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Base-Induced Dehydrogenation of Ruthenium Hydrazine Complexes

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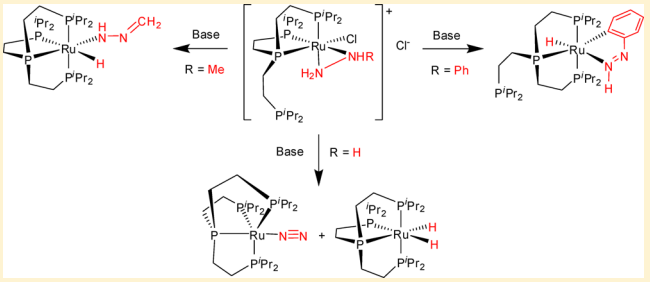
Supporting Information

ABSTRACT: Treatment of $[RuCl(PP_3^{iPr})]^+Cl^-$ (PP_3^{iPr} = $P(CH_2CH_2P^iPr_2)_3$) with hydrazine, phenylhydrazine, and methylhydrazine afforded side-on bound hydrazine complexes $[RuCl(\eta^2\text{-}H_2N\text{-}NH_2)(\eta^3\text{-}PP_3^{iPr})]^+$, $[RuCl(\eta^2\text{-}H_2N\text{-}NHPh)(\eta^3\text{-}PP_3^{iPr})]^+$, and $[RuCl(\eta^2\text{-}H_2N\text{-}NHMe)(\eta^3\text{-}PP_3^{iPr})]^+$. The analogous reactions of $[RuCl_2(PP_3^{Ph})]$ (PP_3^{Ph} = $P(CH_2CH_2PPh_2)_3$) with hydrazine, phenylhydrazine, and methylhydrazine afforded end-on bound hydrazine complexes $[RuCl(\eta^1\text{-}H_2N\text{-}NH_2)(PP_3^{Ph})]^+$, $[RuCl(\eta^1\text{-}H_2N\text{-}NHPh)(PP_3^{Ph})]^+$, and $[RuCl(\eta^1\text{-}H_2N\text{-}NHMe)(PP_3^{Ph})]^+$. Treatment of parent hydrazine complex $[RuCl(N_2H_4)(PP_3^{iPr})]^+$ with strong base afforded the dinitrogen and dihydride complexes $[Ru(N_2)(PP_3^{iPr})]$ and $[RuH_2(PP_3^{iPr})]$. Treatment of phenylhydrazine complex $[RuCl(NH_2NHPh)(PP_3^{iPr})]^+$ with strong base afforded the hydrido ruthenaindazole complex $[RuH(\eta^2\text{-}NH{=}NC_6H_4)(\eta^3\text{-}PP_3^{iPr})]$ while similar treatment of methylhydrazine complex $[RuCl(NH_2NHMe)(PP_3^{iPr})]^+$ afforded the hydrido methylenehydrazide complex $[RuH(NHN{=}CH_2)(PP_3^{iPr})]$. Treatment of the hydrazine complexes $[RuCl(NH_2NHR)(PP_3^{Ph})]^+$ (R = H, Ph, Me) with strong base afforded the dinitrogen complex $[Ru(N_2)(PP_3^{Ph})]$.



INTRODUCTION

Iron-bound hydrazine, diazene, and hydrido species have been shown to be important intermediates in the reduction of dinitrogen at iron by the enzyme nitrogenase.[1] There has been recent interest in the synthesis of iron hydrazine and diazene complexes as well as studies into their interconversions as possible models of the interaction at nitrogenase.[2] There has also been interest in the synthesis of phenyl- and methyl-substituted hydrazine and diazene complexes of iron as well as ruthenium[3−5] since these are considered more stable analogues of the parent unsubstituted species and may be able to shed light on the chemistry and properties of metal hydrazines and diazenes.

Hydrazine (NH_2NH_2) can bind to a metal center in three ways, end-on, bridging, or side-on. Similar bonding modes are known for substituted hydrazines although end-on bound species can be coordinated via the NH_2 terminus or the substituted NHR end.[6] Substituted diazenes can also bind end-on, bridging, or side-on in a variety of modes (Figure 1).[7]

We have previously reported the base-mediated conversion of iron-bound hydrazine to diazene then to dinitrogen in the presence of a strong base.[8] More recently we reported the base-induced conversion of coordinated hydrazine to side-on bound diazene on ruthenium[9] as well as the conversion of coordinated phenylhydrazine to side-on bound phenyldiazene (on iron and ruthenium) and conversion of coordinated methylhydrazine to side-on bound methyldiazene (on ruthenium), respectively.[7]

In these reports, the complexes contained bidentate phosphines as coligands and changes to these coligands were expected to confer changes in reactivity of the resultant complexes due to ligand constraints and sterics. The tetradentate phosphine (PP_3) podand ligands have previously been utilized to bind four sites in an octahedral system leaving the remaining two sites geometry-constrained to a cis arrangement[10] and, where the central atom has been replaced by boron or silicon, to induce electronic effects in the resulting complexes.[11] We now report the synthesis of ruthenium hydrazine, methylhydrazine, and phenylhydrazine complexes containing PP_3 ligands and their reactions with base.

RESULTS AND DISCUSSION

Ru Hydrazine Complexes with the PP_3^{iPr} Ligand. Treatment of $[RuCl(PP_3^{iPr})]^+Cl^-$ (PP_3^{iPr} = tris[2-(diisopropylphosphino)ethyl]phosphine) with hydrazine in tetrahydrofuran (THF) and methanol afforded the complex $[RuCl(\eta^2\text{-}N_2H_4)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**1**) where the hydrazine ligand is bound side-on and the polydentate has one pendant arm that is not coordinated (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of **1** exhibits resonances at δ 108.3, 91.6, and 8.3 in a ratio of 1:2:1 assigned to the central phosphine P_C, the two equivalent terminal phosphines P_T, and the free (uncoordinated) phosphine arm P_F, respectively. The resonance for P_F is close to the resonance for the phosphine arms of the free ligand (δ −15.4)[12] while the resonance for P_C is at higher field than in complexes where all phosphines are coordinated (typically δ 142−162).[12] The ^{31}P solid state NMR spectrum shows similar

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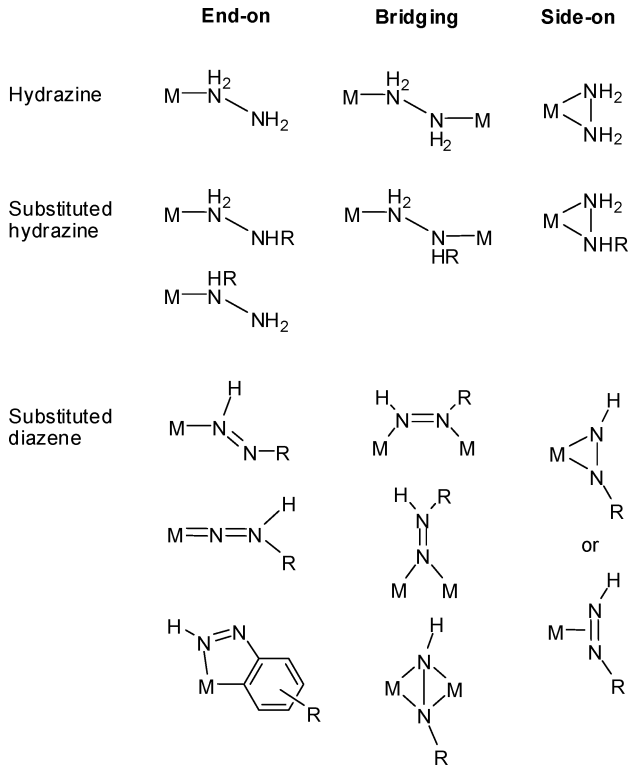
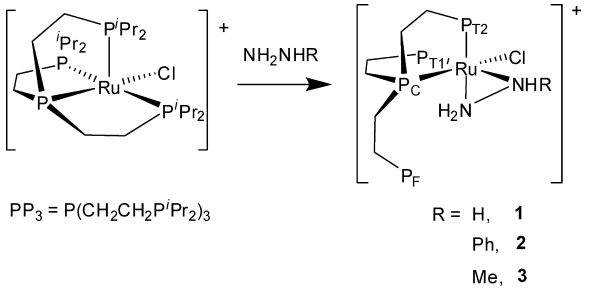


Figure 1. Bonding modes of hydrazine, substituted hydrazine, and substituted diazene complexes.

Scheme 1



chemical shifts to the solution chemical shifts with resonances at δ 109.3, 95.9, 90.5, and 4.3. On labeling with ^{15}N, the P_T resonance gains an extra splitting of about 21 Hz in the $^{31}P\{^1H\}$ NMR spectrum while a single resonance at δ −364.7 is observed in the $^{15}N\{^1H\}$ NMR spectrum indicating that the hydrazine ligand is side-on bound trans to the two equivalent phosphine arms (Figure 2). While the ^{15}N resonance appears superficially as a doublet, there is an underlying complexity due

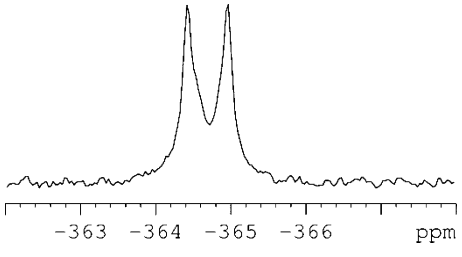


Figure 2. $^{15}N\{^1H\}$ NMR spectrum of $[RuCl(\eta^2\text{-}^{15}N_2H_4)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**1**, methanol/THF/THF-d_8, 41 MHz).

to the symmetry of the complex and the fact that it is part of an AA′XX′ spin system.

Crystals of $[RuCl(\eta^2\text{-}N_2H_4)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**1**) suitable for X-ray crystallography were obtained on layering the reaction mixture with diethyl ether. The crystal structure (Figure 3)

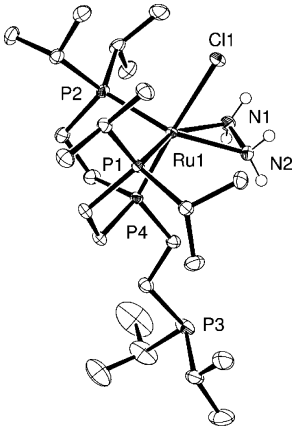


Figure 3. ORTEP plot of $[RuCl(\eta^2\text{-}N_2H_4)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**1**), 50% displacement ellipsoids, chloride counterion, and carbon-bound hydrogen atoms excluded for clarity. Selected bond lengths (Å) and angles (deg): Ru1−N1 2.1242(18), Ru1−N2 2.1324(18), N1−N2 1.444(2), N1−Ru1−N2 39.66(6), N1−Ru1−P4 96.17(7), N2−Ru1−P4 97.50(7), N1−Ru1−P1 153.08(4), N2−Ru1−P1 113.45(6), N1−Ru1−P2 108.36(6), N2−Ru1−P2 148.02(4), P1−Ru1−P2 98.53(5), N1−Ru1−Cl1 82.62(7), N2−Ru1−Cl1 79.42(7), N2−N1−Ru1 70.48(8), N1−N2−Ru1 69.86(8).

clearly shows the side-on bound nature of the hydrazine ligand, the uncoordinated phosphine arm (P3), and the fact that the chloride ligand is trans to the central phosphorus (P4). The geometry about ruthenium is that of a severely distorted octahedron with an acute N1−Ru1−N2 angle of 39.66(6)° and angles of 113.45(6), 108.36(6), and 98.53(5)° for N2−Ru1−P1, N1−Ru1−P2, and P1−Ru1−P2, respectively. The Ru−N bond lengths of 2.1242(18) and 2.1324(18) Å are within the range for previously reported Ru hydrazine complexes (2.101−2.273 Å).[9,13,14] Short contacts were observed from the N atoms of the hydrazine ligand to the chloride anion (3.073 and 3.169 Å), and these may contribute to the stability of the complex in the solid state. Side-on bound hydrazine complexes are still relatively rare[15] and, so far, only one other side-on bound hydrazine complex on ruthenium has been reported.[9] The hydrazine ligand is labile in solution without excess hydrazine. Attempts to isolate the complex as the tetraphenylborate salt by addition of $NaBPh_4$ only afforded orange crystals of the chloro complex $[RuCl(PP_3^{iPr})]^+BPh_4^-$.[12]

Treatment of $[RuCl(PP_3^{iPr})]^+Cl^-$ with phenylhydrazine in THF afforded the side-on bound phenylhydrazine complex $[RuCl(\eta^2\text{-}NH_2NHPh)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**2**) (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture contained resonances at δ 104.8, 83.9, 72.3, and 8.4 for the central phosphine P_C, terminal phosphines P_{T1}, P_{T2}, and the pendant phosphine P_F, respectively. Addition of pentane or hexane to the reaction mixture afforded a pale yellow precipitate. The ^{31}P solid state NMR spectrum of the precipitate showed four resonances at δ 105.1 (P_C), 72.1 (P_{T1}), 68.1 (P_{T2}), and 3.9 (P_F). These chemical shifts are similar to the resonances observed for the reaction mixture by solution $^{31}P\{^1H\}$ NMR spectroscopy, where the chemical shift for P_F is diagnostic of a

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pendant phosphine arm. The ^{31}P solid state NMR spectrum is consistent with the presence of a side-on bound phenylhydrazine similar to that observed for the parent hydrazine complex **1**. The phenylhydrazine ligand in complex **2** is labile in solution, and, on redissolving the precipitate, only signals for $[RuCl(PP_3^{iPr})]^+$ and free phenylhydrazine were observed by NMR spectroscopy.

Treatment of $[RuCl(PP_3^{iPr})]^+Cl^-$ with excess methylhydrazine in THF afforded the methylhydrazine complex $[RuCl(\eta^2\text{-}NH_2NHMe)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**3**) (Scheme 1). The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture exhibits multiple resonances in the region δ 108−6 where up to 5 different geometric isomers are possible, all with one phosphine arm uncoordinated (Supporting Information). In one isomer, the phosphine ligand is facially coordinated with the Cl ligand trans to the central phosphine and the methylhydrazine ligand trans to terminal phosphines, as for hydrazine complex **1** (Figure 4a).

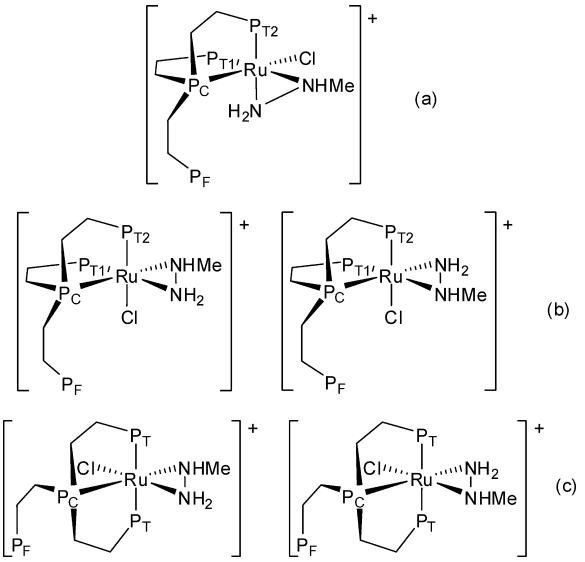

Figure 4. Geometric isomers of $[RuCl(\eta^2\text{-}NH_2NHMe)(\eta^3\text{-}PP_3^{iPr})]^+$ (**3**).

In another two isomers, the phosphine ligand is facially coordinated with the Cl ligand trans to a terminal phosphine (Figure 4b). A further two isomers arise from meridional coordination of the phosphine ligand with the two terminal phosphines trans to each other (Figure 4c). The ^{31}P solid state NMR spectrum is similar to that observed for hydrazine complex **1** with resonances at δ 104.9, 96.8, 83.1, and −3.3 indicating that only one isomer is present in the solid state. As observed for the analogous hydrazine complex **1**, the methylhydrazine ligand in **3** is labile in solution and efforts to isolate the tetraphenylborate salt afforded only the chloro complex $[RuCl(PP_3^{iPr})]^+BPh_4^-$.

Layering the reaction mixture of $[RuCl(PP_3^{iPr})]^+Cl^-$ and methylhydrazine with diethyl ether afforded yellow crystals of **3**. X-ray crystallographic analysis confirmed the side-on bound nature of the methylhydrazine ligand and η^3-coordination of the tripodal phosphine ligand (Figure 5). The chloro ligand is trans to the central phosphine (P4) indicating that geometric isomer (a) was crystallized preferentially. The distorted octahedral geometry about ruthenium is shown by the acute N1−Ru1−N2 angle of 39.54(16)° as well as angles for N2−Ru1−P1, N1−Ru1−P2, and P1−Ru1−P2 of 114.79(12), 107.62(12), and

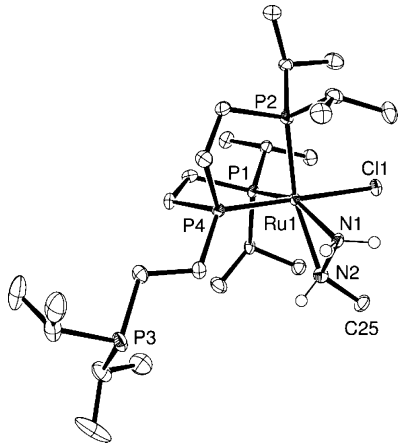

Figure 5. ORTEP plot of $[RuCl(\eta^2\text{-}NH_2NHMe)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**3**), 50% displacement ellipsoids, chloride counterion, and carbon-bound hydrogen atoms excluded for clarity. Only one of two independent molecules is shown. Selected bond lengths (Å) and angles (deg): Ru1−N1 2.116(4), Ru1−N2 2.173(5), N1−N2 1.452(6), N2−C25 1.474(7), N1−Ru1−N2 39.54(16), N1−Ru1−P4 96.74(13), N2−Ru1−P4 94.76(13), N1−Ru1−P1 154.31(13), N2−Ru1−P1 114.79(12), N1−Ru1−P2 107.62(12), N2−Ru1−P2 146.92(12), P1−Ru1−P2 98.06(5), N1−Ru1−Cl1 84.48(13), N2−Ru1−Cl1 85.75(13), N2−N1−Ru1 72.3(3), N1−N2−C25 113.4(4), N1−N2−Ru1 68.1(3), C25−N2−Ru1 130.8(4).

98.06(5), respectively. Short contacts were observed from the N atoms of the methylhydrazine ligand to the chloride counterion (3.119−3.126 Å), and this may contribute to the stability of the complex in the solid state. Methylhydrazine preferentially binds end-on,[16,17] and although bridging examples are known,[18] only one other example of side-on binding[19] has been crystallographically characterized.

Ru Hydrazine Complexes with the PP_3^{Ph} Ligand. Treatment of $[RuCl_2(PP_3^{Ph})]$ (PP_3^{Ph} = tris[2-(diphenylphosphino)ethyl]phosphine) with excess hydrazine in THF resulted in the substitution of one chloride ligand with hydrazine to afford the end-on bound hydrazine complex $[RuCl(N_2H_4)(PP_3^{Ph})]^+$ (**4**) (Scheme 2). On treatment with $NaBPh_4$ in methanol, complex **4** can be isolated as the tetraphenylborate salt. The $^{31}P\{^1H\}$ NMR spectrum of **4** contains three resonances characteristic for an octahedral complex with a tripodal tetradentate phosphine ligand. The low field resonance at δ 142.5 is assigned to the central phosphine P_C, while the resonance at δ 59.2 is assigned to the unique phosphine P_U and the resonance at δ 34.1 with double the intensity of the other signals to the two equivalent terminal phosphines P_T. The hydrazine signals in the ^{1}H NMR spectrum at δ 3.26 and 1.94 correlate to ^{15}N signals at δ −344.8 and −321.1, respectively, in a 2D $^1H-^{15}N$ HSQC (heteronuclear single quantum coherence) experiment indicating that the nitrogen atoms are in different chemical environments. On labeling with ^{15}N, an extra 31 Hz coupling is only observed for P_U in the $^{31}P\{^1H\}$ NMR spectrum indicating that the hydrazine ligand is located trans to P_U and that it must be end-on bound. In the $^{15}N\{^1H\}$ NMR spectrum, the upfield signal exhibits a reciprocal 31 Hz coupling to ^{31}P indicating that it corresponds to the NH_2 directly bonded to Ru. The upfield signal also exhibits a 6 Hz coupling to its partner nitrogen atom in the hydrazine ligand. The downfield signal does not exhibit any measurable ^{31}P coupling and is assigned to the noncoordinated NH_2, again consistent with the fact that the hydrazine ligand is

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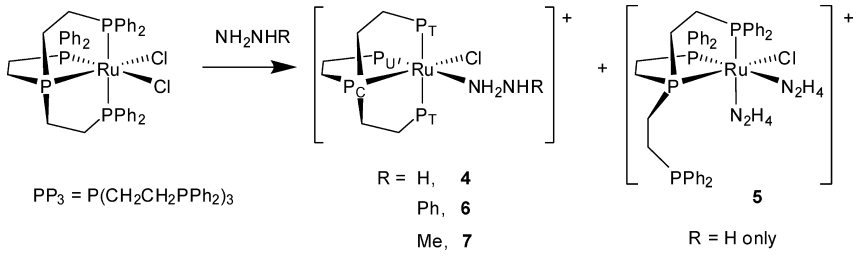
Scheme 2



bound end-on. Microanalysis confirms that there is only one coordinated hydrazine in the solid state for the tetraphenylborate salt of **4**.

Although we were unable to grow crystals of hydrazine complex **4** suitable for X-ray crystallography, we did obtain, from the reaction mixture of $[RuCl_2(PP_3^{Ph})]$ and hydrazine in THF, crystals of the bis-substituted hydrazine complex $[RuCl(\eta^1\text{-}N_2H_4)_2(\eta^3\text{-}PP_3^{Ph})]^+Cl^-$ (**5**). The crystal structure of **5** (Figure 6) clearly shows two hydrazine ligands which are

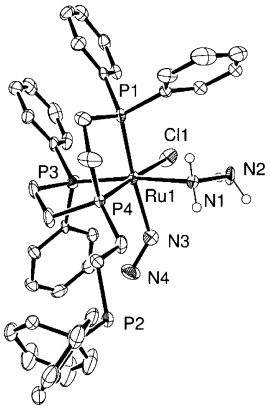


Figure 6. ORTEP plot of $[RuCl(\eta^1\text{-}N_2H_4)_2(\eta^3\text{-}PP_3^{Ph})]^+Cl^-$ (**5**), 50% displacement ellipsoids, chloride counterion, carbon-bound hydrogen atoms, and atoms of less than 50% occupancy excluded for clarity. It was not possible to locate H atom positions on N3 and N4 due to disorder over two positions. Selected bond lengths (Å) and angles (deg): Ru1–N3 2.219(5), Ru1–N1 2.239(4), N1–N2 1.484(6), N3–N4 1.382(8), N3–Ru1–N1 81.18(17), N2–N1–Ru1 121.3(3), N4–N3–Ru1 125.7(5).

both trans to terminal phosphines (P1 and P3) and bound end-on. One arm of the phosphine ligand is a pendant arm and not coordinated to the metal and the chloride ligand is trans to the central phosphorus atom (P4). The Ru–N bond lengths of 2.219(5) and 2.239(4) Å and N–N bond lengths of 1.484(6) and 1.382(8) Å are within the range reported for other ruthenium end-on bound hydrazine complexes (2.126–2.273 and 1.377–1.479 Å, respectively).[9,13] Short contacts were observed from the N atoms of the hydrazine ligands to the chloride counterion (3.205–3.282 Å), and this may contribute to the stability of the bis hydrazine complex in the solid state. Bis-substituted hydrazine complexes have been structurally characterized previously and are known to bind end-on[9,20] and bridging.[21] The ^{31}P solid state NMR spectrum of the bulk of the crystals shows resonances at δ 106.7, 63.3, 58.8, and −2.4 for the central phosphine P_C, two terminal phosphines P_{T1}, P_{T2}, and the pendant phosphine P_F consistent with the crystal structure above. When the crystals were dissolved, only the presence of the monosubstituted complex **4** with all phosphine arms coordinated was detected indicating first the lability of the coordinated hydrazine and second that the structure in the solid state differs from the structure in solution.

Treatment of $[RuCl_2(PP_3^{Ph})]$ with phenylhydrazine or methylhydrazine in THF similarly resulted in the substitution of one chloride ligand to afford end-on bound hydrazine complexes $[RuCl(NH_2NHR)(PP_3^{Ph})]^+$ (R = Ph, **6**; R = Me, **7**) (Scheme 2).

Layering of diethyl ether on the respective reaction mixtures afforded crystals suitable for X-ray crystallography for both complexes $[RuCl(NH_2NHR)(PP_3^{Ph})]^+$ (R = Ph, **6**; R = Me, **7**) (Figures 7 and 8). Both structures show an octahedral

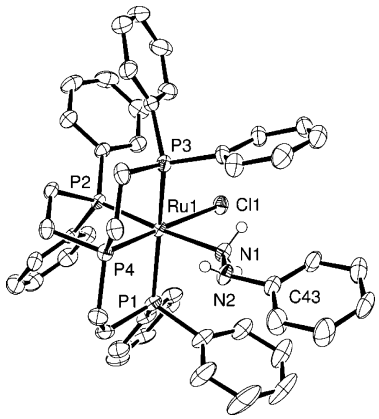


Figure 7. ORTEP plot of $[RuCl(NH_2NHPh)(PP_3^{Ph})]^+Cl^-$ (**6**), 50% displacement ellipsoids, only one of two independent molecules shown. Three phenylhydrazine solvates, chloride counterion, and carbon-bound hydrogen atoms excluded for clarity. Selected bond lengths (Å) and angles (deg): Ru1–N1 2.210(3), N1–N2 1.436(4), N2–C43 1.429(4), N2–N1–Ru1 123.91(19), C43–N2–N1 116.1(3).

arrangement of atoms around the metal center with the chloride ligand trans to the central phosphorus (P4). Both phenylhydrazine and methylhydrazine ligands are bound end-on via the NH_2 group. The N–N bond lengths of the two independent molecules of phenylhydrazine complex **6** (1.436(4), 1.445(4) Å) are within the range reported previously for end-on bound phenylhydrazine complexes (1.41–1.545 Å)[7,22–24] although the Ru–N bonds (2.210(3), 2.222(3) Å) are slightly shorter than the Ru–N bond for $[RuCl(NH_2NHPh)(dmpe)_2]^+$ (2.2504(19) Å).[7] The N–N bond length (1.450(2) Å) for methylhydrazine complex **7** is within the range reported for other end-on bound methylhydrazine complexes (1.421–1.458 Å).[7,17,22,25,26] The Ru–N bond length (2.2103(15) Å) is similar to that for $[RuCl(NH_2NHMe)(dmpe)_2]^+$ where dmpe =1,2-bis(dimethylphosphino)ethane (2.1965(18) Å)[7] and significantly longer than the Ru-methylhydrazine bond in

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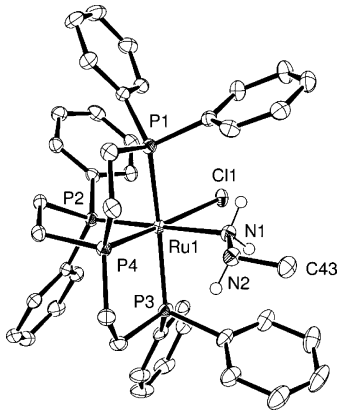


Figure 8. ORTEP plot of $[RuCl(NH_2NHMe)(PP_3^{Ph})]^+Cl^-$ (**7**), 50% displacement ellipsoids, THF solvate, chloride counterion, and carbon-bound hydrogen atoms have been excluded for clarity. Selected bond lengths (Å) and angles (deg): Ru1−N1 2.2103(15), N1−N2 1.450(2), N2−C43 1.468(2), N2−N1−Ru1 123.50(11), N1−N2−C43 110.66(14).

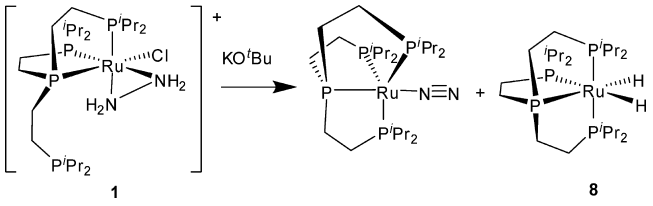
$[Ru(Tp)(NH_2NHMe)\{P(OEt)_3\}(PPh_3)]$ where Tp = hydridotris(pyrazolyl)borate (2.154(3) Å)[26] probably due to the stronger trans influence of the P atom trans to the methylhydrazine ligand in **7** compared to that of the trans N atom in $[Ru(Tp)(NH_2NHMe)\{P(OEt)_3\}(PPh_3)]$.

Both phenylhydrazine complex **6** and methylhydrazine complex **7** can be isolated as the respective tetraphenylborate salts on treatment with $NaBPh_4$ in methanol. The $^{31}P\{^1H\}$ NMR spectrum of phenylhydrazine complex **6** contains three signals at δ 139.8, 59.0, and 32.4 in a ratio of 1:1:2 for P_C, P_U, and P_T, respectively. The ^{31}P solid state NMR spectrum is similar to the solution spectrum with resonances at δ 140.4, 59.4, 37.0, and 30.4 as expected for a complex with all four phosphine atoms coordinated to the metal. In a $^1H-^{15}N$ correlation experiment, the broad ^1H signal integrating to three protons at δ 3.70 correlates to two ^{15}N signals at δ −284.8 and −328.4 for NHPh and $RuNH_2$, respectively. The ^1H signal at δ 5.44 correlates to a ^{13}C signal at δ 112.6 indicating that it is due to CH protons. This highly shielded signal for aromatic protons is likely due to the ortho protons of the phenylhydrazine ligand which are located in the shielding zone (close to the face) of two PP_3^{Ph} phenyl groups as also seen in the crystal structure of **6** (Figure 7).

Similarly, for methylhydrazine complex **7**, three resonances in a ratio of 1:1:2 at δ 140.5, 57.6, and 33.4 are observed in the $^{31}P\{^1H\}$ NMR spectrum for P_C, P_U, and P_T, respectively. In a $^1H-^{15}N$ HSQC experiment, the ^1H NMR signals at δ 3.04 (integrating to two protons) and δ 1.50 (integrating to one proton) correlate to ^{15}N signals at δ −314.5 and −309.6 for $RuNH_2$ and NHMe, respectively. The ^1H NMR signal for the methyl protons of the methylhydrazine ligand is shifted upfield to δ 0.80 as the protons are located in the shielding zone of two phenyl groups from the PP_3^{Ph} ligand, and this can also be seen in the crystal structure of **7** (Figure 8).

Base-Induced Dehydrogenation of Ru Hydrazine Complexes. *$[RuCl(\eta^2\text{-}^{15}N_2H_4)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**1**).* Treatment of ^{15}N-labeled hydrazine complex $[RuCl(\eta^2\text{-}^{15}N_2H_4)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**1**) with KO^{t}Bu in THF-d_8 afforded the Ru(0) dinitrogen $[Ru(^{15}N_2)(PP_3^{iPr})]$ and Ru dihydride $[RuH_2(PP_3^{iPr})]$ (**8**) complexes in a ratio of 1:1.2 (NMR yields of 44% and 54%, respectively) (Scheme 3). The ^1H, ^{31}P, and

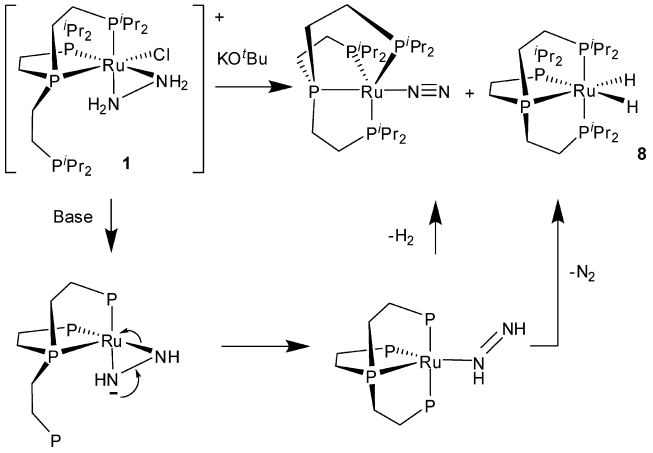
Scheme 3



^{15}N NMR spectra for $[Ru(^{15}N_2)(PP_3^{iPr})]$ match those reported previously.[12] The use of the ^{15}N labeled substrate first confirms that N_2 observed in the product is derived from the labeled hydrazine in **1** and second allows ^{15}N NMR spectroscopy to be used as a further line of evidence to verify the identity of the product.

The reaction probably proceeds by initial deprotonation of the hydrazine species to afford the side-on bound diazene complex (Scheme 4). This first step has been observed in Ru

Scheme 4



dmpe and depe (depe = 1,2-bis(diethylphosphino)ethane) systems where side-on bound diazene complexes have been isolated and characterized.[9] Transfer of electrons onto Ru and into the N−N bond affords a Ru(0) end-on bound diazene complex. Disproportionation of the diazene with loss of H_2 or loss of N_2 forms the Ru dinitrogen and dihydride complexes.

Synthesis and Characterization of $[RuH_2(PP_3^{iPr})]$. The Ru dihydride complex $[RuH_2(PP_3^{iPr})]$ (**8**) has not been previously reported and was synthesized independently by treatment of $[RuCl(PP_3^{iPr})]^+Cl^-$ with sodium in liquid ammonia or potassium triethylborohydride ($KBEt_3H$) in benzene or toluene under argon. The ^1H NMR spectrum exhibits a single broad resonance at −9.13 ppm for the hydride ligands. The $^{31}P\{^1H\}$ NMR spectrum contains a quartet at 154.2 ppm and a doublet at 91.8 ppm in a ratio of 1:3. These features are consistent with exchange occurring between the hydride ligands as well as between the terminal phosphorus environments. On lowering the temperature, the single hydride resonance separates into two signals while the two phosphorus signals give three broad signals in a ratio of 1:2:1 (Figure 9). Such exchange has been observed previously for analogous dihydride complexes with tripodal tetraphosphine ligands.[27]

Crystals of **8** suitable for X-ray crystallography were obtained by slow evaporation of a benzene/benzene-d_6 solution under argon (Figure 10). The geometry of the complex is distorted

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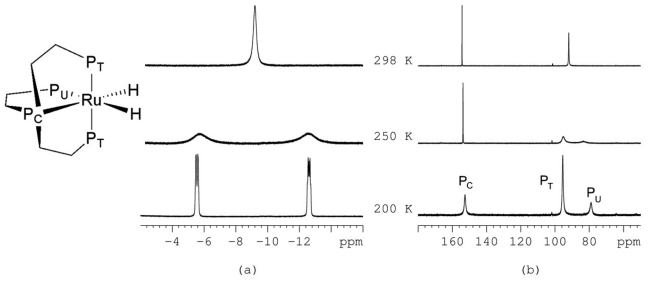


Figure 9. High field ^{1}H (a) and $^{31}P\{^{1}H\}$ (b) NMR spectra of $[RuH_2(PP_3^{iPr})]$ (**8**) (d_8-toluene, 600 and 243 MHz).

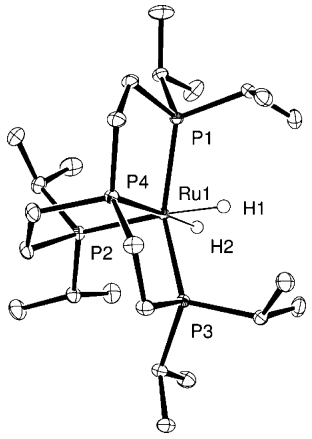
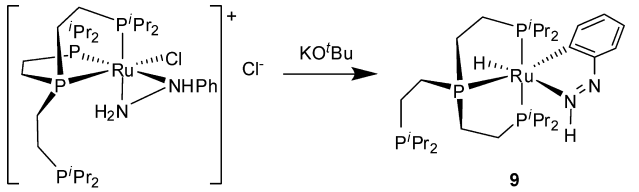


Figure 10. ORTEP plot of $[RuH_2(PP_3^{iPr})]$ (**8**), 50% displacement ellipsoids, carbon bound hydrogen atoms excluded for clarity. Selected bond lengths (Å) and angles (deg): Ru1−P4 2.2322(3), Ru1−P3 2.3002(3), Ru1−P1 2.3090(3), Ru1−P2 2.3415(3), P4−Ru1−P3 84.256(10), P4−Ru1−P1 84.565(10), P3−Ru1−P1 147.883(10), P4−Ru1−P2 85.671(11), P3−Ru1−P2 100.792(10), P1−Ru1−P2 108.259(10).

octahedral with the hydride ligands in mutually cis positions. The structure is analogous to those of $[RuH_2(P(CH_2CH_2CH_2P^iPr_2)_3)]$[28] (which contains the related tetraphosphine ligand with 3-carbon instead of 2-carbon linkers between the phosphines) and $[RuH_2(P(CH_2CH_2CH_2PMe_2)_3)]$[29] (which also contains 3-carbon linkers as well as methyl substituents instead of isopropyl substituents on the terminal phosphines). The P_C-Ru-P_T/P_U angles (84.257(10)−85.671(11)°) are smaller than those of $[RuH_2(P(CH_2CH_2CH_2P^iPr_2)_3)]$ (89.45(4)−94.75(4)°) and $[RuH_2(P(CH_2CH_2CH_2PMe_2)_3)]$ (90.8(2)−96.4(2)°) reflecting the more constrained environment of the ligand with 2-carbon linkers compared to those with 3-carbon linkers.

*$[RuCl(\eta^2\text{-}NH_2NHPh)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**2**).* In contrast to the complex with unsubstituted hydrazine, treatment of phenylhydrazine complex $[RuCl(\eta^2\text{-}NH_2NHPh)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**2**) with KO^{t}Bu in THF afforded the hydrido ruthenaindazole complex $[RuH(C_6H_4N{=}NH)(\eta^3\text{-}PP_3^{iPr})]$ (**9**) as an orange solid (Scheme 5). In the ^{1}H NMR spectrum, a hydride resonance at δ −12.52 and only four aromatic signals at δ 8.08, 8.01, 6.83, and 6.71 which (except for the signal at δ 6.83) exhibit small couplings to ^{31}P indicate the presence of a cyclometalated phenyl ring. A singlet at δ 14.75 is observed for NH at a typical chemical shift for an end-on bound aryldiazene ligand (δ 11−17).[26,30−32] ^{1}H signals for two sets of methyl protons from the phosphine ligand are shifted upfield to δ −0.02 as these protons are in the shielding zone (directly on

Scheme 5



either side of the face) of the five-membered diazoruthenacycle. In a $^{1}H-^{15}N$ HSQC experiment, the diazene proton correlates to a ^{15}N signal at δ 2.4 which is well within the range of reported chemical shifts for aryldiazenyl NH nitrogens (δ 43.6 to −110.7).[26,32] The ^{15}N NMR chemical shift for the aryl N was located at δ 110.7 after synthesizing a ^{15}N-labeled complex $[RuH(C_6H_4{}^{15}N{=}NH)(\eta^3\text{-}PP_3^{iPr})]$. In the $^{31}P\{^{1}H\}$ NMR spectrum, three signals are observed at δ 103.4, 92.5, and 8.2 in a ratio of 1:2:1 for the central phosphine, the two equivalent terminal phosphines, and a free pendant phosphine arm, respectively. Given the presence of three different ligands in the molecule (hydride and cyclometalated phenyldiazene), the only arrangement where the terminal phosphines are equivalent is one where the terminal phosphines are trans to each other.

Crystals suitable for X-ray crystallography were grown by slow evaporation of a toluene solution of **9** (Figure 11). The crystal structure confirms the presence of an orthometalated phenyldiazene ligand, a hydride ligand and the meridional arrangement of the PP_3^{iPr} ligand with two mutually trans terminal phosphine arms and one free phosphine arm. The cyclometalated aryldiazene motif has so far only been observed for iridium complexes, of which several have been crystallo-

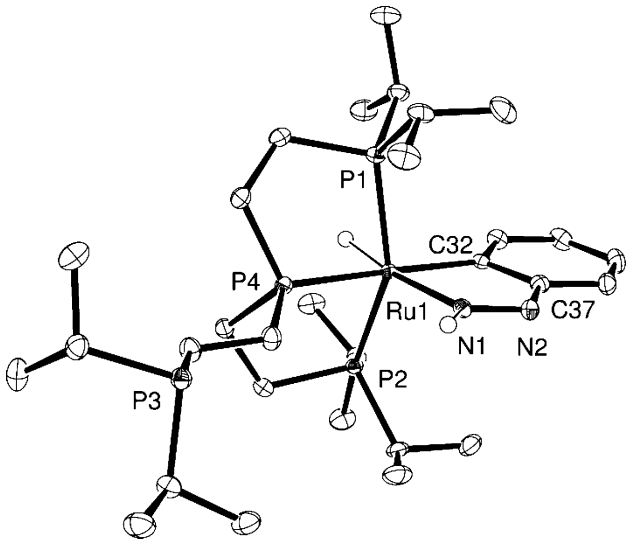


Figure 11. ORTEP plot of $[RuH(C_6H_4N{=}NH)(\eta^3\text{-}PP_3^{iPr})]$ (**9**), 50% displacement ellipsoids, toluene solvate and carbon-bound hydrogen atoms excluded for clarity. Selected bond lengths (Å) and angles (deg): Ru1−N1 2.0388(14), Ru1−C32 2.0781(16), Ru1−P4 2.2642(4), Ru1−P1 2.2803(4), Ru1−P2 2.2934(4), Ru1−H 1.581(18), N1−N2 1.2911(19), N2−C37 1.395(2), C32−C37 1.424(2), N1−Ru1−C32 75.76(6), N1−Ru1−P4 103.15(4), N1−Ru1−P1 104.46(4), P4−Ru1−P1 84.837(16), N1−Ru1−P2 104.73(4), P4−Ru1−P2 83.788(16), P1−Ru1−P2 150.381(17), N1−Ru1−H 170.2(6), N2−N1−Ru1 123.25(11), N1−N2−C37 110.52(13), C37−C32−Ru1 111.93(12), N2−C37−C32 118.54(14).

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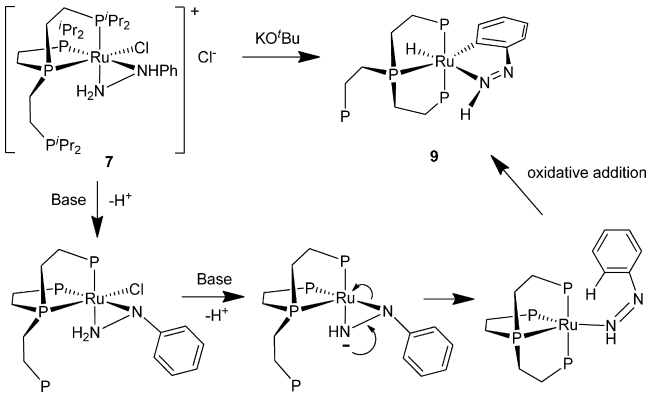
graphically characterized.[33] The N−N bond distance of 1.2911(19) Å in **9** is similar to those in cyclometalated aryldiazene iridium complexes (1.24−1.28 Å) and within the range reported for other aryldiazene complexes (1.13−1.373 Å)[31,34] clearly indicating the presence of an N−N double bond. The N−C bond distance of 1.395(2) Å is also shorter than the analogous bond in phenylhydrazine complex $[RuCl(NH_2NHPh)(PP_3^{Ph})]^+$ (**6**) (1.429(4) Å) indicating partial delocalization of the nitrogen lone pair into the phenyl ring. In fact, the planarity of the ruthenacycle and attached phenyl ring indicates delocalization of electrons throughout the bicyclic structure such that the cyclometalated phenyldiazene moiety can be considered a benzopyrrole or indazole molecule with a ruthenium metal in place of a carbon atom. The aromaticity of the ruthenaindazole moiety is borne out by the significant upfield shifts of the methyl protons located on either side of the face of the ring.

The reaction probably proceeds initially by stepwise deprotonation of the NHPh end of the phenylhydrazine ligand and then deprotonation of the NH_2 group to give a side-on bound phenyldiazene ligand (Scheme 6). These steps have

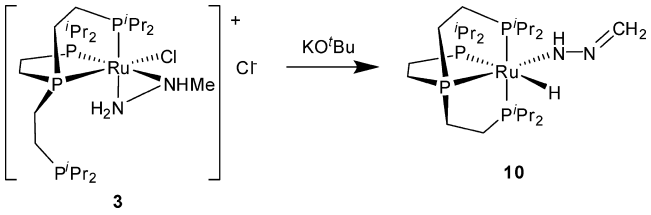
Scheme 6



been observed for Ru dmpe complexes where the side-on phenylhydrazide and phenyldiazene complexes have been isolated and characterized.[7] Subsequent transfer of electrons onto Ru and into the N−N bond affords a Ru(0) end-on bound phenyldiazene complex. Oxidative addition of the phenyl group affords the final hydrido ruthenaindazole complex **9**. This is the first report of an end-on bound phenyldiazene complex being formed on base treatment of a phenylhydrazine complex. It is also the first route to a cyclometalated phenyldiazene by base treatment of phenylhydrazine. The known iridium cyclometalated aryldiazene complexes have been synthesized by reaction of iridium precursor complexes such as $[IrCl(CO)(PPh_3)_2]$, $[IrH_3(PPh_3)_3]$, $[IrH(CO)(PPh_3)_3]$, $[IrH(CO)_2(PPh_3)_2]$, or $[Ir_2(CO)_6(PPh_3)_2]$ with aryldiazonium salts.[33,35]

*$[RuCl(\eta^2\text{-}NH_2NHMe)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**3**).* Treatment of methylhydrazine complex $[RuCl(\eta^2\text{-}NH_2NHMe)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (**3**) with KO^{t}Bu for 5−10 min in THF followed by a quick pentane extraction afforded a mixture of products and we assign the major product as the hydrido 2-methylenehydrazido complex $[RuH(NHN{=}CH_2)(PP_3^{iPr})]$ (**10**) (Scheme 7). Longer reaction times afforded significant amounts of unidentified products. The methylenehydrazide complex **10** is unstable both in solution and in the solid state, and the

Scheme 7



complex was characterized by NMR spectroscopy as soon as possible after synthesis.

In the ^{1}H NMR spectrum of $[RuH(NHN{=}CH_2)(PP_3^{iPr})]$ (**10**), two doublets at δ 6.28 and 5.54 with13.5 Hz coupling are observed for the methylene protons. A doublet at δ 5.27 with a 7.1 Hz coupling to ^{31}P is observed for NH, and a metal hydride signal is observed at δ −10.69. All signals integrate in a ratio of 1:1:1:1. The $^{31}P\{^1H\}$ NMR spectrum indicates that all four P atoms are bound to Ru with signals at δ 145.4, 63.5, and 52.9 for P_C, P_T, and P_U, respectively. The methylene protons correlate to a single ^{13}C signal at δ 104.4 in a $^1H-^{13}C$ HSQC experiment while the NH proton correlates to a ^{15}N signal at δ −266.4 in a low temperature $^1H-^{15}N$ HSQC experiment (Figure 12). No three-bond correlation is detected in a $^1H-^{15}N$ HMBC experiment even at low temperature for N_β.

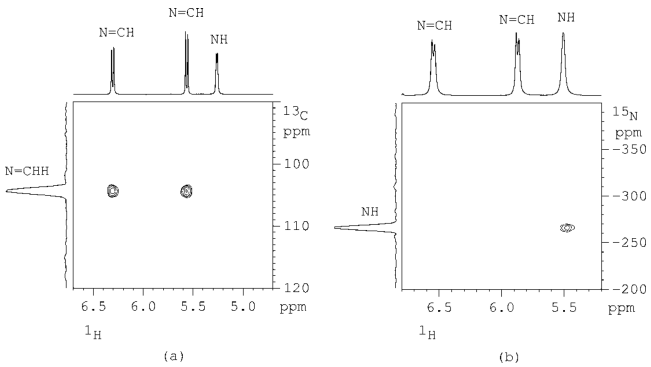


Figure 12. (a) $^1H-^{13}C$ HSQC spectrum (toluene-d_8, 298 K, 600 and 151 MHz) and (b) $^1H-^{15}N$ HSQC spectrum (toluene-d_8, 200 K, 600 and 61 MHz) of $[RuH(NH\text{-}N{=}CH_2)(PP_3^{iPr})]$ (**10**).

Formation of methylenehydrazide complex **10** probably proceeds initially by deprotonation of the methylhydrazine ligand to afford the side-on bound methyldiazene complex (Scheme 8), and an analogous complex has been observed for Ru with dmpe coligands.[7] Electron transfer onto Ru and into the N−N bond leading to decoordination of the NMe end affords a Ru(0) methyldiazene species. Hydride transfer from the methyl group to the Ru center with electron redistribution effectively oxidizes Ru(0) to Ru(II) and furnishes the final hydrido methylenehydrazide complex **10**.

While we have assigned **10** as the methylenehydrazide complex, we cannot completely eliminate the possibility that the nitrogenous ligand could be methyleneimine $(NH{=}CH_2)$ rather than $(^-NH\text{-}N{=}CH_2)$. Albertin and co-workers[36] have reported the formation of methyleneimine complex $[Re(NH{=}CH_2)(CO)P_4]^+$ (P = $P(OEt)_3$) as a mixture with methyldiazene complex $[Re(NH{=}NCH_3)(CO)P_4]^+$ on treatment of methylhydrazine complex $[Re(NH_2NHMe)(CO)P_4]^+$ with $Pb(OAc)_4$ at low temperature. The rhenium methyleneimine complex has a broad ^{1}H NMR signal at δ 13.98 for the NH proton and a

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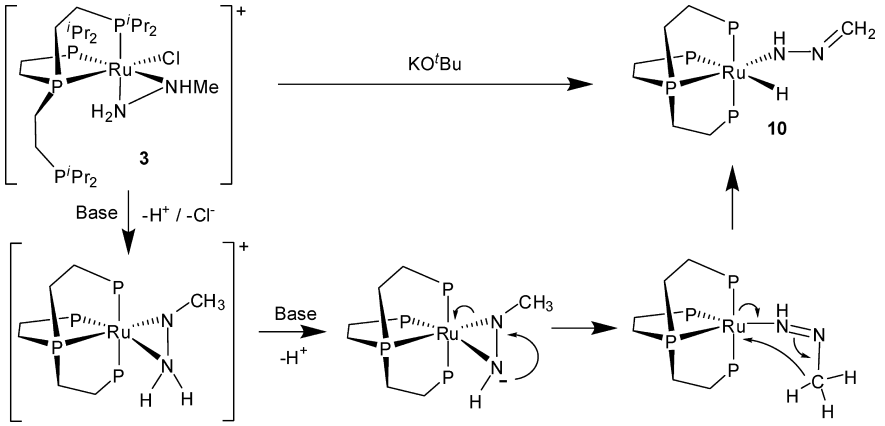
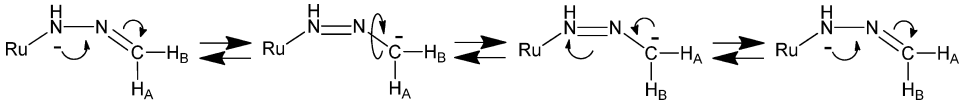
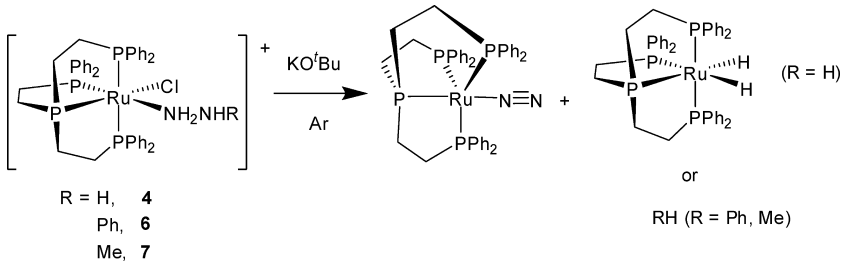
Scheme 8



Scheme 9



Scheme 10



slightly broadened multiplet at δ 3.66 which couples to the NH proton for one of the two N=CH_2 methylene protons (the other methylene proton likely masked by P ligand signals). Albertin et al. have also reported the base-induced tautomerization of methyldiazene complexes $[M(NH{=}NCH_3)(CO)P_4]^{2+}$ (M = Ru, Os; P = $P(OEt)_3$) to formaldehyde hydrazone complexes $[M(NH_2N{=}CH_2)(CO)P_4]^{2+}$ where broad ^{1}H NMR signals at δ 5.86 (M = Ru) and δ 6.26 (M = Os) are observed for the NH_2 groups and AB quartets (J_{AB} = 9.3 Hz) at δ 6.67 (M = Ru) and 6.54 (M = Os) for the methylene protons.[37] The ^{1}H NMR data for complex **10** is more consistent with that for a methylenehydrazide ligand given that the NH resonance is not to low field (i.e., not between δ 11−14) and no coupling is observed from the NH to the methylene protons as reported for free methyleneimine[38] and methyleneimine complexes.[36,39] In addition, a methyleneimine complex would be charged and unlikely to be pentane soluble.

Both mono[40] and bis-substituted[41] methylenehydrazide ($^-$NHN=CHR and $^-$NHN=CRR′) complexes are known, but to the best of our knowledge, methylenehydrazide complex **10** is the first report of a complex containing a parent methylenehydrazide ($^-$NHN=CH_2) ligand. Complex **10** is unstable both in solution and solid states and decomposes over time to afford dinitrogen complex $[Ru(N_2)(PP_3{}^{iPr})]$ and other unidentified products.

An unusual feature of $[RuH(NHN{=}CH_2)(PP_3{}^{iPr})]$ (**10**) is the evidence of chemical exchange between the methylene protons. Selective saturation of the downfield methylene signal (at δ 6.28) shows a dramatic reduction in the intensity of the upfield methylene proton (at δ 5.54) by saturation transfer, indicating chemical exchange between the methylene protons. The rate of exchange was measured to be approximately 2.8 s^{-1} at 298 K using an inversion-transfer-recovery experiment[42] (see the Supporting Information), and this translates to an activation barrier for the exchange process of about 70.4 kJ mol^{-1}. A reasonable rationalization for the facile exchange is that there is an allylic-type delocalization of electrons across the methylenehydrazide ligand (Scheme 9) which facilitates rotation about the N=C bond.

*Base-Induced Reaction of $[RuCl(^{15}N_2H_4)(PP_3{}^{Ph})]^+$ (**4**), $[RuCl(NH_2NHPh)(PP_3{}^{Ph})]^+$ (**6**) $[RuCl(NH_2NHMe)(PP_3{}^{Ph})]^+$ (**7**).* In an analogous reaction to that for $[RuCl(\eta^2\text{-}^{15}N_2H_4)(\eta^3\text{-}PP_3{}^{iPr})]^+$ (**1**), treatment of ^{15}N-labeled hydrazine complex $[RuCl(^{15}N_2H_4)(PP_3{}^{Ph})]^+$ (**4**, chloride or tetraphenylborate salt) with KO^{t}Bu in THF-d_8 afforded the Ru(0) dinitrogen $[Ru(^{15}N_2)(PP_3{}^{Ph})]$ and Ru dihydride $[RuH_2(PP_3{}^{Ph})]$ complexes in a ratio of 6:1 (NMR yields of approximately 72% and 13%, respectively) (Scheme 10). The resonances in the ^{1}H, ^{31}P, and ^{15}N NMR spectra are identical to those for the relevant complexes as previously reported in the literature.[43,44]

Similarly, treatment of phenylhydrazine complex $[RuCl(NH_2NHPh)(PP_3{}^{Ph})]^+$ (**6**) or methylhydrazine complex $[RuCl(NH_2NHMe)(PP_3{}^{Ph})]^+$ (**7**) with KO^{t}Bu under argon afforded the dinitrogen complex $[Ru(N_2)(PP_3{}^{Ph})]$ (85% yield by NMR) and benzene (87% yield by NMR) or methane (39% yield by NMR; the yield of methane is probably understated

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Table 1. Crystallographic Data for $[RuCl(\eta^2\text{-}N_2H_4)(\eta^3\text{-}PP_3{}^{iPr})]^+Cl^-$ (1), $[RuCl(\eta^2\text{-}NH_2NHMe)(\eta^3\text{-}PP_3{}^{iPr})]^+Cl^-$ (3), $[RuCl(\eta^1\text{-}N_2H_4)_2(\eta^3\text{-}PP_3{}^{Ph})]^+Cl^-$ (5), $[RuCl(NH_2NHPh)(PP_3{}^{Ph})]^+Cl^-$ (6), $[RuCl(NH_2NHMe)(PP_3{}^{Ph})]^+Cl^-$ (7), $[RuH_2(PP_3{}^{iPr})]$ (8), and $[RuH(C_6H_4N{=}NH)(\eta^3\text{-}PP_3{}^{iPr})]$ (9)

	1	3	5	6	7	8	9
formula	$C_{24}H_{58}Cl_2N_2P_4Ru$	$C_{25}H_{60}Cl_2N_2P_4Ru$	$C_{42}H_{46}Cl_2N_4P_4Ru$	$C_{114}H_{124}Cl_4N_{10}P_8Ru$	$C_{90}H_{104}Cl_4N_4OP_8Ru_2$	$C_{24}H_{56}P_4Ru$	$C_{37}H_{68}N_2P_4Ru$
M (g mol^{-1})	670.57	684.60	902.68	2225.93	1849.47	569.64	765.88
size (mm^3)	0.40 × 0.30 × 0.28	0.40 × 0.30 × 0.25	0.20 × 0.18 × 0.16	0.30 × 0.25 × 0.23	0.30 × 0.20 × 0.20	0.40 × 0.30 × 0.26	0.25 × 0.20 × 0.15
crystal morphology	colorless block	colorless block	colorless block	colorless block	colorless block	colorless block	orange block
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
space group	*Pbca*	$P2_1/c$ (no. 14)	$P2_1/c$ (no.14)	*Cc*	*Ibca*	$P2_1/n$ (no.14)	*P*-1
a (Å)	13.693(11)	13.6590(10)	14.411(16)	12.117(11)	17.3284(9)	10.7083(4)	12.2635(5)
b (Å)	18.134(15)	18.7193(14)	29.81(4)	27.59(3)	26.8150(12)	19.7253(8)	13.1418(5)
c (Å)	26.76(2)	26.3192(18)	9.912(11)	34.12(3)	36.139(3)	14.3069(6)	14.6359(5)
α (deg)	90	90	90	90	90	90	78.7060(10)
β (deg)	90	91.681(3)	100.35(3)	100.23(2)	90	107.7170(10)	71.3070(10)
γ (deg)	90	90	90	90	90	90	64.7060(10)
V (Å^3)	6 643(9)	6 726.6(8)	4 188(8)	11 228(19)	16 792.2(16)	2 878.6(2)	2015.36(13)
Z	8	8	4	4	8	4	2
D_c (g/cm^3)	1.341	1.352	1.432	1.317	1.463	1.314	1.262
μ (mm^{-1})	0.841	0.833	0.690	0.529	0.690	0.777	0.574
F(000)	2 832	2 896	1 856	4 616	7 648	1 216	816
$2\theta_{max}$ (deg)	60.9	53.5	49.8	52.7	54.4	62.0	54.2
N	79 190	55 357	24 036	86 165	125 524	38 868	32 206
N_{ind}	10 066 (R_{int} = 0.0444)	14 250 (R_{int} = 0.0646)	7 113 (R_{int} = 0.0949)	21 821 (R_{int} = 0.0294)	9 285 (R_{int} = 0.0347)	9 166 (R_{int} = 0.0251)	8 870 (R_{int} = 0.0264)
N_{obs} ($I > 2\sigma(I)$)	8 435	10 628	4 422	20 628	8 177	8 265	7 762
goodness of fit	1.047	1.199	0.984	1.041	1.040	1.046	1.023
$R1$ (F, $I > 2\sigma(I)$)	0.0258	0.0602	0.0504	0.0325	0.0251	0.0187	0.0259
wR2 (F^2, all data)	0.0563	0.1144	0.0867	0.0779	0.0596	0.0447	0.0535
absolute structure parameter				0.011(13)			

due to loss of methane gas from solution into the head space of the reaction mixture), respectively. Reduction of coordinated phenylhydrazine to ammonia and aniline has been reported.[3,17,24,45] Reduction of methylhydrazine to ammonia and methylamine has also been reported.[3,4] Only one report details the formation of dinitrogen and benzene as a mixture with ammonia and aniline from phenylhydrazine.[46] As far as we are aware, there is no precedent for the formation of dinitrogen and methane from coordinated methylhydrazine. The reactions of hydrazine complexes **4**, **6**, and **7** with base probably proceed through a mechanism analogous to that proposed for the reaction of $[RuCl(\eta^2\text{-}N_2H_4)(\eta^3\text{-}PP_3{}^{iPr})]^+$ (**1**) with base (Scheme 4) but with loss of benzene or methane, respectively, for complexes **6** and **7**.

CONCLUSIONS

We have reported the synthesis of tripodal phosphine (PP_3 where PP_3 = $PP_3{}^{iPr}$ = $P(CH_2CH_2P^iPr_2)_3$ and $PP_3{}^{Ph}$ = $P(CH_2CH_2PPh_2)_3$) complexes of Ru containing hydrazine, phenylhydrazine, and methylhydrazine ligands.

Treatment of the Ru hydrazine complexes with base (butoxide) affords the Ru(0) dinitrogen complexes and the Ru dihydride complexes. Treatment of the phenylhydrazine complex $[RuCl(NH_2NHPh)(PP_3{}^{Ph})]^+$ with base affords the Ru(0) dinitrogen complex and benzene. Treatment of the methylhydrazine complex $[RuCl(NH_2NHMe)(PP_3{}^{Ph})]^+$ with base affords the Ru(0) dinitrogen complex and methane.

The treatment of phenylhydrazine complex $[RuCl(\eta^2\text{-}NH_2NHPh)(\eta^3\text{-}PP_3{}^{iPr})]^+$ with base affords a new hydrido ruthenaindazole complex $[RuH(C_6H_4N{=}NH)(\eta^3\text{-}PP_3{}^{iPr})]$ containing a cyclometalated phenyldiazene ligand. This is the first report of formation of an end-on bound phenyldiazene ligand by base treatment of the phenylhydrazine ligand.

The base treatment of methylhydrazine complex $[RuCl(\eta^2\text{-}NH_2NHMe)(\eta^3\text{-}PP_3{}^{iPr})]^+$ affords the hydrido methylenehydrazide complex $[RuH(NHN{=}CH_2)(PP_3{}^{iPr})]$, and this the first report of a complex containing the parent methylenehydrazide ligand.

These reactions, where the Ru center is coordinated by a hindered tripodal PP_3 ligand, in contrast to those reported for Ru complexes with bidentate ligands dmpe and depe, where side-on bound diazene complexes were isolated as stable complexes. These results exemplify how changes in the ligand environment can dramatically impact the reactivity pathways of ruthenium hydrazines and may be due to a number of factors including the balance between the steric and electronic effects of the tripodal phosphine ligands.

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) and dimethoxymagnesium (methanol). Tetrahydrofuran, 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, benzene-d_6, and toluene-d_8 were dried over and distilled from sodium/benzophenone. Hydrazine (1 M in THF) was purchased from Aldrich and deoxygenated before use. Hydrazine-$^{15}N_2$ was prepared by Soxhlet extraction of $^{15}N_2H_4{\cdot}H_2SO_4$ with liquid ammonia.[47] Methylhydrazine

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was dried over barium oxide, vacuum distilled, and stored over activated molecular sieves under nitrogen. Phenylhydrazine was vacuum distilled and stored over activated molecular sieves under nitrogen. $Ph^{15}NHNH_2$ was prepared by diazotization of aniline-^{15}N with sodium nitrite (unlabeled) and subsequent reduction with sodium sulfite. Potassium *t*-butoxide was sublimed twice and stored under an inert atmosphere. Potassium triethylborohydride ($KBEt_3H$) was synthesized by reaction of equimolar amounts of potassium hydride and triethylboron in toluene and hexane. Tris[2-(diphenylphosphino)ethyl]phosphine (PP_3^{Ph}) was purchased from Aldrich and used without further purification. $[RuCl_2(PP_3^{Ph})]$ was prepared from $[RuCl_2(PPh_3)_3]$ according to the literature method.[43] Tris[2-(diisopropylphosphino)ethyl]phosphine (PP_3^{iPr}) and $[RuCl(PP_3^{iPr})]^+Cl^-$ were prepared according to the literature method.[12]

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, ^{31}P, and ^{15}N NMR spectra were recorded on Bruker Avance III 600, 400 or DPX 300 NMR spectrometers at 298 K unless otherwise stated. ^1H NMR spectra were referenced to residual solvent resonances while ^{31}P spectra were referenced to external neat trimethyl phosphite at δ 140.85 ppm. ^{15}N NMR spectra were reference to external neat nitromethane at δ 0.0 ppm. Simulation of ^{31}P spectra were performed iteratively using the simulation program NUMMRIT (SpinWorks 3) where signs for coupling constants are not implied. Infrared spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer as nujol mulls. ^{31}P solid state NMR spectra were recorded on a Bruker Avance III 300 MHz solid state spectrometer equipped with an Oxford 300 magnet. Samples were spun in a 4 mm rotor at 12 or 14 kHz and spectra were referenced to external ammonium dihydrogen phosphate (ADP) at δ 1.0. Mass spectrometric analyses were carried out at the Bioanalytical Mass Spectrometry Facility, UNSW. Microanalyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. X-ray crystallography was carried out on a Bruker Nonius X8 Apex II CCD diffractometer (MoKα radiation, λ = 0.710 73 Å, T = 100(2) K). Crystallographic data are presented in Table 1.

$[RuCl(\eta^2\text{-}N_2H_4)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (1). Methanol (0.4 mL) was added to a suspension of $[RuCl(PP_3^{iPr})]^+Cl^-$ (93 mg, 0.15 mmol) in hydrazine (1 M in THF, 1 mL, 1 mmol) under nitrogen to give a yellow solution. $^{31}P\{^1H\}$ NMR (hydrazine/MeOH/THF, 122 MHz): δ 108.3 (dt, $^2J_{PC\text{-}PT}$ 18 Hz, $^2J_{PC\text{-}PF}$ 21 Hz, 1P, $\mathbf{P_C}$), 91.6 (d, 2P, $\mathbf{P_T}$), 8.3 (d, 1P, $\mathbf{P_F}$). Diethyl ether (5 mL) was added, and yellow crystals precipitated from the reaction mixture overnight. The product was collected by filtration, washed with diethyl ether, then dried *in vacuo* (74 mg, 0.11 mmol, 74%). $C_{24}H_{58}Cl_2N_2P_4Ru$ (670.69) requires C, 43.0; H, 8.7; N, 4.2; found C, 43.2; H, 8.8; N, 4.2%. ^{31}P solid state NMR: δ 109.3 (1P, $\mathbf{P_C}$), 95.9 (1P, $\mathbf{P_{T1}}$), 90.5 (1P, $\mathbf{P_{T2}}$), 4.3 (1P, $\mathbf{P_F}$). IR: 3282m, 3189w, 3113w, 2748w, 1592m, 1561m, 1418m, 1368m, 1245m, 1183w, 1159m, 1139w, 1121w, 1113w, 1100w, 1068w, 1048m, 1026w, 994w, 964w, 930w, 896m, 891m, 885m, 840w, 811m, 782m, 758w, 721s, 708s, 688s, 657s, 636s, 617s, 607s cm^{-1}.

The ^{15}N-labeled analogue $[RuCl(\eta^2\text{-}^{15}N_2H_4)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ was prepared in a similar reaction using $^{15}N_2H_4$. $^{31}P\{^1H\}$ NMR (MeOH/THF/THF-d_8, 122 MHz): δ 108.4 (dt, $^2J_{PC\text{-}PE}$ 18 Hz, $^2J_{PC\text{-}PF}$ 21 Hz, 1P, $\mathbf{P_C}$), 91.9 (dd, $^2J_{PE\text{-}N}$ 21 Hz, 2P, $\mathbf{P_T}$), 8.3 (d, 1P, $\mathbf{P_F}$). $^{15}N\{^1H\}$ NMR (MeOH/THF/THF-d_8, 41 MHz): δ −336.4 (s, free $^{15}N_2H_4$), −364.7 (d, $^2J_{NP}$ 21 Hz, Ru-$\mathbf{N}H_2$).

$[RuCl(\eta^2\text{-}NH_2NHPh)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (2). Methanol (6 drops) was added to a suspension of $[RuCl(PP_3^{iPr})]^+Cl^-$ (0.113 g, 0.177 mmol) and phenylhydrazine (0.307 g, 2.84 mmol) in THF (1 mL) under nitrogen to give a dark orange solution. Hexane (10 mL) was added and yellow solid precipitated from the reaction mixture overnight. The product was collected by filtration, washed with hexane, then dried *in vacuo* (0.146 g, 0.157 mmol, 89%). $C_{30}H_{62}Cl_2N_2P_4Ru{\cdot}C_6H_8N_2{\cdot}C_4H_8O$ (927.07) requires C, 51.8; H, 8.5; N, 6.0; found C, 51.4; H, 8.5; N, 6.3%. $^{31}P\{^1H\}$ NMR (phenylhydrazine/THF/THF-d_8, 162 MHz): δ 104.8 (m, 1P, $\mathbf{P_C}$), 83.9 (br, 1P, $\mathbf{P_{T1}}$), 72.3 (br, 1P, $\mathbf{P_{T2}}$), 8.4 (m, 1P, $\mathbf{P_F}$). ^{31}P solid state NMR: δ 105.1 (1P, $\mathbf{P_C}$), 72.1 (1P, $\mathbf{P_{T1}}$), 68.1 (1P, $\mathbf{P_{T2}}$), 3.9 (1P, $\mathbf{P_F}$).

The ^{15}N-labeled analogue was prepared in a similar manner using $[RuCl(PP_3^{iPr})]^+Cl^-$ (0.103 g, 0.161 mmol) and $Ph^{15}NHNH_2$ (0.249 g, 2.30 mmol) to afford $[RuCl(NH_2{}^{15}NHPh)(PP_3^{iPr})]^+Cl^-$ (0.116 g, 0.125 mmol, 78%).

$[RuCl(\eta^2\text{-}NH_2NHMe)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (3). Methylhydrazine (0.2 mL, 4 mmol) was added to a suspension of $[RuCl(PP_3^{iPr})]^+Cl^-$ (0.136 g, 0.213 mmol) in THF (2 mL) under nitrogen to give a yellow solution. $^{31}P\{^1H\}$ NMR (methylhydrazine/THF/THF-d_8, 162 MHz): δ 105.9 (q, $^2J_{PP}$ 19 Hz, 4.4P), 104.1 (m, 1P), 103.3 (m, 1.3P), 101.9 (dt, $^2J_{PP}$ 26 Hz, $^2J_{PP}$ 19 Hz, 1.4P), 99.9 (q, $^2J_{PP}$ 20 Hz, 4P), 92.3 (t, $^2J_{PP}$ 16 Hz, 4.4P), 91.5 (m, 1.3P), 89.9 (m, 1.5P), 88.6 (t, $^2J_{PP}$ 17 Hz, 4P), 88.2 (m, 1P), 81.4 (t, $^2J_{PP}$ 22 Hz, 1.2P), 72.3 (d, $^2J_{PP}$ 20 Hz, 8.2P), 70.8 (m, 1P), 64.7 (dd, $^2J_{PP}$ 24 Hz, $^2J_{PP}$ 19 Hz, 1.2P), 10.0 (m, 1.3P), 9.4–8.1 (m, 10.5P). Diethyl ether (6 mL) was added and yellow crystals precipitated from the reaction mixture overnight. The product was collected by filtration, washed with diethyl ether, then dried in vacuo (0.129 g, 0.188 mmol, 88%). $C_{25}H_{60}Cl_2N_2P_4Ru$ (684.72) requires C, 43.9; H, 8.9; N, 4.1; found C, 44.0; H, 8.9; N, 4.1%. ^{31}P solid state NMR: δ 104.9 (1P, $\mathbf{P_C}$), 96.8 (1P, $\mathbf{P_{T1}}$), 83.1 (1P, $\mathbf{P_{T2}}$), −3.3 (1P, $\mathbf{P_F}$). IR: 3248w, 3155w, 3079m, 1584s, 1402m, 1379s, 1315w, 1251m, 1183m, 1157w, 1099m, 1061m, 1044s, 1021s, 988w, 965w, 928w, 900m, 885m, 841w, 817m, 784m, 722s, 709s, 691s, 656s, 630m, 616s cm^{-1}.

$[RuCl(N_2H_4)(PP_3^{Ph})]^+X^-$ (4). *X*=*Cl*. $[RuCl_2(PP_3^{Ph})]$ (53 mg, 63 μmol) was dissolved in a hydrazine solution (1 M in THF, 2 mL, 2 mmol) under nitrogen to give a yellow solution. On standing for several days, a yellow crystalline solid precipitated from the reaction mixture. The product was collected by filtration and washed with THF. The product was used directly in the next step without further purification. $^{31}P\{^1H\}$ NMR (MeOH, 122 MHz): δ 144.9 (dt, $^2J_{PC\text{-}PU}$ 11.1 Hz, $^2J_{PC\text{-}PT}$ 10.9 Hz, 1P, $\mathbf{P_C}$), 60.2 (dt, $^2J_{PU\text{-}PT}$ 25.2 Hz, 1P, $\mathbf{P_U}$), 35.1 (dd, 2P, $\mathbf{P_T}$). Crystals of $[RuCl(\eta^1\text{-}N_2H_4)_2(\eta^3\text{-}PP_3^{Ph})]^+Cl^-$ (**5**) suitable for X-ray crystallography were obtained from a similar reaction mixture as above which was left to stand at room temperature for several days. ^{31}P solid state NMR: δ 106.7 (1P, $\mathbf{P_C}$), 63.3 (1P, $\mathbf{P_{T1}}$), 58.8 (1P, $\mathbf{P_{T2}}$), −2.4 (1P, $\mathbf{P_F}$).

The ^{15}N-labeled analogue $[RuCl(^{15}N_2H_4)(PP_3^{Ph})]^+Cl^-$ was prepared in a similar manner using $^{15}N_2H_4$. $^{31}P\{^1H\}$ NMR (MeOH, 121 MHz): δ 144.9 (dt, $^2J_{PC\text{-}PU}$ 10.9 Hz, $^2J_{PC\text{-}PT}$ 10.9 Hz, 1P, $\mathbf{P_C}$), 60.1 (ddt, $^2J_{PU\text{-}PT}$ 25.2 Hz, $^2J_{PU\text{-}N}$ 31.0 Hz 1P, $\mathbf{P_U}$), 35.1 (dd, 2P, $\mathbf{P_T}$). $^{15}N\{^1H\}$ NMR (MeOH, 30 MHz): δ −320.2 (d, $^1J_{NN}$ 6 Hz, $\mathbf{N}H_2$), −345.3 (dd, $^2J_{NP}$ 31 Hz, $^1J_{NN}$ 6 Hz, Ru-$\mathbf{N}H_2$).

X=*BPh*$_4$. A solution of $NaBPh_4$ (49 mg, 0.14 mmol) in methanol (0.5 mL) was added to a solution of $[RuCl(N_2H_4)(PP_3^{Ph})]^+Cl^-$ in methanol (1 mL). The precipitate formed was collected by filtration, washed with methanol (3 × 1 mL), and dried *in vacuo* to afford a yellow solid (56 mg, 48 μmol, 77%). $C_{66}H_{66}BClN_2P_4Ru$ (1158.55) requires C, 68.4; H, 5.8; N, 2.4; found C, 68.3; H, 6.0; N, 2.4%. ^1H NMR (THF-d_8, 400 MHz): δ 7.82 (m, 4H, **Ph**), 7.71–7.24 (m, 22H, **Ph**), 7.09–6.75 (m, 24H, **Ph**), 3.39–3.09 (m, 4H, Ru$\mathbf{N}H_2$, $\mathbf{C}H_2$), 2.65–2.37 (m, 2H, $\mathbf{C}H_2$), 2.36–1.97 (m, 8H, $\mathbf{C}H_2$), 1.94 (br, 2H, $\mathbf{N}H_2$). $^1H\{^{31}P\}$ NMR (THF-d_8, 400 MHz): δ 7.82 (m, 4H, **Ph**), 7.53–7.24 (m, 22H, **Ph**), 7.05–6.74 (m, 24H, **Ph**), 3.34–3.14 (m, 4H, Ru$\mathbf{N}H_2$, $\mathbf{C}H_2$), 2.57–2.42 (m, 2H, $\mathbf{C}H_2$), 2.27 (m, 2H, $\mathbf{C}H_2$), 2.13 (m, 2H, $\mathbf{C}H_2$), 2.03 (br, 4H, $\mathbf{C}H_2$), 1.93 (br t, $^3J_{HH}$ 4 Hz, 2H, $\mathbf{N}H_2$). $^{31}P\{^1H\}$ NMR (THF-d_8, 162 MHz): δ 142.5 (dt, $^2J_{PC\text{-}PU}$ 11.0 Hz, $^2J_{PC\text{-}PT}$ 11.3 Hz, 1P, $\mathbf{P_C}$), 59.2 (dt, $^2J_{PU\text{-}PT}$ 25.2 Hz, 1P, $\mathbf{P_U}$), 34.1 (dd, 2P, $\mathbf{P_T}$). $^{15}N\{^1H\}$ NMR (THF-d_8, 41 MHz, from HN-HSQC): δ −321.1 (corr with ^1H δ 1.94, $\mathbf{N}H_2$), −344.8 (corr with ^1H δ 3.26, Ru$\mathbf{N}H_2$). IR: 3343w, 3296m, 3254w, 3231w, 3053m, 1600w, 1579m, 1482m, 1435s, 1337w, 1306w, 1264w, 1190w, 1160w, 1097m, 1031w, 999w, 972w, 917w, 899w, 885w, 847w, 830w, 801w, 788w, 735s, 720s, 701s, 674m, 612s cm^{-1}.

$[RuCl(NH_2NHPh)(PP_3^{Ph})]^+X^-$ (6). *X*=*Cl*. Phenylhydrazine (0.1 mL, 1 mmol) was added to a suspension of $[RuCl_2(PP_3^{Ph})]$ (32 mg, 38 μmol) in THF (0.6 mL) under nitrogen to give a pale yellow solution. Diethyl ether (2 mL) was added and the reaction mixture left to stand for 1 week. Crystals suitable for X-ray crystallography were obtained from this reaction mixture. The remaining solid was collected

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by filtration, washed with diethyl ether (3 × 1 mL), and dried *in vacuo* (30 mg, 32 μmol, 83%). ^{31}P solid state NMR: δ 140.4 (1P, **P**$_C$), 59.4 (1P, **P**$_U$), 37.0 (d, $^2J_{P-P}$ 283 Hz, 1P, **P**$_{T1}$), 30.4 (d, $^2J_{P-P}$ 283 Hz, 1P, **P**$_{T2}$).

X=*BPh*$_4$. A solution of $NaBPh_4$ (37 mg, 0.11 mmol) in methanol (0.5 mL) was added to a solution of $[RuCl(NH_2NHPh)(PP_3^{Ph})]^+Cl^-$ (37 mg, 39 μmol) in methanol (0.5 mL). The precipitate formed was collected by filtration, washed with methanol (2 × 3 mL), and dried *in vacuo* to afford a yellow solid (39 mg, 32 μmol, 81%). $C_{72}H_{70}BClN_2P_4Ru$ (1234.65) requires C, 70.0; H, 5.7; N, 2.3; found C, 70.0; H, 5.8; N, 2.3%. ^{1}H NMR (THF-d_8, 400 MHz, 281K): δ 7.72 (br, 4H, **Ph**), 7.53 (m, 4H, **Ph**), 7.44 (m, 12H, **Ph**), 7.15−6.74 (m, 32H, **Ph**), 6.64 (m, 1H, **Ph**), 5.44 (m, 2H, **Ph**), 3.70 (br, 3H, RuN**H**$_2$ and N**H**Ph), 3.22 (m, 2H, C**H**$_2$), 2.60 (m, 2H, C**H**$_2$), 2.27−1.94 (m, 8H, C**H**$_2$). ^{1}H{^{31}P} NMR (THF-d_8, 400 MHz, 280K): δ 7.72 (br, 4H, **Ph**), 7.53 (m, 4H, **Ph**), 7.44 (m, 12H, **Ph**), 7.15−6.74 (m, 32H, **Ph**), 6.64 (m, 1H, **Ph**), 5.44 (m, 2H, **Ph**), 3.70 (br, 3H, RuN**H**$_2$ and N**H**Ph), 3.22 (m, 2H, C**H**$_2$), 2.60 (m, 2H, C**H**$_2$), 2.20 (m, 2H, C**H**$_2$), 2.14−1.90 (m, 6H, C**H**$_2$). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz, 280 K): δ 139.8 (app. q, splitting 12 Hz, 1P, **P**$_C$), 59.0 (dt, $^2J_{PU-PT}$ 26 Hz, $^2J_{PU-PC}$ 12 Hz, 1P, **P**$_U$), 32.4 (dd, $^2J_{PU-PT}$ 26 Hz, $^2J_{PT-PC}$ 11 Hz, 2P, **P**$_T$). ^{15}N{^{1}H} NMR (THF-d_8, 41 MHz, from HN-HSQC, 284K): δ −284.8, (corr with ^{1}H δ 3.70, N**H**Ph), −328.4 (corr with ^{1}H δ 3.70, RuN**H**$_2$). IR: 3342w, 3276m, 3191w, 3053s, 1952w, 1889w, 1818w, 1770w, 1601m, 1579m, 1495m, 1483s, 1435s, 1337w, 1308w, 1251m, 1190w, 1159w, 1098m, 1031w, 999w, 971w, 897w, 885w, 847m, 829w, 801w, 787w, 748s, 734s, 720s, 701s, 676m, 623m, 612s cm^{-1}.

[RuCl(NH$_2$NHMe)(PP$_3^{Ph}$)]$^+$X$^-$ (7). *X* = *Cl*. Methylhydrazine (0.1 mL, 2 mmol) was added to a suspension of $[RuCl_2(PP_3^{Ph})]$ (44 mg, 52 μmol) in THF (0.4 mL) under nitrogen to give a very pale yellow solution. Diethyl ether (2 mL) was added, and the reaction mixture was left to stand for 1 month. The pale yellow needles formed were collected by filtration, washed with diethyl ether (3 × 0.5 mL), and dried *in vacuo* (44 mg, 50 μmol, 95%). $C_{43}H_{48}Cl_2N_2P_4Ru$ (888.78) requires C, 58.1; H, 5.5; N, 3.2; found C, 58.3; H, 5.4; N, 3.1%. ^{31}P{^{1}H} NMR (MeOH, 122 MHz): δ 144.9 (dt, $^2J_{PC-PU}$ 11.1 Hz, $^2J_{PC-PT}$ 10.9 Hz, 1P, **P**$_C$), 60.2 (dt, $^2J_{PU-PT}$ 25.2 Hz, 1P, **P**$_U$), 35.1 (dd, 2P, **P**$_T$). IR: 3302w, 3277w, 3193w, 3047w, 3034w, 1572w, 1482s, 1433s, 1334w, 1313w, 1274w, 1191m, 1157w, 1122m, 1098s, 1065m, 1030w, 998m, 973w, 959w, 897m, 847w, 828s, 801m, 787m, 756m, 745s, 719s, 698s, 669m cm^{-1}. Crystals suitable for X-ray crystallography were obtained from a similar reaction mixture to that described above.

X = *BPh*$_4$. A solution of $NaBPh_4$ (46 mg, 0.13 mmol) in methanol (1 mL) was added to a solution of $[RuCl(NH_2NHMe)(PP_3^{Ph})]^+Cl^-$ (53 mg, 60 μmol) in methanol (1 mL). The precipitate formed was collected by filtration, washed with methanol several times, and dried *in vacuo* to afford a pale yellow solid (64 mg, 55 μmol, 91%). ^{1}H NMR (THF-d_8, 400 MHz): δ 7.75 (br, 4H, **Ph**), 7.54 (m, 4H, **Ph**), 7.46−7.26 (m, 18H, **Ph**), 7.03 (m, 2H, **Ph**), 7.00−6.86 (m, 14H, **Ph**), 6.82 (m, 8H, **Ph**), 3.21 (m, 2H, C**H**$_2$), 3.04 (br s, 2H, RuN**H**$_2$), 2.48 (m, 2H, C**H**$_2$), 2.19 (m, 2H, C**H**$_2$), 2.04 (m, 6H, C**H**$_2$), 1.50 (q, $^3J_{HH}$ 6 Hz, 1H, N**H**Me), 0.80 (d, $^3J_{HH}$ 6 Hz, 3H, C**H**$_3$). ^{1}H{^{31}P} NMR (THF-d_8, 400 MHz): δ 7.75 (br, 4H, **Ph**), 7.54 (m, 4H, **Ph**), 7.46−7.25 (m, 18H, **Ph**), 7.03 (m, 2H, **Ph**), 7.00−6.86 (m, 14H, **Ph**), 6.82 (m, 8H, **Ph**), 3.21 (m, 2H, C**H**$_2$), 3.04 (m, 2H, RuN**H**$_2$), 2.47 (m, 2H, C**H**$_2$), 2.19 (m, 2H, C**H**$_2$), 2.04 (m, 6H, C**H**$_2$), 1.50 (q, $^3J_{HH}$ 6 Hz, 1H, N**H**Me), 0.80 (d, $^3J_{HH}$ 6 Hz, 3H, C**H**$_3$). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz): δ 140.5 (app. q, splitting 12 Hz, 1P, **P**$_C$), 57.6 (dt, $^2J_{PU-PT}$ 25 Hz, $^2J_{PU-PC}$ 12 Hz, 1P, **P**$_U$), 33.4 (dd, $^2J_{PU-PT}$ 25 Hz, $^2J_{PT-PC}$ 12 Hz, 2P, **P**$_T$). ^{15}N{^{1}H} NMR (THF-d_8, 41 MHz, from HN-HSQC): δ −309.6 (corr with ^{1}H δ 1.50, N**H**Me), −314.5 (corr with ^{1}H δ 3.04, RuN**H**$_2$). IR: 3319w, 3271w, 3189w, 3053m, 3035m, 1579m, 1483s, 1435s, 1337w, 1310w, 1269w, 1247w, 1191w, 1160w, 1125w, 1098m, 1031w, 1000w, 972w, 948w, 899w, 885w, 847w, 830m, 819w, 802w, 788w, 734s, 701s, 674m, 658w, 612m cm^{-1}.

Reaction of [RuCl(η^2-^{15}N$_2$H$_4$)(η^3-PP$_3^{iPr}$)]$^+$Cl$^-$ with KO^{t}Bu. $[RuCl(\eta^2\text{-}^{15}N_2H_4)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (29 mg, 43 μmol) and KO^{t}Bu (22 mg, 0.20 mmol) were suspended in THF-d_8 under nitrogen to give a dark green then yellow reaction mixture which was filtered into an NMR tube. ^{1}H NMR (THF-d_8, 400 MHz, high field only): δ −9.49 (br, RuH$_2$). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz): δ 162.1 (m, RuN$_2$ **P**$_C$), 155.0 (q, $^2J_{PC-PE}$ 12 Hz, RuH$_2$ **P**$_C$), 92.1 (br, RuH$_2$ **P**$_T$), 88.3 (m, RuN$_2$ **P**$_T$). ^{15}N{^{1}H} NMR (THF-d_8, 41 MHz): δ −12.8 (s, **N**$_\beta$), −53.3 (m, Ru**N**$_\alpha$).

[RuH$_2$(PP$_3^{iPr}$)] (8). A condenser containing dry ice and acetone was attached to a flask containing $[RuCl(PP_3^{iPr})]^+Cl^-$ (0.393 g, 0.615 mmol) and sodium (0.29 g, 13 mmol) under argon. Ammonia (approximately 50 mL) was condensed into the flask, and the mixture refluxed for about 4 h. The ammonia was slowly evaporated off under a stream of argon. The residue was dried *in vacuo* to remove the last traces of ammonia then extracted with pentane (50 mL) and filtered through Celite, and the solvent was removed under reduced pressure. The residue was dried *in vacuo* to afford a pale brown solid (0.129 g, 0.201 mmol, 33% yield). $C_{24}H_{56}P_4Ru{\cdot}C_5H_{12}$ (641.82) requires C, 54.3; H, 10.7; found C, 54.5; H, 10.3%. ^{1}H NMR (benzene-d_6, 400 MHz): δ 1.68 (m, 6H, C**H**), 1.47−1.32 (br m, 12H, C**H**$_2$), 1.27 (m, 18H, C**H**$_3$), 1.20 (m, 18H, C**H**$_3$), −9.13 (br, 2H, Ru**H**). ^{1}H{^{31}P} NMR (benzene-d_6, 400 MHz): δ 1.68 (sep, $^3J_{HH}$ 7 Hz, 6H, C**H**), 1.36 (br m, 12H, C**H**$_2$), 1.27 (d, $^3J_{HH}$ 7 Hz, 18H, C**H**$_3$), 1.20 (d, $^3J_{HH}$ 7 Hz, 18H, C**H**$_3$), −9.13 (br, 2H, Ru**H**). ^{31}P{^{1}H} NMR (benzene-d_6, 162 MHz): δ 154.2 (q, $^2J_{PC-PE}$ 12 Hz, 1P, **P**$_C$), 91.8 (br, 3P, **P**$_E$). ^{1}H NMR (toluene-d_8, 600 MHz, 200 K): δ 2.23−0.53 (C**H**/C**H**$_2$/C**H**$_3$), −5.55 (m, 1H, Ru**H**), −12.61 (m, 1H, Ru**H**). ^{31}P{^{1}H} NMR (toluene-d_8, 243 MHz, 200 K): δ 152.6 (br, 1P, **P**$_C$), 95.5 (br, 2P, **P**$_T$), 79.0 (br, 1P, **P**$_U$). Crystals suitable for X-ray crystallography were obtained by slow evaporation of a benzene/benzene-d_6 solution under argon.

$[RuH_2(PP_3^{iPr})]$ was also synthesized by treatment of $[RuCl(PP_3^{iPr})]^+Cl^-$ (0.302 g, 0.473 mmol) with KBEt$_3$H (0.187 g, 1.36 mmol) in toluene (10 mL) under argon overnight. The solvent was removed under reduced pressure with warming from an oil bath. The residue was extracted with hexane (50 mL), sonicated for 20 min, filtered through Celite and the solvent removed under reduced pressure. The residue was dried *in vacuo* to afford a very pale yellow solid (0.107 g, 0.187 mmol, 40% yield).

[RuH(C$_6$H$_4$N═NH)(η^3-PP$_3^{iPr}$)] (9). $[RuCl(\eta^2\text{-}NH_2NHPh)(\eta^3\text{-}PP_3^{iPr})]^+Cl^-$ (90 mg, 0.12 mmol) and KO^{t}Bu (83 mg, 0.74 mmol) were stirred overnight in THF (2 mL) under nitrogen to give a dark blue-green suspension which gradually turned orange. The reaction mixture was evaporated to dryness under vacuum. The residue was extracted with pentane (15 mL) and filtered through Celite, and the solvent was removed under reduced pressure. The residue was dried *in vacuo* to afford a red-orange solid (30 mg, 45 μmol, 37%). $C_{30}H_{60}N_2P_4Ru$ (673.87) requires C, 53.5; H, 9.0; N, 4.2 found C, 53.8; H, 9.0; N, 4.0%. ^{1}H NMR (THF-d_8, 300 MHz): δ 14.75 (s, 1H, N**H**), 8.08 (m, 1H, **Ph**), 8.01 (m, 1H, **Ph**), 6.83 (m, 1H, **Ph**), 6.71 (m, 1H, **Ph**), 2.23−1.92 (m, 6H, C**H**/C**H**$_2$), 1.90−1.61 (m, 7H, C**H**/C**H**$_2$), 1.47 (m, 2H, C**H**$_2$), 1.32−1.08 (m, 20H, C**H**$_2$/C**H**$_3$), 1.08−0.95 (m, 7H, C**H**$_2$/C**H**$_3$), 0.77 (m, 6H, C**H**$_3$), −0.02 (m, 6H, C**H**$_3$), −12.52 (dt, $^2J_{HP}$ 14 Hz, 28 Hz, 1H, Ru**H**). ^{1}H{^{31}P} NMR (THF-d_8, 300 MHz): δ 14.74 (s, 1H, N**H**), 8.08 (m, 1H, **Ph**), 8.01 (m, 1H, **Ph**), 6.83 (m, 1H, **Ph**), 6.71 (m, 1H, **Ph**), 2.22−1.94 (m, 6H, C**H**/C**H**$_2$), 1.89−1.60 (m, 7H, C**H**/C**H**$_2$), 1.47 (m, 2H, C**H**$_2$), 1.31−1.08 (m, 20H, C**H**$_2$/C**H**$_3$), 1.08−0.97 (m, 7H, C**H**$_2$/C**H**$_3$), 0.77 (d, $^3J_{HH}$ 7 Hz, 6H, C**H**$_3$), −0.02 (d, $^3J_{HH}$ 7 Hz, 6H, C**H**$_3$), −12.52 (s, 1H, Ru**H**). ^{31}P{^{1}H} NMR (THF-d_8, 122 MHz): δ 103.4 (dt, $^2J_{PC-PE}$ 15 Hz, $^2J_{PC-PF}$ 19 Hz, 1P, **P**$_C$), 92.5 (d, 2P, **P**$_T$), 8.2 (d, 1P, **P**$_F$). ^{15}N{^{1}H} NMR (THF-d_8, 30 MHz, from HN-HSQC): δ 2.4 (corr with ^{1}H δ 14.75, Ru**N**H). IR: 3162m, 1928m (ν Ru−H), 1602w, 1574m, 1537w, 1412m, 1364m, 1307s, 1292s, 1238s, 1170m, 1152w, 1095w, 1076w, 1035w, 1020m, 1008m, 923w, 881m, 860m, 835w, 794w, 774m, 751w, 720s, 707s, 695s, 672s, 646s, 625s, 611s, 601s cm^{-1}. MS (ESI, THF): *m*/*z* 675.2836 [100%, (M + H)$^+$]. Crystals suitable for X-ray crystallography were obtained by slow evaporation of a toluene solution under nitrogen.

The ^{15}N-labeled analogue was prepared in a similar manner using $[RuCl(NH_2{}^{15}NHPh)(PP_3^{iPr})]^+Cl^-$ (72 mg, 96 μmol) and KO^{t}Bu (42 mg, 0.37 mmol) to afford $[RuH(C_6H_4{}^{15}N{=}NH)(\eta^3\text{-}PP_3^{iPr})]$ (39 mg, 58 μmol, 60%). ^{15}N NMR (THF-d_8, 41 MHz): δ 110.7 (**N**C$_6$H$_4$).

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[RuH(NHN=CH$_2$)(PP$_3^{iPr}$)] (10). [RuCl(η^2-NH$_2$NHMe)(η^3-PP$_3^{iPr}$)]$^+$Cl$^-$ (60 mg, 88 μmol) and KO^{t}Bu (80 mg, 0.71 mmol) were stirred in THF (2 mL) under nitrogen for 6 min, then the reaction mixture was evaporated to dryness under reduced pressure. The residue was extracted with pentane (12 mL), filtered through Celite, and the solvent was removed under reduced pressure. The residue was dried *in vacuo* to afford a yellow solid (33.6 mg, 54.9 μmol, 62%). ^{1}H NMR (toluene-d_8, 600 MHz): δ 6.28 (d, $^2J_{HH}$ 13.5 Hz, 1H, =CHH), 5.54 (d, $^2J_{HH}$ 13.5 Hz, 1H, =CHH), 5.27 (d, $^2J_{HP}$ 7.1 Hz, 1H, NH), 2.21−0.61 (m, CH/CH$_2$/CH$_3$), −10.69 (ddt, $^2J_{HP}$ 93.5, 29.8, 18.1 Hz, 1H, RuH). ^{1}H{^{31}P} NMR (toluene-d_8, 600 MHz): δ 6.28 (d, $^2J_{HH}$ 13.5 Hz, 1H, =CHH), 5.54 (d, $^2J_{HH}$ 13.5 Hz, 1H, =CHH), 5.27 (s, 1H, NH), 2.21−0.61 (m, CH/CH$_2$/CH$_3$), −10.69 (s, 1H, RuH). ^{31}P{^{1}H} NMR (toluene-d_8, 243 MHz): δ 145.4 (app. q, splitting =11.3 Hz, 1P, $\mathbf{P_C}$), 63.5 (app. t, splitting =13.3 Hz, 2P, $\mathbf{P_T}$), 52.9 (m, 1P, $\mathbf{P_U}$). ^{13}C{^{1}H} NMR (toluene-d_8, 151 MHz, from HC-HSQC): δ 104.4 (corr with ^{1}H δ 6.28 and 5.54, N=CH$_2$). ^{1}H NMR (toluene-d_8, 600 MHz, 200 K): δ 6.55 (d, $^2J_{HH}$ 13 Hz, 1H, =CHH), 5.87 (d, $^2J_{HH}$ 13 Hz, 1H, =CHH), 5.51 (br, 1H, NH), 2.35−0.00 (m, CH/CH$_2$/CH$_3$), −10.61 (m, 1H, RuH). ^{15}N{^{1}H} NMR (toluene-d_8, 61 MHz, from HN-HSQC, 200 K): δ −266.4 (corr with ^{1}H δ 5.51, RuNH).

Reaction of [RuCl(^{15}N$_2$H$_4$)(PP$_3^{Ph}$)]$^+$Cl$^-$ with KO^{t}Bu. [RuCl(^{15}N$_2$H$_4$)(PP$_3^{Ph}$)]$^+$Cl$^-$ (48 mg, 55 μmol) and KO^{t}Bu (15 mg, 0.13 mmol) were suspended in THF-d_8 under nitrogen to give a dark red solution and some insoluble orange solid. The supernatant liquid was decanted into an NMR tube. ^{1}H NMR (THF-d_8, 400 MHz, high field only): δ −7.18 (m, RuH$_2$). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz): δ 160.5 (m, RuN$_2$ $\mathbf{P_C}$), 158.0 (q, $^2J_{PC\text{-}PE}$ 7 Hz, RuH$_2$ $\mathbf{P_C}$), 77.9 (d, RuH$_2$ $\mathbf{P_E}$), 70.5 (m, RuN$_2$ $\mathbf{P_E}$). ^{15}N{^{1}H} NMR (THF-d_8, 41 MHz): δ −24.7 (s, $\mathbf{N}_\beta$), −63.4 (m, RuN$_\alpha$).

Reaction of [RuCl(NH$_2$NHPh)(PP$_3^{Ph}$)]$^+$Cl$^-$ with KO^{t}Bu. [RuCl(NH$_2$NHPh)(PP$_3^{Ph}$)]$^+$Cl$^-$ (25 mg, 26 μmol) and KO^{t}Bu (18 mg, 0.16 mmol) were suspended in THF (0.4 mL) and THF-d_8 (0.15 mL) under argon to give a dark green suspension which on standing turned dark orange-red with some insoluble dark brown solid. ^{1}H NMR (THF/THF-d_8, 400 MHz): δ 7.26 (s, C$_6$H$_6$). ^{31}P{^{1}H} NMR (THF/THF-d_8, 162 MHz): δ 160.2 (q, $^2J_{PC\text{-}PE}$ 24 Hz, RuN$_2$ $\mathbf{P_C}$), 70.1 (d, RuN$_2$ $\mathbf{P_E}$).

Reaction of [RuCl(NH$_2$NHMe)(PP$_3^{Ph}$)]$^+$Cl$^-$ with KO^{t}Bu. [RuCl(NH$_2$NHMe)(PP$_3^{Ph}$)]$^+$Cl$^-$ (17 mg, 19 μmol) and KO^{t}Bu (19 mg, 0.17 mmol) were suspended in THF (0.4 mL) and THF-d_8 (0.15 mL) under argon to give an orange solution and some insoluble orange solid. ^{1}H NMR (THF/THF-d_8, 300 MHz): δ 0.15 (s, CH$_4$). ^{31}P{^{1}H} NMR (THF/THF-d_8, 122 MHz): δ 160.2 (q, $^2J_{PC\text{-}PE}$ 24 Hz, RuN$_2$ $\mathbf{P_C}$), 70.1 (d, RuN$_2$ $\mathbf{P_E}$). IR (orange solid): 2080s (ν(N≡N), RuN$_2$) cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files for **1**, **3**, **5**, **6**, **7**, **8**, and **9**. Figures for ^{31}P{^{1}H} NMR spectrum of **3**; ^{1}H and ^{31}P{^{1}H} NMR spectra of **10**; details of inversion transfer recovery NMR experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Dr. Scott J. Dalgarno and Dr. Ruaraidh D. McIntosh were primarily responsible for the X-ray crystallographic analysis.

Notes

The authors declare no competing financial interest.

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