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Side-on Bound Complexes of Phenyl- and Methyl-diazene

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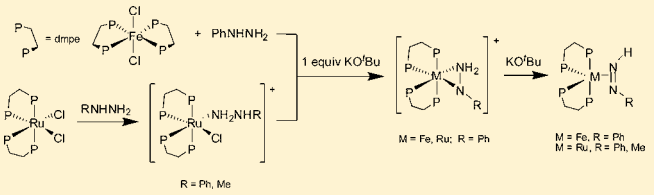
Supporting Information

ABSTRACT: Treatment of *trans*-[$FeCl_2(dmpe)_2$] with phenylhydrazine and 1 equiv of base afforded the side-on bound phenylhydrazido complex *cis*-[$Fe(\eta^2\text{-}NH_2NPh)(dmpe)_2]^+$. Further deprotonation of the phenylhydrazido complex afforded the side-on bound phenyldiazene complex *cis*-[$Fe(\eta^2\text{-}HN{=}NPh)(dmpe)_2$] as a mixture of diastereomers. Treatment of *cis*-[$RuCl_2(dmpe)_2$] with phenylhydrazine or methylhydrazine afforded the end-on bound phenylhydrazine or methylhydrazine complexes *cis*-[$RuCl(\eta^1\text{-}NH_2NHR)(dmpe)_2]^+$ (R = Ph, Me). Treatment of the substituted hydrazine complexes with base afforded the side-on bound phenylhydrazido complex *cis*-[$Ru(\eta^2\text{-}NH_2NPh)(dmpe)_2]^+$ as well as the phenyldiazene and methyldiazene complexes *cis*-[$Ru(\eta^2\text{-}HN{=}NR)(dmpe)_2$] (R = Ph, Me). *cis*-[$RuCl(\eta^1\text{-}NH_2NHR)(dmpe)_2]^+$ (R = Ph, Me), *cis*-[$M(\eta^2\text{-}NH_2NPh)(dmpe)_2]^+$ (M = Fe, Ru) and *cis*-[$Ru(\eta^2\text{-}HN{=}NPh)(dmpe)_2$] were characterized structurally by X-ray crystallography. *cis*-[$Ru(\eta^2\text{-}HN{=}NPh)(dmpe)_2$] is the first side-on bound phenyldiazene complex to be structurally characterized. In the structure of *cis*-[$Ru(\eta^2\text{-}HN{=}NPh)(dmpe)_2$], the geometry of the coordinated diazene fragment is significantly nonplanar (CNNH angle 137°) suggesting that the complex is probably better described as a Ru(II) metallodiaziridine than a Ru(0) diazene π-complex.



INTRODUCTION

Recent studies of enzymatic dinitrogen reduction by nitrogenase support an alternating pathway where N_2H_x species such as hydrazine (N_2H_4), hydrazide ($N_2H_3^-$), and diazene (N_2H_2) are vital intermediates for reaction at iron of the active site.[1] In particular, the binding modes and the reactions by which these species are interconverted are of interest because they may provide a greater understanding of the mode of action of nitrogenases. Given the general instability and reactive nature of coordinated diazene, hydrazide, and hydrazine, we have examined in this paper the synthesis and chemistry of phenyl- and methyl-substituted N_2H_xR complexes as potentially useful models for studying the potential diazene intermediates in nitrogen fixation in either biological or synthetic systems.[2]

We previously reported the synthesis of the first side-on bound diazene complex *cis*-[$Fe(\eta^2\text{-}NH{=}NH)(dmpe)_2$] (dmpe = 1,2-bis(dimethylphosphino)ethane) from the side-on bound hydrazine complex *cis*-[$Fe(\eta^2\text{-}N_2H_4)(dmpe)_2]^{2+}$ either by reduction with potassium graphite[3] or by deprotonation with a strong base.[4] The deprotonation route was also used to synthesize the analogous Ru diazene complexes.[5] The diazene complexes, and in particular the Fe complex, are thermally unstable, extremely air sensitive and fragile; they decompose readily under most laboratory reaction conditions. However, the diphenyldiazene (azobenzene) complex *cis*-[$Fe(\eta^2\text{-}NPh{=}NPh)(dmpe)_2$],[6] is stable, and we initially targeted a synthesis of side-on bound phenyldiazene and methyldiazene complexes where an NH functionality remains (allowing for further reaction) while the phenyl or methyl substituent potentially confers some degree of stability to the resulting diazene complexes.

Although free phenyldiazene or methyldiazene can be prepared in situ by a number of methods,[7] the diazenes are unstable species which readily decompose to give a range of products including the corresponding hydrocarbon (benzene or methane), dinitrogen, hydrazine, mono or disubstituted hydrazines, and azobenzene (for phenyldiazene).[8] Methyldiazene is also very oxygen sensitive and has been reported to react explosively with oxygen at room temperature.[9]

Complexation to transition metals greatly increases the stability of substituted diazenes, and there are now a number of synthetic approaches to metal diazene complexes as well as a number of different binding modes. The first reported route to aryldiazene complexes was by insertion of an aryldiazonium cation into a metal-hydride bond[10] where the resulting aryldiazene ligand is bound end-on, with a bent geometry and with a proton on the metal-coordinated nitrogen atom (Figure 1). Protonation at the coordinated nitrogen of aryldiazenido complexes also afforded aryldiazene complexes.[11] In a related method, the reaction of an aryldiazonium salt with a platinum side-on bound phenylacetylene complex afforded the bent, end-on bound aryldiazene complex containing an end-on bound phenylacetylide ligand.[12] In one example on rhenium, protonation occurs on the noncoordinating nitrogen atom to give the isomeric linear phenyldiazene complex.[13] For several examples of aryldiazenes on iridium, spontaneous hydrogenation of aryldiazenido ligands can also occur via orthometalation of the aryl ring.[14] Aryl- and methyl-diazene complexes have also been formed by the selective oxidation

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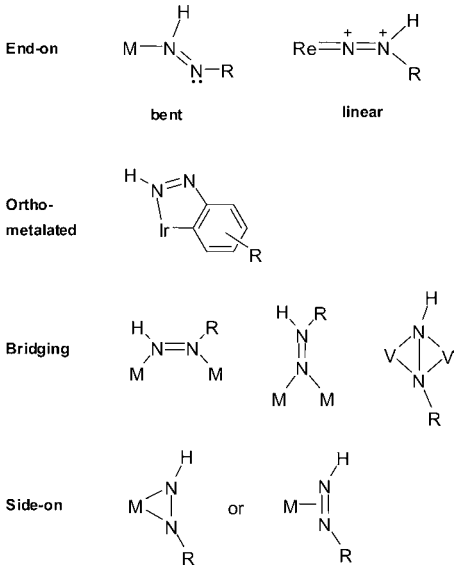


Figure 1. Binding modes of aryl and alkyl substituted diazene complexes.

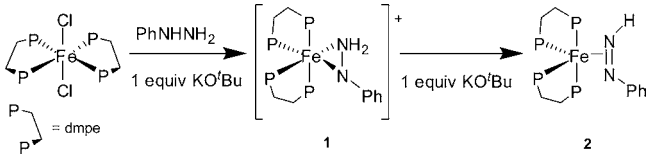
of the corresponding hydrazine complexes with $Pb(OAc)_4$.[15] Bridging phenyl- and methyldiazene complexes have also been reported with both bent and linear (isodiazene) forms[16] as well as a simultaneously bridging and side-on phenyldiazene complex of vanadium (Figure 1).[17]

There is only one report of a η^2-HNNPh ligand on Co[18] (although no crystal structure of the complex was reported) and none reported for HNNMe.

RESULTS AND DISCUSSION

Iron Phenylhydrazido(1-) and Phenyldiazene Complexes. Addition of 1 equiv of strong base (KO^tBu) to an emerald green solution of *trans*-$[FeCl_2(dmpe)_2]$ and phenylhydrazine in tetrahydrofuran (thf) afforded red crystals of the phenylhydrazido(1-) complex *cis*-$[Fe(\eta^2\text{-}NH_2NPh)(dmpe)_2]^+Cl^-$ (**1**) (Scheme 1), and these were characterized by X-ray crystallography (Figure 2).

Scheme 1



The phenylhydrazine is deprotonated only at NPh to give a phenylhydrazido ligand which is coordinated side-on. The Fe–NPh bond (1.939(4) Å) is shorter than the Fe–NH_2 bond (1.998(4) Å) and Fe–N bonds in side-on bound hydrazine *cis*-$[Fe(\eta^2\text{-}N_2H_4)(dmpe)_2]^{2+}$, diazene *cis*-$[Fe(\eta^2\text{-}NH{=}NH)(dmpe)_2]$, and azobenzene *cis*-$[Fe(\eta^2\text{-}NPh{=}NPh)(dmpe)_2]$ complexes (1.981(2)–2.032(7) Å)[3] as well as the Fe–NPh bond in $[(LFe)_2(\mu\text{-}S)(\mu\text{-}NH_2NPh)]$ (L = (HC(CMeN(2,6-diisopropylphenyl))$_2$)$^-$)[19] (1.990(4) Å). The relatively short Fe–N bond probably arises from the nitrogen having a high electron density (formal negative charge) leading to a strong bond to the iron center. The geometry about the NPh nitrogen is almost planar (sum of angles about N1 is 354.6°) and the N–C bond (1.352(6) Å) is also shorter than the corresponding

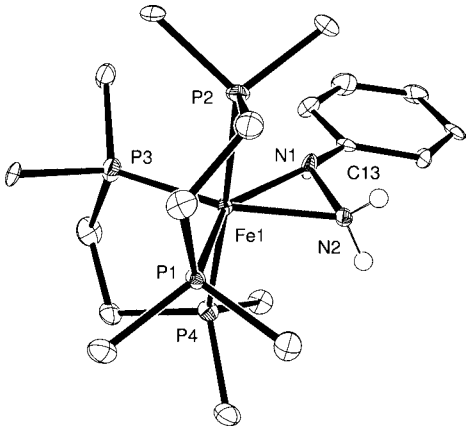


Figure 2. ORTEP plot of *cis*-$[Fe(\eta^2\text{-}NH_2NPh)(dmpe)_2]^+Cl^-$ (**1**, 50% displacement ellipsoids, chloride counterion, thf solvate, and carbon-bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Fe1–N1 1.939(4), Fe1–N2 1.998(4), N1–C13 1.352(6), N1–N2 1.400(5), N1–Fe1–N2 41.63(16), C13–N1–N2 121.8(4), C13–N1–Fe1 161.4(4), N2–N1–Fe1 71.4(2).

bond in the azobenzene complex (1.391(3) Å). The phenyl ring is nearly coplanar with the M–N–N plane as is also observed for the bridging phenylhydrazido ligand in $[(LFe)_2(\mu\text{-}S)(\mu\text{-}NH_2NPh)]$ (L = (HC(CMeN(2,6-diisopropylphenyl))$_2$)$^-$)[19] and side-on phenylhydrazido ligands in $[Ti(Cp)Cl_2(\eta^2\text{-}NH_2NPh)]$,[20] $[Ti(L')Cl_2(\eta^2\text{-}NH_2NPh)]$ (L′ = tris(pyrazolyl)borate),[21] and $[Zr(Cp^*)_2(OH)(\eta^2\text{-}NH_2NPh)]$[22] although unlike that in $[W(Cp)_2(\eta^2\text{-}NH_2NPh)]^+$[23] where the phenyl ring is bent out of the M–N–N plane. The coplanarity of the phenyl group with the M–N–N plane as well as the short N–C bond are consistent with sp^2 hybridization of the NPh nitrogen and partial delocalization of the nitrogen lone pair through the π-system of the phenyl ring.

NMR data for *cis*-$[Fe(\eta^2\text{-}NH_2NPh)(dmpe)_2]^+$ (**1**) is entirely consistent with the structure depicted in Figure 2. Four ddd signals were observed in the $^{31}P\{^1H\}$ NMR spectrum, characteristic of an octahedral complex containing two bidentate dmpe ligands and two additional nonidentical ligands in the remaining cis coordination sites. In the two-dimensional ^1H-^{15}N HSQC (Heteronuclear Single Quantum Coherence) experiment, the two NH proton resonances at δ 5.46 and 3.80 correlate with a single ^{15}N signal at δ −366.6 confirming that both protons reside on the same nitrogen atom (NH_2). A ^{15}N signal at δ −299.0 for NPh is observed when the ligand is $^{15}N_2$-labeled.

Phenylhydrazido complex **1** could also be isolated as the tetraphenylborate salt by counterion exchange in ethanol. Treatment of the tetraphenylborate salt of **1** with KO^tBu afforded the side-on bound phenyldiazene complex *cis*-$[Fe(\eta^2\text{-}HN{=}NPh)(dmpe)_2]$ (**2**) as the major product (Scheme 1). Small amounts of byproducts including $[Fe(N_2)(dmpe)_2]$[24] and $[\{Fe(dmpe)_2\}_2(\mu\text{-dmpe})]$[6] are also formed, presumably because of decomposition of the phenyldiazene complex.

The $^{31}P\{^1H\}$ NMR spectrum of *cis*-$[Fe(\eta^2\text{-}HN{=}NPh)(dmpe)_2]$ (**2**) is broad at room temperature but sharpens up at low temperature showing two sets of resonances in a ratio of approximately 2:1 (Figure 3) due to the presence of a pair of diastereomers. Each diastereomer has an associated enantiomer, and the four possible stereoisomers arise from the diazene coordination to the metal with either face and the helical twist that can be adopted by the bidentate dmpe ligands (Figure 4).

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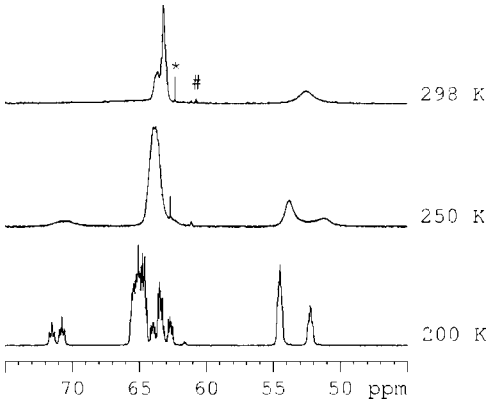


Figure 3. $^{31}P\{^1H\}$ NMR spectra of *cis*-[Fe(η^2-HN═NPh)(dmpe)$_2$] (**2**, toluene-d_8, 243 MHz, * = [Fe(N$_2$)(dmpe)$_2$]; # = [{Fe(dmpe)$_2$}$_2$(μ-dmpe)]).

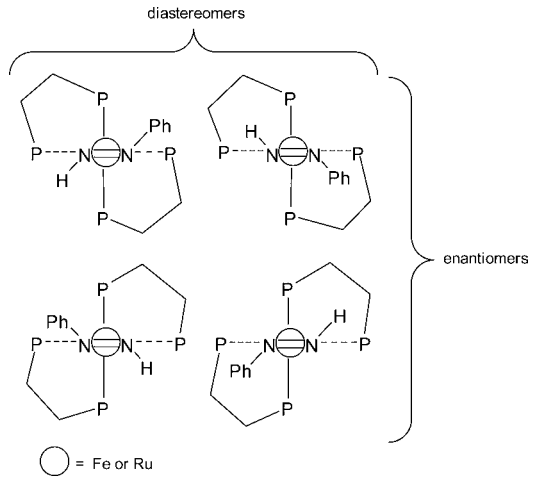


Figure 4. Diastereomers and enantiomers of [M(η^2-HN═NPh)(dmpe)] (M = Fe **2**, Ru **5**).

The observed dynamic behavior which interchanges the ^{31}P nuclei could result from face-to-face flip of the diazene on the metal or a twist of the coordinated phosphine backbone or a combination of the two.

A ^1H-^{15}N HSQC experiment at 200 K identified the ^{15}N resonances for the NH groups at δ −327.1 (major) and −324.5 (minor) correlating to ^1H signals at δ 2.11 and 1.71, respectively. Two ^{15}N signals at δ −246.3 (minor) and −254.3 (major) (200 K) for the ^{15}N resonances for the NPh groups are observed for the ^{15}N-labeled analogue. The ^1H and ^{15}N chemical shifts for the side-on bound diazenes contrast to literature data for end-on bound and bridging diazene complexes,[10,11,25,26] and this can be attributed to the significant back-bonding from the metal to the diazene ligand causing a large upfield shift of the signals.

An analogous reaction between *trans*-[FeCl$_2$(dmpe)$_2$] and methylhydrazine in the presence of KO^{t}Bu did not give any isolable complexes. In an attempt to access stable examples of hydrazine and diazene complexes we further investigated approaches to the synthesis of analogous ruthenium complexes.

Ruthenium Phenylhydrazine, Phenylhydrazido(1-), and Phenyldiazene Complexes. Treatment of *cis*-[RuCl$_2$(dmpe)$_2$] with excess phenylhydrazine in thf resulted in the substitution of one chloride ligand with phenylhydrazine to afford the phenylhydrazine complex *cis*-[RuCl(η^1-NH$_2$NHPh)(dmpe)$_2$]$^+$ (**3**) as the chloride salt (Scheme 2). The complex was isolated as the tetraphenylborate salt by anion exchange with NaBPh$_4$ in methanol. The four signals in the $^{31}P\{^1H\}$ NMR spectrum are characteristic of an octahedral complex containing two bidentate dmpe ligands and two additional nonidentical ligands in the remaining cis coordination sites. The large 298 Hz coupling between P$_C$ and P$_D$ indicate that these two atoms are trans to each other in the coordination sphere. In the ^1H-^{15}N HSQC experiment, the ^1H signal at δ 7.54 correlates to a ^{15}N signal at δ −287.3 for NHPh while the ^1H signals at δ 5.16 and 4.55 correlate to a single ^{15}N signal at δ −356.0 for the NH$_2$ group. The coordination mode of the phenylhydrazine ligand could not be determined conclusively by NMR as all the NH protons exhibit only weak coupling to P and while there are Nuclear Overhauser Effect (NOE; through space) interactions with various CH$_3$ protons, these could not be used to conclusively establish the binding mode of the ligand.

Slow evaporation of a thf-d_8 solution of **3** afforded colorless crystals suitable for X-ray crystallographic analysis (Figure 5).

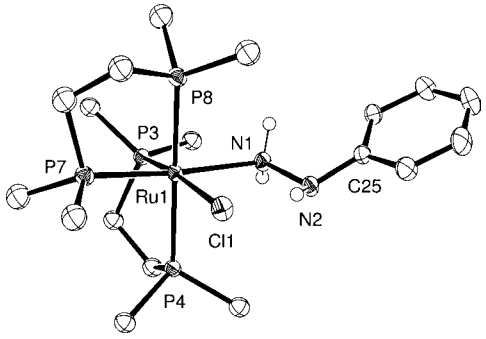
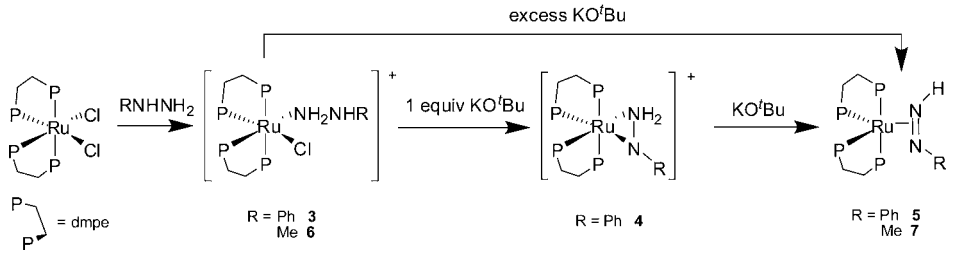


Figure 5. ORTEP plot of *cis*-[RuCl(η^1-NH$_2$NHPh)(dmpe)$_2$]$^+$BPh$_4^-$ (**3**, 50% displacement ellipsoids, BPh$_4$ counterion, atoms of less than 50% occupancy and carbon bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Ru1−N1 2.2504(19), N1−N2 1.436(3), N2−C25 1.412(3), N2−N1−Ru1 117.17(13), C25−N2−N1 117.13(18).

Scheme 2



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The phenylhydrazine is bound to Ru in an end-on fashion through the NH_2 group, and this binding mode is the most common for phenylhydrazine.[27,28] The phenylhydrazine ligand is bent and the proton on the terminal nitrogen is relatively close to protons on the dmpe methyl groups thus accounting for the NOE interactions observed.

Treatment of the chloride salt of phenylhydrazine complex **3** with 1 equiv of KO^{t}Bu base in thf afforded a mixture of unreacted starting material, the phenylhydrazide complex *cis*-[RuCl(η^2-PhNNH$_2$)(dmpe)$_2$]$^+$Cl$^-$ (**4**), and the phenyldiazene complex *cis*-[RuCl(η^2-PhN═NH)(dmpe)$_2$] (**5**) as well as *cis*-[RuCl$_2$(dmpe)$_2$] and free phenylhydrazine (probably because of disassociation of phenylhydrazine from the starting material). However, similar treatment of the tetraphenylborate salt of **3** with 1 equiv of base allowed the isolation of the singly deprotonated phenylhydrazide complex *cis*-[RuCl(η^2-NH$_2$NPh)(dmpe)$_2$]$^+$BPh$_4^-$ (**4**). The signals in the ^{31}P{^{1}H} NMR spectrum are heavily overlapped; however, the eight singlets in the ^{1}H{^{31}P} NMR spectrum (for the dmpe methyl protons) are characteristic of an octahedrally coordinated complex containing two bidentate dmpe ligands and two additional nonidentical ligands in the remaining *cis* coordination sites. In a ^{1}H-^{15}N HSQC experiment at 200 K, both NH proton signals at δ 5.25 and 4.37 correlate to a single ^{15}N signal at δ −365.6 indicating that both protons are located on the same nitrogen atom. The ^{15}N signal at δ −287.0 (a doublet with 20 Hz coupling to P) for NPh was observed on ^{15}N labeling, and this chemical shift is consistent with that observed for the analogous iron complex **1** (δ −299.1).

Crystals of the ruthenium phenylhydrazide complex **4** suitable for X-ray diffraction analysis were grown by layering a thf solution of the ^{15}N-labeled complex with diethyl ether (Figure 6). As for the analogous iron phenylhydrazide complex

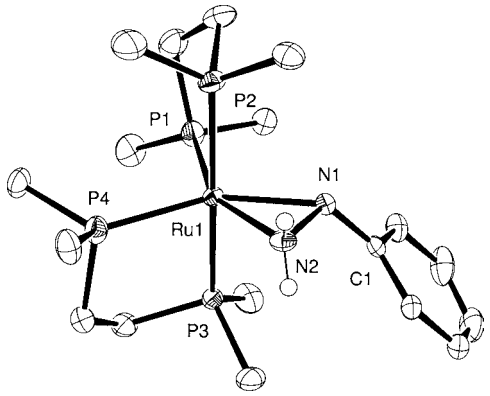

Figure 6. ORTEP plot of *cis*-[Ru(η^2-NH$_2$^{15}NPh)(dmpe)$_2$]$^+$BPh$_4^-$ (**4**, 50% displacement ellipsoids, BPh$_4$ counterion and carbon bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Ru1−N2 2.126(3), Ru1−N1 2.155(3), N1−C1 1.383(5), N1−N2 1.435(4), N2−Ru1−N1 39.16(11), C1−N1−N2 114.6(3), C1−N1−Ru1 129.0(2), N2−N1−Ru1 69.32(16), N1−N2−Ru1 71.52(15).

1, the phenylhydrazide ligand is coordinated side-on and deprotonated at NPh only. However, the phenyl ring is distinctly bent out of the M−N−N plane compared with the coplanar nature of the phenyl ring of the iron complex **1** and other reported phenylhydrazido complexes.[19−22] The out-of-plane phenyl ring resembles that reported for [W(Cp)$_2$(η^2-NH$_2$NPh)]$^+$,[23] and the sum of angles about N1 (312.92°) indicates a more sp^3-like geometry for NPh with little or no delocalization of the nitrogen lone pair into the phenyl ring. The Ru−NPh bond (2.155(3) Å) is significantly longer than the Ru−NH$_2$ bond (2.126(3) Å) unlike all other reported phenylhydrazide complexes where in general the M−NPh bonds are shorter than the M−NH$_2$ bonds. The N−N bond length of 1.435(4) Å is almost the same length as that for the phenylhydrazine complex **3** (1.436(3) Å) and is typical for an N−N single bond.

Treatment of phenylhydrazine complex **3** or phenylhydrazide complex **4** with excess base afforded the side-on bound phenyldiazene complex *cis*-[Ru(η^2-HN═NPh)(dmpe)$_2$] (**5**) (Scheme 2), and crystals of **5** suitable for X-ray crystallography were grown by layering a solution of **5** in benzene-d_6 with pentane (Figure 7). The phenyldiazene ligand is bound side-on

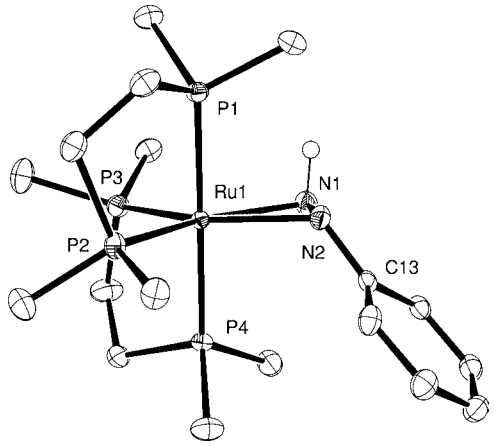

Figure 7. ORTEP plot of *cis*-[RuCl(η^2-HN═NPh)(dmpe)$_2$] (**5**, 50% displacement ellipsoids, carbon bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Ru1−N2 2.1238(16), Ru1−N1 2.1477(16), N1−N2 1.425(2), N2−C13 1.383(2), N2−Ru1−N1 38.96(6), N2−N1−Ru1 69.61(9), C13−N2−N1 114.74(15), C13−N2−Ru1 126.37(13), N1−N2−Ru1 71.42(9).

to Ru with an acute N2−Ru1−N1 angle of 38.96(6)°. The Ru−N distances of 2.1238(16) and 2.1477(16) Å are longer than the Ru−N distances of previously reported ruthenium η^1-aryldiazene complexes (2.080(11)−2.12(1) Å)[25] although within the range of Ru−N distances for the parent Ru η^2-diazene complexes [Ru(η^2-NH═NH)(PP)$_2$] (PP = dmpe, depe) (2.123(4)−2.1589(15) Å).[5] The N−N distance of 1.425(2) Å is significantly longer than those reported for end-on (including several iridium ortho-metalated aryldiazene complexes),[12−14,26] end-on bridging (μ-η^1:η^1)[16] or side-on bridging (μ-η^2:η^2)[17] aryldiazene complexes (1.13(2)−1.373(5) Å) although completely within the range of N−N distances for the parent Ru η^2-diazene complexes (1.414(5)−1.427(3) Å) and slightly shorter than that for the phenylhydrazide complex **4** (1.435(4) Å). The long N−N bond is entirely consistent with back-bonding from the filled d-orbitals of ruthenium to the antibonding π^* orbitals of the phenyldiazene ligand. Complex **5** is the first side-on bound phenyldiazene complex to be structurally characterized.

To date, there have been five side-on bound metal diazenes that have been structurally characterized (Table 1). There is always debate as to whether the metal diazenes are best represented as π complexes of M^n or as metallodiaziridines (metallo diazocyclopropanes) which would be M^{n+2} hydrazides

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Table 1. NN Bond Lengths (Å) and RNNR (R = H, C) Dihedral Angles (deg) in Side-on Bound Metal Diazene Complexes

complex	N−N bond length (Å)	RNNR (R = H, C) dihedral angle (deg)	reference
cis-Fe(NH═NH)(dmpe)$_2$	1.427(7)	156(5)	3
	1.398(8)	149(5)	
cis-Fe(PhN═NPh)(dmpe)$_2$	1.412(4)	113.9(2)	3
cis-Ru(NH═NH)(dmpe)$_2$	1.427(3)	162(2)	5
cis-Ru(NH═NH)(depe)$_2$	1.414(5)	168(4)	5
cis-Ru(PhN═NH)(dmpe)$_2$	1.425(2)	137.2(2)	this work
trans-NH═NH	1.247, 1.266, 1.28	180	34
trans-PhN═NPh	1.173−1.259	180	35

($ML_4N_2H_2^{2-}$).[29] Table 1 indicates that, in all cases, the N−N bond is longer when diazene is complexed than it is in free diazene. In *cis*-[Ru(PhN═NH)(dmpe)$_2$],(**5**), the torsional angle C−N−N−H (137.2(2)°) deviates very significantly from planarity suggesting that **5** should be viewed as more like a metallodiaziridine than a π complex. However, in the parent iron and ruthenium diazene complexes (Fe(NH═NH)(dmpe)$_2$ and Ru(NH═NH)(dmpe)$_2$), the torsion angles are closer to 180°[3,5] (Table 1) suggesting that these are better regarded as M(0)-π complexes. Theoretical calculations on Fe(NH═NH)(dmpe)$_2$[4] were consistent with a π bonded diazene, analogous to the π-bonding of alkenes to transition metals and with little charge localization on the nitrogen atoms.

The coordination and bonding in metal π complexes has been well-studied in alkene complexes, where the out of plane distortions of the substituents on the coordinated alkene is a measure of the metallocyclopropane character of an alkene complex.[30] The HCH angle in cyclopropane has been reported to be 114.4° in liquid crystalline solution[31] and 115.1 ± 1° by gas phase electron diffraction.[32] The corresponding HCH angle in aziridine is 115.72(1)°.[33]

It is likely that, as more side-on-bound complexes of diazene and substituted diazenes are characterized, there will be a continuum of structures ranging from those where the HNNH torsional angle is closer to 180° (where the N atoms are effectively sp^2 hybridized) to those where the torsional angle approaches the tetrahedral angle and the complexes are better described as metallodiaziridines.

In the ^{1}H{^{31}P} NMR spectrum of phenyldiazene complex **5**, the eight singlets for the dmpe methyl groups are characteristic of an octahedrally coordinated complex containing two bidentate dmpe ligands and two additional nonidentical ligands in the remaining *cis* coordination sites. In the ^{31}P{^{1}H} NMR spectrum, three multiplets in the relative ratio 1:2:1 were observed where the signals for P_B and P_C appear as a broad multiplet at δ 38.7 (Figure 8). On lowering the temperature, individual signals for P_B and P_C separate out and these signals exhibit large 335 Hz couplings indicating that they are due to P atoms *trans* to each other in the coordination sphere. In the case of the Ru complex **5**, only one diastereomer is observed at low temperature unlike the iron complex **2** where two diastereomers were observed. Again, the observed dynamic behavior where the ^{31}P nuclei are interchanged at higher temperatures reflects fluxionality in the complex and could result from face-to-face flip of the diazene on the metal or a twist of the coordinated phosphine backbone or a combination of the two.

A low temperature (193 K) ^{1}H-^{15}N HSQC experiment for **5** showed a correlation between the NH proton resonance at δ 2.62 and a ^{15}N signal at δ −324.4. The ^{15}N signal for NPh resonates at δ −251.5 for the ^{15}N-labeled analogue, and this

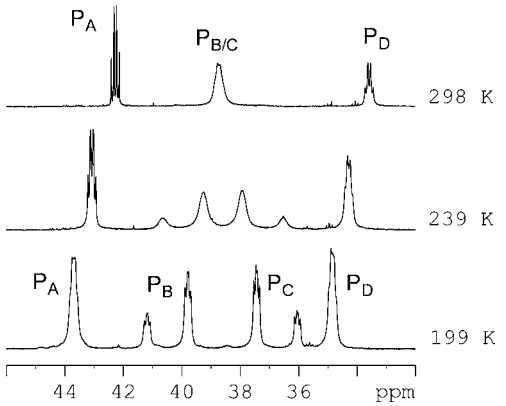

Figure 8. ^{31}P{^{1}H} NMR spectra of *cis*-[Ru(η^2-HN═NPh)(dmpe)$_2$] (**5**, toluene-d_8, 243 MHz).

shift is consistent with the shifts reported for *cis*-[Fe(η^2-NPh═NPh)(dmpe)$_2$] (**2**, δ −246.3 and −254.3 for the minor and major diastereomers respectively). The NPh ^{15}N resonance exhibits a 14 Hz coupling to ^{31}P and in the ^{31}P{^{1}H} NMR spectrum, P_A exhibits the reciprocal coupling to ^{15}N indicating that P_A is the signal for the phosphorus atom trans to NPh.

Ruthenium Methylhydrazine and Methyldiazene Complexes. Treatment of *cis*-[RuCl$_2$(dmpe)$_2$] with excess methylhydrazine in a mixture of thf and methanol afforded the methylhydrazine complex *cis*-[RuCl(η^1-NH$_2$NHMe)(dmpe)$_2$]$^+$ (**6**) as the chloride salt (Scheme 2). Crystals suitable for X-ray crystallography were obtained by layering the reaction mixture with diethyl ether, and only one of the two independent molecules in the unit cell is shown (Figure 9). The methylhydrazine ligand is bound end-on to Ru through the NH_2 group, and this binding mode is the most common for methylhydrazine.[19,28,36]

The methylhydrazine complex **6** was isolated as the tetraphenylborate salt by anion exchange with $NaBPh_4$ in methanol. In the ^{31}P{^{1}H} NMR spectrum, the four ddd signals as well as the large coupling between P_C and P_D of 298 Hz are similar to those for the phenylhydrazine complex **3**. In the ^{1}H-^{15}N HSQC experiment, the ^{1}H signal at 4.29 ppm, which integrates to two protons, correlates to a ^{15}N signal at −335.6 ppm for NH_2 while the ^{1}H signal at 4.04 ppm correlates to a ^{15}N signal at −308.2 ppm for the NHMe group.

Attempted monodeprotonation of the methylhydrazine complex **6** with 1 equiv of KO^{t}Bu afforded a complex mixture of products. Treatment with excess KO^{t}Bu base, however, afforded the side-on bound methyldiazene complex *cis*-[RuCl(η^2-HN═NMe)(dmpe)$_2$] (**7**) as the major product and a small amount of [RuH$_2$(dmpe)$_2$][6] byproduct (Scheme 2). The ^{31}P{^{1}H} NMR spectrum contains multiplets that are overlapping and severely distorted by second order effects. In

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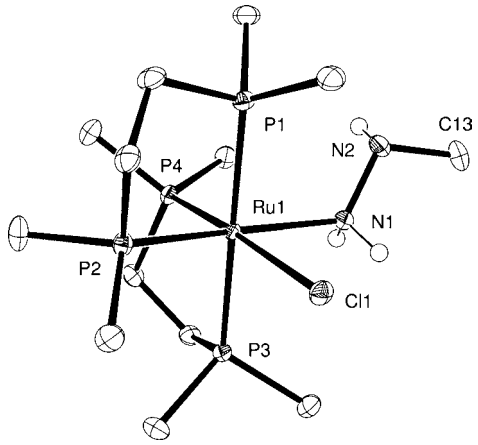

Figure 9. ORTEP plot of *cis*-[RuCl(η^1-NH_2NHMe)(dmpe)$_2$]$^+$Cl$^-$ (**6**, 50% displacement ellipsoids, Cl counterion, carbon bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Ru1−N1 2.1965(18), N1−N2 1.458(3), N2−C13 1.468(3), N2−N1−Ru1 119.57(14), N1−N2−C13 109.74(19).

the $^1H\{^{31}P\}$ NMR spectrum, there are seven resolved singlets (including one which has twice the intensity of the others) for the dmpe methyl groups. Of note in the ^1H NMR spectrum is the NMe resonance at δ 3.22 which exhibits a small coupling to P implying that the NMe group is coordinated to the metal center. In the ^1H-^{15}N HSQC experiment at 193 K, the ^1H resonance at δ 3.9 correlates with a ^{15}N signal at δ −289.5 for NH (Figure 10a). Whereas in the ^1H-^{15}N HMBC (Heteronuclear Multiple Bond Correlation) experiment, the NMe ^1H resonance correlates to two ^{15}N signals at δ −286.7 and −277.3 ppm for NH and NMe respectively (Figure 10b). The methyldiazene complex **7** is unstable in solution and decomposes over several days in benzene-d_6 to afford the solvent activated complex [RuD(Ph-d_5)(dmpe)$_2$][37] ($^{31}P\{^1H\}$ δ 45.8, 39.9, 33.2, 27.1) as the major product with concomitant release of methane (^1H δ 0.15, ^{13}C δ −4.2 in benzene-d_6) and other unidentified products.

CONCLUSIONS

We have reported synthetic approaches to a series of side-on bound iron and ruthenium phenyl and methyl-substituted hydrazide and diazene complexes by stepwise deprotonation of the parent hydrazine complexes. The phenyl- and methyldiazene complexes are the first known side-on bound complexes of substituted diazenes. The complexes have been thoroughly characterized by NMR spectroscopy (^1H, ^{31}P, and ^{15}N) and by X-ray crystallography. Both iron and ruthenium phenyldiazene complexes exhibit fluxional behavior consistent with a facile twist of the diphosphines or face-to-face flip of the coordinated diazenes. The ruthenium methyldiazene complex is thermally unstable and decomposes in benzene-d_6 to afford the phenyl deuteride complex.

Now that there are several side-on bound diazenes that have been structurally characterized, it is apparent that the structure of the coordinated diazene can range from near planar to significantly non-planar. The planar structure would be expected for a complex where Fe(0) or Ru(0) is coordinated to the π-system of a diazene where the nitrogens are effectively sp^2 hybridized and the nitrogen−nitrogen bond is effectively a double bond. The structure where the diazene fragment is a nonplanar structure would be anticipated for a complex where Fe(II) or Ru(II) is coordinated to a diazide $(RNNR)^{2-}$ where the nitrogens are effectively sp^3 hybridized, and the structure is better regarded as a metallodiaziridine.

EXPERIMENTAL SECTION

All manipulations of metal complexes and air-sensitive reagents were carried out using standard Schlenk techniques or in nitrogen or argon filled glove boxes. Solvents were dried and distilled under nitrogen or argon from sodium/benzophenone (benzene, hexane), sodium (heptane), diethoxymagnesium (ethanol), and dimethoxymagnesium (methanol). Tetrahydrofuran (inhibitor free), diethyl ether, toluene, and pentane were dried and deoxygenated using a Pure-Solv 400-4-MD (Innovative Technology) solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Tetrahydrofuran-d_8, toluene-d_8, and benzene-d_6 were dried over and distilled from sodium/benzophenone. Dichloromethane-d_2 was dried over, distilled from, and stored over activated molecular sieves. Phenylhydrazine was purchased from Aldrich, distilled under vacuum, and stored over activated molecular sieves under nitrogen. Methylhydrazine was purchased from Aldrich, dried over barium oxide, vacuum distilled, and stored over activated molecular sieves under nitrogen. Potassium *t*-butoxide was sublimed twice and stored under nitrogen or argon. *trans*-[$FeCl_2$(dmpe)$_2$] was prepared according to the literature method.[38] *cis*-[$RuCl_2$(dmpe)$_2$] was prepared

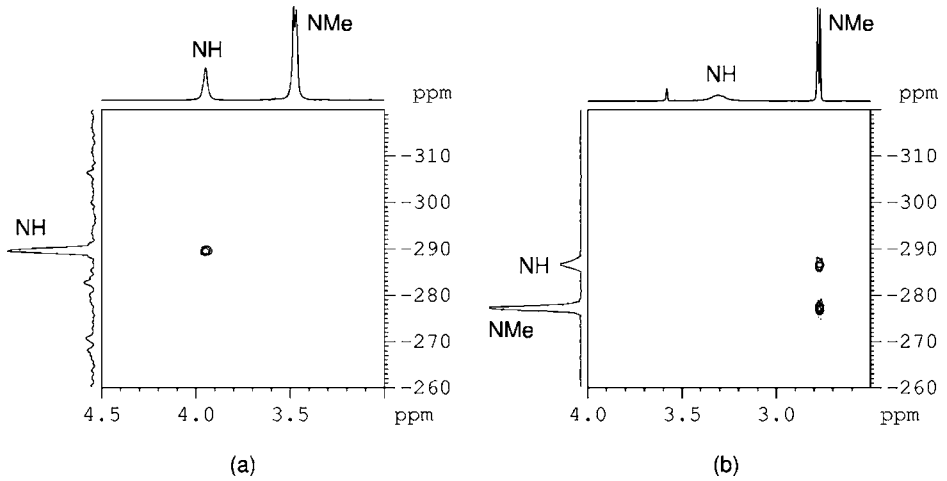

Figure 10. (a) ^1H-^{15}N HSQC spectrum (toluene-d_8, 193 K, 400 and 41 MHz) (b) ^1H-^{15}N HMBC spectrum (thf-d_8, 298 K, 500 and 51 MHz) of *cis*-[RuCl(η^2-HN═NMe)(dmpe)$_2$] (**7**).

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Table 2. Crystallographic Details for *cis*-[Fe(η^2-NH_2NPh)(dmpe)$_2$]$^+$Cl$^-$ (1), *cis*-[RuCl(η^1-NH_2NHPh)(dmpe)$_2$]$^+$$BPh_4^-$ (3), *cis*-[Ru(η^2-NH_2^{15}NPh)(dmpe)$_2$]$^+$$BPh_4^-$ (4), *cis*-[Ru(η^2-HN=NPh)(dmpe)$_2$] (5), and *cis*-[RuCl(η^1-NH_2NHMe)(dmpe)$_2$]$^+$Cl$^-$ (6)

	1	3	4	5	6
formula	$C_{22}H_{47}ClFeN_2OP_4$	$C_{46}H_{78}BClN_2OP_4Ru$	$C_{42}H_{59}BN_2P_4Ru$	$C_{18}H_{38}N_2P_4Ru$	$C_{26}H_{76}Cl_4N_4P_8Ru_2$
M (g mol^{-1})	570.80	946.31	827.67	507.45	1036.61
crystal morphology	red plate	colorless block	yellow block	yellow block	colorless block
size (mm^3)	0.24 × 0.20 × 0.08	0.40 × 0.30 × 0.25	0.40 × 0.25 × 0.20	0.40 × 0.30 × 0.30	0.20 × 0.20 × 0.15
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$C2/c$	$P2_1$	$P2_1/c$	$P2_12_12_1$
a (Å)	17.260(2)	39.212(3)	10.0354(13)	14.5109(8)	13.5246(6)
b (Å)	13.4299(16)	9.8714(7)	16.150(2)	8.6862(4)	13.7540(6)
c (Å)	12.5230(14)	24.3607(17)	13.1828(19)	18.9423(10)	24.5580(11)
β (deg)	106.257(7)	108.174(3)	102.261(7)	102.279(2)	90.00
V (Å^3)	2786.7(6)	8959.2(11)	2087.8(5)	2333.0(2)	4568.2(4)
Z	4	8	2	4	4
D_c (g/cm^3)	1.360	1.403	1.317	1.445	1.507
μ (mm^{-1})	0.884	0.591	0.560	0.952	1.199
F_{000}	1216	4016	868	1056	2144
$2\theta_{max}$ (deg)	58.1	51.4	54.7	52.7	54.4
reflections collected	7171	57171	20297	17917	68743
independent reflections	7173 (R_{int} = 0.0464)	8489 (R_{int} = 0.0398)	9633 (R_{int} = 0.0401)	4752 (R_{int} = 0.0261)	9989 (R_{int} = 0.0348)
observed reflections	4115 [$I > 2\sigma(I)$]	7337 [$I > 2\sigma(I)$]	8610 [$I > 2\sigma(I)$]	4329 [$I > 2\sigma(I)$]	9326 [$I > 2\sigma(I)$]
final GOF	1.010	1.049	1.052	1.019	1.029
R1	0.0714	0.0335	0.0444	0.0228	0.0226
wR2	0.1100	0.0770	0.0857	0.0522	0.0452

by heating a mixture of [{Ru(PMe$_2$Ph)$_3$}$_2$(μ-Cl)$_3$]$^+$Cl$^-$ and dmpe at 200 °C and subsequent Soxhlet extraction with toluene.[39] Phenylhydrazine-$^{15}N_2$ was prepared by diazotization of aniline-^{15}N with sodium nitrite-^{15}N and subsequent reduction with sodium sulfite.[40] Ph^{15}NNH$_2$ was prepared in a similar manner with aniline-^{15}N and unlabeled sodium nitrite.

Air-sensitive NMR samples were prepared in argon or nitrogen filled glove boxes 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, and ^{15}N NMR spectra were recorded on Bruker Avance III 600, 500, 400 or DPX300 NMR spectrometers at 298 K unless otherwise stated. ^{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 referenced to external neat nitromethane at δ 0.0 ppm. Simulation of ^{31}P spectra for cis-unsymmetrical complexes were performed iteratively using the simulation program NUMMRIT (SpinWorks 3), and the signs for coupling constants are not implied. Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer as nujol mulls. Mass spectrometric analysis for this work was carried out at the Bioanalytical Mass Spectrometry Facility, UNSW. Microanalyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand, or on a Thermo Finnigan EA 1112 Series Flash Elemental Analyzer at the Central Science Laboratory, University of Tasmania. X-ray crystallography data were collected on a Bruker Nonius X8 Apex II CCD diffractometer operating with MoKα radiation (λ = 0.71073) at a temperature of 100(2) K. Crystallographic details are summarized in Table 2.

***cis*-[Fe(η^2-NH_2NPh)(dmpe)$_2$]$^+$X$^-$ (1).** *X = Cl.* Potassium *t*-butoxide (36 mg, 0.32 mmol) was added to an emerald green solution of *trans*-[FeCl$_2$(dmpe)$_2$] (0.118 g, 0.276 mmol) and phenylhydrazine (0.130 g, 1.20 mmol) in thf (2 mL) under nitrogen. The resulting dark orange-red solution was left to stand overnight in which time a red crystalline solid precipitated. The solid was collected by filtration, washed with thf (4 mL), and dried in vacuo (0.125 g, 91% yield). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 6.97 (m, 2H, ***m*-Ph**), 6.70 (m, 2H, ***o*-Ph**), 6.44 (m, 1H, ***p*-Ph**), 5.46 (br, 1H, N**H**H), 3.80 (br, 1H, NH**H**), 2.17−1.89 (m, 2H, C**H**$_2$), 1.88−1.78 (m, 6H, C**H**$_3$ and C**H**$_2$), 1.78−1.68 (m, 4H, C**H**$_3$ and C**H**$_2$), 1.63 (s, 3H, C**H**$_3$), 1.58−1.40 (m, 2H, C**H**$_2$), 1.27 (m, 3H, C**H**$_3$), 1.25−1.11 (m, 9H, C**H**$_3$), 0.92 (s, 3H, C**H**$_3$). ^{1}H{^{31}P} NMR (CD_2Cl_2, 400 MHz): δ 6.97 (m, 2H, **Ph**), 6.70 (m, 2H, **Ph**), 6.44 (m, 1H, **Ph**), 5.46 (br, 1H, N**H**H), 3.80 (br, 1H, NH**H**), 2.17−1.89 (m, 2H, C**H**$_2$), 1.82 (m, 6H, C**H**$_3$ and C**H**$_2$), 1.75 (m, 4H, C**H**$_3$ and C**H**$_2$), 1.63 (s, 3H, C**H**$_3$), 1.58−1.40 (m, 2H, C**H**$_2$), 1.27 (s, 3H, C**H**$_3$), 1.23 (s, 3H, C**H**$_3$), 1.21 (s, 3H, C**H**$_3$), 1.20 (s, 3H, C**H**$_3$), 0.92 (s, 3H, C**H**$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 65.6 (ddd, $^2J_{AB}$ 6.5 Hz, $^2J_{AC}$ 24.6 Hz, $^2J_{AD}$ 43.8 Hz, 1P, **P$_A$**), 63.6 (ddd, $^2J_{BC}$ 46.9 Hz, $^2J_{BD}$ 42.5 Hz, 1P, **P$_B$**), 61.0 (ddd, $^2J_{CD}$ 151.2 Hz, 1P, **P$_C$**), 60.4 (ddd, 1P, **P$_D$**). ^{15}N{^{1}H} NMR (CD_2Cl_2, 41 MHz, from HN-HSQC): δ −366.6 (corr with ^{1}H δ 5.46 and 3.80, **N**H$_2$).

The $^{15}N_2$-labeled analogue was prepared in a similar manner using phenylhydrazine-$^{15}N_2$. ^{1}H NMR (CD_2Cl_2, 400 MHz): 5.46 (br d, $^1J_{HN}$ 86 Hz, 1H, N**H**H), 3.80 (br d, $^1J_{HN}$ 79 Hz, 1H, NH**H**). ^{15}N NMR (CD_2Cl_2, 41 MHz): δ −299.0 (m, **N**Ph), −366.8 (m, **N**H$_2$).

The ^{15}N-labeled analogue was prepared in a similar manner using Ph^{15}NNH$_2$.

X = BPh$_4$. Potassium *t*-butoxide (82 mg, 0.73 mmol) was added to a solution of *trans*-[FeCl$_2$(dmpe)$_2$] (0.302 g, 0.707 mmol) and phenylhydrazine (0.121 g, 1.12 mmol) in thf (4 mL) under nitrogen. The resulting dark red solution was left to stand overnight in which time a dark red crystalline solid precipitated. The solid *cis*-[Fe(η^2-NH_2NPh)(dmpe)$_2$]$^+$Cl$^-$ was collected by filtration, washed with thf, and dried in vacuo. The chloride salt was extracted with ethanol (3 mL, 3 × 1 mL), filtered through Celite then added to a solution of sodium tetraphenylborate (0.250 g, 0.731 mmol) in ethanol (4 mL). The resulting orange-red precipitate was collected by filtration, washed with ethanol (3 × 1 mL) and methanol (3 × 1 mL), then dried under vacuum (0.384 g, 0.491 mmol, 69% yield). $C_{42}H_{59}BFeN_2P_4$ (782.57) requires C, 64.5; H, 7.6; N, 3.6; found, C, 64.2; H, 7.8; N, 3.2%. ^{1}H NMR (thf-d_8, 300 MHz): δ 7.29 (m, 8H, ***o*-PhB**), 6.99−6.80 (m, 10H, ***m*-Ph** and ***m*-PhB**), 6.72 (m, 4H, ***p*-PhB**), 6.54 (m, 2H, ***o*-Ph**), 6.40 (m, 1H, ***p*-Ph**), 3.80 (br s, 1H, N**H**H), 3.05 (br s, 1H, NH**H**), 2.07−1.70 (m, 5H, C**H**$_2$), 1.67 (d, $^2J_{HP}$ 8 Hz, 3H, C**H**$_3$), 1.64−1.46 (m, 3H, C**H**$_2$), 1.46−1.35 (m, 6H, C**H**$_3$), 1.21−1.09 (m, 9H, C**H**$_3$), 1.06 (m, 3H, C**H**$_3$), 0.79 (m, 3H, C**H**$_3$). ^{1}H{^{31}P} NMR (thf-d_8, 300 MHz): δ 7.29 (m, 8H, ***o*-PhB**), 6.98−6.82 (m, 10H, ***m*-Ph** and ***m*-PhB**), 6.72 (m, 4H, ***p*-PhB**), 6.54 (m, 2H, ***o*-Ph**), 6.41 (m, 1H, ***p*-Ph**), 3.79 (br s,

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1H, NHH), 3.04 (br s, 1H, NHH), 1.95 (m, 1H, CH_2), 1.83−1.70 (m, 4H, CH_2), 1.67 (s, 3H, CH_3), 1.65−1.47 (m, 3H, CH_2), 1.43 (s,3H, CH_3), 1.41 (s, 3H, CH_3), 1.164 (s, 3H, CH_3), 1.157 (s, 3H, CH_3), 1.13 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 0.79 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (thf-d_8, 122 MHz): δ 66.2 (m, 1P, P_A), 64.2 (m, 1P, P_B), 61.3 (m, 2P, P_C and P_D). $^{15}N\{^1H\}$ NMR (thf-d_8, 30 MHz, from HN-HSQC): δ −376.1 (corr with ^1H δ 3.80 and 3.05, NH_2). IR: 3305w, 3242w, 1942w, 1881w, 1823w, 1765w, 1587s, 1562 m, 1478s, 1427s, 1302s, 1281 m, 1265s, 1179 m, 1147w, 1123w, 1083w, 1068w, 1032w, 988w, 929s, 890s, 831 m, 802w, 757 m, 747s, 737s, 725s, 707s, 649 m, 624w, 613s cm^{-1}.

The ^{15}N-labeled analogue was prepared in a similar manner using *cis*-[Fe(η^2-$NH_2{}^{15}$NPh)(dmpe)$_2$]$^+$Cl$^-$. ^{15}N NMR (thf-d_8, 30 MHz): δ −299.1 (s, NPh).

***cis*-[Fe(η^2-HN═NPh)(dmpe)$_2$] (2).**[41] Potassium *t*-butoxide (24 mg, 0.21 mmol) was added to a solution of *cis*-[Fe(η^2-NH_2NPh)-(dmpe)$_2$]$^+$$BPh_4^-$ (0.148 g, 0.189 mmol) in thf (2 mL) under nitrogen and stirred for 20 min. The resulting red suspension was filtered through Celite, the residue washed with thf (3 × 2 mL), and the filtrate was evaporated to dryness under reduced pressure. The residue was extracted with benzene (3 × 2 mL), filtered through Celite, and evaporated to dryness under reduced pressure to afford a red solid (44.3 mg, 51% yield). ^1H NMR (toluene-d_8, 600 MHz, 200 K): δ 7.88, 7.41, 7.37, 7.20, 6.82, 6.75 (m, **Ph**), 2.11, 1.71 (br s, N**H**), 1.50, 1.44, 1.15, 0.98, 0.86, 0.68, 0.66, 0.63, 0.61, 0.52, 0.38 (m, CH_3), 1.64−0.73 (m, CH_2). $^{31}P\{^1H\}$ NMR (toluene-d_8, 243 MHz, 200 K): δ 71.5, 70.8, 65.9−64.3, 64.0, 63.4, 62.7, 54.5, 52.3 (m, **P**). $^{15}N\{^1H\}$ NMR (toluene-d_8, 61 MHz, from HN-HSQC, 200 K): δ −327.1, (corr with ^1H δ 2.11, **N**H, major diastereomer), −324.5 (corr with ^1H δ 1.71, **N**H, minor diastereomer). IR: 3155w, 3050w, 3034w, 1605w, 1579s, 1548 m, 1415 m, 1358 m, 1316 m, 1291 m, 1281 m, 1272 m, 1244 m, 1150 m, 1121w, 1063w, 1018 m, 1008w, 978 m, 926s, 902 m, 884s, 831 m, 785w, 738 m, 716s, 705s, 694s, 640s, 628 m cm^{-1}.

The ^{15}N-labeled analogue was prepared in a similar manner using *cis*-[Fe(η^2-$NH_2{}^{15}$NPh)(dmpe)$_2$]$^+$$BPh_4^-$. ^{15}N NMR (toluene-d_8, 40 MHz, 200 K): δ −246.3 (s, NPh, minor diastereomer), −254.3 (s, NPh, major diastereomer).

***cis*-[RuCl(η^1-NH_2NHPh)(dmpe)$_2$]$^+$X$^-$ (3).** *X* = *Cl.* Phenylhydrazine (0.4 mL, 4 mmol) was added to a suspension of *cis*-[$RuCl_2$(dmpe)$_2$] (0.148 g, 0.313 mmol) in thf (2 mL) under nitrogen to give a pale yellow solution. Diethyl ether (10 mL) was added, and the mixture left to stand overnight. The white precipitate of *cis*-[RuCl(η^1-NH_2NHPh)(dmpe)$_2$]$^+$Cl$^-$ was collected by filtration and washed with diethyl ether (0.173 g, 95% yield). The compound was used directly without further purification.

The ^{15}N-labeled analogue was prepared in a similar manner using *cis*-[$RuCl_2$(dmpe)$_2$] (0.68 g, 1.4 mmol) and Ph^{15}NHNH_2 (0.17 g, 1.6 mmol), yield 80 mg (10%).

X = *BPh*$_4$. A solution of $NaBPh_4$ (35 mg, 0.10 mmol) in methanol (0.5 mL) was added to a solution of *cis*-[RuCl(η^1-NH_2NHPh)-(dmpe)$_2$]$^+$Cl$^-$ (34 mg, 59 μmol) in methanol (1.2 mL) under nitrogen. The white precipitate of *cis*-[RuCl(η^1-NH_2NHPh)-(dmpe)$_2$]$^+$$BPh_4^-$ formed was collected by filtration, washed with methanol (3 × 0.5 mL), and dried in vacuo (40 mg, 78% yield). $C_{42}H_{60}BClN_2P_4Ru$ (864.25) requires C, 58.4; H, 7.0; N, 3.2; found, C, 58.2; H, 7.0; N, 3.1%. ^1H NMR (thf-d_8, 400 MHz): δ 7.54 (b, 1H, NHPh), 7.28 (m, 8H, ***o*-PhB**), 7.22 (m, 2H, ***m*-Ph**), 6.90−6.81 (m, 9H, ***m*- PhB** and ***p*-Ph**), 6.79−6.68 (m, 6H, ***p*-PhB** and ***o*-Ph**), 5.16 (br, 1H, NHH), 4.55 (br, 1H, NHH), 2.01−1.74 (m, 4H, CH_2), 1.69−1.57 (m, 1H, CH_2), 1.57−1.52 (m, 4H, CH_3 and CH_2), 1.52−1.44 (m, 8H, CH_3 and CH_2), 1.40 (d, $^2J_{HP}$ 10 Hz, 3H, CH_3), 1.36 (dd, $^2J_{HP}$ 8 Hz, $^2J_{HP}$ 2 Hz, 3H, CH_3), 1.33−1.26 (m, 6H, CH_3), 1.18 (d, $^2J_{HP}$ 8 Hz, 3H, CH_3). $^1H\{^{31}P\}$ NMR (thf-d_8, 400 MHz): δ 7.53 (bt, $^2J_{HH}$ 3−4 Hz, 1H, NHPh), 7.28 (m, 8H, ***o*-PhB**), 7.22 (m, 2H, ***m*-Ph**), 6.90−6.81 (m, 9H, ***m*-PhB** and ***p*-Ph**), 6.79−6.68 (m, 6H, ***p*-PhB** and ***o*-Ph**), 5.16 (dd, $^2J_{HH}$ 9 Hz, $^2J_{HH}$ 4 Hz, 1H, NHH), 4.55 (br, $^2J_{HH}$ 9 Hz, $^2J_{HH}$ 3 Hz, 1H, NHH), 1.86 (m, 4H, CH_2), 1.61 (m, 1H, CH_2), 1.57−1.43 (m, 3H, CH_2), 1.55 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.19 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (thf-d_8, 162 MHz): δ 50.8 (m, 1P, P_A), 45.8 (m, 1P, P_B), 40.9 (dm, $^2J_{CD}$ 298 Hz, 1P, P_C), 33.5 (dm, 1P, P_D). $^{15}N\{^1H\}$ NMR (thf-d_8, 41 MHz, from HN-HSQC): δ −287.3 (corr with ^1H δ 7.54, NHPh), −356.0 (corr with ^1H δ 5.16 and 4.55, NH_2). IR: 3225 m, 3054 m, 3030 m, 1600 m, 1578 m, 1559w, 1497 m, 1426 m, 1304 m, 1284 m, 1250 m, 1200w, 1176w, 1153w, 1132w, 1079w, 1064w, 1033w, 1016w, 992w, 929s, 891 m, 838 m, 793w, 750s, 735s, 706s, 691 m, 651 m, 612s cm^{-1}.

***cis*-[Ru(η^2-NH_2NPh)(dmpe)$_2$]$^+$$BPh_4^-$ (4).** Potassium *t*-butoxide (20 mg, 0.18 mmol) was added to a suspension of *cis*-[RuCl(η^1-NH_2NHPh)(dmpe)$_2$]$^+$$BPh_4^-$ (102 mg, 0.118 mmol) in thf (3 mL) under nitrogen. The initial dark blue suspension turned into a cloudy yellow solution on stirring for 30 min. The reaction mixture was filtered through Celite, the residue washed with thf (2 × 1 mL), and the filtrate evaporated to dryness under vacuum. Diethyl ether (10 mL) and thf (0.5 mL) were added, and the mixture was left to stand for 1 h. The yellow solid formed was collected by filtration, washed with diethyl ether twice, and dried under vacuum (68 mg, 70% yield). $C_{42}H_{59}BN_2P_4Ru$ (827.79) requires C, 60.9; H, 7.2; N, 3.4; found, C, 60.5; H, 7.3; N, 3.3%. ^1H NMR (thf-d_8, 400 MHz): δ 7.29 (m, 8H, ***o*-PhB**), 6.95 (m, 2H, ***m*-Ph**), 6.86 (m, 8H, ***m*-PhB**), 6.72 (m, 4H, ***p*-PhB**), 6.56 (m, 2H, ***o*-Ph**), 6.40 (m, 1H, ***p*-Ph**), 4.75 (br, 1H, NHH), 3.92 (br, 1H, NHH), 2.01−1.75 (m, 3H, CH_2), 1.71−1.47 (m, 5H, CH_2), 1.61 (d, $^2J_{HP}$ 8 Hz, 3H, CH_3), 1.44 (d, $^2J_{HP}$ 5 Hz, 3H, CH_3), 1.41 (d, $^2J_{HP}$ 8 Hz, 3H, CH_3), 1.30 (d, $^2J_{HP}$ 8 Hz, 3H, CH_3), 1.28 (d, $^2J_{HP}$ 8 Hz, 3H, CH_3), 1.16 (d, $^2J_{HP}$ 7 Hz, 3H, CH_3), 1.15 (d, $^2J_{HP}$ 6 Hz, 3H, CH_3), 0.76 (d, $^2J_{HP}$ 5 Hz, 3H, CH_3). $^1H\{^{31}P\}$ NMR (thf-d_8, 400 MHz): δ 7.29 (m, 8H, ***o*-PhB**), 6.94 (m, 2H, ***m*-Ph**), 6.86 (m, 8H, ***m*-PhB**), 6.72 (m, 4H, ***p*-PhB**), 6.56 (m, 2H, ***o*-Ph**), 6.40 (m, 1H, ***p*-Ph**), 4.75 (br, 1H, NHH), 3.92 (br, 1H, NHH), 1.92 (m, 1H, CH_2), 1.76 (m, 1H, CH_2), 1.67−1.47 (m, 6H, CH_2), 1.61 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.15 (s, 3H, CH_3), 0.76 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (thf-d_8, 162 MHz): δ 46.9 (m, 2P, P_A and P_B), 36.7 (m, 2P, P_C and P_D). $^{15}N\{^1H\}$ NMR (thf-d_8, 41 MHz, from HN-HSQC, 200 K): δ −365.6 (corr with ^1H δ 5.25 and 4.37, NH_2). Note that NH ^1H NMR resonances shifted on cooling to 200 K. IR: 3320w, 3251w, 3054w, 1941w, 1882w, 1822w, 1764w, 1587s, 1562 m, 1478s, 1426s, 1416s, 1303s, 1282 m, 1263s, 1180 m, 1147w, 1125w, 1075w, 1067w, 1032w, 988w, 929s, 910 m, 890 m, 833 m, 802w, 756 m, 747s, 736s, 707s, 676w, 649 m, 624w, 613s cm^{-1}.

The ^{15}N-labeled analogue was prepared in a similar manner using *cis*-[RuCl(η^1-$NH_2{}^{15}$NHPh)(dmpe)$_2$]$^+$$BPh_4^-$. ^{15}N NMR (thf-d_8, 30 MHz): δ −287.0 (d, $^2J_{NP}$ 20 Hz, NPh).

***cis*-[Ru(η^2-HNNPh)(dmpe)$_2$] (5).** A suspension of *cis*-[RuCl(η^1-NH_2NHPh)(dmpe)$_2$]$^+$Cl$^-$ (62 mg, 0.11 mmol) and potassium *t*-butoxide (42 mg, 0.37 mmol) was stirred in thf (2 mL) under nitrogen for 15 min. The initial blue-green suspension turned into a bright yellow solution which was then evaporated to dryness in vacuo. The residue was washed with hexane (3 × 2 mL) then extracted with benzene (3 × 2 mL), filtered through Celite and the filtrate evaporated to dryness under vacuum. The yellow-brown tacky solid was recrystallized from benzene-d_6 and pentane to afford *cis*-[Ru(η^2-PhNNH)(dmpe)$_2$] as yellow-brown crystals (0.015 g, 27% yield). $C_{18}H_{38}N_2P_4Ru$ (507.53) requires C, 42.6; H, 7.6; N, 5.5; found, C, 42.7; H, 7.8; N, 5.2%. ^1H NMR (benzene-d_6, 300 MHz): δ 7.72 (b, 1H, **Ph**), 7.38−6.95 (m, 3H, **Ph**), 6.65 (m, 1H, **Ph**), 2.89 (br, 1H, N**H**), 1.48−1.32 (m, 1H, CH_2), 1.41 (d, $^2J_{HP}$ 6 Hz, 3H, CH_3), 1.36 (d, $^2J_{HP}$ 7 Hz, 3H, CH_3), 1.32−1.05 (m, 6H, CH_2), 1.09 (m, 3H, CH_3), 1.01 (m, 3H, CH_3), 0.95−0.84 (m, 4H, CH_2 and CH_3), 0.82 (d, $^2J_{HP}$ 7 Hz, 3H, CH_3), 0.81 (d, $^2J_{HP}$ 6 Hz, 3H, CH_3), 0.78 (m, 3H, CH_3). $^1H\{^{31}P\}$ NMR (benzene-d_6, 300 MHz): δ 7.72 (b, 1H, **Ph**), 7.38−6.95 (m, 3H, **Ph**), 6.65 (m, 1H, **Ph**), 2.89 (br, 1H, N**H**), 1.48−1.32 (m, 1H, CH_2), 1.41 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.31−1.10 (m, 6H, CH_2), 1.09 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 0.92−0.81 (m, 1H, CH_2), 0.86 (s, 3H, CH_3), 0.82 (s, 3H, CH_3), 0.81 (s, 3H, CH_3), 0.78 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (benzene-d_6, 122 MHz): δ 42.8 (m, 1P, P_A), 38.9 (m, 2P, P_B and P_C), 34.1 (m, 1P, P_D). $^{15}N\{^1H\}$ NMR (toluene-d_8, 41 MHz, from HN-HSQC, 193 K): δ −324.4 (corr with ^1H δ 2.62, NH). IR: 3143w, 3064w, 3034w, 1596w, 1578 m, 1549w, 1414w, 1342

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m, 1290w, 1277 m, 1232w, 1148 m, 1064w, 1014w, 995w, 973w, 936 m, 923s, 895 m, 883 m, 865w, 826w, 787w, 743 m, 731 m, 716 m, 697 m, 688 m, 642 m, 630 m cm^{-1}.

The ^{15}N-labeled analogue was prepared in a similar manner using *cis*-[RuCl(η^1-NH_2^{15}NHPh)(dmpe)$_2$]$^+$Cl$^-$. ^{15}N NMR (benzene-d_6, 51 MHz): δ −251.5 (d, $^2J_{NP}$ 14 Hz, **N**Ph). $^{15}N\{^1H\}$ NMR (benzene-d_6, 51 MHz): δ −251.5 (d, $^2J_{NP}$ 14 Hz, **N**Ph). $^{15}N\{^1H, ^{31}P\}$ NMR (benzene-d_6, 51 MHz): δ −251.5 (s, **N**Ph).

***cis*-[RuCl(η^1-NH_2NHMe)(dmpe)$_2$]$^+$X$^-$ (6).** *X = Cl.* Methanol (approximately 0.25 mL) was added to a suspension of *cis*-[$RuCl_2$(dmpe)$_2$] (0.105 g, 0.222 mmol) in thf (2 mL) and methylhydrazine (0.209 g, 4.54 mmol) under nitrogen to give a pale yellow solution. Diethyl ether (10 mL) was added and the mixture left to stand for 6 days. The white precipitate of *cis*-[RuCl(η^1-NH_2NHMe)(dmpe)$_2$]$^+$Cl$^-$ was collected by filtration, washed with diethyl ether, and dried under vacuum (90 mg, 78% yield). This compound was used directly without further purification.

X = BPh_4. A solution of $NaBPh_4$ (39 mg, 0.11 mmol) in methanol (1 mL) was added to a solution of *cis*-[RuCl(η^1-NH_2NHMe)(dmpe)$_2$]$^+$Cl$^-$ (35 mg, 68 μmol) in methanol (1 mL) under nitrogen. The white microcrystalline precipitate of *cis*-[RuCl(η^1-NH_2NHMe)(dmpe)$_2$]$^+$$BPh_4^-$ formed was collected by filtration, washed with methanol (3 × 1.5 mL), and dried in vacuo (52 mg, 95% yield). $C_{37}H_{58}BClN_2P_4Ru$ (802.18) requires C, 55.4; H, 7.3; N, 3.5; found, C, 55.7; H, 7.5; N, 3.4%. ^1H NMR (thf-d_8, 400 MHz): δ 7.28 (m, 8H, ***o*-PhB**), 6.86 (m, 8H, ***m*-PhB**), 6.71 (m, 4H, ***p*-PhB**), 4.29 (bm, 2H, N**H**$_2$), 4.04 (m, 1H, N**H**Me), 2.53 (d, $^3J_{HH}$ 6.4 Hz, 3H, NC**H**$_3$), 1.91−1.68 (m, 5H, C**H**$_2$), 1.68−1.53 (m, 2H, C**H**$_2$), 1.60 (dd, $^2J_{HH}$ 9.2 Hz, $^2J_{HH}$ 1.6 Hz, 3H, C**H**$_3$), 1.53−1.45 (m, 10H, C**H**$_2$, 3 × C**H**$_3$), 1.37 (d, $^2J_{HH}$ 9.9 Hz, 3H, C**H**$_3$), 1.30 (d, $^2J_{HH}$ 8.5 Hz, 3H, C**H**$_3$), 1.26 (d, $^2J_{HH}$ 8.1 Hz, 3H, C**H**$_3$), 1.18 (d, $^2J_{HH}$ 8.3 Hz, 3H, C**H**$_3$). $^1H\{^{31}P\}$ NMR (thf-d_8, 400 MHz): δ 7.28 (m, 8H, ***o*-PhB**), 6.86 (m, 8H, ***m*-PhB**), 6.71 (m, 4H, ***p*-PhB**), 4.29 (m, 2H, N**H**$_2$), 4.04 (m, 1H, N**H**Me), 2.53 (d, $^3J_{HH}$ 6.4 Hz, 3H, NC**H**$_3$), 1.91−1.68 (m, 5H, C**H**$_2$), 1.68−1.53 (m, 2H, C**H**$_2$), 1.60 (s, 3H, C**H**$_3$), 1.53−1.45 (m, 1H, C**H**$_2$), 1.51 (s, 3H, C**H**$_3$), 1.48 (s, 3H, C**H**$_3$), 1.46 (s, 3H, C**H**$_3$), 1.37 (s, 3H, C**H**$_3$), 1.30 (s, 3H, C**H**$_3$), 1.26 (s, 3H, C**H**$_3$), 1.18 (s, 3H, C**H**$_3$). $^{31}P\{^1H\}$ NMR (thf-d_8, 162 MHz): δ 51.4 (ddd, $^2J_{AB}$ 32.6 Hz, $^2J_{AC}$ 15.6 Hz, $^2J_{AD}$ 25.1 Hz, 1P, **P$_A$**), 44.6 (ddd, $^2J_{BC}$ 29.3 Hz, $^2J_{BD}$ 16.5 Hz, 1P, **P$_B$**), 39.8 (ddd, $^2J_{CD}$ 298.3 Hz, 1P, **P$_C$**), 33.5 (ddd, 1P, **P$_D$**). $^{15}N\{^1H\}$ NMR (thf-d_8, 41 MHz, from HN-HSQC): δ −308.2 (corr with ^1H δ 4.04, **N**HMe), −335.6 (corr with ^1H δ 4.29, **N**H$_2$). IR: 3307w, 3292w, 3258 m, 3163w, 3053 m, 3030 m, 1614w, 1578 m, 1421 m, 1304 m, 1292 m, 1281 m, 1267w, 1256w, 1242w, 1199w, 1129 m, 1071w, 1032w, 937s, 930s, 912 m, 891s, 838 m, 803w, 749s, 735s, 705s, 647 m, 610s cm^{-1}. MS (ESI, acetonitrile): *m/z* 483.0697 [45%, (RuCl(NH_2NHMe)(dmpe)$_2$)$^+$], 478.0444 [100, (RuCl(dmpe)$_2$(CH_3CN))$^+$], 437.0175 [93, (RuCl(dmpe)$_2$)$^+$].

***cis*-[Ru(η^2-HNNMe)(dmpe)$_2$] (8).**[41] A suspension of *cis*-[RuCl(η^1-NH_2NHMe)(dmpe)$_2$]$^+$Cl$^-$ (33 mg, 64 μmol) and potassium *t*-butoxide (40 mg, 0.36 mmol) was stirred in thf (2 mL) under nitrogen for 5 min. The resulting pale yellow solution was evaporated to dryness in vacuo. The residue was extracted with heptane (3 × 2 mL), filtered through Celite, and the filtrate evaporated to dryness under vacuum to afford *cis*-[Ru(η^2-HNNMe)(dmpe)$_2$] as a yellow solid (0.013 g, 46% yield). ^1H NMR (toluene-d_8, 400 MHz): δ 3.9 (br, 1H, N**H**), 3.22 (d, $^4J_{HP}$ 7 Hz, 3H, NC**H**$_3$), 1.65−1.44 (m, 2H, C**H**$_2$), 1.39 (m, 9H, C**H**$_3$), 1.35−1.16 (m, 4H, C**H**$_2$), 1.12 (d, $^2J_{HP}$ 7 Hz, 3H, C**H**$_3$), 1.05 (d, $^2J_{HP}$ 3 Hz, 3H, C**H**$_3$), 1.00 (d, $^2J_{HP}$ 6 Hz, 3H, C**H**$_3$), 0.89 (d, $^2J_{HP}$ 6 Hz, 3H, C**H**$_3$), 0.84 (d, $^2J_{HP}$ 4 Hz, 3H, C**H**$_3$), 0.87−0.63 (m, 2H, C**H**$_2$). $^1H\{^{31}P\}$ NMR (toluene-d_8, 400 MHz): δ 3.91 (br, 1H, N**H**), 3.22 (s, 3H, NC**H**$_3$), 1.54 (m, 2H, C**H**$_2$), 1.39 (s, 3H, C**H**$_3$), 1.38 (s, 6H, C**H**$_3$), 1.36−1.16 (m, 4H, C**H**$_2$), 1.12 (s, 3H, C**H**$_3$), 1.05 (s, 3H, C**H**$_3$), 1.00 (s, 3H, C**H**$_3$), 0.89 (s, 3H, C**H**$_3$), 0.84 (s, 3H, C**H**$_3$), 0.87−0.77 (m, 1H, C**H**$_2$), 0.70 (m, 1H, C**H**$_2$). $^{31}P\{^1H\}$ NMR (toluene-d_8, 162 MHz): δ 39.2 (m, 1P, **P$_A$**), 36.0 (m, 2P, **P$_B$** and **P$_C$**), 33.9 (m, 1P, **P$_D$**). $^{15}N\{^1H\}$ NMR (toluene-d_8, 41 MHz, from HN-HSQC, 193 K): δ −289.5 (corr with ^1H δ 3.9, **N**H). $^{15}N\{^1H\}$ NMR (toluene-d_8, 41 MHz, from HN-HMBC, 193 K): δ −289.2 (corr with ^1H δ 3.48, **N**H), −281.7 (corr with ^1H δ 3.48, **N**CH$_3$). $^{15}N\{^1H\}$ NMR (thf-d_8, 51 MHz, from HN-HMBC, 298 K): δ −286.7 (corr with ^1H δ 2.77, **N**H), −277.3 (corr with ^1H δ 2.77, **N**CH$_3$). IR: 3172w, 2723w, 1767w, 1574w, 1415s, 1287 m, 1272s, 1213w, 1169w, 1121 m, 1055 m, 983w, 928s, 903s, 883s, 830s, 792 m, 720s, 701s, 684s, 642s cm^{-1}. MS (ESI, thf): *m/z* 996.1839 [25%], 908.0847 [30], 864.0952 [40], 547.1110 [40], 505.0890 [50], 447.0471 [100, (Ru(HNNMe)(dmpe)$_2$H)$^+$], 433.0319 [90], 403.0575 [43, (RuH(dmpe)$_2$)$^+$].

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files for **1**, **3**, **4**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Lukoyanov, D.; Dikanov, S. A.; Yang, Z.-Y.; Barney, B. M.; Samoilova, R. I.; Narasimhulu, K. V.; Dean, D. R.; Seefeldt, L. C.; Hoffman, B. M. *J. Am. Chem. Soc.* **2011**, *133*, 11655.

(2) Parshall, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 1822. Gilchrist, A. B.; Rayner-Canham, G. W.; Sutton, D. *Nature* **1972**, *235*, 42.

(3) Field, L. D.; Li, H. L.; Dalgarno, S. J.; Turner, P. *Chem. Commun.* **2008**, 1680.

(4) Field, L. D.; Li, H. L.; Magill, A. M. *Inorg. Chem.* **2009**, *48*, 5.

(5) Field, L. D.; Li, H. L.; Dalgarno, S. J. *Inorg. Chem.* **2010**, *49*, 6214.

(6) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 4080.

(7) Kosower, E. M. *Acc. Chem. Res.* **1971**, *4*, 193.

(8) Kosower, E. M.; Huang, P. C. *J. Am. Chem. Soc.* **1965**, *87*, 4645. Vidyarthi, S. K.; Willis, C.; Back, R. A. *J. Phys. Chem.* **1976**, *80*, 559.

(9) Ackermann, M. A.; Hallmark, M. R.; Hammond, S. K.; Roe, A. N. *Inorg. Chem.* **1972**, *11*, 3076.

(10) Parshall, G. W. *J. Am. Chem. Soc.* **1965**, *87*, 2133.

(11) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Chem. Commun.* **1973**, 176. Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3052.

(12) Croatto, U.; Toniolo, L.; Immirzi, A.; Bombieri, G. *J. Organomet. Chem.* **1975**, *102*, C31.

(13) Mason, R.; Thomas, K. M.; Zubieta, J. A.; Douglas, P. G.; Galbraith, A. R.; Shaw, B. L. *J. Am. Chem. Soc.* **1974**, *96*, 260.

(14) Einstein, F. W. B.; Sutton, D. *J. Chem. Soc., Dalton Trans.* **1973**, 434.

(15) Smith, M. R.; Keys, R. L.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8312. Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Dolcetti, P. M.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1997**, 4435. Albertin, G.; Antoniutti, S.; Bordignon, E.; Pattaro, S. *J. Chem. Soc., Dalton Trans.* **1997**, 4445. Albertin, G.; Antoniutti, S.; Bacchi, A.; Bergamo, M.; Bordignon, E.; Pelizzi, G. *Inorg. Chem.* **1998**, *37*, 479.

(16) Schollhammer, P.; Guénin, E.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W.; Yufit, D. S. *Organometallics* **1998**, *17*, 1922. Chen, Y.; Zhou, Y.; Chen, P.; Tao, Y.; Li, Y.; Qu, J. *J. Am. Chem. Soc.* **2008**, *130*, 15250.

(17) Kopka, K.; Mattes, R. *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 1675.

(18) Korner, V.; Huttner, G.; Vogel, S.; Barth, A.; Zsolnai, L. *Chem. Ber./Recueil* **1997**, *130*, 489.

(19) Vela, J.; Stoian, S.; Flaschenriem, C. J.; Münck, E.; Holland, P. L. *J. Am. Chem. Soc.* **2004**, *126*, 4522.

(20) Dilworth, J. R.; Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Chem. Commun.* **1983**, 1368.
(21) Hughes, D. L.; Leigh, G. J.; Walker, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, 1413.
(22) Howard, W. A.; Waters, M.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4917.
(23) Carroll, J. A.; Sutton, D.; Cowie, M.; Gauthier, M. D. *J. Chem. Soc., Chem. Commun.* **1979**, 1058.
(24) Leigh, G. J.; Jimenez-Tenorio, M. *J. Am. Chem. Soc.* **1991**, *113*, 5862. Hall, D. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1996**, 3539.
(25) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369. Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *Inorg. Chem.* **1988**, *27*, 829. Albertin, G.; Antoniutti, S.; Bordignon, E.; Pelizzi, G.; Vitali, F. *J. Organomet. Chem.* **1988**, *353*, 229.
(26) End-on (η^1) aryldiazenes: Ittel, S. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4804. Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369. Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *J. Am. Chem. Soc.* **1986**, *108*, 6627. Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *Inorg. Chem.* **1988**, *27*, 829. Albertin, G.; Antoniutti, S.; Bordignon, E.; Pelizzi, G.; Vitali, F. *J. Organomet. Chem.* **1988**, *353*, 229. Peters, J. C.; Hillhouse, G. L.; Rheingold, A. L. *Polyhedron* **1994**, *13*, 1741. Cook, J.; Davison, A.; Davis, W. M.; Jones, A. G. *Organometallics* **1995**, *14*, 650. Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1996**, *35*, 6245. Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Busatto, F.; Pelizzi, G. *Inorg. Chem.* **1997**, *36*, 1296. Albertin, G.; Antoniutti, S.; Bacchi, A.; Ballico, G. B.; Bordignon, E.; Pelizzi, G.; Ranieri, M.; Ugo, P. *Inorg. Chem.* **2000**, *39*, 3265. Melenkivitz, R.; Southern, J. S.; Hillhouse, G. L.; Concolino, T. E.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12068. Albertin, G.; Antoniutti, S.; Bedin, M.; Castro, J.; Garcia-Fontán, S. *Inorg. Chem.* **2006**, *45*, 3816. End-on (η^1) ortho-metallated aryldiazenes: Bellon, P. L.; Caglio, G.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1974**, 897. Carroll, J. A.; Cobbledick, R. E.; Einstein, F. W. B.; Farrell, N.; Sutton, D.; Vogel, P. L. *Inorg. Chem.* **1977**, *16*, 2462. Bellon, P. L.; Demartin, F.; Manassero, M.; Sansoni, M.; Caglio, G. *J. Organomet. Chem.* **1978**, *157*, 209.
(27) Hsieh, T.-C.; Zubieta, J. *Inorg. Chim. Acta* **1987**, *127*, L31. Chilou, V.; Gouzerh, P.; Jeannin, Y.; Olivarès, G.; Robert, F.; Hsieh, T.-C.; Zubieta, J. *Polyhedron* **1989**, *8*, 29. Coucouvanis, D.; Mosier, P. E.; Demadis, K. D.; Patton, S.; Malinak, S. M.; Kim, C. G.; Tyson, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 12193. Hitchcock, P. B.; Hughes, D. L.; Maguire, M. J.; Marjani, K.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1997**, 4747. Murray, H. H.; Novick, S. G.; Armstrong, W. H.; Day, C. S. *J. Cluster Sci.* **1993**, *4*, 439. Hills, A.; Hughes, D. L.; Leigh, G. J.; Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **1991**, 325.
(28) Davies, C. J.; Dodd, I. M.; Harding, M. M.; Heaton, B. T.; Jacob, C.; Ratnam, J. *J. Chem. Soc., Dalton Trans.* **1994**, 787.
(29) Yelle, R. B.; Crossland, J. L.; Szymczak, N. K.; Tyler, D. R. *Inorg. Chem.* **2009**, *48*, 861. Saouma, C. T.; Moore, C. E.; Rheingold, A. L.; Peters, J. C. *Inorg. Chem.* **2011**, *50*, 11285.
(30) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; John Wiley: Hoboken, NJ, 2005; Powell, P. *Principles of Organometallic Chemistry*, 2nd ed.; Chapman and Hall: London, U.K., 1988.
(31) Snyder, L. C.; Meiboom, S. *J. Chem. Phys.* **1967**, *47*, 1480.
(32) Bastianson, O.; Fritsch, F. N.; Hedberg, K. *Acta Crystallogr.* **1964**, *17*, 538.
(33) Blanca, M. B.-D.; Maimon, E.; Kost, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2216.
(34) Demaison, J.; Hegelund, F.; Burger, H. *J. Mol. Struct.* **1997**, *413*−*414*, 447. Jensen, H. J. A.; Jorgensen, P.; Helgaker, T. *J. Am. Chem. Soc.* **1987**, *109*, 2895. Schaad, L. J.; Kinser, H. B. *J. Phys. Chem.* **1969**, *73*, 1901.
(35) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146. Bouwstra, J. A.; Schouten, A.; Kroon, J. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39*, 1121. Harada, J.; Ogawa, K.; Tomoda, S. *Acta Crystallogr., Sect. B: Struct. Sci.* **1997**, *53*, 662. Harada, J.; Ogawa, K. *J. Am. Chem. Soc.* **2004**, *126*, 3539.
(36) Goedken, V. L.; Peng, S.-M. *Chem. Commun.* **1975**, 258. Sellmann, D.; Waeber, M. *Z. Naturforsch., B: Chem. Sci.* **1986**, *41*, 877. Barkley, J. V.; Heaton, B. T.; Jacob, C.; Mageswaran, R.; Sampanthar, J. T. *J. Chem. Soc., Dalton Trans.* **1998**, 697. Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Miani, F.; Pelizzi, G. *Inorg. Chem.* **2000**, *39*, 3283. Redman, J. E.; Feeder, N.; Teat, S. J.; Sanders, J. K. M. *Inorg. Chem.* **2001**, *40*, 3217. Albertin, G.; Antoniutti, S.; Bortoluzzi, M.; Castro-Fojo, J.; Garcia-Fontan, S. *Inorg. Chem.* **2004**, *43*, 4511. Dabb, S. L.; Messerle, B. A.; Otting, G.; Wagler, J.; Willis, A. *Chem.—Eur. J.* **2008**, *14*, 10058.
(37) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.
(38) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 5507.
(39) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 896.
(40) Axenrod, T.; Watnick, C. M.; Wieder, M. J. *Org. Magn. Reson.* **1979**, *12*, 476.
(41) Satisfactory microanalysis could not be obtained because of thermal instability of the compound.