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Operationally Unsaturated Pincer/Rhenium Complexes Form Metal Carbenes from Cycloalkenes and Metal Carbynes from Alkanes

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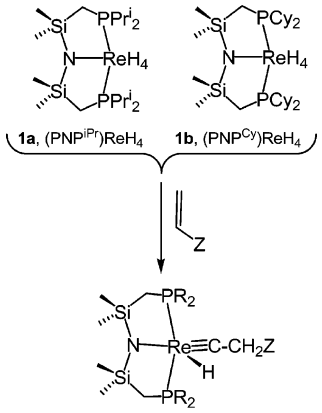
Abstract: Operationally unsaturated (i.e., 16/18-electron) $(PNP^R)Re(H)_4$, where PNP^R is $N(SiMe_2CH_2PR_2)_2$, is reactive at 22 °C with cyclic olefins. The first observed products are generally $(PNP^R)Re(H)_2$-(cycloalkylidene), with hydrogenated olefin as the product of hydrogen abstraction from the tetrahydride. The tetrahydride complex with R = ^{t}Bu generally fails to react (too bulky), that with R = cyclohexyl suffers a (controllable) tendency to abstraction of 3H from one ring, forming an η^3-cyclohexenyl compound, and that with R = ^{i}Pr generally gives the richest bimolecular reactivity. The cyclic monoolefins studied show distinct reactivity, C6 giving first the carbene and then coordinated cyclohexadiene, C5 giving carbene, then diene, and then η^5-C_5H_5, C8 giving carbene and then η^2-cyclooctyne, and C12 giving an η^3-allyl. Norbornene gives a π-complex of the norbornene in thermal equilibrium with its carbene isomer; at 90 °C, hydrocarbon ligand Cα−Cβ bond cleavage occurs to give, for the first time, a carbyne complex from an internal olefin. Two compounds synthesized here have the formal composition "$(PNP^R)Re$ + olefin", and each of these is capable of dehydrogenating the methyl group of a variety of alkanes at 110 °C to form (PNP)ReH(≡CR).

Introduction

Transformations of organic molecules on transition-metal centers are a focal point of organo-transition-metal chemistry. Of particular interest to us are the transformations that occur on strongly π-basic metal centers, capable of rebuilding an organic molecule into a π-acidic ligand complementary to the metal. A recent paper[1] details how the strongly π-basic $M(OSi^tBu_3)_3$ (M = Nb, Ta) isomerizes olefins to alkylidenes. We have previously reported[2,3] that the highly π-basic Re center supported by the PNP ligands, $(R_2PCH_2SiMe_2)_2N^-$, effects the rearrangement of acyclic alkenes into hydrido carbyne complexes. $(PNP^R)ReH_4$ complexes **1** (Scheme 1) react rapidly with 3 mol of acyclic alkenes $H_2C{=}CHR$ at 22 °C to quantitatively produce $(PNP^R)ReH(\equiv CCH_2R)$ and 2 mol of the corresponding alkane H_3CCH_2R. These experimental results, together with the supporting DFT study, demonstrate the strong preference of Re in the PNP complexes for the formation of hydrido carbyne products. In particular, we found that the hydrido carbyne structure is preferred over the isomeric carbene, η^2-alkene, vinyl hydride, or vinylidene dihydride complexes. Our observed

Scheme 1



production of a hydrido carbyne from $(PNP^R)ReH_4$ and alkene requires making and breaking of C−H, Re−C, and Re−H bonds (but not C−C bonds!) and can only occur in hydrocarbons where the metal can migrate to a terminal carbon purely by C−H cleavage. With this background, we were intrigued by the possible outcome of the reaction of $(PNP^R)ReH_4$ with cycloalkenes.

The ultimate focus of our interest was on the C−H activation of alkanes.[4−16] The elements of the hydrido + carbyne set of

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ligands might be formally derived (eq 1a) from an alkane by formal loss of "2H". Thus, we envisioned that, with an appropriate hydrogen acceptor A (eq 1b), conversion of alkanes to hydrido carbynes can be accomplished on the (PNP)Re center.

$$(PNP)Re + H_3CCH_2R \longrightarrow (PNP)Re(H)\equiv CCH_2R + \text{"2H"} \quad \textbf{(1a)}$$

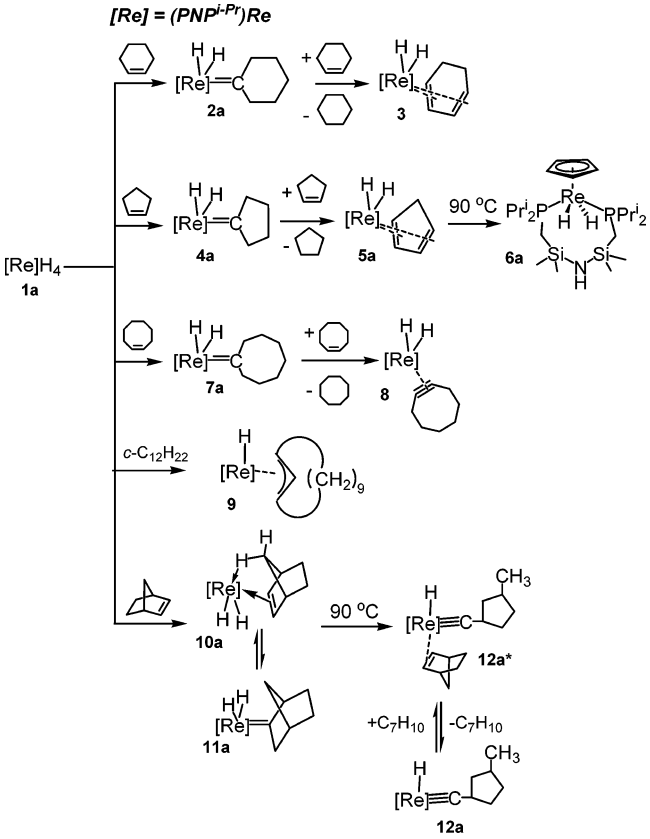
$$(PNP)ReH_4 + H_3CCH_2R + 3A \longrightarrow (PNP)ReH(\equiv CCH_2R) + 3AH_2 \quad \textbf{(1b)}$$

To make the new Re−carbon bonds in the reaction in Scheme 1, the Re center in (PNP)ReH_4 (**1**) must lose the hydrides, which in this case is accomplished by hydrogenation of excess acyclic olefin substrate. To make new Re−C bonds in reactions with substrates that do not possess H_2-accepting functionalities, a different approach must be taken. Either the formation of new bonds to Re is thermodynamically favorable enough to expel free H_2 or an additional, sacrificial H_2 acceptor incapable of carbyne formation must be introduced. We have reported[17] on examples of both types of behavior in activation of pyridine substrates where cyclooctene suitably served as a sacrificial H_2 acceptor. Here we report the dehydrogenation of alkanes to hydrido carbynes with various cycloalkenes as hydrogen acceptors. We also describe the details of the fascinatingly divergent, ring-size-dependent reactivity of the (PNP)ReH_4 complexes with cyclic alkenes involving hydrogen migration, C−H activation, and even C−C bond scission. The influence of the phosphine substituent is also described. Some aspects of this chemistry have been communicated.[18]

Results

Influence of R in PNP^R on the Rate. We have previously reported syntheses of compounds **1a,b** (Scheme 1) that bear different substituents on P. While the (PNP$^{t\text{Bu}}$) analogue ("**1^{t}Bu**") has served to uncover some alluring Ru chemistry,[19] the ^{t}Bu analogue has proven to be too hindered sterically. ^{t}Bu was recovered unchanged after thermolysis (160 °C, 24 h) in mesitylene in the presence of excess cyclopentene, and it was also unreactive toward cyclohexene and cyclooctene. Norbornene did react with ^{t}Bu slowly, but the reaction was found to lead to unselective decomposition. We have previously found that ^{t}Bu reacts with linear alkenes much more slowly than **1a** or **1b**; we ascribed that to the prohibitive steric bulk of the (PNP$^{t\text{Bu}}$) ligand. The rates of reaction of **1a** and **1b** are qualitatively similar, reflecting the comparable steric and electronic influence of ^{i}Pr and Cy. The major difference is that **1b**, upon removal of hydrides from the Re center, is prone to undergo intramolecular C−H activation (vide infra).

Scheme 2



Reactivity of 1a,b with Cycloalkenes. **Solvent Choice**. As will be discussed later, some of the species formed in the reactions of cycloalkenes with **1a,b** are quite reactive, even with many common solvents. Deuterated solvents such as C_6D_6 also can undergo H/D exchange with these reactive Re compounds. We found that cyclohexane, cyclooctane, and hexamethyldisiloxane were effectively inert as solvents.

Reactions with Cyclohexene and C−H Activation of the PNP^{Cy} Ligand (Schemes 2 and 3). The preliminary results of the studies of the reactivity of **1** with cyclohexene have been communicated.[18] At ambient temperature, **1a** and **1b** react with excess cyclohexene in under 1 h to produce **2a** or **2b**, respectively (with concomitant production of cyclohexane). The solid-state structure of **2b** (see below) is unusual as it possesses a β-agostic cyclohexylidene ligand and the geometry about the carbene carbon is strongly distorted toward a T-shape. Solution spectroscopic data suggest a similar β-agostic interaction in **2a**. The formation of **2a** from **1a** was quantitative when at least 2 equiv of cyclohexene was used, and no intermediates were observed during the course of this reaction at 22 °C. In the case of **1b**, reaction with 2 equiv of cyclohexene at 22 °C led to a mixture of **2b** and the purple-blue cyclohexenyl hydride **13** (Scheme 3). Activation of three C−H bonds in cyclohexyl-substituted phosphines to give cyclohexenyl and cyclohexene complexes has been documented in several related systems.[20] We have now identified **13** as the impurity we previously observed[2] in the reactions of **1b** with acyclic alkenes. In those instances, the formation of **13** could be suppressed by using an

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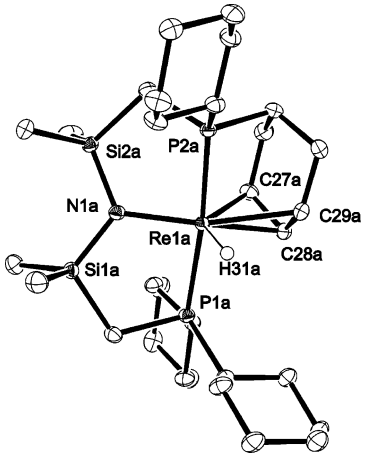


Figure 1. ORTEP plot of **13** (50% thermal ellipsoids). Omitted for clarity: all H atoms except ReH, the second independent molecule, the pentane molecule in the lattice. Selected bond distances (Å) and angles (deg): Re1a−N1a, 2.031(3); Re1a−C27a, 2.181(3); Re1a−C28a, 2.200(3); Re1a−C29a, 2.363(3); Re1a−P1a, 2.3763(8); Re1a−P2a, 2.3004(8); N1a−Re1a−P1a, 87.16(8); N1a−Re1a−P2a, 87.40(8); P1a−Re1a−P2a, 174.52(3); C27a−C28a−C29a, 111.6(3).

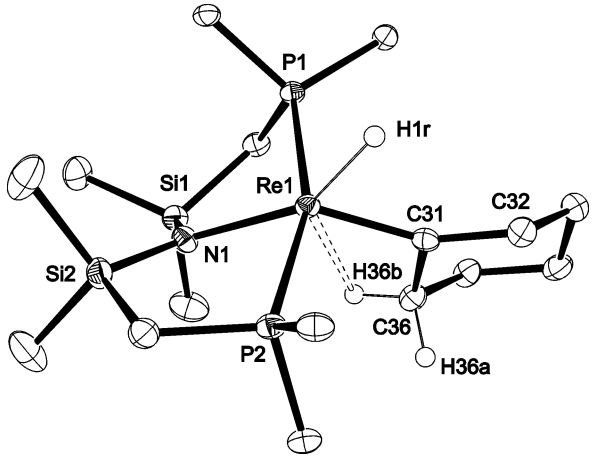
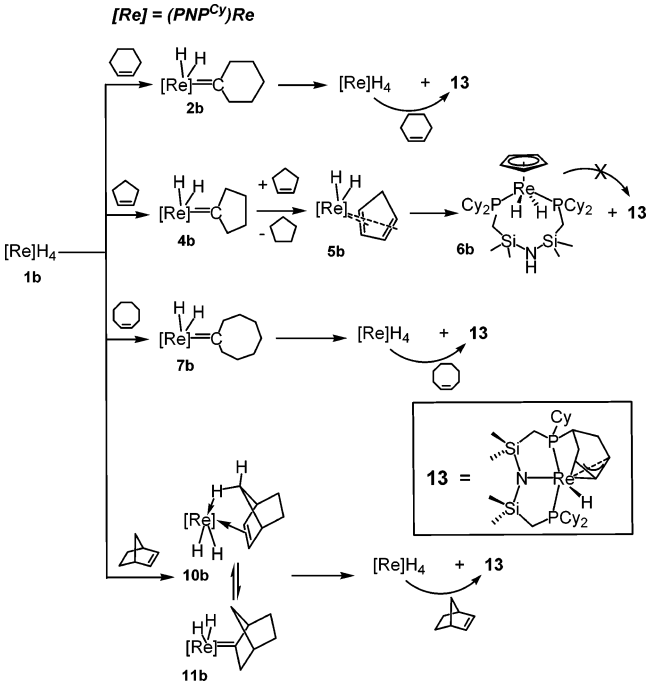


Figure 2. ORTEP plot of **2b** (50% thermal ellipsoids). Omitted for clarity: the CH_2 groups on all P atoms and all H atoms except those on C36 and the one (of two actually present) on Re. Selected bond distances (Å) and angles (deg): Re1−C31, 1.889(4); Re1−N1, 2.182(3); Re1−P1, 2.4091(9); Re1−P2, 2.3715(1); C31−Re1−N1, 136.90(15); N1−Re1−C36, 102.36(13), P1−Re1−P2, 161.30(4); Re1−C31−C32, 147.2(3); Re1−C31−C36, 100.4(3); N1−Re1−P1, 79.88(9).

Scheme 3



excess of the alkene. Similarly, a large (20-fold) excess of cyclohexene eliminates 99% of the formation of **13** (on a <1 h time scale).

$[Cy_2PCH_2SiMe_2NSiMe_2CH_2PCy(C_6H_8)]ReH$, 13. This molecule crystallizes with two molecules in the asymmetric unit, but the two show no significant differences. The two are numbered analogously to facilitate comparison in the Supporting Information. Figure 1 shows how the conformation of one C_6 ring allows the "*meta*" and "*para*" carbons, which each have been singly dehydrogenated, to bind to the metal: P is axial on the C_6 ring, which contrasts to its equatorial site in every other compound reported here. This η^3-allyl binding also makes −(Re−P−C_{ipso}) very small (99.2−99.6°). The Re−N distances are short (<2.04 Å), and the Re−P distance to the dehydrogenated, allyl bound C_6 ring is *shorter* (by >0.08 Å) than to the PCy_2 phosphorus. There is no significant difference in the Re−PCy_2 distance here from the Re−P^iPr_2 groups in compound **8**.

$(PNP^{Cy})Re(H)_2[=C(CH_2)_5]$, 2b. Only one of the two (inequivalent) hydrides known to be present from the NMR spectra and from the diamagnetism of the compound (e.g., observation of ^{31}P NMR signals) was found by X-ray diffraction; only it is illustrated in Figure 2, but there is ample room for the second hydride *cis* to both N1 and H1R. −(P1−Re−P2) is the typical transoid value (161.30(4)°) of PNP in a *mer* arrangement, but the angle N1−Re−C31 is large, 136.90(15)°, allowing ample space for an agostic interaction with C36−H36b. Relevant distances from Re to C36 and H36b are 2.635(4) Å (cf. the norbornene values below) and 2.38 Å (H position not refined). This is accomplished by deforming −(Re−C31−C36) (100.4(3)°) much below that of Re−C31−C32 (147.2(3)°). The Re−C31 distance, 1.889(4) Å, is consistent with a multiple bond, although this is a rare example[21] of a carbene with a β-agostic interaction (cf. β-agostic alkyls). The C−C bond lengths and C−C−C angles in the cyclohexylidene ring are unexceptional, and the molecular mirror symmetry deduced from the NMR spectra requires rapid exchange between H36a and H36b as the agostic donors. The Re−N1 distance, 2.182(3)Å, is longer than that in **1b** (2.063(2)Å), indicative of diminished π-donation from N to Re as a consequence of the agostic donation.

While pure **2a** is stable in solution at ambient temperature for at least several hours, solutions of **2b** readily evolve into a 2:1 mixture of **13** and **1b**. In the presence of excess cyclohexene, pure **3**, a cyclohexa*diene* complex, is ultimately produced from **2b** in solution even though excess cyclohexene retards the transformation kinetically. However, **2b** is stable in the solid state at ambient temperature, which allowed for its characterization by X-ray crystallography and elemental analysis. Thermolysis (120 °C, 30 min) of a solid sample of **2b** in a vacuum transfer apparatus resulted in the production of a mixture of cyclohexane and cyclohexene as volatile products and **13** and **1b** as the organometallic residue (see the Experimental Section

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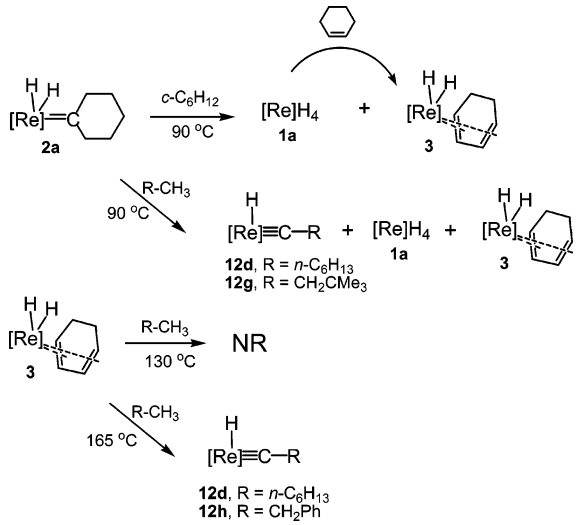
Scheme 4



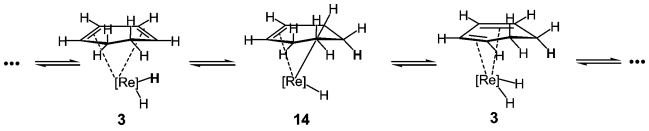
for details). Compound **13** is thermally stable in alkane or arene solvents, although it readily undergoes H/D exchange with C_6D_6 at 22 °C.

Compounds **1a**−**c** are produced by Mg reduction of $(PNP^R)ReOCl_2$[22] in an ethereal solvent under a H_2 atmosphere. When the reduction of **1b**, $(PNP^{Cy})ReOCl_2$, is performed in ether under an atmosphere of pure Ar in an attempt to form merely "(PNP)Re", mixtures with ratios of 3:1 to 10:1 of **13** and **1b** are formed (by ^{31}P NMR in situ) in a few different experiments (see the Experimental Section). The stoichiometric ratio that may be expected is 2:1 (corresponding on average to the elements of $(PNP^{Cy})Re$), and it is not immediately clear how an excess of hydrogen-poor **13** is produced. Compound **13** readily reacts with H_2 to give **1b** in the time of mixing. Reduction of $(PNP^R)ReOCl_2$ under Ar followed by hydrogenolysis is a convenient way of synthesizing **1b** on a large scale. However, these studies show that any attempt to synthesize simply "$(PNP^{Cy})Re$" (or its ether complex) by magnesium reduction in Et_2O has a different outcome, one based on intramolecular attack by the highly reduced, electron-rich rhenium.

Thermolysis (90 °C, 1 h) of **1a** with ≥3 equiv of cyclohexene in cyclohexane led to the exclusive formation of **3**. **2a** is an intermediate in this reaction. Isolated samples of **2a** transform into **3** upon thermolysis in cyclohexane in the presence of ≥1 equiv of cyclohexene. When **1a** was thermolyzed in the presence of <3 equiv of cyclohexene or when a solution of pure **2a** was thermolyzed in cyclohexane, a mixture of **1a** and **3** was formed after the thermolysis. The cyclohexadiene ligand in **3** (as well as cyclohexylidene in **2a**) comes from cyclohexene and not the cyclohexane solvent as evidenced by the invariance of the reaction outcome in cyclooctane or cyclo-C_6D_{12} solvents.

Alkane Dehydrogenation with 2a. Compound **2a** is the formal equivalent of (PNP)Re and cyclohexane and thus is attractive for the alkane reaction of eq 1a. Thermolysis of **2a** in heptane or neohexane led to a mixture of the corresponding hydrido carbynes **12d** and **12g**, together with **3** (the product of competitive C_6 ring dehydrogenation in **2a)**, the hydrogen acceptor product **1a** (Scheme 4), and presumably cyclohexane. The structure and spectroscopic properties of several hydrido carbynes (**12c**, **12g**, and others) were described previously.[2] The new hydrido carbynes **12** prepared in this work display very similar spectroscopic features and a red color. Addition of cyclohexene before thermolysis eliminated **1a** from the products, but it also increased the **3**:**12** ratio. Thermolysis of **2a** in heptane in the presence of a large excess of cyclohexene completely suppressed the formation of **12** (only **3** was formed). Thermolysis of **3** (colorless) in heptane or ethylbenzene at 130 °C did not lead to any NMR-detectable change or any color change. When solutions of **3** in heptane or ethylbenzene were briefly heated at 165 °C, the red color typical of **12** was observed and the corresponding hydrido carbynes **12d** and **12h** were identified by subsequent NMR analysis. However, at 165 °C the onset of unselective decomposition of **12** occurs, and we have not been able to convert **3** into **12** in high yield.

Scheme 5



3 is a colorless compound that dissolves well in aromatic (and sparingly in aliphatic) solvents. The ^{31}P NMR resonance of **3** is broad at 22 °C and decoalesces into two broad peaks at low temperature. This presumably reflects a ground-state orientation of the cyclohexadiene which leaves inequivalent P, but with a modest barrier for rotation of the diene ring. Only one hydride signal ($\delta = -8.33$, br dt, $J_{HH} = 7$ Hz, $J_{HP} = 16$ Hz) could be clearly observed. The presence of the other hydride (presumably obscured by the aliphatic resonances) is inferred from the observed H−H coupling and the similarity with the cyclopentadiene species **5b (**Scheme 3**)**, for which a structure in the solid state was determined (vide infra).

The ^1H NMR resonances of the cyclohexadiene ligand in **3** are somewhat broad. Spin saturation transfer experiments were consistent with the process shown in Scheme 5 that accounts for the site exchange between six of the hydrogens of the cyclohexadiene ligand. Similar observations were made in the case of the $(R_3P)_2ReH_3(\eta^4\text{-diene})$ complexes.[23] The reversible cyclohexadiene/dihydride−cyclohexene/monohydride transformation exchanges the two *endo* hydrogens of the cyclohexadiene ligand with one of the hydrides. The same process also exchanges the remaining six hydrogens of the cyclohexadiene ligand (two *exo* hydrogens from the CH_2 groups and the four $C(sp^2)$−H hydrogens). Irradiation of the hydride signal at −8.33 ppm had no effect on the cyclohexadiene ligand resonances and vice versa, so this hydride does not participate in the exchange process.

The activation barrier for the formation of the hydrido cyclohexenyl intermediate **14** is likely lowered by the π-donating ability of N. While **3** is a saturated, 18-electron complex, **14** is a 16-electron complex without counting the π-donation from N. We have previously demonstrated[3,24] that the π-donation from N in (PNP)Re systems can stabilize operationally unsaturated compounds. Consequently, we expect that **14** is also stabilized by π-donation and thus more accessible energetically. Indeed, we have isolated other closely related allyl hydride complexes

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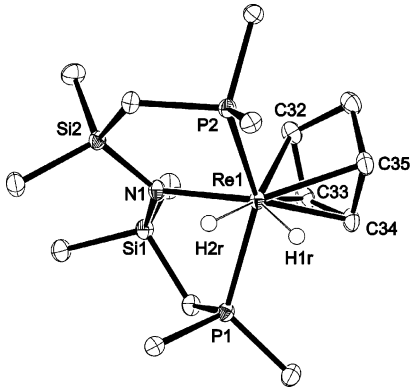


Figure 3. ORTEP plot of **5b** (50% thermal ellipsoids). Omitted for clarity: all H atoms except ReH, the methylene carbons of cyclohexyl groups. Selected bond distances (Å) and angles (deg): Re1−N1, 2.212(2); Re1−P1, 2.4193(4), Re1−P2, 2.3979(4); C32−C33, 1.430(2); C33−C34, 1.440(2); C34−C35, 1.439(2); P1−Re1−P2, 139.51(1); N1−Re1−P1, 76.12(4).

(**13** and **9a**, vide infra). For $(R_3P)_2ReH_3(\eta^4$-diene) it was also proposed[23] that the diene fragment slowly rotates about the Re−centroid axis. Such a slow rotation is likely in **3** as well and may be responsible for the observed low-temperature inequivalence of the two P sites. In addition, we have observed broadening of the observed ^{1}H and ^{31}P resonances at low temperatures as a result of the flexing motion of the PNP backbone in other PNP complexes. The combination of three dynamic processes (Re−H/C−H exchange, diene rotation, and PNP backbone flexing) in **3** is responsible for the observed dynamic features of the NMR spectra.

Cyclopentene (Schemes 2 and 3). Upon mixing of **1a** with a 4-fold excess of cyclopentene at 22 °C (in cyclohexane-d_{12}), a mixture of **4a**, **5a**, and **6a** was initially observed. **4a** could not be isolated and was only identified on the basis of the selected NMR resonances in solution that resembled those of **2a**. A lone singlet was observed in the ^{31}P{^{1}H} NMR spectrum for each (**4a**, δ 49.4), and it became a triplet upon selective decoupling of only the alkyl hydrogens. **5a** was the dominant product after 5 h at 22 °C, and thermolysis of this solution produced **6a** in a >95% yield. **1b** reacted similarly with cyclopentene at 22 °C, except that **13** was also produced. As with cyclohexene and **1b**, the formation of **13** could be suppressed by using a large excess of cyclopentene. **5b** could be isolated as an analytically pure crystalline solid in high yield, including an X-ray-quality single crystal.

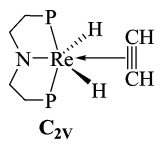
$(PNP^{Cy})Re(H)_2(C_5H_6)$, 5b. The X-ray structure in Figure 3 shows that the bulky PCy_2 groups bend away from C_5H_6 and toward the small hydride H2r. Nevertheless, the amide nitrogen is coplanar (angle sum is 359.98°) with its three substituents. The two *trans* angles in the Re/P_2/N/H1r unit are nearly equal (−(N1−Re−H1r) = 139.9(9)° and −(P1−Re−P2) = 139.51(1)°, the latter unusually small for this pincer ligand), and −(N1−Re−H2r) is cisoid, 76.0(9)°. The distances from Re to the diene terminal carbons (C32 at 2.2963(6) Å and C35 at 2.2608(15) Å) are clearly longer than to the diene internal carbons (C33 at 2.2095(16) Å and C34 at 2.1697(15) Å), and C_5H_6 is oriented in a way which leaves the phosphorus nuclei inequivalent, in agreement with the ^{31}P NMR spectrum. The Re−N1 distance, 2.212(2) Å, is very long, consistent with this amide not participating in N → Re π-donation, but also influenced by the *trans* influence of H1r.

Thermolysis of pure **5b** in C_6D_6 produced a mixture of **13** and **6b**; the formation of either product was irreversible (i.e., the mixture does not change proportion with further heating). **6b** can be isolated in high yield if **5b** or **1b** is thermolyzed in the presence of a large excess of cyclopentene (cosolvent). **6a** and **6b** were identified primarily on the basis of the similarity of the key solution NMR data with those of the known $CpRe(H)_2(PR_3)_2$ compounds.[23] Compounds of the type $CpRe(H)_2(PR_3)_2$ have a four-legged stool geometry, with hydrides being the opposite "legs". The flexible backbone of the η^2-$PN(H)P^{iPr}$ ligand in **6** should not lead to a geometry about Re that is significantly different in $CpRe(H)_2(PR_3)_2$. A single resonance arising from the five Cp hydrogens was observed at ca. 4.5 ppm, as well as a triplet hydride resonance at ca. −12 ppm with a $^2J_{HP}$ = 41 Hz characteristic of the $CpRe(H)_2(PR_3)_2$ complexes. **6a** and **6b** are thermally stable in solution in alkane and arene solvents.

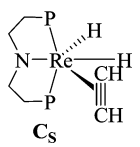
5a,b each gave rise to a single broad ^{31}P NMR resonance and somewhat broad resonances of the cyclopentadiene ligand. One of the ^{1}H NMR hydride signals resonated at ca. −8 ppm, while the other was apparently broad and/or obscured by the aliphatic resonances. Presumably, **5** undergoes the same dynamic processes as **3** (vide supra). We selected **3**, rather than **5a** or **5b**, for the spin saturation transfer and low-temperature NMR studies because of the ease of isolation in a pure state and simpler ^{1}H NMR spectrum (vs **5b**).

Cyclooctene. Cyclooctene reacts (Schemes 2 and 3) with **1a**,**b** more slowly than do cyclohexene and cyclopentene. Initially, the formation of the cyclooctylidene **7** was observed, which further evolves either exclusively into the cyclooctyne/dihydride **8** (from **1a**) or exclusively into **13** (from **1b** and ≥3 equiv of cyclooctene). **7a** and **7b** could not be isolated and were only characterized by their selected NMR resonances that resemble those of **2** and **4**.

$(PNP^{iPr})Re(H)_2$(cyclooctyne). The synthesis of $(PNP^{iPr})Re(H)_2$(cyclooctyne), **8**, was reported earlier, but not discussed in detail there.[17] Thermolysis of **1a** in the presence of ≥3 equiv of cyclooctene in cyclooctane, cyclohexane, or hexamethyldisiloxane led to the exclusive formation of **8**. **8** is thermally stable (<100 °C, 24 h) in these solvents and is light pink in both solution and the solid state (the faint pink color is retained after three recrystallizations). **8** reacts with H_2 to produce cyclooctane and **1a**. It is best formed after treatment of $(PNP^{iPr})Re(H)_4$ with ≥3 mol of cyclooctene at 90 °C. Two moles of cyclooctane is produced from the hydride ligands lost. Proton and ^{31}P{^{1}H} NMR spectra at 22 °C are consistent with a molecule with mirror symmetry, the mirror plane bisecting the P−Re−P angle. The hydrides are observed to be inequivalent, as are the related substituents on the PNP^{iPr} ligand: CH_2, $SiMe_2$, and ^{i}Pr. DFT calculations reported earlier on $(PNP^H)Re(H)_2$(HCCH) establish that the C_s isomer is 27.6 kcal/mol ($\Delta G°_{298}$) more stable than the C_{2v} isomer. Both ^{1}H and ^{13}C{^{1}H} NMR



C_{2v}



C_S

spectra at 22 °C show C_s symmetry of the cyclooctyne ring. The ^{31}P{^{1}H} NMR spectrum at −76 °C shows that the broad

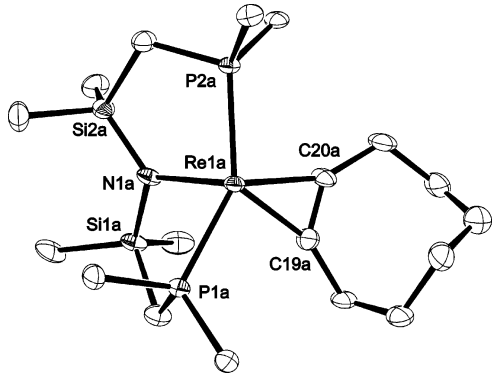


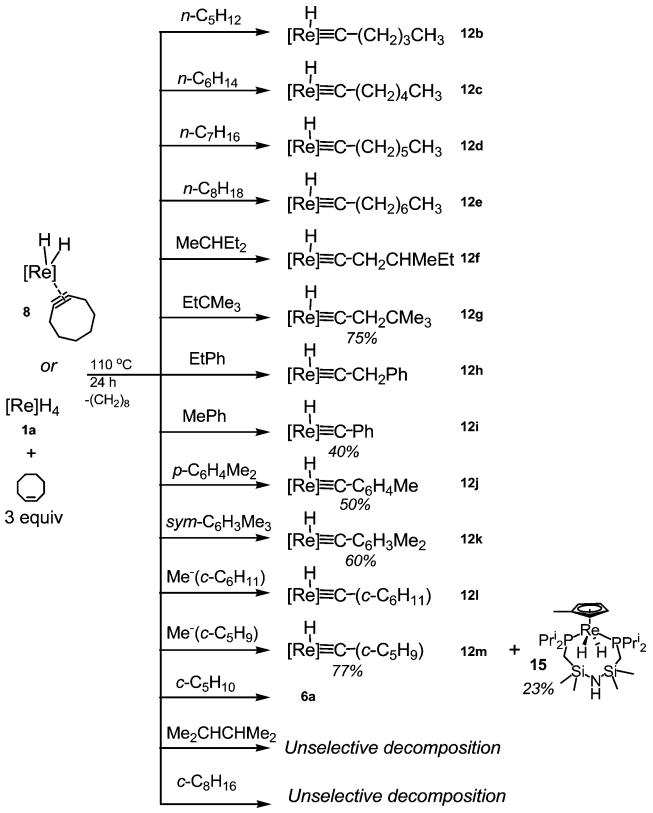
Figure 4. ORTEP plot of **8** (50% thermal ellipsoids). Omitted for clarity: Me groups of isopropyls, all H atoms including two ReH atoms, second independent molecule. Selected bond distances (Å) and angles (deg): Re1a−C19a, 2.026(7); Re1a−C20A, 2.022(7); Re1a−N1a, 2.158(6); Re1a−P1a, 2.4023(18); Re1a−P2a, 2.3872(17); C19a−C20a, 1.320(10); P1a−Re1a−P2a, 145.78(6); N1a−Re1a−P1a, 78.93(16); N1a−Re1a−C19a, 117.4(3).

singlet at 22 °C has decoalesced into two signals, thus breaking the molecular mirror symmetry implied by the 22 °C ^{1}H and ^{13}C NMR spectra; this we attribute to the C≡C vector not exactly eclipsing the P−Re−P plane, as established (see below) in two crystallographically independent molecules in the solid. In addition, P^{i}Pr$_2$/cyclooctyne congestion can lead to the ^{31}P NMR inequivalence by favoring a non-mirror-symmetric conformation at low temperature; this conformation includes lack of mirror symmetry of the two fused rings of the (PNP)Re substructure.

This sample crystallized (Figure 4) with two independent molecules in the unit cell. A least-squares fit shows that the two molecules agree to within 3σ for the core of the Re/ligand molecule; differences involve single bonds at the molecular periphery: the conformation of one ^{i}Pr group and the CH$_2$ groups of the cyclooctyne. The Re−N distances are of intermediate length (∼2.15 Å), the Re−C distances (2.007(7)−2.026(7) Å) are shorter than to the norbornene carbons (∼2.20 Å; see below) and the alkyne C−C distance (1.320(10)−1.328(9) Å) is shorter than that (1.455(2) Å) in coordinated norbornene. −(P−Re−P) is small (∼145.6°), consistent with repulsion from the cyclooctyne, whose C≡C vector the ReP$_2$ plane eclipses. This sterically unfavorable alkyne conformation must be electronically dictated and involves competitive π-donation by amide N and the alkyne-filled π-orbital. The ^{13}C chemical shift, 190.4 ppm, approaches the region characteristic of alkyne 4e donation.[25] The coordinated alkyne has severely bent C(sp^3)−C(sp)−C(sp) angles: 129.1(7)−135.1(7)°. The amide nitrogen is planar. Although the hydrides were located in a difference map, they could not be refined to chemically reasonable positions and thus permit no conclusion.

Prolonged (>24 h) thermolysis of **8** at 130 °C in cyclooctane led to decomposition to unknown products. Several dozen(!) new resonances appeared in the ^{31}P NMR spectrum. Interestingly, the color of the resultant solution was red, reminiscent of the color of the hydrido carbynes **12**. In addition, hydride peaks in the ^{1}H NMR spectrum of this mixture and resonances in the ^{31}P NMR spectrum appeared in the same region as those of **12**. We were not able to characterize the products of this decomposition conclusively. It is possible, however, that some

Scheme 6



compounds similar to **12** form as a result of attack on the ligand or solvent or C−C cleavage in the eight-membered ring of the solvent of the cyclooctyne ligand. This chemistry is much more promising when the hydrocarbon solvent contains a methyl group, as will now be described.

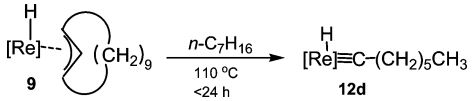
Thermolysis (24 h, 110 °C) of **8** or of **1a** + 3 equiv of cycloooctene in several hydrocarbon solvents (Scheme 6) resulted in liberation of cyclooctane and the formation of the solvent-derived hydrido carbyne products **12**. In general, these reactions were near quantitative (NMR evidence) when the substrate (solvent) contained an ethyl group. Methyl-substituted arenes apparently did produce the hydrido carbynes (**12i**−**k**), but only in ca. 50% yield (the balance is other unidentified products). The carbyne products can only form if the substrate contains a methyl group; the reactive transient is apparently incapable of C−C bond cleavage. While cyclohexane and cyclooctane were not activated to any detectable degree, thermolysis of **8** in cyclopentane resulted in a clean formation of the cyclopentadienyl complex **6a**. Interestingly, thermolysis of **8** in methylcyclopentane produced both the carbyne-containing (**12m**) and the Cp-containing (**15**) products. The higher reactivity of the cyclopentane vs larger cycloalkanes is generally in line with the differences in C−H activation of cycloalkanes described by others.[26,27] 2,3-Dimethylbutane was not activated, instead producing a mixture of unidentified products similar to that produced in larger cycloalkanes. Two substrates offered a choice of different methyl groups within the same molecule. Activation of 3-methylpentane (product **12f**) and of neohexane (product **12g**) was selective for the less hindered methyl group.

(25) Compare, however, Wells, M. B.; White, P. S.; Templeton, J. L. *Organometallics* **1997**, *16*, 1857.

(26) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738.

(27) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.

Scheme 7



Monitoring the reactions at early stages revealed that small amounts of **1a**, cyclooctane, and cyclooctene were produced during the thermolysis of pure **8** in alkanes. This is similar to the observations we made in the activation of alkylpyridines by **8**.[17]

Cyclododecene. Cyclododecene reacted (Scheme 2) slowly with **1a** (reaction with **1b** was not explored) to ultimately give two isomers of **9**. Our attempts at separating the two isomers by recrystallization or at obtaining a suitable crystal for an X-ray diffraction study were not successful. The solution NMR data are consistent with the proposed cyclododecene/hydride formulation. The validity of the proposed structure is reinforced by the similarity (color, allylic, and hydridic NMR resonances) with the structurally authenticated *P*-cyclohexene/hydride **13**. The single hydride and the three allylic hydrogens for each isomer of **9** were clearly identified in the ^{1}H NMR spectrum, as well as the allylic resonances in the ^{13}C NMR spectrum. The hydride signal of each isomer appears as a doublet of doublets at ca. −12 ppm owing to the coupling to two inequivalent phosphines. Accordingly, an AB pattern for each isomer was observed in the ^{31}P{^{1}H} NMR spectrum at ca. 30 ppm (*trans* $^2J_{PP}$ = 241 or 243 Hz). Selective decoupling experiments confirm the proposed assignment in each isomer. All operationally unsaturated (PNP)Re compounds possess distinct colors, and **9** and **13** have similar blue-purple color in solution and the solid state. The exact difference between the two isomers of **9** is not clear from the solution NMR studies. The commercial cyclododecene is a mixture of *cis*- and *trans*-isomers. It is possible that isomerism of the two allyl substituents accounts for the presence of two isomers of **9**. However, the two isomers of **9** do not have to duplicate the population of the two different isomers of cyclododecene because **1a** (and likely other Re−H-containing intermediates) was previously shown[2] to rapidly isomerize olefins (e.g., stilbene). The two isomers of **9** equilibrate, but on a time scale too slow to be the ring reorientation ("rotation") observed for the cyclohexadiene ring of **3**.

Compound **9** reacted with heptane similarly to the cyclooctyne complex **8**. Thermolysis of **9** in heptane (110 °C) produced **12d** in >98% yield (Scheme 7). Monitoring this reaction at early stages revealed the intermediate formation of **1a**. Compound **9** is thus an effective formal source of (PNP)Re, and the allyl + hydride serves as a 2H acceptor in heptane dehydrogenation (eq 1a).

Norbornene. Norbornene reacted (Schemes 2 and 3) rapidly at 22 °C in alkane solvents with **1a(b)** to give a mixture of isomeric **10a(b)** and **11a(b)**. As with other cycloalkenes, in the case of **1b**, a large excess of norbornene was necessary to suppress cyclohexyl dehydrogenation (i.e., the formation of **13)**. Isolated samples of **10a**/**11a** were stable at 22 °C in an alkane solution, whereas dissolution of solid samples of **10b**/**11b** (recrystallized at −30 °C from solutions containing an excess of norbornene) resulted in the formation of a mixture of **10b**, **11b**, **13**, **1b**, and norbornane that evolved into a 2:1 mixture of **13** and **1b** (and also norbornane) over 24 h at 22 °C. Solutions

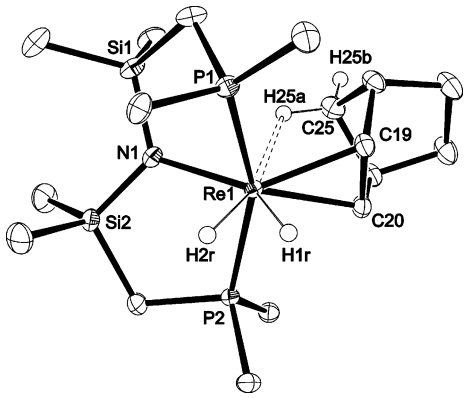


Figure 5. ORTEP plot of **10a** (50% thermal ellipsoids). Omitted for clarity: Me groups of isopropyls, all H atoms except ReH and the hydrogens on the bridgehead carbon of norbornene. Selected bond distances (Å) and angles (deg): Re1−N1, 2.122(1); Re1−P1, 2.3924(4); Re1−P2, 2.3657(4); Re1−C19, 2.191(1); Re1−C20, 2.215(1); C19−C20, 1.455(2); P1−Re1−P2, 154.70(1); N1−Re1−P1, 80.24(4).

of **10**/**11** are dark blue-purple, and the solids obtained by crystallization from such solutions were of the same color as well. **10** was the major isomer for both PNP ligands; e.g., the ratio of **10a** to **11a** was ca. 8:1. This ratio was constant for different batches and remained the same after multiple crystallization/redissolution sequences. Because of the difficulty in isolation of **10b**/**11b**, we concentrated on the characterization of **10a**/**11a**. The NMR resonances of **10**a and **11a** were distinct, indicating that exchange between **10a** and **11a** is slow on the NMR time scale at 22 °C but fast on the time scale of experimental handling. The material obtained by cooling a solution of **10a**/**11a** was highly crystalline, allowing for a facile selection of an X-ray-quality crystal. Visual microscopic inspection revealed the presence of crystals of only one morphology and color (blue-purple). By analogy with **2**, one may expect that **11a** should be of a color closer to orange rather than blue-purple. The intense blue-purple color is probably that of **10a**, and in solution it may conceal the lighter color of **11a**. It seems possible that only **10a** crystallizes out of the solution and rapidly equilibrates into a **10a**/**11a** mixture upon redissolution. Both **10a** and **11a** display two inequivalent upfield hydride resonances. The chemical shifts and the broadness of the hydrides of **11a** resemble those of **2**. While the hydride resonances of **10a** are not as broad as those of **11a**, they show no coupling fine structure at 22 °C. Upon cooling to −40 °C, the H−P coupling becomes resolved. Consistent with the proposed formulations, the NMR spectra of **10a** indicate C_s symmetry with a single ^{31}P resonance observed, while **11a** is C_1-symmetric by NMR and displays an AB pattern in the ^{31}P{^{1}H} NMR spectrum; this lack of symmetry is caused by the chirality in the norbornylidene moiety. The NMR resonances of **11a** are somewhat broad at 22 °C. The alkylidene nature of **11a** was confirmed by the observation of a downfield (δ 281 ppm) ^{13}C resonance corresponding to the α-carbon. Unfortunately, assignment of the other ^{13}C resonances of **11a** was not possible owing to the overlap and low symmetry and concentration.

(PNP^{iPr})Re(H)$_2$(norbornene). The structure (Figure 5) has idealized mirror symmetry, which leaves the hydrides inequivalent (and *cis*) and the two phosphorus atoms equivalent, both in agreement with NMR observations. The amide nitrogen is coplanar with its three substituents (angle sum 359.46°). The angles between N and the norbornene olefinic carbons C19 and

C20 are much larger (138.60(5)° and 138.62(5)°, respectively) than 90°, thereby opening a place for the norbornene CH_2. The Re−C25 and Re−H25 distances, 3.044 and 2.52 Å, respectively, are consistent with an agostic interaction, which accords with one ^{1}H NMR chemical shift observed at −1.51 ppm (i.e., as anticipated for H interacting with a transition metal).[28] The Re−N1 distance, 2.122(1) Å, is of intermediate length, consistent with an agostic interaction completing an 18-electron count but in competition with N → Re π-donation. The olefinic C19−C20 distance, 1.455(2) Å, is long,[29−31] consistent with strong π-basicity of the (PNP^{iPr})Re center.

Thermolysis (90 °C) of **10a**/**11a** in the presence of 5 equiv of norbornene led rather unexpectedly to the hydrido carbyne product **12a** (ca. 90%). **12a** is an isomer of **10a** and **11a**, formed via scission of a $C_\alpha-C_\beta$ bond in **11a**, our first observation of C−C bond cleavage. **12a** is trapped in the reaction mixture as its norbornene adduct **12a***. The coordinated norbornene can be removed in vacuo at 110 °C. The NMR data for **12a** and **12a*** are similar to those of the other hydrido carbynes **12** and their olefin adducts. For **12a**, the chemical shifts of the ^{31}P NMR (δ 60.8 ppm) and Re−H ^{1}H NMR (δ −10.57 ppm) resonances are especially similar to those of the most structurally similar **12m** (^{31}P NMR, δ 60.6 ppm; ^{1}H NMR, δ −10.58 ppm). **12a** possesses a chiral center, but it is fairly remote from the PNP ligand. Consequently, it is evident from the ^{1}H and ^{13}C NMR that the symmetry of **12a** is C_1 (four Si−Me resonances in the ^{1}H and ^{13}C NMR spectra), but the chemical shift difference for several other diastereotopic nuclei is too small to be resolved.

Benzene C−H Cleavage. Because of our frequent observation of isotope exchange of reactive transients produced here with d_6-benzene solvent (and thus our frequent use of d_{12}-cyclohexane as an NMR solvent), we have briefly studied this behavior. In fact, (PNP^{iPr})Re(H)$_2$[=C(CH$_2$)$_5$], **2a**, is 1/3 converted in 10 min at 22 °C in C_6H_6 to a single compound, proposed to be (PNP^{iPr})Re(H)$_3$(Ph). This is apparently an equilibrium state, since the mole ratio of **2a** to this product remains unchanged over an additional 24 h. Consistent with the expectation that cyclohexene is being displaced in this reaction, dissolving **2a** in benzene containing 10 equiv of cyclohexene showed no production of (PNP^{iPr})Re(H)$_3$(Ph).

C−H Bond Competition Experiments. To evaluate the relative reactivity of primary (from *n*-alkanes) vs secondary (from cycloalkane) vs aromatic C−H bonds, several direct competition experiments were performed between **8** and mixtures of equimolar amounts of two hydrocarbons. These were carried out to completion at 110 °C, and the product distribution was assayed by ^{31}P{^{1}H} NMR spectroscopy. These experiments will not paint a detailed picture of C−H bond selectivity, which is undoubtedly highly complex.[32] Results for the chosen hydrocarbons are shown in Table 1. Given that the products are formed under irreversible conditions, these are taken to be kinetic ratios characteristic of the reactive transient. The near identity (experiments a and b) of hexane and heptane in the competition with cyclopentane is consistent with these linear alkanes being reactive preferentially at primary (methyl) C−H bonds. Experiments c and d confirm this and show that aryl C−H bonds are not competitive in terms of formation of irreversible product(s) and that the transient is indiscriminate (i.e., highly reactive) between *n*-alkane and ethylbenzene methyl group C−H bonds. On a per-bond basis, the reactivity ratios are benzyl CH_3 (8.0) > alkyl CH_3 (4.5) > CH_2 (1.0).

Table 1. Product Yields in Competition between Hydrocarbons for (PNP)Re(H)$_2$(cyclooctyne)

reagents	product mole ratio
n-hexane/cyclopentane	**12c**:**6a** = 73:27
n-heptane/cyclopentane	**12d**:**6a** = 73:27
n-hexane/ethylbenzene	**12c**:**12h** = 52:48
n-heptane/ethylbenzene	**12d**:**12h** = 53:47

DFT Computational Study. The questions we hoped to answer with these computations are the following: (a) What are the thermodynamics of synthesis of the cyclooctyne complex, and how necessary is accompanying cyclohexane hydrogenation? (b) Is cyclooctane production (eq 2) required for favorable alkane dehydrogenation to carbyne, or is cyclooctene (eq 3)

$$\text{(PNP)Re(H)}_2\text{(cyclooctyne)} + \text{H}_3\text{CR} \rightarrow \text{(PNP)ReH(}{\equiv}\text{CR)} + (\text{CH}_2)_8 \quad (2)$$

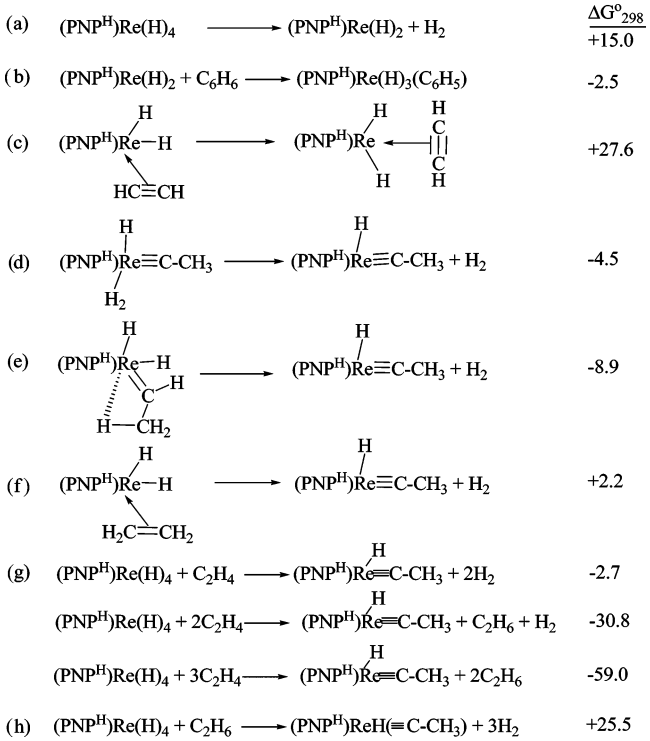
$$\text{(PNP)Re(H)}_2\text{(cyclooctyne)} + \text{H}_3\text{CR} \rightarrow \text{(PNP)ReH(}{\equiv}\text{CR)} + \text{H}_2 + \text{cyclo-C}_8\text{H}_{14} \quad (3)$$

sufficient? (c) Are there any mechanisms whose intermediates have such a high energy that they can be excluded? (d) How do reaction thermodynamics help to understand the lack of equilibrium production of phenyl complexes from benzene with (PNP)Re(H)$_4$, but detectable phenyl products from (PNP^{iPr})Re(H)$_2$(=C(CH$_2$)$_5$)? (e) What is special about the norbornene substrate that causes η^2-olefin and carbene to be in near thermoneutral equilibrium, and why is this the only case where C−C bond scission is observed? (f) Is the norbornylidene isomer β-agostic? (g) What are the thermodynamics of production of (PNP)ReH(η^3-allyl) + free H_2 vs the (PNP)ReH$_2$ (carbene) or η^2-olefin isomers? (h) Is (PNP)Re(H)$_2$(=C(CH$_3$)R) β-agostic, or is this a feature specific to cyclic carbenes?

Features we have already established from our analogous study of *acyclic* alkenes focus on the interconversion between monosubstituted carbenes (PNP)Re(H)$_2$[=CH(R)] and the hydrido carbynes (PNP)ReH(≡CR), so these are complementary to the present paper, in which conversion to carbyne encounters a new and demanding feature: C−C bond scission. Previously established features (Scheme 8) are the following:[2,24] (1) (PNP^H)Re(H)$_2$, while highly reactive (eq b), is too endergonic (eq a) by H_2 loss from (PNP^H)Re(H)$_4$ to be an intermediate in the reactions of unsaturated hydrocarbons with the latter at 22 °C. (2) (PNP^H)Re(H)$_2$(η^2-HCCH) is more stable as the less symmetric isomer (eq c); this is also true for the analogous η^2-H$_2$C=CH$_2$ adduct. (3) H_2 loss from (PNP^H)Re(H)$_3$(≡CCH$_3$) is favorable (eq d), an effect attributed to product stabilization by π-donation from amide N to Re. (4) Dehydrogenation of (PNP^H)Re(H)$_2$(=C(H)CH$_3$) is also favorable (eq e). The β-agostic methyl C−H donor contributes to this rotamer being more stable than that with the carbene plane rotated 180°. (5) Ethylene

(28) For a thoughtful discussion of the uniqueness of norbornene in this regard, see: Budzelaar, P. H. M.; Moonen, N. N. P.; DeGelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2000**, 753.
(29) Yamamoto, Y.; Ohno, T.; Itoh, K. *Organometallics* **2003**, *22*, 2267.
(30) Gorski, M.; Kochel, A.; Szymanska-Buzar, T. *Organometallics* **2004**, *23*, 3037.
(31) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1978**, *100*, 4918.
(32) Vetter, A. J.; Flaschenriem, C.; Jones, W. D. *J. Am. Chem. Soc.* **2005**, *127*, 12315.

Scheme 8

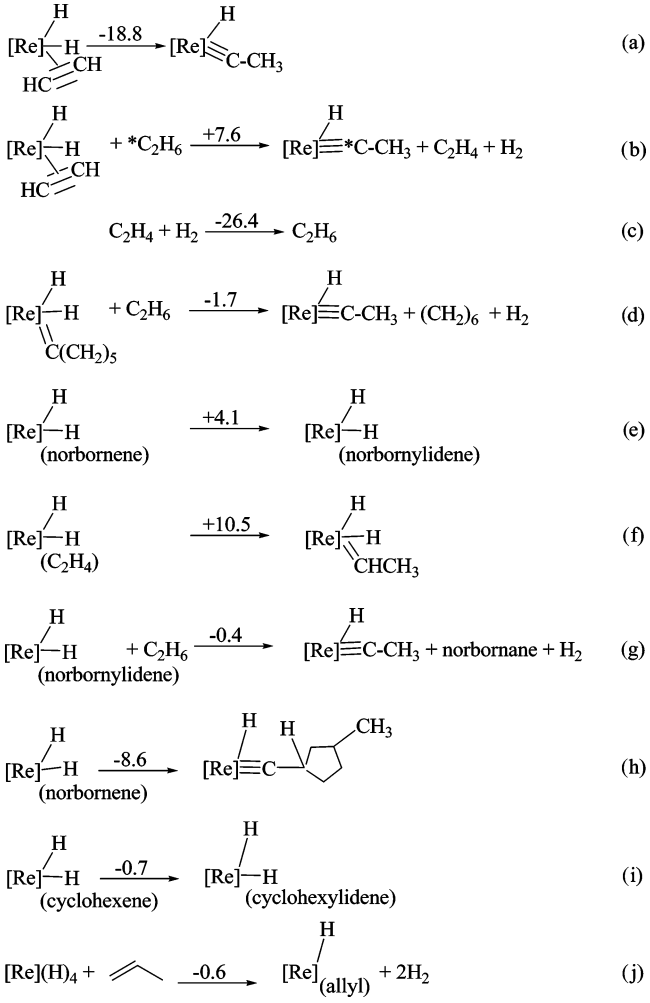


conversion to carbyne and free H_2 is (just barely) favorable, but hydrogenation of available ethylene can dramatically improve the reaction free energy (eqs f and g). (6) Dehydrogenation of ethane by $(PNP^H)Re(H)_4$ is unfavorable (eq h). However, if it were possible to make a species more reactive than $(PNP^H)Re(H)_4$, this challenging reaction might be accomplished. The present paper deals with this goal. The computational method is detailed in the Experimental Section.

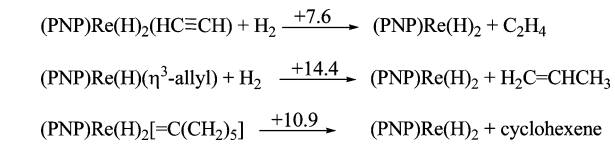
Equation a of Scheme 9 shows that the alkyne isomer is less stable than the alkylidyne, so the cyclooctyne complex contains additional unused chemical potential. However, eq b shows that the alkyne complex lacks the ability to dehydrogenate ethane (or a longer chain alkane, as in the present experimental work) until the ethylene released is hydrogenated to alkane (add eq c to eq b). Equation d shows that the somewhat more "hydrogen rich" cyclohexylidene complex (vs alkyne complex) does have the chemical potential to dehydrogenate ethane, even when free H_2 is the product.

Equation e shows that the η^2-norbornene isomer is more stable than the norbornylidene isomer, in agreement with experiment, and comparison to eq f shows that the norbornyl fragment makes the carbene isomer more thermodynamically accessible (i.e., less unfavorable) than for ethylene. The cyclic C_6 case (eq i) actually reverses the relative stability of these two isomers, accomplishing something that was not true of $RuHCl(P^iPr_3)_2$ as the π-base. Comparison of eq g with eq d shows that the norbornylidene and the cyclohexylidene complexes are comparable in their thermodynamic potential for ethane dehydrogenation. Conversion of $(PNP)Re(H)_4$ by equimolar propylene to $(PNP)ReH(\eta^3\text{-allyl}) + 2H_2$ is nearly thermoneutral, but this observed conversion (with cyclododecene) will be further stabilized by hydrogenation of olefin to alkane; this explains the observed production of the unique allyl product **9**. Equation h shows that C−C bond rupture is favorable, in accord with experiment.

Scheme 9



Scheme 10 [a]



[a] $\Delta G°_{298}$ in kilocalories per mole.

Another provisional way to rank the chemical potential in the three alkane dehydrogenation precursors employed here is shown in Scheme 10 ($\Delta G°_{298}$ values given in kilocalories per mole). Since the product is, in each case, an olefin and the same metal species, the most positive standard free energy change involves the "most stable" reagent complex. By this criterion, the highest chemical potential is the alkyne complex and the lowest the η^3-allyl. Calculations show that $(PNP)Re(H)_2(HCCH)$ lacks the thermodynamic potential to convert cyclohexane to coordinated cyclohexylidene (eq 7, $\Delta G°_{298}$ given in kilocalories per mole).

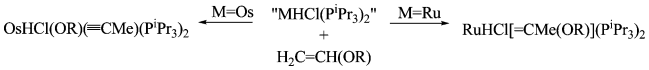
$$(PNP)Re(H)_2(HC{\equiv}CH) + (CH_2)_6 \xrightarrow{+10.5} (PNP)Re(H)_2[{=}C(CH_2)_5] + C_2H_4 \quad (7)$$

Selected Structural Features. Those structures calculated (on a simplified $(H_2PCH_2SiH_2)_2N^-$ model) for which an X-ray structure has been determined showed agreement (see the

Table 2. Selected Structural Features (Å) of DFT-Optimized Species $[(H_2PCH_2SiH_2)_2N]Re(ligand)$

	Re–N	Re–C	Re···C_{ag}	Re···H_{ag}	C–C
$(PNP^H)Re(H)_2(\eta^2$-norbornene)	2.129	2.212, 2.212	2.991	2.430	1.443
$(PNP^H)Re(H)_2(HC{\equiv}CH)$	2.131	2.013, 2.013			1.315
$(PNP^H)Re(H)_2$(cyclohexylidene)	2.183	1.897	2.671	2.471	
$(PNP^H)Re(H)_2$(norbornylidene)	2.158	1.904	2.861	2.848	
$(PNP^H)Re(H)_2(\eta^2$-cyclohexene)	2.136	2.226, 2.249	3.075	2.410	1.430
$(PNP^H)Re(H)(C_3H_5)$	2.030	2.178, 2.244, 2.378			1.437, 1.402

Scheme 11



Supporting Information) sufficient to create confidence in those calculated structures where an experimental determination is lacking. For example, $(PNP^H)Re(H)_2(HC{\equiv}CH)$ has the alkyne C≡C bond eclipsing the P−Re−P plane and Re−C and C−C distances (2.01 and 1.32 Å) which compare well with those in Figure 4. The calculation also captures well the unusually small −(P−Re−P) (150.3° vs 145.8° in Figure 4).

Cyclohexene and norbornene bind to the $(PNP)Re(H)_2$ fragment similarly to η^2-olefin complexes, judging by their Re−C bonds and leaving the C−C distance shorter (by 0.12 Å). The optimized geometry for coordinated cyclohexene puts one H on C4 (i.e., not an allylic H) with a close contact to Re. The η^3-allyl complex has the allyl group oriented as observed in the X-ray structure of **13**.

As shown in Table 2, the agostic CH···Re interaction is much weaker or essentially absent in coordinated norbornylidene vs coordinated cyclohexylidene. This is inversely reflected in the Re−N distances (i.e., increased N → Re π-donation when the agostic disappears). This may be related to the fact that the agostic donor in the norbornylidene is a (less flexible) bridgehead C−H. This destabilization of the norbornylidene may be a factor favoring the thermodynamics of C−C cleavage for the caged C_7 compound.

Summary

The reaction chemistry we reported earlier[33] for $[RuHCl(P^iPr_3)_2]_2$ showed that an unsaturated species devoid of strong π-acid ligands (which diminish the π-basicity of the metal center) had the ability to isomerize olefins carrying a donor substituent (e.g., OR or NR_2) into Fischer carbenes bound to Ru. This Ru also doubly dehydrogenated tetrahydrofuran and *N*-alkyltetrahydropyrroles into their corresponding metal carbene complexes.[33] However, $[RuHCl(P^iPr_3)_2]_2$ lacked the ability to convert an olefinic hydrocarbon to a non-heteroatom-substituted carbene complex. A 5d metal is generally more reducing than its 4d analogue, and this simple idea rationalizes why $Os(H)_3Cl(P^iPr_3)_2$ (this was used in place of the unknown $OsHCl(P^iPr_3)_2$) transforms the above substrates more dramatically, sacrificing the donor substituent from carbon to form a saturated carbyne isomer of the ruthenium products (Scheme 11).

In seeking still more reducing power to accomplish transformations of non-donor-substituted hydrocarbons, we turned to a stronger π-donor substituent to replace chloride; for this, we chose amide. The pincer ligand class pioneered by Fryzuk[34] combined this donor with protection (via the $SiMe_2$ substituents) against β-H migration to which late-transition-metal $N(alkyl)_2$ ligands are vulnerable.[35] The Fryzuk ligand also permits installing variable steric protection at the two phosphorus donor centers to prevent the dimerization which could destroy the unsaturation we hoped to maintain. Finally, we wanted not only the higher reducing power of a 5d metal, but one which has a lower oxidation state than the +2 of our Ru chemistry. We therefore settled on $(PNP^R)Re$ as our goal. Isolated $(PNP)Re^I$ complexes remain inaccessible. We also have no evidence that this low oxidation state is ever reached in the reactions we have studied. It is likely that Re^{III} is the lowest oxidation state accessible in this chemistry. This only reinforces the notion of $(PNP)Re^I$ being an exceptionally reactive, reducing fragment. Furthermore, even though $(PNP)Re^I$ compounds many not have been involved at all, it is convenient to analyze the results from the point of view of the thermodynamic preferences of the $(PNP)Re^I$ fragment. Magnesium reduction of $(PNP^R)ReOCl_2$ proceeded best in the presence of H_2, which then represented a compromise in that we produce $(PNP^R)Re(H)_4$. To reach the desired lower formal oxidation state, we explored scavenging H from $(PNP^R)Re(H)_4$ using sacrificial olefins, which then become the substrate for the more unsaturated transient "(PNP^R)-Re" moiety. In fact, operationally unsaturated $(PNP^R)Re(H)_4$ reacts under mild conditions with olefins, which are indeed hydrogenated and also converted to rearranged hydrocarbon fragments which, being more π-acidic than olefins, are more suited to accommodate the strong π-basicity (reducing power) of the $(PNP^R)Re$ moiety: carbenes, carbynes, a cycloalkyne, conjugated dienes, an allyl, and even a cyclopentadienyl. At 90 °C, a C−C bond of a coordinated norbornyl skeleton is cleaved on the basis of the evident thermodynamic driving force to form a carbyne ligand. These isomerizations of olefins to non-heteroatom-stabilized carbenes are of interest in understanding olefin metathesis catalyst generation when no obvious carbene precursor is supplied and show that a sufficiently reducing metal complex can isomerize an olefin substrate to the necessary carbene complex,[1] provided a hydride ligand is available. In the norbornene case we describe, the carbene complex forms on mixing at 22 °C and is in thermal equilibrium with its olefin isomer.

A brief study shows that the ^{t}Bu substituents in $(PNP^{tBu})Re(H)_4$ apparently shield the metal so effectively that internal olefins cannot react. Cyclohexyl substituents pendent on the reactive rhenium transient are effectively "cannibalized", via triple dehydrogenation, but this ligand degradation reaction can be minimized by feeding excess olefin substrate, so that the bimolecular reaction becomes at least competitive. Because the cyclohexyl carbons that are attacked are those farthest from phosphorus (a fact consistent with intramolecular attack and requisite flexibility to get these C−H bonds back to the reactive

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center of the molecule), an effective antidote is to employ the otherwise sterically similar isopropyl substituent in place of cyclohexyl. While steric factors play a large role in (PNP^R)Re chemistry, the norbornyl species **10** and **11** show considerable tolerance of substrate bulk, and adduct **12a***, containing two norbornyl-derived units, is especially noteworthy. The frequently formed **13** is an especially sterically efficient way to satisfy the electronic demands of the (PNP)Re fragment.

Certain of the molecules we have produced from cyclic olefins, which are thus frustrated from reaching their thermodynamic minimum, (PNP)ReH(≡CR), have been examined as possible reagents for alkane conversion to unsaturated fragments. Each successful example has the ability to accept 2H from the alkane, as predicted in eq 1a. Most studied is the cyclooctyne complex **8**. It effectively converts methyl groups to the carbyne complexes **12**, with ethyl groups reacting faster than (hindered) methyl groups and benzylic methyls showing no major advantage. The lack of formation of any η^6-arene complexes is suggested to be due to the PNP ligand high electron donor number and also its steric bulk. The driving force for binding the smaller η^5-C_5H_4R (R = H or CH_3) is evidently strong, however, since it ultimately forms in every reaction of cyclopentane or methylcyclopentane and then by H migration to the pincer amide nitrogen, generating a pendent secondary amine; this amide nitrogen is thus not only an electron pump/acceptor when PNP is bound η^3 to a metal, but it is also a reactive functionality, involved in bond breaking and making. The allyl monohydride complex **9** also shows an ability to dehydrogenate *n*-heptane. Prerequisite for (PNP)ReL_x species to serve as alkane dehydrogenation reagents is thus the ability to expel the ligands L_x, especially as an alkane, and that L_x cannot rearrange to a carbyne without C−C bond scission.

The idea of "stripping" H ligands from an L_nMH_m species with a sacrificial olefin (e.g., ^{t}BuHC═CH_2) has a long tradition as a way to create a transient capable of attacking unreactive substrates (e.g., alkanes, N_2) and lies at the core of catalytic alkane dehydrogenation, based on the core 14-electron fragment (pincer) Ir^I operating above 200 °C; there, *mechanistic* details have been more carefully established[36] than in our present survey of general reagent features and substrate capability. Here, as there, it is necessary to design the supporting ligand to be resistant to intramolecular attack by the reactive metal center, and analogous cases where a cyclohexyl on phosphorus is dehydrogenated under "hydrogen-poor conditions" (i.e., excess sacrificial olefin) have been reported.[37−39] Our work here has identified additional general principles, as well as unusual structural features of some intermediates and final products. In sum, these establish the (PNP^R)Re fragment as one with the ability to attack unreactive H−C(sp^3) bonds, to make an η^2-olefin/carbene isomerization nearly thermoneutral, and even to cleave C−C bonds. It is accessible to reactants at 22 °C because of the operationally unsaturated character of (PNP)Re$(H)_4$, and the H ligands there represent cooperative leaving groups.

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Experimental Section

General Considerations. All manipulations were performed using standard Schlenk techniques or in an argon-filled glovebox unless otherwise noted. Aliphatic and aromatic hydrocarbons (except norbornene) were dried over and distilled or vacuum transferred from NaK/benzophenone/18-crown-6. Norbornene was dried and vacuum transferred from Na/K alloy into a sufficiently wide mouthed vessel that allowed retrieval of solid norbornene with a spatula. The preparation of compounds **1a**,[2] **1b**,[3] **1c**,[2] **2b**[3], and **8**[17] was described previously. ^{1}H NMR chemical shifts are reported in parts per million relative to the peak for protio impurities in the deuterated solvents. ^{31}P spectra are referenced to external standards of 85% H_3PO_4 (at 0 ppm). NMR spectra were recorded with a Varian Gemini 2000 (300 MHz, ^{1}H; 121 MHz, ^{31}P; 75 MHz, ^{13}C), a Varian Unity Inova instrument (400 MHz, ^{1}H; 162 MHz, ^{31}P; 101 MHz, ^{13}C), or a Varian Unity Inova instrument (500 MHz, 1H; 126 MHz, ^{13}C). Elemental analyses were performed by CALI, Inc. (Parsippany, NJ). ORTEP plots were generated using Ortep-3 for Windows.[40] Full details of compounds not shown below are available as Supporting Information.

Computational Details. All calculations were performed with the Gaussian 98 package[41] at the B3PW91[42] level of theory, with unrestricted wave functions used for all triplet-state calculations. Basis sets used included LANL2DZ for Re and Si and 6-31G** for C, N, and H.[43] The basis set LANL2DZ is the Los Alamos National Laboratory ECP plus a double-ζ valence on Re, P, and Si;[44] additional d polarization functions[45] were added to all phosphorus and silicon atoms in all DFT calculations. All optimizations were performed with C_1 symmetry, and all minima were confirmed by analytical calculation of frequencies, which were also used to compute zero-point energy corrections without scaling.

(PNP^{iPr})ReH_2(═C(CH_2)$_5$) (2a). (PNP^{iPr})ReH_4 (**1a**) (60 mg, 103 μmol) was dissolved in 0.5 mL of cyclohexene. The mixture was allowed to stand for 30 min, during which time the color became orange. The volatiles were removed in vacuum, and the oily residue was dissolved in cyclohexane-d_{12} for NMR characterization. The product thus obtained was 99% pure by NMR, but all attempts to crystallize it failed. ^{1}H NMR (C_6D_{12}): δ 2.53 (br m, 2H, CH_2), 1.55−1.65 (8H, CH_2 and PCH overlapping), 1.35−1.45 (CH_2 overlapping with $C_6D_{11}H$), 2.65 (m, J_{HH} = 7 Hz, 2H, PC*H*), 1.15 (AB dvt, J_{HH} = 15 Hz, J_{HP} = 4 Hz, 2H, PCH_2Si), 1.00−1.12 (four apparent q (dvt) overlapping, for each 8 Hz, 6H, PCHCH_3), 0.65 (AB dvt, J_{HH} = 15 Hz, J_{HP} = 4 Hz, 2H, PCH_2Si), 0.15 (s, 6H, SiCH_3), 0.10 (s, 6H, SiCH_3), −6.7 (v br, 1H, Re*H*), −10.0 (v br, 1H, Re*H*). ^{31}P{^{1}H} NMR (C_6D_{12}): δ 47.4 (s). ^{31}P NMR (C_6D_{12}), selectively decoupled from alkyl hydrogens: δ 47.4 (t, 12 Hz). ^{13}C{^{1}H} NMR (C_6D_{12}): δ 264.9 (t, 9 Hz, Re═*C*), 57.4 (s, Re═CCH_2), 30.2 (t, 9 Hz, P*C*H), 29.9 (s, CH_2), 29.5 (t, 14 Hz, P*C*H), 27.3 (s, CH_2), 25.7 (s, CH_2), 20.3 (s, PCH*C*H_3), 19.9 (s, PCH*C*H_3), 19.0 (br s, 2 s overlapping, PCH*C*H_3), 15.9 (br s, PCH_2Si), 15.6 (s, Re═CCH_2), 5.6 (s, Si*C*H_3), 5.4 (br s, Si*C*H_3). ^{13}C NMR (selected resonances, C_6D_{12}): δ 57.4 (t, J_{CH} = 127 Hz, Re═CCH_2), 15.6 (t, J_{CH} = 117 Hz, Re═CCH_2).

Thermolyses of 2a. (i) In Heptane + 0 equiv of Cyclohexene. 2a was prepared in situ from **1a** (52 mg, 89 μmol) and cyclohexene (150 μL, 1480 μmol) in heptane. The volatiles were removed, and the residue (free from cyclohexene) was redissolved in 0.6 mL of heptane. NMR

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analysis indicated a >99% purity of **2a**. This solution was allowed to stand at 22 °C for 24 h, but only traces of **1**, **12d**, and **3** were observed. After 1 h at 90 °C a 27:60:0:13 ratio of **1a**, **12d**, **2a**, and **3** was observed.

(ii) In Heptane + 8 equiv of Cyclohexene. 1a (30.0 mg, 51.5 μmol) and cyclohexene (52.2 μL, 515 μmol) were mixed in 0.6 mL of heptane. NMR analysis indicated quantitative conversion to **2a**. This solution was heated at 90 °C for 2 h, resulting in a 15:85 mixture of **12d** and **3**. Further heating (90 °C) did not change this ratio.

(iii) In Heptane + 2 equiv of Cyclohexene. 1a (39.6 mg, 68.0 μmol) and cyclohexene (27.5 μL, 272 μmol) were mixed in 0.6 mL of heptane. NMR analysis indicated quantitative conversion to **2a**. This solution was heated at 110 °C for 40 min, resulting in a 43:57 mixture of **12d** and **3**. Further heating (110 °C) did not change this ratio.

(iv) In Neohexane + 1.3 equiv of cyclohexene. 1a (39.6 mg, 68.0 μmol) and cyclohexene (22.6 μL, 224 μmol) were mixed in 0.6 mL of neohexane. NMR analysis indicated quantitative conversion to **2a**. This solution was heated at 110 °C for 18 h, resulting in a 8:92 mixture of **12g** and **3**.

Reaction of 2a with C_6H_6. 1a (20.0 mg, 34.3 μmol) was dissolved in 0.1 mL (ca. 1 mmol) of cyclohexene. The reaction mixture turned orange. The mixture was allowed to stand for 1 h, and then the volatiles were removed. The residue was dissolved in cyclohexane, and then the volatiles were removed. The residue was dissolved in C_6H_6, and the evolution of this solution was monitored by ^{31}P NMR. After 10 min at 22 °C the mixture consisted of a 35:65 mixture of the tentatively identified (PNP^{iPr})ReH$_3$Ph [^{31}P{^{1}H} NMR (C_7D_8): δ 57.1 (s)] and **2a**. This corresponds to $K_{eq} \approx 1 \times 10^{-3}$ ($\Delta G \approx +4$ kcal/mol) for the displacement of C_6H_{10} by C_6H_6. The mixture was allowed to stand for 24 h at 22 °C. The ratio of (PNP^{iPr})ReH$_3$Ph to **2a** did not change significantly, and traces of **5a**, **1a,** and a few unidentified compounds were observed. Dissolution of **2a** (from 50.0 mg (86.8 μmol) of **1a**) in benzene in the presence of excess (87 μL or 860 μmol) cyclohexene does *not* lead to formation of (PNP^{iPr})ReH$_3$Ph; only **2a** was present. Upon dissolution of **2a** in toluene, a broad resonance (or overlapping resonances) at δ ca. 57 ppm was also observed in the ^{31}P NMR spectrum.

(PNP^{Cy})ReH$_2$(=C(CH$_2$)$_5$) (2b) was reported previously.[18]

Thermolysis of 2b. (i) In Solution. A crystalline sample of **2b** (15 mg, 18 μmol) was dissolved in heptane and heated at 90 °C for 30 min. Subsequent NMR analysis detected a 1:2 mixture of **1b** and **13**.

(ii) In the Solid State. A crystalline sample of **2b** (15 mg, 18 μmol) was heated (120 °C, 30 min, in vacuo) in a vacuum transfer apparatus, on the other end of which a J. Young tube with 0.6 mL of C_6D_6 was attached and frozen in liquid nitrogen to trap the volatile products. The solid turned red-purple upon thermolysis. The trap was thawed and analyzed by ^{1}H NMR spectroscopy. A mixture of cyclohexene and cyclohexane in a 55:45 ratio was observed. The purple-red residue was dissolved in C_6D_6 and analyzed by ^{31}P NMR spectroscopy. A 63:37 mixture of **13** and **1b** was measured. If all of **2b** underwent a thermal loss of the C_6 fragment in a 55:45 ratio of C_6H_{10} to C_6H_{12}, then a theoretical ratio of 61:39 of **13** to **1b** would have been expected in the residue.

(κ^2-*P,P*-PN(H)P^{Cy})ReH$_2$(η^5-Cp) (6b). (PNP^{Cy})ReH$_4$ (**1b**) (200 mg, 260 μmol) was dissolved in 2 mL of heptane, and cyclopentene (0.3 mL, 3.5 mmol) was added to it. The mixture was heated at 90 °C for 3 h, and then the resultant colorless solution was placed into the −30 °C freezer. The next day, colorless crystalline material was collected by decantation of the solvent. Yield: 0.186 g (89%). ^{1}H NMR (C_6D_6): δ 4.67 (s, 5H, η-C_5H_5), 1.20−2.08 (several m, 48H, PC$_6$*H*$_{11}$, PC*H*$_2$Si), 0.30 (s, 12 H, Si*Me*), −12.11 (t, 2H, 41 Hz, Re*H*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 75.0 (η-C_5H_5), 45.5 (m, P*C*H), 30.7 (s, C*H*$_2$ of Cy), 29.7 (s, C*H*$_2$ of Cy), 28.0 (t, 5 Hz, C*H*$_2$ of Cy), 27.8 (t, 5 Hz, C*H*$_2$ of Cy), 27.4 (s, C*H*$_2$ of Cy), 4.9 (s, Si*Me*). ^{31}P{^{1}H} NMR (C_6D_6): δ 16.8 (s). Anal. Calcd (Found) for $C_{35}H_{68}NP_2ReSi_2$ (**6b**): C, 52.08 (52.17); H, 8.49 (8.80); N, 1.74 (1.67).

Observation of (PNP^{iPr})ReH$_2$(=C(CH$_2$)$_7$) (7a). 1a (30.0 mg, 51.5 μmol) was dissolved in 0.6 mL of heptane and treated with cyclooctene (67 μL, 515 μmol). The evolution of the reaction mixture was followed by ^{31}P NMR. After 45 min at 22 °C, **7a** was observed (14%) along with the remaining **1a**. After 18 h at 22 °C, **8** was the major component (70%) along with a small amount of **7a**. After the mixture was heated at 90 °C for 2 h, complete conversion to **8** was observed. NMR data for **7a** follow. ^{31}P{^{1}H} NMR (C_7H_{16}): δ 45.8 (s). ^{31}P NMR, with selective decoupling of aliphatic hydrogens (C_7H_{16}): δ 45.8 (dd).

Observation of (PNP^{Cy})ReH$_2$(=C(CH$_2$)$_7$) (7b). 1b (41 mg, 53 μmol) was dissolved in 0.6 mL of heptane and treated with 0.1 mL of cyclooctene (0.77 mmol). The evolution of the reaction mixture was followed by ^{31}P and ^{1}H NMR. After 1.5 h at 22 °C, **7b** was observed (20%) along with unreacted **1b** (80%). The mixture was allowed to stand at 22 °C, and over 2 d, conversion to **13** was observed. Extensive H/D scrambling involving the C_6D_6 NMR solvent, cyclooctene, and the PNP ligand was registered. NMR data for **7b** follow. ^{1}H NMR (C_6D_6, selected resonances): δ 0.47 (s, 6H, Si*CH*$_3$), 0.42 (s, 6H, Si*CH*$_3$), −6.08 (br, 1H, Re*H*), −7.96 (br, 1H, Re*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 35.6 (br s).

(PNP^{iPr})ReH$_2$(cyclooctyne) (8) was reported previously.[17]

Decomposition of 8. **8** (30 mg, 44 μmol) was heated in 0.6 mL of cyclooctane for 48 h. After this time, ^{31}P NMR analysis indicated near complete disappearance of **8**. More than 30 resonances were observed by ^{31}P NMR in the 20−90 ppm region. Thermolysis of **8** (30 mg) in (a) cyclohexane, (b) 2,3-dimethylbutane, and (c) a 5:1 mixture of cyclohexane and SiMe$_4$ for 48 h at 110 °C led to essentially the same mixtures.

(PNP^{iPr})ReH(cyclododecenyl) (9). 1a (61 mg, 105 μmol) and cyclododecene (0.200 mL, 1.05 mmol, mixture of *cis*- and *trans*-isomers) were dissolved in 0.6 mL of hexamethyldisiloxane and heated for 3 h at 90 °C. The deep-blue solution was transferred to a 10 mL flask with a Kontes stopcock and dried in vacuo at 90 °C for 15 min. The oily residue was dissolved in 1 mL of a SiMe$_4$/pentane mixture and placed in the freezer at −30 °C for 2 days. The blue crystalline precipitate was isolated by decantation, washed with cold SiMe$_4$, and dried in vacuo. Yield: 56 mg (72%). Ten minutes after dissolution at 22 °C, NMR analysis shows a 10:1 mixture of isomers; after <1 h at 22 °C, the mixture equilibrates to a ca. 5:1 ratio. Anal. Calcd (Found) for $C_{30}H_{66}NP_2ReSi_2$ (**9**): C, 48.35 (48.26); H, 8.93 (8.88); N, 1.88 (1.79).

Data for the Major Isomer of 9. ^{1}H NMR (C_6D_6): δ 4.11 (m, 1H, allyl CH), 2.99 (m, 1H, allyl CH), 2.81 (m, 1H, allyl CH), 2.49 (br d, 12 Hz, 1H), 2.24 (quintet, 6 Hz, 1H), 1.3−2.05 (several m, C_{12} ring CH_2 groups and PCH groups), 1.23 (dd, 8 Hz, 13 Hz, 3H, PCHC*H*$_3$), 1.15 (dd, 8 Hz, 13 Hz, 3H, PCHC*H*$_3$), 1.09 (dd, 8 Hz, 13 Hz, 3H, PCHC*H*$_3$), 1.05 (2 dd overlapping, 6H, PCHC*H*$_3$), 0.99 (2 dd overlapping, 6H, PCHC*H*$_3$), 0.75 (dd, 8 Hz, 13 Hz, 3H, PCHC*H*$_3$), 0.63 (s, 3H, SiC*H*$_3$), 0.59 (s, 3H, SiC*H*$_3$), 0.28 (s, 3H, SiC*H*$_3$), 0.12 (s, 3H, SiC*H*$_3$), −11.96 (dd, 14 Hz, 20 Hz, 1H, Re*H*). PC*H*$_2$Si proton signals are concealed by other aliphatic resonances. ^{31}P{^{1}H} NMR (C_6D_6): δ 30.0 (AB d, 241 Hz), 26.1 (AB d, 241 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 71.6 (s, CH of the C_{12} ring), 46.7 (s, CH of the C_{12} ring), 42.8 (s, CH of the C_{12} ring), 36.8 (s), 32.6 (d, 26 Hz, P*C*H), 33.5 (s), 31.3 (d, 25 Hz, P*C*H), 29.8 (s), 29.4 (s), 28.4 (s), 25.0−27.5 (several s, P*C*H and *C*H$_2$ or the C_{12} ring), 21.1 (s, PCH*C*H$_3$), 20.1 (s, PCH*C*H$_3$), 19.44 (s, PCH*C*H$_3$), 19.39 (s, PCH*C*H$_3$), 19.30 (s, PCH*C*H$_3$), 18.9 (s, PCH*C*H$_3$), 18.4 (s, PCH*C*H$_3$), 17.2 (s, PCH*C*H$_3$), 13.5 (s, P*C*H$_2$Si), 11.3 (s, P*C*H$_2$-Si), 7.9 (s, Si*C*H$_3$), 6.6 (s, Si*C*H$_3$), 5.0 (2 s overlapping, Si*C*H$_3$).

Data for the Minor Isomer of 9. ^{1}H NMR (C_6D_6): δ 4.22 (m, 1H, allyl CH), 3.69 (m, 1H, allyl CH), 3.38 (m, 1H, allyl CH), 0.49 (s, 3H, SiC*H*$_3$), 0.41 (s, 3H, SiC*H*$_3$), 0.34 (s, 3H, SiC*H*$_3$), 0.31 (s, 3H, SiC*H*$_3$), −11.91 (dd, 14 Hz, 20 Hz, 1H, Re*H*). Other resonances are obscured and cannot be reliably assigned. ^{31}P{^{1}H} NMR (C_6D_6): δ 29.4 (AB d, 243 Hz), 28.6 (AB d, 243 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 67.2 (s, CH of the C_{12} ring), 46.1 (s, CH of the C_{12} ring), 42.1 (s, CH of the C_{12}

ring), multiple singlets in the 16−36 ppm region cannot be reliably assigned, 10.7 (s, P*C*H$_2$Si), 9.8 (s, P*C*H$_2$Si), 7.8 (s, Si*C*H$_3$), 6.4 (s, Si*C*H$_3$), 5.9 (2 s overlapping, Si*C*H$_3$).

Alkane Activation by 9. 1a (15.0 mg, 25.8 μmol) and cyclododecene (16.4 μL, 85.0 μmol) were dissolved in 0.6 mL of heptane. This mixture was heated and periodically monitored by NMR. The ratio of **1a** to **12d** to **9** observed after (a) 2 h at 22 °C was 99:0:1, (b) that after 1.5 h at 90 °C was 41:3:56, (c) that after 18 h at 90 °C was 13:63:24, and (d) that after 3 h at 110 °C was 2:98:0. The volatiles were removed from the mixture, and the red residue was dissolved in C_6D_6. ^{1}H, ^{13}C, and ^{31}P NMR data were collected and were identical to **12d** obtained by other methods.

(PNP$^{i\mathrm{Pr}}$)ReH$_2$(norbornene) (10a) and (PNP$^{i\mathrm{Pr}}$)ReH$_2$(norbornylidene) (11a). 1a (30 mg, 52 μmol) was dissolved in 0.6 mL of pentane and treated with norbornene (34 mg, 360 μmol). The mixture immediately became deep blue-purple, and NMR analysis showed essentially quantitative conversion to the products. The volatiles were removed in a vacuum, and the residue was redissolved in 0.5 mL of $Me_3SiOSiMe_3$ and placed in the freezer at −30 °C overnight. The blue-purple crystals were separated by decantation, washed with cold $SiMe_4$, and dried in vacuo. Yield: 31 mg (89%). Upon dissolution, a mixture of **10a** and **11a** was observed by NMR (ca. 8:1 ratio) in solution. Anal. Calcd (Found) for $C_{25}H_{56}NP_2ReSi_2$ (**10a**/**11a**): C, 44.48 (44.32); H, 8.36 (8.42); N, 2.07 (1.97).

Data for the Major Isomer (Norbornene Complex 10a). ^{1}H NMR (C_7D_8): δ 3.01 (br s, 2H), 2.67 (br s, 2H), 2.65 (m, J_{HH} = 7 Hz, 2H, PC*H*), 1.80 (m, J_{HH} = 7 Hz, 2H, PC*H*), 1.59 (AB dvt, J_{HH} = 15 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$Si), 1.51 (br, 4H), 1.25 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.11 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.08 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.06 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 0.64 (AB dvt, J_{HH} = 15 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$Si), 0.39 (s, 6H, SiC*H*$_3$), 0.25 (s, 6H, SiC*H*$_3$), −1.51 (d, 8 Hz, 1H), agostic CH, −12.7 (v br, 1H, Re*H*), −15.8 (v br, 1H, Re*H*). ^{1}H NMR (C_7D_8, −40 °C, selected resonances): δ −12.65 (t, 10 Hz, 1H, Re*H*), −15.82 (t, 21 Hz, 1H, Re*H*). ^{31}P{^{1}H} NMR (C_7D_8): δ 44.4 (s). ^{13}C{^{1}H} NMR (C_7D_8): δ 48.9 (s, norbornene), 38.8 (t, 6 Hz, norbornene), 34.9 (s, norbornene), 33.1 (s, norbornene), 32.6 (t, 12 Hz, P*C*H), 28.7 (t, 9 Hz, P*C*H), 20.2 (s, PCH*C*H$_3$), 19.7 (s, PCH*C*H$_3$), 18.7 (s, PCH*C*H$_3$), 18.6 (s, PCH*C*H$_3$), 16.1 (br s, P*C*H$_2$Si), 5.9 (s, Si*C*H$_3$), 4.5 (br s, Si*C*H$_3$).

Data for the Minor Isomer (Norbornylidene Complex 11a), Selected Resonances. ^{1}H NMR (C_7D_8, −40 °C): δ −5.98 (br s, Re*H*), −13.04 (br s, Re*H*); at 22 °C the hydride peaks are too broad to be detected. ^{13}C{^{1}H} NMR (C_7D_8): δ 281.0 (br, Re=*C*). ^{31}P{^{1}H} NMR (C_7D_8): δ 51.6 (AB d, 187 Hz), 47.1 (AB br d, 187 Hz).

(PNP$^{\mathrm{Cy}}$)ReH$_2$(norbornene) (10b) and (PNP$^{\mathrm{Cy}}$)ReH$_2$(norbornylidene) (11b). 1b (44 mg, 56 μmol) was dissolved in 0.6 mL of C_6D_6 and treated with norbornene (35 mg, 380 μmol). The mixture turned purple immediately. Extensive H/D scrambling occurred as evidenced by the broad multiplets in the ^{31}P{^{1}H} NMR spectrum and the low intensity of the hydride signals. Because of the great congestion in the ^{1}H NMR spectrum, only selected resonances could be assigned. Removal of volatiles (including norbornene) and dissolution of the residue in toluene led to decomposition to a mixture of **13** and **1b**, complete in 24 h at 22 °C (the end ratio of **13** to **1b** was 2:1). NMR data for **10b** follow. ^{1}H NMR (C_6D_6): δ 0.49 (s, 6H, Si*Me*), 0.32 (s, 6H, Si*Me*), −1.47 (d, 8 Hz, 1H), agostic CH, −12.7 (v br, 1H, Re*H*), −15.9 (v br, 1H, Re*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 35.8 (br s). A minor (ca. 15%) isomer (**11b**) was also detected by ^{31}P NMR at δ 40.1 (br m). Anal. Calcd (Found) for $C_{37}H_{72}NP_2ReSi_2$ (**10b**/**11b**): C, 53.20 (52.98); H, 8.69 (8.51); N, 1.68 (1.69).

(PNP$^{i\mathrm{Pr}}$)ReH(≡C(3-methylcyclopentyl)) (12a) and (PNP$^{i\mathrm{Pr}}$)ReH(≡C(3-methylcyclopentyl))(norbornene) (12a*). 1a (40 mg, 68 μmol) was dissolved in 0.5 mL of heptane, and norbornene (32 mg, 340 μmol) was added to it. The mixture was heated for 2 h at 90 °C. NMR indicated complete conversion to **12a***. The volatiles were removed in vacuo, the oily residue was heated at 110 °C in vacuo for 2 h to convert **12a*** to **12a**, and then the residue was dissolved in C_6D_6 for NMR characterization.

Data for 12a. ^{1}H NMR (C_6D_6): δ 1.4−2.5 (several m, PCH and 3-methylcyclopentyl), 1.31 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.21 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.08 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.06 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 0.94 (d, 3H, 8 Hz, 3-*H*$_3$C(cyclopentyl)), 0.82 (AB dvt, J_{HH} = 14 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$Si), 0.78 (AB dvt, J_{HH} = 14 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$-Si), 0.370 (two s overlapping, 6H, SiC*H*$_3$), 0.324 (s, 3H, SiC*H*$_3$), 0.319 (s, 3H, SiC*H*$_3$), −10.57 (t, 15 Hz, Re*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 60.8 (s). ^{13}C{^{1}H} NMR (C_6D_6): 281.7 (br t, 12 Hz, Re≡*C*), 62.2 (s, Re≡C*C*H), 41.1 (s, methylcyclopentyl), 34.6 (s, methylcyclopentyl), 34.0 (s, methylcyclopentyl), 30.7 (s, methylcyclopentyl), 29.2−29.8 (4 overlapping m, P*C*H), 21.0 (t, 5 Hz, 1C, PCH*C*H$_3$), 20.8 (t, 5 Hz, 1C, PCH*C*H$_3$), 20.7 (s, methylcyclopentyl), 19.2 (br dd, 2C, PCH*C*H$_3$), 19.1 (br t, 2C, PCH*C*H$_3$), 17.2 (br s, 2C, PCH*C*H$_3$), 10.4 (br s, P*C*H$_2$Si), 7.5 (s, 1C, Si*C*H$_3$), 7.4 (s, 1C, Si*C*H$_3$), 6.3 (br dd, 2C, Si*C*H$_3$).

Data for 12a*. ^{1}H NMR (C_6D_6, selected resonances): δ 0.26 (s, 6H, SiC*H*$_3$), 0.19 (s, 6H, SiC*H*$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 44.0 (s). ^{13}C{^{1}H} NMR (C_7H_{14}, selected resonance): 270.3 (t, 12 Hz, Re≡*C*).

(PNP$^{i\mathrm{Pr}}$)ReH(≡C*C*H$_2$Ph) (12h). 8 (25 mg, 36 μmol) was dissolved in 0.6 mL of ethylbenzene in a J. Young tube. The tube was inserted into a 110 °C oil bath. After 24 h the conversion was essentially quantitative by NMR. The volatiles were removed from the solution in vacuo, leaving behind a viscous red oil. It was redissolved in C_6D_6 for full NMR characterization. ^{1}H NMR (C_6D_6): δ 7.44 (d, 8 Hz, 2H, *o*-Ph), 7.16 (t, 8 Hz, 2H, *m*-Ph), 7.04 (t, 8 Hz, 1H, *p*-Ph), 2.85 (m, 2H, Re≡CC*H*$_2$), 1.91 (m, J_{HH} = 7 Hz, 2H, PC*H*), 1.75 (m, J_{HH} = 7 Hz, 2H, PC*H*), 1.18 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.11 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.03 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 0.96 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 0.83 (AB dvt, J_{HH} = 15 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$Si),), 0.73 (AB dvt, J_{HH} = 15 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$Si), 0.39 (s, 6H, SiC*H*$_3$), 0.33 (s, 6H, SiC*H*$_3$), −9.69 (t, 14 Hz, 1H, Re*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 60.34 (s). ^{13}C-{^{1}H} NMR (C_6D_6): δ 273.0 (t, 12 Hz, Re≡*C*), 136.2 (s, arom C), 128.8 (s, arom CH), 127.8 (s, arom CH), 126.2 (s, arom CH), 56.4 (s, Re≡C*C*H$_2$), 29.5 (t, 13 Hz, P*C*H), 29.0 (t, 11 Hz, P*C*H), 20.1 (s, PCH*C*H$_3$), 18.9 (s, PCH*C*H$_3$), 18.8 (s, PCH*C*H$_3$), 17.3 (s, PCH*C*H$_3$), 10.5 (s, P*C*H$_2$Si), 7.2 (s, Si*C*H$_3$), 6.3 (t, 2 Hz, Si*C*H$_3$).

Activation of C$_6$H$_n$Me$_{6-n}$. Three portions of **8** (each 25 mg, 36 μmol) were dissolved in 0.6 mL of toluene, *p*-xylene, and mesitylene, respectively. These solutions were thermolyzed at 110 °C for 24 h and then analyzed by ^{31}P NMR. In each case, the solution became brown-red and a ^{31}P NMR resonance assignable to an aryl-substituted carbyne emerged (ca. 40% for **12i**, ca. 50% for **12j**, ca. 60% for **12k**). Upon partial decoupling of aliphatic hydrogens, these ^{31}P NMR resonances were observed as doublets. The highly lipophilic nature of the resultant mixtures did not allow us to isolate the products in a pure state.

Data for 12i. ^{31}P{^{1}H} NMR (C_7H_8): δ 59.3 (s).

Data for 12j. ^{31}P{^{1}H} NMR (*p*-xylene): δ 59.4 (s).

Data for 12k. ^{31}P{^{1}H} NMR (mesitylene): δ 59.3 (s).

(PNP$^{i\mathrm{Pr}}$)ReH(≡C(cyclohexyl)) (12l). 8 (25 mg, 36 μmol) was dissolved in 0.6 mL of methylcyclohexane in a J. Young tube. The tube was inserted into a 110 °C oil bath. After 24 h the conversion was essentially quantitative by NMR. The volatiles were removed from the solution in vacuo, leaving behind a viscous red oil. It was redissolved in C_6D_6 for full NMR characterization. ^{1}H NMR (C_6D_6): δ 2.17 (m, J_{HH} = 7 Hz, 2H, PC*H*), 2.11 (m, 1H, Re≡CC*H*), 1.76 (m, J_{HH} = 7 Hz, 2H, PC*H*), 1.0−1.7 (several m of the CH_2 groups of cyclohexyl), 1.32 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.21 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.08 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.06 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 0.83 (AB dvt, J_{HH} = 14 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$Si), 0.75 (AB dvt, J_{HH} = 14 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$Si), 0.38 (s, 6H, SiC*H*$_3$), 0.33 (s, 6H, SiC*H*$_3$), −10.33 (t, 15 Hz, 1H, Re*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 61.13 (s). ^{13}C-{^{1}H} NMR (C_6D_6): δ 283.8 (t, 11 Hz, Re≡*C*), 60.9(s, Re≡C*C*H), 31.6

(s, CH_2 of cyclohexyl), 29.8 (t, 11 Hz, P*C*H), 29.3 (t, 13 Hz, P*C*H), 26.8 (s, CH_2 of cyclohexyl), 26.4 (s, CH_2 of cyclohexyl), 20.9 (s, PCH*C*H_3), 19.3 (s, PCH*C*H_3), 19.0 (s, PCH*C*H_3), 17.2 (s, PCH*C*H_3), 10.3 (s, P*C*H_2Si), 7.5 (s, Si*C*H_3), 6.3 (br s, Si*C*H_3).

(PNP^{iPr})ReH(≡C(cyclopentyl)) (12m) and (κ^2-*P*,*P*-PN(H)P^{iPr})-ReH$_2$(η^5-C$_5$H$_4$Me) (15). 1a (26 mg, 45 μmol) was dissolved in 0.5 mL of methylcyclopentane, and 0.2 mL cyclooctene was added to it. The mixture was heated at 110 °C for 18 h. A 77:23 mixture of **12m** and **15** formed (NMR evidence in situ). The volatiles were removed in vacuo, and the residue was redissolved in C_6D_6 for NMR characterization. Extensive overlap precluded assignment of all the ^{1}H NMR resonances in this mixture. Therefore, only selected NMR data are reported.

Data for 12m. ^{1}H NMR (C_6D_6): δ 1.30 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.21 (apparent q (dvt), 8 Hz, 6H, PCHC*H*$_3$), 1.02−1.14 (two apparent q (dvt) overlapping, 12H, PCHC*H*$_3$), 0.83 (AB dvt, J_{HH} = 14 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$Si), 0.76 (AB dvt, J_{HH} = 14 Hz, J_{HP} = 4 Hz, 2H, PC*H*$_2$Si), 0.37 (s, 6H, SiC*H*$_3$), 0.33 (s, 6H, SiC*H*$_3$), −10.58 (t, 15 Hz, 1H, Re*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 60.6 (s). ^{31}P NMR, with selective decoupling of aliphatic hydrogens (C_6D_6): δ 60.6 (d).

Data for 15. ^{1}H NMR (C_6D_6): δ 4.58 (br t, 2H, C*H* of η^5-C$_5$H$_4$-Me), 4.39 (br t, 2H, C*H* of η^5-C$_5$H$_4$Me), 0.24 (s, 12H, SiC*H*$_3$), −12.30 (t, 2H, 41 Hz, ReH). ^{31}P{^{1}H} NMR (C_6D_6): δ 27.1 (s). ^{31}P NMR, with selective decoupling of aliphatic hydrogens (C_6D_6): δ 27.1 (t).

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Supporting Information Available: CIF files for X-ray structures and drawings of DFT-geometry-optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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