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Synthesis and Characterization of Iron(II) and Ruthenium(II) Hydrido Hydrazine Complexes

Leslie D. Field,*[,†] Hsiu L. Li,[†,‡] Scott J. Dalgarno,[§,⊥] Paul Jensen,[‡] and Ruaraidh D. McIntosh[⊥]

[†]School of Chemistry, University of New South Wales, New South Wales 2052, Australia

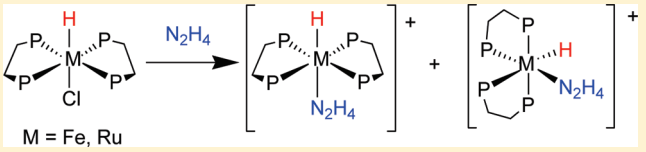
[‡]School of Chemistry, University of Sydney, New South Wales 2006, Australia

[§]Department of Chemistry, University of Missouri—Columbia, Columbia, Missouri 65211, United States

[⊥]School of Engineering and Physical Sciences-Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, U.K.

Supporting Information

ABSTRACT: Treatment of *trans*-[MHCl(dmpe)$_2$] (M = Fe, Ru) with hydrazine afforded the hydrido hydrazine complexes *cis*- and *trans*-[MH(N$_2$H$_4$)(dmpe)$_2$]$^+$ which have been characterized by NMR spectroscopy (^{1}H, ^{31}P, and ^{15}N). Both cis and trans isomers of the Fe complex and the trans isomer of the Ru complex were characterized by X-ray crystallography. Reactions with acid and base afforded a range of N$_2$H$_x$ complexes, including several unstable hydrido hydrazido complexes.



INTRODUCTION

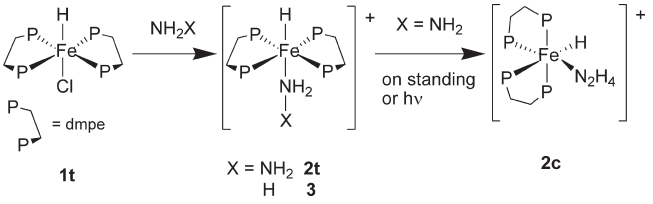
The conversion of dinitrogen to ammonia can be achieved biologically by the nitrogenase metalloenzymes or industrially by the Haber−Bosch process. One feature common to both of these processes is that iron is the key metal in the active catalyst.[1] Ruthenium compounds are also used as industrial catalysts for ammonia synthesis,[2] and ruthenium complexes are of interest as they frequently stabilize reactive intermediates that are too unstable to be isolated or characterized on the analogous iron complexes.[3] Research into the mechanism of nitrogenase action has highlighted that metal-bound hydrides[4] and hydrazines[5] are important potential reaction intermediates in dinitrogen reduction. Metal complexes containing both hydride and hydrazine ligands are known for Ru, Ir, Os, and Re[6] although only one example on Fe is known [FeH(N$_2$H$_4$){P(OEt)$_3$}]$^+$ where the hydride and hydrazine ligands were shown to be in mutually cis coordination sites.[7] None of these hydrido hydrazine complexes have been structurally characterized.

In this paper we report the synthesis and characterization of iron and ruthenium phosphine complexes containing both hydride and hydrazine ligands. This type of metal complex may play an important role as an intermediate in the Leigh[8] or Tyler[9] systems for dinitrogen conversion to ammonia. While several mechanistic pathways have been proposed for dinitrogen reduction in iron phosphines and some have been investigated computationally,[10] none of the postulated intermediate structures have so far contained both hydride and hydrazine ligands.

RESULTS AND DISCUSSION

Iron Hydrido Hydrazine Complexes. Treatment of *trans*-[FeHCl(dmpe)$_2$] (dmpe =1,2-bis(dimethylphosphino)ethane) (**1t**) with approximately 6 equiv of hydrazine in tetrahydrofuran afforded a mixture of the starting material **1t** and the hydrazine complex *trans*-[FeH(N$_2$H$_4$)(dmpe)$_2$]$^+$ (**2t**) (Scheme 1) in an approximate ratio of 1.3:1 (by ^{31}P{^{1}H} NMR spectroscopy). This is probably an equilibrium mixture with competition between chloride and hydrazine for the metal coordination site. On standing, yellow needles of the chloride salt of the hydrido hydrazine complex *trans*-[FeH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ (**2t-Cl**) formed, and these were characterized by X-ray crystallography. An ORTEP depiction of **2t-Cl** is shown in Figure 1. The geometry about iron is that of a slightly distorted octahedron with the hydride and hydrazine ligands in mutually trans positions. The hydrazine is bound end-on, and the Fe−N distance of 2.0927(11) Å is within the range of those reported for other iron complexes containing end-on bound hydrazine ligands (2.042(3)−2.224(5) Å).[11,12] The N−N bond length of 1.4635(17) Å is slightly longer than those reported for other iron−hydrazine complexes (1.432(10)−1.460 Å), including those with side-on or bridging hydrazines,[11−14] although shorter than the bridging hydrazine ligand in {[PhBP$^{Ph}_3$]Fe}$_2$($\mu-\eta^1$:η^1-N$_2$H$_4$)($\mu-\eta^2$:η^2-N$_2$H$_2$) (PhBP$^{Ph}_3$ = PhB(CH$_2$PPh$_2$)$_3^-$) (1.465(3) Å).[15] One proton on the terminal nitrogen is disordered over two positions at 50% occupancy each.

Scheme 1



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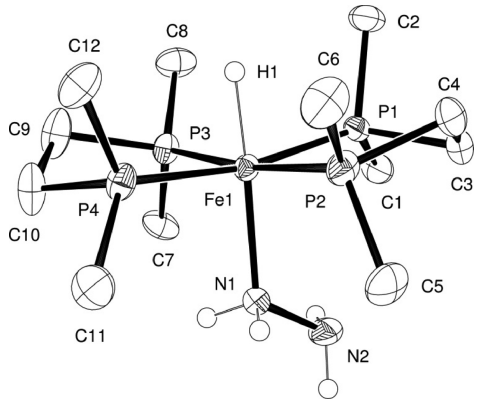

Figure 1. ORTEP depiction of *trans*-$[FeH(N_2H_4)(dmpe)_2]^+Cl^-$ (**2t-Cl**) (50% displacement ellipsoids, chloride counterion, hydrazine solvate, hydrogen atoms on the phosphine ligands, and one of the two disordered hydrogen atoms on the terminal nitrogen with 50% occupancy have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Fe1−N1, 2.0927(11); Fe1−P3, 2.1867(4); Fe1−P4, 2.1961(4); Fe1−P2, 2.2050(4); Fe1−P1, 2.2149(4); Fe1−H1, 1.49(2); N1−N2, 1.4635(17); N1−Fe1−P3, 95.50(4); N1−Fe1−P4, 91.54(3); P3−Fe1−P4, 85.914(16); N1−Fe1−P2, 92.28(4); P3−Fe1−P2, 171.959(17); P4−Fe1−P2, 95.931(17); N1−Fe1−P1, 99.37(3); P3−Fe1−P1, 91.975(16); P4−Fe1−P1, 169.039(16); P2−Fe1−P1, 84.734(17); N1−Fe1−H1, 175.9(8); P3−Fe1−H1, 85.0(8); P4−Fe1−H1, 84.4(8); P2−Fe1−H1, 87.4(8); P1−Fe1−H1, 84.7(8); N2−N1−Fe1, 119.28(8).

The hydrazine complex **2t-Cl** is unstable in solution and, in the absence of excess hydrazine, loses hydrazine and reverts to the starting material **1t** within a matter of hours. NMR data were acquired as quickly as possible after dissolution of the sample or in the presence of excess $^{15}N_2$-hydrazine for the collection of ^{15}N NMR spectra. The pentet at −28.9 ppm ($^2J_{HP}$ = 49 Hz) for the hydride ligand in the ^1H NMR spectrum and the singlet at 68.9 ppm in the $^{31}P\{^1H\}$ NMR spectrum (broad doublet, $^2J_{HP}$ = 49 Hz, without ^1H decoupling) confirm the trans configuration of the complex. The two ^{15}N signals at −311.1 and −371.3 ppm confirm the end-on binding of the hydrazine ligand.

The hydrido hydrazine complex was isolated as the tetraphenylborate salt *trans*-$[FeH(N_2H_4)(dmpe)_2]^+BPh_4^-$ (**2t-BPh$_4$**) in moderate yield on addition of $NaBPh_4$ to a solution of **2t-Cl** in methanol under an argon atmosphere. If the anion exchange reaction was carried out under nitrogen, an appreciable quantity of the dinitrogen complex[16] *trans*-$[FeH(N_2)(dmpe)_2]^+BPh_4^-$ was also formed, underlining the inherent lability of the hydrazine ligand. The hydride and phosphine chemical shifts are similar to those for the Cl salt **2t-Cl**.

The nitrogen-bound protons of the coordinated hydrazine ligand of **2t-BPh$_4$** appear at 2.78 and 2.34 ppm in the ^1H NMR spectrum. Only the downfield resonance exhibits weak coupling to ^{31}P, and, on this basis, we assign this to the protons on the nitrogen bound to iron ($N_\alpha H$). The ^{15}N chemical shifts of the hydrazine ligand were obtained from a 2D $^1H-^{15}N$ correlation experiment (at natural abundance) where the ^1H resonance at 2.78 ppm correlates to the ^{15}N signal at −373.2 ppm, while the ^1H resonance at 2.34 ppm correlates to the ^{15}N signal at −311.0 ppm (Figure 2). In this way the ^{15}N signals at −373.2 and −311.0 ppm were assigned to N_α and N_β, respectively. These shifts are comparable to those reported for Rh and Ru complexes with end-on bound hydrazine ligands where $\delta(N_\alpha)$ appears to high field of $\delta(N_\beta)$.[17,18]

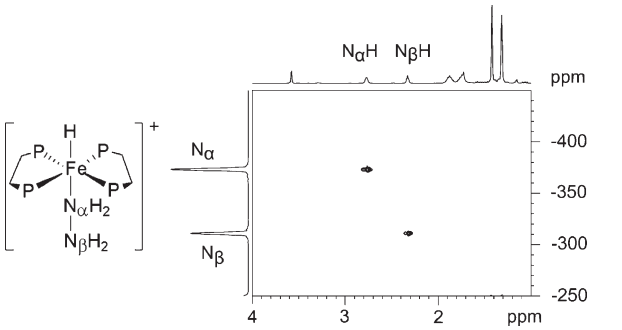

Figure 2. $^1H-^{15}N$ HSQC spectrum of *trans*-$[FeH(N_2H_4)(dmpe)_2]^+$-$[BPh_4]^-$ (**2t-BPh$_4$**) (300 K, thf-d_8).

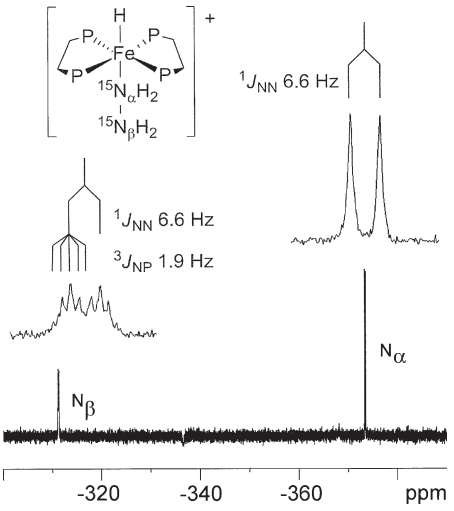

Figure 3. $^{15}N\{^1H\}$ spectrum of *trans*-$[FeH(^{15}N_2H_4)(dmpe)_2]^+$-$[BPh_4]^-$ (**2t-BPh$_4$**) (300 K, thf-d_8).

The $^{15}N_2$ analogue of hydrazine complex **2t-BPh$_4$** was prepared in an analogous fashion to that used to synthesize unlabeled **2t-BPh$_4$** using $^{15}N_2$-hydrazine. In the ^1H NMR spectrum, both signals for the nitrogen-bound protons of the coordinated hydrazine ligand exhibit additional coupling to ^{15}N ($^1J_{HN_\alpha}$ = 69.4 Hz, $^1J_{HN_\beta}$ = 63.9 Hz). In the $^{15}N\{^1H\}$ spectrum (Figure 3), the downfield signal (assigned to N_β) is a doublet of pentets due to coupling to the other N atom ($^1J_{NN}$ = 6.6 Hz) and coupling to four equivalent P atoms (J_{NP} = 1.9 Hz). The upfield signal (N_α) does not exhibit any discernible coupling to phosphorus, and this is unusual as in this case, $|^3J_{NP}| > |^2J_{NP}|$, unlike the case for dinitrogen complexes $[FeH(N_2)(PP)_2]^+$ where typically $|^2J_{NP}| > |^3J_{NP}|$.[19] In the ^{15}N spectrum with decoupling of the low-field proton region, the signal for N_α shows an additional splitting due to the metal-bound hydride ligand which is again consistent with the nitrogen assignments.

The hydrido hydrazine complex **2t-BPh$_4$** is unstable in solution; however, unlike the chloride salt **2t-Cl** which readily loses hydrazine to regenerate **1t**, **2t-BPh$_4$** reacts over time with N−N bond cleavage to form the hydrido ammine complex *trans*-$[FeH(NH_3)(dmpe)_2]^+$ (**3**) on standing as observed by ^1H, ^{31}P, and ^{15}N NMR spectroscopies. In the several hours required to acquire the ^{15}N data for **2t-BPh$_4$**, the signal for **3** at −433.7 ppm can already be observed, and small amounts of free $^{15}N_2$ (−72.3 ppm) and *trans*-$[FeH(^{15}N_2)(dmpe)_2]^+$ (−48.2 and −63.2 ppm)[19] are also observable in the ^{15}N NMR spectrum.

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The decomposition reaction proceeds at a relatively slow rate and is most likely the result of disproportionation. Hydrazine is known to disproportionate to ammonia and dinitrogen or diazene especially in the presence of metal complexes.[20] Crossland and Tyler have reported a similar decomposition of coordinated hydrazine in *trans*-$[FeH(N_2H_4)(DMeOPrPE)_2]^+$ (DMeOPrPE = 1,2-bis(dimethoxypropylphosphino)ethane).[1]

An authentic sample of the hydrido ammine complex *trans*-$[FeH(NH_3)(dmpe)_2]^+[BPh_4]^-$ (**3-BPh$_4$**) was prepared independently, in good yield, by reaction of **1t** with ammonia in the presence of sodium tetraphenylborate in ethanol (Scheme 1). Care had to be taken to maintain an atmosphere of ammonia when the complex was in solution because there was relatively facile substitution of ammonia by dinitrogen. The pentet at −30.1 ppm in the ^{1}H NMR spectrum and the singlet at 69.0 ppm in the ^{31}P NMR spectrum confirm that the complex has a trans geometry in solution. A 2D ^{1}H−^{15}N correlation experiment shows the ^{1}H NH_3 resonance at −0.09 ppm correlates to a ^{15}N signal at −433.1 ppm. The ^{15}N labeled analogue of **3** was prepared by allowing a solution of ^{15}N-labeled hydrazine complex **2t-BPh$_4$** to stand for several days. The nitrogen-bound protons of the coordinated ammonia ligand in the ^{1}H NMR spectrum show coupling to ^{15}N ($^1J_{HN}$ = 65.5 Hz) as well as to ^{31}P ($^3J_{HP}$ = 2.9 Hz). Bergman et al. have synthesized this hydrido ammine complex, albeit with different counterions, via protonation of the amido group in $[FeH(NH_2)(dmpe)_2]$ with fluorene or water.[21]

Crystals of *cis*-$[FeH(N_2H_4)(dmpe)_2]^+Cl^-$ (**2c-Cl**, Scheme 1) were obtained from a tetrahydrofuran (THF) solution of a mixture of **1t**, hydrazine, and the hydrazine complex **2t-Cl** when it was left to stand over an extended period (months). Presumably there is an equilibrium between the cis and trans isomers, and while the equilibrium favors the trans isomer, the cis isomer forms a stable crystalline solid which precipitates from solution over time. An ORTEP diagram of **2c-Cl** is shown in Figure 4. The geometry about iron is that of a slightly distorted octahedron with the hydride and hydrazine ligands occupying mutually cis coordination sites. The hydrazine ligand is bound end-on, and the Fe−N and N−N bond distances of 2.095(3) and 1.462(5) Å are similar to those observed for the trans isomer **2t-Cl**.

The multiplet at −11.2 ppm for the hydride ligand in the ^{1}H NMR spectrum and the four ddd signals in the ^{31}P NMR spectrum confirm the presence of two different ligands in mutually cis coordination sites. ^{15}N NMR signals at −298.0 and −377.6 ppm are similar to those for **2t-Cl** and confirm the presence of an end-on bound hydrazine ligand.

The cis isomer **2c-Cl** was also obtained by irradiation of a solution of **1t** and hydrazine in tetrahydrofuran (Scheme 1). Apart from slow crystallization, complex **2c-Cl** could not be isolated isomerically pure in a bulk reaction and the product typically contained variable amounts of trans isomer **2t-Cl**. Irradiation of **1t** in the absence of hydrazine afforded a mixture of **1t** and the cis isomer **1c** in an approximate ratio of 7.5:1. The cis isomer **1c** has a hydride resonance at −10.96 ppm and four ^{31}P resonances at 80.5, 73.6, 67.4, and 53.2 ppm. However, on standing overnight, **1c** reverts back to **1t**.

Reactions of Iron Hydrido Hydrazine Complexes. Treatment of ^{15}N-labeled hydrido hydrazine complex **2t-BPh$_4$** with an excess of a weak acid (2,6-lutidinium triflate) in tetrahydrofuran, afforded a mixture of reaction products of which the known side-on bound hydrazine complex $[Fe(\eta^2\text{-}N_2H_4)(dmpe)_2]^{2+}$ ($\delta(^{15}N)$ = −389.0 ppm)[13] and NH_4^+ ($\delta(^{15}N)$ = −365.4 ppm) were detected

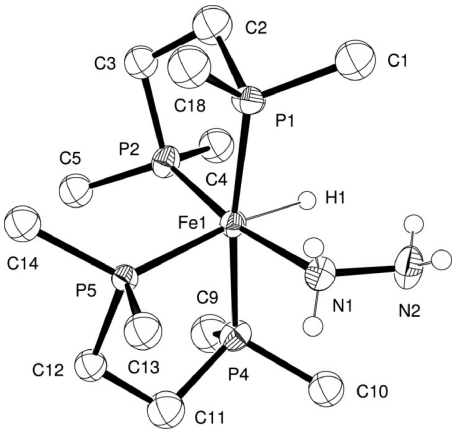

Figure 4. ORTEP depiction of *cis*-$[FeH(N_2H_4)(dmpe)_2]^+Cl^-$ (**2c-Cl**) (50% displacement ellipsoids, chloride counterion, hydrazine solvate, hydrogen atoms on the phosphine ligands, and atoms with 20% occupancy have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Fe1−N1, 2.095(3); Fe1−P2, 2.172(3); Fe1−P1, 2.2091(11); Fe1−P4, 2.2105(11); Fe1−P5, 2.247(2); Fe1−H1, 1.60(4); N1−N2, 1.462(5); N1−Fe1−P2, 170.24(12); N1−Fe1−P1, 89.19(10); P2−Fe1−P1, 84.40(7); N1−Fe1−P4, 88.41(10); P2−Fe1−P4, 96.91(7); P1−Fe1−P4, 171.71(5); N1−Fe1−P5, 91.00(11); P2−Fe1−P5, 97.54(9); P1−Fe1−P5, 102.27(5); P4−Fe1−P5, 85.70(5); N1−Fe1−H1, 86.9(14); P2−Fe1−H1, 85.3(14); P1−Fe1−H1, 85.7(14); P4−Fe1−H1, 86.2(14); P5−Fe1−H1, 171.7(14); N2−N1−Fe1, 117.4(2).

by ^{15}N NMR spectroscopy (Scheme 2). In this reaction, the hydride ligand is presumably protonated and lost as H_2 by reaction with acid and the pendant NH_2 of the hydrazine ligand fills the vacant coordination site resulting in a side-on bound hydrazine. Subsequent reaction of $[Fe(\eta^2\text{-}N_2H_4)(dmpe)_2]^{2+}$ with acid affords ammonium as previously described.[22]

Treatment of ^{15}N-labeled **2t-BPh$_4$** with excess KO^{t}Bu in tetrahydrofuran afforded a complex mixture of reaction products including the iron diazene complex $[Fe(\eta^2\text{-}N_2H_2)(dmpe)_2]$ ($\delta(^{15}N)$ = −312.8 ppm), the iron(0) dinitrogen complex $[Fe(N_2)(dmpe)_2]$ ($\delta(^{15}N)$ = −44.9, −49.0 ppm), and the iron(II) dihydride complex $[FeH_2(dmpe)_2]$ as the major identifiable products (Scheme 3). Both H_2 and N_2 are products of the disproportionation of diazene, so the formation of $[Fe(N_2)(dmpe)_2]$ and $[FeH_2(dmpe)_2]$ in the reaction mixture is not unreasonable. During the early stages of the reaction, the side-on bound hydrazine complex $[Fe(\eta^2\text{-}N_2H_4)(dmpe)_2]^{2+}$ ($\delta(^{15}N)$ = −388.0 ppm) is also observed as a minor product. This is presumably formed by deprotonation of the metal hydride **2t-BPh$_4$** and oxidation under the reaction conditions. $[Fe(\eta^2\text{-}N_2H_4)(dmpe)_2]^{2+}$ is known to form the diazene complex $[Fe(\eta^2\text{-}N_2H_2)(dmpe)_2]$ under basic conditions[22] and disappears as the reaction progresses.

Interestingly, if, instead of the tetraphenylborate salt, the chloride salt **2t-Cl** was treated with KO^{t}Bu, the major products appear to result from single deprotonation of the coordinated hydrazine to give the hydrido hydrazido complexes $[FeH(N_2H_3)(dmpe)_2]$ as a mixture of cis (**4c**) and trans (**4t**) isomers (Scheme 3). The products are highly unstable and rapidly decompose to form $[Fe(N_2)(dmpe)_2]$, $[FeH_2(dmpe)_2]$, and a suite of other unidentified products presumably via the metal diazene complex. Isomers **4c** and **4t** have only been characterized as transient species spectroscopically, and while the structure of these complexes is speculative

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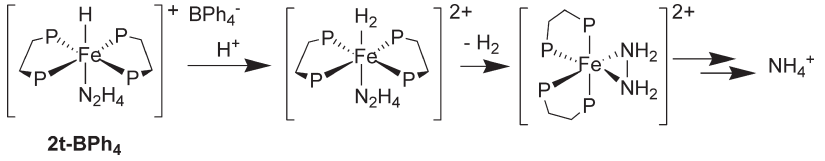
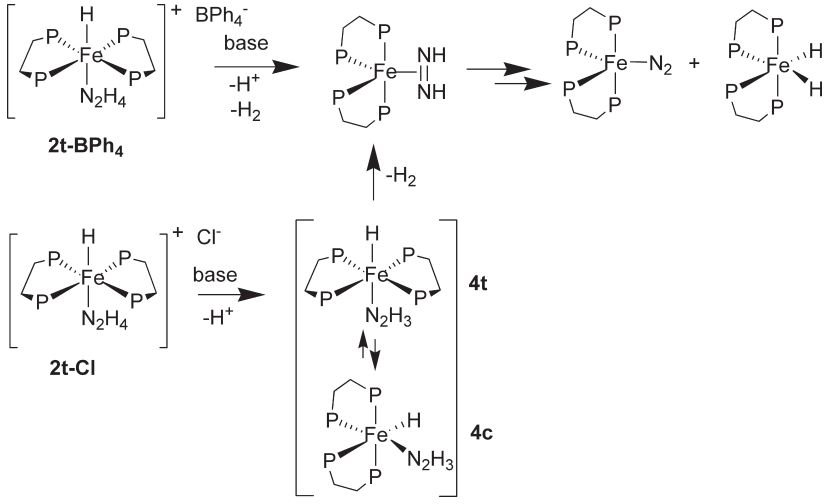
Scheme 2



Scheme 3

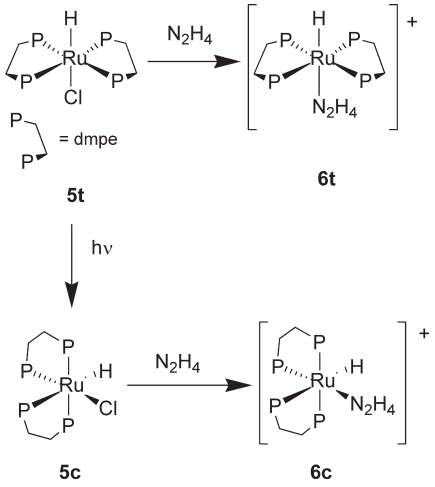


at this stage, the hydride resonances at −11.27 and −26.05 ppm for **4c** and **4t**, respectively, are close to those reported by Bergman for the analogous hydrido amido complexes *cis*- and *trans*-[FeH(NH_2)-$(dmpe)_2$] (−11.30 and −25.97 ppm, respectively).[23] Four resonances were observed in the ^{15}N NMR spectrum at −275.9, −308.8, −369.6, and −378.4 ppm for the two different nitrogen atoms in the two isomeric complexes. No NH protons were observed probably due to rapid exchange on the NMR time scale under the reaction conditions. Only one example of an iron hydrazido(1−) complex has been reported so far, *cis*-[Fe-$(DMeOPrPE)_2(N_2H_3)]^+$, where the hydrazido ligand is bound side-on ($\delta(^{15}N)$ = −375 ppm at room temperature, −367.6, −369.9 ppm at 193 K).[24] No iron hydrazido(1−) complexes have been reported with a hydride coligand. Hydrazido(1−) complexes are considered rare and also known to be unstable.[25]

The difference in reactivity between **2t-Cl** and **2t-BPh$_4$** is surprising but could be attributed to their different stabilities, solubilities, and ease of deprotonation. Complex **2t-BPh$_4$** is more soluble in the reaction mixture and probably reacts more rapidly with the *tert*-butoxide base.

Ruthenium Hydrido Hydrazine Complexes. Treatment of *trans*-[RuHCl$(dmpe)_2$] (**5t**) with hydrazine afforded *trans*-[RuH-$(N_2H_4)(dmpe)_2]^+Cl^-$ (**6t-Cl**) as a white solid (Scheme 4). Although **6t-Cl** loses hydrazine in solution to reform **5t** such as its iron analogue, it does not readily coordinate nitrogen while dissolved in methanol or ethanol. Thus, the anion exchange with $NaBPh_4$ in methanol could be carried out under nitrogen and afforded the complex as the tetraphenylborate salt *trans*-[RuH-$(N_2H_4)(dmpe)_2]^+BPh_4^-$ (**6t-BPh$_4$**). Crystals of **6t-BPh$_4$** suitable for X-ray crystallography were obtained from a solution of **6t-Cl** and $NaBPh_4$ in methanol, and an ORTEP depiction is shown in Figure 5. There is a slightly distorted octahedral arrangement of donors about ruthenium with the hydride and

Scheme 4



hydrazine (bound end-on) ligands in mutually trans positions. The Ru−N distance of 2.2728(13) Å is longer than those previously reported for ruthenium hydrazine complexes (2.162(2)−2.225(3) Å),[3,12,18,26] perhaps reflecting the large trans influence of the hydride ligand. The N−N distance of 1.4632(18) Å is within the range reported for other ruthenium hydrazine complexes (1.378(10)−1.479(5) Å).

As for the analogous Fe complex, the pentet at −20.56 ppm in the ^1H NMR spectrum and the singlet at 41.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum confirm the trans geometry of **6t-BPh$_4$**. The broad resonances at 3.42 and 2.64 ppm correlate to ^{15}N signals at −372.9 and −310.1 ppm for N_α and N_β, respectively.

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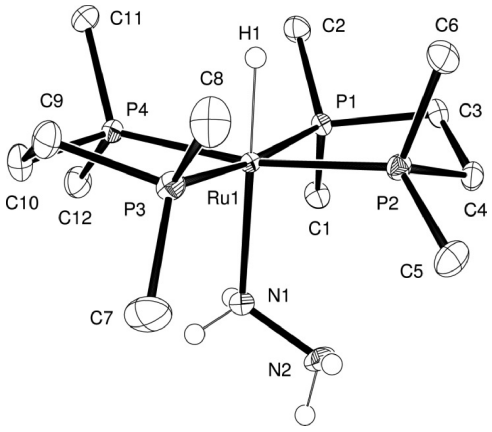
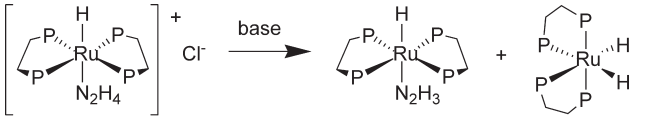


Figure 5. ORTEP depiction of *trans*-$[RuH(N_2H_4)(dmpe)_2]^+BPh_4^-$ (**6t-BPh$_4$**) (50% displacement ellipsoids, tetraphenylborate counterion, and hydrogen atoms on the phosphine ligands have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Ru1−N1, 2.2728(13); Ru1−P3, 2.3135(5); Ru1−P4, 2.3203(5); Ru1−P1, 2.3263(5); Ru1−P2, 2.3291(6); Ru1−H1, 1.603(13); N1−N2, 1.4632(18); N1−Ru1−P3, 95.91(4); N1−Ru1−P4, 92.32(4); P3−Ru1−P4, 83.97(2); N1−Ru1−P1, 91.52(4); P3−Ru1−P1. 172.540(15); P4−Ru1−P1, 96.36(2); N1−Ru1−P2, 98.32(4); P3−Ru1−P2, 95.39(2); P4−Ru1−P2, 169.347(15); P1−Ru1−P2, 82.90(2); N1−Ru1−H1, 177.5(6); P3−Ru1−H1, 85.9(6); P4−Ru1−H1, 86.2(6); P1−Ru1−H1, 86.7(6); P2−Ru1−H1, 83.2(6); N2−N1−Ru1, 117.42(9).

Irradiation of **5t** afforded a mixture enriched in the cis isomer (*cis*-$[RuHCl(dmpe)_2]$, **5c**) where the approximate ratio of cis and trans isomers was 5.7:1, respectively (Scheme 4). Complete conversion of the trans isomer to the cis isomer was not achieved despite prolonged irradiation. Unlike the case for iron, where **1c** reverted to the trans isomer **1t** on standing overnight, **5c** was stable indefinitely. Addition of hydrazine afforded *cis*-$[RuH(N_2H_4)(dmpe)_2]^+Cl^-$ (**6c-Cl**) (Scheme 4) and variable amounts of the trans isomer **6t-Cl**. The multiplet at −8.33 ppm in the ^{1}H NMR spectrum and the four multiplets in the $^{31}P\{^1H\}$ NMR spectrum at 49.6, 42.3, 39.9, and 31.3 ppm confirm the presence of two different ligands in mutually cis positions. ^{15}N resonances at −298.4 and −374.2 ppm for N_β and N_α, respectively, were obtained from a $^{15}N_2$ analogue of **6c-Cl** where couplings to ^{31}P ranging from 2 to 25 Hz were observed. Crystals of **6c-Cl** were examined by X-ray crystallography; although refinement to acceptable publication standard was not possible, the atom connectivity and stereochemistry of the complex were clearly demonstrated with the hydrazine and hydrido ligands in mutually cis positions.

Treatment of **6t-Cl** with KO^{t}Bu afforded the unstable hydrido hydrazido complex *trans*-$[RuH(N_2H_3)(dmpe)_2]$ (**7t**) as well as $[RuH_2(dmpe)_2]$ and other unidentified products (Scheme 5). Only the trans isomer was observed unlike the case for the analogous iron complexes which were a mixture of cis and trans isomers (**4c**/**4t**). The hydride resonance at −19.33 ppm is upfield of the resonance for the hydrido amido complex *trans*-$[RuH(NH_2)(dmpe)_2]$ (−16.57 ppm).[27] The two resonances in the ^{15}N spectrum are observed at −306.8 and −365.9 ppm and do not exhibit proton coupling even at 200 K, similar to the analogous iron hydrido hydrazido complexes **4c**/**4t**. No mononuclear ruthenium hydrazido(1−) complexes have been reported previously. Dinuclear and trinuclear ruthenium complexes are known with

Scheme 5



bridging hydrazido(1−) ligands, and two examples have been described with bridging hydride coligands.[28]

CONCLUSIONS

In this paper we have reported the synthesis and characterization of a series of iron and ruthenium complexes containing both hydride and hydrazine ligands. In particular, both cis and trans isomers of iron and ruthenium were characterized by NMR spectroscopy (^{1}H, ^{31}P, and ^{15}N) and X-ray crystallography. To the best of our knowledge, these are the first complexes containing both hydride and hydrazine ligands to be structurally characterized. The iron hydrido hydrazine complexes are unstable in solution, and the hydrazine ligand is labile and readily displaced by chloride or dinitrogen. The coordinated hydrazine in *trans*-$[FeH(N_2H_4)(dmpe)_2]^+BPh_4^-$ (**2t-BPh$_4$**) breaks down with N−N bond cleavage to give the hydrido ammine complex *trans*-$[FeH(NH_3)(dmpe)_2]^+$ (**3-BPh$_4$**). Treatment of **2t-BPh$_4$** with a weak acid produces $[Fe(\eta^2\text{-}N_2H_4)(dmpe)_2]^{2+}$ with a side-on bound hydrazine ligand. Treatment with base produces the known iron diazene complex $[Fe(\eta^2\text{-}N_2H_2)(dmpe)_2]$. Treatment of the chloride salts of either *trans*-$[FeH(N_2H_4)(dmpe)_2]^+$ (**2t-Cl**) or *trans*-$[RuH(N_2H_4)(dmpe)_2]^+$ (**6t-Cl**) with base produces the hydrazido hydride complexes $[MH(N_2H_3)(dmpe)_2]$ (**4t**, **4c**, and **7t**).

EXPERIMENTAL SECTION

All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk techniques or in nitrogen- or argon-filled gloveboxes. Solvents were dried and distilled under nitrogen or argon from sodium/benzophenone (tetrahydrofuran, hexane, and diethyl ether), calcium hydride (acetonitrile), dimethoxymagnesium (methanol), and diethoxymagnesium (ethanol). Tetrahydrofuran (inhibitor-free) and pentane were dried and deoxygenated using a Pure Solv 400-4-MD (Innovative Technology) solvent purification system. Deuterated solvents were purchased from Aldrich, Merck, or Cambridge Isotope Laboratories. Tetrahydrofuran-d_8, toluene-d_8, and benzene-d_6 were dried over and distilled from sodium/benzophenone.

Potassium *tert*-butoxide was resublimed before use. 2,6-Lutidinium triflate was prepared by reaction of 2,6-lutidine with an equimolar amount of triflic acid in toluene. Hydrazine (1 M in tetrahydrofuran) was purchased from Aldrich and deoxygenated before use. Hydrazine-$^{15}N_2$ was prepared by Soxhlet extraction of $^{15}N_2H_4\cdot H_2SO_4$ with liquid ammonia.[29] Ammonia saturated ethanol or tetrahydrofuran was obtained by bubbling anhydrous ammonia gas into the appropriate solvent for several minutes. The complexes *trans*-$[FeHCl(dmpe)_2]$ (**1t**) and *trans*-$[RuHCl(dmpe)_2]$ (**5t**) were prepared using modifications of the literature methods.[22,30] Irradiation was carried out using a 300 W high-pressure mercury vapor lamp with the incident beam directed through a water-filled jacket to filter out infrared radiation.

Air-sensitive NMR samples were prepared in argon- or nitrogen-filled gloveboxes or on a high-vacuum line by vacuum transfer of solvent into an NMR tube fitted with a concentric Teflon valve. ^{1}H, ^{31}P, ^{15}N, and two-dimensional NMR spectra were recorded on a Bruker DMX600,

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Table 1. Crystallographic Data for *trans*-$[FeH(N_2H_4)(dmpe)_2]^+Cl^-$ (2t-Cl), *cis*-$[FeH(N_2H_4)(dmpe)_2]^+Cl^-$ (2c-Cl), and *trans*-$[RuH(N_2H_4)(dmpe)_2]^+BPh_4^-$ (6t-BPh_4)

	2t-Cl	2c-Cl	6t-BPh_4
formula	$C_{12}H_{40}ClFeN_{3.5}P_4$	$C_{12}H_{41}ClFeN_4P_4$	$C_{36}H_{57}BN_2P_4Ru$
M (g mol^{-1})	448.66	456.67	753.60
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$	$P2_1/n$ (No. 14)
a (Å)	9.0906(8)	16.404(3)	13.252(3)
b (Å)	27.982(2)	9.0876(14)	18.373(4)
c (Å)	9.9025(8)	17.938(2)	15.893(4)
β (deg)	115.2990(10)	121.583(12)	98.759(10)
V (Å^3)	2277.3(3)	2278.0(6)	3824.5(14)
D_c (g cm^{-3})	1.309	1.332	1.309
Z	4	4	4
T (K)	150(2)	173(2)	100(2)
μ(Mo K$_\alpha$) (mm^{-1})	1.061	1.062	0.604
cryst size (mm)	0.47 × 0.22 × 0.10	0.23 × 0.14 × 0.10	0.20 × 0.10 × 0.10
cryst color	yellow	colorless	colorless
cryst habit	needle	prism	block
T(Gaussian)$_{min,max}$	0.775, 0.901	0.7922, 0.9012	0.8887, 0.9421
$2\theta_{max}$ (deg)	56.66	54.24	73.14
hkl range	−11 11, −36 36, −13 13	−20 21, −10 11, −22 17	−20 22, −30 30, −26 26
N	22 420	15 848	70 455
N_{ind}	5488 (R_{merge} 0.0248)	5009 (R_{int} = 0.0283)	18153 (R_{int} = 0.0512)
N_{obs} ($I > 2\sigma(I)$)	4882	4344	12547
goodness of fit	1.085	1.180	1.019
$R1$ (F, $I > 2\sigma(I)$)	0.0264	0.0557	0.0391
wR2 (F^2, all data)	0.0718	0.1295	0.0702

DMX500, DRX400, or DPX300 NMR spectrometer. The center of ^{1}H decoupling for ^{31}P spectroscopy of hydride complexes was set at −10 or −20 ppm. ^{1}H NMR spectra were referenced to residual solvent resonances while ^{31}P spectra were referenced to external neat trimethyl phosphite at δ 140.85 ppm. ^{15}N NMR spectra were reference to external neat nitromethane at δ 0.00 ppm. Simulations of spectra for cis-unsymmetrical complexes were performed iteratively using the simulation program NUMMRIT (SpinWorks), and the signs for coupling constants are not implied. Infrared spectra were recorded on a Shimadzu 8400 series or a Nicolet Avatar 360 FTIR spectrometer as Nujol mulls. Electrospray mass spectra were recorded on a Finnigan LCQ mass spectrometer (at the University of Sydney) or carried out at the Bioanalytical Mass Spectrometry Facility (at the University of New South Wales). Crystallographic details are given in Table 1.

Preparation of *trans*-$[FeH(N_2H_4)(dmpe)_2]^+Cl^-$ (2t-Cl). *trans*-$[FeHCl(dmpe)_2]$ (**1t**; 33 mg, 84 μmol) was dissolved in a solution of hydrazine in thf (0.5 mL, 1 M, 0.5 mmol) under nitrogen to give an orange solution. After standing for 4 days at room temperature, the yellow needles formed were collected by filtration and dried in vacuo (27 mg, 76% yield), mp 128° (dec.). ^{1}H NMR (thf-d_8, 600 MHz): δ 4.41 (b, 2H, N**H**), 2.71 (b, 2H, N**H**), 2.30 (b, 4H, C**H**$_2$), 1.66 (bs, 16H, C**H**$_2$ and C**H**$_3$), 1.11 (bs, 12H, C**H**$_3$), −28.9 (p, $^2J_{HP}$ = 49 Hz, 1H, Fe**H**). ^{31}P{^{1}H} NMR (thf-d_8, 243 MHz): δ 68.9 (s). ^{31}P NMR (thf-d_8, 202 MHz): δ 68.8 (bd, $^2J_{HP}$ = 49 Hz). Yellow needles suitable for X-ray crystallography were grown from a similar solution of **1t** in hydrazine, thf, and thf-d_8.

The ^{15}N-labeled analogue of **2t-Cl** was prepared in situ by dissolving **1t** (28 mg, 71 μmol) in a solution of ^{15}N-hydrazine in thf (0.1 mL, 0.5 M, 50 μmol)/thf-d_8 (0.4 mL). The solution contained a mixture of **1t** and ^{15}N-labeled **2t-Cl**. ^{15}N{^{1}H} NMR (thf/thf-d_8, 30 MHz): δ −311.1 (s, $FeNH_2\mathbf{N}H_2$), −371.3 (s, $Fe\mathbf{N}H_2$).

Preparation of *trans*-$[FeH(N_2H_4)(dmpe)_2]^+BPh_4^-$ (2t-BPh_4). *trans*-$[FeHCl(dmpe)_2]$ (**1t**; 0.117 g, 0.297 mmol) was dissolved in a solution of hydrazine in thf (3 mL, 1 M, 3 mmol) under argon, and the solution was stirred overnight during which time a yellow solid precipitated from solution. Diethyl ether (10 mL) was added, and the yellow solid was collected by filtration, washed with diethyl ether (10 mL), and dried in vacuo. A solution of $NaBPh_4$ (0.12 g, 0.35 mmol) in methanol (5 mL) was added to a solution of the yellow solid in methanol (5 mL) under argon. The yellow precipitate formed was collected by filtration, washed with methanol (10 mL, 5 mL), and dried in vacuo (75.4 mg, 36% yield). Anal. Calcd for $C_{36}H_{57}BFeN_2P_4$ (708.38): C, 61.0; H, 8.1; N, 4.0. Found C, 61.2; H, 8.3; N, 3.9%. ^{1}H NMR (thf-d_8, 400 MHz): δ 7.27 (m, 8H, ***o*-Ph**), 6.86 (m, 8H, ***m*-Ph**), 6.72 (m, 4H, ***p*-Ph**), 2.78 (m, 2H, $FeN\mathbf{H}_2$), 2.34 (bt, $^3J_{HH}$ = 4.2 Hz, 2H, $FeNH_2N\mathbf{H}_2$), 1.89 (m, 4H, C**H**$_2$), 1.76 (m, 4H, C**H**$_2$), 1.43 (bs, 12H, C**H**$_3$), 1.33 (bs, 12H, C**H**$_3$), −29.75 (p, $^2J_{HP}$ = 50.1 Hz, 1H, Fe**H**). ^{1}H{^{31}P} NMR (thf-d_8, 400 MHz): δ 7.27 (m, 8H, ***o*-Ph**), 6.86 (m, 8H, ***m*-Ph**), 6.72 (m, 4H, ***p*-Ph**), 2.78 (bt, $^3J_{HH}$ = 4.2 Hz, 2H, $FeN\mathbf{H}_2$), 2.34 (bt, $^3J_{HH}$ = 4.2 Hz, 2H, $FeNH_2N\mathbf{H}_2$), 1.89 (m, 4H, C**H**$_2$), 1.76 (m, 4H, C**H**$_2$), 1.43 (s, 12H, C**H**$_3$), 1.33 (s, 12H, C**H**$_3$), −29.75 (s, 1H, Fe**H**). ^{31}P{^{1}H} NMR (thf-d_8, 162 MHz): δ 67.4 (s). ^{15}N{^{1}H} NMR (thf-d_8, from HN-HSQC, 41 MHz): δ −311.0 (corr with ^{1}H δ 2.34, $FeNH_2\mathbf{N}H_2$), −373.2 (corr with ^{1}H δ 2.78, $Fe\mathbf{N}H_2$). IR: 3306 w, 3247 w, 3037 w (ν(N−H)), 1828 m (ν(Fe−H)), 1596 m, 1578 m, 1422 s, 1300 w, 1283 m, 1231 w, 1144 w, 1065 w, 1034 w, 930 s, 883 m, 848 m, 832 m, 793 w, 733 s, 702 s, 645 s, 624 m, 612 m cm^{-1}.

The ^{15}N-labeled analogue of **2t-BPh_4** was prepared by adding a solution of $^{15}N_2$-hydrazine in thf (2.6 mL, 0.6 M, 1.6 mmol) to a solution of **1t** (0.107 g, 0.273 mmol) in ethanol (5 mL) under argon. A solution of $NaBPh_4$ (0.111 g, 0.324 mmol) in ethanol (5 mL) was then added. The yellow precipitate was collected by filtration, washed with ethanol, and

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dried in vacuo (0.101 g, 52% yield). All ^{1}H and ^{31}P NMR data were identical to the above except the following. ^{1}H NMR (thf-d_8, 400 MHz): δ 2.79 (bd, $^1J_{HN}$ = 69.4 Hz, 2H, Fe^{15}N**H**$_2$), 2.34 (dt, $^1J_{HN}$ 63.9 Hz, $^3J_{HH}$ = 4.7 Hz, 2H, Fe^{15}N**H**$_2$^{15}N**H**$_2$). ^{1}H{^{31}P} NMR (thf-d_8, 400 MHz): δ 2.79 (dt, $^1J_{HN}$ = 69.4 Hz, $^3J_{HH}$ = 4.7 Hz, 2H, Fe^{15}N**H**$_2$), 2.34 (dt, $^1J_{HN}$ = 63.9 Hz, $^3J_{HH}$ = 4.7 Hz, 2H, Fe^{15}N**H**$_2$^{15}N**H**$_2$). ^{15}N{^{1}H at 2.5 ppm} NMR (thf-d_8, 41 MHz): δ −311.3 (dp, $^1J_{NN}$ = 6.6 Hz, $^3J_{NP}$ = 1.9 Hz, Fe^{15}NH$_2$^{15}N**H**$_2$), −373.4 (dd, $^1J_{NN}$ = 6.6 Hz, $^2J_{N-hydride}$ = 1.1 Hz, Fe^{15}N**H**$_2$^{15}NH$_2$). ^{15}N{^{1}H at 2.5, −30 ppm} NMR (thf-d_8, 41 MHz): δ −311.3 (dp, $^1J_{NN}$ = 6.6 Hz, $^3J_{NP}$ = 1.9 Hz, Fe^{15}NH$_2$^{15}N**H**$_2$), −373.4 (d, $^1J_{NN}$ = 6.6 Hz, Fe^{15}N**H**$_2$^{15}NH$_2$). ESI (acetonitrile): m/z 432 [5%, FeH(^{15}N$_2$H$_4$)(dmpe)$_2$(CH$_3$CN)$^+$], 396 [100, Fe(dmpe)$_2$(CH$_3$CN)−H$^+$], 355 [43, Fe(dmpe)$_2$−H$^+$], 308 [22], 280 [23, Fe(^{15}N$_2$H$_4$)(dmpe)(CH$_3$CN)−H$^+$], 219 [30, Fe(CH$_3$CN)$_4$−H$^+$]. IR: 3352 w, 3300 w, 3236 w, 3160 w, 3043 w (ν(N−H)), 2056 w, 1828 m (ν(Fe−H)), 1592 m, 1578 m, 1422 m, 1300 w, 1282 m, 1231 w, 1138 w, 1065 w, 1034 w, 930 s, 908 m, 884 m, 832 m, 792 w, 732 s, 700 s, 645 m, 612 s cm^{-1}.

Preparation of *trans*-[FeH(NH$_3$)(dmpe)$_2$]$^+$[BPh$_4$]$^-$ (3-BPh$_4$). *trans*-[FeHCl(dmpe)$_2$] (**1t**; 110 mg, 0.28 mmol) was dissolved in ammonia saturated ethanol (5 mL) under nitrogen to give a deep orange solution. After several minutes, a color change to yellow was observed. A solution of NaBPh$_4$ (120 mg, 0.35 mmol in 5 mL of ammonia saturated ethanol) was added to the reaction mixture. The precipitate formed was collected by filtration, washed with ammonia saturated ethanol (3 mL), and dried in vacuo to give a yellow crystalline solid (72 mg, 37% yield), mp 208 °C (dec.). Anal. Calcd for C$_{36}$H$_{56}$BFeNP$_4$ (693.36): C, 62.4; H, 8.1; N, 2.0. Found: C, 62.1; H, 8.1; N, 2.0%. ^{1}H NMR (thf-d_8, 400 MHz): δ 7.26 (m, 8H, ***o*-Ph**), 6.86 (m, 8H, ***m*-Ph**), 6.71 (m, 4H, ***p*-Ph**), 1.78 (m, 8H, C**H**$_2$), 1.34 (bs, 12H, C**H**$_3$), 1.30 (bs, 12H, C**H**$_3$), −0.09 (b, 3H, FeN**H**$_3$), −30.08 (p, $^2J_{HP}$ = 49.5 Hz, 1H, Fe**H**). ^{1}H{^{31}P} NMR (thf-d_8, 400 MHz): δ 7.26 (m, 8H, ***o*-Ph**), 6.86 (m, 8H, ***m*-Ph**), 6.71 (m, 4H, ***p*-Ph**), 1.78 (m, 8H, C**H**$_2$), 1.34 (s, 12H, C**H**$_3$), 1.30 (s, 12H, C**H**$_3$), −0.09 (b, 3H, FeN**H**$_3$), −30.08 (s, 1H, Fe**H**). ^{31}P{^{1}H} NMR (thf-d_8, 162 MHz): δ 69.0 (s). ^{15}N{^{1}H} NMR (thf-d_8, 41 MHz, from HN-HSQC): δ −433.1 (corr with ^{1}H δ −0.09, FeN**H**$_3$). ESI (acetonitrile): m/z 415 [98%, FeH(NH$_3$)(dmpe)$_2$(CH$_3$CN)$^+$], 398 [70, FeH(dmpe)$_2$(CH$_3$CN)$^+$], 357 [100, FeH(dmpe)$_2^+$], 265 [80, FeH(NH$_3$)(dmpe)(CH$_3$CN)$^+$], 248 [54, FeH(dmpe)(CH$_3$CN)$^+$]. IR: 3354 w, 3281 w, 3048 m, 3032 m (ν(N−H)), 1836 (ν(Fe−H)), 1579 w, 1422 s, 1304 w, 1297 m, 1286 m, 1263 m, 1179 w, 1157 w, 1121 w, 1066 w, 1032 w, 997 w, 929 s, 909 m, 886 s, 866 w, 846 m, 834 m, 805 w, 793 w, 753 w, 730 m, 704 s, 644 m, 611 m cm^{-1}.

[FeH(^{15}NH$_3$)(dmpe)$_2$]$^+$[BPh$_4$]$^-$ (**3t-BPh$_4$**) was observed on allowing [FeH(^{15}N$_2$H$_4$)(dmpe)$_2$]$^+$[BPh$_4$]$^-$ (**2t-BPh$_4$**) to stand in thf-d_8 solution. All ^{1}H and ^{31}P NMR data were identical to the above except the following: ^{1}H NMR (thf-d_8, 400 MHz): δ −0.10 (dp, $^1J_{HN}$ 65.5 Hz, $^3J_{HP}$ = 2.9 Hz, Fe^{15}N**H**$_3$). ^{15}N{^{1}H} (thf-d_8, 41 MHz): δ −433.7 (s).

Preparation of *cis*-[FeH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ (2c-Cl). *trans*-[FeHCl(dmpe)$_2$] (18 mg, 46 μmol) was dissolved in a solution of hydrazine in thf (0.3 mL, 1 M, 0.3 mmol) and thf-d_8 (0.1 mL) under nitrogen to give an orange solution. After 2 days, yellow needles of *trans*-[FeH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ (**2t-Cl**) were formed. After 2.5 months, the yellow needles had re-dissolved and new prismatic crystals of *cis*-[FeH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ (**2c-Cl**) formed and these were suitable for X-ray crystal analysis. The solution contained a mixture of **1t**, **2t-Cl**, and **2c-Cl** in an approximate ratio of 1.5:1:9. ^{1}H NMR (thf/thf-d_8, 300 MHz, high field only): δ −11.2 (dddd, $^2J_{HP}$ = 36.7 Hz, $^2J_{HP}$ = 51.8 Hz, $^2J_{HP}$ = 64.6 Hz, $^2J_{HP}$ = 53.0 Hz, Fe**H**). ^{31}P{^{1}H} NMR (thf/thf-d_8, 121 MHz): δ 73.2 (ddd, $^2J_{P_AP_B}$ = 17.6 Hz, $^2J_{P_AP_C}$ = 39.2 Hz, $^2J_{P_AP_D}$ = 29.2 Hz, 1P, **P$_A$**), 69.4 (ddd, $^2J_{P_BP_C}$ = 101.3 Hz, $^2J_{P_BP_D}$ = 38.5 Hz, 1P, **P$_B$**), 68.1 (ddd, $^2J_{P_CP_D}$ = 25.4 Hz, 1P, **P$_C$**), 57.4 (ddd, 1P, **P$_D$**).

Alternative synthesis: Compound **1t** (90.7 mg, 0.231 mmol) was dissolved in a solution of hydrazine in thf (0.8 mL, 1 M, 0.8 mmol) and thf-d_8 (0.1 mL) under argon to give an orange solution. The reaction mixture was irradiated for 5−6 h and then left to stand for several days. The yellow precipitate was collected by filtration and washed with diethyl ether (5 mL). The solid contained a mixture of cis and trans isomers in an approximate ratio of 7.8:1 (79 mg, 81% yield). ^{1}H NMR (thf-d_8, 400 MHz): δ 5.04 (br m, 1H, FeN**H**H), 4.65 (br m, 1H, FeNH**H**), 2.98 (m, 2H, N**H**$_2$), 2.66 (m, 1H, C**H**$_2$), 2.14 (m, 1H, C**H**$_2$), 1.99 (d, $^2J_{HP}$ = 9 Hz, 3H, C**H**$_3$), 1.92 (d, $^2J_{HP}$ = 8 Hz, 3H, C**H**$_3$), 1.87−1.94 (m, 1H, C**H**$_2$), 1.78 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), 1.62−1.76 (m, 2H, C**H**$_2$), 1.52 (m, 1H, C**H**$_2$), 1.48 (d, $^2J_{HP}$ = 6 Hz, 3H, C**H**$_3$), 1.44 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), 1.37 (m, 1H, C**H**$_2$), 1.31 (d, $^2J_{HP}$ = 6 Hz, 3H, C**H**$_3$), 1.17 (m, 1H, C**H**$_2$), 1.05 (d, $^2J_{HP}$ = 8 Hz, 3H, C**H**$_3$), 0.97 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), −11.23 (dddd, $^2J_{HP}$ = 36.7 Hz, $^2J_{HP}$ = 51.8 Hz, $^2J_{HP}$ = 63.3 Hz, $^2J_{HP}$ = 54.2 Hz, Fe**H**). ^{1}H{^{31}P} NMR (thf-d_8, 400 MHz): δ 5.04 (br m, 1H, FeN**H**H), 4.65 (br m, 1H, FeNH**H**), 2.98 (m, 2H, N**H**$_2$), 2.66 (m, 1H, C**H**$_2$), 2.14 (m, 1H, C**H**$_2$), 1.99 (s, 3H, C**H**$_3$), 1.92 (s, 3H, C**H**$_3$), 1.87−1.94 (m, 1H, C**H**$_2$), 1.78 (s, 3H, C**H**$_3$), 1.62−1.76 (m, 2H, C**H**$_2$), 1.52 (m, 1H, C**H**$_2$), 1.48 (s, 3H, C**H**$_3$), 1.44 (s, 3H, C**H**$_3$), 1.37 (m, 1H, C**H**$_2$), 1.31 (s, 3H, C**H**$_3$), 1.17 (m, 1H, C**H**$_2$), 1.05 (s, 3H, C**H**$_3$), 0.97 (s, 3H, C**H**$_3$), −11.23 (s, 1H, Fe**H**). ^{31}P{^{1}H} NMR (thf-d_8, 162 MHz): δ 72.8 (m, 1P, **P$_A$**), 68.8 (m, 1P, **P$_B$**), 66.9 (m, 1P, **P$_C$**), 57.5 (m, 1P, **P$_D$**).

The ^{15}N-labeled analogue of **2c-Cl** was prepared in situ by allowing a solution of **1t** (33 mg, 84 μmol) in ^{15}N$_2$-hydrazine in thf (0.3 mL, 0.5 M, 0.15 mmol)/thf-d_8 (0.1 mL) to stand for 1 month. The solution contained a mixture of **1t**, ^{15}N-labeled **2t-Cl**, and ^{15}N-labeled **2c-Cl** in an approximate ratio of 29:3:1. ^{15}N{^{1}H} NMR (thf/thf-d_8, 30 MHz): δ −298.0 (s, FeNH$_2$**N**H$_2$), −377.6 (s, Fe**N**H$_2$).

Preparation of *cis*- and *trans*-[FeH(N$_2$H$_3$)(dmpe)$_2$] (4c and 4t). A suspension of *trans*-[FeH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ (**2t-Cl**; 30.8 mg, 72.5 μmol) and KO^{t}Bu (30.4 mg, 0.271 mmol) in tetrahydrofuran (0.5 mL) was shaken under argon for several minutes; then the solvent was removed under reduced pressure. Benzene-d_6 was added by vacuum transfer to the residue to afford a dark orange solution.

Compound **4c**. ^{1}H NMR (benzene-d_6, 400 MHz): δ 1.89 (d, $^2J_{HP}$ = 8 Hz, 3H, C**H**$_3$), 1.72 (d, $^2J_{HP}$ = 8 Hz, 3H, C**H**$_3$), 1.23 (d, $^2J_{HP}$ = 6 Hz, 3H, C**H**$_3$), 1.18 (d, $^2J_{HP}$ = 5 Hz, 3H, C**H**$_3$), 0.93 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), 0.89 (d, $^2J_{H-P}$ = 7 Hz, 3H, C**H**$_3$), 0.87 (d, $^2J_{HP}$ = 5 Hz, 3H, C**H**$_3$), 0.61 (d, $^2J_{HP}$ = 5 Hz, 3H, C**H**$_3$), −11.27 (m, Fe**H**) (C**H**$_2$ resonances obscured by overlapping signals). ^{1}H{^{31}P} NMR (benzene-d_6, 400 MHz): δ 1.89 (s, 3H, C**H**$_3$), 1.72 (s, 3H, C**H**$_3$), 1.23 (s, 3H, C**H**$_3$), 1.18 (s, 3H, C**H**$_3$), 0.93 (s, 3H, C**H**$_3$), 0.89 (s, 3H, C**H**$_3$), 0.87 (s, 3H, C**H**$_3$), 0.61 (s, 3H, C**H**$_3$), −11.27 (s, Fe**H**) (C**H**$_2$ resonances obscured by overlapping signals). ^{31}P{^{1}H} NMR (benzene-d_6, 162 MHz): δ 72.5 (m, 1P), 70.3 (m, 1P), 66.0 (m, 1P), 59.6 (m, 1P).

Compound **4t**. ^{1}H NMR (benzene-d_6, 400 MHz): δ 1.76 (m, 4H, C**H**$_2$), 1.42 (m, 4H, C**H**$_2$), 1.38 (bs, 12H, C**H**$_3$), 1.13 (bs, 12H, C**H**$_3$), −26.05 (p, $^2J_{HP}$ = 46 Hz, Fe**H**). ^{1}H{^{31}P} NMR (benzene-d_6, 400 MHz): δ 1.76 (m, 4H, C**H**$_2$), 1.42 (m, 4H, C**H**$_2$), 1.38 (s, 12H, C**H**$_3$), 1.13 (s, 12H, C**H**$_3$), −26.05 (s, Fe**H**). ^{31}P{^{1}H} NMR (benzene-d_6, 162 MHz): δ 72.0 (s).

The ^{15}N-labeled analogues of **4c** and **4t** were prepared similarly by reaction of ^{15}N-labeled **2t-Cl** (13 mg, 30 μmol) and KO^{t}Bu (21 mg, 0.19 mmol) in tetrahydrofuran (2 mL) and extraction with pentane (7 mL).

Compound **4c**. ^{1}H NMR (toluene-d_8, 400 MHz): δ 1.90 (d, $^2J_{HP}$ = 8 Hz, 3H, C**H**$_3$), 1.72 (d, $^2J_{HP}$ = 8 Hz, 3H, C**H**$_3$), 1.23 (d, $^2J_{HP}$ = 6 Hz, 3H, C**H**$_3$), 1.19 (d, $^2J_{HP}$ = 5 Hz, 3H, C**H**$_3$), 0.91 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), 0.90 (d, $^2J_{HP}$ = 5 Hz, 3H, C**H**$_3$), 0.87 (d, $^2J_{HP}$ = 6 Hz, 3H, C**H**$_3$), 0.64 (d, $^2J_{HP}$ = 6 Hz, 3H, C**H**$_3$), −11.39 (m, Fe**H**) (C**H**$_2$ resonances obscured by overlapping signals). ^{1}H{^{31}P} NMR (toluene-d_8, 400 MHz): δ 1.90 (s, 3H, C**H**$_3$), 1.72 (s, 3H, C**H**$_3$), 1.23 (s, 3H, C**H**$_3$), 1.19 (s, 3H, C**H**$_3$), 0.91 (s, 3H, C**H**$_3$), 0.90 (s, 3H, C**H**$_3$), 0.87 (s, 3H, C**H**$_3$), 0.64 (s, 3H, C**H**$_3$), −11.39 (s, Fe**H**) (C**H**$_2$ resonances obscured by overlapping signals). ^{31}P{^{1}H} NMR (toluene-d_8, 162 MHz): δ 72.5 (m, 1P), 70.6 (m, 1P), 66.3 (m, 1P), 59.4 (m, 1P).

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Compound **4t**: ^{1}H NMR (toluene-d_8, 400 MHz): δ 1.97 (m, 4H, C**H**$_2$), 1.43 (bs, 12H, C**H**$_3$), 1.33 (m, 4H, C**H**$_2$), 1.00 (bs, 12H, C**H**$_3$), −27.66 (p, $^2J_{H-P}$ = 48 Hz, Fe**H**). ^{1}H{^{31}P} NMR (toluene-d_8, 400 MHz): δ 1.97 (m, 4H, C**H**$_2$), 1.43 (s, 12H, C**H**$_3$), 1.33 (m, 4H, C**H**$_2$), 1.00 (s, 12H, C**H**$_3$), −27.66 (s, Fe**H**). ^{31}P{^{1}H} NMR (toluene-d_8, 162 MHz): δ 70.0 (s).

Compounds **4c**/**4t**. ^{15}N{^{1}H} NMR (toluene-d_8, 41 MHz, 198K): δ −275.9 (m), −308.8 (m), −369.6 (b), −378.4 (b). ^{15}N NMR (toluene-d_8, 41 MHz, 198 K): δ −275.9 (m), −308.8 (m), −369.6 (b), −378.4 (b).

Preparation of *trans*-[RuH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ (6t-Cl). *trans*-[RuHCl(dmpe)$_2$] (**5t**; 26.9 mg, 61.4 μmol) was dissolved in a solution of hydrazine in thf (0.3 mL, 1 M, 0.3 mmol) and thf-d_8 (0.2 mL) under argon to give a nearly colorless solution. After standing for 3 days at room temperature, the fine colorless needles of *trans*-[RuH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ formed were collected by filtration under nitrogen and washed with diethyl ether (4 × 1 mL; 24 mg, 83% yield). ^{1}H NMR (MeOH, 500 MHz, high field only): δ −20.1 (p, $^2J_{HP}$ = 21 Hz, 1H, Ru**H**). ^{31}P{^{1}H} NMR (MeOH, 202 MHz): δ 41.1 (s).

The ^{15}N-labeled analogue of **6t-Cl** was prepared in situ by allowing a solution of **5t** and **5c** in ^{15}N$_2$-hydrazine in thf and thf-d_8 to stand for several days. The solution contained a mixture of **5t**, **5c**, ^{15}N-labeled **6t-Cl**, and ^{15}N-labeled **6c-Cl** in an approximate ratio of 2.4:6.8:1:4.2. ^{15}N{^{31}P, ^{1}H} NMR (thf/thf-d_8, 51 MHz): δ −309.7 (d, $^1J_{NN}$ = 6.1 Hz, RuNH$_2$**N**H$_2$), −370.5 (d, Ru**N**H$_2$). ^{15}N{^{1}H} NMR (thf/thf-d_8, 51 MHz): δ −309.7 (dp, $^1J_{NN}$ = 6.1 Hz, $^3J_{NP}$ = 1.6 Hz, RuNH$_2$**N**H$_2$), −370.5 (d, Ru**N**H$_2$). ^{15}N NMR (thf/thf-d_8, 51 MHz): δ −309.7 (bt, $^1J_{NH}$ = 60 Hz, RuNH$_2$**N**H$_2$), −370.5 (bt, $^1J_{NH}$ 70 Hz, Ru**N**H$_2$).

Preparation of *trans*-[RuH(N$_2$H$_4$)(dmpe)$_2$]$^+$ BPh$_4^-$ (6t-BPh$_4$). Compound **5t** (29.8 mg, 68.1 μmol) was dissolved in a solution of hydrazine in thf (0.4 mL, 1 M, 0.4 mmol) and thf-d_8 (0.25 mL) under argon. The white solid formed was collected by filtration under nitrogen and washed with diethyl ether (3 × 1 mL). A solution of NaBPh$_4$ (27 mg, 79 μmol) in methanol (1 mL) was added to a solution of the white solid in methanol (0.5 mL). Compound **6t-BPh$_4$** was formed as a white solid which was collected by filtration, washed with methanol (2 × 0.5 mL), and dried in vacuo (36 mg, 70% yield). Anal. Calcd for $C_{36}H_{57}BN_2P_4Ru$ (753.71): C, 57.4; H, 7.6; N, 3.7. Found: C, 57.4; H, 7.5; N, 3.4%. ^{1}H NMR (thf-d_8, 500 MHz): δ 7.27 (m, 8H, ***o*-Ph**), 6.86 (m, 8H, ***m*-Ph**), 6.72 (m, 4H, ***p*-Ph**), 3.42 (br, 2H, RuN**H**$_2$), 2.64 (b, 2H, RuNH$_2$N**H**$_2$), 1.57−1.77 (m, 8H, C**H**$_2$), 1.40 (bs, 24H, C**H**$_3$), −20.56 (p, $^2J_{HP}$ = 22 Hz, 1H, Ru**H**). ^{1}H{^{31}P} NMR (thf-d_8, 500 MHz): δ 7.27 (m, 8H, ***o*-Ph**), 6.86 (m, 8H, ***m*-Ph**), 6.72 (m, 4H, ***p*-Ph**), 3.42 (br, 2H, RuN**H**$_2$), 2.64 (b, 2H, RuNH$_2$N**H**$_2$), 1.71 (m, 4H, C**H**$_2$), 1.63 (m, 4H, C**H**$_2$), 1.40 (bs, 24H, C**H**$_3$), −20.56 (s, 1H, Ru**H**). ^{31}P{^{1}H} NMR (thf-d_8, 202 MHz): δ 41.1 (s). ^{15}N{^{1}H} NMR (thf-d_8, from HN-HSQC, 41 MHz): δ −310.1 (corr with ^{1}H δ 2.64, RuNH$_2$**N**H$_2$), −372.9 (corr with ^{1}H δ 3.42, Ru**N**H$_2$). ESI (acetonitrile): m/z 444.08 [20%, RuH(dmpe)$_2$(CH$_3$CN)$^+$], 435.05 [20, RuH(N$_2$H$_4$)(dmpe)$_2^+$], 403.06 [20, RuH(dmpe)$_2^+$]. IR: 3367 w, 3322 w, 3257 w (ν(N−H)), 1929 s (ν(Ru−H)), 1596 m, 1578 m, 1422 s, 1299 w, 1284 m, 1134 w, 1081 w, 1034 w, 933 s, 910 m, 887 m, 835 m, 794 w, 734 s, 702 s, 648 s, 613 s cm^{-1}. Crystals suitable for X-ray crystallography were grown from a solution of **6t-Cl** and NaBPh$_4$ in methanol.

Preparation of *cis*-[RuHCl(dmpe)$_2$] (5c). A solution of **5t** (31.5 mg, 71.9 μmol) in thf-d_8 (0.5 mL) was irradiated for 2 h under argon. The solution contained a mixture of the cis and trans isomers in an approximate ratio of 5.7:1. ^{1}H NMR (thf-d_8, 400 MHz): δ 1.61−1.82 (m, 4H, C**H**$_2$), 1.56 (m, 6H, C**H**$_3$), 1.46−1.59 (m, 2H, C**H**$_2$), 1.41 (m, 6H, C**H**$_3$), 1.32 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), 1.23−1.39 (m, 2H, C**H**$_2$), 1.26 (d, $^2J_{HP}$ = 6 Hz, 6H, C**H**$_3$), 1.15 (d, $^2J_{HP}$ = 8 Hz, 3H, C**H**$_3$), −8.52 (dddd, $^2J_{HP}$ = 104.0 Hz, $^2J_{HP}$ = 22.0 Hz, $^2J_{HP}$ = 30.7 Hz, $^2J_{HP}$ = 24.3 Hz, 1H, Ru**H**). ^{1}H{^{31}P} NMR (thf-d_8, 400 MHz): δ 1.64−1.76 (m, 4H, C**H**$_2$), 1.57 (s, 3H, C**H**$_3$), 1.55 (s, 3H, C**H**$_3$), 1.46−1.59 (m, 2H, C**H**$_2$), 1.42 (s, 3H, C**H**$_3$), 1.41 (s, 3H, C**H**$_3$), 1.32 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), 1.23−1.39 (m, 2H, C**H**$_2$), 1.26 (s, 6H, C**H**$_3$), 1.15 (s, 3H, C**H**$_3$), −8.52 (s, 1H, Ru**H**). ^{31}P{^{1}H} NMR (thf-d_8, 162 MHz): δ 56.3 (ddd, $^2J_{P_AP_B}$ = 23.2 Hz, $^2J_{P_AP_C}$ = 28.3 Hz, $^2J_{P_AP_D}$ = 13.6 Hz, 1P, **P$_A$**), 48.3 (ddd, $^2J_{P_BP_C}$ = 304.5 Hz, $^2J_{P_BP_D}$ = 23.7 Hz, 1P, **P$_B$**), 38.6 (ddd, $^2J_{P_CP_D}$ = 14.5 Hz, 1P, **P$_C$**), 27.3 (ddd, 1P, **P$_D$**).

Preparation of *cis*-[RuH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ (6c-Cl). A solution of **5c** in thf-d_8 as prepared above was treated with a solution of hydrazine (0.5 mL, 1 M, 0.5 mmol) under argon. After standing for approximately 1 month, colorless crystals of **6c-Cl** formed and were collected by filtration and washed with hexane (3 × 1 mL; 8 mg, 24% yield). ^{1}H NMR (thf-d_8, 500 MHz): δ 6.15 (bm, 1H, RuN**H**H), 5.53 (bm, 1H, RuNH**H**), 3.26 (br, 2H, N**H**$_2$), 2.50 (m, 2H, C**H**$_2$), 2.00 (m, 1H, C**H**$_2$), 1.97 (d, $^2J_{HP}$ = 8 Hz, 3H, C**H**$_3$), 1.92 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), 1.79−1.87 (m, 2H, C**H**$_2$), 1.75 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), 1.58−1.66 (m, 1H, C**H**$_2$), 1.51 (d, $^2J_{HP}$ = 6 Hz, 3H, C**H**$_3$), 1.47 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), 1.30 (d, $^2J_{HP}$ = 6 Hz, 3H, C**H**$_3$), 1.26−1.18 (m, 2H, C**H**$_2$), 1.20 (d, $^2J_{H-P}$ = 8 Hz, 3H, C**H**$_3$), 1.16 (d, $^2J_{HP}$ = 7 Hz, 3H, C**H**$_3$), −8.33 (dm, $^2J_{HP}$ = 86.1 Hz, Ru**H**). ^{1}H{^{31}P} NMR (thf-d_8, 500 MHz): δ 6.15 (d, $^2J_{HH}$ = 11.5 Hz, 1H, RuN**H**H), 5.53 (d, $^2J_{HH}$ = 11.5 Hz, 1H, RuNH**H**), 3.26 (br, 2H, N**H**$_2$), 2.50 (m, 2H, C**H**$_2$), 2.00 (m, 1H, C**H**$_2$), 1.97 (s, 3H, C**H**$_3$), 1.92 (s, 3H, C**H**$_3$), 1.79−1.87 (m, 2H, C**H**$_2$), 1.75 (s, 3H, C**H**$_3$), 1.58−1.66 (m, 1H, C**H**$_2$), 1.51 (s, 3H, C**H**$_3$), 1.47 (s, 3H, C**H**$_3$), 1.30 (s, 3H, C**H**$_3$), 1.18−1.26 (m, 2H, C**H**$_2$), 1.20 (s, 3H, C**H**$_3$), 1.16 (s, 3H, C**H**$_3$), −8.33 (s, 1H, Ru**H**). ^{31}P{^{1}H} NMR (thf-d_8, 202 MHz): δ 49.6 (m, 1P, **P$_A$**), 42.3 (m, 1P, **P$_B$**), 39.9 (m, 1P, **P$_C$**), 31.3 (m, 1P, **P$_D$**).

The ^{15}N-labeled analogue of **6c-Cl** was prepared in situ by allowing a solution **5t** and **5c** in ^{15}N$_2$-hydrazine in thf and thf-d_8 to stand for several days. The solution contained a mixture of **5t**, **5c**, ^{15}N-labeled **6t-Cl**, and ^{15}N-labeled **6c-Cl** in an approximate ratio of 2.4:6.8:1:4.2. ^{15}N{^{31}P, ^{1}H} NMR (thf/thf-d_8, 51 MHz): δ −298.4 (d, $^1J_{NN}$ = 4.6 Hz, RuNH$_2$**N**H$_2$), −374.2 (d, Ru**N**H$_2$). ^{15}N{^{1}H} NMR (thf/thf-d_8, 51 MHz): δ −298.4 (dd, $^1J_{NN}$ = 4.6 Hz, $^3J_{NP}$ = 4.6 Hz, RuNH$_2$**N**H$_2$), −374.2 (ddt, $^3J_{NP}$ = 25.3 Hz, $^3J_{NP}$ = 1.9 Hz, Ru**N**H$_2$). ^{15}N NMR (thf/thf-d_8, 51 MHz): δ −298.4 (t, $^1J_{NH}$ = 64.3 Hz, RuNH$_2$**N**H$_2$), −374.2 (td, $^1J_{NH}$ = 71.5 Hz, $^3J_{NP}$ = 25.3 Hz, Ru**N**H$_2$).

Preparation of *trans*-[RuH(N$_2$H$_3$)(dmpe)$_2$] (7t). A suspension of **6t-Cl** (31 mg, 66 μmol) and KO^{t}Bu (32 mg, 0.29 mmol) in tetrahydrofuran (1 mL) was stirred under nitrogen for several minutes; then the solvent was removed under reduced pressure. The residue was extracted with pentane (6 mL), filtered through Celite, and the filtrate evaporated to dryness under reduced pressure to afford **7t** as an off-white solid. ^{1}H NMR (benzene-d_6, 300 MHz): δ 5.77 (b, N**H**), 1.89 (m, 4H, C**H**$_2$), 1.44 (bs, 12H, C**H**$_3$), 1.17 (m, 4H, C**H**$_2$), 1.02 (bs, 12H, C**H**$_3$), −19.33 (p, $^2J_{HP}$ = 21.7 Hz, Ru**H**). ^{1}H{^{31}P} NMR (benzene-d_6, 300 MHz): δ 5.76 (b, N**H**), 1.89 (m, 4H, C**H**$_2$), 1.44 (s, 12H, C**H**$_3$), 1.17 (m, 4H, C**H**$_2$), 1.02 (s, 12H, C**H**$_3$), −19.33 (s, Ru**H**). ^{31}P{^{1}H} NMR (benzene-d_6, 122 MHz): δ 42.0 (s).

The ^{15}N-labeled analogue of **7t** was prepared similarly by reaction of ^{15}N-labeled **6t-Cl** (28 mg, 59 μmol) and KO^{t}Bu (28 mg, 0.25 mmol) in tetrahydrofuran (2 mL) and extraction with hexane (6 mL). ^{1}H NMR (benzene-d_6, 400 MHz): δ 5.54 (b, N**H**), 1.93 (m, 4H, C**H**$_2$), 1.44 (bs, 12H, C**H**$_3$), 1.17 (m, 4H, C**H**$_2$), 1.02 (bs, 12H, C**H**$_3$), −19.28 (dp, $^2J_{HP}$ 21.7 Hz, $^2J_{H-N}$ 8.1 Hz, Ru**H**). ^{1}H{^{31}P} NMR (benzene-d_6, 400 MHz): δ 5.54 (b, N**H**), 1.93 (m, 4H, C**H**$_2$), 1.44 (s, 12H, C**H**$_3$), 1.17 (m, 4H, C**H**$_2$), 1.02 (s, 12H, C**H**$_3$), −19.28 (d, $^2J_{HN}$ = 8.1 Hz, Ru**H**). ^{31}P{^{1}H} NMR (benzene-d_6, 162 MHz): δ 42.0 (s). ^{15}N{^{1}H} NMR (benzene-d_6, 41 MHz): δ −306.8 (s), −365.7 (bs). ^{15}N NMR (benzene-d_6, 41 MHz): δ −306.8 (s), −365.9 (bs).

■ ASSOCIATED CONTENT

Supporting Information. Crystallographic data for *trans*-[FeH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ (**2t-Cl**), *cis*-[FeH(N$_2$H$_4$)(dmpe)$_2$]$^+$Cl$^-$ (**2c-Cl**), and *trans*-[RuH(N$_2$H$_4$)(dmpe)$_2$]$^+$BPh$_4^-$ (**6t-BPh$_4$**) (cif), and figures showing selected ^{1}H, ^{31}P{^{1}H} (cif) and figures

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showing $^{15}N\{^1H\}$ NMR spectra for complexes *cis*-[FeH(N_2H_3)-(dmpe)$_2$] (**4c**), *trans*-[FeH(N_2H_3)(dmpe)$_2$] (**4t**), and *trans*-[RuH-(N_2H_3)(dmpe)$_2$] (**7t**) (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: L.Field@unsw.edu.au.

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