Amido/phosphine pincer hydrides of ruthenium

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The chemistry of the ligand \((R_2PCH_2SiMe_2)N\) on ruthenium is developed, including RuH(PNP-Cy)(PPh₃) and (HPNP-R)RuH₂Cl. The latter contains a protonated nitrogen (i.e., amine as a donor to Ru) and one H₂ ligand (X-ray structure for R = tBu). This compound can be dehydrohalogenated to give (PNP-Cy)RuH₃, which undergoes H/D exchange of D₂ into its cyclohexyl rings, and is itself dehydrogenated by excess H₂C=CHR to give \([Cy_2PCH_2SiMe_2NSiMe_2CH_2PCy(C_6H_8)]\) Ru, which contains a triply dehydrogenated cyclohexyl ring π-allyl bonded to Ru. (PNP-Cy)RuH₃ reacts with dihydrofurans to give the heteroatom-stabilized carbene complex (PNP-Cy)RuH\([=CO(CH_2)_3\])

The many pincer ligands I that have been reported recently¹⁻¹⁰ fall into two general categories, those with a neutral donor G (e.g., pyridine-based), and those with an anionic donor G (e.g., phenyl-based). The neutral donor D₀ can be phosphorous or nitrogen, and this D₀RR' group can have controllable electronic and steric (including chiral) features, leading to a versatile set of pincer ligands.⁵,¹¹,¹² Depending on the nature of the "arm" that links G to D₀, the donor can be at the amine or imine oxidation level. We have been attracted to the pincer ligands II pioneered by Fryzuk because the group G is anionic and, unlike phenyl, bears a lone pair.¹³

The ability of an amide N to participate in π-donation to the metal is something we have developed as a way to access, under mild conditions (e.g., 20 °C), unsaturated (poly)hydride molecules; the ligand π-lone pair can donate to an otherwise unsaturated metal, making it metastable (persistent), but nevertheless leaving it operationally unsaturated. Amides of the late transition metals with 16 valence electrons are quite prone to β-hydrogen migration to give a hydride and an imine, III; the presence of silicon on nitrogen in the Fryzuk ligand helps to prevent such a degradation, albeit at the price of a somewhat diminished nitrogen nucleophilicity.

We report here our efforts to develop ruthenium polyhydride chemistry with the PNP ligand carrying primarily cyclohexyl substituents, since ligand steric bulk has been proven effective in preventing reagent deactivation via dimerization.

Results and discussion
Preparation of the PNP-R ligands

One additional advantage of the Fryzuk ligand class is the possibility of systematic modification of phosphine alkyl groups; a variety of these have been prepared.¹ The synthesis of the PNP-R ligands in this study followed a modified preparation in which the desired phosphines, HPR₂, are deprotonated at −78 °C in THF to yield the lithium phosphide in situ; this was then reacted with the silylamide to form the desired LiPNP-R salt. Recrystallization from ether gives 60−75% yield of the corresponding etherate (Scheme 1). Both the N-protonated and N-TMS-protected PNP-R ligands can also be synthesized. The protonated ligand, HPNP-R, has been found to be a useful source of the ligand in this study. Made from treatment of the Li–PNP salt with 1 M HCl in ether at 0 °C, the HPNP-R ligand (a clear oil) is typically used as a solution in benzene. The TMS-protected version of the PNP ligand can be prepared by treatment of an ether solution of the corresponding Li salt with TMS–OTf. The TMS-protected ligand was initially prepared so as to minimize protonation of the amide in subsequent synthesis steps.

![Scheme 1](https://example.com/scheme1.png)

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The reaction of the lithium salt of the PNP-R ligand with Ru hydrido-chlorides forms the hydride-phosphine complex RuH(PNP-R)(PR₃) (Scheme 2). Both the PPh₃ and P(PR₃)₂ derivatives can be synthesized; the former from reaction of a toluene solution of RuHCl(PPh₃)₃ with the LiPNP-R salt, and the latter from [RuHCl(P(PR₃)₂)]₂.

Reaction of LiPNP-Ph or Cy with the ruthenium hydrides at room temperature gives quantitative conversion to the appropriate RuH(PNP-R)(PR₃) (Scheme 2). In each case, a hydride signal was observed as a doublet of triplets, showing splitting from both the pincer ligand and non-chelating phosphine. Two diastereotopic Si-Me signals were also observed, each integrating to six hydrogens. The ³¹P{H} NMR exhibits a doublet, due to the interaction of PR₂ with PR₃, and a downfield triplet from PR₃ coupling to PNP-PR₂. Synthetic scale purification of the PNP ligand is a suitable ligand for the ruthenium system and can form unsaturated hydride complexes. The next goal was the synthesis of a polyhydride complex that could participate in C–H activation reactions.

Synthesis and characterization of RuH(PNP-R)(PR₃)

A successful entry into polyhydride PNP-Ru chemistry involves the synthesis and isolation of the pincer-protonated (HPNP-Cy)RuHCl₂ as a precursor to a 16 e⁻ Ru species. (HPNP-Cy)RuHCl₂ can be made [eqn. (1)] in poor (isolated) yield from the corresponding protonated HPNP-Cy ligand and RuHCl₂(PCy₃)₂, liberating 2 equiv of PCy₃.

\[
\text{HPNP-Cy} + \text{RuHCl}_2(\text{PCy}_3)_2 \rightarrow \text{RuH}_2(\text{PCy}_3)_2 + 2\text{PCy}_3
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A single crystal suitable for X-ray diffraction studies was obtained from slow evaporation of a toluene solution of RuH(PNP-Cy)(PPh₃). The molecular structure and selected atom labelling are illustrated in Fig. 1. Details of the structural determination are presented in Tables 1 and 2. The hydride, while not located in the crystal structure refinement, was located by DFT calculations, which placed the hydride at 1.562 Å from the Ru metal center (Fig. 2). Good agreement with the above crystal structure data was achieved with all other bond lengths and angles in the optimized structure (Table 2). The calculated N–Ru–PH₃ angle of 158.5° compares favorably to the experimentally determined angle of 164.2°.

These reactions and accompanying crystal structure show that the PNP ligand is a suitable ligand for the ruthenium system and can form unsaturated hydride complexes. The next goal was the synthesis of a polyhydride complex that could participate in C–H activation reactions.

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\[
\text{Solid-state structure of RuH(PNP-Cy)(PPh₃)}
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Ru–PR3 2.275 2.24
P–Ru 2.326 2.37
C–P 1.850 1.83
N–Si 1.734 1.71
Ru–N 2.118 2.15
RuH(H2) structure with a long H–H bond. The

Table 2 Comparison of calculated and experimental values for (PNP)RuHL (L = H or Ph)

<table>
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(HPNP-Cy)RuH3Cl exhibits one hydride resonance at −12.46 ppm (t, J = 14.2 Hz). This hydride resonance remains a sharp triplet to −20 °C, where it begins to broaden; at −80 °C, the resonance is a broad singlet. A T1(min) was found at 59.1 ms (C3D8, 400 MHz, −30 °C), suggesting a trihydride structure with relatively small Ru–H and H–Ru–H or an RuH(H2) structure with a long H–H bond. The t-Bu analog (see below) helps resolve this uncertainty. The N–H resonance of the ligand amine is observed as a singlet at 3.10 ppm. While the cyclohexyl region of the spectrum is quite crowded, the cyclohexyl resonances integrate to approximately 44H.

Synthesis and structure of (HPNP-Cy)RuH3Cl

Although (PNP-Cy)Li served to introduce the PNP-Cy ligand onto Ru via a number of common Ru starting materials (vide supra), attempts to use (PNP-Cy-Bu)Li analogously were unsuccessful. Reactions of (PNP-Cy-Bu)Li with RuHCl(PH3)3, [RuHCl(PPr3)2]2 and [arene]RuCl2: only resulted in low (<50%) conversion to the desired products and were plagued by side reactions. Encouraged by our success in surmounting similar problems in the introduction of the PNP ligand onto Re via the utilization of Mg derivatives of PNP, we decided to try this approach here. The reaction between (PNP-Cy-Bu)MgCl(dioxane) and [p-cymene]RuCl2 in C6D6, followed by exposure to H2 atmosphere, cleanly produces (HPNP-Cy)RuH3Cl (95% purity by NMR). Solid (HPNP-Cy-Bu)RuH3Cl was isolated in the form of X-ray quality crystals in 61% yield. The RuH3 spin system gives rise to a single resonance in the 1H NMR spectrum at −12.96 ppm (t, JHP = 15 Hz) and selective decoupling of only the alkyl hydrogens gives rise to a quartet (from three H on Ru) in the 31P NMR spectrum for the equivalent P nuclei of the HNPN ligand. The environment around Ru in the solid state structure (Fig. 3 and Table 3) can be described as approximately octahedral. The results of the X-ray diffraction study are consistent with a dihydrogen ligand occupying the position trans to the NH ligand and a hydride ligand trans to Cl. The compression of the P–Ru–P angle to 163.725(11)° from the idealized octahedral value of 180° can be attributed to the pincer ligand constraints. In spite of such constraints, the Ru–N distance is nearly as long as the distance from Ru to the much larger atom, phosphorus. The chloride ligand is also somewhat displaced from an idealized octahedral position towards the NH functionality (∧Ru1–N1–Cl1 = 82.6°), presumably due to the N–H–Cl hydrogen bonding. This hydrogen bonding is also evident in the unusually small ∧Ru1–N1–Ru1–Cl1 is 23°. The participation of Cl in hydrogen bonding is likely facilitated by the trans influence of the hydride ligand weakening the Ru–Cl bond; indeed, the Ru–Cl distance is rather long at 2.5263(3) Å. Normally, M–P and M–Cl distances to Ru are essentially equal, but here the Ru–Cl distance is longer by 0.16 Å. A similar intramolecular hydrogen bond between an NH of an HNPN ligand and a metal-bound halide was observed in Ir complexes of protonated PNP ligand.

Reactivity of (HPNP-Cy)RuH3Cl

Attempts to form (HPNP-Cy)RuH4 from (HPNP-Cy)RuH3Cl by using various hydride transfer reagents [NaBH4, LiAlH4, Cp2ZrHCl, Et3SiH, Me2PhSH], t-BuSiH] were unsuccessful; when reacting at all, only intractable mixtures of products were formed. Neither could the lone chloride ligand be replaced by a more weakly binding anion, using such reagents as AgOTf. No exchange with the hydrogen ligands was observed when (HPNP-Cy)RuH3Cl was allowed to react with 1 atm of D2, even at elevated temperatures (60 °C for 20 h in C6D6).

However, some ligand replacement reactions were moderately successful. (HPNP-Cy)RuHCl(PPPr3)2 can be formed by the independent reaction of [RuHCl(PPPr3)2] with HPNP-Cy, which produced (HPNP-Cy)RuHCl(PPPr3) in quantitative yield. The N–H signal of the

Fig. 2  Geometry optimized structure of (PNP)RuH(PH3) (see Table 2 for parameters).

Fig. 3  X-ray crystal structure of (HPNP-Cy)RuH(H2)Cl.
Table 3  Selected distances (Å) and angles (deg) for [HPNP-Cy]RuH(Cl)

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amine is observed slightly upfield of (HPNP-Cy)RuH(Cl) at 3.08 ppm, and two diastereotropic Si–Me signals are observed at 0.35 and 0.13 ppm. As in the case of (PNP-Cy)RuH(PP3), the 31P{1H} NMR spectrum is characterized by two signals, a doublet, due to PCy2/PP3 coupling, and a downfield triplet from PPr3.

Reaction of (HPNP-Cy)RuH(Cl) with 1 atm of CO in C6D6 immediately results in the formation of a yellow solution (from the red-brown of the starting materials) and the evolution of H2 (as seen by 1H NMR). Within 1 h the reaction is complete, while signals for H2 and for (PNP-Cy)RuH3 are resolved on the 1H NMR time scale (kf is small) at 95°C [eqn. (4)]. The hydrides within the resulting (PNP-Cy)RuH3 are never fully decoalesced (kH*(H–H) enhanced by the π-donor amide ligand trans to itself). RuH bond lengths to H2 hydrogens are ~0.1 Å longer than to Ru–H (1.66 Å vs 1.56 Å), consistent with neutron diffraction structural data on MH(H2) compounds.22

Reactivity of (PNP-Cy)RuH3

Reactivity of (PNP-Cy)RuH3 toward H2. H2 (1 atm) adds reversibly (but incompletely) to form (PNP-Cy)RuH4 at room temperature [Fig. 5 and eqn. (4)]. The hydrides within the resulting (PNP-Cy)RuH3 are never fully decoalesced (kH*(H–H) enhanced by the π-donor amide ligand trans to itself). RuH bond lengths to H2 hydrogens are ~0.1 Å longer than to Ru–H (1.66 Å vs 1.56 Å), consistent with neutron diffraction structural data on MH(H2) compounds.22

Fig. 4 DFT calculated, geometry-optimized structures of (PNP)RuH5.
Reactivity of (PNP-Cy)RuH₃ toward olefins. The reaction (typically 5–10 h at room temperature followed by 10–15 h at 60 °C in C₆D₆) of (PNP-Cy)RuH₃ with a variety of olefins (typically in a 1:4 mole ratio) results in the formation of an η¹-cyclohexenyl ring [eqn. (5)], in addition to small amounts of bound or isomerized (to a carbene in the case of dihydrofuran) olefin as well as equivalent amounts of hydrogenated olefin. These reactions are thus net dehydrogenations, even of sp³ carbons, by an olefin acting as a hydrogen acceptor.

\[
\text{(PNP-Cy)RuH₃} + \text{H}_2 \rightarrow \text{(PNP-Cy)RuH₃/H}_2 \text{coalesced signal at 12.39 ppm).}
\]

In the reaction mixture, the η¹-cyclohexenyl(cyclohexyl)-phosphine complex is characterized by an AB pattern at \(\text{δ} = 10.51 \text{ and } 32.58 \text{ (J}_{P-H} = 303 \text{ Hz), as well as four SiC₃H₃} \text{chemical shifts. The proposed structure is based on such reactions with other cyclohexyl-substituted phosphines.}

The addition of [NEt₃H]Cl minimizes the formation of the η¹-metallated cyclohexyl phosphine ring, allowing, for example, in the case of the dihydrofuran, progression to the carbene F [eqn. (6)].

\[
\begin{align*}
\text{(PNP-Cy)RuH₃} & + \text{H}_2 \rightarrow \text{(PNP-Cy)RuH₃/H}_2 \text{ coalesced signal at 12.39 ppm.}
\end{align*}
\]

One possible mechanism that accounts for the observed intermediates and the influence of the addition of [NEt₃H]Cl upon the product distribution is detailed in Scheme 3.

The formation of A can be observed as the first signals resulting from the reaction of any amount of 2,3-dihydrofuran with (PNP-Cy)RuH₃. Within 5 min of their mixing, there is a complete disappearance of the signals due to (PNP-Cy)RuH₃ (i.e. the hydride at –15.03 ppm and the accompanying \(\delta^{31P}\) signal) and the appearance of only one hydride resonance, a triplet at –17.6 ppm. A \(\delta^{31P}\) singlet and other \(\delta^1H\) resonances are also shifted from those of the starting material, although the multiplicities and relative separations are nearly identical. A small amount of free THF is also seen. This complex is persistent, existing in the reaction mixture at room temperature as long as there is still some unreacted olefin.

By following this reaction by NMR at room temperature, the production of additional THF can be observed. If H₂ is added at this point, all excess 2,3-dihydrofuran is converted to tetrahydrofuran. Some (approximately 10% of the reaction mixture after 3 h) of the η¹-metallated cyclohexyl product (identified by the AB \(\delta^{31P}\) [H] NMR pattern) is also formed. After approximately 5 h, the first evidence for the carbene is seen (hydride triplet at –16.86 ppm). After allowing the reaction to proceed at room temperature for 2.5 days, an equilibrium mixture consisting of 20–30% of the η¹-metallated product, 20–30% of the carbene, and 40–60% of complex A is obtained. The addition of a catalytic amount of [NEt₃H]Cl at this point decreases the amount of the η¹-cyclole metallated product in solution; thus B and C are in equilibrium under H₂.

Heating the reaction mixture without the addition of [NEt₃H]Cl results in the conversion of A to the carbene species, with little change in the amount of η¹ product observed. After 15 h at 60 °C, about 80% of the reaction mixture has converted to the carbene, with the remainder being primarily the η¹-cyclole metallated product. If [NEt₃H]Cl is added at any point, nearly quantitative conversion to the carbene is seen.

Addition of [NEt₃H]Cl to a solution of (PNP-Cy)RuH₃ and subsequent addition of the other olefins under consideration (styrene, Bu-ethylene) results simply in the olefin adduct of the (PNP-Cy)RuH₃ product in solution; thus, B and C are in equilibrium under H₂.

Identical products are observed [eqn. (7)] from the reaction of (HPNP-Cy)RuH₃Cl and NEt₃, which allows the in situ...
Dehydrohalogenation of the 18 e− species and the formation of a reactive 16 e− complex, presumably (PNP-Cy)RuH3.

\[ \text{(HPNP-Cy)RuH}_3	ext{Cl} + \text{NEt}_3 \rightarrow \text{(PNP-Cy)RuH}_3 + \text{NeCl} \]  

This transient unsaturated complex was trapped by the addition of excess 2,3-dihydrofuran to a benzene solution of equimolar (HPNP-Cy)RuH3Cl and NEt3. After 2 days at 60 °C complete conversion to the carbene complex \( \text{F} \) could be seen (eqn. (7)), together with 1 equiv of tetrahydrofuran. The hydride resonance of \( \text{F} \) is found as a triplet at \( \delta = 16.82 \) ppm, with the \( ^{31}\text{P}{\{}\text{H}\} \) NMR signal appearing as a singlet at 41.2 ppm. Additional hydrogen signals corresponding to the hydrogens on the heterocycle appear as triplets at 3.90 and 3.27 ppm, and as a broad triplet at 1.97 ppm. A carbon signal at 297.8 ppm, a broad singlet due to unresolved coupling to P, further confirms the assignment of this species to a carbene moiety. Such reactivity has also been seen with the unsaturated Ru complex \( \text{RuHCl(PiPr}_3)_2 \). The slow reactivity of (HPNP-Cy)RuH3Cl with 2,3-dihydrofuran without base must be due to its saturated character, with no good leaving group available.

Similar to (PNP-Cy)RuH3 above, this \textit{in situ} formed complex can also isomerize 2,5-dihydrofuran to the identical carbene [eqn. (8)]. With the addition of 2,5-dihydrofuran and NEt3, (HPNP-Cy)RuH3Cl forms (PNP-Cy)RuH3(=COC3H6) quantitatively in 5 days at 60 °C, again producing 1 equiv of THF. In both cases, an insoluble material ([NEt3H]Cl) precipitates from the benzene solution.

\[ \text{(HPNP-Cy)RuH}_3	ext{Cl} + \text{NEt}_3 \rightarrow \text{(PNP-Cy)RuH}_3\text{Cl} \]  

Reactivity of (PNP-Cy)RuH3 toward C–H bonds. (PNP-Cy)RuH3 also participates in C(sp3)–H activation processes. This was first observed as H/D exchange in \( \text{C}_6\text{D}_6 \). While a triplet at \(-15.04 \) ppm is seen for (PNP-Cy)RuH3 in the hydride region of the \( ^1\text{H} \) NMR spectrum (if a spectrum is taken immediately upon dissolution, allowing (PNP-Cy)RuH3 to stand in deuterated solvent causes the signal to broaden from H/D exchange (Fig. 6). To slow the H/D exchange rate, a 1:1 mixture of \( \text{C}_6\text{H}_6/\text{C}_6\text{D}_6 \) was employed. With phosphorus decoupling, two signals can be resolved in as little as 15 min in contact with \( \text{C}_6\text{D}_6 \). After 30 min, \(^{31}\text{P} \) decoupling of the hydride signal reveals a downfield 1:1:1 triplet (with \( J_{\text{H-D}} = 5 \) Hz) due to the formation of (PNP-Cy)RuH2D as well a singlet still assignable to (PNP-Ru)H3. These signals overlap, forming a triplet with a downfield shoulder with \( J_{\text{H-P}} = 12.8 \) Hz if phosphorus decoupling is not employed. Complete disappearance of a hydride signal (and thus complete conversion to (PNP-Cy)Ru(D)3) in the \( ^1\text{H} \) NMR occurs after 8 h in pure \( \text{C}_6\text{D}_6 \).

Interestingly, such H/D exchange also occurs with aliphatic solvents. In cyclohexane-d12, for example, (PNP-Cy)RuH3 gives a triplet at \(-15.49 \) ppm (with \( J_{\text{P-H}} = 12.8 \) Hz) upon initial dissolution. In THF-d8, broadening of the resonance is seen, indicating a significant amount of H/D exchange. Analysis of this sample by \( ^1\text{H} \) NMR (using solvent suppression techniques to minimize the interference of \( \text{C}_6\text{D}_{12} \)) reveals a deuterium signal at \(-15.4 \) ppm, which corresponds to at least the partial formation of (PNP-Cy)RuH(D)3 (Fig. 7).

The C–H bonds in the cyclohexyl rings in (PNP-Cy)RuH3 also undergo H/D exchange. By dissolving (PNP-Cy)RuH3 [made either from allowing (PNP-Cy)RuH3 to stir overnight in \( \text{C}_6\text{D}_6 \) or from reacting (PNP-Cy)RuH3 with \( \text{D}_2 \) in deuterated solvent, then removing volatiles \text{in vacuo}] in toluene-d8 at room temperature, the presence of \(^2\text{H} \) as a broad resonance at \( \delta = 1.83 \) ppm indicates the deuterium signal at \( \delta = 1.83 \) ppm, which corresponds to at least the partial formation of (PNP-Cy)RuH(D)3 (Fig. 7).

Conclusions

The pincer-ligated compounds reported here can be compared to those with chloride in place of amide; (PNP-Cy)RuH(H2) then can be compared with RuH(H2)(PCy3)2. Both of
these compounds share the hydride/dihydrogen ground state structure and thus both show a preference for Ru(tet) and so an aversion to a higher metal oxidation state. The greater π-donor power of amide vs. chloride then fails to reduce H₂ to 2 H⁻. On the other hand, the greater donor power of the amide gives intact (PNP-Cy)RuH(H₂) enough π-basicity at Ru to improve the thermodynamics of binding additional H₂, to give (PNP-Cy)RuH₂. Perhaps even more demonstrative of the π-basicty (i.e., reducing power) of (PNP-Cy)RuH(H₂) is its ability to react, by (endothermic, but thermally accessible) oxidative addition, with arenes, with its own cyclohexyl C–H, and with free cyclohexane H–C(sp³) bonds, all evidenced by H/D exchange. The endothermic character of all these except the intramolecular version is characteristic of a 4d metal, and might be reversed for the 5d analog, Os, otherwise unsaturated Ru, this and other reactions reported here are slower than desired. The activation energies implicated are probably due at least in part to steric effects, and thus the four cyclohexyl substituents in most of the molecules reported here may represent “overprotection” in PNP-Cy, which may be ameliorated by changing to smaller phosphine substituents.

**Experimental**

**General considerations**

All manipulations were performed using standard Schlenk techniques or in an argon-filled glovebox unless otherwise noted. Solvents were distilled from Na/benzophenone, CaH₂, or 4 Å molecular sieves, degassed prior to use, and stored in air-tight vessels. RuCl₃(PPh₃)₂, RuHCl[PPh₃]₂, C₆H₆,₂₈ RuCl₂(PCy₃)₂(CHCHCMe₂),₂₉ RuHCl[P(Pr)₂]₂,₂₅ HN(SiMe₂CH₂PPh₂)₃,²₀ LiN(SiMe₂CH₂PPh₂)₂,²₀ HP₄Bu₂,²₀ and RuH₃Cl(PCy₃)₂ were prepared according to published procedures. All other reagents were used as received from commercial vendors. ¹H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents. ³¹P spectra are referenced to an external standard of 85% H₃PO₄ at 0 ppm. NMR spectra were recorded with a Varian Gemini 2000 (300 MHz ¹H; 121 MHz ³¹P; 75 MHz ¹³C), a Varian Unity Inova (400 MHz ¹H; 162 MHz ³¹P; 101 MHz ¹³C), or a Varian Unity Inova (500 MHz ¹H, 126 MHz ¹³C) instrument.

**Syntheses**

(PNP'Bu)MgCl(dioxane). ³¹P{¹H} NMR (C₆D₆): δ 3.37 (s, 8H, dioxane), 1.14 (d, 13 Hz, 36H, CMe₃), 0.58 (d, 10 Hz, 4H, P—CH₂—Si), 0.44 (s, 12H, Si—CH₃). ¹H NMR (C₆D₆): δ 17.9 (s).

(HPNP'Bu)RuH₃Cl (PNP'Bu)MgCl(dioxane) (24.2 mg, 40.5 μmol) and [(cymene)RuCl₂] (12.4 mg, 40.5 μmol) were mixed in a J. Young tube in 0.6 mL C₆D₆. After shaking for 1 h, the NMR spectrum revealed the formation of (PNP'Bu)RuCl and an equivalent amount of free cymene. This suspension was treated with 2 mL of pentane, filtered, and stripped to a yellow oil. This oil was dissolved in 0.6 mL C₆D₆ in vacuo removed in vacuo and RuH₃Cl(PCy₃)₂ was prepared according to published procedures. All other reagents were used as received from commercial vendors. ¹H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents. ³¹P spectra are referenced to an external standard of 85% H₃PO₄ at 0 ppm. NMR spectra were recorded with a Varian Gemini 2000 (300 MHz ¹H; 121 MHz ³¹P; 75 MHz ¹³C), a Varian Unity Inova (400 MHz ¹H; 162 MHz ³¹P; 101 MHz ¹³C), or a Varian Unity Inova (500 MHz ¹H, 126 MHz ¹³C) instrument.
was layered with ca. 0.5 mL of pentane. After standing for 24 h at ambient temperature large, X-ray quality crystals of the product formed. Yield: 14.5 mg (61%). (HPNP-P-Bu)RuH2Cl: 1H NMR (CD2Cl2): δ 3.15 (br, 1H, NH), 1.42 (vt, 5 Hz, 18H, CMe3), 1.15 (vt, 5 Hz, 18H, CMe3), 0.41 (s, 6H, Si-CH3), 0.23 (s, 6H, Si-CH3), −12.96 (t, 15 Hz, 3H, RuH2). 31P{1H} NMR (CD2Cl2): δ 75.4 (s).

Li(NiMe2CH2P(Cy2))2·0.75Et2O. This procedure is a slight modification of Fryazkin’s preparations for analogous compounds Li[NiMe2CH2PR3], where R = Me, Pr, Bu.12 LiBu (17 mL of 2.5 M in hexanes, 42.5 mmol) was added to a solution of 7.50 g (37.8 mmol) HPCy2 in 75 mL hexane at room temperature. The white slurry was allowed to stir for 5 days, the supernatant was decanted via cannula, and the product was washed with 75 mL pentane. Drying in vacuo yielded 7.70 g of LiPCy2 (quantitative). The lithio salt (7.70 g, 37.7 mmol) for 3 days produced a white crystalline solid, which was unaffected.

For convenience, the reagent was used as a 0.44 M solution in CD2Cl2 unless generated in situ. 1H NMR (400 MHz, CD2Cl2, 20 °C): NH proton not observed: δ 0.35 (s, 12H, SiMe2). 60 mg (0.74 mmol) LiN(SiMe2CH2PPh2)2 was added to a solution of 2.107 g (9.12 mmol) 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisilazane in 25 mL THF. After stirring at room temperature for 5 h, a solution of 2.90 g (12.6 mmol) 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisilazane in 25 mL THF was added dropwise over 20 min at −78 °C. The resulting red solution was filtered and the supernatant was decanted and sublimated to yield 2.24 g (56%) of the title compound. 1H NMR (400 MHz, CD2Cl2, 20 °C): δ 26.47 (dt, 2JPr-H = 4 Hz, 3JCy-H = 3 Hz, BuLi, then 3 h of stirring at room temperature). The red solution was filtered and the free PPh3 liberated in the reaction was removed by sublimation (60 °C, 0.003 torr, 1 week). Isolated yield: 620 mg (91%). 1H NMR (400 MHz, CD2Cl2, 20 °C): 31P{1H} NMR (162 MHz, CD2Cl2, 20 °C): δ 18.8 (s).

Ru(dpny)(PPh3). RuCl(PPh3)2Cl2 (150 mg, 0.74 mmol) was added to a solution of 10 mL of 2.0 M in pentane, 1.06 equiv.) was added to a solution of 4.0 g (27.4 mmol) HPBu2 in 40 mL THF. Dropwise over 20 min at −78 °C. The yellow solution was allowed to stir for 2 h, then recooled to −78 °C. Over a period of 1.5 h, a solution of 2.107 g (9.12 mmol), 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisilazane (HNiMe2CH2Cl2) in 25 mL THF was added dropwise via addition funnel. The mixture was allowed to warm to room temperature and stirred 30 min before removal of the volatiles to a liquid N2 trap. The resulting red solid was filtered and washed with pentane (2 × 75 mL), filtered, and reduced to dryness in vacuo. The residue was extracted with pentane (2 × 75 mL), filtered, and reduced to dryness in vacuo. Attempts to isolate product from the viscous yellow oil by crystallization from hexane or pentane failed, yielding only a trace of LiCl precipitate. The LiCl was separated via cannula, and the mother liquor volatiles were removed to a liquid N2 trap. Drying the residue in a minimum of ether and cooling to −70 °C for 5 days produced a white crystalline solid, which was washed with 90 mL cold ether (−70 °C) and dried in vacuo to yield 2.24 g (56%) of the title compound. 1H NMR (400 MHz, CD2Cl2, 20 °C): δ 0.35 (s, 12H, SiMe2), 0.56 (d, JPr-H = 4 Hz, 3JCy-H = 3 Hz, BuLi, then 3 h of stirring at room temperature).
Ru[HPNP-Cy]2(P3Pr). [RuHCl(P3Pr)2] (10 mg, 0.011 mmol) and 11.7 mg (0.022 mmol) Li(N(SiMe2CH2PPh2)2 were combined in 0.5 mL C6D6 and added to an NMR tube. 1H and 31P{1H} spectra recorded 20 min later revealed quantitative conversion to the title compound with liberation of 1 equiv of free P2I5. 1H NMR (400 MHz, C6D6, 20°C): δ 0.47 (d, 3JH–P = 24 Hz, 2H, PNP-C6H5 overlapping with PPN-C6H5). 

Ru[HPNP-Cy][PH][P3Pr]. [RuHCl(P3Pr)2] (10 mg, 0.011 mmol) and 11.7 mg (0.022 mmol) Li(N(SiMe2CH2PPh2)2 were combined in 0.5 mL C6D6 and added to an NMR tube. 1H and 31P{1H} spectra recorded 20 min later revealed quantitative conversion to the title compound with liberation of 1 equiv of free P2I5. 1H NMR (400 MHz, C6D6, 20°C): δ −22.74 (d, 2JH–P = 46 Hz, 2H, RuH), −0.24 (s, 6H, PNP-SiMe2), 0.46 (s, 6H, PNP-SiMe2), 0.92 (dd, [JH–P = 12 Hz, 2JH–P = 7 Hz, 1H, RuH], 1.37 [3JH–P = 14 Hz, 2H, PNP-C6H5, 3.08 (br s, 1H, P–H)]. 

Ru[HPNP-Cy]3Cl. Method 1. LiN(SiMe2CH2PPh2)2)0.75Et2O (1.032 g, 1.87 mmol) and 470.1 mg (1.002 mmol) of [RuHCl(PiPr3)2]2 were combined in 125 mL of C6D6 and placed in an NMR tube. This solution was degassed and the head space of the 300 mL flask was evacuated and refilled with THF at room temperature to form a reddish brown slurry. Within 5 min, the red-brown solution had become bright yellow. (HPNP-Cy)RuH5, was present at 62.5 ppm, corresponding to approximately 10% of the reaction mixture at 20°C. Reaction of (HPNP-Cy)RuH(CO)Cl.

Ru[PNP-Cy]3H. (HPNP-Cy)RuHCl3 (24.3 mg, 0.0363 mmol) was dissolved in approximately 0.5 mL C6D6 and placed in an NMR tube. P3Pr (7.1 μL, 1.02 equiv) was added via syringe. No reaction was observed by NMR after 18 h at room temperature. Heating the solution for an additional 5 days at 60°C resulted in the formation of (HPNP-Cy)RuHCl(P3Pr) (35% yield), among other decomposition products. 1H NMR (400 MHz, C6D6, 20°C): δ −12.50 (br s, 1H, RuH), 0.13 (s, 6H, PNP-SiMe2), 0.35 (s, 6H, PNP-SiMe2), 1.30 [br d, 3JH–P = 9 Hz, 18H, (PCH2)2], 1.0–2.2 [m, 43H, PNP-C6H5 overlapping with PPN-C6H5]. 2.24 [br d, JH–P = 14 Hz, 2H, PNP-CH2 or PNP-C6H5(methylene)]. 2.30 [br d, JH–P = 12 Hz, 2H, PNP-CH2 or PNP-C6H5(methylene)]. 2.53 [br d, JH–P = 12 Hz, 2H, PNP-CH2 or PNP-C6H5(methylene)]. 3.08 (br s, 1H, HPNP). 

Reaction of (HPNP-Cy)RuH(CO)Cl. (HPNP-Cy)RuHCl3 (10 mg, 0.0148 mmol) was dissolved in approximately 0.5 mL C6D6 and placed in an NMR tube. This solution was placed under 1 atm of CO by standard gas line techniques. Within 5 min, the red-brown solution had become bright yellow. (HPNP-Cy)RuH(CO)Cl was identified by NMR. 1H NMR (400 MHz, C6D6, 20°C): δ −5.47 (t, JH–P = 12 Hz, 1H, RuH), 0.43 (m, 12H, PNP-SiMe2), 0.37 (s, 6H, PNP-SiMe2), 0.9–2.1 (m, 48H, PNP-C6H5, PNP-CH3, 3) (31P{1H} NMR (162 MHz, C6D6, 20°C): δ 53.7 (s). 

Ru[PNP-Cy]3H. (HPNP-Cy)RuHCl3 (199.9 mg, 0.2989 mmol) was dissolved in approximately 15 mL of C6H6. LiTMP (74.1 mg, 1.68 equiv, in 5 mL C6H6) was added dropwise over 20 min at 0°C to the red-brown solution and allowed to stir at room temperature for 20 min. The solvent was removed in vacuo, and the resulting reddish brown solid was extracted with pentane and filtered through Celite, yielding an off-white solid (LiCl) and a red filtrate. The solution was concentrated in vacuo and cooled to −40°C; (HPNP-Cy)RuH3 was obtained as a reddish powder (isolated yield 46%; yield of the crude product 71%). Following the identical procedure with (Me)SiCH2Li gives comparable yields and product purity. 1H NMR (400 MHz, C6D6, 20°C): δ −15.03 (t, JH–P = 12 Hz, 1H, RuH), 0.49 (s, 12H, PNP-SiMe2), 0.9–1.89 (m, 48H, PNP-C6H5, PNP-CH3, 3) (31P{1H} NMR (162 MHz, C6D6, 20°C): δ 53.4 (s). Attempts to obtain a 31P{1H} NMR spectrum were unsuccessful, due to decomposition of (PNP)RuH3 over several hours in solution.

Ru[PNP-Cy]2H. (HPNP-Cy)RuHCl3 (9.6 mg, 0.0152 mmol) was dissolved in approximately 0.5 mL C6D6 and placed in a gas tight NMR tube. The solution was degassed and the head space gasses removed. One atmosphere (20°C) of H2 was added via standard gas line techniques. After 10 min, 1H NMR revealed a new broad singlet at −8.90 ppm, and a shifting and broadening of the RuH3 signal, formerly found at −15.0 ppm, to approximately −11 ppm (exact value is determined by the amount of hydrogen present in the system). Similarly, a new 31P signal, which can be assigned to (PNP-Cy)RuH3, was present at 62.5 ppm, corresponding to approximately 10% of the reaction mixture at 20°C. Removal of all volatiles and redissolution in C6D6 gave 100% (PNP-Cy)RuH3, as shown by a broad singlet (formerly a triplet, but broadened by the H-D solvent exchange described elsewhere) at −14.98 ppm and a singlet in the 31P at 55.3 ppm. Variable temperature experiments did not decoalesce the RuH3 hydrogens, though a reduction in temperature to less
than −20 °C allowed the nearly quantitative production of (PNP-Cy)RuH2 from (PNP-Cy)RuH3.

**RuH(PNP-Cy)(CO(CH2)2).** Method 1. (HPNP-Cy)RuH2Cl (10 mg, 0.015 mmol) was dissolved in 0.5 mL C6D6; 2.2 µL (1.02 equiv) of NEt3 and 6.0 µL of C6H8O (2.3-dihydrofuran, 5.15 equiv) were added via syringe. The solution was transferred to an NMR tube. NMR spectra taken through 12 h at room temperature showed no change in the observed spectra. After 2 h of heating at 60 °C, 14% conversion to the title product was seen; this increased to 95%+ after 2 days of heating at 60 °C.1H NMR (400 MHz, C6D6, 20 °C): δ −16.82 (t, JH–P = 22 Hz, 1H, RuP); 0.43 (s, 6H, PNP-SiMe2); 0.28 (s, 6H, PNP-SiMe2); 0.80 (dt, JH–P = 9 Hz, JPH = 4Hz, 2H, PNP–CH2); 1.1–2.2 (m, PNP–C6H11, PNP–CH2), 1.97 (br t, 2H, 3.27 (t, J = 7.2 Hz), 3.90 (t, J = 5.6 Hz). 31P{1H} NMR (162 MHz, C6D6, 20 °C): δ 41.23 (s).13C{1H} NMR (101 MHz, C6D6, 20 °C), 29.6 (s, PNP–CH2), 75.9 (s, Ru =COCH2CH2). 24.9 (s, PNP–C6H11), 26.8 (s, PNP–C6H11), 27.1 (s, PNP–C6H11), 28.0 (s, PNP–C6H11), 28.2 (s, PNP–CH2), 29.3 (s, PNP–C6H11), 30.2 (s, PNP–C6H11), 36.7 (s, PNP–C6H11), 53.2 (s, Ru =COCH2CH2), 77.9 (s, Ru =COCH2CH2), 297.8 (s, Ru =COCH2CH2).

Method 2. (HPNP-Cy)RuH2Cl (10.3 mg, 0.0158 mmol) was dissolved in 0.5 mL C6D6; 2.5 µL (1.07 equiv) of NEt3 and 5.0 µL of C6H8O (2.5-dihydrofuran, 4.18 equiv) were added via syringe. The solution was transferred to an NMR tube. NMR spectra taken through 12 h at room temperature showed no change. After 4 days heating at 60 °C, 95%+ conversion to indicated product was observed.

Method 3. (PNP-Cy)RuH2 (11.1 mg, 0.01756 mmol) was dissolved in 0.5 mL C6D6; 3.0 mg (1.24 equiv) of NEt3 and 6.0 µL of C6H8O (2.3-dihydrofuran, 4.52 equiv) were added via syringe. The solution was transferred to an NMR tube. After 2 h at 25 °C, NMR spectra showed 60% of (HPNP-Cy)RuH2Cl, 30% the end carbide (characterization above), and 10% (HPNP-Cy)RuH2. After 4 h of heating at 60 °C, 95% conversion to the hydrido carbene was seen.

Method 4. (HPNP-Cy)RuH2Cl (10.3 mg, 0.01382 mmol) was dissolved in 0.5 mL C6D6; 2.2 µL (0.99 equiv) of NEt3 and 5.0 µL of C6H8O (2.5-dihydrofuran, 4.18 equiv) were added via syringe. The solution was transferred to an NMR tube. After 5 days at 60 °C, NMR spectra showed quantitative conversion to the hydrido carbene.

Reaction of Ru(PNP-Cy)H4 with C6H8CH2CH2. (PNP-Cy)RuH2 (10 mg, 0.0161 mmol) was dissolved in 0.5 mL of C6H8. Styrene, C6H8CH2CH2 (5.5 µL, 5.28 µL) was added via syringe. After 3 h at room temperature, two products [bound olefin and an η1-cyclohexenyl(cyclohexyl) phosphine complex in an approximately 3:1 ratio] were observed. After 15 h at 60 °C, 95% conversion to the η1-cyclohexenyl(cyclohexyl) phosphine complex was seen.1H NMR (400 MHz, C6D6, 20 °C) of the olefin complex: δ −22.72 (dt, JH–P = 24 Hz, JPH = 20 Hz, 3H, RuP); 0.59 (s, 3H, PNP-SiMe2); 0.48 (s, 3H, PNP-SiMe2); 0.39 (s, 3H, PNP-SiMe2); 0.19 (s, 3H, PNP-SiMe2); 0.9–1.89 (m, 48H, PNP–C6H11, PNP–CH2), bound styrene resonances are located under free styrene and evidenced by broadening only.31P{1H} NMR (162 MHz, C6D6, 20 °C) of the olefin complex: δ 44.6 and 35.0 (AB pattern, JF = 319 Hz).1H NMR (400 MHz, C6D6, 20 °C) of the η1 complex: δ 0.76 (s, 3H, PNP-SiMe2), 0.53 (s, 3H, PNP-SiMe2), 0.42 (s, 3H, PNP-SiMe2), 0.23 (s, 3H, PNP-SiMe2), 0.9–2.40 (m, 47H, PNP–C6H11, PNP–CH2).31P{1H} NMR (162 MHz, C6D6, 20 °C) of the η1 complex: δ 104.51 and 32.58 (AB pattern, JF = 303 Hz). No hydrides are observed.

**Reaction of Ru(PNP-Cy)H4 with CH2CH(CH3)2.** (PNP-Cy)RuH2 (7.4 mg, 0.0117 mmol) was dissolved in 0.5 mL of C6H8. Bu-ethylene, CH2(CH3)(CH3), (7.5 µL, 4.97 equiv) was added via syringe. After 15 min at room temperature, two products [bound olefin and an η1-cyclohexenyl(cyclohexyl) phosphine complex in an approximately 0.8:1 ratio] were observed, along with some liberated neohexane. After 15 h at 60 °C, 95% conversion to the η1-cyclohexenyl(cyclohexyl) phosphine complex was seen.1H NMR (400 MHz, C6D6, 20 °C) of the olefin complex: δ −19.97 (br t, JH–P = 19 Hz, 3H, RuP); 0.41 (s, 3H, PNP-SiMe2); 0.36 (s, 3H, PNP-SiMe2); 0.31 (s, 3H, PNP-SiMe2); 0.28 (s, 3H, PNP-SiMe2); 0.9–1.94 (m, 48H, PNP–C6H11, PNP–CH2), bound η1 Bu ethylene resonances are located under free η1 Bu ethylene and evidenced by broadening only.31P{1H} NMR (162 MHz, C6D6, 20 °C) of the olefin complex: δ 63.1 and 36.0 (AB pattern, JF = 326 Hz).1H NMR and 31P{1H} NMR of the η1 complex are the same as reported above.

**C–H/D exchange**

In a typical experiment, 10 mg of (PNP-Cy)RuH2 was dissolved in the appropriate solvent in a gas-tight NMR tube; 25 mg of the Ru complex was used for 2H spectra. In order to clearly follow H/D exchange in benzene at room temperature and within reasonable time intervals, a 1:1 mixture of C6D6/C6D6 was employed; positions of deuteriation were determined by 1H and 2H NMR. In cyclohexane-δ2, no resolved coupling for (PNP-Cy)RuH2D was seen in the 1H NMR; in all cases, a broad singlet results after the specified time periods.

**X-Ray structure determinations**

RuH(PPh3)[N(SiMe2CH2PCy2)2]. The orange crystal of RuH(PPh3)[N(SiMe2CH2PCy2)2] grown from a saturated toluene solution by slow evaporation, was affixed to a glass fiber using silicone grease. The sample was then transferred from the glove bag to the goniostat where it was cooled to 113 K using a gas-flow cooling system of local design. The data were collected on a Bruker SMART 6000 diffractometer at 113 K using 5 s frames with an omega scan of 0.30 degrees. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged using the Bruker SAINT software as well as utility programs from the XEL2 library. The structure was readily solved using SHELXTL and Fourier techniques. With the exception of the hydride hydrogen, all hydrogen atoms were readily located in a difference Fourier phased on the non-hydrogen atoms. All hydrogen atoms located were allowed to vary isotropically in the final cycles of refinement. A careful examination of the final difference Fourier map did not locate any peaks that could be readily identified as the metal hydride position. A final difference Fourier map was featureless, the largest peak being 1.32 eÅ−3 at the metal site.

(RHPNP-Bu)RuH2Cl. A yellow crystal, grown from C6D6, and ether by layering, was cut to the approximate dimensions 0.30 × 0.30 × 0.30 mm3 and was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a SMART6000 (Bruker) at 113(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 460 reflections. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 10 s and a detector distance of 5.01 cm. A randomly oriented
region of reciprocal space was surveyed to the extent of 1.5 spheres and to a resolution of 0.51 Å. Five major sections of frames were collected with 0.30° steps in ω at five different ϕ settings and a detector position of −43° in 2θ. An additional set of 50 frames was collected in order to model decay. The intensity data were corrected for absorption and decay (SADABS). The final full-matrix least-squares refinement converged to R = 0.0305 and wR2 = 0.0776 (F², all data). The remaining electron density is located around the metal and the chlorine atom.

Acknowledgements

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References

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