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Effects of Phosphine Ligand Chelation on the Reactivity of Monomeric Parent Amido Ruthenium Complexes: Synthesis and Reactivity of Such a Complex Bearing Monodentate Ligands

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Abstract: The parent amido complex *cis*-$(PMe_3)_4Ru(H)(NH_2)$ (**2**) has been prepared via the deprotonation of [*cis*-$(PMe_3)_4Ru(H)(NH_3)^+$][BPh_4^-]. The amido complex is a somewhat weaker base than the DMPE analogue *trans*-$(DMPE)_2Ru(H)(NH_2)$ but is still basic enough to quantitatively deprotonate fluorene and reversibly deprotonate 1,3-cyclohexadiene and toluene. Complex **2** exhibits very labile phosphine ligands, two of which can be replaced by DMPE to yield the mixed complex *cis*-$(PMe_3)_2(DMPE)Ru(H)(NH_2)$. Because of the ligand lability, **2** also undergoes hydrogenolysis and rapid exchange with labeled NH_3. The amide complex reacts with alkyl halides to yield E2 and S_N2 products, along with ruthenium hydrido halide complexes including the ruthenium fluoride *cis*-$(PMe_3)_4Ru(H)(F)$. Ruthenium hydrido ammonia halide ion pair intermediates [*cis*-$(PMe_3)_4Ru(H)(NH_3)^+$][X^-] are observed in some deprotonation and E2 reactions, and measurement of the equilibrium constants for NH_3 displacement from these complexes suggests that they benefit from significant hydrogen bonding between X^- and NH_3 groups. Cumulenes also react with complex **2** to afford the products of insertion into an NH bond. The rates of neither these NH insertion reactions nor the reversible deprotonation reactions show any dependence on the concentration of PMe_3 present, suggesting that these reactions take place directly at the NH_2 group and do not involve precoordination of substrate to the metal center.

Introduction

Late metal complexes featuring alkoxide and amide ligands have long been implicated as intermediates in important catalytic reactions.[1−6] Amide complexes[7] in particular are postulated to be formed as intermediates in the catalytic cycles of important synthetic processes including hydroamination,[8−10] asymmetric hydrogenation,[11] and C−N coupling reactions.[12−15] Nonetheless, late metal amide complexes still remain rare relative to their alkoxide counterparts,[5,16] and the chemistry of the most fundamental amide complexes, parent amido species ($M-NH_2$), is particularly underdeveloped.[17−20] This is a consequence of both the rarity of practical NH_2^- sources and the relative instability of most reported parent amido complexes.

Our group recently reported the synthesis of *trans*-$(DMPE)_2Ru(H)(NH_2)$ (**1**) (DMPE = 1,2-bisdimethylphosphinoethane), the first isolable monomeric structurally characterized late-metal parent amido complex.[21−23] This complex proved to be remarkably basic, and the pK_a of the corresponding ammonia complex was estimated to be approximately 23−24 (as measured in THF).[23] Complex **1** quantitatively deprotonates weak carbon acids such as fluorene and undergoes H/D exchange with weaker acids (including toluene) via reversible proton transfer.[23]

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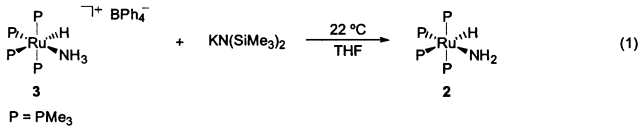
One unfortunate feature of the DMPE ligands of complex **1** is that their dechelation is not detectable by typical kinetic experiments, and thus, the role of phosphine dissociation in the reactivity of **1** is beyond the reach of conventional experiments. Additionally, the chelation of DMPE strongly disfavors phosphine dissociation and, thus, retards any reactivity that does require an open site at the metal center.[3,24] When given the frequency with which organometallic complexes require such sites for both stoichiometric and catalytic reactions,[3,24] this is likely to interfere with attempts to extend the reactivity of amide complexes such as **1** beyond reactions that occur directly at the NH_2 group.

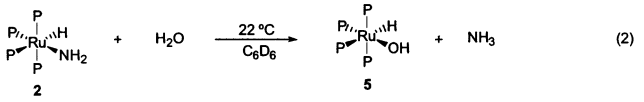
We have thus sought to prepare an analogue of **1** featuring at least one monodentate phosphine ligand. Our hope was that such a complex, while perhaps less stable than **1**, would exhibit novel reactivity and lend itself to a mechanistic investigation more readily. To this end, we have now synthesized the complex *cis*-$(PMe_3)_4Ru(H)(NH_2)$ (**2**), and we report herein on its reactivity.

Results

Synthesis and Characterization of *cis*-$(PMe_3)_4Ru(H)(NH_2)$. The ammonia complex [*cis*-$(PMe_3)_4Ru(H)(NH_3)^+$][BPh_4^-] (**3**) has been prepared previously and found to form the dihydride *cis*-$(PMe_3)_4Ru(H)_2$ (**4**) upon treatment with hydride bases.[25] Treatment of **3** with $KN(SiMe_3)_2$, however, cleanly affords amide complex *cis*-$(PMe_3)_4Ru(H)(NH_2)$ (**2**) (eq 1). Complex **2**



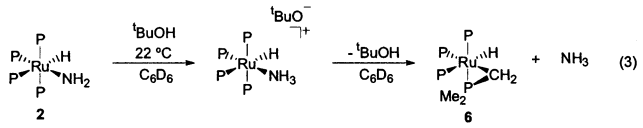
(1)



(2)

is produced in 95% yield as a crude yellow-tan oil of 95% purity, and subsequent crystallization of the highly soluble complex from pentane affords pure **2** as off-white crystals in 60% yield. The cis geometry of **2** is indicated by the presence of resonances for three chemically inequivalent PMe_3 ligands in the ^1H, ^{13}C, and ^{31}P NMR spectra. The RuH signal (δ −8.49 ppm) also indicates a cis geometry, featuring one large coupling (J = 99 Hz) to a phosphorus atom trans to the hydride and a doublet of triplets pattern arising from two smaller couplings (J = 29, 24 Hz) to the three cis disposed phosphorus groups. The NH_2 protons appear in the ^1H NMR spectrum as a single, sharp peak at δ −2.39 ppm, in roughly the same region as the corresponding signal associated with DMPE analogue **1** (δ −3.42 ppm).[21] The shape and chemical shift of this peak are strongly dependent on the purity of the sample; it broadens and generally shifts downfield in the presence of impurities.

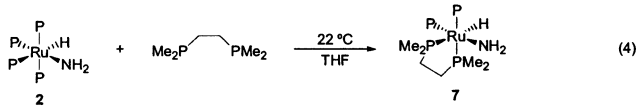
When pure, amide complex **2** is stable indefinitely in the solid state at room temperature and stable in solution in halide free, nonacidic solvents below 75 °C. At this temperature, it slowly decomposes to multiple products over the course of several days. The complex decomposes quickly in air and reacts rapidly with traces of water to liberate ammonia and form the known hydroxide complex *cis*-$(PMe_3)_4Ru(H)(OH)$[26] (**5**) (eq 2). In the presence of catalytic quantities of some acids, including ^{t}BuOH, Ph_2NH, and molecular sieves, complex **2** decomposes to cleanly form the known cyclometalated complex *cis*-$(PMe_3)_3Ru(CH_2PMe_2)(H)$[27] (**6**) and liberate ammonia (eq 3). In the cases of



(3)

^{t}BuOH and Ph_2NH, this transformation has been observed to proceed via an ion pair intermediate [*cis*-$(PMe_3)_4Ru(H)(NH_3)^+$]-[A^-] which forms immediately and is converted to **6** in 2−4 days (at ambient temperature).

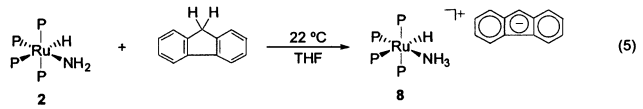
Complex **2** was prepared in the hope that its PMe_3 ligands would prove sufficiently labile to allow for the investigation and extension of the chemistry exhibited by DMPE analogue **1**, and evidence suggests that at least some of the PMe_3 ligands are indeed quite labile. Reaction of **2** with either CO or ^{t}BuNC results in the liberation of PMe_3 and the formation of multiple ruthenium hydride products featuring PMe_3 displacement both trans and/or cis to the hydride. Treatment of **2** with 2 equiv of DMPE results in the displacement of only two PMe_3 ligands to form a new amide complex $(PMe_3)_2$(DMPE)Ru(H)(NH_2) (**7**) (eq 4). The ^{31}P NMR spectrum of **7** features two resonances in



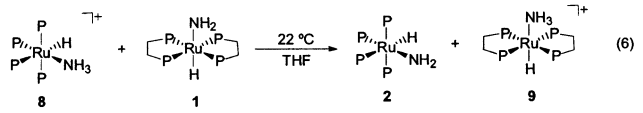
(4)

the DMPE region ($\sim\delta$ 60−30 ppm) and two in the PMe_3 region ($\sim\delta$ 20 to −10 ppm), including an upfield DMPE signal corresponding to a phosphorus atom positioned trans to a hydride (δ 30.03 ppm) and a PMe_3 signal (δ 3.67 ppm) very similar to that observed for the phosphorus atom trans to the NH_2 group in complex **2** (δ 3.12 ppm). The other two phosphorus atoms are disposed trans to each other and are, thus, strongly coupled (J = 323 Hz).

Acid−Base Reactivity. The basicity of complex **2** was probed by exploring its reactivity toward sterically encumbered weak acids. Complex **2** was found to quantitatively deprotonate fluorene to form the fluorenide salt **8** (eq 5), but no reaction



(5)



(6)

was observed between **2** and triphenylmethane (which is reversibly deprotonated by **1**). Like its DMPE analogue, fluorenide salt **8** did not undergo NH_3 displacement, even upon

(24) Crabtree, R. H. *The Organometallic Chemistry of Transition Metals*, 2nd ed.; John Wiley & Sons: New York, 1994.
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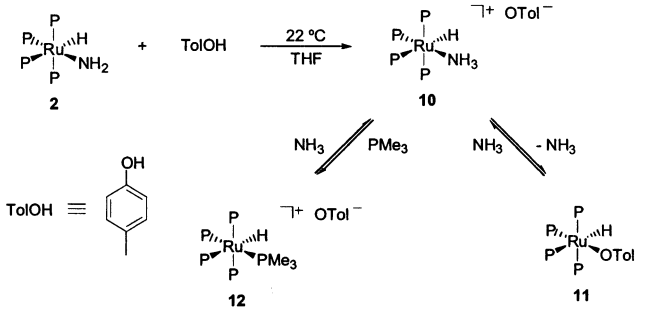
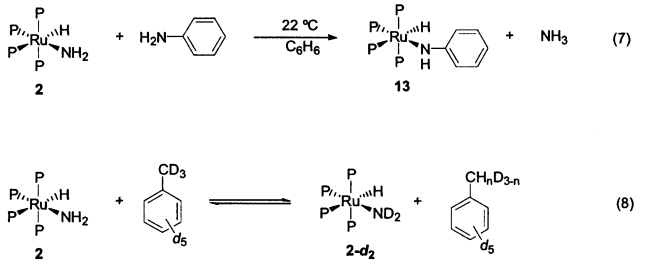
Scheme 1



prolonged heating. To directly compare the relative basicities of **2** and the *trans*-DMPE analogue **1**, ammonia complex **8** was treated with **1**. This resulted in an immediate quantitative proton transfer to yield **2** and DMPE ammonia complex **9** (eq 6). Salt **3** displayed similar proton transfer reactivity.

Like DMPE analogue **1**, amide complex **2** quantitatively deprotonates *p*-cresol (TolOH) upon mixing to yield the ammonia−aryloxide ion pair **10** (Scheme 1). This species exists in slow equilibrium with the inner-sphere cresolate **11**[28] ($K_{eq} \approx 400\ M^{-1}$), in which the ammonia has been displaced by the aryloxide. Efforts to investigate the effect of [PMe_3] on the rate of this displacement reaction were complicated by the reversible displacement of ammonia by PMe_3 to yield the pentaphosphino hydride cation **12**. Species **12** is characterized by a doublet of quintets in the RuH region of its ^{1}H NMR spectrum and the presence of both a doublet and quintet in the ^{31}P NMR spectrum.[29] This equilibrium, and the significance of its position, is discussed further below. Complex **2** also reacts with aniline to yield the protonolysis product *cis*-$(PMe_3)_4Ru(H)(NHPh)$[28] (**13**) and NH_3 (eq 7), although in this case the ion pair intermediate was not observed.



In contrast to **1**, amide complex **2** does not react significantly with neat toluene-d_8 at room temperature, but slow H/D exchange between the benzylic position of the solvent and complex **2** does occur at 45 °C (eq 8). The $RuNH_2$ protons are exchanged first (90% deuteration in 2 d), and deuteration of the phosphine ligands is observed thereafter (90% deuteration in 5 d). Addition of PMe_3 to this reaction mixture has no significant effect on the rate of initial decay of the $RuNH_2$ resonance, although deuteration of the free phosphine is eventually observed. Complex **2** also catalyzes the equilibration of 1,3-cyclohexadiene with its 1,4 isomer (eq 9), and this

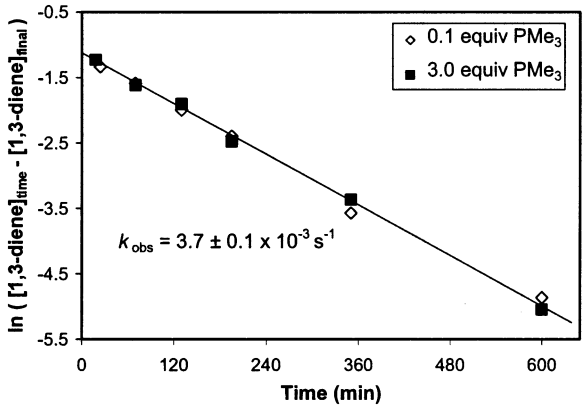
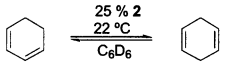


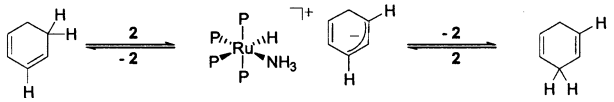
Figure 1. Pseudo-first-order plot for kinetics of the isomerization of 1,4-cyclohexadiene (0.15 M) by **2** (0.038 M = 25 mol %) in the presence of PMe_3 (0.005 M, ◇; or 0.11 M, ■) in C_6D_6 at 22 °C.

equilibration takes place with a half-life of approximately 90 min when a catalyst loading of 25% **2** is used. The kinetics of

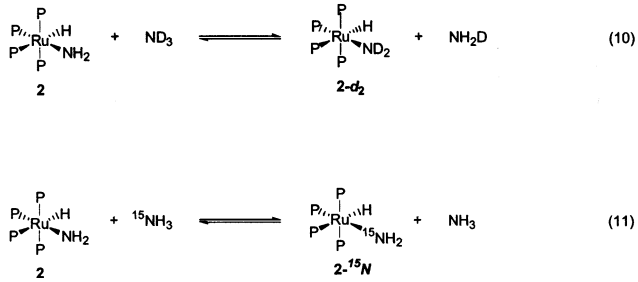


this process were investigated in the presence of both 0.1 and 3.0 equiv of PMe_3, and the rate law was found to be first order in [substrate] and independent of [PMe_3] (Figure 1). This suggests that phosphine dissociation is not required and implies a mechanism involving reversible, direct, intermolecular deprotonation of diene by **2** (Scheme 2).

Scheme 2



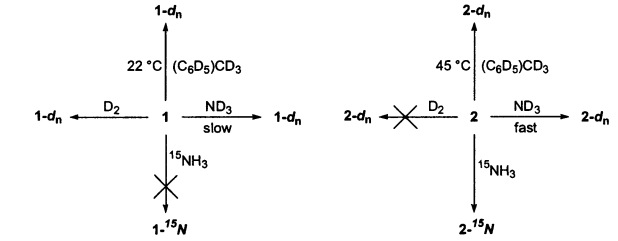
Treatment of **2** with ND_3 results in a rapid decrease in the intensity of the $RuNH_2$ signal and appearance of NH_nD_{3-n} in the ^{1}H NMR spectrum of the mixture (eq 10). As in the case of



H/D exchange with toluene-d_8, exchange into the phosphine ligands eventually occurs thereafter. When ND_3 is removed after deuteration of the $RuNH_2$ group (∼10 min), the amide group is almost entirely reprotonated and the phosphine ligands become partially deuterated over the course of the next 24 h. The initial exchange between ND_3 and the NH_2 group occurs much more readily than that between ND_3 and **1**, suggesting that a different mechanism may be operative for the less basic complex (exchange processes involving amide complexes **1** and **2** are compared in Scheme 3). Treatment of **2** with $^{15}NH_3$ (δ −0.18 ppm (d, J = 60.8 Hz)) results in rapid liberation of $^{14}NH_3$ (δ −0.18 ppm (t, J = 42.8 Hz)) (eq 11), and the mass spectrum of the isolated product *cis*-$(PMe_3)_4Ru(H)(^{15}NH_2)$ (**2-^{15}N**) confirms

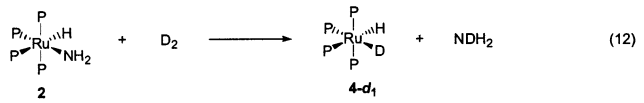
(26) Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875.
(27) Werner, H.; Werner, R. *J. Organomet. Chem.* **1981**, *209*(3), C60.
(28) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *Organometallics* **1991**, *10*, 1875.
(29) A very similar complex has been reported previously: Burn, M. J.; Bergman, R. G. *J. Organomet. Chem.* **1994**, *472*, 43.

Scheme 3



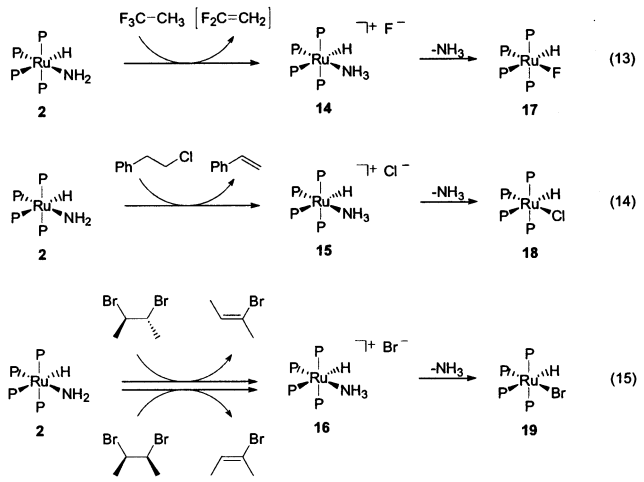
it to be enriched in ^{15}N (m/z = 424). This exchange, which does not take place at all with DMPE analogue **1**, occurs too rapidly at room temperature to allow convenient exploration of the phosphine dependence of the reaction rate.

Amide complex **2** reacts slowly with D_2 to yield NH_2D and P_4RuHD (**4-*d*$_1$**) (eq 12) rather than H/D exchange products analogous to those observed with **1**. This reaction is slowed dramatically in the presence of 2 equiv of PMe_3, but H/D exchange into the $RuNH_2$ of the starting material still is not observed by ^1H NMR spectroscopy.



(12)

While complex **2** does not appear to behave strictly as a Brønsted base in its reactions with ND_3 and D_2, its considerable basicity is reflected in its reactivity toward various alkyl halides. Complex **2** reacts with 1,1,1-trifluoroethane, 1-chloro-2-phenylethane, and 2,3-dibromobutane to form protonated organometallic products [*cis*-$(PMe_3)_4Ru(H)(NH_3)^+][X^-]$ (X = F, **14**; X = Cl, **15**; X = Br, **16**) featuring the halides as outer-sphere anions (eq 13−15). Over several hours at room temperature,



(13)

(14)

(15)

the ammonia is displaced to form the corresponding ruthenium hydrido fluoride (**17**), chloride (**18**), or bromide (**19**) complex. The organic dehydrohalogenation products styrene and 2-bromobutene are cleanly generated in these reactions, but 1,1-difluoroethylene has not been observed. The stereochemistry of the elimination was investigated using *rac*- and *meso*-2,3-dibromobutane. Dehydrobromination of the rac isomer yielded the *Z*-2-bromobutane with 98% selectivity, whereas the meso compound yielded 97% of the *E* isomer (eq 15).

Nucleophilic Reactivity. The reaction of amide complex **2** with ethyl bromide highlights the nucleophilic reactivity of the

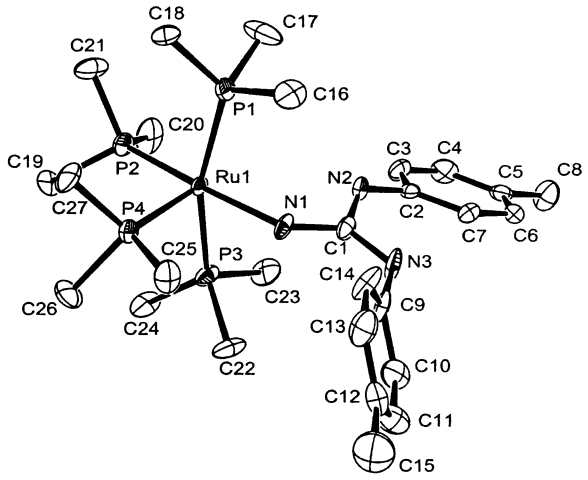
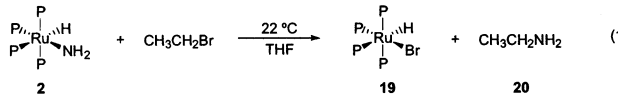


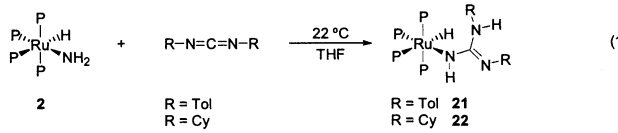
Figure 2. ORTEP diagram of **21** (thermal ellipsoids at 50% probability). Hydrogen atoms, second molecule of unit cell, and solvent have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru−N1, 2.180(6); Ru1−P1, 2.349(2); Ru1−P2, 2.283(2); Ru1−P3, 2.339(2); Ru1−P4, 2.346(3); C1−N1, 1.341(9); C1−N2, 1.408(10); C1−N3, 1.313-(10); Ru1−N1−C1, 133.1(6); N1−C1−N2, 114.4(7); N2−C1−N3, 117.6-(7); P2−Ru1−N1, 172.8(2); P1−Ru1−P3, 162.59(9); P4−Ru1−N1, 89.9-(2); Ru1−N1−C1−N2, 11(1).

complex. While traces of ethylene and ammonia bromide complex **16** are observed in this reaction, the major products are ethylamine (**20**) and bromide complex **19** (eq 16). Even when the reaction is monitored within minutes of mixing, no intermediate ethylamine-bound cation is observed.



(16)

Treatment of complex **2** with di-*p*-tolyl carbodiimide results in an overall insertion of the carbodiimide into the NH bond of the amide complex to yield guanidinate **21** (eq 17). The ^1H NMR



(17)

spectrum of the product is characterized by the presence of two tolyl groups (δ 2.35, 2.21 ppm) and a single RuNH proton at δ 9.02 ppm. (The second NH proton is not observed even at reduced (−80 °C) or elevated (75 °C) temperatures, presumably because of quadrupole broadening). The ^{31}P NMR spectrum features a downfield resonance at δ 5.37 ppm, which is consistent with the presence of an anionic nitrogen group trans to the corresponding phosphine. The structure of complex **21** was confirmed by an X-ray diffraction study, and the ORTEP diagram and significant bond lengths and angles are shown in Figure 2. In an effort to determine whether the insertion shown in eq 17 takes place via precoordination of the carbodiimide (following phosphine loss) or by a direct nucleophilic attack of the NH_2 group on the substrate, we attempted to study the dependence of the rate of the reaction on [PMe_3]. Unfortunately, even in the presence of 10 equiv of PMe_3, the reaction proceeded too rapidly at −80 °C for its rate to be measured. Dicyclohexyl carbodiimide reacts with amide complex **2** in a similar manner, yielding N−H insertion product **22** (eq 17). In this case, the

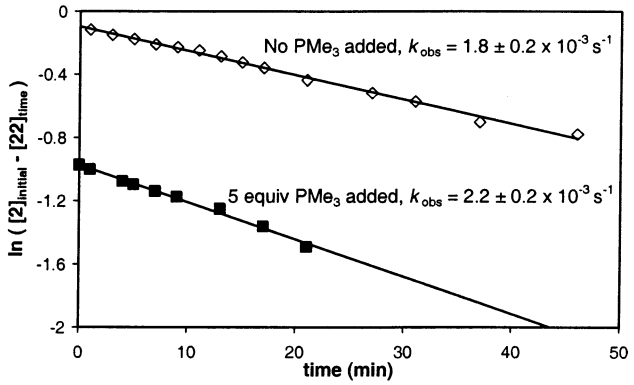


Figure 3. Pseudo-first-order plot for kinetics of the reaction of **2** (0.032 M) with dicyclohexyl carbodiimide (0.30 M) in the presence of PMe_3 (0.003 M, ◇; or 0.16 M, ■) in THF-d_8 at −29 °C.

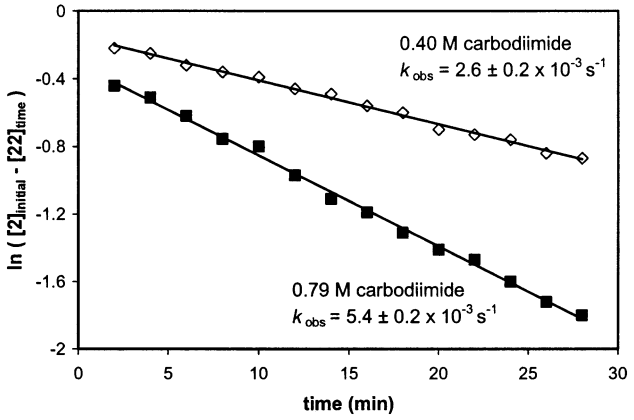
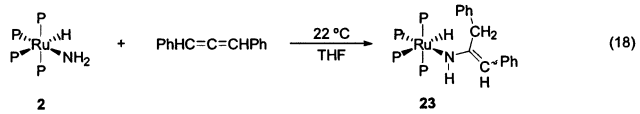


Figure 4. Pseudo-first-order plot for kinetics of the reaction of **2** (0.040 M) with dicyclohexyl carbodiimide (0.40 M, ◇; or 0.79 M, ■) in THF-d_8 at −31 °C.

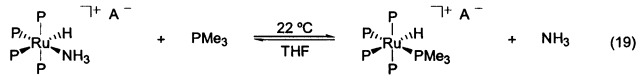
reaction proceeds sufficiently slowly that it can be monitored at −30 °C. The pseudo-first-order plots of two parallel experiments using 0.1 and 5.0 equiv of PMe_3 are shown in Figure 3; they show that the concentration of PMe_3 is not a factor in the rate of the reaction. In a separate experiment employing various concentrations of carbodiimide (Figure 4), the reaction was found to be cleanly first order in the carbodiimide.

The N−H insertion reactivity of complex **2** is not limited to heterocumulenes, as diphenyl allene also reacts rapidly with **2** to yield product **23** (eq 18). Again, both the ^1H and ^{31}P NMR spectra of this product are consistent with its formulation as an N-bound N−H insertion product.



2 **23** (18)

Investigation of Hydrogen Bonding in Ion Pairs. As described earlier, ammonia cresolate complex **10** reacts reversibly with PMe_3 to yield the pentaphosphino ruthenium hydride cresolate **12** (Scheme 1). This equilibrium provided an opportunity to investigate the energetic significance of hydrogen bonding interactions in $[(PMe_3)_4RuH(NH_3)^+][A^-]$ products resulting from proton transfer to **2**. To the extent that hydrogen bonding is possible in ion pairs such as **10**, we suspected that such interactions would favor the ammonia complexes relative to phosphine displacement products such as **12**. Thus, the positions of related equilibria (eq 19) should be sensitive to the hydrogen bonding capabilities of A^- if such interactions are significant in these species. The position of this equilibrium was



(19)

investigated for ion pairs $[(PMe_3)_4RuH(NH_3)^+][A^-]$ where A^- = BPh_4^- (**3**), $C_{13}H_9^-$ (**8**), $OTol^-$ (**10**), OTf^- (**24**), BF_4^- (**25**), and BAr_f^- (BAr_f = B(3-5-$C_6H_3(CF_3)_2)_4$) (**26**), and the resulting equilibrium constants are shown in Table 1. The data show that the ammonia complex is more favored for anions with localized charges and steric properties suitable for hydrogen bonding. Unfortunately, ammonia halide complexes **14**−**16** collapsed irreversibly to hydrido halide complexes **17**−**19** before equilibrium with PMe_3 was attained.

Table 1. Equilibrium Constants for Displacement of NH_3 by PMe_3 in Eq 19

entry	anion (compd)	K_{eq}
1	$OTol^-$ (**10**)	0.45 ± 0.05
2	OTf^- (**24**)	1.0 ± 0.1
3	$C_{13}H_9^-$ (**8**)	1.4 ± 0.1
4	BF_4^- (**25**)	4.5 ± 0.1
5	BPh_4^- (**3**)	16 ± 1
6	BAr_f^- (**26**)	19 ± 1
7	F^- (**14**)	*a*

[a] No product.

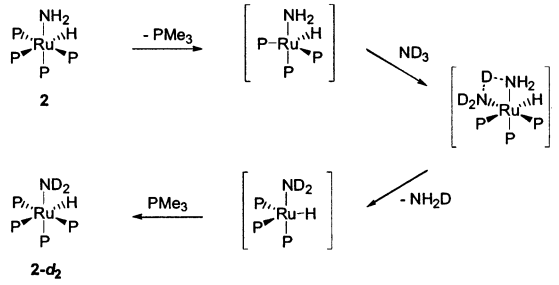
Discussion

Synthesis and Stability. While amide complex **2** can be prepared by $NaNH_2/NH_{3(l)}$ methodology analogous to that used in the synthesis of DMPE analogue **1**,[21] we found the deprotonation route shown in eq 1 to be more effective. Deprotonation by hydride and alkyllithium bases has been used to prepare parent amido complexes previously,[18,20] but these bases were ineffective in performing this deprotonation cleanly. The sterically hindered base $KN(SiMe_3)_2$, however, affords product **2** in excellent purity and high crude yield, presumably because of the inability of the base to displace the ammonia ligand. Unfortunately, the extremely high solubility of **2** even in pentane (∼0.5 g/mL) renders its isolation somewhat difficult, limiting the yield of its synthesis.

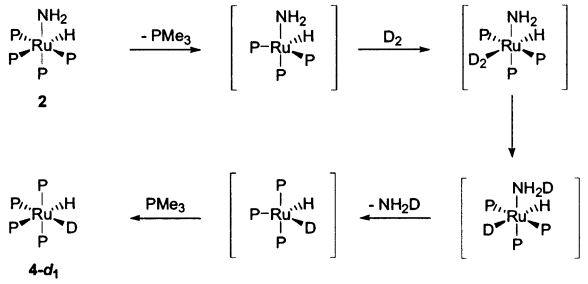
Unlike DMPE analogue **1**, complex **2** assumes a cis geometry. This geometry is common to almost all $(PMe_3)_4Ru(H)(X)$ complexes and is presumably due largely to the steric preference against crowding the relatively large PMe_3 groups into an equatorial plane. In this case, the cis geometry also allows the alignment of the strongly π-donating NH_2 ligand trans to a PMe_3 ligand (which is weakly π-acidic) rather than a hydride (which is not π-accepting). The adoption of the trans geometry in the DMPE system is probably a result of steric influences imposed by the chelating ligands and may be either a thermodynamic or kinetic phenomenon.

Complex **2** is reasonably stable at moderate temperatures, although it is very air sensitive (turning brown rapidly upon exposure) and reacts with traces of water to liberate ammonia and produce the corresponding hydroxide complex **5**. The amide group is reactive toward protonolysis by stronger acids such as cresol as well, although this takes place by an initial formation of an ion pair followed by subsequent ammonia displacement,

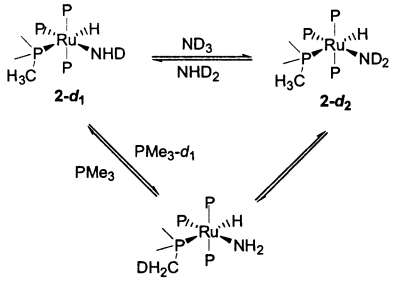
Scheme 4



Scheme 5



Scheme 6



as is observed for DMPE analogue **1**. It is not clear why the protonolysis by water is particularly rapid and does not involve an observable ion pair intermediate. In cases where ammonia displacement by the anion is sterically prohibitive, as with ^{t}BuOH and Ph_2NH, these ion pairs sometimes decompose by ammonia displacement and PMe_3 cyclometalation to yield complex **6**. The cyclometalation could take place via deprotonation of the P−CH_3 group by the strongly basic anion (we have independently observed related base-induced cyclometalation in a similar ruthenium ammonia complex[30]) or by initial dissociation of either NH_3 or PMe_3; further experiments may well distinguish among these mechanisms. The conversion of **2** to **6** and NH_3 occurs even when catalytic amounts of acid are used, and the addition of 4 atm of NH_3 to the reaction mixture does not regenerate amide **2**. This suggests that the amide complex is less stable than the cyclometalation products.

Basicity and Exchange Processes. All evidence suggests that **2** is moderately less basic than its DMPE analogue **1**. Species **2** undergoes H/D exchange with toluene and cyclohexadienes more slowly than does **1**, and direct comparison of the two species results in quantitative deprotonation of ammonia complex **8** by **1** ($pK_a = 23-24$ in THF)[23] (eq 8). Although **2** is sufficiently basic to cleanly deprotonate fluorene ($pK_a = 22.9$ in THF)[31] to yield ion pair **8**, this result gives an overestimate of the pK_a of **8** because of ion pairing effects that we have discussed at length elsewhere.[23] The most reasonable estimate of the pK_a of **8** is probably 20−21 (in THF) on the basis of the two results above. The attenuated basicity of **2** relative to DMPE analogue **1** can be attributed largely to its cis geometry and the resulting stabilization of its NH_2 lone pair by its interaction with the weakly π-accepting P−C σ^* orbitals of the trans PMe_3 ligand. The presence of π-acidic substituents or ligands has previously been observed to reduce the basicity of amide complexes,[20] and a ligand in the trans orientation would be expected to have the greatest impact in this regard.[3] Geometric constraints imposed by chelating ligands have previously been observed to enhance the basicity of transition metal centers.[32]

Another striking difference between complexes **1** and **2** is the lability of the PMe_3 ligands in **2** compared with the tightly bound chelating DMPE ligands of **1**. While **1** exchanges only slowly with ND_3 and does not exchange with $^{15}NH_3$ at all, **2** exchanges rapidly with both substrates at room temperature. When given the lower basicity of **2**, we presume that its exchange reactions with labeled ammonia take place via phosphine displacement by the incoming NH_3 group, rather than by its initial deprotonation (Scheme 4). Additionally, complex **2** reacts with D_2 to yield the hydrido deuteride **4-d_1** and NDH_2 rather than H/D exchange products (like those observed in the analogous reaction of **1**), and this reaction is retarded by the addition of phosphine. This suggests the mechanism shown in Scheme 5, which has previously been proposed for the hydrogenolysis of related amide and alkoxide complexes,[28] in which phosphine dissociation is a key step.

The lability of the phosphine ligands in **2** is not surprising. Not only are they monodentate ligands in contrast to the chelating DMPE groups in **1**, but the PMe_3 ligand located trans to the hydride is labilized by both the strong trans effect of the hydride ligand and the strong cis effect of the π-donating NH_2 group.[3] The reaction of complex **2** with DMPE highlights the regiochemistry of phosphine dissociation (product **7** appears to be the kinetic product) as a new complex substituted trans to the hydride and cis to the NH_2 group is formed (eq 4). This substitution reaction also suggests that complex **2** may indeed be a useful synthon in the preparation of new amide complexes featuring a variety of ligands, and we have begun to explore this possibility.

Role of Phosphine Dissociation. While amide complex **2** has relatively labile phosphine ligands, this feature does not appear to play a significant role in many of the basic and nucleophilic reactions the complex undergoes. H/D exchange reactions involving complex **2** are kinetically complicated, because of the fact that exchange with the NH_2 group is only moderately faster than the exchange between the NH_2 protons and those of the PMe_3 ligands. Additionally, efforts to investigate the effect of added phosphine on H/D exchange were complicated by an apparent exchange between free phosphine and partially deuterated bound phosphine. These exchange processes result in the overall catalytic H/D exchange of ND_3 with PMe_3, and a representative cycle for this deuterium transfer is illustrated in Scheme 6. The isomerization of 1,3-cyclohexadiene to the 1,4 isomer (eq 9) provides a more useful probe into the rate of proton transfer and occurs at a rate qualitatively similar to that for H/D exchange into the diene. The isomerization proceeds at a rate independent of phosphine concentration (Figure 1), indicating that the process takes place by direct,

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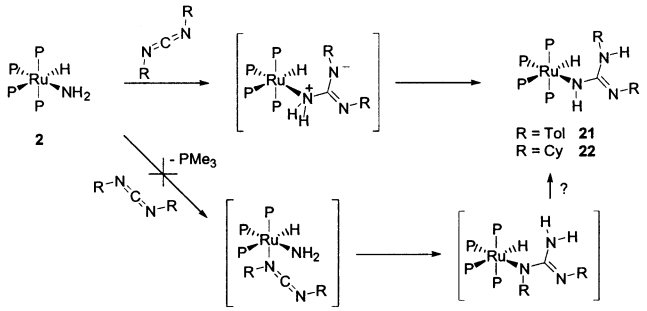
Scheme 7



reversible proton transfer to **2** (Scheme 2) rather than any pathway requiring coordination of the substrate to the metal center.

The rate of insertion of dicyclohexyl carbodiimide into an NH bond of complex **2** is also independent of [PMe_3] (Figure 3). This reaction is rapid at room temperature despite the steric demands of the cyclohexyl groups, and the corresponding reaction of di-*p*-tolyl carbodiimide is rapid even at −80 °C. This is consistent with a mechanism involving direct nucleophilic attack by the NH_2 group on the electrophilic carbon (Scheme 7), which proceeds more rapidly at the more electrophilic (and less sterically congested) carbon in the aryl substituted carbodiimide. This mechanism is also consistent with the formation of an N−H insertion product rather than the product of M−N insertion that would be anticipated to result from intramolecular NH_2 migration (Scheme 7, bottom path). While these two isomers could potentially interconvert by an intramolecular proton transfer and displacement, such a reaction would be expected to be slow at low temperature in the presence of excess phosphine. Similar regiochemistry consistent with N−H insertion is observed in the reaction of diphenyl acetylene with DMPE analogue **1**.[23]

Alkyl Halide Reactions. Unlike complex **1**, amide **2** reacts cleanly with a variety of alkyl halides to yield either E2 or S_N2 products. In the case of the E2 reactions, complex **2** behaves in a manner expected for a more conventional base such as KO^{t}Bu. An investigation of the stereochemistry of E2 eliminations involving **2** conducted using the rac and meso isomers of 2,3-dibromobutane showed that both isomers reacted to give almost exclusively the anti elimination product. In this regard, complex **2** behaves no differently than a more conventional base.[33] These reactions do, however, also yield organometallic products of the type [$(PMe_3)_4RuH(NH_3)^+$][X^-], and ultimately their displacement products $(PMe_3)_4Ru(H)(X)$. In the case of the reaction between **2** and trifluoroethane, this provides a novel route to a relatively rare late metal fluoride species, **17** (eq 13). In this reaction, no olefin or other simple organic product is observed; we attribute this to some combination of the volatility and reactivity of 1,1-difluoroethylene. We have independently confirmed that 1,1-difluoroethylene reacts with amide complex **2** to yield multiple products.

The S_N2 reaction of complex **2** with ethyl bromide shows that it is possible to use complex **2** to deliver an NH_2^- unit to an organic substrate. This is typically a difficult transformation because of the unavailablility of soluble NH_2^- sources and the propensity for over-alkylation in the reactions of alkyl halides with ammonia.[34] Efforts to exploit this reactivity to effect the amination of alkyl halides using a catalytic amount of complex **2** are underway.

Hydrogen Bonding. While the displacement of ammonia from ion pairs [$(PMe_3)_4RuH(NH_3)^+$][A^-] by PMe_3 prevented us from conveniently exploring the significance of phosphine dissociation in these reactions, it also offered an opportunity to explore the extent of hydrogen bonding in these systems. The crystal structures and NMR behavior of some ion pairs involving DMPE analogue **1** showed evidence of strong hydrogen bonding interactions,[23] and such interactions would be important to the energetics involved in deprotonation reactions involving amides such as **1** and **2** and in the subsequent displacement reactions of initial proton transfer products. To explore the role of solution-phase hydrogen bonding in these systems, we investigated the effect of the anion on the position of the equilibrium shown in eq 19 and found that anions capable of functioning as hydrogen bonding acceptors favored the corresponding ammonia complex over the pentaphosphino displacement product. Cresolate favored the ammonia complex most strongly, and triflate, while a very weak base, favored the ammonia complex more strongly than did the sterically hindered and delocalized fluorenide anion. These results demonstrate that hydrogen bonding has a significant effect on the energetics of this system in solution. Unfortunately, the N−H stretching vibrations in the IR spectra of these complexes were too weak and complicated to be of use in investigating hydrogen bonding in these ion pairs.

Various scales have been developed for evaluating the extent to which "noncoordinating" anions donate electron density to metal centers,[35−39] but fewer *directly* compare these anions in terms of their abilities as hydrogen bonding acceptors. Such evaluation is clearly important in any reactions featuring such anions and weakly acidic metal species such as aquo or amine complexes. We investigated the relative hydrogen bonding abilities of BF_4^-, BPh_4^-, and BAr_f^- using the equilibrium in eq 19 and found BF_4 to engage in significantly more H bonding than the other two anions and the fluorinated borate BAr_f^- to engage in the least. All three complexes favored the pentaphosphino displacement product much more than did triflate or fluorenide anions.

Conclusion

In summary, we have found that the amide complex $(PMe_3)_4Ru(H)(NH_2)$ (**2**) can be conveniently prepared by deprotonation. The complex is slightly less basic than DMPE analogue **1**, although it is still sufficiently basic to deprotonate fluorene, isomerize cyclohexadiene, and serve as a potent base for E2 eliminations. Complex **2** is also nucleophilic, reacting with ethyl bromide to yield ethylamine and with carbodiimides and diphenylallene to yield N−H insertion products, even at temperatures well below room temperature. Neither the basic nor nucleophilic reactivity of the complex involves phosphine dissociation, and it appears instead to originate directly at the ruthenium-bound NH_2 group. Efforts to exploit the reactivity

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of this complex as an H/D exchange catalyst and soluble NH_2 source are underway.

Experimental Section

General Procedures and Materials. General procedures have been described elsewhere.[40] In NMR assignments, phosphine groups are identified by a subscript indicating the element to which they are oriented trans. 1,3,5-trimethoxybenzene (Aldrich, recrystallized from pentane) was employed as an internal standard in NMR tube reactions. Gas chromatography (GC) was performed using a Hewlett-Packard model 5890 series II gas chromatograph equipped with a 30-m HP-1 column. Chromatographic separations were achieved using isothermal conditions (50 °C) and a constant flow rate of 1 mL/min. The X-ray structure determination was performed by Dr. Fred Hollander and Dr. Allen Oliver at the UCB CHEXRAY facility.

Unless otherwise indicated, all reagents were purchased from commercial suppliers and used as received. Solvent purification methods have been described elsewhere.[40,41] All alkyl halides were degassed and dried over 4-Å molecular sieves for 2 d and then distilled prior to use. Aniline and cresol were dried over 4-Å molecular sieves. Fluorene was recrystallized from pentane prior to use. Trimethylphosphine (Aldrich) was vacuum transferred from sodium metal prior to use. Complexes **1**,[21] **3**,[25] and **9**,[23] diphenyl allene,[42] $NaBAr_f$,[43] and dibromobutanes[44] were prepared according to published procedures.

***cis*-$(PMe_3)_4Ru(H)(NH_2)$ (2).** In two vials, ammonia complex **3** (2.16 g, 2.91 mmol) and $KN(SiMe_3)_2$ (0.585 g, 2.94 mmol) were each dissolved separately in THF (10 mL each). A stirbar was added to the solution of the ammonia complex, and the base solution was then added dropwise to the stirred solution of **3**. This resulted in the formation of flocculent white material and a slight yellowing of the previously pale tan solution. The mixture was stirred for 1 h and then filtered through Celite. After the yellow filtrate was collected, its volatile materials were removed in vacuo. The yellow residue was extracted with pentane (2 × 10 mL), and the extract was concentrated to 3 mL in vacuo. This solution was chilled to −35 °C, and three batches of off-white crystals of **2** (0.738 g, 60% yield) were collected over the course of 8 d. ^{1}H NMR (C_6D_6): δ 1.37 (18H, t, J = 2.6 Hz, $P_P(CH_3)_3$), 1.14 (9H, d, J = 6.4 Hz, $P_N(CH_3)_3$), 1.12 (9H, d, J = 5.0 Hz, $P_H(CH_3)_3$), −2.39 (2H, s, $RuNH_2$), −8.49 (1H, dtd, J = 99.2, 29.6, 24.4 Hz, Ru*H*) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 3.12 (td, J = 26, 21 Hz, P_N), −1.50 (t, J = 26 Hz, P_P), −11.04 (q, J = 22 Hz, P_H) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 28.8 (dd, J = 20, 2 Hz, $P_N(CH_3)_3$), 23.4 (td, J = 14, 4 Hz, $P_P(CH_3)_3$), 22.3 (dq, J = 14, 2 Hz, $P_H(CH_3)_3$) ppm. IR (C_6H_6, cm^{-1}): 3364 (w), 2964 (s), 2903 (s), 1808 (s), 1418 (s), 1292 (s), 1275 (s), 937 (s). MS *m*/*z* (EI): 423 (M), 406 (M − NH_3), 347 (M − PMe_3). Anal. Calcd for $C_{12}H_{39}NP_4Ru$: C, 34.12; H, 9.30; N, 3.31. Found: C, 34.02; H, 9.10; N, 2.98.

***cis*-$(PMe_3)_4Ru(H)(OH)$ (5).** Complex **2** (25 mg, 59 μmol) was dissolved in C_6D_6 (1 mL), and the solution was transferred to an NMR tube which was capped with a septum. Degassed H_2O (1.0 μL, 56 μmol) was then added by syringe, and after 5 min, ^{1}H and ^{31}P NMR spectra were acquired showing quantitative conversion of **2** to hydroxide complex **5**. The spectroscopic features of this complex matched those reported in the literature.[26]

***cis*-$(PMe_3)_3Ru(CH_2PMe_2)(H)$ (6).** Complex **2** (104 mg, 246 μmol) was dissolved in THF (5 mL), and Ph_2NH (14 mg, 83 μmol) was added. The solution was heated to 45 °C for 4 h, after which time the volatile materials were removed in vacuo to yield a white residue. This was recrystallized from pentane at −35 °C to yield **6** (65 mg, 65% yield) as a white solid. The spectroscopic features of this complex matched those reported in the literature.[27]

***cis*-$(PMe_3)_2(DMPE)Ru(H)(NH_2)$ (7).** Amide complex **2** (276 mg, 654 μmol) was dissolved in benzene (5 mL), and DMPE (100 mg, 666 μmol) was added. The solution was allowed to stand at room temperature for 24 h, after which the volatile materials were removed in vacuo and the oily residue was redissolved in benzene (5 mL). After an additional 24 h, the volatile materials were again removed, yielding 95% pure **7** according to ^{1}H and ^{31}P NMR spectra. The oily residue was extracted with pentane (5 mL), and the extract was concentrated to 0.3 mL in vacuo and crystallized at −35 °C to yield **7** (103 mg, 38% yield) as an off-white oily solid after 2 d. ^{1}H NMR (C_6D_6): δ 1.71, (3H, d, J = 8.6 Hz, $P(CH_3)$), 1.40 (4H, m, $P(CH_2)_2P$), 1.33 (9H, dd, J = 6.3, 1.7 Hz, $P(CH_3)_3$), 1.20 (6H, d, J = 5.9 Hz, 2 × $P(CH_3)$), 1.12 (3H, d, J = 7.8 Hz, $P(CH_3)$), 1.02 (9H, d, J = 7.72 Hz, $P(CH_3)_3$), −2.51 (2H, s, $RuNH_2$), −7.51 (1H, dq, J = 99.6, 24.8 Hz, Ru*H*) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 44.11 (ddd, J = 323, 27, 12 Hz, $P(CH_2)_2P_P$), 30.03 (q, J = 18 Hz, $P(CH_2)_2P_H$), 3.67 (br, $(CH_3)_3P_N$), 0.04 (dt, J = 323, 18 Hz, $(CH_3)_3P_P$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 34.3 (m, $P(CH_3)$), 28.6 (m, $P(CH_3)_3$), 27.6 (m, $P(CH_3)_3$), 22.6 (m, $P(CH_3)$), 21.0 (m, $P(CH_3)$), 15.8 (m, $P(CH_3)$) ppm. IR (C_6H_6, cm^{-1}): 3332 (w), 3261 (w), 2967 (s), 2901 (s), 1794 (s), 1420 (s), 1295 (s), 1273 (s), 1039 (s), 924 (s). MS *m*/*z* (EI): 421 (M^+), 404 (M − NH_3). Anal. Calcd for $C_{12}H_{37}NP_4Ru$: C, 34.28; H, 8.80; N, 3.33. Found: C, 34.23; H, 9.12; N, 3.01.

[*cis*-$(PMe_3)_4Ru(H)(NH_3)^+$][$C_{13}H_9^-$] (8). Amide complex **2** (432 mg, 1.02 mmol) was dissolved in pentane (10 mL), and a pentane solution of fluorene (183 mg, 1.10 mmol) was added dropwise with swirling. Orange powder formed during the addition, and this was collected by filtration and recrystallized from THF (10 mL) layered with pentane (10 mL) at −35 °C. After 24 h, red-orange crystals of **8** (530 mg, 89% yield) were collected. ^{1}H NMR (THF-d_8): δ 7.85 (d, J = 7.6 Hz, 2H, Ar), 7.26 (d, J = 8.0 Hz, 2H, Ar), 6.78 (t, J = 7.6 Hz, 2H, Ar), 6.40 (t, J = 7.2 Hz, 2H, Ar), 5.95 (s, 1H, Ar), 1.17 (9H, d, J = 7.6 Hz, $P_N(CH_3)_3$), 1.08 (18H, t, J = 2.8 Hz, $P_P(CH_3)_3$), 0.96 (9H, d, J = 5.6 Hz, $P_H(CH_3)_3$), −0.24 (s, 3H, $RuNH_3$), −10.00 (dtd, J = 92, 32, 20 Hz, 1H, Ru*H*) ppm. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 13.57 (dt, J = 37, 23 Hz, P_N), −4.73 (dd, J = 37, 23 Hz, P_P), −15.72 (q, J = 23 Hz, P_H) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8): δ 138.1 (s, Ar), 123.3 (s, Ar), 119.9 (s, Ar), 119.5 (s, Ar), 117.0 (s, Ar), 108.8 (s, Ar), 83.7 (s, Ar), 25.9 (d, J = 23.9 Hz, $P_N(CH_3)_3$), 22.7 (td, J = 13.5, 3.4 Hz, $P_P(CH_3)_3$), 21.7 (d, J = 17.9 Hz, $P_H(CH_3)_3$). IR (THF, cm^{-1}): 3397 (w), 3340 (w), 1799 (s), 1658 (m), 1596 (s). MS *m*/*z* (FAB): 424 (M − $C_{13}H_9$). Anal. Calcd for $C_{25}H_{49}NP_4Ru$: C, 51.01; H, 8.39; N, 2.38. Found: C, 51.02; H, 8.14; N, 2.29.

Reaction of 8 with 1. Complex **1** (12 mg, 29 μmol) and internal standard (1 mg, 6 μmol) were dissolved in THF-d_8 (0.5 mL) and transferred to an NMR tube, and an initial ^{1}H NMR spectrum was acquired. Complex **8** (12 mg, 29 μmol) was then added to the sample, and new ^{31}P and ^{1}H NMR spectra were acquired within 10 min. These showed complete conversion to complexes **2** (^{1}H NMR (THF-d_8): δ −8.86 (dq, Ru*H*) ppm; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 3.65 (td, P_N) ppm) and **9** (^{1}H NMR (THF-d_8) δ −20.32 (dq, Ru*H*) ppm; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 43.08 ppm).[45]

[*cis*-$(PMe_3)_4Ru(H)(NH_3)^+$][OTol$^-$] (10). Complex **2** (186 mg, 443 μmol) was dissolved in pentane (2 mL), and *p*-cresol (48 mg, 0.44 μmol) was added as a pentane solution (1 mL). The solution was then chilled to −35 °C, resulting in the formation of white precipitate **10** (210 mg, 90% yield). Elemental analysis was consistent with this material being pure, although in solution phase **10** was always contaminated with displacement product **11**. Addition of 1 atm of NH_3 to these solutions suppressed this contamination. ^{1}H NMR (THF-d_8):

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(41) Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Educ.* **2001**, *78*, 64.
(42) Elsevier, C. J.; Stehouwer, P. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1983**, *48*, 1103.
(43) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.
(44) Young, W. G.; Dillon, R. J.; Lucas, H. J. *J. Am. Chem. Soc.* **1929**, *51*, 2528.

(45) The identification of this compound was confirmed by comparison to an authentic sample.

6.50 (2H, d, $J = 7.5$ Hz, Ar), 5.93 (2H, d, $J = 7.5$ Hz, Ar), 2.40 (3H, s, RuNH_3), 2.10 (3H, s, ArCH_3), 1.47 (18H, t, $J = 3.0$ Hz, $P_P(CH_3)_3$), 1.46 (9H, d, $J = 6.6$ Hz, $P_N(CH_3)_3$), 1.39 (9H, d, $J = 8.2$ Hz, $P_H(CH_3)_3$), −9.46 (dtd, $J = 92$, 32, 20 Hz, 1H, Ru*H*) ppm. $^{31}P\{^1H\}$ NMR (THF-d_8): δ 14.36 (dt, $J = 38$, 24 Hz, P_N), −3.90 (dd, $J = 38$, 24 Hz, P_P), −14.32 (q, $J = 24$ Hz, P_H) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8): δ 169.7 (s, Ar), 129.9 (s, Ar), 120.5 (s, Ar), 117.6 (s, Ar), 26.3 (d, $J = 26$ Hz, $P_N(CH_3)_3$), 23.3 (td, $J = 14$, 3 Hz, $P_P(CH_3)_3$), 22.4 (d, $J = 18$ Hz, $P_H(CH_3)_3$), 21.8 (s, ArCH_3) ppm. IR (THF, cm^{-1}): 3401 (w), 3342 (w), 1798 (s), 1655 (m), 1597 (s). MS *m*/*z* (FAB, sulfolane): 424 (M − OTol). Anal. Calcd for $C_{19}H_{47}NOP_4Ru$: C, 43.01; H, 8.93; N, 2.64. Found: C, 43.06; H, 8.76; N, 2.30.

***cis*-(PMe$_3$)$_4$Ru(H)(OTol) (11).** Complex **2** (204 mg, 483 μmol) and cresol (53 mg, 491 μmol) were dissolved in C_6H_6 (5 mL), and the solution and a stirbar were loaded into a glass vessel equipped with a Teflon stopcock. The solution was degassed and stirred at room temperature for 24 h. After this time, the volatile materials were removed in vacuo, and the remaining off-white solid was recrystallized from pentane (2 mL) at −35 °C for 48 h to yield **11** as white crystals (174 mg, 70% yield). The spectroscopic features of this complex matched those reported in the literature.[28]

***cis*-(PMe$_3$)$_4$Ru(H)(NHPh) (13).** Complex **2** (142 mg, 338 μmol) and aniline (33 mg, 350 μmol) were dissolved in C_6H_6 (5 mL), and the solution was stirred at room temperature for 24 h. After this time, the volatile materials were removed in vacuo, and the remaining off-white solid was recrystallized from pentane (2 mL) at −35 °C for 48 h to yield **13** (101 mg, 59% yield) as a yellow-white solid. The spectroscopic features of this complex matched those reported in the literature.[28]

H/D Exchange between 2 and Toluene-d_8. Complex **2** (18 mg, 43 μmol) and internal standard were dissolved in toluene-d_8 (300 μL), and the mixture was divided evenly between two NMR tubes. Both solutions were degassed, and PMe_3 (66 mL × 12 Torr, 43 μmol) was added to one tube by vacuum transfer from a known volume bulb. Both tubes were flame sealed under vacuum, heated to 45 °C, and monitored periodically by ^1H and ^{31}P NMR spectroscopy. Slow decreases in the intensities of the $P(CH_3)_3$ and RuNH_2 resonances were observed in both samples and took place at approximately the same initial rate in the two samples. In the sample containing PMe_3, isotopomers PMe_3-d_n (δ −57.58 − (0.33)*n* ppm) were observed in the ^{31}P NMR spectrum, and an increasing degree of deuterium incorporation in this group was observed as the reaction progressed. Deuteration of the Ru*H* was not observed. After 3 d, the samples were evaporated to dryness in vacuo. C_6H_6 (300 μL) was added, and deuterium incorporation was confirmed by $^2H\{^1H\}$ NMR spectroscopy: δ 1.4 (18D), 1.1 (18D), −2.4 (2D) ppm.

Isomerization of 1,3-Cyclohexadiene by 2. A solution of 1,3-cyclohexadiene (7.0 mg, 88 μmol), **2** (9.2 mg, 22 μmol), and internal standard (3.0 mg, 18 μmol) in C_6D_6 (580 μL) was quickly prepared and divided evenly between two NMR tubes. The tubes were fitted to Cajon adapters and frozen at −196 °C within 2 min of mixing the diene and **2**. PMe_3 (6.6 mL × 3.2 Torr, 2.6 μmol; 6.6 mL × 90 Torr, 32 μmol) was then added to each tube via vacuum transfer from a known volume bulb, and the tubes were sealed under vacuum. The samples were then kept in a water bath at 22 °C, and the ratio of 1,3-cyclohexadiene (δ 5.86 (2H, d), 5.67 (2H, d), 1.95 (3H, s) ppm) and 1,4 cyclohexadiene (δ 5.60 (4H, s), 2.51 (3H, s) ppm)[45] was monitored by ^1H NMR over the course of several hours. No loss of diene or **2** was observed during this time. The results are shown in Figure 1.

***cis*-(PMe$_3$)$_4$Ru(H)(NH$_2$)-d_n via ND$_3$.** Amide complex **2** (10 mg, 24 μmol) and internal standard were dissolved in C_6D_6, (0.5 mL) and this solution was loaded into an NMR tube equipped with a Teflon stopcock. After an initial ^1H NMR spectrum was acquired, the solution was degassed on the vacuum line, ND_3 (6.6 mL × 720 Torr, 260 μmol) was added by vacuum transfer from a known volume bulb, and the tube was closed. A ^1H NMR spectrum of the resulting solution was acquired within 5 min and showed a 30% decrease in the integration of the RuNH_2 signal at −2.39 ppm and an NH_nD_{3-n} signal at δ −0.17 ppm, accounting for the missing intensity. No other peaks were significantly changed. After 3 h, only 20% of the original RuNH_2 signal remained, and the $P(CH_3)_3$ signals were broadened and less intense. The ^{31}P NMR showed broadening in the $P(CH_3)_3$ signals as well. After 24 h, the $P(CH_3)_3$ signals had further decreased in intensity, while the RuNH_2 signal had actually increased slightly. After 72 h, both $P(CH_3)_3$ and RuNH_2 signals appeared at ∼50% of their original intensities, and the Ru*H* signal remained unchanged. The solution was evaporated to dryness in vacuo, and a mass spectrum (EI) of the resulting off-white oily solid showed a broad envelope centered at $m/z = 441$, corresponding to ∼50% deuteration. The $^2H\{^1H\}$ NMR (C_6H_6) of this material was consistent with deuteration at all positions except RuH: δ 1.4 (18D), 1.1 (18D), −2.4 (2D) ppm.

***cis*-(PMe$_3$)$_4$Ru(H)(^{15}NH$_2$) (2-^{15}N).** Complex **2** (21 mg, 50 μmol) was dissolved in C_6D_6 (300 μL) in an NMR tube equipped with a Teflon stopcock, the solution was degassed, and $^{15}NH_3$ (6.6 mL × 141 Torr, 50 μmol) was added by vacuum transfer from a known volume bulb. The ^1H NMR spectrum of the solution after 5 min showed a 1:1 mixture of free $^{15}NH_3$ (δ −0.17 (d, $J = 60.8$ Hz) ppm) and $^{14}NH_3$ (δ −0.17 (t, $J = 42.8$ Hz) ppm) and slight broadening in the NH_2 signal (δ −2.40 ppm). The solution was briefly degassed under vacuum, and additional $^{15}NH_3$ (6.6 mL × 412 Torr, 150 μmol) was added. This addition resulted in the liberation of additional $^{14}NH_3$ and further broadening of the RuNH_2 signal in the ^1H NMR spectrum. The volatile materials were then removed, and **2-^{15}N** (20 mg, 96% yield) was collected as a pale yellow oil. EIMS *m*/*z*: = 424 (M^+).

Reaction of 2 with D$_2$. Amide complex **2** (19 mg, 45 μmol) was dissolved in THF-d_8 (1 mL), and this solution was divided evenly between two NMR tubes, each equipped with a Teflon stopcock. The tubes were then degassed on the vacuum line, and PMe_3 (29 mL × 12 Torr, 19 μmol) was added to one of the samples by vacuum transfer from a known volume bulb. Both tubes were then charged with D_2 (754 Torr) and closed. The samples were shaken and kept at 22 °C and monitored by ^1H NMR spectroscopy. After 2 h, the solution containing no PMe_3 had undergone 40% conversion to P_4RuHD[28] (^1H NMR (THF-d_8) δ 1.31 (36H, br, $P(CH_3)_3$), −10.13 (1H, m, Ru*H*); $^2H\{^1H\}$ NMR (THF-d_8) δ − 10.1 (br); $^{31}P\{^1H\}$ NMR (THF-d_8) δ 0.7 (t), −6.7 (t) ppm) and NH_2D (δ 0.34 (2H, t) ppm), and the sample containing PMe_3 had undergone <5% conversion to the same products. After 8 h, the respective extents of conversion in the two tubes were 85 and 5%, respectively. In neither case was any deuteration of remaining **2** or additional deuteration of P_4RuHD observed.

[*cis*-(PMe$_3$)$_4$Ru(H)(NH$_3$)$^+$][F$^-$] (14). Complex **2** (253 mg, 602 μmol) was dissolved in benzene (5 mL), and the solution and a stirbar were loaded into a glass vessel equipped with a Teflon stopcock. The solution was degassed, and 1,1,1-trifluoroethane (66 mL × 170 Torr, 613 μmol) was added via vacuum transfer from a known volume bulb. The stopcock was then closed, and the solution was stirred at room temperature for 48 h, during which time the color changed from pale yellow to bright orange. The sample was evaporated to dryness in vacuo, then dissolved in THF (2 mL), layered with pentane (10 mL), and chilled to −35 °C. Complex **14** (156 mg, 59% yield) was collected as an off-white solid after 24 h. ^1H NMR (THF-d_8): δ 3.94 (3H, s, RuNH_3), 1.53 (18H, s, $P_P(CH_3)_3$), 1.49 (9H, d, $J = 6.2$ Hz, $P_N(CH_3)_3$), 1.32 (9H, d, $J = 8.2$ Hz, $P_H(CH_3)_3$), −9.77 (dtd, $J = 89.2$, 32.4, 20.0 Hz, 1H, Ru*H*) ppm. ^{19}F NMR (THF-d_8): δ −82.8 (br) ppm.$^{31}P\{^1H\}$ NMR (THF-d_8): δ 13.90 (dt, $J = 36$, 28 Hz, P_N), −2.55 (dd, $J = 36$, 23 Hz, P_P), −12.37 (q, $J = 24$ Hz, P_H) ppm. $^{13}C\{^1H\}$ NMR (THF-d_8): δ 26.8 (dq, $J = 25$, 3 Hz, $P_N(CH_3)_3$), 24.0 (td, $J = 15$, 3 Hz, $P_P(CH_3)_3$), 23.2 (d, $J = 17$ Hz, $P_H(CH_3)_3$) ppm. IR (THF, cm^{-1}): 3395 (w), 3334 (w), 1799 (s). Anal. Calcd for $C_{12}H_{40}FNP_4Ru$: C, 32.57; H, 9.11; N, 3.17. Found: C, 32.20; H, 8.84; N, 2.89.

Reaction of 2 with PhCH$_2$CH$_2$Cl. Complex **2** (23 mg, 55 μmol) was dissolved in THF-d_8 (300 μL), 1-phenyl-2-chloroethane (7.7 mg, 55 μmol) was added, and the solution was loaded into an NMR tube.

The ^{1}H NMR spectrum of this solution after 30 min showed equal amounts of styrene (^{1}H NMR (THF-d_8) δ 7.3−7 (5H, m, Ph), 6.56 (1H, dd, PhC*H*═CH_2), 5.59 (d, PhCH═C*H*H), 5.05 (1H, d, PhCH═CH*H*)) and an organometallic complex with spectroscopic characteristics consistent with an ammonia cation complex **15**. Efforts to isolate complex **15** from this product mixture were unsuccessful. Over the course of 24 h, the resonances assigned to **15** decreased in intensity and were replaced by those for NH_3 displacement product **18**. The volatile materials were then removed in vacuo, and the residue was recrystallized from pentane (0.5 mL) at −35 °C for 24 h to yield **18** (14 mg, 55% yield). **15**: ^{1}H NMR (THF-d_8) δ 2.87 (s, 3H, RuNH_3), 1.52 (18H, t, J = 3.1 Hz, P(CH_3)$_3$), 1.49 (9H, d, J = 6.2 Hz, P(CH_3)$_3$), 1.35 (9H, d, J = 7.6 Hz, P(CH_3)$_3$), −9.63 (1H, dtd, J = 92.1, 31.8, 20.8 Hz, Ru*H*) ppm; ^{31}P{^{1}H} NMR (THF-d_8) δ 14.91 (td, J = 37, 24 Hz, P_N), −2.85 (dd, J = 36, 23 Hz, P_P), −13.75 (q, J = 23 Hz, P_H) ppm. **18**: ^{1}H NMR (C_6D_6) 1.49 (18H, t), 1.24 (9H, d), 1.09 (9H, d), −8.51 (1H, dq) ppm; ^{31}P{^{1}H} NMR (THF-d_8) δ 16.65 (td), −4.85 (dd), −16.61 (q) ppm; Lit.[46] ^{1}H NMR (C_6D_6) 1.48 (18H, t), 1.24 (9H, d), 1.09 (9H, d), −8.50 (1H, dq) ppm; ^{31}P{^{1}H} NMR (THF-d_8) δ 16.7 (td), −4.9 (dd), −16.6 (q) ppm.

[*cis*-(PMe$_3$)$_4$Ru(H)(NH$_3$)$^+$][Br$^-$] (16). Complex **2** (105 mg, 249 μmol) and *rac*-2,3-dibromobutane (56 mg, 259 μmol) were each dissolved in pentane (1 mL each), and the bromobutane solution was then added dropwise to **2**. The resulting solution was chilled to −35 °C for 4 h, yielding **16** (82 mg, 65% yield) as a white solid. ^{1}H NMR (THF-d_8): δ 2.57 (3H, s, RuNH_3), 1.53 (18H, t, J = 3.1 Hz, P(CH_3)$_3$), 1.48 (9H, d, J = 6.4 Hz, P(CH_3)$_3$), 1.36 (9H, d, J = 7.4 Hz, P(CH_3)$_3$), −9.60 (dtd, J = 92, 32, 20 Hz, 1H, Ru*H*) ppm. ^{31}P{^{1}H} NMR (THF-d_8): δ 15.23 (dt, J = 37, 24 Hz, P_N), −2.65 (dd, J = 36, 23 Hz, P_P), −13.98 (q, J = 23 Hz, P_H) ppm. ^{13}C{^{1}H} NMR (THF-d_8): δ 26.2 (d, J = 26 Hz, P(*C*H$_3$)$_3$), 23.2 (td, J = 14, 3 Hz, P(*C*H$_3$)$_3$), 22.2 (d, J = 17 Hz, P(*C*H$_3$)$_3$) ppm. IR (THF): 3400 (w), 3341 (w), 11819 (s) cm^{-1}. MS m/z (FAB, sulfolane): 424 (M − Br). Anal. Calcd for $C_{12}H_{40}$BrNP$_4$Ru: C, 28.63; H, 8.01; N, 2.78. Found: C, 28.39; H, 8.16; N, 2.64.

Dehydrobromination of *meso*- and *rac*-2,3-Dibromobutane by 2. In a typical experiment, amide complex **2** (8.4 mg, 20 μmol) and *rac*-2,3-dibromobutane (4.4 mg, 20 μmol) were each dissolved separately in C_6D_6 (0.25 mL), and then the base solution was added dropwise to the stirred dibromobutane solution. The resulting solution was transferred into an NMR tube and the ^{1}H NMR spectrum of the mixture showed *Z*-2-bromobutene (δ 5.21 (1H, q, J = 7.3 Hz), 1.97 (3H, s), 0.84 (3H, d, J = 7.3 Hz) ppm)[45] to be the only significant product. The experiment was repeated in *o*-xylene and filtered through a plug of silica, and GC analysis of the product showed *Z* (t_r = 1.50 min) and *E* (t_r = 1.40 min) isomers in a 98:2 ratio. The analogous experiments using *meso*-2,3-dibromobutane produced the *E* isomer according to ^{1}H NMR spectroscopy (δ 5.71 (1H, q, J = 6.0 Hz), 1.85 (3H, s), 1.12 (3H, d, J = 6.0 Hz) ppm)[45] and the *Z* and *E* isomers in a 3:97 ratio by GC analysis. In both NMR experiments, **16** was the only initial organometallic product observed, and it was replaced by **19** and NH_3 over the course of 48 h.

***cis*-(PMe$_3$)$_4$Ru(H)F (17).** Complex **14** (50 mg, 110 μmol) was dissolved in C_6D_6 (0.5 mL), and the solution was loaded into an NMR tube. The tube was affixed to a Cajon adaptor, degassed, and flame sealed under vacuum. The sample was heated for 24 h at 45 °C, yielding **17** and NH_3 as the only products observed by NMR spectroscopy. The volatile materials were removed in vacuo, and the residue was recrystallized from THF (0.5 mL) and pentane (5 mL) to yield **17** (35 mg, 72% yield) as yellow crystals.^{1}H NMR (C_6D_6): δ 1.38 (18H, br, P(CH_3)$_3$), 1.19 (9H, d, J = 6.4 Hz, P(CH_3)$_3$), 0.98 (9H, d, J = 7.6 Hz, P(CH_3)$_3$), −7.61 (1H, dq, J = 104.0, 29.6 Hz, Ru*H*) ppm. ^{31}P{^{1}H} NMR (THF-d_8): δ 18.86 (dtd, J = 150, 34, 18 Hz, P_F), −0.29 (dt, J = 34, 26 Hz, P_P), −6.78 (p, J = 34 Hz, P_H) ppm. ^{13}C{^{1}H} NMR (THF-d_8): δ 27.5 (d, J = 25 Hz, P(*C*H$_3$)$_3$), 22.4 (td, J = 15, 4 Hz, P(*C*H$_3$)$_3$), 20.0 (dq, J = 15, 2 Hz, P(*C*H$_3$)$_3$) ppm. ^{19}F NMR (THF-d_8): δ −396.1 (dq, J = 150, 35 Hz). IR (KBr): 1803 (s) cm^{-1}. MS m/z (EI): 426 (M$^+$), 350 (M − PMe$_3$). Anal. Calcd for $C_{12}H_{37}FP_4Ru$: C, 33.88; H, 8.77. Found: C, 34.00; H, 8.94.

***cis*-(PMe$_3$)$_4$Ru(H)Br (19).** Complex **16** (70 mg, 140 μmol) was dissolved in C_6D_6 (0.5 mL), and the solution was loaded into an NMR tube. The tube was affixed to a Cajon adaptor, degassed, and flame sealed under vacuum. The sample was heated for 24 h at 45 °C, yielding **19** and NH_3 as the only products observed by NMR spectroscopy. The volatile materials were removed in vacuo, and the residue was recrystallized from THF (0.5 mL) and pentane (3 mL) to yield **19** (55 mg, 81% yield) as yellow crystals. ^{1}H NMR (C_6D_6): δ 1.48 (18H, t, J = 2.7 Hz, P(CH_3)$_3$), 1.19 (9H, d, J = 5.5 Hz, P(CH_3)$_3$), 1.04 (9H, d, J = 7.8 Hz, P(CH_3)$_3$), −8.90 (1H, dq, J = 103.2, 29.6 Hz, Ru*H*) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 17.95 (td, J = 34, 19 Hz, P_{Br}), −7.02 (dd, J = 34, 26 Hz, P_P), −19.55 (q, J = 23 Hz, P_H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 28.2 (dq, J = 24, 3 Hz, P(*C*H$_3$)$_3$), 24.8 (td, J = 14, 3 Hz, P(*C*H$_3$)$_3$), 22.9 (dq, J = 17, 2 Hz, P(*C*H$_3$)$_3$) ppm. IR (KBr): 2994 (s), 1805 (s) cm^{-1}. MS m/z (EI): 487 (M$^+$). Anal. Calcd for $C_{12}H_{37}BrP_4$-Ru: C, 29.63; H, 7.67. Found: C, 29.88; H, 7.74.

Reaction of 2 with CH$_3$CH$_2$Br. Complex **2** (40 mg, 100 μmol) and ethyl bromide (12 mg, 110 μmol) were each dissolved separately in THF-d_8 (0.25 mL). The solution of ethyl bromide was then added dropwise to **2**, and the resulting solution was loaded into an NMR tube capped with a Teflon stopcock. The ^{1}H and ^{13}C NMR spectra of this solution showed ethylamine (**20**) (^{1}H NMR (THF-d_8) δ 2.63 (2H, q, J = 7.0 Hz, $CH_3CH_2NH_2$), 1.37 (2H, br, $CH_3CH_2NH_2$), 1.01 (3H, t, J = 7.0 Hz, *C*H$_3$CH$_2$NH$_2$) ppm; ^{13}C{^{1}H} NMR (THF-d_8) δ 37.9 (s, CH_3CH_2-NH_2), 19.9 (s, *C*H$_3$CH$_2$NH$_2$) ppm)[45] and ethylene (δ 5.37 ppm) in a 10:1 molar ratio, as well as a trace of ammonia. Complex **19** and a small amount of **16** were the only organometallic products observed. Ethylamine was readily separated from the organometallic products by vacuum transfer of the volatile materials.

***cis*-(PMe$_3$)$_4$Ru(H)(NHC(NTol)(NHTol)) (21).** Complex **2** (245 mg, 580 μmol) was dissolved in toluene (3 mL), and di-*p*-tolyl carbodiimide (135 mg, 608 μmol) was added. The solution was allowed to stand at room temperature for 3 h, layered with pentane (10 mL), and chilled to −35 °C for 48 h to yield **21** (231 mg, 62% yield) as off-white crystals. ^{1}H NMR (C_6D_6): δ 9.02 (1H, s, RuN*H*), 8.38 (2H, d, J = 8.4 Hz, Ar), 7.30 (2H, d, J = 8.1 Hz, Ar), 7.24 (2H, d, J = 8.1 Hz, Ar), 7.16 (2H, d, J = 8.4 Hz, Ar), 2.35 (3H, s, ArCH_3), 2.21 (3H, s, ArCH_3), 1.10 (18H, t, J = 5.6 Hz, P$_P$(CH_3)$_3$), 0.92 (9H, d, J = 7.4 Hz, P$_N$(CH_3)$_3$), 0.74 (9H, d, J = 7.2 Hz, P$_H$(CH_3)$_3$), −8.57 (1H, dq, J = 90.0, 27.2 Hz, Ru*H*) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 5.37 (td, J = 29.2, 22.3 Hz, P_N), −2.81 (t, J = 29.2 Hz, P_P), −11.27 (q, J = 24.3 Hz, P_H) ppm. ^{13}C-{^{1}H} NMR (C_6D_6): δ 158.0 (s, *C*N$_3$), 154.3 (s, Ar), 143.0 (s, Ar), 130.1 (s, Ar), 129.7 (s, Ar), 127.2 (s, Ar), 127.1 (s, Ar), 126.1 (s, Ar), 117.7 (s, Ar), 27.3 (d, J = 24.6 Hz, P$_N$(*C*H$_3$)$_3$), 23.2 (td, J = 13.4, 2.4 Hz, P$_P$(*C*H$_3$)$_3$), 21.8 (d, J = 17.0 Hz, P$_H$(*C*H$_3$)$_3$), 21.6 (s, Ar*C*H$_3$), 21.3 (s, Ar*C*H$_3$) ppm. IR (KBr): 3232 (w), 3216 (w), 2998 (m), 2971 (m), 2907 (m), 1803 (s), 1614 (s), 1591 (s), 1512 (s), 1428 (m), 1313 (m) 945 (s), 855 (m), 712 (m). MS m/z (EI): 645 (M+), 569 (M − PMe$_3$). Anal. Calcd for $C_{27}H_{53}N_3P_4Ru$: C, 50.30; H, 8.29; N, 6.52. Found: C, 50.34; H, 8.15; N, 6.41.

X-ray Diffraction Study of 21. Colorless plates of **21** were grown from THF/pentane at −30 °C. A fragment measuring 0.35 × 0.30 × 0.09 mm^3 was mounted on a glass fiber using Paratone N hydrocarbon oil and studied using a SMART CCD area detector with graphite monochromated Mo Kα radiation. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. Some nonhydrogen atoms were refined anisotropically, while the rest were refined isotropically. The hydride hydrogens and the hydrogens on the nitrogens were located as peaks in reasonable locations on a difference

(46) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511.

Fourier map and included without refinement. Other hydrogen atoms were also included but not refined.

The compound crystallizes in space group $P\bar{1}$ (#2) with four molecules in the triclinic unit cell together with two molecules of solvent. The theoretical formula consists of one molecule of the complex and half a molecule of THF. However, the solvent in this crystal appears to be a mixture of THF and pentane in an approximately 70:30 ratio. Thus, the calculated cell contents and the model cell contents are slightly different. One PMe_3 ligand was torsionally disordered, but all atoms refined normally other than those carbons and the atoms in the THF/pentane solvent region.

The two molecules of **21** in the unit cell are chemically identical and very similar (but not identical) in terms of their conformations and bond distances. The orientations of the imine-bound tolyl group and the PMe_3 group trans to the nitrogen are slightly different in the two molecules. Selected bond lengths and angles for one molecule are given in Figure 1; all crystallographic data are included in the Supporting Information. A short summary of crystallographic data follows. Space group $P\bar{1}$ (#2), $a = 11.8161(2)$ Å, $b = 14.1196(4)$ Å, $c = 22.7184(6)$ Å, $V = 3573.1(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.26$ g/cm^3, μ(Mo Kα) = 6.41 cm^{-1}, no. of unique reflections = 11 447, no. of reflections with $I > 2.50\sigma(I) = 6091$, $R = 5.2\%$.

***cis*-(PMe$_3$)$_4$Ru(H)(NHC(NCy)(NHCy) (22).** Complex **2** (145 mg, 343 μmol) was dissolved in diethyl ether (10 mL), and dicyclohexyl carbodiimide (78 mg, 380 μmol) was added. The solution was allowed to stand at room temperature for 3 h and was then concentrated to 2 mL in vacuo and chilled to −35 °C. White crystals of **22** (123 mg, 54% yield) were collected after 24 h. ^{1}H NMR (C_6D_6): δ 5.35 (1H, d, $J = 7.2$ Hz, RuN*H*), 4.37 (1H, m, Cy), 3.29 (1H, m, Cy), 2.51 (2H, m, Cy), 2.26 (2H, m, Cy), 2.10 (2H, m, Cy), 1.9−1.3 (14H, m, Cy), 1.25 (18H, t, $J = 2.8$ Hz, $P_P(CH_3)_3$), 1.01 (9H, d, $J = 5.1$ Hz, $P_N(CH_3)_3$), 0.98 (9H, d, $J = 6.9$ Hz, $P_H(CH_3)_3$), −8.46 (1H, dq, $J = 120.8$, 26.4 Hz, Ru*H*) ppm. ^{31}P{^{1}H} NMR (THF-d_8): δ 5.33 (td, $J = 30.8$, 20.4, P_N), −0.77 (t, $J = 30.8$ Hz, P_P), −14.57 (q, $J = 25.1$ Hz, P_H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 159.6 (s, *C*N$_3$), 57.4 (C=N*C*), 49.7 (s, N*C*), 38.2 (s, Cy), 36.2 (s, Cy), 28.0 (s, Cy), 27.6 (d, $J = 28.2$ Hz, $P_N(CH_3)_3$), 27.6 (s, Cy), 27.3 (s, Cy), 26.7 (s, Cy), 23.6 (td, $J = 13.2$, 3.6 Hz, $P_P(CH_3)_3$), 21.1 (d, $J = 15.9$ Hz, $P_H(CH_3)_3$) ppm. IR (KBr, cm^{-1}): 3267 (w), 2969 (m), 2905 (m), 1807 (s), 1514 (m), 1313 (m), 944 (s), 858 (m), 710 (m). MS *m*/*z* (EI): 629 (M$^+$), 553 (M − PMe$_3$). Anal. Calcd for $C_{25}H_{61}N_3P_4Ru$: C, 47.76; H, 9.78; N, 6.68. Found: C, 47.80; H, 9.93; N, 6.80.

Kinetic Studies of the Formation of 22. In a typical experiment, complex **2** (9.6 mg, 23 μmol) and internal standard were dissolved in THF-d_8 (0.4 mL), and 0.20 mL of this solution was added to an NMR tube. The tube was affixed to a Cajon adaptor, degassed, and charged with PMe_3 (6.6 mL × 3.0 Torr, 1.1 μmol) via vacuum transfer from a known volume bulb. The tube was then chilled to −78 °C and opened to a positive pressure of N_2. The stopcock of the Cajon adapter was then removed, and the dicyclohexyl carbodiimide was added slowly as a THF-d_8 solution (50 μL × 0.44 M, 22 μmol). The carbodiimide solution was allowed to run down the walls of the tube so that it would cool before reaching the solution of **2**. The walls of the tube were then rinsed with THF-d_8 (50 μL). The stopcock was replaced, the sample was frozen at −196 °C, and the tube was flame sealed under vacuum. The sample was then thawed at −78 °C and introduced to a NMR spectrometer whose probe was precooled to −29 °C. Kinetic data were acquired at this temperature by monitoring the change in the product resonance at δ 5.11 ppm (RuNH) and total hydride resonances (two overlapping overlapping signals, δ 8−9 ppm) relative to internal standard. The results are reported in Figures 3 and 4.

***cis*-(PMe$_3$)$_4$Ru(H)(NHC(CHPh)(CH$_2$Ph)) (23).** Complex **2** (65 mg, 154 μmol) was dissolved in toluene (4 mL), and diphenylallene (29 mg, 155 μmol) was added. The resulting bright red solution was allowed to stand at room temperature for 3 h and was then layered with pentane (10 mL) and chilled to −35 °C for 72 h to yield **23** (46 mg, 49% yield) as an orange-red solid. ^{1}H NMR (C_6D_6): δ 7.53 (2H, d, $J = 7.8$ Hz, Ar), 7.34 (2H, t, $J = 7.4$ Hz, Ar), 7.24 (2H, t, $J = 7.3$ Hz, Ar), 7.15 (2H, d, $J = 7.3$ Hz, Ar), 7.03 (1H, t, $J = 7.3$ Hz, Ar), 6.85 (1H, t, $J = 7.5$ Hz, Ar), 6.21 (1H, s, C=C*H*(Ph)), 4.11 (2H, s, C*H*$_2$(Ph)), 1.72 (1H, d, $J = 5.7$ Hz, RuN*H*), 1.18 (18H, t, $J = 2.7$ Hz, $P_P(CH_3)_3$), 0.99 (9H, d, $J = 6.9$ Hz, $P_N(CH_3)_3$), 0.76 (9H, d, $J = 4.8$ Hz, $P_H(CH_3)_3$), −7.78 (1H, dq, $J = 100.0$, 28.0 Hz, Ru*H*) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 5.45 (td, $J = 30.8$, 17.8 Hz, P_N), −1.57 (t, $J = 30.8$ Hz, P_P), −14.68 (q, $J = 21.6$ Hz, P_H) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ 157.8 (s, *C*NC$_2$), 154.3 (s, Ar), 146.5 (s, Ar), 141.8 (s, Ar), 131.1 (s, Ar), 128.8 (s, Ar), 128.6 (s, Ar), 126.2 (s, Ar), 125.4 (s, Ar), 117.4 (s, C=*C*H(Ph)), 43.5 (s, *C*H$_2$Ph), 27.7 (d, $J = 24.0$ Hz, $P_N(CH_3)_3$), 23.7 (td, $J = 14.6$, 4.0 Hz, $P_H(CH_3)_3$), 21.9 (d, $J = 15.0$ Hz, $P_H(CH_3)_3$) ppm. IR (KBr, cm^{-1}): 3321 (w), 1631 (w), 1805 (s). MS *m*/*z* (EI): 629 (M$^+$). Anal. Calcd for $C_{27}H_{49}NP_4Ru$: C, 52.75; H, 8.36; N, 2.28. Found: C, 52.55; H, 8.34; N, 2.15.

***cis*-[(PMe$_3$)$_4$Ru(H)(NH$_3$)$^+$][OTf$^-$] (24).** Complex **2** (89 mg, 210 μmol) was dissolved in pentane (5 mL), and HOTf (30 mg, 200 μmol) was added as a pentane solution (2 mL). This resulted in precipitation of an off-white solid, which was collected by filtration and recrystallized from THF (3 mL) layered with pentane (10 mL) at −35 °C. After 48 h, **24** (49 mg, 41% yield) was collected as off-white crystals. ^{1}H NMR (THF-d_8): δ 2.01 (3H, s, RuN*H*$_3$), 1.47 (18H, t, $J = 3.0$ Hz, $P_P(CH_3)_3$), 1.46 (9H, d, $J = 6.6$ Hz, $P_N(CH_3)_3$), 1.39 (9H, d, $J = 8.2$ Hz, $P_H(CH_3)_3$), −9.46 (dtd, $J = 92$, 32, 20 Hz, 1H, Ru*H*) ppm. ^{31}P{^{1}H} NMR (THF-d_8): δ 15.00 (dt, $J = 35$, 24 Hz, P_N), −2.44 (dd, $J = 35$, 24 Hz, P_P), −14.47 (q, $J = 24$ Hz, P_H) ppm. ^{19}F NMR (THF-d_8): δ −75.29 ppm. ^{13}C{^{1}H} NMR (THF-d_8): δ 26.2 (d, $J = 27$ Hz, $P_N(CH_3)_3$), 23.2 (td, $J = 14$, 3 Hz, $P_P(CH_3)_3$), 22.3 (d, $J = 18$ Hz, $P_H(CH_3)_3$). IR (THF, cm^{-1}): 3401 (w), 1821 (s). Anal. Calcd for $C_{13}H_{40}F_3NO_3P_4RuS$: C, 27.27; H, 7.04; N, 2.45. Found: C, 27.41; H, 7.25; N, 2.30.

***cis*-[(PMe$_3$)$_4$Ru(H)(NH$_3$)$^+$][BF$_4^-$] (25).** Complex **2** (123 mg, 291 μmol) was dissolved in pentane (3 mL), and HBF_4·Et_2O (45 mg, 280 μmol) was added as a pentane solution (1 mL). This resulted in precipitation of yellow oil, which was collected and recrystallized from THF (1 mL) layered with pentane (5 mL) at −35 °C. After 48 h, **25** (72 mg, 43% yield) was collected as a yellow-beige solid. ^{1}H NMR (THF-d_8): δ 1.91 (s, 3H, RuN*H*$_3$), 1.56 (18H, t, $J = 3.2$ Hz, $P_P(CH_3)_3$), 1.46 (9H, d, $J = 6.2$ Hz, $P_N(CH_3)_3$), 1.37 (9H, d, $J = 7.6$ Hz, $P_H(CH_3)_3$), −9.49 (dtd, $J = 94$, 32, 20 Hz, 1H, Ru*H*) ppm. ^{31}P{^{1}H} NMR (THF-d_8): δ 15.00 (dt, $J = 36$, 25 Hz, P_N), −2.45 (dd, $J = 36$, 25 Hz, P_P), −14.55 (q, $J = 25$ Hz, P_H) ppm. ^{19}F NMR (THF-d_8): δ 148.8 (br) ppm. ^{13}C{^{1}H} NMR (THF-d_8): δ 26.4 (d, $J = 26$ Hz, $P_N(CH_3)_3$), 23.1 (td, $J = 15$, 3 Hz, $P_P(CH_3)_3$), 22.3 (d, $J = 18$ Hz, $P_H(CH_3)_3$). IR (THF, cm^{-1}): 3398 (w), 1818 (s). Anal. Calcd for $C_{12}H_{40}BF_4NP_4Ru$: C, 28.24; H, 7.90; N, 2.75. Found: C, 28.12; H, 7.69; N, 2.69.

***cis*-[(PMe$_3$)$_4$Ru(H)(NH$_3$)$^+$][BAr$_f^-$] (26).** Complex **3** (143 mg, 193 μmol) was suspended in ether (5 mL), and $NaBAr_f$ (177 mg, 200 μmol) was added. The resulting mixture was stirred for 6 h and then filtered through Celite. The filtrate was layered with pentane (10 mL) and chilled to −35 °C for 12h, and **26** (133 mg, 54% yield) was collected as a white solid. ^{1}H NMR (THF-d_8): δ 7.80 (8H, br, BAr$_f$), 7.59 (4H, br, BAr$_f$), 1.87 (3H, s, RuN*H*$_3$), 1.57 (18H, t, $J = 3.0$ Hz, P(C*H*$_3$)$_3$), 1.46 (9H, d, $J = 6.0$ Hz, P(C*H*$_3$)$_3$), 1.38 (9H, d, $J = 7.4$ Hz, P(C*H*$_3$)$_3$), −9.41 (dtd, $J = 92$, 33, 21 Hz, 1H, Ru*H*) ppm. ^{31}P{^{1}H} NMR (THF-d_8): δ 15.00 (dt, $J = 36$, 25 Hz, P_N), −2.42 (dd, $J = 36$, 25 Hz, P_P), −14.60 (q, $J = 25$ Hz, P_H) ppm. ^{19}F NMR (THF-d_8): δ −59.61 ppm. ^{13}C{^{1}H} NMR (THF-d_8): δ 26.3 (d, $J = 26$ Hz, $P_N(CH_3)_3$), 23.2 (td, $J = 15$, 3 Hz, $P_P(CH_3)_3$), 22.1 (d, $J = 18$ Hz, $P_H(CH_3)_3$). IR (THF, cm^{-1}): 3351 (w), 3194 (w), 1822 (s), 1610 (m). Anal. Calcd for $C_{44}H_{52}F_{24}BNP_4Ru$: C, 41.07; H, 4.07; N, 1.09. Found: C, 41.09; H, 3.86; N, 0.98.

***cis*-[(PMe$_3$)$_4$Ru(H)(PMe$_3$)$^+$][BPh$_4^-$] (27).** Complex **3** (240 mg, 323 μmol) was dissolved in THF (3 mL), and the solution was loaded into a glass vessel equipped with a Teflon stopcock. The solution was degassed, and PMe_3 (66 mL × 100 Torr, 360 μmol)was added via

vacuum transfer from a known volume bulb. Complex **27** (184 mg, 70% yield) precipitated as a white solid. ^{1}H NMR (THF-d_8): 7.27 (8H, br, Ar), 6.85 (8H, t, J = 7.3 Hz, Ar), 6.72 (4H, t, J = 7.3 Hz, Ar), 1.51 (36H, br, $P_P(CH_3)_3$), 1.35 (9H, d, J = 6.3 Hz, $P_H(CH_3)_3$), −11.36 (dquin, J = 72, 24 Hz, 1H, Ru*H*) ppm. ^{31}P{^{1}H} NMR (THF-d_8): δ −9.11 (d, J = 27 Hz, P_P), −22.22 (quin, J = 27 Hz, P_H) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 164.6 (q, J_{BC} = 100 Hz), 136.4 (s, Ar), 126.2 (s, Ar), 122.3 (s, Ar), 26.8 (m $P_P(CH_3)_3$), 26.2 (d, J = 20 Hz, $P_H(CH_3)_3$). IR (THF, cm^{-1}): 1841 (s). Anal. Calcd for $C_{39}H_{66}BP_5Ru$: C, 58.43; H, 8.30. Found: C, 58.24; H, 8.41.

Measurement of K_{eq} for Equilibrium between $[(PMe_3)_4Ru(H)(NH_3)^+][A^-]$ and $[(PMe_3)_4Ru(H)(PMe_3)^+][A^-]$. In a typical experiment, **3** (11 mg, 15 μmol) and internal standard were dissolved in THF-d_8 (300 μL) and the solution was loaded into an NMR tube equipped with a Teflon stopcock. The solution was then degassed, and PMe_3 (6.6 mL × 34 Torr, 13 μmol) was added via vacuum transfer from a known volume bulb. The tube was then closed and left at room temperature, and the concentrations of **3** (δ −9.48 (1H, dtd) ppm), **27** (δ −11.33 (1H, dquin) ppm), NH_3 (δ −0.17 (3H, t) ppm), and PMe_3 (δ 0.94 (9H, s) ppm) were monitored by ^{1}H NMR at 20 °C. When the relative concentrations stopped changing, they were measured and used to calculate K_{eq} (15.9). Additional NH_3 (6.6 mL × 30 Torr, 12 μmol) was added to the tube via vacuum transfer from a known volume bulb. The tube was again monitored by ^{1}H NMR, and the K_{eq} (16.1) recorded after equilibrium was achieved.

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Supporting Information Available: Full details of the X-ray diffraction study of **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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