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(SiMe2CH2PR2)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 = tBu generally fails to react (too bulky), that with R = cyclohexyl suffers a (controllable) tendency to abstraction of 3H from one ring, forming an η3-cyclohexenyl compound, and that with R = iPr 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 η2-C5H5, C8 giving carbene and then η2-cyclooctyne, and C12 giving an η2-allyl. Norbornene gives a (complex of the norbornene in thermal equilibrium with its carbene isomer; at 90 °C, hydrocarbon ligand Câ-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 details how the strongly π-basic M(OSi t-Bu3)3 (M = Nb, Ta) isomerizes olefins to alkylidenes. We have previously reported that the highly π-basic Re center supported by the PNP ligands, (R2PCH2SiMe2)2N-, effects the rearrangement of acyclic alkenes into hydrido carbyne complexes. (PNP5)ReH4 complexes (Scheme 1) react rapidly with 3 mol of acyclic alkenes H2C=CHR at 22 °C to quantitatively produce (PNP5)ReH(=CCHR) and 2 mol of the corresponding alkane H3CCH2R. 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, η2-alkene, vinyl hydride, or vinylidene dihydride complexes. Our observed production of a hydrido carbyne from (PNP5)ReH4 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 (PNP5)ReH4 with cycloalkenes.

The ultimate focus of our interest was on the C−H activation of alkanes. 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 “\(2\text{H}\)”. 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.

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\begin{align*}
\text{(PNP)Re} + \text{H}_2\text{CCH}_2\text{R} & \rightarrow \text{(PNP)Re=CH}_2\text{R} + "2\text{H}" \\
\text{(PNP)ReH}_4 + \text{H}_2\text{CCH}_2\text{R} + 3\text{A} & \rightarrow \text{(PNP)ReH=CH}_2\text{R} + 3\text{A}\text{H}_2
\end{align*}
\] (1a) (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 \(\text{H}_2\)-accepting functionalities, a qualitatively similar, reflecting the comparable steric and electronic influence of \(\text{Pr}\) and \(\text{Cy}\). The major difference is that 1b, upon removal of hydrides from the Re center, is prone to undergo intramolecular \(\text{C—H}\) activation (vide infra).

**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\(^{\text{Bu}}\)) analogue ("iPrBu") has served to uncover some alluring Ru chemistry,\(^{19}\) the \(\text{tBu}\) analogue has proven to be too hindered sterically. \(\text{tBu}\) 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 \(\text{tBu}\) slowly, but the reaction was found to lead to unselective decomposition. We have previously found that \(\text{tBu}\) reacts with linear alkenes much more slowly than 1a or 1b; we ascribed that to the prohibitive steric bulk of the (PNP\(^{\text{Bu}}\)) ligand. The rates of reaction of 1a and 1b are qualitatively similar, reflecting the comparable steric and electronic influence of \(\text{Pr}\) and \(\text{Cy}\). The major difference is that 1b, upon removal of hydrides from the Re center, is prone to undergo intramolecular \(\text{C—H}\) activation (vide infra).

**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 \(\text{C}_6\text{D}_6\) 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 \(\text{C—H}\) Activation of the PNP\(^{\text{Cy}}\) 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 \(\beta\)-agostic cyclohexylidene ligand and the geometry about the carbene carbon is strongly distorted toward a T-shape. Solution spectroscopic data suggest a similar \(\beta\)-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 \(\text{C—H}\) 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 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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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).

[Cy3PCH2SiMe2NSiMe2CH2PCy(C6H8)]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 C6 ring is established from a pre-existing C6 ring, which contrasts to its equatorial site in every other compound reported here. This η3-allyl binding also makes (Re−P−Cipso) 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 C6 ring is shorter (by >0.08 Å) than to the PCy2 phosphorus. There is no significant difference in the Re−PCy2 distance here from the Re−PPR2 groups in compound 8.

(PNP-3)ReH(C)(=C(CH3)3), 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 31P 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 (161.3°) 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 example21 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 cyclohexadiene 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)

for details). Compound 13 is thermally stable in alkane or arene solvents, although it readily undergoes H/D exchange with C₆D₆ at 22 °C.

Compounds 1a–c are produced by Mg reduction of (PNP⁶)-ReOCl₂ in an ethereal solvent under a H₂ atmosphere. When the reduction of 1b, (PNP⁶)ReOCl₂, is performed in ether under an atmosphere of pure Ar in an attempt to form merely “(PNP⁶)-Re”, mixtures with ratios of 3:1 to 10:1 of 13 and 1b are formed (by 31P 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 (PNP⁶)-Re), and it is not immediately clear how an excess of hydrogen-poor 13 is produced. Compound 13 readily reacts with H₂ to give 1b in the time of mixing. Reduction of (PNP⁶)-ReOCl₂ 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 “(PNP⁶)-Re” (or its ether complex) by magnesium reduction in Et₂O 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 cyclohexene solvent as evidenced by the invariance of the reaction outcome in cyclooctane or cyclo-C₆D₁₂ solvents.

**Alkane Dehydrogenation with 2a.** Compound 2a is the formal equivalent of (PNP⁶)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 C₆ 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. 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.

3 is a colorless compound that dissolves well in aromatic (and sparingly in aliphatic) solvents. The 3¹P 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 (δ = −8.33, br dt, J₈₂₈ = 7 Hz, J₈₉ = 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 (R₂P₃)ReH₃(η¹-diene) complexes. 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 CH₂ groups and the four C(sp³)–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 that the π-donation from N in (PNP⁶)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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C5 H 6 is oriented in a way which leaves the phosphorus nuclei carbons (C33 at 2.2095(16) Å and C34 at 2.1697(15) Å), and the diene terminal carbons (C32 at 2.2963(6) Å and C35 at 1.439(2) Å) influenced by the trans broadening of the observed 1H and 31P resonances at low temperatures of the two P sites. In addition, we have observed may be responsible for the observed low-temperature inequivalence 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-δ2, 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 31P{1H} 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)3Re(H)2(C5H6), 5b. The X-ray structure in Figure 3 shows that the bulky PCy2 groups bend away from C5H6 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 ReP2/NH1r 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 C5H6 is oriented in a way which leaves the phosphorus nuclei inequivalent, in agreement with the 31P NMR spectrum. The Re−N1 distance, 2.212(2) Å, is very long, consistent with this amide not participating in N−Re σ-donation, but also influenced by the trans influence of H1r.

Thermolysis of pure 5b in C6D6 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−(H2(PR3)) compounds.23 Compounds of the type CpRe(H2−(PR3)) have a four-legged stool geometry, with hydrides being the opposite “legs”. The flexible backbone of the η2-PN(PR3) ligand in 6 should not lead to a geometry about Re that is significantly different in CpRe(H2(PR3))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 2JHP = 41 Hz characteristic of the CpRe(H2(PR3))2 complexes. 6a and 6b are thermally stable in solution in alkane and arene solvents.

5a,b each gave rise to a single broad 31P NMR resonance and somewhat broad resonances of the cyclopentadiene ligand. One of the 1H 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 1H 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)3Re(H)2(cyclooctyne). The synthesis of (PNP)3Re−(H2)(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 H2 to produce cyclooctane and 1a. It is best formed after treatment of (PNP)3Re−(H2) with ≥3 mol of cyclooctene at 90 °C. Two moles of cyclooctane is produced from the hydride ligands lost. Proton and 31P{1H} 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 ligand: CH2, SiMe2, and 'Pr. DFT calculations reported earlier on (PNP)3Re(H2−(HCCH) establish that the C4 isomer is 27.6 kcal/mol (∆G°298k) more stable than the C2v isomer. Both 1H and 13C{1H} NMR spectra at 22 °C show C4 symmetry of the cyclooctyne ring. The 31P{1H} 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 1H and 13C 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, PPr2/cyclooctyne congestion can lead to the 31P 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 iPr group and the CH₂ periphery: the conformation of one iPr group and the CH₂

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 cyclooctene 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.


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 1H NMR spectrum, as well as the allylic resonances in the 13C 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 31P{1H} NMR spectrum at ca. 30 ppm (trans JPP = 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 shown2 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 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 10a 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 C1 symmetry with a single 31P resonance observed, while 11a is C1-symmetric by NMR and displays an AB pattern in the 31P{1H} 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) 13C resonance corresponding to the α-carbon. Unfortunately, assignment of the other 13C resonances of 11a was not possible owing to the overlap and low symmetry and concentration. (PNP)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

**Scheme 7**

![Scheme 7](image)

**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).
C20 are much larger (138.60(5)° and 138.62(5)°, respectively) than 90°, thereby opening a place for the norbornene CH2. The Re−C25 and Re−H25 distances, 3.044 and 2.52 Å, respectively, are consistent with an agostic interaction, which accords with one 1H 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)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 C8−C9 bond in 11a, our first observation of C−C bond cleavage. 12a is trapped in the reaction mixture as its norbornene adduct 12a8. The coordinated norbornene can be removed in vacuo at 110 °C. The NMR data for 12a and 12a8 are similar to those of the other hydrido carbynes 12 and their olefin adducts. For 12a, the chemical shifts of the 31P NMR (δ 60.8 ppm) and Re=H 1H NMR (δ −10.57 ppm) resonances are especially similar to those of the most structurally similar 12m (31P NMR, δ 60.6 ppm; 1H 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 1H and 13C NMR spectra, that the symmetry of 12a is C1 (four Si−Me resonances in the 1H and 13C NMR spectra), but the chemical shift difference for several other diastereotopic nuclei is too small to be resolved.

Benzenec−H Cleavage. Because of our frequent observation of isotope exchange of reactive transients produced here with d6-benzene solvent (and thus our frequent use of d12-cyclohexane as an NMR solvent), we have briefly studied this behavior. In fact, (PNP)Re(H)2(C(CH3)3)2, 2a, is 1/3 converted in 10 min at 22 °C in C6H6 to a single compound, proposed to be (PNP)Re(H)2(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)Re(H)2(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 31P(1H) 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 reaction ratios are benzyl CH3 (8.0) > alkyl CH3 (4.5) > CH2 (1.0).

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)

Table 1. Product Yields in Competition between Hydrocarbons for (PNP)Re(H)2(cyclooctyne)

<table>
<thead>
<tr>
<th>reagents</th>
<th>product mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane/cyclopentane</td>
<td>12c:6a = 73:27</td>
</tr>
<tr>
<td>n-heptane/cyclopentane</td>
<td>12d:6a = 73:27</td>
</tr>
<tr>
<td>n-hexane/ethylbenzene</td>
<td>12c:12h = 52:48</td>
</tr>
<tr>
<td>n-heptane/ethylbenzene</td>
<td>12d:12h = 53:47</td>
</tr>
</tbody>
</table>

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)3, but detectable phenyl products from (PNP)Re(H)2(=C(CH3)2)? (e) What is special about the norbornene substrate that causes π−olefin and carbyne 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)Re(H)(η5-allyl) + free H2 vs the (PNP)ReH2 (carbene) or π−olefin isomers? (h) Is (PNP)Re(H)2(=C(CH3)2) 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 monooxygenated carbenes (PNP)Re[H]2[=CH(R)] and the hydrido carbenes (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)Re(H)2, while highly reactive (eq b), is too endergonic (eq a) by H2 loss from (PNP)ReH2 to be an intermediate in the reactions of unsaturated hydrocarbons with the latter at 22 °C. (2) (PNP)Re(H)(η5-HCCH) is more stable as the less symmetric isomer (eq c); this is also true for the analogous π−HCCH adduct. (3) H2 loss from (PNP)Re(H)(==CCH3) is favorable (eq d), an effect attributed to product stabilization by π-donation from amide N to Re. (4) Dehydrogenation of (PNP)Re(H)(==C(H)CH3) 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

conversion to carbyne and free H₂ 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 \((\text{PNP})\text{Re(H)₄}\) is unfavorable (eq h). However, if it were possible to make a species more reactive than \((\text{PNP})\text{Re(H)₄}\), 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 alkylidyne 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 H₂ is the product.

Equation e shows that the \(\eta^3\)-norbornene isomer is more stable than the norbornylidene isomer, in agreement with experiment, and comparison to eq f shows that the norbornylidene makes the carbene isomer more thermodynamically accessible (i.e., less unfavorable) than for ethylene. The cyclic C₆ case (eq i) actually reverses the relative stability of these two isomers, accomplishing something that was not true of RuHCl(PPr₃)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 \((\text{PNP})\text{Re(H)₄}\) by equimolar propylene to \((\text{PNP})\text{Re(\text{H)₄(\text{C}CH)}₃)}\) + 2H₂ is nearly thermoneutral, but this observed conversion (with cyclooctene) 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.

Another provisional way to rank the chemical potential in the three alkane dehydrogenation precursors employed here is shown in Scheme 10 (\(\Delta G^\circ_{298}\) 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 \(\eta^3\)-allyl. Calculations show that \((\text{PNP})\text{Re(H)₂\[C(CH₂)₅\]}\) lacks the thermodynamic potential to convert cyclohexene to coordinated cyclohexylidene (eq 7, \(\Delta G^\circ_{298}\) given in kilocalories per mole).

\[
\text{(PNP)}\text{Re(H)₂(\text{HC≡CH}) + H₂} \rightarrow \text{(PNP)}\text{Re(H)₂ + C₂H₄} + 7.6 \text{ kca}\mbox{mol}^{-1}
\]
\[
\text{(PNP)}\text{Re(H)(\text{η}^3\text{-allyl}) + H₂} \rightarrow \text{(PNP)}\text{Re(H)₂ + H₂C≡CH₃} + 14.4 \text{ kca}\mbox{mol}^{-1}
\]
\[
\text{(PNP)}\text{Re(H)₂[\text{C(CH₂)}₃]} \rightarrow \text{(PNP)}\text{Re(H)₂ + cyclohexene} + 10.9 \text{ kca}\mbox{mol}^{-1}
\]

Selected Structural Features. Those structures calculated (on a simplified \((\text{H₂PCH₂SiH₂})₂\)N⁻ model) for which an X-ray structure has been determined showed agreement (see the
Table 2. Selected Structural Features (Å) of DFT-Optimized Species [(H₂PCH₂SiH₂)₂N]Re(ligand)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Re-N</th>
<th>Re-C</th>
<th>Re–C₉</th>
<th>Re–H₉</th>
<th>C–C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(PNP)²Re(H₂)(η²-norbornene)</td>
<td>2.129</td>
<td>2.212</td>
<td>2.991</td>
<td>2.430</td>
<td>1.443</td>
</tr>
<tr>
<td>(PNP)²Re(H₂)(HC=CH)</td>
<td>2.131</td>
<td>2.013</td>
<td>1.897</td>
<td>2.671</td>
<td>2.471</td>
</tr>
<tr>
<td>(PNP)²Re(H₂)(cyclohexylidene)</td>
<td>2.183</td>
<td>1.904</td>
<td>2.861</td>
<td>2.848</td>
<td></td>
</tr>
<tr>
<td>(PNP)²Re(H)(norbornylene)</td>
<td>2.158</td>
<td>1.904</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(PNP)²Re(H)(η²-cyclohexene)</td>
<td>2.136</td>
<td>2.226</td>
<td>3.075</td>
<td>2.410</td>
<td>1.430</td>
</tr>
<tr>
<td>(PNP)²Re(H)(C₃H₅)</td>
<td>2.030</td>
<td>2.178</td>
<td>2.244</td>
<td>2.378</td>
<td>1.437</td>
</tr>
</tbody>
</table>

Scheme 11

Supporting Information) sufficient to create confidence in those calculated structures where an experimental determination is lacking. For example, (PNP)²Re(H₂)(HC=CH) has the alkyn 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)²Re(H₂) fragment similarly to η²-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 η²-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 C₇ compound.

Summary

The reaction chemistry we reported earlier for [RuHCl(P₃)₃]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 NR₂) into Fischer carbene bound to Ru. This Ru also doubly dehydrogenated tetrahydrofuran and N-alkylnorbornylidene into their corresponding metal carbene complexes. However, [RuHCl(P₃)₃]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(H₂)Cl-(P₃)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 chlorine; for this, we chose amide. The pincer ligand class pioneered by Fryzuk combined this donor with protection (via the SiMe₂ substituents) against β-H migration to which late-transition-metal N(alkyl)₂ ligands are vulnerable. The Fryzuk ligand also permits installing variable steric protection at the two phosphorus donor centers to prevent the dimerization which could render 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)²Re as our goal. Isolated (PNP)²Re 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 ReIII is the lowest oxidation state accessible in this chemistry. This only reinforces the notion of (PNP)²Re being an exceptionally reactive, reducing fragment. Furthermore, even though (PNP)²Re compounds may 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)²Re fragment. Magnesium reduction of (PNP)²ReOCl₃ proceeded best in the presence of H₂, which then represented a compromise in that we produce (PNP)²Re(H₂). To reach the desired lower formal oxidation state, we explored scavenging H from (PNP)²Re(H₂) using sacrificial olefins, which then become the substrate for the more unsaturated transient “(PNP)²Re²” moiety. In fact, operationally unsaturated (PNP)²Re(H₂) 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)²Re moiety: carbones, 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 carbones 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, 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 tBu substituents in (PNP)²Re(H₂) 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

cyclohexyl. While steric factors play a large role in (PNPR)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 carbonyl complexes 12, with ethyl groups reacting faster than (hindered) methyl groups and benzyl methyls showing no major advantage. The lack of formation of any η6-arene complexes is suggested to be due to the PNP ligand high electronic demand and also its steric bulk. The driving force for binding the smaller η5-C5H4R (R = H or CH3) 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 but η3 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)ReL9 species to serve as alkane dehydrogenation reagents is thus the ability to expel the ligands L9, especially as an alkane, and that L9 cannot rearrange to a carbonyl without C–C bond scission.

The idea of “stripping” H ligands from an L9MHn species with a sacrificial olefin (e.g., BuHCCl=CH2) has a long tradition as a way to create a transient capable of attacking unreactive substrates (e.g., alkanes, N2) and lies at the core of catalytic alkane dehydrogenation, based on the core 14-electron fragment (pincer) Ir2 operating above 200°C; there, mechanistic details have been more carefully established than in our present survey of the operationally unsaturated character of (PNP)Re(H)4, and analogous cases where a cyclohexyl on phosphorus is the H ligands there represent cooperative leaving groups. (36) Zhu, K.; Achord, P. D.; Zhang, Z.; Krogh-Jespersen, K.; Goldman, A. S. J. Am. Chem. Soc. 2004, 126, 13044.


(38) Baya, M.; Bual, M. L.; Esteban@email, M. A.; Onate, E. Organometallics 2004, 23, 1416.


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 Na/K 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, 1b, 1c, 2b, and 87 was described previously. 31P NMR chemical shifts are reported in parts per million relative to the peak for proton impurities in the deuterated solvents. 31P spectra are referenced to external standards of 85% H3PO4 (at 0 ppm). NMR spectra were recorded with a Varian Gemini 2000 (300 MHz, 1H; 121 MHz, 31P; 57 MHz, 13C), a Varian Unity Inova instrument (400 MHz, 1H; 162 MHz, 31P; 101 MHz, 13C), or a Varian Unity Inova instrument (500 MHz, 1H; 126 MHz, 13C). Elemental analyses were performed by CALL Inc. (Parsippany, NJ). ORTEP plots were generated using Ortep-3 for Windows. 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 3P21G** 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. (38) The basis set LANL2DZ is the Los Alamos National Laboratory ECP plus a double-ζ valence on Re, P, and Si; additional polarization functions were added to all phosphorus and silicon atoms in all DFT calculations. All optimizations were performed with C1 symmetry, and all minima were confirmed by analytical calculation of gradients, which were also used to compute zero-point energy corrections without scaling.

(PNP)ReH2(C(CH3)2) (2a). In situ preparation of (PNP)ReH2 (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-d12 for NMR characterization. The product thus obtained was 99% pure by NMR, but all attempts to crystallize it failed. (1H NMR (C6D12): δ 2.53 (br m, 2H, CHZ), 1.55–1.65 (8H, CH3 and PCH2 overlapping), 1.35–1.45 (CH2 overlapping with C6D12, 2.65 (m, Jav = 7 Hz, 2H, PCH2), 1.15 (AB dvt, Jav = 15 Hz, Jav = 4 Hz, 2H, 2H, PCHSi), 1.00–1.12 (four apparent q (dvt) overlapping, for each 8H, 6H, PCHCH3, 0.65 (AB dvt, Jav = 15 Hz, Jav = 4 Hz, 2H, PCH2Si), 0.15 (s, 6H, SiCH3), 0.10 (s, 6H, SiCH3), –6.7 (v br, 1H, ReHl), –10.0 (v br, 1H, ReH2). 31P(1H) NMR (C6D12): δ 47.4 (s). 31P NMR (C6D12), selectively decoupled from alkyl hydrogens: δ 47.4 (12 Hz). 13C{1H} NMR (C6D12): δ 264.9 (t, 9 Hz, Re=C), 57.4 (s, Re=CCH3), 30.2 (t, 9 Hz, PCH2), 29.9 (s, CH2), 29.5 (14 Hz, PCH2), 27.3 (s, CH2), 25.7 (s, CH3), 20.3 (s, PCH3), 19.9 (s, PCH3), 19.0 (br s, 2 s overlapping, PCHCH3), 15.9 (br s, PCH2Si), 15.6 (s, Re=CCH3), 5.6 (s, SiCH3), 5.4 (br s, SiCH3). 13C NMR (selected resonances, C6D12): δ 57.4 (t, JCH = 127 Hz, Re=CCH3), 15.6 (t, JCH = 117 Hz, Re=CCH3).

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
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 C5H5. 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 cyclohexene, and then the volatiles were removed. The residue was dissolved in C6D6, and the evolution of this solution was monitored by 31P 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 SiMe3 for 48 h at 110 °C led to essentially the same mixtures.

(PNP)ReH2(C=C(CH2)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 C6D6 was attached and frozen in liquid nitrogen to trap the volatile products. The solid turned red-purple upon thermolysis. The trap was thawed and the evolution of this solution was monitored by 31P NMR. After 10 min at 22 °C the mixture consisted of a 35:65 mixture of the tentatively identified (PNP)ReH2Ph; only more than 30 resonances were observed. The oily residue was dissolved in 1 mL of a SiMe4/pentane mixture and placed in the freezer at −22 °C. The next day, colorless crystalline material was collected from 0.4 mL (ca. 1 mmol) of cyclohexene. The reaction mixture turned purple-red upon thermolysis. The trap was thawed and the evolution of this solution was monitored by 31P 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 SiMe3 for 48 h at 110 °C led to essentially the same mixtures.

(PNP)ReH2(cyclooctylen) (8). 8 was the major component of 9, 1H NMR (C6D6): δ 4.11 (m, 1H, allyl CH), 2.99 (m, 1H, allyl CH), 2.81 (m, 1H, allyl CH), 2.49 (br d, 243 Hz), 28.6 (AB d, 243 Hz). 13C NMR (C6D6): δ 57.1 (s) and 2a. This corresponds to Keq ≈ 1 x 10−3 (AG ≈ +4 kcal/mol) for the displacement of C5H5 by C6H5.

Decomposition of 8. 8 (30 mg, 44 µmol) was heated in 0.6 mL of cyclooctene for 48 h. After this time, 1H NMR analysis indicated near complete disappearance of 8. More than 30 resonances were observed by 31P 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 SiMe3 for 48 h at 110 °C led to essentially the same mixtures.

(PNP)ReH2(cyclooctylen) (9). 1a (61 mg, 105 µmol) and cyclooctylen (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 SiMe3/pentane mixture and placed in the freezer at −30 °C for 2 days. The blue crystalline precipitate was isolated by decantation, washed with cold SiMe3, and dried in vacuo. Yield: 56% (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. Calcld (Found) for C20H35NP,ReSi3: C, 48.35 (48.26); H, 8.93 (8.88); N, 1.88 (1.79).

Data for the Major Isomer of 9. 1H NMR (C6D6): 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, C12 ring CH3 groups and PCH3 groups), 1.23 (dd, 8 Hz, 13 Hz, 3H, PCH3), 1.15 (dd, 8 Hz, 13 Hz, 3H, PCH3), 1.05 (2 d overlapping, 6H, PCH3), 0.99 (2 d overlapping, 6H, PCH3), 0.75 (dd, 8 Hz, 13 Hz, 3H, PCH3), 0.63 (s, 3H, SiCH3), 0.59 (s, 3H, SiCH3), 0.28 (s, 3H, SiCH3), 0.12 (s, 3H, SiCH3), −1.96 (dd, 14 Hz, 20 Hz, 1H, ReH), PCH3Si proton signals are concealed by other aliphatic resonances. 31P{1H} NMR (C6D6): δ 30.0 (AB d, 241 Hz), 26.1 (AB d, 241 Hz). 13C{1H} NMR (C6D6): δ 76.1 (s, CH of the C12 ring), 46.7 (s, CH of the C12 ring), 42.8 (s, CH of the C12 ring), 36.8 (s, 32.6 (d, 26 Hz, PCH3), 33.5 (s, 31.3 (d, 25 Hz, PCH3), 29.8 (s), 29.4 (s), 28.4 (s), 25.0–27.5 (several s, PCH and CH2 or the C12 ring), 21.1 (s, PCH3), 20.1 (s, PCH3), 19.44 (s, PCH3), 19.39 (s, PCH3), 19.30 (s, PCH3), 18.9 (s, PCH3), 18.4 (s, PCH3), 17.2 (s, PCH3), 13.5 (s, PCH3), 11.3 (s, PCH2-Si), 7.9 (s, SiCH3), 6.6 (s, SiCH3), 5.0 (2 s overlapping, SiCH3).

Data for the Minor Isomer of 9. 1H NMR (C6D6): δ 4.22 (m, 1H, allyl CH), 3.69 (m, 1H, allyl CH), 3.38 (m, 1H, allyl CH), 0.49 (s, 3H, SiCH3), 0.41 (s, 3H, SiCH3), 0.34 (s, 3H, SiCH3), 0.31 (s, 3H, SiCH3), −1.91 (dd, 14 Hz, 20 Hz, 1H, ReH). Other resonances are obscured and cannot be reliably assigned. 31P{1H} NMR (C6D6): δ 29.4 (AB d, 243 Hz), 28.6 (AB d, 243 Hz). 13C{1H} NMR (C6D6): δ 67.2 (s, CH of the C12 ring), 46.1 (s, CH of the C12 ring), 42.1 (s, CH of the C12 ring).
ring), multiple singlets in the 16–36 ppm region cannot be reliably assigned, 10.7 (s, PCH2Si), 9.8 (s, PCH3Si), 7.8 (s, SiCH3), 6.4 (s, SiCH3), 5.9 (2 s overlapping, SiCH3).

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 41:35:6 (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 CD3OD. 1H, 13C, and 31P NMR data were collected and were identical to 12d obtained by other methods.

(PNP)3PReH2(norbornene) (10a) and (PNP)3PReH2(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 Me6SiOSiMe3 and placed in the freezer at −30 °C overnight. The blue-purple crystals were separated by decantation, washed with cold SiMe3, 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 for C37H72NP2ReSi2: C, 70.04; H, 9.85; N, 3.91. Found: C, 70.07; H, 9.81; N, 3.92. It 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 reddissolved in C6D6 for full NMR characterization. 1H NMR (CD6): δ 7.44 (d, 8 H, 2-Ph), 7.16 (t, 8 H, 2, m-Ph), 7.04 (t, 8 H, 1H, p-Ph), 2.85 (m, 2 H, Re=C=C(CH3)), 1.91 (m, Jm = 7 H, 2H, PCH), 1.75 (m, Jm = 7 H, 2H, PCH), 1.18 (apparent q, d, 8 H, 6H, PCH3), 1.11 (apparent q, d, 8 H, 6H, PCH3), 1.03 (apparent q, d, 8 H, 6H, PCH3), 0.83 (apparent q, d, 8 H, 6H, PCH3), 0.73 (AB d, Jm = 15 H, Jm = 4 H, 2H, PCH), 0.39 (s, 6H, SiCH3), 0.25 (s, 6H, SiCH3), −1.51 (d, 8 H, 1H), agostic CH3, −12.7 (v br, 1H, ReH), −15.8 (v br, 1H, ReH). 13C NMR (CD6): δ 273.0 (t, 12 Hz, Re=C=C(CH3)), 136.2 (s, ar-C(6)), 128.8 (s, ar-C(5)), 127.8 (s, ar-C(4)), 126.2 (s, ar-C(3)), 56.4 (s, Re=C=C(CH3)), 29.5 (t, 13 Hz, PCH), 29.0 (t, 11 Hz, PCH), 20.1 (s, 1H, PCHH3), 18.9 (s, PCH3), 18.5 (s, PCHH3), 17.3 (s, PCH3), 10.5 (s, PCH3), 7.2 (s, SiCH3), 6.3 (t, 2 Hz, SiCH3).

Activation of C6HMe3-xylene. 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 thermoloyed at 110 °C for 24 h and then analyzed by 31P NMR. In each case, the solution became brown-red. 31P NMR resonance attributable to an aryl-substituted carbene emerged (ca. 40% for 12i, ca. 50% for 12j, ca. 60% for 12k). Upon partial decoupling of aliphatic hydrogens, these 31P 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.
(s, CH$_2$ of cyclohexyl), 29.8 (t, 11 Hz, PCH), 29.3 (t, 13 Hz, PCH), 26.8 (s, CH$_2$ of cyclohexyl), 26.4 (s, CH$_2$ of cyclohexyl), 20.9 (s, PCHCH$_3$), 19.3 (s, PCHCH$_3$), 19.0 (s, PCHCH$_3$), 17.2 (s, PCHCH$_3$), 10.3 (s, PCH$_2$Si), 7.5 (s, SiCH$_3$), 6.3 (br s, SiCH$_3$).

(PNP$^{2+}$)ReH(C(cyclopentyl)) (12m) and (κ$^2$-P,P-PN(H)P$^{2+}$)-ReH$_2$(η$^3$-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$_6$D$_6$ 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$_6$D$_6$): δ 1.30 (apparent q (dvt), 8 Hz, 6H, PCH$_3$), 1.21 (apparent q (dvt), 8 Hz, 6H, PCH$_3$), 1.02–1.14 (two apparent q (dvt) overlapping, 12H, PCHCH$_3$), 0.83 (AB dvt, $J_{HH} = 14$ Hz, $J_{HP} = 4$ Hz, 2H, PCH$_2$Si), 0.76 (AB dvt, $J_{HH} = 14$ Hz, $J_{HP} = 4$ Hz, 2H, PCH$_2$Si), 0.37 (s, 6H, SiCH$_3$), 0.33 (s, 6H, SiCH$_3$), −10.58 (t, 15 Hz, 1H, ReH). $^{31}$P($^1$H) NMR (C$_6$D$_6$): δ 60.6 (s). $^{31}$P NMR, with selective decoupling of aliphatic hydrogens (C$_6$D$_6$): δ 60.6 (d).

Data for 15. $^1$H NMR (C$_6$D$_6$): δ 4.58 (br t, 2H, CH of η$^3$-C$_5$H$_4$-Me), 4.39 (br t, 2H, CH of η$^3$-C$_5$H$_4$Me), 0.24 (s, 12H, SiCH$_3$), −12.30 (t, 2H, 41 Hz, ReH). $^{31}$P($^1$H) NMR (C$_6$D$_6$): δ 27.1 (s). $^{31}$P NMR, with selective decoupling of aliphatic hydrogens (C$_6$D$_6$): 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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