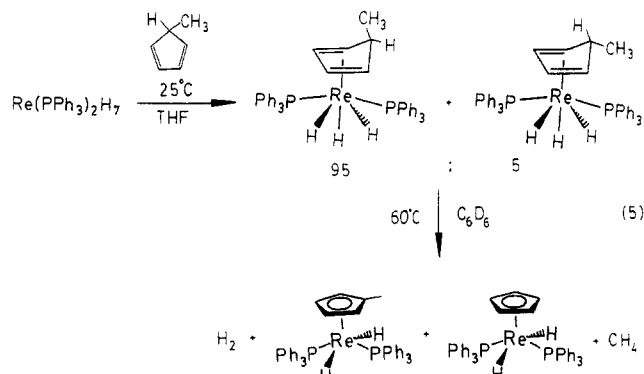
The exo isomer shows spin saturation transfer between the endo-C_5H_5Me hydrogen and the hydride ligands just as in the case of **1**. Irradiation of either the hydride or endo resonance results in the collapse of the partner at 45 °C in C_6D_6 solution.

Discussion

The formation and isolation of **1** represents the first structurally characterized example of an unsubstituted η^4-C_5H_6 complex. A great deal of activity involving reactions of cyclopentadiene with metal complexes followed the discovery of ferrocene in 1956. Complexes such as $CpCo(\eta^4$-$C_5H_6)$ (and its rhodium and iridium analogues) were isolated from reduction of cobaltecene with borohydride, although structures of the molecules were not determined.[20] Since that time, more than a dozen reports

(20) Churchill, M. R.; Mason, R. *Proc. Chem. Soc. London* **1963**, 112–113. Churchill, M. R. *J. Organomet. Chem.* **1965**, *4*, 258–260. Churchill, M. R.; Mason, R. *Proc. R. Soc. London, Ser. A* **1964**, *279*, 191–209. Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1965**, 177–178.

Table IV. Fractional Atomic Coordinates for CpRe(PPh₃)H₄[a]

| atom	x	y	z	B, Å²
Re	0.26146 (1)	0.02377 (1)	0.19598 (1)	2.489 (3)
P	0.37700 (7)	0.21358 (7)	0.31697 (8)	2.05 (1)
C1	0.1921 (5)	−0.1559 (4)	0.2711 (5)	4.8 (1)
C2	0.0840 (5)	−0.1384 (4)	0.1639 (5)	4.8 (1)
C3	0.0269 (4)	−0.0393 (4)	0.2149 (5)	4.65 (9)
C4	0.1026 (4)	0.0055 (4)	0.3569 (5)	4.77 (9)
C5	0.1999 (6)	−0.0647 (4)	0.3927 (5)	5.7 (1)
C6	0.5695 (3)	0.2521 (3)	0.3390 (3)	2.41 (6)
C7	0.6433 4)	0.2025 (4)	0.2379 (4)	3.41 (7)
C8	0.7883 (4)	0.2344 (4)	0.2548 (5)	4.41 (9)
C9	0.8601 (4)	0.3163 (4)	0.3728 (5)	4.23 (9)
C10	0.7870 (4)	0.3665 (3)	0.4719 (4)	3.35 (7)
C11	0.6427 (3)	0.3357 (3)	0.4557 (4)	2.92 (6)
C12	0.3265 (3)	0.3442 (3)	0.2319 (3)	2.27 (6)
C13	0.4211 (4)	0.4425 (3)	0.2012 (4)	3.17 (7)
C14	0.3759 (4)	0.5345 (3)	0.1317 (5)	4.02 (8)
C15	0.2349 (4)	0.5320 (3)	0.0917 (4)	3.93 (8)
C16	0.1394 (4)	0.4363 (3)	0.1231 (4)	3.81 (8)
C17	0.1845 (3)	0.3431 (3)	0.1901 (4)	2.92 (6)
C18	0.3443 (3)	0.2402 (3)	0.5108 (3)	2.28 (6)
C19	0.3959 (4)	0.1684 (3)	0.6145 (4)	3.02 (7)
C20	0.3647 (4)	0.1788 (3)	0.7595 (4)	3.54 (7)
C21	0.2810 (4)	0.2562 (4)	0.8022 (4)	3.75 (8)
C22	0.2325 (4)	0.3298 (4)	0.7028 (4)	3.78 (8)
C23	0.2634 (3)	0.3223 (3)	0.5574 (4)	2.96 (6)
H1A	0.188 (4)	0.098 (3)	0.075 (4)	3.4 (8)*
H1B	0.377 (4)	0.108 (4)	0.114 (4)	4.2 (9)*
H1C	0.277 (5)	0.953 (4)	0.032 (5)	7 (1)*
H1D	0.417 (4)	−0.002 (4)	0.208 (5)	5 (1)*
H1	0.242 (4)	−0.221 (4)	0.250 (5)	5 (1)*
H2	0.058 (4)	−0.172 (3)	0.105 (4)	4.5 (8)*
H3	−0.054 (4)	0.015 (4)	0.157 (5)	5 (1)*
H4	0.088 (6)	0.064 (5)	0.385 (7)	10 (2)*
H5	0.260 (5)	−0.068 (4)	0.486 (5)	6 (1)*
H7	0.597 (3)	0.143 (3)	0.157 (4)	2.7 (7)*
H8	0.823 (6)	0.189 (5)	0.206 ()	9 (2)*
H9	0.959 (4)	0.340 (4)	0.398 (4)	5 (1)*
H10	0.833 (3)	0.419 3)	0.548 (4)	3.0 (7)*
H11	0.593 (3)	0.373 (3)	0.520 (4)	2.6 (7)*
H13	0.505 (4)	0.447 (3)	0.213 (4)	4.2 (9)*
H14	0.445 (4)	0.593 (4)	0.112 (4)	4.5 (9)*
H15	0.214 (5)	0.596 (4)	0.050 (5)	6 (1)*
H16	0.041 (4)	0.430 (4)	0.097 (5)	5 (1)*
H17	0.128 4)	0.283 (3)	0.203 (4)	3.1 (8)*
H19	0.461 (4)	0.110 (4)	0.577 (5)	5 (1)*
H20	0.398 (3)	0.133 (3)	0.828 (3)	2.2 (6)*
H21	0.252 (5)	0.273 (4)	0.918 (5)	6 (1)*
H22	0.180 (4)	0.390 (4)	0.734 (5)	6 (1)*
H23	0.221 (3)	0.367 (3)	0.479 (4)	2.6 (7)*
CEN	0.1220	−0.0790	0.2790	

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)b(2,3)]$.

of either isolated or proposed η^4-C_5H_5R complexes have appeared.[21-23]

(21) (a) Wilkinson, G. *J. Am. Chem. Soc.* **1954**, *76*, 209–211. Fischer, E. O.; Werner, H. *Chem. Ber.* **1959**, *92*, 1423–1427. Paulson, P. L. *Proc. Chem. Soc.* **1960**, 297–305. Fischer, E. O.; Zahn, U. *Chem. Ber.* **1959**, *92*, 1624–1628. Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710–1714. Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1969**, 616–617. Kreiter, C. G.; Nist, K.; Kogler, J. XI International Conference on Organometallic Chemistry, 1983, Pine Mountain, abstracts, p. 18. (b) Green, M. L. H.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1985**, 1383–1384.

(22) Green, M. L. H.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1959**, 3753–3767. Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3172–3177. Darensbourg, M. Y. *J. Organomet. Chem.* **1972**, *38*, 133–138. Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047–3077. Davies, S. G.; Moon, S. D.; Simpson, S. J.; Thomas, S. E. *J. Chem. Soc., Dalton Trans.* **1983**, 1805–1806. Davies, S. G.; Simpson, S. J.; Felkin, H.; Fillebeen-Khan, T. *Organometallics* **1983**, *2*, 539–541. Whitesides, T. H.; Shelly, J. *J. Organomet. Chem.* **1975**, *92*, 215–226. Bullock, R. M.; Headford, C. E. L.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 727–729.

Scheme II

Scheme III
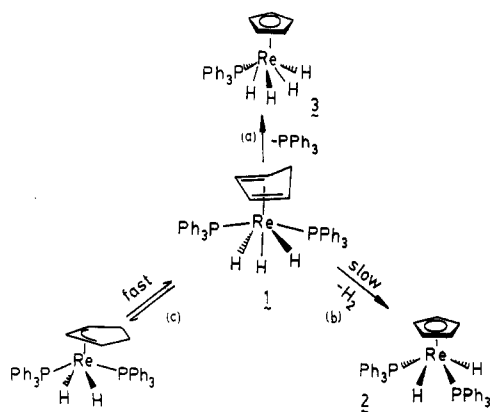
In general, three separate routes have been used to prepare the η^4-C_5H_5R ligand: (1) the direct reaction of cyclopentadiene with a metal,[21] (2) the reaction of a cyclopentadienyl metal complex with a hydridic reagent, usually involving exo attack on the η^5-C_5H_5 ring,[22] and (3) the reaction of a cyclopentadienyl metal hydride complex with a ligand, inducing migration of hydride to the ring.[23] Several examples are shown in Scheme I.

The η^4 complex described in this paper differs from those of earlier reports in that the complex also contains coordinated hydride ligands. The low symmetry of the complex results in the observation of three distinct fluxional processes. The processes with the lowest barriers involve equilibration of the two distinct types of hydride and phosphine ligands. The similar barriers for both of these processes could be accounted for by a single mechanism that includes both types of exchange. Pairwise hydrogen atom exchange has been seen by Ginsberg in $ReH_3(phosphine)_4$ molecules,[4] and the polytopal rearrangements of seven-coordinate molecules in general has been discussed by Hoffmann and Muetterties.[24] We suspect that the phosphine ligands are equilibrated by rotation of the C_5H_6 ring and that a pairwise hydride exchange can occur during the rotation.

The third fluxional exchange equilibrates the hydride ligands with the endo-η^4-C_5H_6 hydrogen. Several possible mechanisms can be envisioned for this exchange. First, migration of the endo hydrogen down to the metal center should be preceeded by the loss of a ligand such as phosphine (Scheme IIa) or dihydrogen (Scheme IIb). The loss of phosphine from 1 can be ruled out since no reaction is observed between 1 and free $P(C_6D_5)_3$ over several hours time. Similarly, loss of dihydrogen followed by migration would generate the known molecule $CpRe(PPh_3)_2H_2$ which does not react with hydrogen (1000 psi, 40 °C).

An alternative mechanism involves hydrogen migration from the metal up to the C_5H_6 ring, generating a symmetrical π-allyl dihydride intermediate (Scheme IIc). This intermediate is expected to be quite reactive since it is formally 16-electron and is probably responsible for the ring displacement reaction observed with PPh_3. The reaction of this intermediate with hydrogen is apparently quite slow, since only traces of $Re(PPh_3)_2H_7$ were seen in
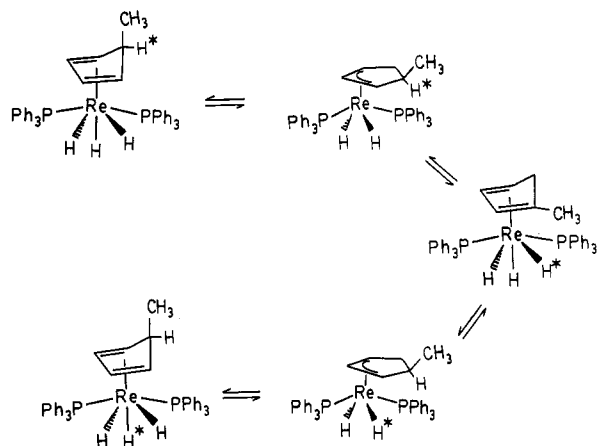
the reaction with hydrogen. Ethylene apparently reacts with this species and is then hydrogenated, leaving behind 2. Since reactions of 1 with PPh_3, H_2, and ethylene are much slower than the rate of endo-H/hydride exchange, the formation of the η^3-cyclopentenyl intermediate must be a rapid and reversible process with trapping by the substrate being rate determining (or at least prior to the rate-determining step).

This type of migration has been postulated in several other systems,[23] most notably the (η^4-cyclohexadiene)Re-$(PPh_3)_2H_3$.[25] Both spin saturation transfer and temperature-dependent line-shape analysis have been used to demonstrate the migration of a hydride ligand from the metal to the hexadiene ligand, generating an intermediate π-allyl similar to the one proposed here. The reported temperature and frequency separations for this process in the hexadiene complex (k = 3700 s⁻¹ at 75 °C) are comparable to those given here for 1, implying that the barriers for hydrogen migration are comparable in both molecules ($\Delta G^{\ddagger} \approx 15$ kcal/mol).

A second related example of reversible metal to olefin migration involves the complex $Re(C_2H_4)_2[PPh(i\text{-}Pr)_2]_2H_3$ reported by Spencer, Howard, and Hazel.[18] Facile exchange between the ethylene hydrogens and the hydride ligands occurs at 70 °C, as evidenced by both spin saturation transfer and temperature-dependent line shapes. It is interesting to note that the related complex (η^4-C_5H_6)W(PMe_3)_3H_2$ was not reported to show any evidence of dynamic behavior.[22] Also, while (η^4-c-C_8H_{10})Re-$(PMe_2Ph)_2H_3$ undergoes metal to ring migration to form (η^5-c-C_8H_{11})Re(PMe_2Ph)_2H_2$, no reverse migration is observed.[26]

Complex 1 also displays a low-energy C–H stretch at 2755 cm⁻¹ as is typical of the η^4-C_5H_6 moiety. As the structural determination shows no interaction between the metal and the endo C–H bond, the low energy of this stretch cannot be attributed to an agostic interaction but rather to the asymmetric combination of the C–H_{exo} and C–H_{endo} stretches. A discussion of this effect has been given by Faller, including the demonstration of the averaging of the stretching frequencies upon monodeuteriation of the η^4-C_5H_6 ring.[27]

Substitution of the endo hydrogen in 1 for a methyl group still apparently results in migration of the endo group to the metal by way of a C–C cleavage reaction. In

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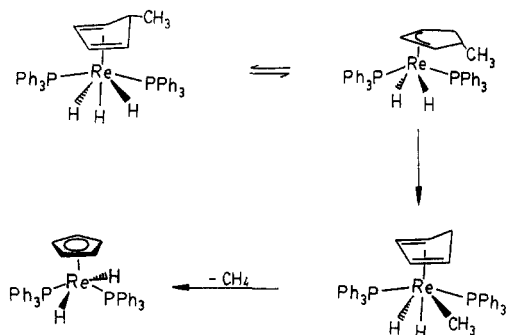(24) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* 1977, 16, 511–522.

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Scheme IV

the reaction of methylcyclopentadiene with $Re(PPh_3)_2H_7$ a large preference for the formation of *exo*- over *endo*-$(\eta^4\text{-}C_5H_5Me)Re(PPh_3)_2H_3$ was observed. The conversion of the exo isomer to $(C_5H_4Me)Re(PPh_3)_2H_2$ undoubtedly involves a mechanism similar to that for the dehydrogenation of 1. The observation of spin transfer between the hydride and the endo hydrogen is interesting in that a simple reversible migration of the hydride ligand to the η^4 ring will not exchange the magnetically distinct sites. A second reversible migration of the –CHMe– hydrogen to the metal must also occur reversibly (the hydride ligands must also scramble during this process) in order for the exchange to occur (Scheme III). The preference for the methyl group in the methylene position of the $\eta^4\text{-}C_5H_5Me$ ring is consistent with the observation of only the exo and endo isomers but no 1- or 2-substituted methylcyclopentadiene complexes despite the fact that the latter are the major isomers in free methylcyclopentadiene.

The observation of a 20:1 ratio of *exo*- to *endo*-$(\eta^4\text{-}C_5H_5Me)Re(PPh_3)_2H_3$ from the reaction of $Re(PPh_3)_2H_7$ with methylcyclopentadiene is worth commenting on further. Since free C_5H_5Me is present as a 47:47:6 ratio of 1-:2-:5-methyl isomers, coordination of the [Re-$(PPh_3)_2H_5$] to the diene will be followed by an isomerization of the endo hydrogen to the carbon containing the methyl group, giving the exo-$(\eta^4\text{-}C_5H_5Me)$ rhenium complex. *Only* in the case of 5-methylcyclopentadiene can *endo*-$(\eta^4\text{-}C_5H_5Me)Re(PPh_3)_2H_3$ be formed, and this only will occur if the rhenium complexes to the same side of the ring as the methyl group. The ratio of exo- to endo-$(\eta^4\text{-}C_5H_5Me)$ complex formed therefore arises from the requirements of the mechanism of formation.

The formation of the small amount of methane and 2 probably arises from the endo isomer by the pathway shown in Scheme IV. Here, migration of hydrogen from the metal to the C_5H_5Me ring is followed by migration of the endo-methyl group to the metal. The methyl hydride complex formed then quickly eliminates methane and forms 2. The ring to metal migration of alkyl groups in $\eta^4\text{-}C_5H_5R$ complexes has been observed previously in several systems.[28]

Complex 1 is also unique in that it was found to undergo an unusual hydrogen-transfer reaction. The complex $Re(PPh_3)_2H_7$ has been used by Felkin and Ephritikhine as a convenient thermal source of the unsaturated complex $[Re(PPh_3)_2H_5]$ and has been reported to react with cyclopentadiene at 60 °C to produce $CpRe(PPh_3)_2H_2$.[12] While evidence for the intermediacy of 1 was seen in the

^{1}H NMR spectrum, the observation of the complex was difficult to reproduce.[19] Similarly, photolysis of Re-$(PPh_3)_3H_5$ has been reported to produce the same coordinatively unsaturated intermediate $[Re(PPh_3)_2H_5]^{3,10}$ and to react with cyclopentadiene to produce $CpRe(PPh_3)_2H_2$.[2]

In the thermolysis of 1 in the presence of $Re(PPh_3)_2H_7$, the intermediate $[Re(PPh_3)_2H_5]$ is apparently capable of abstracting dihydrogen from 1 in a bimolecular fashion. A first-order plot of this bimolecular reaction is linear since the $Re(PPh_3)_2H_7$ remains constant during the reaction.

The inhibition by added PPh_3 cannot be accounted for in terms of the trapping of the unsaturated intermediate $[(\eta^3\text{-}C_5H_7)Re(PPh_3)_2H_2]$ with the ultimate formation of the observed product $Re(PPh_3)_3H_5$, since this reaction could only serve to *increase* the rate of disappearance of 1. Apparently, PPh_3 traps the unsaturated species [Re-$(PPh_3)_2H_5$] to form $Re(PPh_3)_3H_5$, shutting down the bimolecular pathway. The slight inhibition by added H_2 is interpreted in terms of shifting the equilibrium between thermally labile $Re(PPh_3)_2H_7$ and $[Re(PPh_3)_2H_5]$ + H_2 toward the former, decreasing the concentration of the catalyst.

The anticipated structure of the transition state or intermediate for this reaction (4) is held together by only
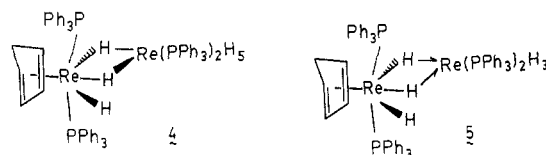
a pair of bridging hydrogen atoms. The electron counting scheme for bridging hydrogen put forth by M. L. H. Green would involve each hydrogen acting as a two-electron donor toward *each* metal center and would formally produce a 20-electron count for the rhenium bis(phosphine) pentahydride fragment in complex 4.[29] A structure that accommodates the formalism by Green would instead have to involve a species of reduced coordination number, such as 5, in which the catalytic species has lost an additional molecule of H_2. Felkin postulated the reversible equilibrium $2[Re(PPh_3)_2H_5] \rightleftharpoons [Re(PPh_3)_2H_7] + [Re(PPh_3)_2H_3]$, which could be involved.

Very few other reactions have been postulated to proceed by this type of intermediate or transition state.[30] One of these reported by Harrod involves a rapid and reversible reaction between $fac,cis\text{-}Ir(PR_3)_2(CO)H_3$ and $trans$-Ir-$(PR_3)_2(CO)H$ (R = 4-chlorophenyl) to give an $Ir(\mu\text{-}H)_2Ir$ intermediate (eq 6). While the bridging species was not

P = PPh_3
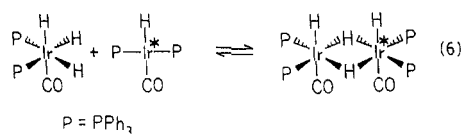
directly observed, the hydrides trans to phosphorus were observed to collapse at temperatures above ~ 0 °C whereas the hydride trans to CO remained sharp at all temperatures.[31] A second example was reported in a similar compound by Eisenberg, in which the phosphine ligands were incorporated into the chelate bis(diphenylphosphino)propane.[32] Moore has observed the formation

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(31) Drouin, M.; Harrod, J. F. *Inorg. Chem.* **1983**, *22*, 999–1001. Harrod, J. F.; Yorke, W. J. *Inorg. Chem.* **1981**, *20*, 1156–1159.

of a stable $Rh(\mu\text{-}H)_2M$ species in the reaction of Cp_2MH_2 (M = Mo, W) with $[Rh(O\!\!=\!\!CMe_2)_2(PPh_3)_2H_2]^+$ (eq 7).[33] A similar reaction occurs with the iridium solvate dihydride, except that there are two additional terminal hydrogens on the iridium.

P = PPh$_3$

M = Mo, W
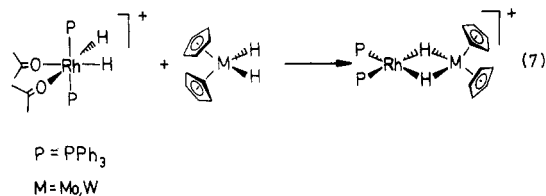
Finally, two studies have been reported that are more closely related to the one presented here. In one, Spencer found that Pt(0) phosphine complexes accelerate the reaction of $Re[PPh(i\text{-}Pr)_2]_2H_7$ with ethylene to generate $Re(C_2H_4)_2[PPh(i\text{-}Pr)_2]_2H_3$, although no details of the mechanism of the reaction were given.[18] In the other, Geoffroy postulated the transfer of dihydrogen between $Re(PR_3)_3H_5$ and $Re(PR_3)_2H_5$ to give $Re(PR_3)_3H_3$ and $Re(PR_3)_2H_7$.[3]

It is interesting to note that the thermal and photochemical behavior of complex 1 are fundamentally different. While the complex undergoes reductive elimination of dihydrogen thermally, irradiation induces loss of phosphine. The preferential photochemical loss of phosphine over dihydrogen was also observed with $Re(PR_3)_3H_5$.[3,10]

Conclusion

The presence of an $\eta^4\text{-}C_5H_6$ ring in $(\eta^4\text{-}C_5H_6)Re(PPh_3)_2H_3$ is found to generate several reactive pathways for the molecule. Dynamic processes include facile phosphine and hydride ligand interchange and reversible metal to ring hydride migration. This ability to intramolecularly form a vacant coordination site permits reactions with substrates that can displace hydrogen or the C_5H_6 ring. While the complex loses hydrogen thermally, loss of phosphine is observed photochemically. Hydrogen loss can be catalyzed by the transfer of dihydrogen to $[Re(PPh_3)_2H_5]$. Also, C–C bond cleavage can be seen when an endo-methyl group is present on the $\eta^4\text{-}C_5H_5R$ ring in the form of alkyl group migration to the metal.

Experimental Section

Nearly all compounds that were used in the course of this work are only slightly air sensitive in the solid state but most are unstable to oxygen and moisture in solution and undergo considerable decomposition over several minutes. All operations involving these compounds were performed under vacuum or an inert atmosphere of dry nitrogen, either on a high vacuum line with modified Schlenk techniques or in a Vacuum Atmospheres Corporation dri-lab glovebox.

Rhenium metal was purchased from Strem Chemicals, Inc., and was used for the preparation of $ReOCl_3(PPh_3)_2$. Triphenylphosphine was also purchased from Strem Chemicals and was recrystallized from dichloromethane/ethanol and dried under reduced pressure. Tri-p-tolylphosphine and triphenylphosphine-d_{15} were prepared by using standard literature procedures and recrystallized from concentrated ether solution.

Dicyclopentadiene was purchased from Mallinkrodt Chemical Co. and was cracked to cyclopentadiene by using a 1-ft vacuum-jacketed vigreux column. The fraction from 40 to 42 °C was saved

and put through three freeze–pump–thaw cycles for degassing before vacuum distillation into the reaction vessel. Di(methylcyclopentadiene) was purchased from Aldrich and was cracked in a similar fashion. All other reagents were obtained commercially and used without further purification.

Tetrahydrofuran and diethyl ether were distilled from purple solutions of sodium benzophenone ketyl under vacuum. Aliphatic and aromatic hydrocarbon solvents were vacuum distilled from purple solutions of potassium benzophenone ketyl with a small amount of tetraglyme. Before distillation, aliphatic hydrocarbon solvents were stirred over H_2SO_4 for at least 48 h, washed successively with saturated $KMnO_4$ in 10% H_2SO_4, three portions of H_2O, and one portion of saturated Na_2CO_3, and stored over $CaCl_2$. Elevated temperatures were maintained by using a thermostated silicone oil bath.

High-field ^1H (400.13-MHz) and ^{31}P (162.00 MHz) NMR spectra were recorded on a Bruker WH-400 NMR spectrometer. ^1H NMR spectra are reported in units of δ (parts per million downfield from tetramethylsilane) but were usually measured relative to residual proton resonances in deuterated solvents: C_6D_6 (7.150), THF-d_8 (1.730), or toluene-d_8 (2.090). ^{31}P NMR spectra are reported in units of δ (parts per million downfield from a coaxially mounted sealed capillary of 30% phosphoric acid). Temperature was regulated during variable-temperature NMR experiments by a Bruker BVT-1000 temperature control unit (0.1 °C). Temperatures were calibrated by using standard methanol or ethylene glycol calibration samples obtained from Wilmad Glass Co.

Single-crystal X-ray diffraction studies were carried out by using an Enraf-Nonius CAD4 diffractometer. Calculations were carried out on the Molecular Structure Corporation Texray 230 computer system using a PDP 11/23 processor and Enraf-Nonius CAD4 and SDP-Plus programs. The perspective thermal ellipsoid plots were done using the SDP version of C. K. Johnson's ORTEP plotting program.

Perdeuteriated benzene (99.6% D), toluene (99.5% D), and tetrahydrofuran (98% D) were obtained from Aldrich or Cambridge Isotopes and were vacuum distilled (25 °C, 10^{-4} mm) from sodium or potassium benzophenone ketyl containing a small amount of tetraglyme and were stored under vacuum in glass ampules fitted with teflon stopcocks.

Elemental analyses were performed by MicAnal Laboratories or by Kodak Instrumental Support facilities. Photolyses were carried out by using a high-pressure 200-W Hg focused beam Oriel lamp fitted with an infrared absorbing water filter and a 2 in. × 2 in. borosilicate glass filter. Low-temperature photolyses were carried out in a plexiglas chamber fitted with a 2 in. × 2 in. square of quartz glass window. Temperature was maintained by a continuous stream of cold water monitored with a thermometer. Experiments involving more than one sample to be photolyzed under the same conditions were carried out in a merry-go-round type apparatus.

Preparation of $Re(PPh_3)_2H_7$. In a slight modification of an earlier preparation,[19] the complex $ReOCl_3(PPh_3)_2$ (2.0 g, 2.4 mmol) was placed in a 100-mL round-bottom flask under vacuum for 1 h. Ether (40 mL) was vacuum transferred into the flask. Lithium aluminum hydride (0.385 g, 10.1 mmol) was added to the stirring slurry over 10 m. After 30 min (when only a flocculent white solid was visible) the mixture was filtered through a medium fritted funnel and the filtrate was transferred to a two-neck 100 mL flask fitted with a septum. Solvent was removed with reduced pressure. Wet CH_2Cl_2 (30 mL) was added through the septum to the cooled solution (~40 °C). The mixture was allowed to stir until bubbling stopped and it then warmed to 0 °C. H_2O (5 mL) was introduced with a syringe and the mixture quickly filtered in air through a cotton plug by using minimum vacuum. The filtrate was quickly cooled by direct addition of LN_2 to the solution, freezing water droplets to the walls of the flask. The solution was then placed in a 50-mL flask, the solvent removed (10^{-3} mm), and Et_2O (5 mL) vacuum transferred into the flask containing the crude product. Upon stirring the less soluble white product complex remained solid while the yellow colored impurities were extracted. The mixture was quickly filtered in air and dried under vacuum (yield 1.15 g, 64%). ^1H NMR (C_6D_6): δ 7.80 (br s, 12 H), 6.97 (br s, 18 H), −4.20 (t, J = 18 Hz, 7 H). Identical procedures were used to prepare the complexes with

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P(p-tolyl)₃, P(p-C₆H₄F)₃, and P(C₆H₄OMe)₃ ligands.

Preparation of (η⁴-C₅H₆)Re(PPh₃)₂H₃. The crude complex Re(PPh₃)₂H₇ was prepared from ReOCl₃(PPh₃)₂ (2.0 g, 2.4 mmol) as described above. THF (8 mL) was then vacuum transferred into the flask followed by cyclopentadiene (2 mL, 100 equiv). The mixture was stirred at room temperature (23 °C) for 24 h after which the solvent volume was reduced under vacuum to about 5 mL. Ether (10 mL) was vacuum distilled into the flask and the mixture stirred. Large colorless crystals formed in good yield (1.10 g, 56% based on ReOCl₃(PPh₃)₂). The ¹H NMR spectrum recorded at –50 °C in C₆D₅CD₃ is δ 8.093 (s, 6 H), 7.718 (s, 6 H), 7.06 (m, 18 H), 5.764 (dd, J = 10.9, 9.4 Hz, 1 H), 3.943 (b s, 2 H), 3.353 (d, J = 6.5 Hz, 1 H), 2.723 (b s, 2 H), –2.358 (t, J = 38.8 Hz, 1 H), and –7.087 (t, J = 19.4 Hz, 2 H). Anal. Calcd (Found) for ReP₂C₄₁H₃₉: C, 63.14 (63.44); H, 5.04 (4.98).

Preparation of CpRe(PPh₃)₂H₂. The complex (η⁴-C₅H₆)-Re(PPh₃)₂H₃ (1.0 g, 1.28 mmol) was dissolved in a minimum of C₆H₆ (10 mL) and allowed to stand for 1 week. Large pale yellow crystals of CpRe(PPh₃)₂H₂·C₆H₆ (yield 1.03 g, 94%) were filtered, washed with hexanes, and dried under vacuum. ¹H NMR (C₆D₆): δ 7.620 (t, J = 7.3 Hz, 12 H), 6.973 (m, 18 H), 4.268 (s, 5 H), –9.952 (t, J = 40.1 Hz, 2 H).

Preparation of CpRe(PR₃)₂H₂ (R = p-C₆H₄F, p-C₆H₄Me, and p-C₆H₄OMe). These CpRe(PR₃)₂H₂ complexes have been prepared in a fashion similar to that for CpRe(PPh₃)₂H₂, except that the η⁴ complexes were not isolated as intermediates. The heptahydride complexes were observed to be less thermally sensitive than the PPh₃ analogue, and the slight heating required to induce reaction with cyclopentadiene was found to also result in the dehydrogenation of the η⁴ complexes. ¹H NMR (C₆D₆) for R = p-C₆H₄F: δ 7.28 (dd, J = 13.3, 7.5 Hz, 12 H), 6.65 (t, J = 8.5 Hz, 12 H), 4.14 (s, 5 H), –10.30 (t, J = 40.2 Hz, 2H). Anal. Calcd (Found) for ReP₂F₆C₄₁H₃₁: C, 56.3 (56.3); H, 4.3 (4.3); P, 6.5 (6.5). ¹H NMR (C₆D₆) for R = p-C₆H₄Me: δ 7.67 (t, J = 7.2 Hz, 12 H), 6.90 (t, J = 7.2 Hz, 12 H), 4.39 (s, 5 H), 2.04 (s, 18 H), –9.91 (t, 39.8 Hz, 2 H). ¹H NMR (C₆D₆) for R = p-C₆H₄OMe: δ 7.695 (t, J = 8.4 Hz, 12 H), 6.681 (d, J = 8.4 Hz, 12 H), 4.472 (s, 5 H), 3.248 (s, 18 H), –9.888 (t, J = 40.2 Hz, 2 H). Anal. Calcd (Found) ReP₂O₆C₄₇H₄₉: C, 58.9 (58.4); H, 5.2 (4.9); P, 6.5 (6.4).

Preparation of Re(PPh₃)₃H₅. A benzene (50-mL) solution of Re(PPh₃)₂H₇ (500 mg, 0.696 mmol) and PPh₃ (550 mg, 2.090 mmol) was heated to 50 °C for 2 h. Solvent was removed with reduced pressure and replaced with ether (10 mL). The large yellow crystals that precipitated as the ether slowly evaporated were washed with hexanes and dried under vacuum (611 mg, 90%). ¹H NMR (C₆D₆): δ 7.602 (s, 18 H), 6.970 (s, 27 H), –4.670 (q, J = 19.0 Hz, 5 H).

Irradiation of Re(PPh₃)₃H₅ with Excess Cyclopentadiene. Re(PPh₃)₃H₅ (5 mg, 0.005 mmol) was placed in an NMR tube under vacuum. THF-d₈ (0.4 mL) was vacuum transferred into the tube followed by cyclopentadiene (5 equiv) and the tube sealed. Irradiation was carried out at 0 °C (maintained by placing the NMR tube in an ice bath) through a 328-nm bandpass filter, and the reaction was followed by ¹H NMR. The only products observable by ¹H NMR after 15-min irradiation and upon precipitation with Et₂O were starting material and (η⁴-C₅H₆)ReH₃(PPh₃)₂ in a molar ratio of 1:9, respectively.

Irradiation of (η⁴-C₅H₆)Re(PPh₃)₂H₃ at 0 °C. (η⁴-C₅H₆)-Re(PPh₃)₂H₃ (5 mg, 0.0064 mmol) was placed in an NMR tube under vacuum where THF-d₈ (0.4 mL) was vacuum transferred into the tube, and the tube was sealed and maintained at LN₂ temperature until the irradiation was begun. During irradiation the tube was maintained at 0 °C in an ice water bath, and irradiation was through a 328-nm band pass filter. A ¹H NMR spectrum showed only resonances for CpRe(PPh₃)H₄ and free PPh₃ after 15 min of irradiation.

A larger scale reaction was conducted by using 300 mg (0.38 mmol) of (η⁴-C₅H₆)Re(PPh₃)₂H₃ in 3 mL of THF. Irradiation for 20 min at 0 °C followed by evaporation of the solvent and recrystallization from toluene at –20 °C gave pure product in 52% isolated yield. Anal. Calcd (Found) for RePC₂₃H₂₄: C, 53.37 (52.74); H, 4.67 (4.54).

Kinetics of Conversion of (η⁴-C₅H₆)Re(PPh₃)₂H₃ to CpRe(PPh₃)₂H₂. Recrystallized (η⁴-C₅H₆)Re(PPh₃)₂H₃ (20 mg, 0.026 mmol) was placed in an NMR tube under vacuum. C₆D₆ (0.4 mL) was vacuum transferred into the tube, and an atmosphere

of N₂ (600 torr to avoid solvent bumping during the experiment) was placed in the tube before it was sealed. ¹H NMR spectra were used to follow the progress of the reaction at 60 °C in the NMR probe by monitoring the disappearance of the (η⁴-C₅H₆)Re-(PPh₃)₂H₃ resonance at δ 3.990 by comparison with a small amount of silicone grease added to the sample.

Kinetics of Decomposition of (η⁴-C₅H₆)Re(PPh₃)₂H₃ in the Presence of Re(PPh₃)₂H₇. (η⁴-C₅H₆)Re(PPh₃)₂H₃ (24 mg, 0.031 mmol) and Re(PPh₃)₂H₇ (2.8 mg, 0.0039 mmol, 0.125 equiv) were placed under vacuum in an NMR tube. THF-d₈ (0.4 mL) was vacuum transferred into the tube, and an atmosphere of N₂ (600 torr) was placed over the frozen solid before the tube was sealed. The tube was thawed and immediately dropped into the NMR probe that was previously equilibrated at 60 °C. ¹H NMR spectra were used to follow the progress of the reaction by monitoring the disappearance of the (η⁴-C₅H₆)Re(PPh₃)₂H₃ resonance at δ 3.990 by comparison with a small amount of silicone grease added to the sample. A separate sample was prepared by using (η⁴-C₅H₆)Re(PPh₃)₂H₃ (10.6 mg, 0.014 mmol) and Re(PPh₃)₂H₇ (9.4 mg, 0.013 mmol, 1.0 equiv) and examined in a similar fashion.

Decomposition of (η⁴-C₅H₆)Re(PPh₃)₂H₃ in the Presence of PPh₃. (η⁴-C₅H₆)Re(PPh₃)₂H₃ (5 mg, 0.0064 mmol) and PPh₃ (4 mg, 0.0152 mmol) were placed under vacuum in an NMR tube. C₆D₆ (0.4 mL) was transferred into the tube, and it was sealed. Upon heating to 60 °C, ¹H NMR resonances were observed for CpRe(PPh₃)₂H₂, Re(PPh₃)₃H₅, and cyclopentene in a 2:1:1 ratio. The presence of cyclopentene was confirmed by gas chromatography.

Reaction of Re(PPh₃)₂H₇ with 2 Equiv of Cyclopentadiene. Re(PPh₃)₂H₇ (5 mg, 0.007 mmol) was placed in an NMR tube under vacuum. C₆D₆ (0.4 mL) and cyclopentadiene (2 equiv) were vacuum transferred into the tube, and the tube was sealed and maintained at –195 °C until the experiment was begun. Upon thawing, the tube was dropped into the NMR probe already being maintained at 60 °C. A spectrum was taken each minute for 15 min by using an automated data collection routine. Integration of the spectra produced the relative product yields indicated in Figure S4.

Reaction of (η⁴-C₅H₆)Re(PPh₃)₂H₃ with PPh₃-d₁₅. (η⁴-C₅H₆)Re(PPh₃)₂H₃ (3 mg, 0.0039 mmol) and PPh₃-d₁₅ (3 mg, 0.0097 mmol) were placed under vacuum in an NMR tube. C₆D₆ (0.4 mL) was vacuum distilled into the tube, and it was sealed. ¹H NMR spectra showed the decomposition of 1 to 2 without the appearance of resonances indicating the presence of free PPh₃.

Preparation and Thermolysis of (η⁴-C₅H₅Me)ReH₃(PPh₃)₂. Re(PPh₃)₂H₇ (150 mg, 0.21 mmol), was placed in a flask into which methylcyclopentadiene (2 mL, 100 equiv) and THF (10 mL) were vacuum distilled. The mixture was stirred at 23 °C for 24 h, the volume reduced to 3 mL, and ether (5 mL) added with stirring. The colorless microcrystalline product (122 mg, 79%) was isolated by filtration, washed with hexane, and dried under vacuum. ¹H NMR spectroscopy indicated the presence of a 20:1 ratio of exo to endo isomers. Anal. Calcd (Found) for ReP₂C₄₂H₄₁: C, 63.54 (63.98); H, 5.20 (5.15).

A mixture of the exo and endo complexes (5 mg, 0.0064 mmol) was sealed in an NMR tube along with 0.4 mL of C₆D₆. The tube was heated to 110 °C for 45 min and an ¹H NMR spectrum recorded, showing two organometallic products (see text). GC analysis of the volatiles above the reaction mixture confirmed the presence of methane by comparison with an authentic sample.

X-ray Structural Determination of CpRe(PPh₃)₂H₂ (2). Colorless crystals of 2 were obtained by evaporation of a benzene solution. A crystal was mounted on a glass fiber and then cooled to –41.5 °C on the diffractometer. A total of 25 reflections with values of χ between 5° and 60° were used to determine a primitive monoclinic unit cell with crystal parameters as shown in Table I. Systematic absences showed the presence of only an n-glide plane, consistent with either space group Pn or P2/n. Collection of a quadrant of 2888 unique data with F₀ > 3σ from 4 < 2θ < 47° followed by a Patterson map solution of the structure in acentric space group Pn revealed the structure for 1 shown in Figure 5. The location of the rhenium in a nonspecial position confirms the selection of Pn as the space group. A benzene solvent molecule of crystallization was located on a difference Fourier map. Following placement of the hydrogen atoms on the aromatic groups and Cp ring in idealized locations, anisotropic refinement

of all non-hydrogen atoms with data $>3\sigma$ converged with $R = 0.0298$ and $R_w = 0.0475$. Interchanging enantiomers in this noncentric space group improved refinement indices by $\sim1\%$, rendering the latter enantiomer a more reasonable choice. A difference Fourier map now showed two peaks near the rhenium atom in positions expected for the two trans hydride atoms. Final refinement was carried out by varying all non-hydrogen atoms anisotropically and the hydride ligands isotropically while holding hydrogens attached to carbon fixed with thermal parameters of 5.0 Å^2. Table III lists final parameters.

X-ray Structural Determination of CpRe(PPh$_3$)H$_4$ (3). Colorless crystals of CpRe(PPh$_3$)H$_4$ were obtained by evaporation of a Et$_2$O solution. A crystal was mounted on a glass fiber and 25 reflections with values of χ between 5° and 60° were used to determine a triclinic unit cell. Crystal parameters are shown in Table I and are consistent with either space group $P1$ or $P\bar{1}$. Collection of a hemisphere of 3390 unique data with $F_o > 3\sigma$ from $4 < 2\theta < 50°$ was followed by the successful Patterson map solution of the structure in centric space group $P\bar{1}$. Hydrogen atoms on the phenyl groups and Cp ring were placed in idealized locations

and their positions and thermal parameters refined along with those of the non-hydrogen atoms. A difference Fourier map now revealed four peaks within bonding position to the metal center corresponding to the expected locations of the hydride ligands. Final refinement of the positions of all atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and the isotropic thermal parameters of the hydrogen atoms revealed the structure shown in Figure 6. Table IV lists final parameters.

Supplementary Material Available: Figures S1–S4, NMR spectra of 1, and tables of data collection parameters, hydrogen positional parameters, thermal parameters, least-squares planes, and bond angles and distances (26 pages); tables of structure factors (61 pages). Ordering information is given on any current masthead page.

N–N Double Bond Cleavage and the Ortho Metalation of Azoarenes Using Ru$_3$(NPh)(CO)$_{10}$

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The reaction of Ru$_3$(NAr)(CO)$_{10}$ with azoarenes under CO results in the cleavage of the N–N double bond to yield Ru$_3$(NAr)$_2$(CO)$_9$ and ArNCO. In the absence of CO the insertion into one of the C–H bonds ortho to the azo functional group also occurs. The product distribution is sensitive to the para substituent on the azobenzene, with electron-withdrawing groups favoring N=N bond cleavage, while ortho metalation is favored with electron-donating groups. A single-crystal X-ray crystallographic study of one of the clusters containing an ortho-metalated azoarene, HRu$_3$(NPh)(CH$_3$OC$_6$H$_3$NNC$_6$H$_4$OCH$_3$)(CO)$_8$ [$P\bar{1}$ space group, $a = 9.237$ (4) Å, $b = 10.917$ (6) Å, $c = 17.199$ (6) Å, $\alpha = 100.47$ (3)°, $\beta = 99.80$ (3)°, $\gamma = 90.59$ (4)°, $Z = 2$], revealed a closed trinuclear cluster containing a triply bridging NPh, a semibridging carbonyl, an ortho-metalated azoarene, and a bridging hydride trans to the carbon of the ortho-metalated ring. Spectroscopic methods indicate the cluster interconverts in solution at room temperature among three isomers. Reaction of HRu$_3$(NPh)(CH$_3$OC$_6$H$_3$NNC$_6$H$_4$OCH$_3$)(CO)$_8$ with carbon monoxide leads to N–N double bond cleavage, while the reaction with excess azoarene yields a new cluster containing two ortho-metalated azoarenes. The analogous reaction of Ru$_3$(NPh)(CO)$_{10}$ with *N*-phenylbenzaldimine was also examined and found to give only the product resulting from ortho metalation of the phenyl ring.

Introduction

The reaction of azoarenes with metal complexes has been extensively studied.[1] One of the most common avenues of reaction involves metalation of one of the C–H bonds ortho to the azo functional group. Recently, the symmetric cleavage of the N–N double bond has also been reported with complexes of some of the early transition metals.[2–4] More complex rearrangements involving both of the above processes along with the additional formation of a C–N bond are known[5–10] and have resulted in com-

plexes containing the *N*-phenyl-*o*-phenylenediamine ligand (eq 1). In one recent study,[11] this rearrangement was found in a useful ruthenium carbonyl catalyzed reaction (eq 2).

Fe$_3$(CO)$_{12}$ + ArNNAr $\longrightarrow$ (1)

+ Bu$^n_3$N $\longrightarrow$ (2)
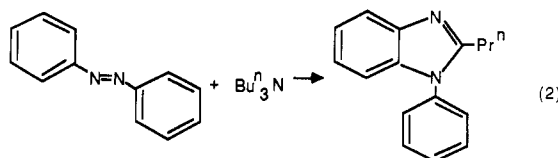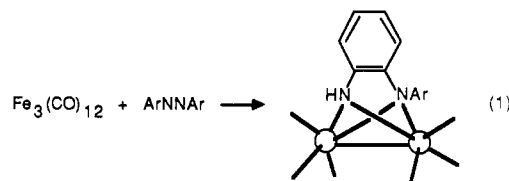
We report here the results of our study on the reaction of Ru$_3$(NPh)(CO)$_{10}$ with azoarenes. The nature of the products is sensitive to reaction conditions as well as to the substituents on the azoarene. Under certain conditions, new trinuclear clusters containing ortho-metalated

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