Amido/phosphine pincer hydrides of ruthenium

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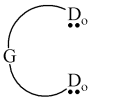
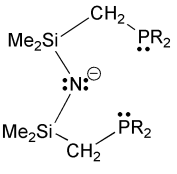
The chemistry of the ligand $(R_2PCH_2SiMe_2)_2N^-$ (R = cyclohexyl and ^{t}Bu), "PNP-R", on ruthenium is developed, including RuH(PNP-Cy)(PPh_3) and (HPNP-R)RuH_3Cl. The latter contains a protonated nitrogen (*i.e.*, amine as a donor to Ru) and one H_2 ligand (X-ray structure for R = ^{t}Bu). This compound can be dehydrohalogenated to give (PNP-Cy)RuH_3, which undergoes H/D exchange of D_2 into its cyclohexyl rings, and is itself dehydrogenated by excess H_2C=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)RuH_3 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 recently[1–10] 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 D_o can be phosphorous or nitrogen, and this D_oRR' 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 D_o, 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]

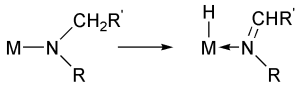


I



II

The ability of an amide N to participate in π-donation to the metal is something we have developed[14] 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 (persistant), 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.



III

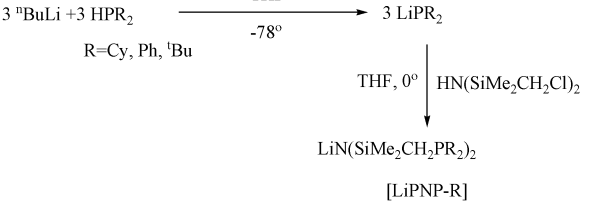
We report here our efforts to develop ruthenium polyhydride chemistry with the PNP ligand carrying primarily cyclohexyl substituents, since ligand steric bulk has been proven effective in preventing reagent deactivation *via* dimerization.

Results and discussion

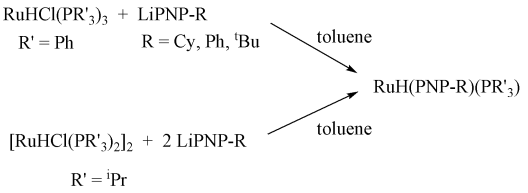
Preparation of the PNP-R ligands

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, HPR_2, 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



Scheme 2

Synthesis and characterization of RuH(PNP-R)(PR′$_3$)

The reaction of the lithium salt of the PNP-R ligand with Ru hydrido-chlorides forms the hydride-phosphine complex RuH(PNP-R)(PR′$_3$) (Scheme 2).

Both the PPh_3 and P^iPr_3 derivatives can be synthesized; the former from reaction of a toluene solution of $RuHCl(PPh_3)_3$ with the LiPNP-R salt, and the latter from $[RuHCl(PR'_3)_2]_2$.

Reaction of LiPNP-Ph or Cy with the ruthenium hydrides at room temperature gives quantitative conversion to the appropriate RuH(PNP-R)(PR′$_3$). 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 $^{31}P\{H\}$ NMR exhibits a doublet, due to the interaction of PR_2 with PR′$_3$, and a downfield triplet from PR′$_3$ coupling to PNP-PR_2. Synthetic scale purification of RuH(PNP-R)(PPh_3) was performed by removal of the liberated phosphine *via* sublimation.

Solid-state structure of Ru(H)(PNP-Cy)(PPh_3)

A single crystal suitable for X-ray diffraction studies was obtained from slow evaporation of a toluene solution of RuH(PNP-Cy)(PPh_3). 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 molecular structure of RuH(PNP-Cy)(PPh_3) shows the expected coordination geometry of two trans PR_2 groups [with a P_1–Ru–P_2 angle of 161.71(5)°] mutually cis to the amide nitrogen. The amide nitrogen lies 2.145(4) Å away from the Ru center and shows no pyramidalization (sum of angles around the nitrogen center is 359.96°). The Ru–P (PNP) bond lengths are 2.3764(15) and 2.3538(14) Å for P_1 and P_2, respectively, slightly shorter than the corresponding Ru–P distances [2.3892(8) and 2.3998(7) Å] in the previously characterized structure of $RuCl(C_6H_4PPh_2)[NH(SiMe_2CH_2PPh_2)_2]$.[13] PPh_3 has a Ru–P bond length of 2.235 Å with distances and angles in the structure suggesting that no agostic Cy or Ph is present. The PNP pincer ligand is approximately coplanar with the ruthenium metal center; however, the triphenylphosphine ligand is bent away from that plane, suggesting a Y-shaped structure, **IV**.

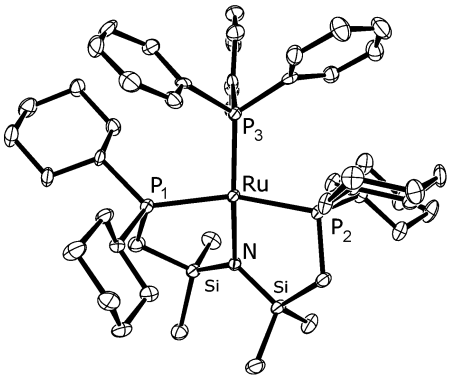
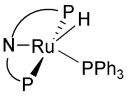


Fig. 1 Crystal structure determination of (PNP-Cy)RuH(PCy_3).



IV

The hydride, while not located in the crystal structure refinement, was located by DFT calculations,[15] 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–PH_3 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.

Synthesis and characterization of (HPNP-Cy)RuH_3Cl

A successful entry into polyhydride PNP-Ru chemistry involves the synthesis and isolation of the pincer-protonated (HPNP-Cy)RuH_3Cl as a precursor to a 16 e$^-$ Ru species. (HPNP-Cy)RuH_3Cl can be made [eqn. (1)] in poor (isolated) yield from the corresponding protonated HPNP-Cy ligand and $RuH_3Cl(PCy_3)_2$, liberating 2 equiv of PCy_3.

$$\text{HPNP-Cy} + \text{RuH}_3\text{Cl}(\text{PCy}_3)_2 \xrightarrow{\text{C}_6\text{H}_6} (\text{HPNP-Cy})\text{RuH}_3\text{Cl} + 2\text{PCy}_3 \quad (1)$$

Synthesis of (HPNP-Cy)RuH_3Cl is also possible from a variety of common Ru starting materials, including $[(p\text{-cymene})RuCl_2]_2$, $[(COD)RuCl_2]_n$ or $[(C_6H_6)RuCl_2]_2$, by the use of the LiPNP-Cy salt under an atmosphere of hydrogen [eqn. (2)]. Stirring this solution overnight in THF at room temperature produces (HPNP-Cy)RuH_3Cl; this 18 e$^-$ complex has proven relatively easy to isolate in good yield by recrystallization from pentane.

$$0.5[p\text{-cymene})\text{RuCl}_2\text{l}_2$$
or
$$1/n[\text{COD}]\text{RuCl}_2]_n + \text{LiPNP-Cy} \xrightarrow[\text{H}_2]{\text{THF}} (\text{HPNP-Cy})\text{RuH}_3\text{Cl}$$
or
$$0.5[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2 \quad (2)$$

Table 1 Crystal structure parameters

Chemical formula	Ru(H)(PPh_3)(N($SiMe_2CH_2PCy_2$)$_2$)	RuH_3Cl[NH($SiMe_2$-$CH_2P^tBu_2$)$_2$]
Empirical formula	$C_{48}H_{76}NP_3RuSi_2$	$C_{22}H_{76}NP_3RuSi_2$
Molecular weight	917.30	589.32
Crystal system	Triclinic	Orthorhombic
Space group	*P*1 bar	*Pbca*
T/K	113	113(2)
μ/mm^{-1}	0.509	0.786
U/Å^3	2399.75	6170.1(2)
a/Å	11.083(1)	14.8336(3)
b/Å	12.643(1)	13.0180(3)
c/Å	18.442(1)	31.9522(7)
α/°	88.64(1)	90
β/°	88.80(1)	90
γ/°	68.28(1)	90
Z	2	8
Total reflections collected	11017	19135
Unique reflections	10301	14501
R_{int}	0.067	0.050
Observed reflections [$I > 2.3\sigma(I)$]	6091	9648
$R(F)$ (all data)	0.046	0.0305
$R_w(F)$ (all data)	0.037	0.0776

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

	(PNP)RuH(PH_3) Calcd (B3PW91)	(PNP)RuH(PPh_3) Exptal
Ru–N	2.118	2.15
N–Si	1.734	1.71
Si–C	1.876	1.87
C–P	1.850	1.83
P–Ru	2.326	2.37
Ru–PR_3	2.275	2.24
Ru–H	1.562	N/A
N–Ru–H	113.0	N/A
N–Ru–PR_3	164.2	158.5

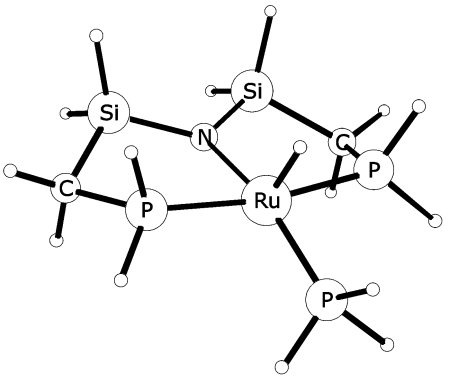


Fig. 2 Geometry optimized structure of (PNP)RuH(PH_3) (see Table 2 for parameters).

(HPNP-Cy)RuH_3Cl 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 T_1(min) was found at 59(1) ms (C_7D_8, 400 MHz, −30 °C), suggesting a trihydride structure with relatively small R_{H-H} and ∠H–Ru–H or an $RuH(H_2)$ 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-^{t}Bu)RuH_3Cl

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-^{t}Bu)Li analogously were unsuccessful. Reactions of (PNP-^{t}Bu)Li with $RuHCl(PPh_3)_3$, $[RuHCl(PR_3)_2]_2$ and $[(arene)RuCl_2]_2$ 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,[16] we decided to try this approach here. The reaction between (PNP-^{t}Bu)MgCl(dioxane) and $[(p\text{-cymene})RuCl_2]_2$ in C_6D_6, followed by exposure to H_2 atmosphere, cleanly produces (HPNP-^{t}Bu)RuH_3Cl (95% purity by NMR). Solid (HPNP-^{t}Bu)RuH_3Cl was isolated in the form of X-ray quality crystals in 61% yield. The RuH_3 spin system gives rise to a single resonance in the ^{1}H NMR spectrum at −12.96 ppm (t, J_{HP} = 15 Hz) and selective decoupling of only the alkyl hydrogens gives rise to a quartet (from three H on Ru) in the ^{31}P NMR spectrum for the equivalent P nuclei of the HPNP 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 (∠N1–Ru–Cl1 = 82.6°), presumably due to the N–H···Cl hydrogen bonding. This hydrogen bonding is also evident in the unusually small ∠Ru–N–H of 91.0(16)°, which has the effect of shortening this very nonlinear (*i.e.*, unfavorable) hydrogen bond. The dihedral angle H1N–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 HPNP ligand and a metal-bound halide was observed in Ir complexes of protonated PNP ligand.[17,18]

Reactivity of (HPNP-Cy)RuH_3Cl

Attempts to form (HPNP-Cy)RuH_4 from (HPNP-Cy)RuH_3Cl by using various hydride transfer reagents [$NaBH_4$, $LiAlH_4$, Cp_2ZrHCl, Et_3SiH, Me_2PhSiH, $(^tBu)_3SiH$] 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)RuH_3Cl was allowed to react with 1 atm of D_2, even at elevated temperatures (60 °C for 20 h in C_6D_6).

However, some ligand replacement reactions were moderately successful. (HPNP-Cy)$RuHCl(P^iPr_3)$ can be formed in 35% yield by reaction of (HPNP-Cy)RuH_3Cl with a stoichiometric amount of P^iPr_3 for 5 days at 60 °C. This slow rate is apparently the result of the complex being saturated. No change in yield or identity of products formed is observed with the addition of excess phosphine. The synthesis of (HPNP-Cy)$RuHCl(P^iPr_3)$ was confirmed by the independent reaction of $[RuHCl(P^iPr_3)_2]_2$ with HPNP-Cy, which produced (HPNP-Cy)$RuHCl(P^iPr_3)$ in quantitative yield. The N–H signal of the

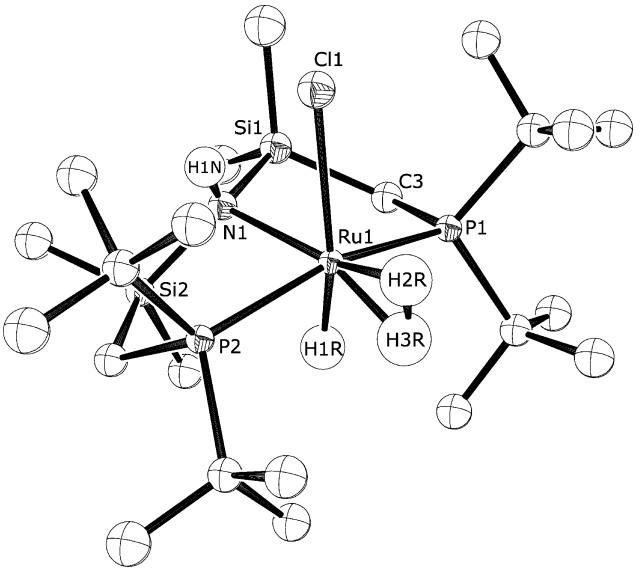


Fig. 3 X-Ray crystal structure of (HPNP-^{t}Bu)$RuH(H_2)Cl$.

Table 3 Selected distances (Å) and angles (deg) for [HPNP-^{t}Bu]-RuH(H$_2$)Cl

Ru(1)–N(1)	2.3115(10)	Ru(1)–H(3R)	1.52(3)
Ru(1)–P(2)	2.3520(3)	Si(1)–N(1)	1.7919(11)
Ru(1)–P(1)	2.3636(3)	Si(2)–N(1)	1.7672(11)
Ru(1)–Cl(1)	2.5263(3)	N(1)–H(1N)	0.79(2)
Ru(1)–H(1R)	1.48(2)	H(2R)–H(3R)	1.12(3)
Ru(1)–H(2R)	1.61(2)		
N(1)–Ru(1)–P(2)	87.89(3)	P(1)–Ru(1)–H(1R)	81.9(9)
N(1)–Ru(1)–P(1)	90.27(3)	Cl(1)–Ru(1)–H(1R)	165.4(8)
P(2)–Ru(1)–P(1)	163.725(11)	Si(2)–N(1)–Si(1)	124.06(6)
N(1)–Ru(1)–Cl(1)	82.56(3)	Si(2)–N(1)–Ru(1)	107.21(5)
P(2)–Ru(1)–Cl(1)	98.691(11)	Si(1)–N(1)–Ru(1)	112.25(5)
P(1)–Ru(1)–Cl(1)	97.098(11)	Si(2)–N(1)–H(1N)	111.6(16)
N(1)–Ru(1)–H(1R)	82.9(8)	Si(1)–N(1)–H(1N)	105.7(16)
P(2)–Ru(1)–H(1R)	81.8(9)	Ru(1)–N(1)–H(1N)	91.0(16)

amine is observed slightly upfield of (HPNP-Cy)RuH$_3$Cl, at 3.08 ppm, and two diastereotopic Si–Me signals are observed at 0.35 and 0.13 ppm. As in the case of (PNP-Cy)RuH(P^{i}Pr$_3$), the ^{31}P{^{1}H} NMR spectrum is characterized by two signals, a doublet, due to PCy$_2$/P^{i}Pr$_3$ coupling, and a downfield triplet from P^{i}Pr$_3$.

Reaction of (HPNP-Cy)RuH$_3$Cl with 1 atm of CO in C$_6$D$_6$ immediately results in the formation of a yellow solution (from the red-brown of the starting materials) and the evolution of H$_2$ (as seen by ^{1}H NMR). Within 1 h the reaction is complete, forming primarily (HPNP-Cy)RuH(CO)Cl, which is characterized by two diastereotopic Si–methyl signals at 0.43 and 0.37 ppm, integrating to 6 hydrogens each, as well as a triplet in the hydride region at −5.47 ppm (J_{P-H} = 19 Hz). The ^{31}P NMR resonance can be observed as a singlet at 53.7 ppm.

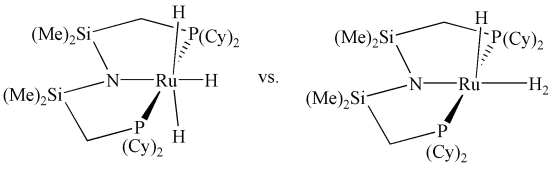
Formation of an unsaturated polyhydride

(PNP-Cy)RuH$_3$ can be prepared in poor (isolated) yield by the reaction of RuH$_3$Cl(PCy$_3$)$_2$ with the corresponding LiPNP-Cy salt. Because of the difficulty in separating free phosphine from the reaction mixture, it was thought that reaction of (HPNP)RuH$_3$Cl with agents that would affect removal of HCl was a more promising synthetic route. (HPNP-Cy)-RuH$_3$Cl reacts quantitatively with lithium 2,2,6,6-tetramethylpiperidide (LiTMP) or Me$_3$SiCH$_2$Li to form (PNP-Cy)RuH$_3$, LiCl, and the protonated base [eqn. (3)]. Recrystallization from pentane gives a 45% yield of the unsaturated Ru species.

$$\begin{aligned}&(\text{HPNP-Cy})\text{RuH}_3\text{Cl} + \text{LiTMP}\\ &\xrightarrow{-\text{LiCl}} (\text{PNP-Cy})\text{RuH}_3 + \text{TMP-H}\\ &(\text{HPNP-Cy})\text{RuH}_3\text{Cl} + \text{Me}_3\text{SiCH}_2\text{Li}\\ &\xrightarrow{-\text{LiCl}} (\text{PNP-Cy})\text{RuH}_3 + \text{Si(CH}_3)_4 \qquad (3)\end{aligned}$$

A triplet at −15.04 ppm is seen for (PNP-Cy)RuH$_3$ in the hydride region of the ^{1}H NMR spectrum if a spectrum is taken immediately upon dissolution [allowing (PNP-Cy)RuH$_3$ to stand in deuterated solvent causes the signal to broaden from H–D exchange, as detailed in the C–H activation section later in this paper]. The Si(Me)$_2$ groups are equivalent at all available temperatures, and a ^{31}P singlet is observed at 55.4 ppm. Even at −90 °C, only one signal is observed. A T_1(min) of 45(2) ms (C$_7$D$_8$, 300 MHz, −60 °C) was measured. As in the case of (HPNP-Cy)RuH$_3$Cl, this does not unequivocally confirm a structure, but is consistent with an averaged T_1 from a hydride/dihydrogen system *or* with three independent hydrides placed in close proximity to each other (short R_{H-H}).[19,20]

Thus, two structures consistent with the spectral data can be considered, **V** and **VI**. The redox isomer containing Ru(II) has been seen for the corresponding chloro-bisphosphine Ru complex, RuH(Cl)(H$_2$)(PCy$_3$)$_2$.[21]



V **VI**

DFT calculation of these RuH$_3$ complexes[15] revealed that the geometry optimizes to a (PNP)RuH(H$_2$) structure (Fig. 4, structure **VI** above but with all Me and Cy replaced by H), regardless of the initial geometry (trihydride or hydride/dihydrogen) employed. The Ru(IV) form, (PNP)Ru(H)$_3$, is not a minimum on the potential energy surface. The Ru species is calculated to have an H–H distance of 0.95 Å, lengthened considerably from the value calculated in free H$_2$ (0.74 Å), due to back donation into σ*(H–H) enhanced by the π-donor amide ligand trans to itself. RuH bond lengths to H$_2$ 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(H$_2$) compounds.[22]

Reactivity of (PNP-Cy)RuH$_3$

Reactivity of (PNP-Cy)RuH$_3$ toward H$_2$. H$_2$ (1 atm) adds reversibly (but incompletely) to form (PNP-Cy)RuH$_5$ at room temperature [Fig. 5 and eqn. (4)]. The hydrides *within* the resulting (PNP-Cy)RuH$_5$ are never fully decoalesced (k_i for intramolecular site exchange is very large), even at −95 °C, while signals for H$_2$ and for (PNP-Cy)RuH$_3$ are resolved on the ^{1}H NMR time scale (k_f is small) at −95 °C [eqn. (4)].

$$\underbrace{(\text{PNP-Cy})\text{RuH}_3 + \text{H}_2}_{^1\text{H (20 °C) coalesced at } \delta -10.72} \overset{k_f}{\rightleftharpoons} \underbrace{(\text{PNP-Cy})\text{RuH}_5}_{k_i,\,^1\text{H (20 °C) } \delta -9.06} \qquad (4)$$

At 20 °C in d$_8$-toluene, the (PNP-Cy)RuH$_3$ resonance, usually observed at −15.04 ppm, is coalesced with the dissolved hydrogen, forming a broad singlet at −10.72 ppm with 1 atm H$_2$ added (the position of the signal is dependent on the pressure of hydrogen added and the temperature of the

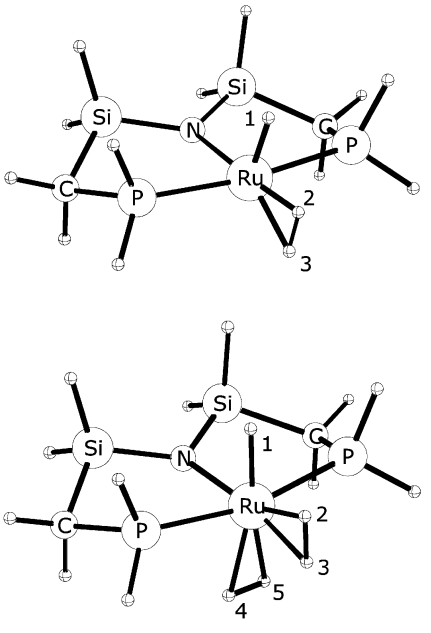


Fig. 4 DFT calculated, geometry-optimized structures of (PNP)RuH$_n$.

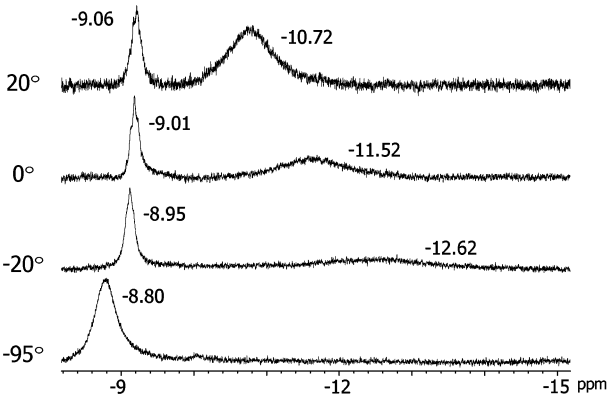


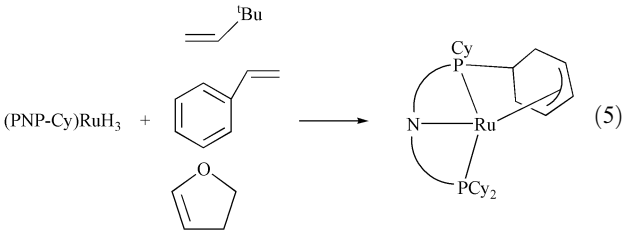
Fig. 5 Variable temperature NMR spectra of the (PNP-Cy)RuH_3/(PNP-Cy)RuH_5 equilibrium.

sample). With a reduction in temperature, the increased mole fraction of (PNP)RuH_5 increases the signal intensity at −9.06 ppm. As the mole fraction of (PNP)RuH_3 and H_2 decrease, a substantial shift and broadening of the (PNP)RuH_3/H_2 coalesced signal is seen, broadening almost completely at −20 °C (−12.62 ppm). No additional signal beside that assigned to (PNP)RuH_5 is observed at −95 °C (Fig. 5), where the equilibrium in eqn. (4) is shifted nearly fully to the right. Returning the sample to room temperature results in complete reversal of the temperature-dependent shifts to their original values. Evacuation of the sample, followed by redissolution in deuterated solvent confirms that only (PNP)RuH_3 (and its H–D exchange products) are present.

Performing a similar experiment as above in C_7H_8 and following the reaction by ^2H NMR also results in the appearance of a coalesced (PNP-Cy)RuH_3 and D_2 signal at −12.39 ppm (0.9 atm of D_2 added at ambient laboratory temperature). By ^{31}P NMR, the reaction mixture contained 34 mole percent of the (PNP-Cy)Ru(H/D)$_5$ product, while the remainder was (PNP-Cy)Ru(H/D)$_3$. The addition of D_2 was again reversible; removal of the solvent *in vacuo* and redissolution of the remaining reddish-brown solid in C_6D_6 showed only the presence of (PNP-Cy)Ru(H/D)$_3$ by ^1H and ^{31}P NMR.

As mentioned above, the hydride ligands within (PNP)RuH_5 are not decoalesced even at low temperature; therefore, an experimental determination of the hydride/dihydrogen nature of these ligands is not possible. A DFT study of the (PNP)RuH_5 complex,[15] using the same model as described above for the (PNP)RuH_3 calculation, found that (PNP)RuH_5 converges to a hydride/bis-dihydrogen structure, with the H_2 trans to N having a longer H/H distance (0.92 Å) than that trans to hydride (0.80 Å), consistent with differential back-donation into each of the σ*(H–H) caused by the trans ligand, H or N (Fig. 4). The Ru–H(hydride) distance (1.58 Å) is shorter than those to H_2, and a shorter H–H distance (H4 to H5), 0.80 Å, correlates with a longer Ru–H distance, 1.88 Å (*cf.* ∼1.68 Å to H2 and H3). The two H_2 molecules are orthogonal, which is a symptom of their interaction with *different* d_π orbitals for back-donation.

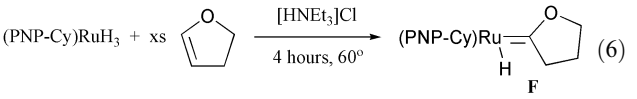
Reactivity of (PNP-Cy)RuH_3 toward olefins. The reaction (typically 5–10 h at room temperature followed by 10–15 h at 60 °C in C_6D_6) of (PNP-Cy)RuH_3 with a variety of olefins (typically in a 1:4 mole ratio) results in the formation of an η^3-cyclohexenyl ring [eqn. (5)], in addition to small amounts 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 sp^3 carbons, by an olefin acting as a hydrogen acceptor.



(5)

In the reaction mixture, the η^3-cyclohexenyl(cyclohexyl)-phosphine complex is characterized by an AB pattern at $^{31}P\{^1H\}$ δ 104.51 and 32.58 (J_{P-P} = 303 Hz), as well as *four* $SiCH_3$chemical shifts. The proposed structure is based on such reactions with other cyclohexyl-substituted phosphines.

The addition of [NEt_3H]Cl minimizes the formation of the η^3-metallated cyclohexyl phosphine ring, allowing, for example, in the case of the dihydrofuran, progression to the carbene **F** [eqn. (6)].



(6)

F

One possible mechanism that accounts for the observed intermediates and the influence of the addition of [NEt_3H]Cl upon the product distribution is detailed in Scheme 3.

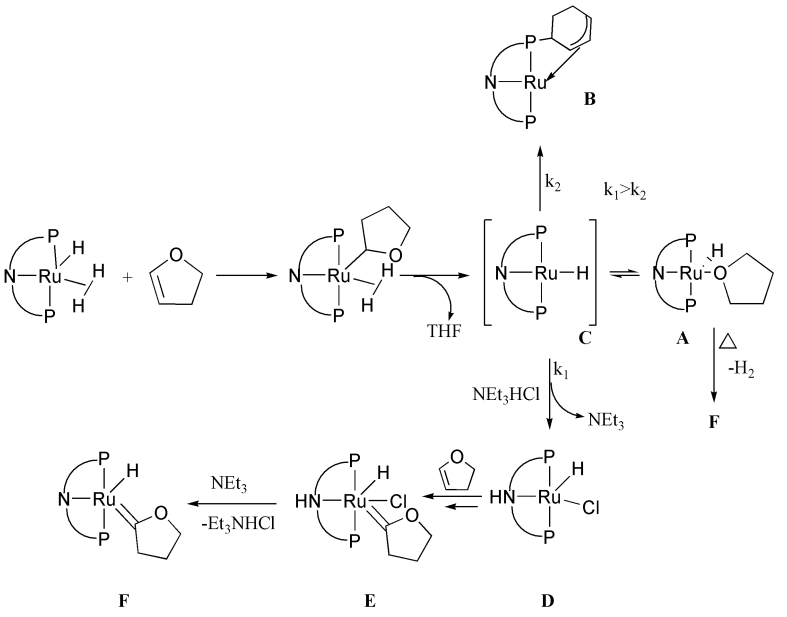
The formation of **A** can be observed as the first signals resulting from the reaction of any amount of 2,3-dihydrofuran with (PNP-Cy)RuH_3. Within 5 min of their mixing, there is a complete disappearance of the signals due to (PNP)RuH_3 (*i.e.*, the hydride at −15.03 ppm and the accompanying ^{31}P signal) and the appearance of only one hydride resonance, a triplet at −17.6 ppm. A $^{31}P\{^1H\}$ *singlet* and other ^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 H_2 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 η^3-metallated cyclohexyl product (identified by the AB $^{31}P\{H\}$ 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 η^3-metallated product, 20–30% of the carbene, and 40–60% of complex **A** is obtained. The addition of a catalytic amount of [NEt_3H]Cl at this point decreases the amount of the η^3-cyclometallated product in solution; thus, **B** and **C** are in equilibrium under H_2.

Heating the reaction mixture without the addition of [NEt_3H]Cl results in the conversion of **A** to the carbene species, with little change in the amount of η^3 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 η^3-cyclometallated product. If [NEt_3H]Cl is added at any point, nearly quantitative conversion to the carbene is seen.

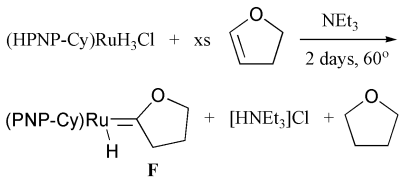
Addition of [NEt_3H]Cl to a solution of (PNP-Cy)RuH_3 and subsequent addition of the other olefins under consideration (styrene, ^{t}Bu-ethylene) results simply in the olefin adduct of the unsaturated (PNP-Cy)RuH_3 complex, an addition that is reversible upon removal of volatiles *in vacuo*. Each olefin complex shows a $^{31}P\{^1H\}$ NMR AB pattern, due to the prochiral character of the olefin.

Identical products are observed [eqn. (7)] from the reaction of (HPNP-Cy)RuH_3Cl and NEt_3, which allows the *in situ*



Scheme 3

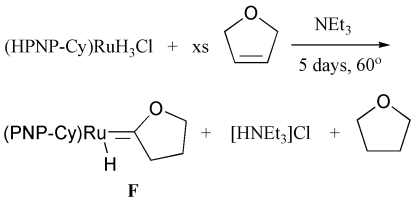
dehydrohalogenation of the 18 e^- species and the formation of a reactive 16 e^- complex, presumably (PNP-Cy)RuH_3.



(7)

This transient unsaturated complex was trapped by the addition of excess 2,3-dihydrofuran to a benzene solution of equimolar (HPNP-Cy)RuH_3Cl and NEt_3. After 2 days at 60 °C complete conversion to the carbene complex **F** could be seen [eqn. (7)], together with 1 equiv of tetrahydrofuran. The hydride resonance of **F** is found as a triplet at −16.82 ppm, with the $^{31}P\{H\}$ 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 $RuHCl(P^iPr_3)_2$.[23] The slow reactivity of (HPNP-Cy)RuH_3Cl with 2,3-dihydrofuran *without* base must be due to its saturated character, with no good leaving group available.

Similar to (PNP-Cy)RuH_3 above, this *in situ* formed complex can also isomerize 2,5-dihydrofuran to the identical carbene [eqn. (8)]. With the addition of 2,5-dihydrofuran and NEt_3, (HPNP-Cy)RuH_3Cl forms (PNP-Cy)Ru(H)(=COC_3H_6) quantitatively in 5 days at 60 °C, again producing 1 equiv of THF. In both cases, an insoluble material ([NEt_3H]Cl) precipitates from the benzene solution.



(8)

Reactivity of (PNP-Cy)RuH_3 toward C–H bonds. (PNP-Cy)RuH_3 also participates in C(sp^3)–H activation processes.[24–26] This was first observed as H/D exchange in C_6D_6. While a triplet at −15.04 ppm is seen for (PNP-Cy)RuH_3 in the hydride region of the ^1H NMR spectrum if a spectrum is taken immediately upon dissolution, allowing (PNP-Cy)RuH_3 to stand in deuterated solvent causes the signal to broaden from H/D exchange (Fig. 6). To slow the H/D exchange at room temperature, a 1:1 mixture of C_6H_6/C_6D_6 was employed. With phosphorus decoupling, two signals can be resolved in as little as 15 min in contact with C_6D_6. After 30 min, ^{31}P decoupling of the hydride signal reveals a downfield 1:1:1 triplet (with $J_{H-D} = 5$ Hz) due to the formation of (PNP-Cy)RuH_2D as well a singlet still assignable to (PNP-Ru)H_3. These signals overlap, forming a triplet with a downfield shoulder with $J_{H-P} = 12.8$ Hz if phosphorus decoupling is not employed. Complete disappearance of a hydride signal (and thus complete conversion to (PNP-Cy)RuD_3) in the ^1H NMR occurs after 8 h in pure C_6D_6.

Interestingly, such H/D exchange also occurs with aliphatic solvents. In cyclohexane-d_{12}, for example, (PNP-Cy)RuH_3 gives a triplet at δ −15.49 (with $J_{P-H} = 12.8$ Hz) upon initial dissolution. Within 2 h, broadening of the resonance is seen, indicating a significant amount of H/D exchange. Analysis of this sample by ^2H NMR (using solvent suppression techniques to minimize the interference of C_6D_{12}) reveals a deuterium signal at −15.4 ppm, which corresponds to at least the partial formation of (PNP-Cy)Ru(H/D)$_3$ (Fig. 7).

The C–H bonds in the cyclohexyl rings in (PNP-Cy)RuH_3 also undego H/D exchange. By dissolving (PNP-Cy)RuD_3 [made either from allowing (PNP-Cy)RuH_3 to stir overnight in C_6D_6 or from reacting (PNP-Cy)RuH_3 with D_2 in deuterated solvent, then removing volatiles *in vacuo*] in toluene-d_8 at room temperature, the presence of ^2H as a broad resonance at δ 1.83 in the cyclohexyl region of the spectrum was observed. Following the D/H exchange of (PNP—Cy)RuD_3 with toluene-H_8 by ^2H NMR, the percent deuteration at the hydride site decreased more rapidly than that observed at the cyclohexyl phosphine sites.

Conclusions

The pincer-ligated compounds reported here can be compared to those with chloride in place of amide; (PNP-Cy)$RuH(H_2)$ then can be compared with $RuH(H_2)Cl(PCy_3)_2$. Both of

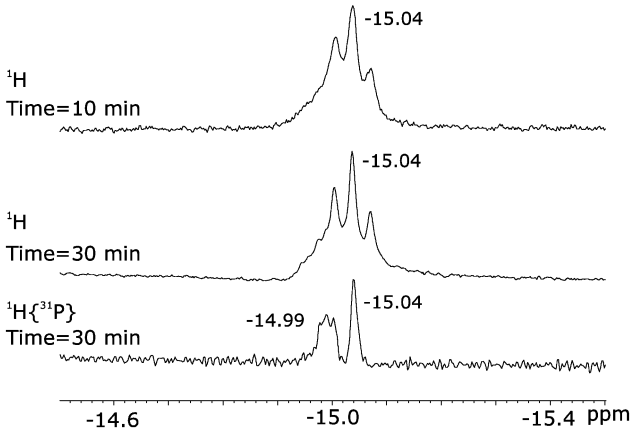


Fig. 6 Time-dependent 400 MHz ^{1}H NMR spectra (20 °C) of (PNP-Cy)RuH_3 in a 1:1 C_6H_6–C_6D_6 solvent mixture.

these compounds share the hydride/dihydrogen ground state structure and thus both show a preference for Ru(II) and so an aversion to a higher metal oxidation state. The greater π-donor power of amide *vs.* chloride then fails to reduce H_2 to 2 H^{-1}. On the other hand, the greater donor power of the amide gives intact (PNP-Cy)$RuH(H_2)$ enough π-basicity at Ru to improve the thermodynamics of binding *additional* H_2, to give (PNP-Cy)RuH_5. Perhaps even more demonstrative of the π-basicity (*i.e.*, reducing power) of (PNP-Cy)$RuH(H_2)$ 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(sp^3) 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, because of the generally stronger M–H and M–C bonds for 5d *vs.* 4d metals.

Synthetic access here to (PNP-Cy)$RuH(H_2)$ involves dehydrochlorination: removal of H from N and Cl from Ru in (HPNP-Cy)RuH_3Cl. While this reaction is successful (with a strong base), and probably benefits thermodynamically from donation of the resulting amide nitrogen lone pair to an 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.

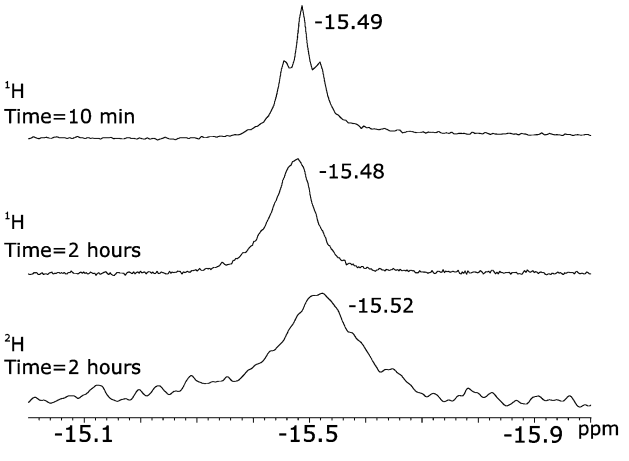


Fig. 7 Time-dependent ^{1}H and ^{2}H NMR spectra (20 °C) of (PNP-Cy)RuH_3 in C_6D_{12}.

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, CaH_2, or 4 Å molecular sieves, degassed prior to use, and stored in air-tight vessels. $RuCl_2(PPh_3)_3$,[27] $RuHCl(PPh_3)_3 \cdot C_7H_8$,[28] $RuCl_2(PCy_3)_2(CHCHCMe_2)$,[29] $[RuHCl(P^iPr_3)_2]_2$,[23] $HN(SiMe_2CH_2PPh_2)_2$,[30] $LiN(SiMe_2CH_2PPh_2)_2$,[30] HP^tBu_2[31] and $RuH_3Cl(PCy_3)_2$[21] were prepared according to published procedures. All other reagents were used as received from commercial vendors. ^{1}H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents. ^{31}P spectra are referenced to an external standard of 85% H_3PO_4at 0 ppm. NMR spectra were recorded with a Varian Gemini 2000 (300 MHz ^{1}H; 121 MHz ^{31}P; 75 MHz ^{13}C), a Varian Unity Inova (400 MHz ^{1}H; 162 MHz ^{31}P; 101 MHz ^{13}C), or a Varian Unity Inova (500 MHz ^{1}H, 126 MHz ^{13}C) instrument.

Syntheses

(PNP^{t}Bu)MgCl(dioxane). ^{t}Bu_2PH (6.33 mL, 34.2 mmol) was dissolved in 100 mL of 1:1 toluene–THF mixture. *n*-BuLi (21.4 mL of 1.6 M in hexanes, 34.2 mmol) was added to this solution, and the yellow color of ^{t}Bu_2PLi appeared. The mixture was stirred for 15 min and then $HN(SiMe_2CH_2Cl)_2$ (2.49 mL, 11.4 mmol) was added and the color dissipated. *n*-BuLi (7.1 mL of 1.6 M in hexanes, 11.4 mmol) was added to this solution. The mixture was stirred for 15 min and then $HN(SiMe_2CH_2Cl)_2$ (0.83 mL, 3.8 mmol) was added. *n*-BuLi (2.4 mL of 1.6 M in hexanes, 3.8 mmol) was added to this solution. The resulting mixture was stirred for 15 min and then $HN(SiMe_2CH_2Cl)_2$ (0.28 mL, 1.27 mmol) was added. The resulting mixture was stirred for 15 min more and then the solvent removed *in vacuo*. The residue was extracted with pentane, filtered and stripped to dryness. The remaining white solid was treated with 25 mL of THF and anhydrous $MgCl_2$ (1.90 g, 20 mmol) was added. This was stirred for 24 h, then treated with 4 mL of 1,4-dioxane, stirred for 4 h and filtered. The filtrate was stripped to dryness, redissolved in Et_2O–dioxane, and stripped again. The residue was extracted with ether, filtered, and the volume of the filtrate was reduced to *ca.* 10 mL. This was treated with 60 mL of pentane and placed in a freezer (−30 °C) for 24 h. The fluffy white solid was filtered off, washed with cold pentane and dried *in vacuo* to give the first crop of the product (4.61 g, 45%). The combined washings from the last step were reduced in volume to *ca.* 10 mL and after 24 h at −30 °C the second crop of the product (0.99 g, 11%) was collected. Total yield: 5.60 g (56%). (PNP-^{t}Bu)MgCl(dioxane): ^{1}H NMR (C_6D_6): δ 3.37 (s, 8H, dioxane), 1.14 (d, 13 Hz, 36H, CMe_3), 0.58 (d, 10 Hz, 4H, P–CH_2–Si), 0.44 (s, 12H, Si–CH_3). ^{31}P{^{1}H} NMR (C_6D_6): δ 17.9 (s).

(HPNP-^{t}Bu)RuH_3Cl. (PNP-^{t}Bu)MgCl(dioxane) (24.2 mg, 40.5 μmol) and [(cymene)$RuCl_2$] (12.4 mg, 40.5 μmol) were mixed in a J. Young tube in 0.6 mL C_6D_6. After shaking for 1 h, the NMR spectrum revealed the formation of (PNP-^{t}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 C_6D_6 in a J. Young tube and then degassed by two freeze-pump-thaw cycles. The tube was back-filled with H_2 at 1 atm. This caused a change of color to blue-green in the time of mixing. After *ca.* 20 min under an H_2 atmosphere, the color again became yellow and the NMR indicated the formation of (HPNP-^{t}Bu)RuH_3Cl (>90% purity). The volatiles were removed *in vacuo* in a small flask and the resultant yellow oil

was layered with *ca.* 0.3 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-^{t}Bu)-RuH$_3$Cl: ^{1}H NMR (C_6D_6): δ 3.15 (br, 1H, NH), 1.42 (vt, 5 Hz, 18H, CMe$_3$), 1.15 (vt, 5 Hz, 18H, CMe$_3$), 0.41 (s, 6H, Si–CH$_3$), 0.23 (s, 6H, Si–CH$_3$), −12.96 (t, 15 Hz, 3H, Ru*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 75.4 (s).

LiN(SiMe$_2$CH$_2$PCy$_2$)$_2$·0.75Et$_2$O. This procedure is a slight modification of Fryzuk's preparations for analogous compounds LiN(SiMe$_2$CH$_2$PR$_2$), where R = Me, ^{i}Pr, ^{t}Bu.[32] ^{n}BuLi (17 mL of 2.5 M in hexanes, 42.5 mmol) was added to a solution of 7.50 g (37.8 mmol) HPCy$_2$ 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 LiPCy$_2$ (quantitative). The lithio salt (7.70 g, 37.7 mmol) was slurried in 30 mL toluene, diluted with 100 mL THF, and cooled to 0 °C. Over a period of 15 min, a solution of 2.90 g (12.6 mmol) 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisilazane [HN(SiMe$_2$CH$_2$Cl)$_2$] in 10 mL THF was added dropwise *via* syringe. The mixture was allowed to warm to room temperature and stirred 30 min before removal of the volatiles to a liquid N$_2$ trap. 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 N$_2$ trap. Dissolving the residue in a minimum of ether and cooling to −70 °C for 5 days produced a white crystalline solid, which was washed with 10 mL cold ether (−70 °C) and dried *in vacuo* to yield 4.50 g (58%) of the title compound as a 4:3 diethyl etherate (^{1}H NMR integration). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.50 (s, 12H, Si*Me*$_2$), 0.78 (d, J_{P-H} = 4 Hz, 4H, C*H*$_2$), 1.12 [t, 4.5H, $^3J_{H-H}$ = 7 Hz, O(CH$_2$C*H*$_3$)$_2$], 1.26 [br m, 20H, P(C$_6$*H*$_{11}$)$_2$], 1.64 [br t, 8H, J_{H-H} = 12 Hz, P(C$_6$*H*$_{11}$)$_2$], 1.77 [br s, 8H, P(C$_6$*H*$_{11}$)$_2$], 1.90 [br s, 8H, P(C$_6$*H*$_{11}$)$_2$], 3.30 [q, 3H, $^3J_{H-H}$ = 7 Hz, O(C*H*$_2$CH$_3$)$_2$]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ −9.3 (very br s). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 20 °C): δ 7.3 (s, Si*Me*$_2$), 11.4 (d, J_{P-C} = 24 Hz, *C*H$_2$), 15.4 [s, O(CH$_2$*C*H$_3$)$_2$], 26.9 [s, P(4-*C*$_6$H$_{11}$)$_2$], 27.9 [d, J_{P-C} = 9 Hz, P(3/5-*C*$_6$H$_{11}$)$_2$], 28.0 [d, J_{P-C} = 9 Hz, P(3/5-*C*$_6$H$_{11}$)$_2$], 30.3 [d, J_{P-C} = 9 Hz, P(2/6-*C*$_6$H$_{11}$)$_2$], 30.6 [d, J_{P-C} = 9 Hz, P(2/6-*C*$_6$H$_{11}$)$_2$], 34.4 [br s, P(1-*C*$_6$H$_{11}$)$_2$], 65.8 [s, O(*C*H$_2$CH$_3$)$_2$]. Notes: (1) The lithium phosphide salt need not be isolated, but can also be prepared and used *in situ* (THF, −78 °C addition of ^{n}BuLi, then 3 h of stirring at room temperature). (2) Over several months, the lattice-bound ether is lost (^{1}H NMR, C_6D_6) to yield a material less soluble in aliphatic solvents, though reactivity is unaffected.

LiN(SiMe$_2$CH$_2$P^{t}Bu$_2$)$_2$·0.75Et$_2$O. ^{n}BuLi (14.5 mL of 2.0 M in pentane, 1.06 equiv.) was added to a solution of 4.0 g (27.4 mmol) HP^{t}Bu$_2$ 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 (9.1 mmol) 1,3-bis(chloromethyl)-1,1,3,3-tetramethyldisilazane [HN(SiMe$_2$CH$_2$Cl)$_2$] 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 N$_2$ trap. The residue was extracted with pentane (2 × 75 mL), filtered, and reduced to dryness *in vacuo*. Dissolving the residue in a minimum of ether and cooling to −70 °C for 3 days produced a white crystalline solid, which was washed with 10 mL cold ether (−70 °C) and dried *in vacuo* to yield 2.24 g (56%) of the title compound. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.33 (s, 12H, Si*Me*$_2$), 0.56 (d, J_{P-H} = 4 Hz, 4H, C*H*$_2$), 1.10 [d, J = 10.8 Hz, 36H, P(^{t}*Bu*)$_2$]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 19.0 (s).

HN(SiMe$_2$CH$_2$PCy$_2$)$_2$. LiN(SiMe$_2$CH$_2$PCy$_2$)$_2$·0.75Et$_2$O (850 mg, 1.38 mmol) was dissolved in 20 mL ether and cooled to 0 °C in an ice bath. *via* syringe, 1.4 mL (1.4 mmol) of 1 M HCl in ether was added, and the reaction was stirred for 15 min before warming to room temperature and stirring an additional 45 min. The solution was filtered through a fine frit and the LiCl residue was extracted with 10 mL ether. The combined ether extracts were concentrated to 3 mL *in vacuo*, but cooling overnight at −70 °C produced no precipitate. The remaining volatiles were removed to a liquid N$_2$ trap to yield the title compound as a viscous oil. Yield: 525 mg (95%). For convenience, the reagent was used as a 0.44 M solution in C_6D_6 unless generated *in situ*. ^{1}H NMR (400 MHz, C_6D_6, 20 °C; N*H* proton not observed): δ 0.35 (s, 12H, Si*Me*$_2$), 0.60 (d, J_{P-H} = 4 Hz, 4H, C*H*$_2$), 1.1–1.3, 1.5, 1.6, 1.7–1.9 [br m, 44H, P(C$_6$*H*$_{11}$)$_2$]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ −12.6 (s). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 20 °C): δ 2.9 (d, J_{P-C} = 5 Hz, Si*Me*$_2$), 9.1 (d, J_{P-C} = 37 Hz, *C*H$_2$), 27.0 [s, P(4-*C*$_6$H$_{11}$)$_2$], 27.7 [s, P(3/5-*C*$_6$H$_{11}$)$_2$], 27.8 [s, P(3/5-*C*$_6$H$_{11}$)$_2$], 29.5 [d, J_{P-C} = 11 Hz, P(2/6-*C*$_6$H$_{11}$)$_2$], 30.3 [d, J_{P-C} = 14 Hz, P(2/6-*C*$_6$H$_{11}$)$_2$], 35.1 [d, J_{P-C} = 17 Hz, P(1-*C*$_6$H$_{11}$)$_2$]. HN(SiMe$_2$CH$_2$P^{t}Bu$_2$)$_2$ can be prepared identically, beginning from the LiPNP-^{t}Bu salt; an 82% isolated yield is obtained of the very thick clear oil. ^{1}H NMR (400 MHz, C_6D_6, 20 °C; N*H* proton not observed): δ 0.30 (s, 12H, Si*Me*$_2$), 0.53 (d, J_{P-H} = 3.6 Hz, 4H, C*H*$_2$), 1.09 [d, J = 11.2 Hz, 36H, P(^{t}*Bu*)$_2$]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 18.8 (s).

RuH(PNP-Cy)(PPh$_3$). RuHCl(PPh$_3$)$_3$·C$_7$H$_8$ (750 mg, 0.74 mmol) and 454 mg (0.74 mmol) LiN(SiMe$_2$CH$_2$P-Cy$_2$)$_2$·0.75Et$_2$O were added to a Schlenk flask and stirred in 30 mL toluene for 48 h at room temperature. The red solution was filtered and the volatiles were removed to a liquid N$_2$ trap. The resulting red solid was powdered in a mortar and pestle and the free PPh$_3$ liberated in the reaction was removed by sublimation (60 °C, 0.003 torr, 1 week). Isolated yield: 620 mg (92%). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ −26.47 (dt, $^2J_{P'-H}$ = 44 Hz, $^2J_{P-H}$ = 19 Hz, 1H, Ru*H*), 0.59 (s, 6H, PNP-Si*Me*$_2$), 0.61 (s, 6H, PNP-Si*Me*$_2$), 0.7–1.8 (m, 46H, PNP-C$_6$*H*$_{11}$ overlapping with PNP-C*H*$_2$), 2.21 (br d, 2H, J = 8Hz, PNP-C*H*$_2$), 7.03 [apparent q, J_{H-H} = 6 Hz, 3H, P(p-C$_6$*H*$_5$)$_3$], 7.09 [apparent t, J_{H-H} = 8 Hz, 6H, P(m-C$_6$*H*$_5$)$_3$], 7.84 [apparent t, J_{H-H} = J_{P-H} = 9 Hz, 6H, P(o-C$_6$*H*$_5$)$_3$]. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 48.8 (d, $J_{P-P'}$ = 26 Hz, 2P, PNP-*P*Cy$_2$), 73.3 (t, $J_{P'-P}$ = 26 Hz, 1P, *P*Ph$_3$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 20 °C): δ 6.1 (s, PNP-Si*Me*$_2$), 7.4 (s, PNP-Si*Me*$_2$), 10.7 (s, PNP-*C*H$_2$), 26.7 [s, P(C$_6$*H*$_{11}$)$_2$], 27.2 [s, P(C$_6$*H*$_{11}$)$_2$], 27.5 [vt, J_{P-C} = 7 Hz, P(2/6-C$_6$*H*$_{11}$)$_2$], 27.6 [vt, J_{P-C} = 5 Hz, P(2/6-C$_6$*H*$_{11}$)$_2$], 27.95 [vt, J_{P-C} = 2 Hz, P(2/6-C$_6$*H*$_{11}$)$_2$], 28.02 [vt, J_{P-C} = 4 Hz, P(2/6-C$_6$*H*$_{11}$)$_2$], 29.2 [s, P(C$_6$*H*$_{11}$)$_2$], 29.5 [s, P(C$_6$*H*$_{11}$)$_2$], 30.6 [s, P(C$_6$*H*$_{11}$)$_2$], 31.9 [s, P(C$_6$*H*$_{11}$)$_2$], 34.7 [vt, J_{P-C} = 8 Hz, P(4-C$_6$*H*$_{11}$)$_2$], 39.0 [vt, J_{P-C} = 11 Hz, P(4-C$_6$*H*$_{11}$)$_2$], 127.4 [d, J_{P-C} = 8 Hz, P(m-*C*$_6$H$_6$)$_3$], 128.5 [s, P(p-*C*$_6$H$_6$)$_3$], 135.0 [d, J_{P-C} = 10 Hz, P(o-*C*$_6$H$_6$)$_3$], 142.7 [d, J_{P-C} = 33 Hz, P(i-*C*$_6$H$_6$)$_3$].

RuH(PNP-Ph)(PPh$_3$). RuHCl(PPh$_3$)$_3$·C$_7$H$_8$ (750 mg, 0.74 mmol) and 396 mg (0.74 mmol) LiN(SiMe$_2$CH$_2$PPh$_2$)$_2$ were added to a Schlenk flask and stirred in 50 mL toluene for 48 h at room temperature. The red solution was filtered and the volatiles were removed to a liquid N$_2$ trap. The resulting red solid was powdered in a mortar and pestle and the free PPh$_3$ liberated in the reaction was removed by sublimation (60 °C, 0.003 torr, 1 week). Isolated yield: 600 mg (91%). ^{1}H NMR (300 MHz, C_6D_6, 20 °C): δ −20.45 (dt, $^2J_{P'-H}$ = 42 Hz, $^2J_{P-H}$ = 20 Hz, 1H, Ru*H*), 0.01 (s, 6H, PNP-Si*Me*$_2$), 0.54 (s,

6H, PNP-SiMe_2), 1.79 (2nd order dvt, $^2J_{H-H}$ = 13 Hz, J_{P-H} = 4 Hz, 2H, PNP-CH_2), 1.89 (2nd order dvt, $^2J_{H-H}$ = 13 Hz, J_{P-H} = 5 Hz, 2H, PNP-CH_2), 6.8–7.7, 8.1 (m, 35H, PNP-C_6H_5 overlapping with PPh_3-C_6H_5). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20 °C): δ 40.7 (d, $J_{P-P'}$ = 19 Hz, 2P, PNP-PPh_2), 85.7 (t, $J_{P'-P}$ = 19 Hz, 1P, PPh_3).

RuH(PNP-Cy)(P^iPr_3). $[RuHCl(P^iPr_3)_2]_2$ (10 mg, 0.011 mmol) and 13.5 mg (0.022 mmol) LiN($SiMe_2CH_2P$-$Cy_2)_2$·0.75Et_2O were combined in 0.5 mL C_6D_6 and added to an NMR tube. ^1H and $^{31}P\{^1H\}$ spectra recorded 20 min later revealed quantitative conversion to the title compound with liberation of 1 equiv of free P^iPr_3. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ −23.52 (dt, $^2J_{P'-H}$ = 48 Hz, $^2J_{P-H}$ = 20 Hz, 1H, Ru*H*), 0.47 (s, 6H, PNP-SiMe_2), 0.51 (s, 6H, PNP-SiMe_2), δ 1.29 [dd, $^3J_{P-H}$ = 12 Hz, $^3J_{H-H}$ = 8 Hz, 18H, P(CH$Me_2)_3$], 1.0–2.2 (m, 43H, PNP-C_6H_{11} overlapping with P^iPr_3-C*H*Me_2), 2.00 [br d, $J_{(H)P-H}$ = 13 Hz, 2H, PNP-CH_2 or PNP-C_6H_{11}(methine)], 2.13 [br d, $J_{(H)P-H}$ = 12 Hz, 2H, PNP-CH_2 or PNP-C_6H_{11}(methine)], 2.36 [br d, $J_{(H)P-H}$ = 12 Hz, 2H, PNP-CH_2 or PNP-C_6H_{11}(methine)], 2.52 [br d, $J_{(H)P-H}$ = 12 Hz, 2H, PNP-CH_2 or PNP-C_6H_{11}(methine)]. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 41.4 (d, $J_{P-P'}$ = 22 Hz, 2P, PNP-PCy_2), 91.1 (t, $J_{P'-P}$ = 19 Hz, 1P, P^iPr_3).

RuH(PNP-Ph)(P^iPr_3). $[RuHCl(P^iPr_3)_2]_2$ (10 mg, 0.011 mmol) and 11.7 mg (0.022 mmol) LiN($SiMe_2CH_2PPh_2)_2$ were combined in 0.5 mL C_6D_6 and added to an NMR tube. ^1H and $^{31}P\{^1H\}$ spectra recorded 20 min later revealed 85% conversion to the title compound with liberation of 1 equiv of free P^iPr_3. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ −22.74 (dt, $^2J_{P'-H}$ = 46 Hz, $^2J_{P-H}$ = 20 Hz, 1H, Ru*H*), −0.24 (s, 6H, PNP-SiMe_2), 0.46 (s, 6H, PNP-SiMe_2), 0.92 [dd, $^3J_{P-H}$ = 12 Hz, $^3J_{H-H}$ = 7 Hz, 18H, P(CH$Me_2)_3$], 1.37 [m, 3H, P(C*H*-$Me_2)_3$], 1.41 (br vt, J_{P-H} = 4 Hz, 2H, PNP-CH_2), 1.94 (br vt, J_{P-H} = 3 Hz, 2H, PNP-CH_2), 6.9–7.2, 7.5, 8.2 (m, 20H, PNP-C_6H_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 39.9 (d, $J_{P-P'}$ = 24 Hz, 2P, PNP-PPh_2), 93.1 (t, $J_{P'-P}$ = 19 Hz, 1P, P^iPr_3).

Ru(HPNP-Cy)H_3Cl. *Method 1.* LiN($SiMe_2CH_2P$-$Cy_2)_2$·0.75Et_2O (1.0032 g, 1.87 mmol) and 470.1 mg (1.002 equivalents) of $](C_6H_6)RuCl_2]_2$ were combined in 125 mL of THF at room temperature to form a reddish brown slurry. The head space of the 300 mL flask was evacuated and refilled with H_2 (1 atm). The reaction mixture was allowed to stir for 3 h before the flask was refilled with H_2 (1 atm). Stirring overnight yielded a reddish homogeneous solution. Removal of the solvent *in vacuo* gave a red-brown solid that was then extracted with toluene. The solvent was removed from the toluene filtrate and the resulting red solid washed with cold pentane and dried under vacuum for 3 h (587.4 mg, 93.7%). [(*p*-cymene)$RuCl_2]_2$ and $[(COD)RuCl_2]_n$ can be used under identical conditions to give comparable yields.

Method 2. $RuH_3Cl(PCy_3)_2$ (10.0 mg, 0.0143 mmol) was dissolved in 0.5 mL C_6D_6 in an NMR tube and 32.5 µL of HPNP-Cy (0.44 M in C_6D_6) was added *via* syringe. Quantitative conversion to (HPNP-Cy)RuH_3Cl was seen within 1 h; attempts to scale up this reaction led to diminished yields and problems with product isolation. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ −12.46 (t, $^2J_{P-H}$ = 13.6 Hz, 3H, RuH_3), 0.223, 0.216, (singlets, 12H total, PNP-SiMe_2), 0.9–1.89 (m, 44H, PNP-C_6H_{11}), 0.96 (dt, J_{HH} = 14 Hz, J_{PH} = 4Hz, 2H, PNP-CH_2), 1.20 (dt, J_{HH} = 14 Hz, J_{PH} = 4Hz, 2H, PNP-CH_2), 3.10 [s, 1H, *H*N-($SiMe_2CH_2PCy_2)_2RuH_3Cl$]. $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 48.01 (s). $^{13}C\{^1H, ^{31}P\}$ NMR (101 MHz, C_6D_6, 20 °C): δ 12.0 (PNP-SiMe_2), 3.1 (s, PNP-SiMe_2), 15.4 (s, PNP-CH_2), 26.7 (s, PNP-C_6H_{11}), 26.9 (s, PNP-C_6H_{11}), 27.5 (s, PNP-C_6H_{11}), 28.0 (s, PNP-C_6H_{11}), 28.1 (s, PNP-C_6H_{11}), 28.5 (s, PNP-C_6H_{11}), 29.6 (s, PNP-C_6H_{11}), 30.0 (s, PNP-C_6H_{11}), 30.3 (s, PNP-C_6H_{11}), 31.4 (s, PNP-C_6H_{11}), 37.7 (s, PNP-C_6H_{11}), 39.0 (s, PNP-C_6H_{11}).

(HPNP-Cy)RuHCl (P^iPr_3). (HPNP-Cy)RuH_3Cl (24.3 mg, 0.0363 mmol) was dissolved in approximately 0.5 mL C_7D_8 and placed in an NMR tube. P^iPr_3 (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(P^iPr_3) (35% yield), among other decomposition products. ^1H NMR (400 MHz, C_7D_8, 20 °C): δ −12.50 (br s, 1H, Ru*H*), 0.13 (s, 6H, PNP-SiMe_2), 0.35 (s, 6H, PNP-SiMe_2), 1.30 [br d, $^3J_{P-H}$ = 9 Hz, 18H, P(CH$Me_2)_3$], 1.0–2.2 [m, 43H, PNP-C_6H_{11} overlapping with P^iPr_3-C*H*Me_2], 2.24 [br d, $J_{(H)P-H}$ = 14 Hz, 2H, PNP-CH_2 or PNP-C_6H_{11}(methine)], 2.30 [br d, $J_{(H)P-H}$ = 12 Hz, 2H, PNP-CH_2 or PNP-C_6H_{11}(methine)], 2.53 [br d, $J_{(H)P-H}$ = 24 Hz, 2H, PNP-CH_2 or PNP-C_6H_{11}(methine)], 2.66 [br d, $J_{(H)P-H}$ = 13 Hz, 2H, PNP-CH_2 or PNP-C_6H_{11}(methine)], 3.08 (br s, 1H, *H*PNP). $^{31}P\{^1H\}$ NMR (162 MHz, C_7D_8, 20 °C): δ 51.8 (d, $J_{P-P'}$ = 21 Hz, 2P, PNP-PCy_2), 73.4 (t, $J_{P'-P}$ = 19 Hz, 1P, P^iPr_3).

Reaction of (HPNP-Cy)RuH(CO)Cl. (HPNP-Cy)RuH_3Cl (10 mg, 0.0148 mmol) was dissolved in approximately 0.5 mL C_6D_6 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, C_6D_6, 20 °C): δ −5.47 (t, $^2J_{P-H}$ = 19 Hz, 1H, Ru*H*), 0.43 (s, 6H, PNP-SiMe_2), 0.37 (s, 6H, PNP-SiMe_2), 0.9–2.1 (m, 48H, PNP-C_6H_{11}, PNP-CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 53.7 (s).

Ru(PNP-Cy)H_3. (HPNP-Cy)RuH_3Cl (199.9 mg, 0.2989 mmol) was dissolved in approximately 15 mL of C_6H_6. LiTMP (74.1 mg, 1.68 equiv, in 5 mL C_6H_6) 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; (PNP-Cy)RuH_3 was obtained as a reddish powder (isolated yield 46%; yield of the crude product 71%). Following the identical procedure with $(Me)_3SiCH_2Li$ gives comparable yields and product purity. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ −15.03 (t, $^2J_{P-H}$ = 13.0 Hz, 3H, RuH_3), 0.49 (s, 12H, PNP-SiMe_2), 0.9–1.89 (m, 48H, PNP-C_6H_{11}, PNP-CH_2). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 55.48 (s). Attempts to obtain a $^{13}C\{^1H\}$ NMR spectrum were unsuccessful, due to decomposition of (PNP)RuH_3 over several hours in solution.

Ru(PNP-Cy)H_5. (PNP-Cy)RuH_3 (9.6 mg, 0.0152 mmol) was dissolved in approximately 0.5 mL C_6D_6 and placed in a gas tight NMR tube. The solution was degassed and the head space gasses removed. One atmosphere (20 °C) of H_2 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 RuH_3 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 ^{31}P signal, which can be assigned to (PNP-Cy)RuH_5, was present at 62.5 ppm, corresponding to approximately 10% of the reaction mixture at 20 °C. Removal of all volatiles and redissolution in C_6D_6 gave 100% (PNP-Cy)RuH_3, 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 ^{31}P at 55.3 ppm. Variable temperature experiments did not decoalesce the RuH_5 hydrogens, though a reduction in temperature to less

than −20 °C allowed the nearly quantitative production of (PNP-Cy)RuH_5 from (PNP-Cy)RuH_3.

RuH(PNP-Cy)(CO(CH$_2$)$_3$). *Method 1.* (HPNP-Cy)RuH_3Cl (10 mg, 0.015 mmol) was dissolved in 0.5 mL C_6D_6; 2.2 μL (1.02 equiv) of NEt_3 and 6.0 μL of C_4H_6O (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. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ −16.82 (t, $^2J_{P-H}$ = 22 Hz, 1H, Ru*H*), 0.43 (s, 6H, PNP-Si*Me*$_2$), 0.28 (s, 6H, PNP-Si*Me*$_2$), 0.80 (dt, J_{HH} = 9 Hz, J_{PH} = 4Hz, 2H, PNP-C*H*$_2$), 1.1–2.2 (m, PNP-C$_6$*H*$_{11}$, PNP-C*H*$_2$), 1.97 (br t, 2H), 3.27 (t, *J* = 7.2 Hz), 3.90 (t, *J* = 5.6 Hz). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 41.23 (s). ^{13}C{^{1}H, ^{31}P} NMR (101 MHz, C_6D_6, 20 °C): δ 2.9 (s, PNP-Si*Me*$_2$), 3.3 (s, PNP-Si*Me*$_2$), 12.7 (s, PNP-*CH*$_2$), 24.1 (s, Ru=COCH$_2$*C*H$_2$-CH$_2$), 24.9 (s, PNP-*C*$_6$H$_{11}$), 25.7 (s, PNP-*C*$_6$H$_{11}$), 26.1 (s, PNP-*C*$_6$H$_{11}$), 26.8 (s, PNP-*C*$_6$H$_{11}$), 27.1 (s, PNP-*C*$_6$H$_{11}$), 28.0 (s, PNP-*C*$_6$H$_{11}$), . 28.2 (s, PNP-*C*$_6$H$_{11}$), 28.3 (s, PNP-*C*$_6$H$_{11}$), 29.6 (s, PNP-*C*$_6$H$_{11}$), 30.2 (s, PNP-*C*$_6$H$_{11}$), 36.7 (s, PNP-*C*$_6$H$_{11}$), 37.8 (s, PNP-*C*$_6$H$_{11}$), 53.2 (s, Ru=COCH$_2$CH$_2$*C*H$_2$), 75.9 (s, Ru=CO*C*H$_2$CH$_2$CH$_2$), 297.8 (s, Ru=*C*OCH$_2$CH$_2$-CH$_2$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 20 °C, selected resonance): δ 297.8 (t, J_{PC} = 7.4 Hz, Ru=*C*OCH$_2$CH$_2$CH$_2$).
Method 2. (HPNP-Cy)RuH_3Cl (10.3 mg, 0.0158 mmol) was dissolved in 0.5 mL C_6D_6; 2.3 μL (1.07 equiv) of NEt_3 and 5.0 μL of C_4H_6O (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)RuH_3 (11.1 mg, 0.01756 mmol) was dissolved in 0.5 mL C_6D_6; 3.0 mg (1.24 equiv) of NEt_3·HCl and 6.0 μL of C_4H_6O (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)RuH_3Cl, 30% the end carbine (characterization above), and 10% (PNP-Cy)RuH_3. After 4 h of heating at 60 °C, 95% conversion to the hydrido carbene was seen.
Method 4. (HPNP-Cy)RuH_3Cl (10.3 mg, 0.01582 mmol) was dissolved in 0.5 mL C_6D_6; 2.2 .μL (0.99 equiv) of NEt_3 and 5.0 μL of C_4H_6O (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)H$_3$ with C$_6$H$_5$CHCH$_2$. (PNP-Cy)RuH_3 (10 mg, 0.0161 mmol)was dissolved in 0.5 mL of C_6H_6. Styrene, $C_6H_5CHCH_2$, (5.5 μL, 2.98 equiv) was added *via* syringe. After 3 h at room temperature, two products [bound olefin and an η^3-cyclohexenyl(cyclohexyl) phosphine complex in an approximately 3:1 ratio] were observed. After 15 h at 60 °C, 95% conversion to the η^3-cyclohexenyl(cyclohexyl) phosphine complex was seen. ^{1}H NMR (400 MHz, C_6D_6, 20 °C) of the olefin complex: δ −22.72 (dd, J_{P-H} = 24 Hz, $J_{P'-H}$ = 20 Hz, 3H, Ru*H*$_3$), 0.59 (s, 3H, PNP-Si*Me*$_2$), 0.48 (s, 3H, PNP-Si*Me*$_2$), 0.39 (s, 3H, PNP-Si*Me*$_2$), 0.19 (s, 3H, PNP-Si*Me*$_2$), 0.9–1.89 (m, 48H, PNP-C$_6$*H*$_{11}$, PNP-C*H*$_2$), bound styrene resonances are located under free styrene and evidenced by broadening only. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C) of the olefin complex: δ 44.6 and 35.0 (AB pattern, $J_{P-P'}$ = 319 Hz). ^{1}H NMR (400 MHz, C_6D_6, 20 °C) of the η^3 complex: δ 0.76 (s, 3H, PNP-Si*Me*$_2$), 0.53 (s, 3H, PNP-Si*Me*$_2$), 0.42 (s, 3H, PNP-Si*Me*$_2$), 0.23 (s, 3H, PNP-Si*Me*$_2$), 0.9–2.40 (m, 47H, PNP-C$_6$*H*$_{11}$, PNP-C*H*$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C) of the η^3 complex: δ 104.51 and 32.58 (AB pattern, $J_{P-P'}$ = 303 Hz). No hydrides are observed.

Reaction of Ru(PNP-Cy)H$_3$ with CH$_2$CHC(CH$_3$)$_3$. (PNP-Cy)RuH_3 (7.4 mg, 0.0117 mmol)was dissolved in 0.5 mL of C_6H_6. ^{t}Bu-ethylene, $CH_2CHC(CH_3)_3$, (7.5 μL, 4.97 equiv) was added *via* syringe. After 15 min at room temperature, two products [bound olefin and an η^3-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 η^3-cyclohexenyl(cyclohexyl) phosphine complex was seen. ^{1}H NMR (400 MHz, C_6D_6, 20 °C) of the olefin complex: δ −19.97 (br t, J_{P-H} = 19 Hz, 3H, Ru*H*$_3$), 0.41 (s, 3H, PNP-Si*Me*$_2$), 0.36 (s, 3H, PNP-Si*Me*$_2$), 0.31 (s, 3H, PNP-Si*Me*$_2$), 0.28 (s, 3H, PNP-Si*Me*$_2$), 0.9–1.94 (m, 48H, PNP-C$_6$*H*$_{11}$, PNP-C*H*$_2$), bound ^{t}Bu ethylene resonances are located under free ^{t}Bu ethylene and evidenced by broadening only. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C) of the olefin complex: δ 63.1 and 36.0 (AB pattern, $J_{P-P'}$ = 326 Hz). ^{1}H NMR and ^{31}P{^{1}H} NMR of the η^3 complex are the same as reported above.

C–H/D exchange

In a typical experiment, 10 mg of (PNP-Cy)RuH_3 was dissolved in the appropriate solvent in a gas-tight NMR tube; 25 mg of the Ru complex was used for ^{2}H spectra. In order to clearly follow H/D exchange in benzene at room temperature and within reasonable time intervals, a 1:1 mixture of C_6H_6/C_6D_6 was employed; positions of deuteration were determined by ^{1}H and ^{2}H NMR. In cyclohexane-d$_{12}$, no resolved coupling for (PNP-Cy)RuH_2D was seen in the ^{1}H NMR; in all cases, a broad singlet results after the specified time periods.

X-Ray structure determinations

RuH(PPh$_3$)[N(SiMe$_2$CH$_2$PCy$_2$)$_2$]. The orange crystal of $RuH(PPh_3)[N(SiMe_2CH_2PCy_2)_2]$, 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 XTEL 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 e Å^{-3} at the metal site.

(HPNP-^{t}Bu)RuH$_3$Cl. A yellow crystal, grown from C_6D_6 and ether by layering, was cut to the approximate dimensions 0.30 × 0.30 × 0.30 mm^3 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).[33] Final cell constants were calculated from the *xyz* centroids of 9648 strong reflections from the actual data collection after integration (SAINT).[34] The space group *Pbca* was determined based on systematic absences and intensity statistics. The structure was solved using SIR-923[35] and refined with SHELXL-97.[36] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed ,which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic displacement parameters except for the hydrogen atoms bonded to Ru and N, which were refined for all parameters. The final full-matrix least-squares refinement converged to $R_1 = 0.0305$ and $wR_2 = 0.0776$ (F^2, all data). The remaining electron density is located around the metal and the chlorine atom.

CCDC reference numbers 197075–6. See http://www.rsc.org/suppdata/nj/b2/b206202j/ for crystallographic files in CIF or other electronic format.

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