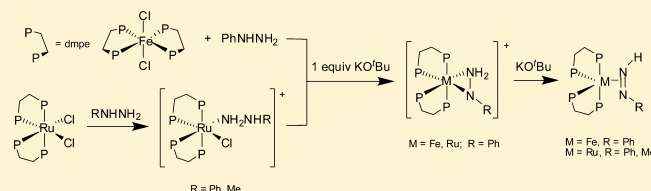


Side-on Bound Complexes of Phenyl- and Methyl-diazene

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S Supporting Information

ABSTRACT: Treatment of *trans*-[FeCl₂(dmpe)₂] with phenylhydrazine and 1 equiv of base afforded the side-on bound phenylhydrazido complex *cis*-[Fe(η²-NH₂NPh)(dmpe)₂]⁺. Further deprotonation of the phenylhydrazido complex afforded the side-on bound phenyldiazene complex *cis*-[Fe(η²-HN=NPh)(dmpe)₂] as a mixture of diastereomers. Treatment of *cis*-[RuCl₂(dmpe)₂] with phenylhydrazine or methylhydrazine afforded the end-on bound phenylhydrazine or methylhydrazine complexes *cis*-[RuCl(η¹-NH₂NHR)(dmpe)₂]⁺ (R = Ph, Me). Treatment of the substituted hydrazine complexes with base afforded the side-on bound phenylhydrazido complex *cis*-[Ru(η²-NH₂NPh)(dmpe)₂]⁺ as well as the phenyldiazene and methyl-diazene complexes *cis*-[Ru(η²-HN=NR)(dmpe)₂] (R = Ph, Me). *cis*-[RuCl(η¹-NH₂NHR)(dmpe)₂]⁺ (R = Ph, Me), *cis*-[M(η²-NH₂NPh)(dmpe)₂]⁺ (M = Fe, Ru) and *cis*-[Ru(η²-HN=NPh)(dmpe)₂] were characterized structurally by X-ray crystallography. *cis*-[Ru(η²-HN=NPh)(dmpe)₂] is the first side-on bound phenyldiazene complex to be structurally characterized. In the structure of *cis*-[Ru(η²-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 N₂H_x species such as hydrazine (N₂H₄), hydrazide (N₂H₃⁻), and diazene (N₂H₂) 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 N₂H_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(η²-NH=NH)(dmpe)₂] (dmpe = 1,2-bis(dimethylphosphino)ethane) from the side-on bound hydrazine complex *cis*-[Fe(η²-N₂H₄)(dmpe)₂]²⁺ either by reduction with potassium graphite³ 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(η²-NPh=NPh)(dmpe)₂]⁶ is stable, and we initially targeted a synthesis of side-on bound phenyldiazene and methyl-diazene 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 methyl-diazene 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 Methyl-diazene 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 bond¹⁰ 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 aryldiazene 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 aryldiazene complexes on iridium, spontaneous hydrogenation of aryldiazene ligands can also occur via ortho-metalation of the aryl ring.¹⁴ Aryl- and methyl-diazene complexes have also been formed by the selective oxidation

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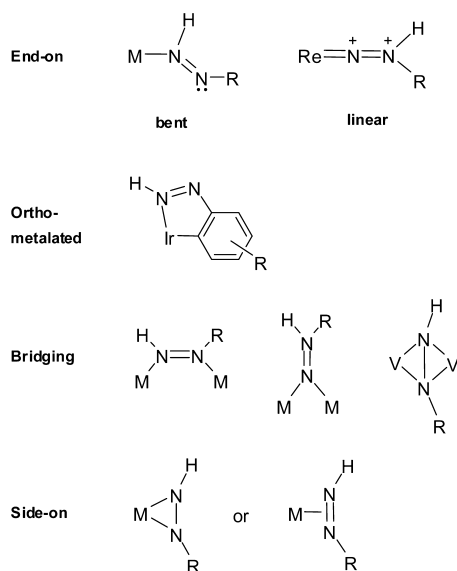


Figure 1. Binding modes of aryl and alkyl substituted diazene complexes.

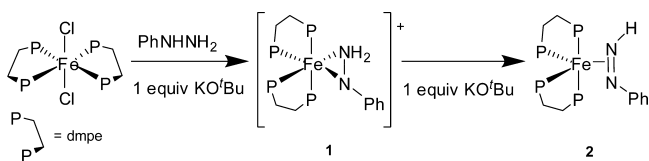
of the corresponding hydrazine complexes with $\text{Pb}(\text{OAc})_4$.¹⁵ Bridging phenyl- and methylhydrazine complexes have also been reported with both bent and linear (isodiazene) forms¹⁶ as well as a simultaneously bridging and side-on phenyldiazene complex of vanadium (Figure 1).¹⁷

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*- $[\text{FeCl}_2(\text{dmpe})_2]$ and phenylhydrazine in tetrahydrofuran (thf) afforded red crystals of the phenylhydrazido(1-) complex *cis*- $[\text{Fe}(\eta^2\text{-NH}_2\text{NPh})(\text{dmpe})_2]^+\text{Cl}^-$ (**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–NH₂ bond (1.998(4) Å) and Fe–N bonds in side-on bound hydrazine *cis*- $[\text{Fe}(\eta^2\text{-N}_2\text{H}_4)(\text{dmpe})_2]^{2+}$, diazene *cis*- $[\text{Fe}(\eta^2\text{-NH=NH})(\text{dmpe})_2]$, and azobenzene *cis*- $[\text{Fe}(\eta^2\text{-NPh=NPh})(\text{dmpe})_2]$ complexes (1.981(2)–2.032(7) Å)³ as well as the Fe–NPh bond in $[(\text{LFe})_2(\mu\text{-S})(\mu\text{-NH}_2\text{NPh})]$ (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

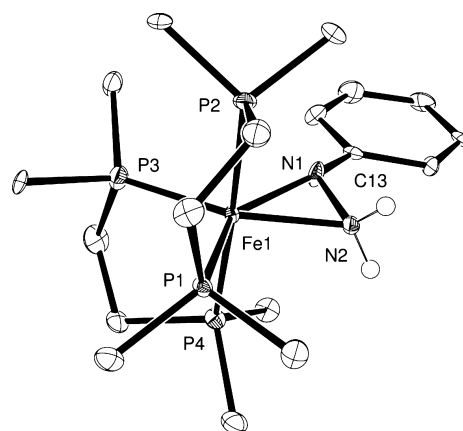


Figure 2. ORTEP plot of *cis*- $[\text{Fe}(\eta^2\text{-NH}_2\text{NPh})(\text{dmpe})_2]^+\text{Cl}^-$ (**1**, 50% displacement ellipsoids, chloride counterion, thf solvate, and carbon-bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Fe1–N1 1.939(4), Fe1–N2 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 $[(\text{LFe})_2(\mu\text{-S})(\mu\text{-NH}_2\text{NPh})]$ (L = (HC(CMeN(2,6-diisopropylphenyl))₂)[–])¹⁹ and side-on phenylhydrazido ligands in $[\text{Ti}(\text{Cp})\text{Cl}_2(\eta^2\text{-NH}_2\text{NPh})]$,²⁰ $[\text{Ti}(\text{L}')\text{Cl}_2(\eta^2\text{-NH}_2\text{NPh})]$ (L' = tris-(pyrazolyl)borate),²¹ and $[\text{Zr}(\text{Cp}^*)_2(\text{OH})(\eta^2\text{-NH}_2\text{NPh})]$ ²² although unlike that in $[\text{W}(\text{Cp})_2(\eta^2\text{-NH}_2\text{NPh})]^{+23}$ 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*- $[\text{Fe}(\eta^2\text{-NH}_2\text{NPh})(\text{dmpe})_2]^+$ (**1**) is entirely consistent with the structure depicted in Figure 2. Four ddd signals were observed in the $^{31}\text{P}\{^1\text{H}\}$ 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 (NH₂). A ^{15}N signal at δ –299.0 for NPh is observed when the ligand is $^{15}\text{N}_2$ -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*- $[\text{Fe}(\eta^2\text{-HN=NPh})(\text{dmpe})_2]$ (**2**) as the major product (Scheme 1). Small amounts of byproducts including $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$ ²⁴ and $[\{\text{Fe}(\text{dmpe})_2\}_2(\mu\text{-dmpe})]$ ⁶ are also formed, presumably because of decomposition of the phenyldiazene complex.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of *cis*- $[\text{Fe}(\eta^2\text{-HN=NPh})(\text{dmpe})_2]$ (**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).

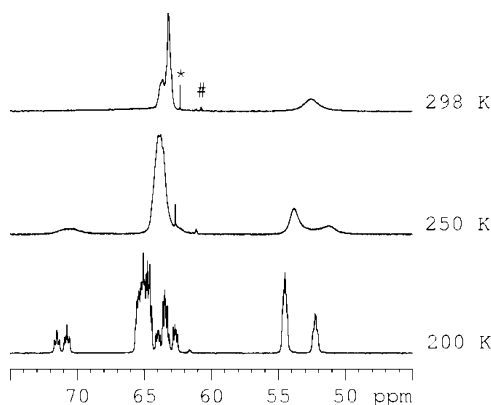


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{cis-}[\text{Fe}(\eta^2\text{-HN=NPh})(\text{dmpe})_2]$ (**2**, toluene- d_8 , 243 MHz, * = $[\text{Fe}(\text{N}_2)(\text{dmpe})_2]$; # = $[\{\text{Fe}(\text{dmpe})_2\}_2(\mu\text{-dmpe})]$).

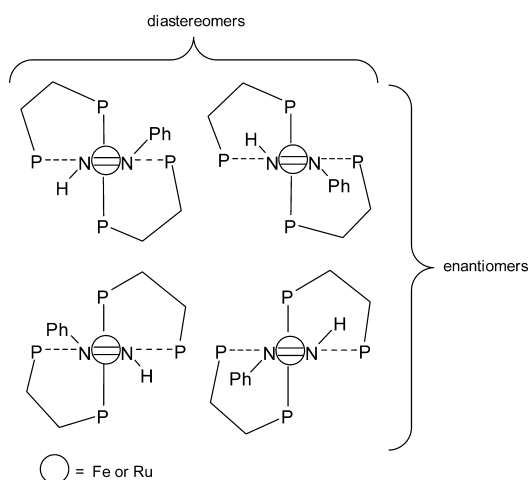


Figure 4. Diastereomers and enantiomers of $[\text{M}(\eta^2\text{-HN=NPh})(\text{dmpe})]$ ($\text{M} = \text{Fe}$ **2**, Ru **5**).

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 $\text{trans-}[\text{FeCl}_2(\text{dmpe})_2]$ and methylhydrazine in the presence of KO^tBu 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 $\text{cis-}[\text{RuCl}_2(\text{dmpe})_2]$ with excess phenylhydrazine in thf resulted in the substitution of one chloride ligand with phenylhydrazine to afford the phenylhydrazine complex $\text{cis-}[\text{RuCl}(\eta^1\text{-NH}_2\text{NHP})(\text{dmpe})_2]^+$ (**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 $^{31}\text{P}\{^1\text{H}\}$ 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 NHP 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).

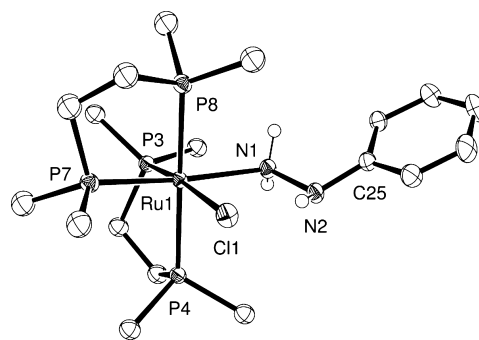
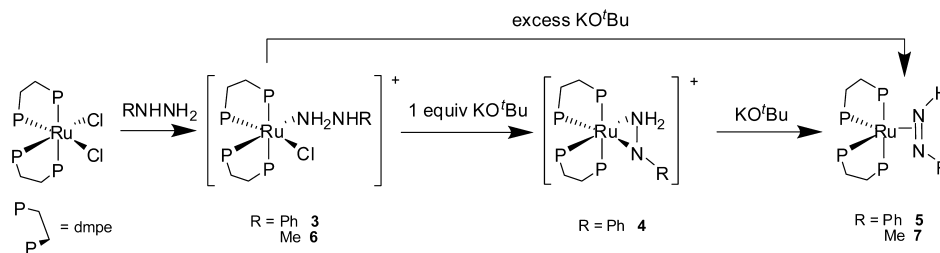


Figure 5. ORTEP plot of $\text{cis-}[\text{RuCl}(\eta^1\text{-NH}_2\text{NHP})(\text{dmpe})_2]^+\text{BPh}_4^-$ (**3**, 50% displacement ellipsoids, BPh_4^- counterion, atoms of less than 50% occupancy and carbon bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (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



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^tBu base in thf afforded a mixture of unreacted starting material, the phenylhydrazide complex $\text{cis-}[\text{RuCl}(\eta^2\text{-PhNNH}_2)(\text{dmpe})_2]^+\text{Cl}^-$ (**4**), and the phenyldiazene complex $\text{cis-}[\text{RuCl}(\eta^2\text{-PhN=NH})(\text{dmpe})_2]$ (**5**) as well as $\text{cis-}[\text{RuCl}_2(\text{dmpe})_2]$ 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 $\text{cis-}[\text{RuCl}(\eta^2\text{-NH}_2\text{NPh})(\text{dmpe})_2]^+\text{BPh}_4^-$ (**4**). The signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum are heavily overlapped; however, the eight singlets in the $^1\text{H}\{^{31}\text{P}\}$ 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 ^1H - ^{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

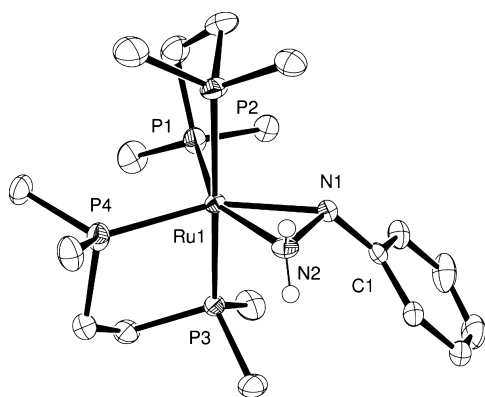


Figure 6. ORTEP plot of $\text{cis-}[\text{Ru}(\eta^2\text{-NH}_2^{15}\text{NPh})(\text{dmpe})_2]^+\text{BPh}_4^-$ (**4**, 50% displacement ellipsoids, BPh_4^- counterion and carbon bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Ru1–N2 2.126(3), Ru1–N1 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 $[\text{W}(\text{Cp})_2(\eta^2\text{-NH}_2\text{NPh})]^+$,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–NH₂ bond (2.126(3) Å) unlike all other reported phenylhydrazide complexes where in general the M–NPh bonds are shorter than the M–NH₂ 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 $\text{cis-}[\text{Ru}(\eta^2\text{-HN=NH})(\text{dmpe})_2]$ (**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

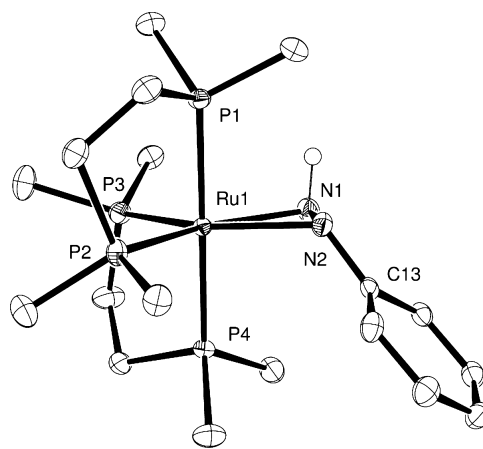


Figure 7. ORTEP plot of $\text{cis-}[\text{RuCl}(\eta^2\text{-HN=NH})(\text{dmpe})_2]$ (**5**, 50% displacement ellipsoids, carbon bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Ru1–N2 2.1238(16), Ru1–N1 2.1477(16), N1–N2 1.425(2), N2–C13 1.383(2), N2–Ru1–N1 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 $[\text{Ru}(\eta^2\text{-NH=NH})(\text{PP})_2]$ (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 ($\mu\text{-}\eta^1\text{:}\eta^1$)¹⁶ or side-on bridging ($\mu\text{-}\eta^2\text{:}\eta^2$)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

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
<i>cis</i> -Fe(NH=NH)(dmpe) ₂	1.427(7)	156(5)	3
	1.398(8)	149(5)	
<i>cis</i> -Fe(PhN=NPh)(dmpe) ₂	1.412(4)	113.9(2)	3
<i>cis</i> -Ru(NH=NH)(dmpe) ₂	1.427(3)	162(2)	5
<i>cis</i> -Ru(NH=NH)(depe) ₂	1.414(5)	168(4)	5
<i>cis</i> -Ru(PhN=NPh)(dmpe) ₂	1.425(2)	137.2(2)	this work
<i>trans</i> -NH=NH	1.247, 1.266, 1.28	180	34
<i>trans</i> -PhN=NPh	1.173–1.259	180	35

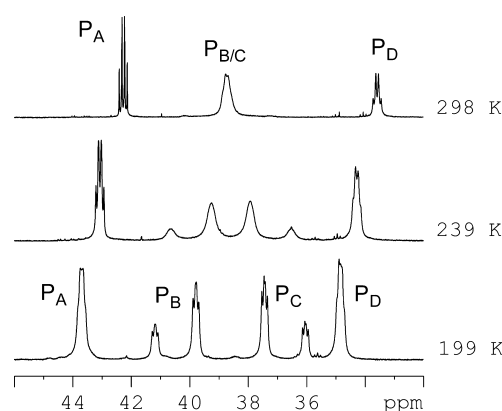
(ML₄N₂H₂²⁻).²⁹ Table 1 indicates that, in all cases, the N–N bond is longer when diazene is complexed than it is in free diazene. In *cis*-[Ru(PhN=NPh)(dmpe)₂](5), the torsional angle C–N–N–H (137.2(2)°) deviates very significantly from planarity suggesting that 5 should be viewed as more like a metallodiaziridine 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 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 solution³¹ 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 sp² hybridized) to those where the torsional angle approaches the tetrahedral angle and the complexes are better described as metallodiaziridines.

In the ¹H{³¹P} 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 ³¹P{¹H} 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 ³¹P 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) ¹H-¹⁵N HSQC experiment for 5 showed a correlation between the NH proton resonance at δ 2.62 and a ¹⁵N signal at δ -324.4. The ¹⁵N signal for NPh resonates at δ -251.5 for the ¹⁵N-labeled analogue, and this

**Figure 8.** ³¹P{¹H} 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 ¹⁵N resonance exhibits a 14 Hz coupling to ³¹P and in the ³¹P{¹H} NMR spectrum, P_A exhibits the reciprocal coupling to ¹⁵N indicating that P_A is the signal for the phosphorus atom *trans* to NPh.

Ruthenium Methylhydrazine and Methylidiazene Complexes. Treatment of *cis*-[RuCl₂(dmpe)₂] with excess methylhydrazine in a mixture of thf and methanol afforded the methylhydrazine complex *cis*-[RuCl(η^1 -NH₂NHMe)(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 NH₂ 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 NaBPh₄ in methanol. In the ³¹P{¹H} 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 ¹H-¹⁵N HSQC experiment, the ¹H signal at 4.29 ppm, which integrates to two protons, correlates to a ¹⁵N signal at -335.6 ppm for NH₂ while the ¹H signal at 4.04 ppm correlates to a ¹⁵N signal at -308.2 ppm for the NHMe group.

Attempted monodeprotonation of the methylhydrazine complex 6 with 1 equiv of KO^tBu afforded a complex mixture of products. Treatment with excess KO^tBu base, however, afforded the side-on bound methylidiazene complex *cis*-[RuCl(η^2 -HN=NMe)(dmpe)₂] (7) as the major product and a small amount of [RuH₂(dmpe)₂]⁶ byproduct (Scheme 2). The ³¹P{¹H} NMR spectrum contains multiplets that are overlapping and severely distorted by second order effects. In

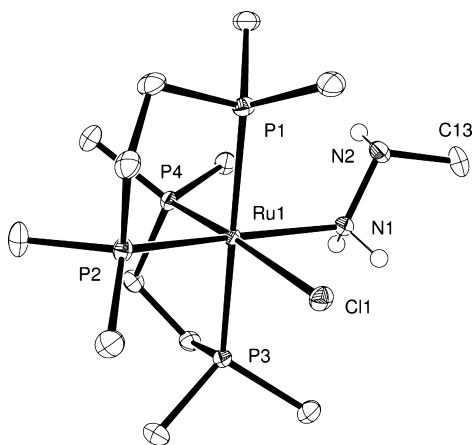


Figure 9. ORTEP plot of *cis*-[RuCl(η^1 -NH₂NHMe)(dmpe)₂]⁺Cl[−] (**6**, 50% displacement ellipsoids, Cl counterion, carbon bound hydrogen atoms have been excluded for clarity). Selected bond lengths (Å) and angles (deg): Ru1–N1 2.1965(18), N1–N2 1.458(3), N2–C13 1.468(3), N2–N1–Ru1 119.57(14), N1–N2–C13 109.74(19).

the ¹H{³¹P} 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-¹⁵N HSQC experiment at 193 K, the ¹H resonance at δ 3.9 correlates with a ¹⁵N signal at δ −289.5 for NH (Figure 10a). Whereas in the ¹H-¹⁵N HMBC (Heteronuclear Multiple Bond Correlation) experiment, the NMe ¹H resonance correlates to two ¹⁵N signals at δ −286.7 and −277.3 ppm for NH and NMe respectively (Figure 10b). The methylidiazene 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 (³¹P{¹H} δ 45.8, 39.9, 33.2, 27.1) as the major product with concomitant release of methane (¹H δ 0.15, ¹³C 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 methyl-diazene complexes are the first known side-on bound complexes of substituted diazenes. The complexes have been thoroughly characterized by NMR spectroscopy (¹H, ³¹P, and ¹⁵N) 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 methylidiazene 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 sp² 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 sp³ 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*-[FeCl₂(dmpe)₂] was prepared according to the literature method.³⁸ *cis*-[RuCl₂(dmpe)₂] was prepared

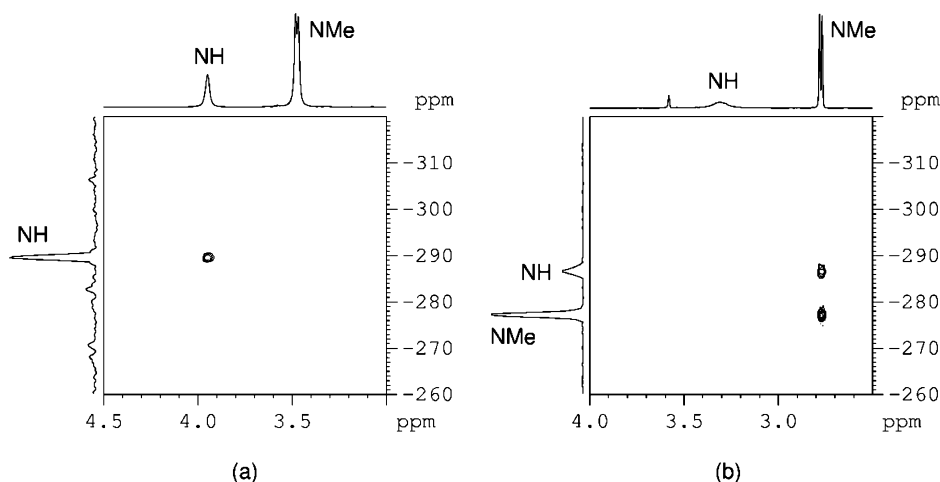


Figure 10. (a) ¹H-¹⁵N HSQC spectrum (toluene-*d*₈, 193 K, 400 and 41 MHz) (b) ¹H-¹⁵N HMBC spectrum (thf-*d*₈, 298 K, 500 and 51 MHz) of *cis*-[RuCl(η^2 -HN=NMe)(dmpe)₂] (**7**).

Table 2. Crystallographic Details for *cis*-[Fe(η^2 -NH₂NPh)(dmpe)₂]⁺Cl[−] (1), *cis*-[RuCl(η^1 -NH₂NHPh)(dmpe)₂]⁺BPh₄[−] (3), *cis*-[Ru(η^2 -NH₂¹⁵NPh)(dmpe)₂]⁺BPh₄[−] (4), *cis*-[Ru(η^2 -HN=NPh)(dmpe)₂] (5), and *cis*-[RuCl(η^1 -NH₂NHMe)(dmpe)₂]⁺Cl[−] (6)

	1	3	4	5	6
formula	C ₂₂ H ₄₇ ClFeN ₂ OP ₄	C ₄₆ H ₇₈ BClN ₂ OP ₄ Ru	C ₄₂ H ₅₉ BN ₂ P ₄ Ru	C ₁₈ H ₃₈ N ₂ P ₄ Ru	C ₂₆ H ₇₆ Cl ₄ N ₄ P ₈ Ru ₂
<i>M</i> (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	<i>P</i> ₂ ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> ₂ ₁	<i>P</i> ₂ ₁ / <i>c</i>	<i>P</i> ₂ ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	17.260(2)	39.212(3)	10.0354(13)	14.5109(8)	13.5246(6)
<i>b</i> (Å)	13.4299(16)	9.8714(7)	16.150(2)	8.6862(4)	13.7540(6)
<i>c</i> (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
<i>V</i> (Å ³)	2786.7(6)	8959.2(11)	2087.8(5)	2333.0(2)	4568.2(4)
<i>Z</i>	4	8	2	4	4
<i>D</i> _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
<i>F</i> ₀₀₀	1216	4016	868	1056	2144
2 θ _{max} (deg)	58.1	51.4	54.7	52.7	54.4
reflections collected	7171	57171	20297	17917	68743
independent reflections	7173 (<i>R</i> _{int} = 0.0464)	8489 (<i>R</i> _{int} = 0.0398)	9633 (<i>R</i> _{int} = 0.0401)	4752 (<i>R</i> _{int} = 0.0261)	9989 (<i>R</i> _{int} = 0.0348)
observed reflections	4115 [<i>I</i> > 2 σ (<i>I</i>)]	7337 [<i>I</i> > 2 σ (<i>I</i>)]	8610 [<i>I</i> > 2 σ (<i>I</i>)]	4329 [<i>I</i> > 2 σ (<i>I</i>)]	9326 [<i>I</i> > 2 σ (<i>I</i>)]
final GOF	1.010	1.049	1.052	1.019	1.029
<i>R</i> ₁	0.0714	0.0335	0.0444	0.0228	0.0226
<i>wR</i> ₂	0.1100	0.0770	0.0857	0.0522	0.0452

by heating a mixture of [Ru(PMe₂Ph)₃]₂(μ-Cl)₃⁺Cl[−] and dmpe at 200 °C and subsequent Soxhlet extraction with toluene.³⁹ Phenylhydrazine-¹⁵N₂ was prepared by diazotization of aniline-¹⁵N with sodium nitrite-¹⁵N and subsequent reduction with sodium sulfite.⁴⁰ Ph¹⁵NNH₂ was prepared in a similar manner with aniline-¹⁵N 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. ¹H, ³¹P, and ¹⁵N NMR spectra were recorded on Bruker Avance III 600, 500, 400 or DPX300 NMR spectrometers at 298 K unless otherwise stated. ¹H NMR spectra were referenced to residual solvent resonances while ³¹P spectra were referenced to external neat trimethyl phosphite at δ 140.85 ppm. ¹⁵N NMR spectra were referenced to external neat nitromethane at δ 0.0 ppm. Simulation of ³¹P 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 MoK α radiation (λ = 0.71073) at a temperature of 100(2) K. Crystallographic details are summarized in Table 2.

***cis*-[Fe(η^2 -NH₂NPh)(dmpe)₂]⁺X[−] (1).** *X* = Cl. Potassium *t*-butoxide (36 mg, 0.32 mmol) was added to an emerald green solution of *trans*-[FeCl₂(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). ¹H NMR (CD₂Cl₂, 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, NHH), 3.80 (br, 1H, NHH), 2.17–1.89 (m, 2H, CH₂), 1.88–1.78 (m, 6H, CH₃ and CH₂), 1.78–1.68 (m, 4H, CH₃ and CH₂), 1.63 (s, 3H,

CH₃), 1.58–1.40 (m, 2H, CH₂), 1.27 (m, 3H, CH₃), 1.25–1.11 (m, 9H, CH₃), 0.92 (s, 3H, CH₃). ¹H{³¹P} NMR (CD₂Cl₂, 400 MHz): δ 6.97 (m, 2H, Ph), 6.70 (m, 2H, Ph), 6.44 (m, 1H, Ph), 5.46 (br, 1H, NHH), 3.80 (br, 1H, NHH), 2.17–1.89 (m, 2H, CH₂), 1.82 (m, 6H, CH₃ and CH₂), 1.75 (m, 4H, CH₃ and CH₂), 1.63 (s, 3H, CH₃), 1.58–1.40 (m, 2H, CH₂), 1.27 (s, 3H, CH₃), 1.23 (s, 3H, CH₃), 1.21 (s, 3H, CH₃), 1.20 (s, 3H, CH₃), 0.92 (s, 3H, CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 162 MHz): δ 65.6 (ddd, ²*J*_{AB} 6.5 Hz, ²*J*_{AC} 24.6 Hz, ²*J*_{AD} 43.8 Hz, 1P, P_A), 63.6 (ddd, ²*J*_{BC} 46.9 Hz, ²*J*_{BD} 42.5 Hz, 1P, P_B), 61.0 (ddd, ²*J*_{CD} 151.2 Hz, 1P, P_C), 60.4 (ddd, 1P, P_D). ¹⁵N{¹H} NMR (CD₂Cl₂, 41 MHz, from HN-HSQC): δ −366.6 (corr with ¹H δ 5.46 and 3.80, NH₂).

The ¹⁵N₂-labeled analogue was prepared in a similar manner using phenylhydrazine-¹⁵N₂. ¹H NMR (CD₂Cl₂, 400 MHz): 5.46 (br d, ¹*J*_{HN} 86 Hz, 1H, NHH), 3.80 (br d, ¹*J*_{HN} 79 Hz, 1H, NHH). ¹⁵N NMR (CD₂Cl₂, 41 MHz): δ −299.0 (m, NPh), −366.8 (m, NH₂).

The ¹⁵N-labeled analogue was prepared in a similar manner using Ph¹⁵NNH₂.

X = BPh₄. Potassium *t*-butoxide (82 mg, 0.73 mmol) was added to a solution of *trans*-[FeCl₂(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 -NH₂NPh)(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). C₄₂H₅₉BF₄N₂P₄ (782.57) requires C, 64.5; H, 7.6; N, 3.6; found, C, 64.2; H, 7.8; N, 3.2%. ¹H NMR (thf-*d*₈, 300 MHz): δ 7.29 (m, 8H, *o*-PhB), 6.99–6.80 (m, 10H, *m*-Ph and *p*-PhB), 6.72 (m, 4H, *p*-PhB), 6.54 (m, 2H, *o*-Ph), 6.40 (m, 1H, *p*-Ph), 3.80 (br s, 1H, NHH), 3.05 (br s, 1H, NHH), 2.07–1.70 (m, 5H, CH₂), 1.67 (d, ²*J*_{HP} 8 Hz, 3H, CH₃), 1.64–1.46 (m, 3H, CH₂), 1.46–1.35 (m, 6H, CH₃), 1.21–1.09 (m, 9H, CH₃), 1.06 (m, 3H, CH₃), 0.79 (m, 3H, CH₃). ¹H{³¹P} NMR (thf-*d*₈, 300 MHz): δ 7.29 (m, 8H, *o*-PhB), 6.98–6.82 (m, 10H, *m*-Ph and *p*-PhB), 6.72 (m, 4H, *p*-PhB), 6.54 (m, 2H, *o*-Ph), 6.41 (m, 1H, *p*-Ph), 3.79 (br s,

1H, NHH), 3.04 (br s, 1H, NHH), 1.95 (m, 1H, CH₂), 1.83–1.70 (m, 4H, CH₂), 1.67 (s, 3H, CH₃), 1.65–1.47 (m, 3H, CH₂), 1.43 (s, 3H, CH₃), 1.41 (s, 3H, CH₃), 1.164 (s, 3H, CH₃), 1.157 (s, 3H, CH₃), 1.13 (s, 3H, CH₃), 1.06 (s, 3H, CH₃), 0.79 (s, 3H, CH₃). ³¹P{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). ¹⁵N{¹H} NMR (thf-*d*₈, 30 MHz, from HN-HSQC): δ –376.1 (corr with ¹H δ 3.80 and 3.05, NH₂). 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 ¹⁵N-labeled analogue was prepared in a similar manner using *cis*-[Fe(η²-NH₂¹⁵NPh)(dmpe)₂]⁺Cl[–]. ¹⁵N NMR (thf-*d*₈, 30 MHz): δ –299.1 (s, NPh).

***cis*-[Fe(η²-HN=NPh)(dmpe)₂] (2).**⁴¹ Potassium *t*-butoxide (24 mg, 0.21 mmol) was added to a solution of *cis*-[Fe(η²-NH₂NPh)(dmpe)₂]⁺BPh₄[–] (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, NH), 1.50, 1.44, 1.15, 0.98, 0.86, 0.68, 0.66, 0.63, 0.61, 0.52, 0.38 (m, CH₃), 1.64–0.73 (m, CH₂). ³¹P{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). ¹⁵N{¹H} NMR (toluene-*d*₈, 61 MHz, from HN-HSQC, 200 K): δ –327.1, (corr with ¹H δ 2.11, NH, major diastereomer), –324.5 (corr with ¹H δ 1.71, NH, minor diastereomer). IR: 3155w, 3050w, 3034w, 1605w, 1579s, 1548 m, 1415 m, 1358 m, 1316 m, 1291 m, 1281 m, 1272 m, 1249 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 ¹⁵N-labeled analogue was prepared in a similar manner using *cis*-[Fe(η²-NH₂¹⁵NPh)(dmpe)₂]⁺BPh₄[–]. ¹⁵N NMR (toluene-*d*₈, 40 MHz, 200 K): δ –246.3 (s, NPh, minor diastereomer), –254.3 (s, NPh, major diastereomer).

***cis*-[RuCl(η¹-NH₂NHPh)(dmpe)₂]⁺X[–] (3).** X = Cl. Phenylhydrazine (0.4 mL, 4 mmol) was added to a suspension of *cis*-[RuCl₂(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(η¹-NH₂NHPh)(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 ¹⁵N-labeled analogue was prepared in a similar manner using *cis*-[RuCl₂(dmpe)₂] (0.68 g, 1.4 mmol) and Ph¹⁵NHNH₂ (0.17 g, 1.6 mmol), yield 80 mg (10%).

X = BPh₄. A solution of NaBPh₄ (35 mg, 0.10 mmol) in methanol (0.5 mL) was added to a solution of *cis*-[RuCl(η¹-NH₂NHPh)(dmpe)₂]⁺Cl[–] (34 mg, 59 μmol) in methanol (1.2 mL) under nitrogen. The white precipitate of *cis*-[RuCl(η¹-NH₂NHPh)(dmpe)₂]⁺BPh₄[–] formed was collected by filtration, washed with methanol (3 × 0.5 mL), and dried in vacuo (40 mg, 78% yield). C₄₂H₆₀BClN₂P₄Ru (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, CH₂), 1.69–1.57 (m, 1H, CH₂), 1.57–1.52 (m, 4H, CH₃ and CH₂), 1.52–1.44 (m, 8H, CH₃ and CH₂), 1.40 (d, ²J_{HP} 10 Hz, 3H, CH₃), 1.36 (dd, ²J_{HP} 8 Hz, ²J_{HP} 2 Hz, 3H, CH₃), 1.33–1.26 (m, 6H, CH₃), 1.18 (d, ²J_{HP} 8 Hz, 3H, CH₃). ¹H{³¹P} NMR (thf-*d*₈, 400 MHz): δ 7.53 (bt, ²J_{HP} 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, CH₂), 1.61 (m, 1H, CH₂), 1.57–1.43 (m, 3H, CH₂), 1.55 (s, 3H, CH₃), 1.50 (s, 3H, CH₃), 1.49 (s, 3H, CH₃), 1.40 (s, 3H, CH₃), 1.36 (s, 3H, CH₃), 1.31 (s, 3H, CH₃), 1.29 (s, 3H,

CH₃), 1.19 (s, 3H, CH₃). ³¹P{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). ¹⁵N{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, NH₂). 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(η²-NH₂NPh)(dmpe)₂]⁺BPh₄[–] (4).** Potassium *t*-butoxide (20 mg, 0.18 mmol) was added to a suspension of *cis*-[RuCl(η¹-NH₂NHPh)(dmpe)₂]⁺BPh₄[–] (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). C₄₂H₅₉BN₂P₄Ru (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, CH₂), 1.71–1.47 (m, 5H, CH₂), 1.61 (d, ²J_{HP} 8 Hz, 3H, CH₃), 1.44 (d, ²J_{HP} 5 Hz, 3H, CH₃), 1.41 (d, ²J_{HP} 8 Hz, 3H, CH₃), 1.30 (d, ²J_{HP} 8 Hz, 3H, CH₃), 1.28 (d, ²J_{HP} 8 Hz, 3H, CH₃), 1.16 (d, ²J_{HP} 7 Hz, 3H, CH₃), 1.15 (d, ²J_{HP} 6 Hz, 3H, CH₃), 0.76 (d, ²J_{HP} 5 Hz, 3H, CH₃). ¹H{³¹P} 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, CH₂), 1.76 (m, 1H, CH₂), 1.67–1.47 (m, 6H, CH₂), 1.61 (s, 3H, CH₃), 1.44 (s, 3H, CH₃), 1.41 (s, 3H, CH₃), 1.30 (s, 3H, CH₃), 1.28 (s, 3H, CH₃), 1.16 (s, 3H, CH₃), 1.15 (s, 3H, CH₃), 0.76 (s, 3H, CH₃). ³¹P{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). ¹⁵N{¹H} NMR (thf-*d*₈, 41 MHz, from HN-HSQC, 200 K): δ –365.6 (corr with ¹H δ 5.25 and 4.37, NH₂). 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 ¹⁵N-labeled analogue was prepared in a similar manner using *cis*-[RuCl(η¹-NH₂¹⁵NHPh)(dmpe)₂]⁺BPh₄[–]. ¹⁵N NMR (thf-*d*₈, 30 MHz): δ –287.0 (d, ²J_{NP} 20 Hz, NPh).

***cis*-[Ru(η²-HNNPh)(dmpe)₂] (5).** A suspension of *cis*-[RuCl(η¹-NH₂NHPh)(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(η²-PhNNH)(dmpe)₂] as yellow-brown crystals (0.015 g, 27% yield). C₁₈H₃₈N₂P₄Ru (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, NH), 1.48–1.32 (m, 1H, CH₂), 1.41 (d, ²J_{HP} 6 Hz, 3H, CH₃), 1.36 (d, ²J_{HP} 7 Hz, 3H, CH₃), 1.32–1.05 (m, 6H, CH₂), 1.09 (m, 3H, CH₃), 1.01 (m, 3H, CH₃), 0.95–0.84 (m, 4H, CH₂ and CH₃), 0.82 (d, ²J_{HP} 7 Hz, 3H, CH₃), 0.81 (d, ²J_{HP} 6 Hz, 3H, CH₃), 0.78 (m, 3H, CH₃). ¹H{³¹P} 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, NH), 1.48–1.32 (m, 1H, CH₂), 1.41 (s, 3H, CH₃), 1.36 (s, 3H, CH₃), 1.31–1.10 (m, 6H, CH₂), 1.09 (s, 3H, CH₃), 1.01 (s, 3H, CH₃), 0.92–0.81 (m, 1H, CH₂), 0.86 (s, 3H, CH₃), 0.82 (s, 3H, CH₃), 0.81 (s, 3H, CH₃), 0.78 (s, 3H, CH₃). ³¹P{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). ¹⁵N{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

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 $\text{cis-}[\text{RuCl}(\eta^1\text{-NH}_2^{15}\text{NHP})(\text{dmpe})_2]^+\text{Cl}^-$. ^{15}N NMR (benzene- d_6 , 51 MHz): δ -251.5 (d, $^2J_{\text{NP}}$ 14 Hz, NPh). $^{15}\text{N}\{^1\text{H}\}$ NMR (benzene- d_6 , 51 MHz): δ -251.5 (d, $^2J_{\text{NP}}$ 14 Hz, NPh). $^{15}\text{N}\{^1\text{H}, ^{31}\text{P}\}$ NMR (benzene- d_6 , 51 MHz): δ -251.5 (s, NPh).

$\text{cis-}[\text{RuCl}(\eta^1\text{-NH}_2\text{NHMe})(\text{dmpe})_2]^+\text{X}^-$ (6). $\text{X} = \text{Cl}$. Methanol (approximately 0.25 mL) was added to a suspension of $\text{cis-}[\text{RuCl}_2(\text{dmpe})_2]$ (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 $\text{cis-}[\text{RuCl}(\eta^1\text{-NH}_2\text{NHMe})(\text{dmpe})_2]^+\text{Cl}^-$ was collected by filtration, washed with diethyl ether, and dried under vacuum (90 mg, 78% yield). This compound was used directly without further purification.

$\text{X} = \text{BPh}_4$. A solution of NaBPh_4 (39 mg, 0.11 mmol) in methanol (1 mL) was added to a solution of $\text{cis-}[\text{RuCl}(\eta^1\text{-NH}_2\text{NHMe})(\text{dmpe})_2]^+\text{Cl}^-$ (35 mg, 68 μmol) in methanol (1 mL) under nitrogen. The white microcrystalline precipitate of $\text{cis-}[\text{RuCl}(\eta^1\text{-NH}_2\text{NHMe})(\text{dmpe})_2]^+\text{BPh}_4^-$ formed was collected by filtration, washed with methanol (3×1.5 mL), and dried in vacuo (52 mg, 95% yield). $\text{C}_{37}\text{H}_{58}\text{BClN}_2\text{P}_4\text{Ru}$ (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, NH_2), 4.04 (m, 1H, NHMe), 2.53 (d, $^3J_{\text{HH}}$ 6.4 Hz, 3H, NCH_3), 1.91–1.68 (m, 5H, CH_2), 1.68–1.53 (m, 2H, CH_2), 1.60 (dd, $^2J_{\text{HH}}$ 9.2 Hz, $^2J_{\text{HH}}$ 1.6 Hz, 3H, CH_3), 1.53–1.45 (m, 10H, CH_2 , $3 \times \text{CH}_3$), 1.37 (d, $^2J_{\text{HH}}$ 9.9 Hz, 3H, CH_3), 1.30 (d, $^2J_{\text{HH}}$ 8.5 Hz, 3H, CH_3), 1.26 (d, $^2J_{\text{HH}}$ 8.1 Hz, 3H, CH_3), 1.18 (d, $^2J_{\text{HH}}$ 8.3 Hz, 3H, CH_3). $^1\text{H}\{^{31}\text{P}\}$ 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, NH_2), 4.04 (m, 1H, NHMe), 2.53 (d, $^3J_{\text{HH}}$ 6.4 Hz, 3H, NCH_3), 1.91–1.68 (m, 5H, CH_2), 1.68–1.53 (m, 2H, CH_2), 1.60 (s, 3H, CH_3), 1.53–1.45 (m, 1H, CH_2), 1.51 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.18 (s, 3H, CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (thf- d_8 , 162 MHz): δ 51.4 (ddd, $^2J_{\text{AB}}$ 32.6 Hz, $^2J_{\text{AC}}$ 15.6 Hz, $^2J_{\text{AD}}$ 25.1 Hz, 1P, P_A), 44.6 (ddd, $^2J_{\text{BC}}$ 29.3 Hz, $^2J_{\text{BD}}$ 16.5 Hz, 1P, P_B), 39.8 (ddd, $^2J_{\text{CD}}$ 29.3 Hz, 1P, P_C), 33.5 (ddd, 1P, P_D). $^{15}\text{N}\{^1\text{H}\}$ NMR (thf- d_8 , 41 MHz, from HN-HSQC): δ -308.2 (corr with ^1H δ 4.04, NHMe), -335.6 (corr with ^1H δ 4.29, NH_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%, $(\text{RuCl}(\text{NH}_2\text{NHMe})(\text{dmpe})_2)^+$], 478.0444 [100, $(\text{RuCl}(\text{dmpe})_2(\text{CH}_3\text{CN}))^+$], 437.0175 [93, $(\text{RuCl}(\text{dmpe})_2)^+$].

$\text{cis-}[\text{Ru}(\eta^2\text{-HNNMe})(\text{dmpe})_2]$ (8).⁴¹ A suspension of $\text{cis-}[\text{RuCl}(\eta^1\text{-NH}_2\text{NHMe})(\text{dmpe})_2]^+\text{Cl}^-$ (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 $\text{cis-}[\text{Ru}(\eta^2\text{-HNNMe})(\text{dmpe})_2]$ as a yellow solid (0.013 g, 46% yield). ^1H NMR (toluene- d_8 , 400 MHz): δ 3.9 (br, 1H, NH), 3.22 (d, $^4J_{\text{HP}}$ 7 Hz, 3H, NCH_3), 1.65–1.44 (m, 2H, CH_2), 1.39 (m, 9H, CH_3), 1.35–1.16 (m, 4H, CH_2), 1.12 (d, $^2J_{\text{HP}}$ 7 Hz, 3H, CH_3), 1.05 (d, $^2J_{\text{HP}}$ 3 Hz, 3H, CH_3), 1.00 (d, $^2J_{\text{HP}}$ 6 Hz, 3H, CH_3), 0.89 (d, $^2J_{\text{HP}}$ 6 Hz, 3H, CH_3), 0.84 (d, $^2J_{\text{HP}}$ 4 Hz, 3H, CH_3), 0.87–0.63 (m, 2H, CH_2). $^1\text{H}\{^{31}\text{P}\}$ NMR (toluene- d_8 , 400 MHz): δ 3.91 (br, 1H, NH), 3.22 (s, 3H, NCH_3), 1.54 (m, 2H, CH_2), 1.39 (s, 3H, CH_3), 1.38 (s, 6H, CH_3), 1.36–1.16 (m, 4H, CH_2), 1.12 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 0.84 (s, 3H, CH_3), 0.87–0.77 (m, 1H, CH_2), 0.70 (m, 1H, CH_2). $^{31}\text{P}\{^1\text{H}\}$ 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). $^{15}\text{N}\{^1\text{H}\}$ NMR (toluene- d_8 , 41 MHz, from HN-HSQC, 193 K): δ -289.5 (corr with ^1H δ 3.9, NH). $^{15}\text{N}\{^1\text{H}\}$ NMR

(toluene- d_8 , 41 MHz, from HN-HMBC, 193 K): δ -289.2 (corr with ^1H δ 3.48, NH), -281.7 (corr with ^1H δ 3.48, NCH_3). $^{15}\text{N}\{^1\text{H}\}$ NMR (thf- d_8 , 51 MHz, from HN-HMBC, 298 K): δ -286.7 (corr with ^1H δ 2.77, NH), -277.3 (corr with ^1H δ 2.77, NCH_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, $(\text{Ru}(\text{HNNMe})(\text{dmpe})_2\text{H})^+$], 433.0319 [90], 403.0575 [43, $(\text{RuH}(\text{dmpe})_2)^+$].

■ 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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