has been reported, for example, in the oxidation of acetyl-substituted ferrocene, even though that oxidation involves an orbital which is mainly metal centered.[65] Substituent effects on $E°$ potentials may be a deceptive indicator of relative metal–ligand contributions to the redox orbital.[66]

Finally, a comparison may be made with the isoelectronic and isocharged complexes (η^6-arene)Cr(CO)$_3$. The latter reduce to dianions in a two-electron step which is chemically reversible if the arene is naphthalene. It is probable that the extra electrons in the chromium arene dianions are accommodated in an orbital mostly metal in character, and that the arene distorts to the tetrahapto form in the dianion to relieve the electronic strain on the metal.[67,68] It has been postulated that the arene distortion occurs after uptake of the first electron to give an intermediate which is actually electron deficient (17 e^- at the metal), leading directly to facile uptake of a second electron to give a 18 e^- metal in the dianion. Our nitrosyl analogue appears to avoid the necessity for a similar multielectron reduction by accommodating the extra electron in a predominantly nitrosyl-based orbital. There is a concomitant change in the M–N–O angle, but not necessarily in the mode of metal–polyolefin bonding (i.e., the M–Cp bond). Thus, the consequences to bonding of the metal–polyolefin unit are affected by the conceptual substitution of NO for CO, and they reflect the fact that the nitrosyl group is an effective "electron sink" in organometallic redox processes.

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Registry No. 1, 36312-04-6; **2**, 64539-47-5; **3**, 12128-13-1; CpCr(CO)$_2$NO^{-}·, 92366-16-0; CpMo(CO)$_2$NO^{-}·, 92396-57-1.

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Mechanistic Features of C–H Activation by ReH$_7$[P(C$_6$H$_{11}$)$_3$]$_2$

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Abstract: The synthesis and characterization of ReH$_7$(PCy$_3$)$_2$ (Cy = cyclohexyl) is reported. This compound is thermally resistant to the dimerization reaction exhibited by other ReH$_7$(PR$_3$)$_2$ compounds, which allows mechanistic features of C–H activation to be studied. Thus, in the temperature range 60–80 °C, ReH$_7$(PCy$_3$)$_2$ exchanges hydrogen with deuteriobenzene. Deuterium is incorporated into the complex not only as hydride ligands but also selectively at the C2 and C3 carbons of all cyclohexyl rings. Only one of the two methylene hydrogens at each of these carbons is exchangeable. It is also shown that exchange at the two adjacent carbons does *not* proceed by concerted dehydrogenation via a cyclohexenyl intermediate; the rate of deuterium incorporation at C3 differs from that at C2. On the basis of observation of exchange with D$_2$, and also kinetic studies of the reaction of ReH$_7$(PCy$_3$)$_2$ with phosphine and olefinic nucleophiles, all of the thermal reactions observed here are concluded to arise from the reductive elimination transient ReH$_5$(PCy$_3$)$_2$.

The majority of neutral phosphine polyhydride complexes (MH$_x$(PR$_3$)$_y$, $x \geq 3$) of the second and third transition series metals are coordinatively saturated and relatively unreactive. We have reported that photolysis of several coordinatively saturated (18 electron) transition-metal polyhydride phosphine complexes leads (by H$_2$ or phosphine photodissociation) to transients of high reactivity toward olefins, CO, Lewis bases, and even saturated hydrocarbons.[1-3] It is our objective to broaden the utility of polyhydride complexes by making them susceptible to thermal activation (cf. OsH$_4$(PMe$_2$Ph)$_3$,[3] which may be quantitatively recovered after 24 h at 100 °C).

The approach described here has been to incorporate a particularly bulky phosphine ligand into the complex in order to promote (phosphine?) ligand dissociation or perhaps even the isolation of a 16-electron complex. Our flash photolysis study[4] of ReH$_5$(PMe$_2$Ph)$_2$, which is the reactive transient in our photochemistry derived from ReH$_5$(PMe$_2$Ph)$_3$, gave evidence for undesirable stabilization of this phototransient by an aryl ring attached to the phosphine ligand. Additionally, in another case we have isolated a product of aryl ring orthometalation.[2] Consequently, we decided to avoid aryl phosphines altogether. We report here on results using tricyclohexyl phosphine which confirm a thermal route to ligand dissociation and permit rather detailed examination of the reactivity of the resulting 16-electron transient. Intramolecular attack on aliphatic C–H bonds has been observed to occur via a 16-electron Re(V) complex.

Experimental Section

General. All manipulations were carried out under N$_2$ with use of standard Schlenk and glove box techniques. Benzene, toluene, cyclohexane, and THF were vacuum transferred from sodium benzophenone

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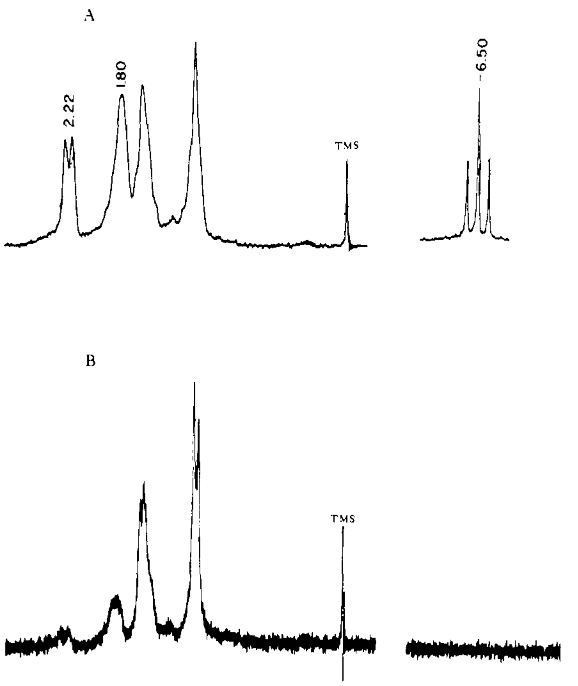

Figure 1. (A) ^{1}H NMR spectrum (220 MHz) of $ReH_7(PCy_3)_2$ in C_6D_6. Chemical shifts (δ) are noted. (B) ^{1}H NMR spectrum (220 MHz) of $ReH_7(PCy_3)_2$ after 14 h at 60 °C in C_6D_6.

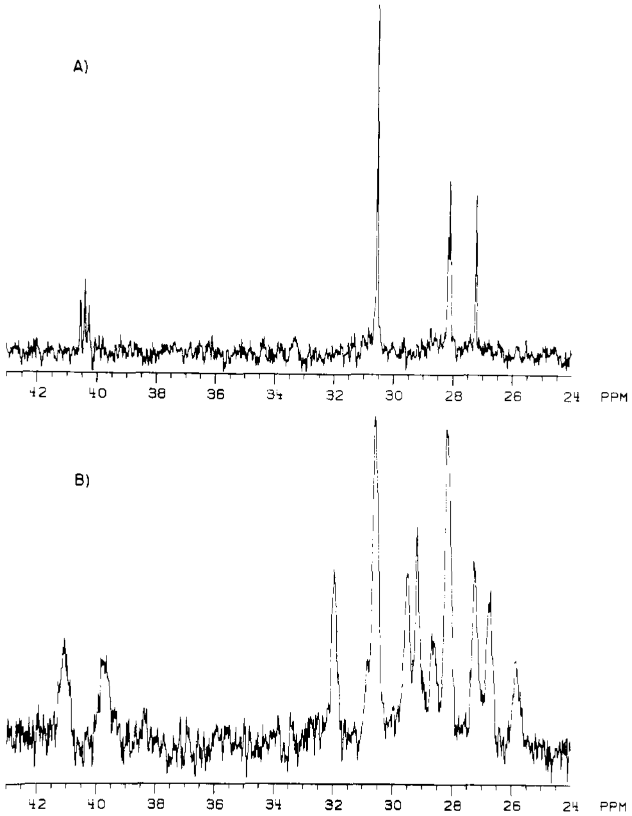

Figure 2. (A) The $^{13}C\{^1H\}$ spectrum of $ReH_7(PCy_3)_2$ before hydrogen/deuterium exchange. (B) Same sample, but proton coupled.

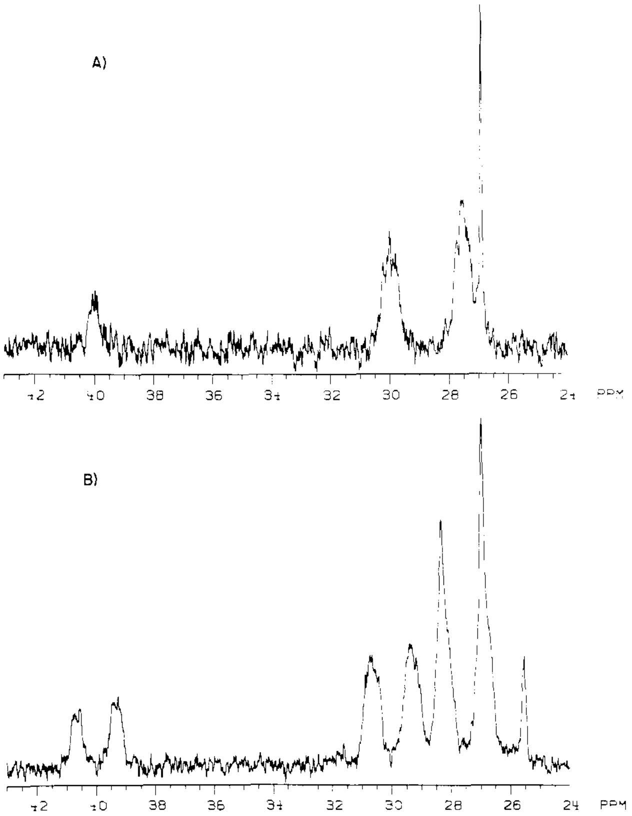

Figure 3. (A) The $^{13}C\{^1H\}$ spectrum of $ReH_7(PCy_3)_2$ after hydrogen/deuterium exchange for 1 h at 80 °C in C_6D_6. (B) Same sample, but proton coupled.

ketyl. Tricyclohexylphosphine (very air sensitive) was supplied by Pressure Chemical Co. ^{1}H NMR spectra were recorded at 220 MHz (Varian HR-220), ^{2}D NMR spectra at 55.4 MHz and ^{13}C NMR spectra at 90.8 MHz (both on a Nicolet NT-360), and ^{31}P NMR spectra at 40.5 MHz (Varian XL-100). Chemical shifts downfield of the reference are uniformly recorded as positive.

$ReOCl_3(PCy_3)_2$. $ReOCl_3(PPh_3)_2$[5] (1.9 g; 2.3 mmol) was slurried in 200 mL of benzene. Excess PCy_3 (2.9 g; 10 mmol) was added via an addition tube. The yellow slurry gives a clear green solution in 10–20 min. Stirring was continued for 1 h until a green slurry appeared. The solvent was removed under vacuum and the green solid residue was extracted with 5 × 20 mL portions of diethyl ether to give a green solution (containing $OPPh_3$ and PPh_3) and a yellow powder ($ReOCl_3(PCy_3)_2$). The yield of product is quantitative (2.0 g; 2.3 mmol). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -27.0. IR (KBr): $\nu_{Re=O}$ 969 cm^{-1}; ν_{CH} 2850, 2930 cm^{-1}. Anal. Calcd: C, 49.73; H, 7.60; Cl, 12.26. Found: C, 49.02; H, 7.70, Cl, 12.73. This material was used without recrystallization to prepare $ReH_7(PCy_3)_2$.

$ReH_7(PCy_3)_2$. $ReOCl_3(PCy_3)_2$ (1.5 g; 1.7 mmol) and $NaBH_4$ (1.8 g; 48 mmol) were added to 100 mL of absolute ethanol and the mixture stirred for 20 h at room temperature. After removal of the ethanol under vacuum, the residue was extracted with 4 × 20 mL benzene. The benzene was removed under vacuum and the residue washed with absolute ethanol, giving a beige product in 70% yield. This material could normally be used without further purification, although purified material was used in the kinetic studies. Further purification to a white powder could be achieved by two or three recrystallizations from benzene/hexane. Anal. Calcd for $C_{36}H_{73}P_2Re$: C, 57.36; H, 9.69. Found: C, 57.56; H, 9.64. NMR (in C_6D_6): $^{31}P\{^1H\}$ δ 47.2 (s); ^{1}H δ 2.22 (d, J = 13 Hz, 12 H), 1.80 (18 H), 1.64 (18 H), 1.20 (18 H), (all CH), -6.50 (t, J_{P-H} = 20 Hz); ^{13}C δ 40.4 (d of t, P–C spacing = 13 Hz, J_{C-H} = 127, 1 C), 30.5 (t, J_{C-H} = 127, 2 C), 28.1 (t of t, P–C spacing = 5 Hz, J_{C-H} = 126, 2 C), 27.2 (t, J_{C-H} = 129, 1 C). See Figure 2. Infrared Spectrum (KBr): ν_{Re-H} 1970 (w br), 1935 (sh), 1915 cm^{-1} (s).

Deuteration Studies. (a) With C_6D_6. A sample of $ReH_7(PCy_3)_2$ was dissolved in C_6D_6 and sealed in an NMR tube. After the mixture was heated at 80 °C for 1 h, the following spectral observations were recorded. $^{31}P\{^1H\}$ NMR: δ 47.0 (br due to coupling to ^{2}D). ^{1}H NMR (Figure 1): δ 1.20, 1.64, 1.80 (w); the δ 2.22 doublet and the Re–H resonance are not detectable. The persistence of some (reduced) intensity at δ 1.80 is due to the fact that this resonance is comprised of 18 hydrogens (2 unresolved chemical shifts), 12 of which exchange and 6 of which do not. These two chemical shifts are separated by 0.05 ppm at 360 MHz. ^{13}C NMR: δ 40.6 (d of t), 30.5 (br d), 28.1 (br d), 27.2 (t); see Figure 3.

The sequential nature of deuterium incorporation at the two carbon sites was established by heating $ReH_7(PCy_3)_2$ in 25 mL of C_6D_6 at 60

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°C. Samples were withdrawn every 2 h over a 12-h period. Each was stripped of C_6D_6 and dissolved in C_6H_6 for recording of the ^2D NMR spectrum. Aliphatic resonances (in addition to Re–D at δ −6.4) grew in at δ 1.80 and 2.22, the former (D on C3) growing more rapidly during the first 6 h.

(b) With D_2. Approximately 5 mL of a saturated cyclohexane solution of $ReH_7(PCy_3)_2$ was placed in a 1-L flask equipped with a Teflon valve. The solution was freeze–thaw degassed and the flask finally charged with 1 atm of D_2. The flask was heated in an oil bath at 55 °C for 13 h. At the end of this time, the solvent was stripped and benzene was added. The ^2D NMR of this sample showed resonances at δ 1.8 and −6.4 relative amplitude (1:10); no deuterons are detectable at δ 2.2. This C_6H_6 solution was next heated in the sealed NMR tube at 80 °C for 1 h. ^2D NMR: δ 2.2 and 1.8, with only a very weak residual peak at δ −6.4. This ^2D spectrum is weak due to dilution of the isotope by C_6H_6.

Kinetics of Phosphine Substitution. Samples for kinetic runs were prepared in a glove box by dissolving appropriate quantities of $ReH_7(PCy_3)_2$ and nucleophile (L) in toluene and transferring to NMR tubes, which were subsequently sealed under vacuum. For each L, a series of runs was carried out with $[ReH_7(PCy_3)_2]$ held constant near 5×10^{-2} M with concentrations of L varied in pseudo-first-order ($\geq$10-fold) excess.

The reactions were monitored by ^{31}P NMR. Good kinetic data could be obtained by following either decay of the $ReH_7(PCy_3)_2$ singlet (47.7 ppm at 67 °C) or growth of the doublet for PCy_3 in the product $ReH_5(PCy_3)_2L$. In a typical run, the sample was inserted into the preheated and equilibrated NMR probe (66.8 ± 0.2 °C), and the first spectrum was begun after allowing 5 min for thermal equilibration. The sample was left in the probe without changing spectrometer settings throughout the reaction, a period of about 3 h ($t_{1/2} \geq 60$ min). For each spectrum, the time for data acquisition (100 scans) was 6 min. Although this introduces some imprecision in individual points, the effect on precision of rate constants (the slope of a plot of these points) is minimized by taking the time at a consistent point in the acquisition period for each spectrum (at the beginning) and by keeping the period between spectra as along as possible.

No decomposition products, intermediates, or evidence of secondary reactions were detected in the NMR at any time during the reactions. In addition, the total integrated intensity (I_T) of PCy_3 signals (i.e., $ReH_7(PCy_3)_2$ singlet + $ReH_5(PCy_3)_2L$ doublet) varied less than ±10% (randomly) during the time that data were taken.

The reactions displayed good first-order behavior over 3 half-lives. Rate constants (k_{obsd}) were obtained as least-squares slopes of plots of both $\ln(I_s)$ vs. t (I_s = integrated intensity of $ReH_7(PCy_3)_2$ singlet) and $\ln(I_T - I_D)$ vs. t (I_D = integrated intensity of $ReH_5(PCy_3)_2L$ doublet and I_T = integrated intensity of product doublet at infinite time). In a given run, the values of k_{obsd} obtained by following reactant disappearance and product formation agreed to well within experimental error (±10%).

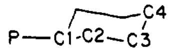
The $^{31}P\{^1H\}$ NMR spectra (67 °C, toluene) of the $ReH_5(PCy_3)_2P'$ products show the expected AB_2 patterns ($P' = PEt_2Ph$): δ 42.2 (d), 5.0 (t, $J_{PP'} = 11.3$ Hz); ($P' = PPh_3$) δ 38.0 (d), 32.0 (t, $J_{PP'} = 10.5$ Hz). The ^{31}P resonance of $ReH_5(PCy_3)_3$ at δ 32.88 shows sextet structure when selectively coupled to hydride hydrogens. The ^1H NMR hydride chemical shift of $ReH_5(PCy_3)_3$ is a quartet ($J_{P-H} = 20$ Hz) at δ −8.1 in C_6D_6.

Results

Reaction of $ReOCl_3(PPh_3)_2$, as a slurry in benzene, with two or more equivalents of PCy_3 yields $ReOCl_3(PCy_3)_2$. There is no evidence for reduction of Re(V), or of coordination of more than two tricyclohexylphosphines. Treatment of $ReOCl_3(PCy_3)_2$ with excess $NaBH_4$ in ethanol at 25 °C gives $ReH_7(PCy_3)_2$. The ^1H NMR shows a triplet for the hydride hydrogens, consistent with the bis-phosphine stoichiometry. The ^{31}P NMR, selectively coupled to the hydride hydrogens, shows six of the expected eight lines. The observed intensities of these (1:3:6:6:3:1) are in better agreement with the ReH_7 stoichiometry ($^1/_7$:1:3:5:5:3:1:$^1/_7$) than with ReH_5 (1:5:10:10:5:1). In addition, integration of cyclohexyl against hydride resonances gives a ratio of 64:7, compared to 66:7 calculated for $ReH_7(PCy_3)_2$.

The compounds ReH_7P_2 (P = PMe_2Ph, PEt_2Ph, $PMePh_2$, and PPh_3) are all converted to $Re_2H_8P_4$ on heating in solution.[6,7] This conversion is easier for $PMePh_2$ and PPh_3 than for the smaller phosphines. In marked contrast, $ReH_7(PCy_3)_2$ shows no change (^1H and ^{31}P NMR) after heating at 80 °C for 2 h in benzene. Moreover, the 360-MHz ^1H NMR spectrum shows no change of pattern or intensity after heating $ReH_7(PCy_3)_2$ for 22 h at 120 °C in cyclohexane-d_{12}; H/D exchange with perdeuterocyclohexane does not occur.

Moderate temperatures (60–80 °C) are sufficient to cause H/D exchange between $ReH_7(PCy_3)_2$ and C_6D_6 solvent. Thus, heating a sealed tube of $ReH_7(PCy_3)_2$ in C_6D_6 for 1 h at 80 °C causes disappearance of the hydride triplet in the ^1H NMR spectrum, concurrent with an increase in the $C_6(H,D)_6$ resonance. Such thermal exchange has been detected for other high valent metal hydrides.[8,9] In addition, however, a dramatic decrease in the intensities of certain of the cyclohexyl resonances also takes place (Figure 1), indicating selective ring deuteration. The 12-proton δ 2.22 doublet (due to coupling to phosphorus) undergoes complete deuteration, while the 18-proton resonance at δ 1.80 experiences partial decay. The (undeuterated) hydrogens at δ 1.8 are attached to a different carbon than those which exchange (see Experimental Section). The doublet structure at δ 2.2 marks this as hydrogen on C2, since the three-bond J_{P-H} is generally the largest along any aliphatic carbon chain.[10] Location and quantitation of the sites of deuteration are best accomplished by ^{13}C NMR spectroscopy.



The room-temperature natural-abundance $^{13}C\{^1H\}$ NMR spectrum of isotopically normal $ReH_7(PCy_3)_2$ shows four resonances: two of unit intensity, one a singlet (C4) and one a virtual triplet (C1, line spacing = 13 Hz), and two of double intensity, one a singlet (C2) and one a virtual triplet (C3, line spacing = 5 Hz), Figure 2. The assignment of C3 rather than C2 to the virtual triplet follows from the observation,[11,12] in related alkyl phosphine complexes, that $^3J_{P-C}$ is greater than $^2J_{PC}$. Proton coupling of the ^{13}C NMR doubles the lines assigned to C1 and converts those assigned to C2, C3, and C4 to apparent triplets.

A sample of $ReH_7(PCy_3)_2$ which had been heated for 1 h at 80 °C in C_6D_6 (Figure 3) exhibits a $^{13}C\{^1H\}$ NMR spectrum with a sharp singlet for C4, a virtual triplet for C1, but broad (full width at half height = 55 Hz) and unresolved resonances for C2 and C3. This broadening indicates selective deuteration at C2 and C3. The number of deuteria incorporated is established by the proton-*coupled* ^{13}C NMR spectrum: the C2 and C3 resonances are each split into doublets (line spacing ~125 Hz), characteristic of one attached hydrogen. The C1 resonance becomes a doublet and the C4 resonance a triplet, consistent with no detueration at either site. There is no evidence for undeuterated (i.e., CH_2) groups at C2 or C3, indicating that detueration has gone to completion under these conditions. Thus, monodeuteration is the limiting situation at C2 and C3.

In view of the fact that monodeuteration takes place at two adjacent sites in the cyclohexyl rings, we sought to establish whether or not exchange at C2 and C3 was a simultaneous process (via a cyclohexenylphosphine A). The alternative, exchange at C2 and C3 by two independent events, would be governed by distinct activation energies for the two processes. By monitoring the ^2D NMR in the aliphatic region during the course of H/D exchange between C_6D_6 and $ReH_7[P(C_6H_{11})_3]_2$ at 60 °C, it is possible to establish the reaction profile at low conversion. Such studies show distinctly faster exchange at C3 than at C2, pre-

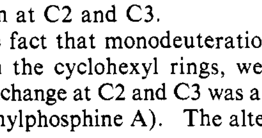


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Table I. Observed Rate Constants for Reaction of $ReH_7(PCy_3)_2$ with Nucleophiles at 66.8 °C in Toluene

L	[L], mol/L	10^3k_{obsd},[a] min^{-1}
PEt_2Ph	0.634	11.62 ± 0.44
	1.19	11.56 ± 0.36
PPh_3	0.543	8.06 ± 0.21
	0.968	9.09 ± 0.22
	1.50	10.24 ± 0.34
PCy_3	0.588	~5[b]
$C_{12}H_8$, *C*	0.517	9.11 ± 0.37
	0.998	11.43 ± 0.48
	1.83	11.25 ± 0.11
$C_{12}H_{10}$, *E*	1.03	c
$C_{10}H_8$, *D*	1.15	c

[a] ±1 standard deviation. [b] Reaction comes to equilibrium at ~15% conversion to $ReH_5(PCy_3)_3$; k_{obsd} ~ 60% that of PPh_3, as estimated by comparing initial rates at similar concentrations. [c] Acenaphthene and naphthalene are totally unreactive after 10.5 h (>10 half-lives for the $C_{12}H_8$ reaction).

cluding a mechanism involving net dehydrogenation of the cyclohexyl ring.

We have performed several studies directed at establishing the identity of the species responsible (i.e., the mechanism), for the isotopic exchange with benzene and with pendant cyclohexyl rings. *If* the reaction begins with a reversible reductive elimination of dihydrogen (eq 1), exchange with D_2 is predicted under the same

$$ReH_7(PCy_3)_2 \rightleftharpoons \underset{B}{ReH_5(PCy_3)_2} + H_2 \qquad (1)$$

thermal conditions as H/D exchange with C–H bonds. In fact, heating $ReH_7(PCy_3)_2$ at 60 °C for 10 h in cyclohexane under an excess of D_2 at 1 atm effects (^2D NMR) deuteration at the hydridic site and also, to a lesser extent, at the aliphatic chemical shift of the hydrogen on C3. With this sample in hand, it is possible to confirm transfer of deuterium from rhenium to cyclohexyl carbon in the absence of D_2 or C_6D_6. Thus, removal of D_2 from the above sample, followed by heating at 80 °C for 1 h, causes migration (^2D NMR) of deuterium to the cyclohexyl rings. In this instance (i.e., higher temperature), deuterium is now seen at both the δ 1.8 and 2.2 sites (C2 and C3). This series of experiments represents additional confirmation that deuterium is incorporated at C2 and C3 with different rates. The driving force for non-statistical transfer of deuterium from rhenium to carbon is the preference for the heavier isotope in the site of higher vibrational frequency (C–H).

Kinetic methods have also been used to probe eq 1 and the reactivity of the transient $ReH_5(PCy_3)_2$ (B) to nucleophilic attack. It was found that phosphines (P′) react cleanly with $ReH_7(PCy_3)_2$ at 60–80 °C in toluene to give $ReH_5(PCy_3)_2(P')$. Application of the steady-state approximation to transient B in Scheme I yields the following rate equation:

$$\frac{-d[ReH_7(PCy_3)_2]}{dt} = \frac{k_1k_2[P'][ReH_7(PCy_3)_2]}{k_{-1}[H_2] + k_2[P']} \qquad (2)$$

Scheme I

$$ReH_7(PCy_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{B}{ReH_5(PCy_3)_2} + H_2$$

$$B + P' \xrightarrow{k_2} ReH_5(PCy_3)_2(P')$$

With P′ present in large excess, this mechanism predicts a rate law first order in $ReH_7(PCy_3)_2$ with observed pseudo-first-order rate constants (k_{obsd}) approaching a limiting value (k_1) as [P′] increases (i.e., H_2 elimination becomes rate determining as $k_2[P']$ becomes greater than $k_{-1}[H_2]$). Because the initial $[ReH_7(PCy_3)_2]$ in each run is considerably greater than the molar solubility of H_2 under these conditions, the solution becomes saturated with H_2 early in the run; thus first-order behavior is expected even when $k_2[P'] \lesssim k_{-1}[H_2]$, since the $[H_2]$ term in the k_{obsd} expression remains invariant during the portion of the run where data are collected.

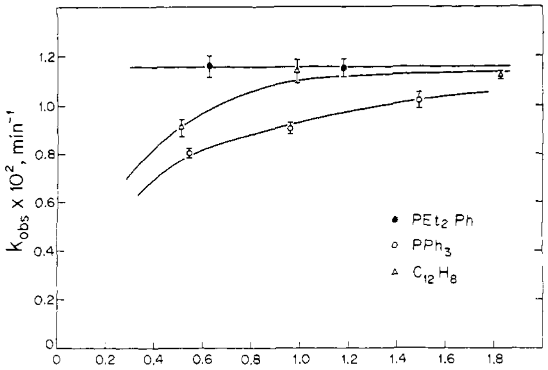
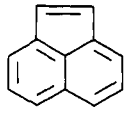
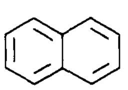


Figure 4. Plot of k_{obsd} vs. concentration of nucleophile, L, for reaction of L with $ReH_7(PCy_3)_2$ at 66.8 °C in toluene.

Good first-order kinetics are observed over at least 3 half-lives. Values of k_{obsd} for reaction with the various nucleophiles are summarized in Table I. The dependence of k_{obsd} on concentration (Figure 4) is clearly consistent with the mechanism in Scheme I. PEt_2Ph reacts at the limiting rate (i.e., $k_1 = k_{obsd} = 1.16 \times 10^{-2}$ min^{-1} at 66.8 °C) throughout the concentration range studied. On the other hand, the less basic and bulkier PPh_3 reacts at less than the limiting rate in the same concentration range, although its approach to a limiting value is evident in Figure 4. (Further increases in $[PPh_3]$ were prohibited by limited solubility.) The limiting values of k_{obsd} (i.e., k_1 in eq 2) for PPh_3 as nucleophile can be obtained from the intercept ($^1/k_1$) of a plot of k_{obsd}^{-1} vs. $[PPh_3]^{-1}$; a least-squares fit of the points gives the intercept 85.1 ± 2.8 and $k_1 = (1.18 \pm 0.04) \times 10^{-2}$ min^{-1}. The effect of steric bulk is further indicated by the behavior of PCy_3, which reacts more slowly than PPh_3 and comes to equilibrium with only ca. 15% conversion to $ReH_5(PCy_3)_3$; the initial rate is estimated to be 60% that of PPh_3 at similar concentrations.

In order to broaden the above study of the reactivity of $ReH_5(PCy_3)_2$, scavenging was attemped with the olefinic hydrocarbons acenaphthalene ($C_{12}H_8$, C), naphthalene (D), and acenaphthene ($C_{12}H_{10}$, E). As seen in Table I and Figure 4, the


C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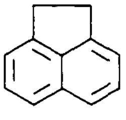
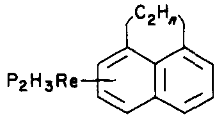
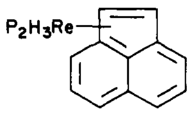

E

kinetic behavior of acenaphthalene is similar to that of the phosphine nucleophiles, approaching the limiting rate somewhat more readily than does PPh_3 in the same concentration range. In the context of Scheme I, this places $C_{12}H_8$ between PPh_3 and PEt_2Ph in ability to compete for transient B. It is significant that $C_{12}H_8$ achieves (within experimental error) the same limiting rate as do PPh_3 and PEt_2Ph, as is required by the proposed mechanism. In contrast, both naphthalene (1.15 M) and acenaphthene (1.03 M) effect no net reaction with the transient $ReH_5(PCy_3)_2$ over 10.5 h at 66.8 °C (more than 10 half-lives for the $C_{12}H_8$ reaction).

The ultimate product of the thermal reaction of $ReH_7(PCy_3)_2$ with acenaphthalene is quite different from that found with phosphine reagents. The compound is a bis-phosphine species (an AB pattern in the $^{31}P\{^1H\}$ NMR), with three hydride ligands (three hydride chemical shifts). This loss of additional hydride ligands over that found in the phosphine reactions can be traced to the capacity of the olefinic bond between *peri* carbons to accept hydrogen. Thus, a coproduct in this reaction is observed to be the hydrogenated hydrocarbon acenaphthene. The ligand complement ReH_3P_2 lacks 4 electrons from an 18-electron configuration, suggesting that a C_{12} hydrocarbon must function as a η^4 ligand in the product. Several modes of binding of C_{12} hydrocarbons (e.g., F, G) are consistent with the low symmetry implicit in the ^{31}P and hydride ^1H NMR spectra. We will report separately on the molecular structure of this material.



F, *n* = 2 or 4



G

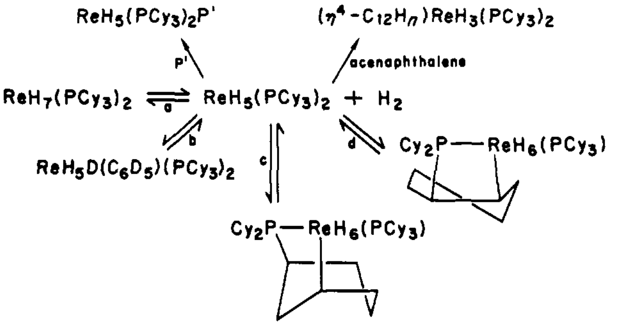
Discussion

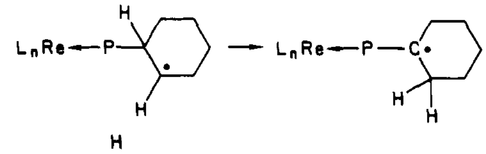
The fluxional complex $ReH_7(PCy_3)_2$ undergoes thermal loss of H_2 at temperatures as low as 60 °C. This reductive elimination (eq 1) has been detected by exchange with dissolved D_2 and by trapping the transient $ReH_5(PCy_3)_2$ not only with phosphines of varying basicity and steric requirements but also with the olefin acenaphthalene. The lack of any net transformation, at this same temperature, with either acenaphthene or naphthalene strongly suggests that it is the double bond between the two *peri* positions which initially coordinates to ReH_5P_2. The fact that the rate of disappearance of ReH_7P_2 and the rate of appearance of product show the same limiting rate constant (at high concentration of trapping reagent) for a diverse array of reagents strongly supports a single mechanism up to the rate-determining step. The observed reduction of k_{obsd} below the limiting values gives direct evidence that H_2 loss is reversible.

In the same temperature range (60–80 °C), it is possible to demonstrate isotopic exchange of benzene-d_6 with the Re–H bonds of $ReH_7(PCy_3)_2$. At such temperatures, certain of the cyclohexyl hydrogens also exchange with Re–D. The isotopic exchange with the C(sp^3)–H bonds occurs only at the C2 and C3 cyclohexyl carbons, and for only one of the two hydrogens on each such carbon. This regiochemistry is diagnostic of an intramolecular mechanism. It is also found that the rate of isotopic exchange is different at these two carbon sites, thus ruling out a mechanism with concerted dehydrogenation to a cyclohexenyl intermediate. The lack of *net* reaction with the arenes benzene, naphthalene, and acenaphthene precludes conventional kinetic determination of whether these olefins form metastable adducts with $ReH_5(PCy_3)_2$, but we suggest that they do, and that these are involved in the Re–H/C_6D_6 exchange. We likewise suggest that $ReH_5(PCy_3)_2$, with the input of a small additional increment of thermal activation, undergoes intramolecular oxidative addition of cyclohexyl C–H bonds to effect the observed isotopic exchange at these sites. These ideas are detailed in Scheme II, in which equilibrium a accounts for exchange with dissolved D_2. In principle, isotopic exchange of ReH units with D_2 could proceed by direct attack of D_2 on either $ReH_7(PCy_3)_2$ or ReH_7PCy_3 (formed in a hypothetical phosphine-dissociation equilibrium). While each is a d^0 species, attack of H_2 on d^0 metal centers has its precedents.[13] However, the phosphine substitution kinetic studies presented here provide direct evidence for eq a as the step preceding such substitution, and thus make the d^2 species $ReH_5(PCy_3)_2$ an established transient. Note in particular that the kinetic evidence for a saturation effect (i.e., the $k_{-1}[H_2]$ term in eq 2) identifies H_2 loss as the pre-equilibrium process. The clean formation of $ReH_5(PCy_3)_2P'$, unaccompanied by any $ReH_7(PCy_3)P'$, convincingly precludes any accompanying phosphine-loss equilibrium (forming ReH_7PCy_3).

With $ReH_5(PCy_3)_2$ established as the transient formed at 60 °C, oxidative addition of C–H bonds to this species will effect the other observed isotopic exchanges. Exchange with deuterobenzene follows readily (eq b). Exchange with pendant cyclohexyl rings follows from an internal "metallation" (oxidative addition) mechanism. The relative rates at the C2 and C3 positions rule out concerted ring dehydrogenation. The observed relative rates, C3 faster than C2, are consistent with a lower activation energy to form a five-membered ring ($\overline{\mathrm{RePC(H)CH_2CH}}$...), eq c, than to form a four-membered ring ($\overline{\mathrm{RePCHCH}}$...), eq d. Part of the activation energy for these metallations is the energy of conversion from P equatorial on the cyclohexyl ring to P axial. The single exchange at each C2 and C3 site follows from the fact that any substituent (i.e., P) immediately destroys the equivalence of the two faces of a cyclohexyl ring (rapid boat/chair interconversion and rapid rotation about P–C and Re–P bonds notwithstanding). While we have been unable to establish the relative stereochemistry of the adjacent deuteria introduced due to the complexity of the aliphatic region in the ^{1}H and ^{2}D NMR spectra, the expectation of cis-ring fusion in the bicyclo compound involving the four-membered ring ($\overline{\mathrm{RePCHCH}}$...) leads to the prediction of cis-vicinal dideuteration which is also cis to the phosphorus substituent. The observed regiospecificity rules out a radical mechanism proceeding through H, since this should rapidly rearrange (eq 3)

Scheme II





(3)

to the more stable radical which would lead to deuteration at C1 and, more importantly, would render equivalent both faces of the cyclohexyl ring, thereby opening a route for production of CD_2 groups.

The ability to detect experimentally the occurrence of distinct rates of deuteration at C2 and C3 clearly establishes processes c and d of Scheme II as requiring further activation energy above that required to reach $ReH_5(PCy_3)_2$. It is noteworthy that we find unequivocal evidence for intramolecular activation at cyclohexyl C2 and C3 by independent activated processes in unsaturated $ReH_5(PCy_3)_2$. Work of the groups of Vrieze[14] and of Robinson and James[15] has permitted isolation of rhodium- and iridium-coordinated (and chelated) cyclohexenyldicyclohexylphosphine, a species which is excluded as an intermediate in the rhenium(V) system. On the other hand, the bulky character of PCy_3 has been shown[16] to lead to a short (2.3 Å) H···Ru contact in unsaturated $RuCl_2CO(PCy_3)_2$; the stage is thus set for internal metalation.

Exchange of M–D and pendant C(sp^3)–H isotopes has been studied in some detail by Masters et al.[17] With M = Pt^{II}, and the hydrocarbon attachment being via $PR_2(CH_2)_nCH_3$, the general conclusions were (1) the preference for exchange in the *n*-alkyl chain is C3 ≫ C4 ≫ C2, with others essentially untouchable, and (2) exchange at the less favored positions is promoted by very bulky groups R. The latter influence has been attributed to minimal loss of internal entropy.[18] Certainly PCy_3 provides the required neighboring group "steric pressure", and previous reports of deuteration of rings in PCy_3 have appeared, but without definitive determination of carbon site preference and of mechanism.[19]

Several additional conclusions derived from this work warrant explicit mention:

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(19) Moers, F. G.; Müskens, P. J. W. M. *Trans. Met. Chem.* **1982**, *7*, 261.

(1) With the proof that ReH$_5$(PCy$_3$)$_2$ is a transient produced at or above 60 °C, there arises the question of why there is no evidence for "dimerization" of this unsaturated fragment to Re$_2$H$_8$(PCy$_3$)$_4$. Several additional conclusions derived from this work warrant explicit mention: (1) With the proof that ReH$_5$(PCy$_3$)$_2$ is a transient produced at or above 60 °C, the re arises the question of why there is no evidence for "dimerization" of this unsaturated fragment to Re$_2$H$_8$(PCy$_3$)$_4$. ReH$_7$(PPh$_3$)$_2$, ReH$_7$(PMePh$_2$)$_2$, and ReH$_7$(PMe$_2$Ph)$_2$ all transform thermally to Re$_2$H$_8$(PR$_3$)$_4$, with decreasing ease along the series as written. One might then expect the complex of the bulkiest phosphine, PCy$_3$, to dimerize most rapidly. The mechanism of formation of Re$_2$H$_8$(PR$_3$)$_4$ dimers from monomers has been established only for the case of photogenerated ReH$_5$(PMe$_2$Ph)$_2$,[4] and it proceeds not by dimerization of two transients but instead by reaction of ReH$_5$(PMe$_2$Ph)$_2$ with ReH$_5$(PMe$_2$Ph)$_3$. Perhaps ReH$_5$(PCy$_3$)$_2$ does not effectively condense with ReH$_7$(PCy$_3$)$_2$ for steric reasons. On the other hand, the above trend in ease of conversion from ReH$_7$P$_2$ to Re$_2$H$_8$P$_4$ also correlates inversely with phosphine basicity. Since PCy$_3$ is very basic, it may be that dimerization of ReH$_7$(PCy$_3$)$_2$ fails because re-addition of H$_2$ to ReH$_5$(PCy$_3$)$_2$ is very fast compared to attack by ReH$_7$(PCy$_3$)$_2$.

(2) In spite of the high formal oxidation state and low d electron count (d^2) of rhenium in transient ReH$_5$(PCy$_3$)$_2$, it is subject to "oxidative" addition by H$_2$ and the C–H bonds of benzene and pendant cyclohexyl groups. An electron-rich metal center is not essential to aliphatic C–H activation in this system. For example, the substitution kinetics with PPh$_3$ allows calculation of a value for $k_{-1}[\mathrm{H_2}]/k_2$ of 0.25. An estimate of the hydrogen concentration yields $k_{-1}/k_2 \simeq 10^2$, indicating addition of H$_2$ to ReH$_5$(PCy$_3$)$_2$ is more favorable than addition of PPh$_3$.

(3) In spite of the evidence for activation of the C–H bonds of benzene, and the likelihood that a η^2-C$_6$H$_6$ complex mediates this reaction, the transient Re(C$_6$H$_6$)H$_5$(PCy$_3$)$_2$ never proceeds on to stable products containing a coordinated C$_6$-cycle in any state of hydrogenation. A hydrogen acceptor (e.g., acenaphthalene) is required to generate sub-16-electron species before η^4 binding of aromatic-derived fragments can be produced. This is also a feature of the C–H activation systems of the Ephritikhine/Felkin group.[20] It is also noteworthy that our work (with PCy$_3$) provides concrete evidence for the proposal of these French workers that H$_2$ elimination is a thermal equilibrium process from ReH$_7$(PPh$_3$)$_2$.

Returning to the original objectives of this work, the complex ReH$_5$(PCy$_3$)$_3$ does not form from borohydride reduction of ReOCl$_3$(PCy$_3$)$_2$ in the presence of excess PCy$_3$. The pentahydride complex can be made, however, by inefficient displacement of H$_2$ by PCy$_3$ from the actual product of the borohydride reaction, ReH$_7$(PCy$_3$)$_2$. While there is no evidence for our initial objective of an isolable unsaturated polyhydride, ReH$_7$(PCy$_3$)$_2$ has been shown to produce ReH$_5$(PCy$_3$)$_2$ in a thermal reaction at moderate temperatures, and this species exhibits the intermolecular hydrogen isotope exchange reactions detected for photogenerated ReH$_5$(PMe$_2$Ph)$_2$.[2] The attempt to preclude interactions between rhenium and pendant aryl phosphine by utilizing an alkyl phosphine reveals transient interactions even with certain aliphatic C–H bonds of coordinated PCy$_3$. ReH$_5$(PCy$_3$)$_2$ is therefore characterized as a transient of high reactivity.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. David DeWit thanks Augustana College, Rock Island, Illinois, for support in the form of a sabbatical leave. The high-field NMR spectrometer employed was purchased under NSF Grant CHE-8105004. We thank Cleveland Refractory Metals for material support.

Registry No. B, 92284-94-1; C, 208-96-8; D, 91-20-3; E, 83-32-9; ReOCl$_3$(PCy$_3$)$_2$, 92284-89-4; ReH$_7$(PCy$_3$)$_2$, 92284-90-7; ReH$_5$(PCy$_3$)$_2$(PEt$_2$Ph), 92284-91-8; ReH$_5$(PCy$_3$)$_2$PPh$_3$, 92284-92-9; ReH$_5$(PCy$_3$)$_3$, 92284-93-0; ReOCl$_3$(PPh$_3$)$_2$, 17442-18-1.

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Monomeric Manganese(II) Alkoxides: Syntheses and X-ray Crystal Structures of Novel Three- and Four-Coordinate Manganese Complexes of the Tri-*tert*-butylmethoxide Ligand

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Abstract: Two novel alkoxides of manganese(II) containing the tri-*tert*-butylmethoxide ligand have been prepared in high yield. X-ray diffraction and elemental analysis were used to identify the products. The new alkoxide complexes are extremely air and moisture sensitive in solution and in the solid state. The molecular structures of [Li{Mn(N(SiMe$_3$)$_2$)(OC-*t*-Bu$_3$)$_2$}] (**4**) and [Li$_2${MnBr$_2$(OC-*t*-Bu$_3$)$_2$}·(THF)$_2$] (**5**) have been determined by X-ray diffraction. The crystal data at 140 K are as follows: **4**, Mo Kα (λ = 0.71069 Å), a = 21.243 (4) Å, b = 11.814 (1) Å, c = 20.334 (3) Å, β = 133.60 (1)°, Z = 4, space group Cc; **5**, Cu Kα (λ = 1.54178 Å), a = 17.868 (11) Å, b = 8.563 (6) Å, c = 26.075 (20) Å, β = 98.39 (6)°, Z = 4, space group $P2_1/c$. For **4**, R = 0.033, and for **5**, R = 0.088. The geometry at the manganese atom in **4** is distorted trigonal planar. Complexes **4** and **5** are the first manganese alkoxides to be structurally characterized. Both **4** and **5** contain a close Li···CH$_3$ interaction. Complex **4** is also unique in that it is a rare example of three-coordinate manganese(II).

In recent years, a number of authentic three-coordinate monomeric transition-metal complexes have been isolated.[1-9] These compounds usually involve sterically hindering groups such as N(SiMe$_3$)$_2$$^-$, CH(SiMe$_3$)$_2$$^-$, or a bulky phosphine which reduce

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