Formation of Metallacyclobutene Complexes via the Addition of Hydrazines to Ruthenium Vinylidene Complexes

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The reaction between monosubstituted hydrazines and Ru(II) vinylidene complexes $[RuCl(P\cap N)_2(=C=CH(R))]BPh_4$ (where R = Ph, *n*-Bu and P∩N = 3,5-dimethyl[1-((2-diphenylphosphino)ethyl)]pyrazole (Me_2PyP)) afforded metallacyclobutene derivatives of the general formula $[RuCl(\kappa^1P\text{-}Me_2PyP)(\kappa^2P,N\text{-}Me_2PyP)(\kappa^2N,C\text{-}NH_2N'(R^1)C(CH_2R^2))]BPh_4$ (where R^1, R^2 = Me, Ph, *n*-Bu). The new metallacyclic ruthenium complexes contain a four-membered ring (−Ru=C−N−N−) and one pendant P,N-donor ligand, Me_2PyP, bound through the P-donor atom. The solid-state and solution-state structures of these complexes were confirmed through X-ray crystallographic analysis and extensive 2D NMR spectroscopic studies. The reactivity of $[RuCl(Me_2PyP)_2(=C=CH(R))]BPh_4$ toward amines and disubstituted hydrazines was also investigated. The Me_2PyP ligand exhibited hemilabile behavior on reaction of $[RuCl(Me_2PyP)_2(=C=CH(R))]BPh_4$ with aniline. The mechanism of the formation of the four-membered metallacycle was investigated, and it was found that the formation of N−C bonds from hydrazines and vinylidene was only possible when facilitated by displacement of the N-donor atom of the P,N-donor ligand Me_2PyP by the $-NH_2$ group of the monosubstituted hydrazines.

Introduction

Metal vinylidene complexes have been studied widely due to their potential role in catalysis, either as catalyst precursors or as postulated reactive intermediates in catalytic reactions.[1,2] The metal vinylidene species of the later transition metals (such as Ru and Os) contain electrophilic α-carbon atoms which readily react with nitrogen-containing nucleophiles, such as amines, to form new N−C bonds.[2,3] The metal-mediated formation of N−C bonds from alkynes and hydrazines has potential benefits for the atom-efficient synthesis of new organonitrogen compounds. Hydrazine is an important substrate for such reactions, as it has been implicated as an intermediate in the biological reduction of N_2 to ammonia.[4,5]

Primary and secondary amines are known to react with the vinylidene ligand of metal complexes to form aminocarbene complexes,[2,3] which are postulated to form as a result of nucleophilic attack at the metal-bound vinylidene α-carbon by the amine, followed by proton transfer.[6] This mechanism for aminocarbene formation has been described as an "intermolecular-concerted" process in which the primary amine adds across the highly polarized carbon−carbon double bond (Figure 1a).[7] A second mechanism has also been postulated in which formation of the aminocarbene species proceeds via the deprotonation of the *β*-carbon of the vinylidene group by one molecule of the amine, while another molecule of amine binds to the metal center before being transferred onto the α-carbon of a *σ*-alkynyl intermediate.[7]

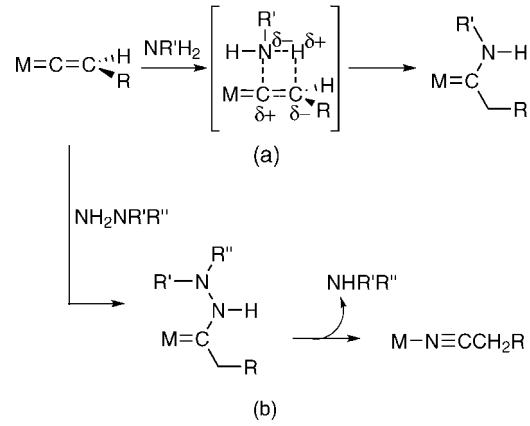

Figure 1. Reaction of a metal vinylidene complex with (a) a primary amine and (b) a hydrazine.

There are only a few reported examples of the reaction of hydrazines with metal vinylidene complexes, and in each case the reaction yielded a metal-bound nitrile product, as opposed to the expected hydrazinocarbene derivative (Figure 1b).[8,9]

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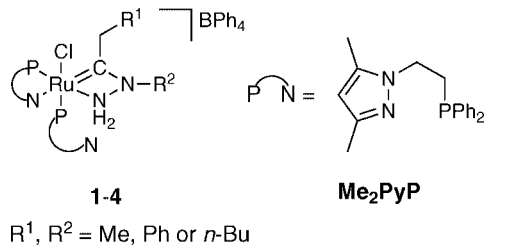
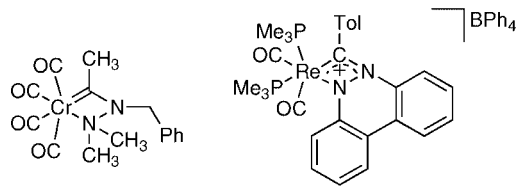
Chart 1



1-4 **Me$_2$PyP**

R^1, R^2 = Me, Ph or *n*-Bu

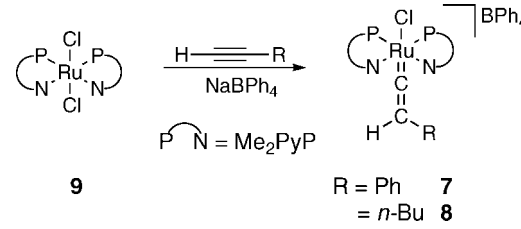


5[21,22] **6**[23]

Addition of substituted hydrazines to both $[FeCp(CCH_2)(CO)(PPh_3)]BF_4$ and $MnCp'(\eta^2\text{-}C_2H_2)(CO)_2$ (where $Cp' = C_5H_5$, C_5Me_5, C_5H_4Me) yielded the acetonitrile complexes $[FeCp(CO)(NCCH_3)(PPh_3)]BF_4$[8] and $MnCp'(CO)_2(NCCH_3)$.[9] The mechanism of this reaction is thought to model the Beckmann rearrangement of oximes.[8] The formation of organic nitrile products from metal-promoted reactions of 1,1-disubstituted hydrazines with alkyne substrates has been catalyzed by a range of ruthenium complexes.[10] The conversion of terminal alkynes to nitrile products with general formula $NCCH_2R$ (where R is a range of organic groups) was catalyzed most effectively by $TpRuCl(PPh_3)_2$ (Tp = hydrotris(pyrazolyl)borate). The proposed mechanism of the catalytic reaction is thought to proceed via a ruthenium vinylidene intermediate.[10]

The most straightforward route to metal vinylidene complexes is through the 1,2-hydrogen shift undergone by many terminal alkynes upon reaction with a transition-metal center.[1–3] Complexes with the general formula $RuCl_2(P\cap N)_2$, containing P,N-donor ligands (P∩N), typically react with terminal alkynes in this way.[11,12] In this paper we describe the synthesis of a new family of ruthenium complexes which contain a four-membered metallacycle (−Ru=C−N−N−) and the P,N-donor ligand 3,5-dimethyl[1-((2-diphenylphoshino)ethyl)]pyrazole (Me$_2$PyP) (**1**−**4**, Chart 1). Metallacyclobutene complexes where one or more members of the four-membered ring is a heteroatom (such as oxygen, phosphorus, or nitrogen) are rare.[13−19] The syntheses of complexes **1**−**4** are the first examples of the formation of such a metallacycle from the reaction of a hydrazine with a vinylidene ligand. The only other examples of metal complexes containing a −M−C−N−N− ring were derived from a *N*-acetylhydrazine ligand bound to chromium[20−22] (e.g., **5**) or the reaction between a diazene species and a rhenium carbyne complex[23] (e.g., **6**) (Chart 1).

Scheme 1



9 R = Ph **7**, = *n*-Bu **8**

Results and Discussion

Synthesis of Ruthenium Vinylidene Complexes Containing P,N-Donor Ligands. The ruthenium vinylidene complexes $[RuCl(Me_2PyP)_2(=C=C(H)Ph)]BPh_4$ (**7**) and $[RuCl(Me_2PyP)_2(=C=C(H)\text{-}n\text{-}Bu)]BPh_4$ (**8**) were synthesized from the ruthenium dichloride complex *trans,cis,cis*-$RuCl_2(Me_2PyP)_2$ (**9**) (Scheme 1). The analogous complex $[RuCl(Me_2PyP)_2(=C=C(H)Ph)]PF_6$ has been reported previously.[11] Complex **9** was synthesized from the addition of 2 equiv of Me$_2$PyP to a dichloromethane solution of $RuCl_2(PPh_3)_3$ using a method adapted from the literature.[11] Excess alkyne, phenylethyne or 1-hexyne, and 1 molar equiv of sodium tetraphenylborate were added successively to a dichloromethane solution of **9** (Scheme 1). The reaction mixture was stirred overnight to give **7** and **8** in good yields, 75% and 67%, respectively. Attempted synthesis of the analogous vinylidene complexes $[RuCl(PyP)_2(=C=C(H)Ph)]X$ (X = BPh_4, PF_6), where PyP is the unmethylated analogue of Me$_2$PyP ((1-(2-diphenylphosphino)ethyl)pyrazole) from $RuCl_2(PyP)_2$ led to the formation of either a mixture of products or formation of the dimeric species $[Ru(\mu\text{-}Cl)(PyP)_2]_2[PF_6]_2$, respectively. Dimeric ruthenium complexes with the formula $[Ru(\mu\text{-}Cl)(PyP)_2]_2[X]_2$ (where X = BPh_4, BArF (tetrakis[3,5-bis(trifluoromethyl)phenyl]borate)) have been synthesized previously from the reaction of $NaBPh_4$ or NaBArF with $RuCl_2(PyP)_2$.[24]

Vinylidene complexes **7** and **8** each exhibited a pair of doublets in the $^{31}P\{^1H\}$ NMR spectra, at 25.8 and 25.0 ppm for **7** and 26.9 and 26.1 ppm for **8**, due to the magnetic inequivalence of the P-donor atoms. The pairs of doublets each exist with a pronounced AB splitting pattern, which was also observed for the analogous literature complex $[RuCl(Me_2PyP)_2(=C=C(H)Ph)]PF_6$.[11] The $^{13}C\{^1H\}$ NMR spectra for **7** and **8** clearly indicate the presence of the vinylidene group. The typically downfield ^{13}C resonance for the α-carbon appears as an apparent triplet at 355.6 ppm for **7** ($^2J_{C-P}$ = 17.3 Hz) and as an apparent triplet at 350.3 ppm for **8** ($^2J_{C-P}$ = 17.4 Hz), while the ^{13}C resonance of the *β*-carbon appears as a singlet at 110.8

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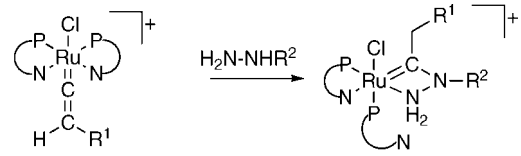
Scheme 2



and 106.1 ppm, respectively. Mass spectrometry and elemental analysis confirmed the structures of **7** and **8**.

Synthesis of Metallacyclic Ruthenium Complexes. The ruthenium vinylidene complexes synthesized above, [RuCl(Me_2-PyP)$_2$(=C=C(H)Ph)]BPh_4 (**7**) and [RuCl(Me_2PyP)$_2$(=C=C(H)-*n*-Bu)]BPh_4 (**8**), were tested for their reactivity toward the monosubstituted hydrazines methylhydrazine and phenylhydrazine. Addition of phenylhydrazine to a dichloromethane solution of the metal vinylidene complex [RuCl(Me_2PyP)$_2$(=C=C(H)Ph)]BPh_4 (**7**) produced the metallacyclic ruthenium complex [RuCl(κ^1*P*-Me_2PyP)(κ^2*P*,*N*-Me_2PyP)(κ^2*N*,*C*-(*N*′-phenylhydrazinyl)benzylcarbene)]BPh_4 (**1**) in 80% yield (Scheme 2). The reaction was performed with methylhydrazine in place of phenylhydrazine under the same reaction conditions, 1 h at room temperature, to give the analogous product [RuCl(κ^1*P*-Me_2PyP)(κ^2*P*,*N*-Me_2PyP)(κ^2*N*,*C*-(NH$_2$N′(CH$_3$)C(CH$_2$Ph))]BPh_4 (**2**) in 70% yield (Scheme 2). The reactivity of phenylhydrazine and methylhydrazine was also tested with the alkyl-substituted vinylidene complex **8**, and the ruthenium carbene complexes [RuCl(κ^1*P*-Me_2PyP)(κ^2*P*,*N*-Me_2PyP)(κ^2*N*,*C*-NH$_2$-N′(R)C(CH$_2$(*n*-Bu)))]BPh_4 (R = Ph (**3**), R = Me (**4**)) were synthesized in yields of 62 and 50%, respectively (Scheme 2).

The reactivity of **1** with phenylethyne was tested to determine the potential of these complexes as intermediates in a catalytic cycle. Phenylethyne was added to a solution of **1** in dichloromethane, and the solution was stirred for 6 days. The main complex isolated from the reaction mixture was the starting material **1**, and no regeneration of the original vinylidene complex [RuCl(Me_2PyP)$_2$(=C=C(H)Ph)]BPh_4 (**7**) was observed under the reaction conditions investigated here.

Solution-State Structures of 1−4. The solution-state structure of each of the complexes **1**−**4** of general formula [RuCl(κ^1*P*-Me_2PyP)(κ^2*P*,*N*-Me_2PyP)(κ^2*N*,*C*-NH$_2$N′(R^1)C(CH$_2$-R^2))]BPh_4 (where R^1 = Me, Ph and R^2 = *n*-Bu, Ph), was determined using 1D and 2D NMR spectroscopy. The protons of the ethylene backbone (−NCH$_2$CH$_2$P−) of both of the Me_2PyP ligands result in eight separate resonances in the ^{1}H NMR spectrum, each integrating to one proton, due to the asymmetry of the molecule. The resonances due to the diastereotopic geminal protons of the −CH$_2$Ph group of both **1** and **2** appear as a pair of doublets, at 5.07 and 4.37 ppm ($^2J_{H-H}$ = −16.8 Hz) for **1**. The protons of the CH$_2$ group adjacent to the carbene atom of **3** and **4** are also magnetically inequivalent, and the resonances due to these protons appear as two multiplets.

The resonances due to the two protons of the NH$_2$ (NH and NH′) group of each of the four complexes **1**−**4** each appear at significantly different chemical shifts, due to the very different environments of each proton, as a result of the asymmetry of the molecular structures. One of the two NH$_2$ protons (NH) is located close to the ethylene backbone of the pendant Me_2PyP ligand, and the resonances due to this proton for the four

Table 1. NMR Spectroscopic Data for 1−4

	$\delta(^1H)$ (ppm)		$\delta(^{31}P)$ (ppm)			
	NH*H*′	NH*H*′			$^2J_{P-P}$ (Hz)	$\delta(^{13}C)$ (ppm) Ru=*C*
1	10.64	6.41	41.1	35.0	33	262.2
2	9.21	5.84	40.3	33.6	34	255.1
3	10.84	6.45	38.9	34.7	33	263.9
4	9.94	5.72[a]	39.6	35.0	34	256.3

[a] Overlapped with another resonance.

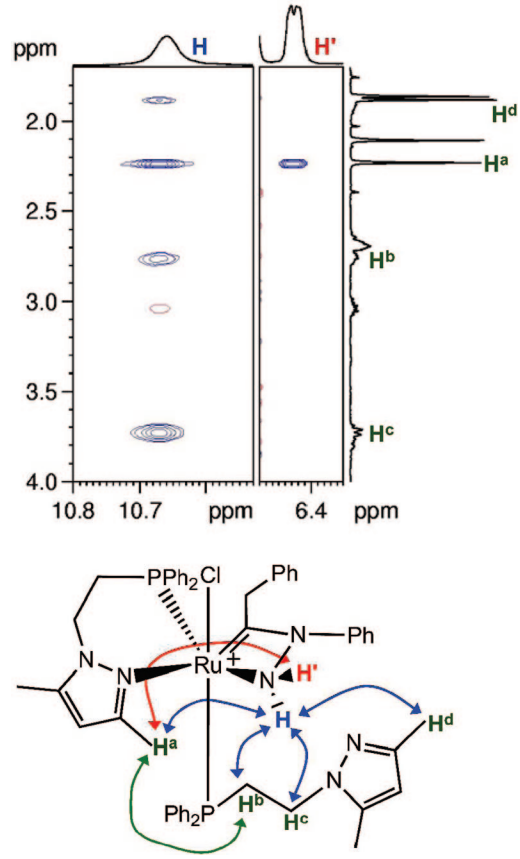


Figure 2. Two sections of the ^{1}H−^{1}H NOESY spectrum of **1** and a diagram depicting the structure of **1** and the ^{1}H−^{1}H NOESY interactions between the protons of **1** (CD_2Cl_2, 500 MHz).

complexes **1**−**4** appear as broad singlets between 10.84 and 9.21 ppm. The resonances due to the second proton of the NH$_2$ group (NH′) for each of the four complexes appear as doublets between 6.45 and 5.72 ppm (Table 1). This assignment was determined using 2D NMR spectroscopy. Sections of the NOESY spectrum of **1**, which show the interaction between the two NH$_2$ protons and the protons of the Me_2PyP ligands, are shown in Figure 2, along with a pictorial representation of the ^{1}H−^{1}H NOESY interactions observed for **1**. Analogous ^{1}H−^{1}H NOESY interactions were observed for **2**. NOE cross-peaks were observed between the resonances due to both NH$_2$ protons and the protons on the methyl substituent at the C3 position of the pyrazole group bound to the metal center. NOE cross-peaks due to the close through-space interaction between the NH proton of NH$_2$ and the CH$_2$ protons of the ethylene backbone of the pendant Me_2PyP ligand were also observed, as well as the CH$_3$ group at the C3 position of the labile pyrazole. An NOE cross-peak was also observed between the resonances due to the protons of the methyl substituent at the C3 position of the pyrazole of the bidentate Me_2PyP ligand and the resonances due to the protons of the PCH$_2$ group of the pendant Me_2PyP ligand. The ^{1}H−^{1}H NOESY spectra of the two pentyl−carbene complexes

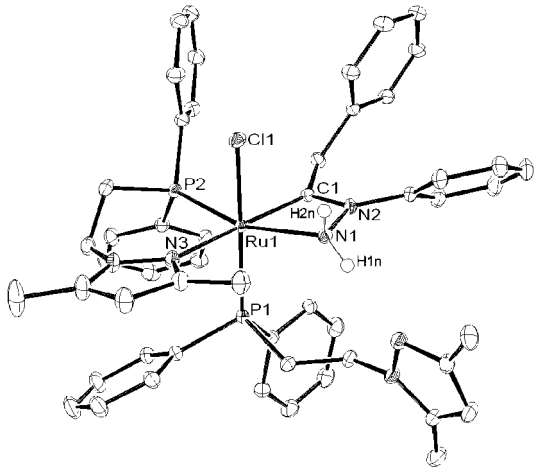


Figure 3. ORTEP depiction of the cation of **1** with thermal ellipsoids at the 50% probability level. All C-bound hydrogen atoms have been omitted for clarity.

3 and **4** exhibited NOE cross-peaks between the resonances due to both NH_2 protons and the protons on the methyl group bound to the adjacent nitrogen atom, in addition to the NOESY interactions analogous to those observed for **1** and **2**.

All four metallacyclic ruthenium complexes **1**−**4** exhibited a pair of doublets in the $^{31}P\{^1H\}$ NMR spectra, between 41.1 and 38.9 ppm and between 35.0 and 33.6 ppm ($^2J_{P-P} = 33-34$ Hz) (Table 1). This splitting pattern is indicative of inequivalent P-donor atoms which are bound to a metal center in a cis fashion. The $^{13}C\{^1H\}$ NMR spectra for **1**−**4** clearly indicate the presence of the carbene group. The typically downfield ^{13}C resonance for the Ru=C carbon appears as an apparent triplet or multiplet between 263.9 and 255.1 ppm for each of the four complexes **1**−**4** (Table 1).

Solid-State Structures of 1−4. To confirm the solid-state structures of the metallacyclic complexes, X-ray diffraction analysis was performed on crystals of [RuCl(κ^1P-Me_2PyP)(κ^2P,N-Me_2PyP)(κ^2N,C-NH_2N'(Ph)C(CH_2Ph))]BPh_4 (**1**) and [RuCl(κ^1P-Me_2PyP)(κ^2P,N-Me_2PyP)(κ^2N,C-NH_2N'(R^1)C(CH_2(*n*-Bu)))]BPh_4 (R^1 = Ph (**3**), Me (**4**)). The ORTEP diagrams for **1**, **3**, and **4** containing the atomic numbering schemes are shown in Figures 3−5. Selected bond lengths and bond angles for **1**, **3**, and **4** are presented in Table 2. Crystallographic data for the three complexes **1**, **3**, and **4** are given in Table 3.

Complexes **1**, **3**, and **4** each have a distorted-octahedral geometry about the metal center, with the hydrazino−carbene ligand acting as a chelating ligand through both N(1) and C(1). The four-membered ring is planar in each of the three complexes. All the bond angles about the metal center are distorted from the ideal angles of 90 and 180°, due to the highly strained four-membered ring. The bite angle of the ligand, N(1)−Ru(1)−C(1), is particularly acute, ranging from 63.12 to 63.27° across **1**, **3**, and **4**. The Ru(1)−C(1)−N(2) bond angles (between 103.29 and 103.81°) are also much narrower than the 120° expected for an atom center with trigonal-planar geometry. The H(1n)−N(1)−H(2n) and Ru(1)−N(1)−H(2n) bond angles do not show any large deviation from the expected tetrahedral arrangement; however, the Ru(1)−N(1)−H(1n) bond angles (with values of 129.0−136.0°) are significantly wider than the ideal 109.5°, indicating that the lone pair of N(1) does not point directly toward the ruthenium atom. The Ru(1)−N(1)−H(1n) bond angle of **4** (129(2)°) is much smaller than those of **1** and **3** (136.0(1) and 134.5(19)°, respectively). This is possibly due to the different steric demands of the methyl substituent on N(2) of **4**, compared to the phenyl substituent of **1** and **3**.

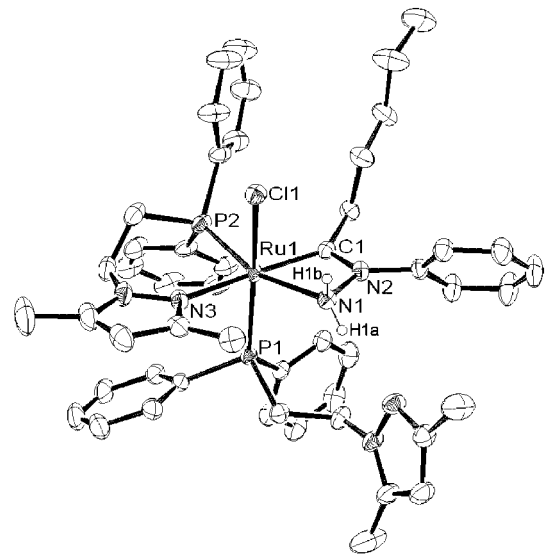


Figure 4. ORTEP depiction of the cation of **3** with thermal ellipsoids at the 30% probability level. All C-bound hydrogen atoms have been omitted for clarity.

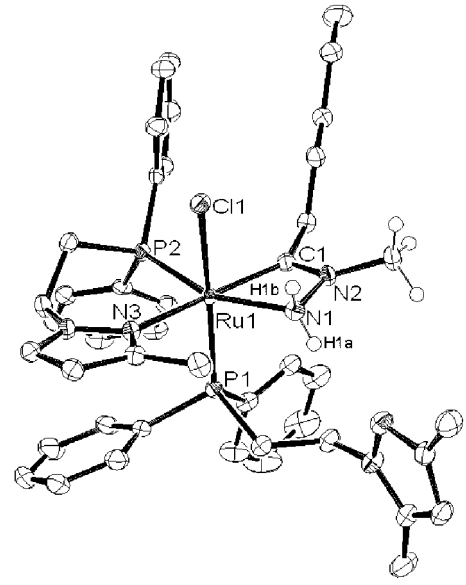


Figure 5. ORTEP depiction of the cation of **4** with thermal ellipsoids at the 50% probability level. All C-bound hydrogen atoms have been omitted for clarity.

The bond lengths and bond angles of the four-membered metallacycles of **1**, **3**, and **4** are almost identical with those found for chromium complexes containing the same motif, such as tetracarbonyl[(*N*-benzyl-*N*′,*N*′-dimethylhydrazinyl)methylcarbene]chromium(0) (**5**, Chart 1).[21,22]

The average Ru(1)−C(1) bond length of **1**, **3**, and **4**, 1.97 Å, is similar to those found in other complexes of ruthenium containing a Ru=CNRR′ group.[7,13,25,26] The N(1)−N(2) bond length of the hydrazine unit, 1.442(12)−1.438(3) Å, for **1**, **3**, and **4** is comparable to that found in both free and metal-bound hydrazines.[27−29] The bond lengths for Ru(1)−N(1) decrease in

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for the Solid-State Structures of 1, 3, and 4

	1	3[a]	4[a]
	Bond Lengths		
Ru(1)−C(1)	1.965(1)	1.966(2)	1.977(2)
C(1)−N(2)	1.3400(1)	1.329(3)	1.314(3)
N(2)−N(1)	1.442(1)	1.438(3)	1.439(3)
Ru(1)−N(1)	2.2634(8)	2.249(2)	2.237(2)
Ru(1)−N(3)	2.2378(9)	2.253(3)	2.239(2)
Ru(1)−P(1)	2.3392(3)	2.3382(7)	2.3096(7)
Ru(1)−P(2)	2.2774(3)	2.2802(7)	2.2846(7)
	Bond Angles		
Ru(1)−C(1)−N(2)	103.29(7)	102.81(16)	102.48(17)
C(1)−N(2)−N(1)	106.48(8)	106.90(19)	107.2(2)
N(2)−N(1)−Ru(1)	87.03(5)	87.02(13)	87.14(13)
N(1)−Ru(1)−C(1)	63.20(4)	63.27(9)	63.12(9)
H(1n)−N(1)−H(2n)	105.7(15)	108(3)	111(3)
Ru(1)−N(1)−H(1n)	136.0(10)	134.5(19)	129(2)
Ru(1)−N(1)−H(2n)	105.6(11)	107.7(17)	107.9(19)

[a] H1n = H1a; H2n = H1b.

order from **1** to **3** to **4**, but all are noticeably longer than those found in other ruthenium complexes containing the Ru−$NH_2NR'R''$ moiety, the majority of which fall within the range of 2.10−2.20 Å.[28–32] The longer Ru(1)−N(1) bond lengths of the complexes **1**, **3**, and **4** are most likely due to the ring strain induced by the four-membered metallacycle.

Reaction of the Ruthenium Vinylidene Complexes with Disubstituted Hydrazines and Amines. The reactions of the ruthenium vinylidene complex [RuCl(Me_2PyP)$_2$(=C=C(H)Ph]-BPh_4 (**7**) with the disubstituted hydrazines 1,1-dimethylhydrazine and 1,2-diphenylhydrazine led to outcomes very different from those observed above for the reactivity of **7** with monosubstituted hydrazines.

The addition of excess 1,2-diphenylhydrazine to a solution of **7** in dichloromethane resulted in no reaction, even after stirring for 24 h. This indicated that the $-NH_2$ group of the hydrazine reagent (such as phenylhydrazine) is necessary for formation of the metallacyclobutene species.

The reaction of 1,1-dimethylhydrazine with **7** was initially performed on an NMR scale and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Addition of excess 1,1-dimethylhydrazine to a dichloromethane-d_2 solution of **7** at room temperature resulted in the rapid formation of a variety of unidentified products, as observed by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction of methylhydrazine with **7** results in the immediate formation of [RuCl(κ^1P-Me_2PyP)(κ^2P,N-Me_2PyP)(κ^2N,C-$NH_2N(Me)C(CH_2$-Ph))]BPh_4 (**2**) at room temperature. The two different reactivities of 1,1-dimethylhydrazine and methylhydrazine with **7** indicate that the extra substituent on the β-nitrogen of the hydrazine has a significant effect on the reaction process.

Large-scale reactions of excess 1,1-dimethylhydrazine with **7** were performed at room temperature and at −70 °C in dichloromethane. In each case mixtures of products were obtained, which could not be isolated and purified due to decomposition.

The reactivity of the ruthenium vinylidene complex **7** was also tested with aniline, *N*-methylaniline, and *n*-propylamine in place of the hydrazines already tested. An amine can act as both a base to deprotonate the β-carbon of the vinylidene group and as a nucleophile to bind to the α-carbon of the vinylidene.[1,6] Although in each case excess amine was added to a solution of **7** in dichloromethane at room temperature and the solution stirred for up to 48 h, only starting material was recovered in the reactions with aniline and *N*-methylaniline. The apparent lack of reactivity of **7** toward primary and secondary aromatic amines may be due to the phenyl substituent on the vinylidene, as less activated vinylidenes are less likely to react with nucleophiles than electron-poor vinylidenes such as unsubstituted vinylidene (=C=CH_2).[33,34] Propylamine is a stronger base and nucleophile than either aniline or *N*-methylaniline and was expected to react with **7**, while the aromatic amines did not. Addition of propylamine to a dichloromethane solution of [RuCl(Me_2PyP)$_2$(=C=C(H)Ph)]BPh_4 (**7**) caused **7** to decompose and no products were isolated. The reaction of propylamine with **7** was also performed on an NMR scale at low temperatures. A broad range of products was formed initially from the addition of propylamine to **7** at −80 °C, as observed by $^{31}P\{^1H\}$ NMR spectroscopy. When the reaction mixture was warmed to room temperature, one major decomposition product was formed, which exhibited a singlet in the $^{31}P\{^1H\}$ NMR spectrum at 41.9 ppm (270 K).

Mechanism of Metallacyclic Hydrazino−Carbene Formation. Two possible mechanisms for the formation of the metallacyclic complexes of general formula [RuCl(κ^1P-Me_2PyP)-(κ^2P,N-Me_2PyP)(κ^2N,C-$NH_2N'(R^1)C(CH_2R^2)$)]BPh_4 (**1**−**4**, where R^1 = Me, Ph and R^2 = *n*-Bu, Ph) are outlined in Figure 6. The metallacyclic complexes **1**−**4** could be formed first through nucleophilic attack at the α-carbon of the vinylidene by the $-NHR^1$ group of the hydrazine, which is then followed by displacement of the pyrazole group of one of the Me_2PyP ligands by the $-NH_2$ group of the hydrazine (mechanism A, Figure 6). Alternatively, the N-donor of the P,N-donor ligand could dissociate followed by binding of the NH_2 group of the substituted hydrazine to the metal center. Subsequent reaction of the $-NHR^1$ group with the vinylidene would form the four-membered ring (mechanism B, Figure 6).

Mechanism A (Figure 6) is the less likely mechanism. First, there is no literature precedent describing the reaction of the more substituted nitrogen of hydrazine reacting with the vinylidene group of a metal complex. Second, the substituted β-nitrogen of phenylhydrazine is less nucleophilic than the α-nitrogen and is also more sterically hindered. The fact that aromatic amines do not react irreversibly with the vinylidene group of **7** was confirmed here by the attempted reactions of aniline, *N*-methylaniline, and 1,2-diphenylhydrazine with **7**, which yielded only starting material in each case. In mechanism B (Figure 6), however, the initial binding of the hydrazine substrate to the metal via the $-NH_2$ group is likely to increase the reactivity of $-NHR^1$ toward nucleophilic attack of the vinylidene. Mechanism B is also supported by similar reactions described in the literature.[35,36] The displacement of a labile ligand by a primary amine, in preference to reaction with a vinylidene group, has been demonstrated previously with vinylidene complexes of osmium.[35] Nucleophilic attack of the unsaturated carbon atom of an acetonitrile ligand by the

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Table 3. Summary of Crystallographic Data for 1, 3, and 4

	1	3	4
empirical formula	$C_{76}H_{76}BClN_6P_2Ru \cdot CH_2Cl_2$	$C_{74}H_{80}BClN_6P_2Ru \cdot C_4H_8O$	$C_{69}H_{78}BClN_6P_2Ru \cdot 3.5C_4H_8O$
M_r	1367.62	1334.81	1453.01
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	12.4426(2)	19.9209(4)	29.5138(9)
b (Å)	13.8014(2)	12.9488(3)	19.7724(6)
c (Å)	20.2734(3)	25.4091(6)	26.3039(6)
β (deg)	100.399(1)	92.960(1)	95.834(2)
V (Å^3)	3392.35(9)	7051.1(3)	15270.4(7)
D_c (g cm^{-3})	1.339	1.257	1.264
Z	2	4	8
T (K)	100(2)	250(2)	90(2)
cryst size (mm)	0.33 × 0.30 × 0.29	0.30 × 0.22 × 0.20	0.32 × 0.25 × 0.18
θ range (deg)	2.73−35	2.36−27	1.94−27
completeness (%)	99.6	99.9	99.8
index ranges	$-19 \geq h \geq 20$	$-21 \geq h \geq 25$	$-37 \geq h \geq 37$
	$-22 \geq k \geq 21$	$-17 \geq k \geq 17$	$-25 \geq k \geq 25$
	$-32 \geq l \geq 32$	$-32 \geq l \geq 32$	$-33 \geq l \geq 33$
no. of rflns measd	102 318	60 170	64 105
unique reflns	29 739	15 371	16 636
R_{int}	0.0415	0.0526	0.0507
GOF (all)	1.048	1.026	1.060
R1 ($I > 2\sigma(I)$)	0.0327	0.0430	0.0427
wR2 ($I > 2\sigma(I)$)	0.0772	0.1010	0.1033
R1 (all data)	0.0444	0.0793	0.0784
wR2 (all data)	0.0805	0.1118	0.1138

β-nitrogen of a methylhydrazine ligand has been observed in ruthenium and osmium complexes.[36]

Experimental evidence supporting mechanism B (Figure 6) was obtained here through variable-temperature NMR spectroscopy experiments of the reaction of the vinylidene complex $[RuCl(Me_2PyP)_2(=C=C(H)Ph)]BPh_4$ (**7**) with aniline, 1,1-dimethylhydrazine, and phenylhydrazine. Excess aniline, phenylhydrazine, or 1,1-dimethylhydrazine was added to a CD_2Cl_2 solution of **7** at either −70 °C or room temperature. The reactions were then monitored by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy (Figure 7).

No reaction was observed between aniline and **7** at low temperatures, but when excess aniline was added to a solution of **7** at room temperature, a new product was formed reversibly (Figure 7b). The new product formed exhibited a pair of doublets with a pronounced AB splitting pattern in the $^{31}P\{^1H\}$ NMR spectrum, at 38.7 and 37.6 ppm (J = 39.3 Hz), which is a downfield shift of approximately 9 ppm relative to the ^{31}P resonances of the starting vinylidene complex **7** (Figure 7a).

Addition of excess phenylhydrazine to a solution of **7** at room temperature immediately yields the hydrazino−carbene product $[RuCl(\kappa^1P\text{-}Me_2PyP)(\kappa^2P,N\text{-}Me_2PyP)(\kappa^2N,C\text{-}NH_2N(Ph)C(CH_2Ph))]BPh_4$ (**1**) (Figure 7d). When the reaction was performed at −70 °C, however, an initial product was formed which gives a $^{31}P\{^1H\}$ NMR spectrum (Figure 7c) which is very different from that of the final product **1** but very similar to that of the product formed on addition of aniline to **7** (Figure 7b). The $^{31}P\{^1H\}$ spectrum of the initial product formed on addition of phenylhydrazine to **7** exhibits a pair of doublets with a pronounced AB splitting pattern, at 39.4 and 37.4 ppm (J = 36.9 Hz). As the reaction mixture was warmed to room temperature, the initial product was converted to the expected hydrazino−carbene product **1**.

The observed reactivity of aniline and phenylhydrazine with $[RuCl(Me_2PyP)_2(=C=C(H)Ph)]BPh_4$ (**7**) can best be explained using mechanism B (Figure 6). The first step of mechanism B, dissociation of one of the pyrazole arms of the Me_2PyP ligand followed by the binding of the primary amine to the metal

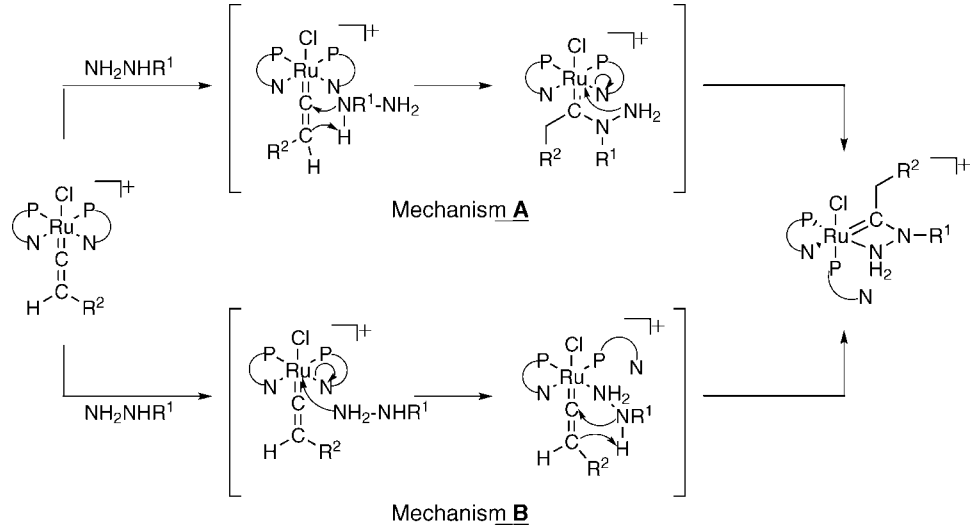

Figure 6. Two possible mechanisms for the synthesis of ruthenium complexes **1**−**4**.

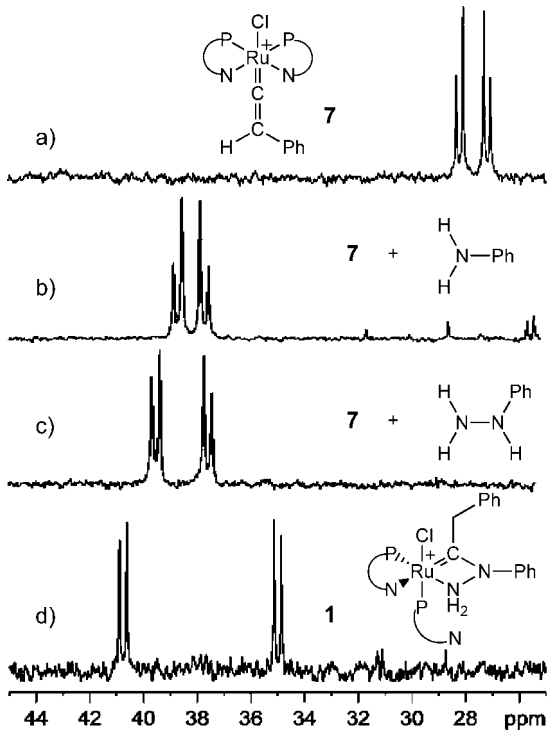

Figure 7. $^{31}P\{^1H\}$ NMR spectra of CD_2Cl_2 solutions of (a) $[RuCl(Me_2PyP)_2(=C=C(H)Ph)]BPh_4$ (**7**), (b) **7** and aniline (excess) at 230 K, (c) **7** and phenylhydrazine (excess) at 190 K, and (d) $[RuCl(\kappa^1 P\text{-}Me_2PyP)(\kappa^2 P,N\text{-}Me_2PyP)(\kappa^2 N,C\text{-}NH_2N(Ph)\text{-}C(CH_2Ph))]BPh_4$ (**1**) at 298 K.

center, is reversible, unlike the first step of mechanism A. The potential for pyrazole−phosphorus ligand PyP to be hemilabile has been shown previously.[24] It appears therefore that the N-donor atom of Me_2PyP is being displaced by aniline and then reassociating once aniline is removed from the reaction mixture to regenerate the starting vinylidene **7**. Once the $-NH_2$ group of phenylhydrazine has displaced the pyrazole arm, however, the −NHPh group then reacts with the α-carbon of the vinylidene to form the four-membered ring of **1**.

The reaction of 1,1-dimethylhydrazine with $[RuCl(Me_2PyP)_2(=C=C(H)Ph)]BPh_4$ (**7**) was also performed on an NMR scale at −70 °C. Two products are present in the reaction mixture at low temperatures (190−210 K): one with a chemical shift at approximately 45.5 ppm and one at approximately 34.0 ppm. The splitting pattern of the two resonances changes and is temperature dependent, with the resonances at 45.5 ppm appearing as either a pair of doublets or a singlet and the resonance at 34.0 ppm appearing as a doublet or a singlet. The two species which are observed may be due to stereoisomerization of the initial product formed in mechanism B (Figure 6) or to the formation of a charged four-membered ring via nucleophilic attack of the $-N(CH_3)_2$ group on the α-carbon of the vinylidene. Subsequent proton transfer is not possible to yield the stable metallacyclic species analogous to **1**, however, as the dimethyl-substituted nitrogen contains no −NH group.

Conclusions

The reaction of the monosubstituted hydrazines methylhydrazine and phenylhydrazine with ruthenium vinylidene complexes $[RuCl(Me_2PyP)_2(=C=C(H)Ph)]BPh_4$ (**7**) and $[RuCl(Me_2PyP)_2(=C=C(H)\text{-}n\text{-}Bu)]BPh_4$ (**8**) yielded the unexpected metallacyclic complexes of general formula $[RuCl(\kappa^1 P\text{-}Me_2PyP)(\kappa^2 P,N\text{-}Me_2PyP)(\kappa^2 N,C\text{-}NH_2N(R^1)C(CH_2R^2))]BPh_4$ (where $R^1 = R^2 = Ph$ (**1**), $R^2 = Ph$, $R^1 = Me$ (**2**), $R^2 = n\text{-}Bu$, $R^1 = Ph$, (**3**), and $R^2 = n\text{-}Bu$, $R^1 = Me$ (**4**)). The synthesis of complexes **1**−**4** is the first example of the synthesis of a metal complex containing the −M−C−N−N− four-membered-ring motif from a metal−vinylidene group and a hydrazine. The solid-state and solution-state structures of complexes **1**−**4** were confirmed using X-ray crystallography and 2D NMR spectroscopy.

Mechanistic studies involving reactions of the ruthenium vinylidene starting material $[RuCl(Me_2PyP)_2(=C=C(H)Ph)]BPh_4$ (**7**) with a series of amines and hydrazines were performed. The reaction of 1,1-dimethylhydrazine with **7** led to decomposition products. There was no reaction of **7** with *N*-methylaniline or 1,2-diphenylhydrazine under the reaction conditions tested here. A reversible reaction does occur between **7** and aniline, confirming the hemilabile nature of the Me_2PyP ligand. The observed reactivities of the mono- and disubstituted hydrazines and the amines with **7** suggest that the formation of **1**−**4** occurs through the displacement of one pyrazole by the $-NH_2$ group of either methylhydrazine or phenylhydrazine, followed by reaction of the $-NHR^1$ group of the hydrazine with the metal-bound vinylidene, leading to formation of the four-membered metallacycle.

The selectivity of the reactions between the vinylidene complexes and amines tested highlight the importance of the lability of mixed-donor ligands in organometallic synthesis. The formation of N−C bonds from hydrazines and vinylidene was only possible when facilitated by dissociation of the N-donor atom of the P,N-donor ligand followed by binding of the $-NH_2$ group of the monosubstituted hydrazines. The pendant Me_2PyP ligand also increases the potential of this reaction to be catalytic, as the N-donor atom can rebind to the metal center to stabilize intermediates in a catalytic cycle.

Experimental Section

All reactions were performed under N_2(g) or Ar(g). Solvents were purified and dried under Ar(g) using conventional methods.[37] Except where specified, chemicals were purchased from either Aldrich Chemical Co. Inc., Precious Metals Online PMO P/L, or Cambridge Isotope Laboratory and used as received unless otherwise stated. The ^1H, ^{31}P, and ^{13}C spectra were recorded on Bruker DPX300, DMX500, and DMX600 spectrometers. ^1H NMR and ^{13}C NMR chemical shifts were referenced internally to residual solvent resonances. ^{31}P NMR was referenced externally using H_3PO_4 (85% in D_2O) in a capillary, taken to be at 0.0 ppm. All NMR spectra were recorded at 298 K unless otherwise specified. Elemental analyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. Single-crystal X-ray analysis was performed by Dr. Jörg Wagler at the Research School of Chemistry, Australian National University, Canberra, Australia, and Institut für Anorganische Chemie, TU Bergakademie Freiberg, Freiberg, Germany. X-ray diffraction data were collected in ψ and ω scans on a Nonius KappaCCD diffractometer (**1**) or a Bruker Nonius X8 APEX2 CCD diffractometer (**3**, **4**) using Mo Kα radiation. The structures were solved with direct methods (SHELXS97) and refined by full-matrix least-squares refinement of F^2 using SHELXL97. Mass spectra were acquired at the BioAnalytical Mass Spectrometry Facility (BMSF), University of New South Wales. In reports of the mass spectral data, M is defined as the molecular weight of the compound of interest. In the case

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of the ESI-MS of cationic compounds, M is defined as the molecular weight of the cationic fragments. The complexes $RuCl_2(PyP)_2$[24] and $RuCl_2(Me_2PyP)_2$[11] were synthesized by following the reported methods.

Synthesis of [RuCl(Me$_2$PyP)$_2$(=C=C(H)Ph)]BPh$_4$ (7). Phenylethyne (0.1 mL, 0.911 mmol) and $NaBPh_4$ (0.154 g, 0.449 mmol) were added successively to a solution of *trans,cis,cis*-$RuCl_2(Me_2PyP)_2$ (**9**; 0.338 g, 0.429 mmol) in DCM (40 mL). The red suspension was stirred overnight, during which time it turned yellow. The suspension was filtered, the filtrate concentrated in vacuo, and Et_2O added. The subsequent precipitate was washed with Et_2O (3 × 2 mL) and dried in vacuo to give a light brown solid. Yield: 0.381 g, 75%. Anal. Found: C, 69.65; H, 5.63; N, 4.78. Calcd for $C_{70}H_{68}BClN_4P_2Ru \cdot 0.5CH_2Cl_2$: C, 69.57; H, 5.71; N, 4.60. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (apparent t, J = 9.4 Hz, 2H, Ar*H*), 7.48−678 (m, 39 H, BC_6H_5, PC_6H_5, =C(H)C_6H_5), 6.64 (apparent t, J = 9.5 Hz, 2H, Ar*H*), 6.30−6.25 (m, 1H, N*CH*H′), 6.06 (apparent d, J = 7.5 Hz, 2H, Ar*H*), 5.92 (s, 1H, Py*H*), 5.90 (s, 1H, Py*H*), 4.40−4.26 (m, 2H, NCH*H*′, N*C*H*H*′), 3.96−3.86 (m, 1H, NC*H*H′), 2.63−2.60 (m, 3H, P*CH_2, =C(*H*)Ph), 2.56−2.49 (m, 1H, PC*H*H′), 2.27 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.92−1.84 (m, 1H, PCH*H*′), 1.47 (s, 3H, CH_3) ppm. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ 25.8 (d, $^2J_{P-P}$ = 31.2 Hz), 25.0 (d, $^2J_{P-P}$ = 31.2 Hz) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 355.6 (apparent t, J = 17.3 Hz, Ru=*C*), 164.1 (q, J = 48.5 Hz, B−*C*), 156.8 (s, *C*CH$_3$), 154.0 (s, *C*CH$_3$), 144.2 (s, *C*CH$_3$), 143.2 (s, *C*CH$_3$), 136.2 (s, *o-C* of BPh_4), 134.6 (d, J = 9.0 Hz, Ar*C*), 133.8 (d, J = 9.0 Hz, Ar*C*), 133.1 (d, J = 9.0 Hz, Ar*C*), 132.1 (s, Ar*C*), 131.8 (d, J = 7.5 Hz, Ar*C*), 131.5 (s, Ar*C*), 131.1 (s, Ar*C*), 130.7 (s, Ar*C*), 128.7 (d, J = 10.5 Hz, Ar*C*), 128.5−128.4 (m, Ar*C*), 128.3−128.2 (m, Ar*C*), 127.9 (m, Ar*C*), 127.0 (s, Ar*C*), 126.6 (s, Ar*C*), 126.4 (s, Ar*C*), 125.5 (d, J = 2.7 Hz, *m-C* of BPh_4), 121.7 (s, *p-C* of BPh_4), 110.8 (s, Ru=C=*C*(H)Ph), 110.0 (s, Py*C*H), 108.8 (s, Py*C*H), 43.8 (s, N*C*H$_2$), 43.5 (s, N*C*H$_2$), 32.8 (d, $^1J_{C-P}$ = 31.5 Hz, P*C*H$_2$), 30.0 (d, $^1J_{C-P}$ = 33 Hz, P*C*H$_2$), 15.4 (d, J = 10.8 Hz, C*C*H$_3$), 15.3 (s, C*C*H$_3$), 12.2 (s, 2 × C*C*H$_3$) ppm. ESI-MS (DCM; *m*/*z* (%)): 819.22 (100) $[M - Cl]^{2+}$, 855.37 (80) $[M]^+$.

Synthesis of [RuCl(Me$_2$PyP)$_2$(=C=C(H)*n*-Bu)]BPh$_4$ (8). 1-Hexyne (0.1 mL, 0.870 mmol) and $NaBPh_4$ (0.108 g, 0.316 mmol) were added successively to a solution of $RuCl_2(Me_2PyP)_2$ (**9**; 0.229 g, 0.290 mmol) in DCM (30 mL). The red suspension was stirred overnight, during which time it turned brown. The suspension was filtered through Celite, the filtrate concentrated in vacuo, and Et_2O added to the solution. The subsequent precipitate was washed with Et_2O (3 × 2 mL) and dried in vacuo to give the product as a brown solid. Yield: 0.228 g, 67%. Anal. Found: C, 69.97; H, 6.15; N, 4.86. Calcd for $C_{68}H_{72}BClN_4P_2Ru \cdot H_2Cl_2$: C, 66.86; H, 6.02; N, 4.52. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.68−7.64 (m, 2H, Ar*H*), 7.48−7.43 (m, 2H, 2 × Ar*H*), 7.40−7.20 (m, 20H, *o*-C*H* of BPh_4, 12 × Ar*H*), 7.11−7.09 (m, 2H, Ar*H*), 6.99 (apparent t, J = 7.4 Hz, 8H, *m*-C*H* of BPh_4), 6.86−6.83 (m, 4H, *p*-C*H* of BPh_4), 6.69−6.65 (m, 2H, Ar*H*), 6.44−6.38 (m, 1H, NCH*H*′), 6.06 (s, 1H, Py*H*), 6.03 (s, 1H, Py*H*), 4.56−4.43 (m, 3H, NC*H*H′, N*CH_2), 2.85−2.70 (m, 3H, PC*H*H′ and P*CH_2), 2.40 (s, 3H, CH_3), 2.37−2.28 (m, 4H, CH_3 and PCH*H*′), 1.99 (s, 3H, CH_3), 1.89−1.85 (m, 2H, =C(H)CH_2−), 1.67−1.63 (m, 1H, =C(*H*)*n*-Bu), 1.50 (s, 3H, CH_3), 0.88−0.82 (m, 2H, −$CH_2CH_2CH_2CH_3$), 0.73−0.67 (m, 5H, −$CH_2CH_2CH_2CH_3$) ppm. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ 26.9 (d, $^2J_{P-P}$ = 30.2 Hz), 26.1 (d, $^2J_{P-P}$ = 30.2 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 350.3 (apparent t, J = 17.4 Hz, Ru=*C*), 163.9 (q, J = 49.4 Hz, B−*C*), 156.1 (s, *C*CH$_3$), 153.4 (s, *C*CH$_3$), 143.0 (s, *C*CH$_3$), 142.9 (s, *C*CH$_3$), 135.8 (s, *o-C*H of BPh_4), 134.5 (d, J = 9.3 Hz, Ar*C*H), 133.9 (d, J = 7.9 Hz, Ar*C*H), 133.5 (d, J = 8.5 Hz, Ar*C*H), 131.7 (d, J = 8.0 Hz, Ar*C*H), 131.4 (s, Ar*C*H), 131.0 (s, Ar*C*H), 130.3 (s, Ar*C*H), 130.2 (s, Ar*C*H), 128.2−128.0 (m, 3 × Ar*C*H), 127.6 (d, J = 9.6 Hz, Ar*C*H), 125.4 (m, *m-C*H of BPh_4), 121.6 (s, *p-C*H of BPh_4), 109.8 (s, Py*C*H), 108.8 (s, Py*C*H), 106.1 (s, Ru=C=*C*(H)*n*-Bu), 43.9 (s, N**C*H$_2$), 43.7 (s, N*C*H$_2$), 34.7 (d, $^1J_{C-P}$ = 31.7 Hz, P*C*H$_2$), 32.6 (s, −*C*H$_2$CH$_3$), 31.7 (d, $^1J_{C-P}$ = 31.2 Hz, P**C*H$_2$), 21.5 (s, −$CH_2CH_2CH_2CH_3$), 14.8 (s, C*C*H$_3$), 14.7 (s, C*C*H$_3$), 13.2 (s, −CH_2CH_3), 12.0 (s, C*C*H$_3$), 11.8 (s, C*C*H$_3$) ppm (*i-C* of PPh_2 was not observed). ESI-MS (DCM; *m*/*z* (%)): 781.1 (100) $[M + CO]^+$, 835.2 (30) $[M]^+$, 753.12 (20) $[M - (=C=CH(n\text{-Bu}))]^+$.

Synthesis of the Metallacyclic Complexes [RuCl(κ^1*P*-Me$_2$PyP)(κ^2*P*,*N*-Me$_2$PyP)(κ^2*N*,*C*-NH$_2$N(R^2)C(CH$_2$R^1))]BPh$_4$ (R^1 = R^2 = Ph (1), R^1 = Ph, R^2 = Me (2), R^1 = *n*-Bu, R^2 = Ph (3), and R^1 = *n*-Bu, R^2 = Me (4)). A 15-fold excess of the appropriate hydrazine was added to a solution of the vinylidene complex **7** or **8** (∼0.082 mmol) in DCM (10 mL). The red solution was stirred for 1 h and then concentrated in vacuo. Et_2O was added to the solution, and the subsequent precipitate was collected by filtration, washed with Et_2O (3 × 2 mL), and dried in vacuo to give the product as a red or yellow solid. Crystals of **1**, **3**, and **4** suitable for X-ray crystallography were grown from layering *n*-hexane over a concentrated DCM or THF solution of the product.

[RuCl(κ^1*P*-Me$_2$PyP)(κ^2*P*,*N*-Me$_2$PyP)(κ^2*N*,*C*-(*N*′-phenylhydrazinyl)benzylcarbene)]BPh$_4$ (1). Red solid. Yield: 80%. Anal. Found: C, 64.39; H, 5.40; N, 5.85. Calcd for $C_{76}H_{76}BClN_6P_2Ru \cdot CH_2Cl_2$: C, 64.62; H, 5.75; N, 6.14. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 10.64 (br s, 1H, N*H*H′), 7.72−7.66 (m, 3H, Ar*H*), 7.60−7.56 (m, 4H, Ar*H*), 7.46−7.42 (m, 4H, Ar*H*), 7.30 (m, 8H, *o*-C*H* of BPh_4), 7.27 (m, 1H, *p*-C*H* of Ph^1), 7.20 (t, J = 7.5 Hz, 1H, *p*-C*H* of Ph^3), 7.14−7.11 (m, 4H, *m*-C*H* of Ph^3 and Ar*H*), 7.09−7.07 (m, 2H, Ar*H*), 7.00 (apparent t, J = 7.5 Hz, 10H, *m*-C*H* of BPh_4 and *o*-C*H* of Ph^3), 6.87−6.83 (m, 7H, *p*-C*H* of BPh_4, *p*-C*H* of Ph^2, *m*-C*H* of Ph^1), 6.77 (apparent t, J = 7.5 Hz, 2H, *m*-C*H* of Ph^2), 6.48 (apparent d, J = 7.5 Hz, 2H, *o*-C*H* of Ph^2), 6.41 (br d, J = 4.2 Hz, 1H, NH*H*′), 6.04 (s, 1H, κ^2-Py*H*), 5.74 (br t, J = 7.9 Hz, 2H, *o*-C*H* of Ph^1), 5.64 (s, 1H, κ^1-Py*H*), 5.07 (d, J = 16.8 Hz, 1H, CH_2Ph), 4.37 (d, J = 16.8 Hz, 1H, CH_2Ph), 3.78−3.68 (m, 2H, κ^1-NC*H*H′ and κ^2-NC*H*H′), 3.06−2.95 (m, 1H, κ^1-NCH*H*′), 2.78−2.61 (m, 4H, 2 × PCH_2), 2.21 (s, 3H, κ^2-C^{3}CH_3), 2.09 (s, 3H, κ^2-C^{5}CH_3), 1.94−1.82 (m, 7H, κ^2-NCH*H*′ and 2 × κ^1-CH_3) ppm. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ 41.1 (d, $^2J_{P-P}$ = 32.8 Hz), 35.0 (d, $^2J_{P-P}$ = 32.8 Hz) ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 262.2 (apparent t, J = 10.8 Hz, Ru=*C*), 163.9 (q, J = 49.3 Hz, B−*C*), 151.8 (s, C_q), 148.1 (s, C_q), 143.9 (s, C_q), 142.4 (s, C_q), 139.1 (s, C_q), 136.4 (m, *i-C* of PPh_2), 135.8 (s, *o-C* of BPh_4), 135.2 (m, *i-C* of PPh_2), 133.6−133.5 (m, C_q and Ar*C*H), 133.2 (d, J = 9.3 Hz, Ar*C*H), 132.9 (d, J = 10.8 Hz, Ar*C*H), 131.7 (s, Ar*C*H), 131.4 (d, J = 8.0 Hz, *o-C* of Ph^1), 131.2 (d, J = 3.1 Hz, Ar*C*H), 129.7 (d, J = 6.2 Hz, *p-C* of Ph^1), 129.7 (s, *p-C* of Ph^3), 129.5 (s, Ar*C*H), 129.0 (s, *o-C* of Ph^2), 128.9 (d, J = 9.4 Hz, Ar*C*H), 128.5 (d, J = 9.2 Hz, Ar*C*H), 127.8 (d, J = 8.6 Hz, Ar*C*H), 127.6 (d, J = 9.4 Hz, Ar*C*H), 127.5 (s, *m-C* of Ph^2), 126.1 (s, Ar*C*H), 125.5 (apparent q, J = 2.8 Hz, *m-C* of BPh_4), 124.5 (s, Ar*C*H), 121.6 (s, *p-C* of BPh_4), 109.0 (s, κ^2-Py*C*H), 105.2 (s, κ^1-Py*C*H), 51.5 (d, J = 3.1 Hz, *C*H$_2$Ph), 43.0 (d, J = 4.6 Hz, κ^1-N*C*H$_2$), 40.1 (s, κ^2-N*C*H$_2$), 35.8 (d, J = 23.1 Hz, κ^1-P*C*H$_2$), 24.7 (d, J = 29.3 Hz, κ^2-P*C*H$_2$), 14.8 (s, κ^2-C^3*C*H$_3$), 12.5 (s, *C*H$_3$), 11.9 (s, κ^2-C^5*C*H$_3$), 10.0 (s, *C*H$_3$) ppm. ESI-MS (DCM; *m*/*z* (%)): 963.3 (100) $[M]^+$.

[RuCl(κ^1*P*-Me$_2$PyP)(κ^2*P*,*N*-Me$_2$PyP)(κ^2*N*,*C*-(*N*′-methylhydrazinyl)benzylcarbene)]BPh$_4$ (2). Yellow solid. Yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.21 (br s, 1H, N*H*H′), 7.60−6.91 (m, 39H, Ar*H*), 6.81 (apparent t, J = 7.5 Hz, 4H, *p*-C*H* of BPh_4), 6.13 (br t, J = 7.0 Hz, 2H, Ar*H*), 5.97 (s, 1H, κ^2-Py*H*), 5.84 (br d, J = 6.2 Hz, 1H, NH*H*′), 5.68 (s, 1H, κ^1-Py*H*), 4.95 (d, J = 16.4 Hz, 1H, CH_2Ph), 3.85−3.75 (m, 1H, κ^2-NC*H*H′), 3.59−3.55 (m, 1H, CH_2Ph), 3.52−3.447 (m, 1H, κ^1-NC*H*H′), 3.07−3.02 (m, 1H, κ^1-NCH*H*′), 2.94 (s, 3H, NCH_3), 2.83−2.76 (m, 1H, κ^1-PCH*H*′), 2.61−2.45 (m, 4H, κ^2-PCH_2, κ^1-PC*H*H′ and κ^2-NCH*H*′), 2.19 (s, 3H, κ^2-C^{3}CH_3), 2.14 (s, 3H, κ^1-C^{3}CH_3), 2.07 (s, 3H, κ^2-C^{5}CH_3), 1.80 (s, 3H, κ^1-C^{5}CH_3) ppm. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2): δ 40.3 (d, $^2J_{P-P}$ = 33.6 Hz), 33.6 (d, $^2J_{P-P}$ = 33.6 Hz) ppm.

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 255.1 (br s, Ru=*C*), 164.7 (q, $J = 49.2$ Hz, B−*C*), 152.2 (s, C_q), 148.5 (s, C_q), 142.6 (s, C_q), 139.7 (s, C_q), 136.6 (s, *o*-*C* of BPh_4), 134.2 (s, Ar*C*), 134.1 (Ar*C*), 133.3 (d, $J = 9.0$ Hz, Ar*C*), 132.9 (d, $J = 10.5$ Hz, Ar*C*), 131.9 (d, $J = 7.5$ Hz, Ar*C*), 131.8 (s, Ar*C*), 131.2 (s, Ar*C*), 130.5 (s, Ar*C*), 130.2 (s, Ar*C*), 129.5 (s, Ar*C*), 129.4 (s, Ar*C*), 129.1 (s, Ar*C*), 128.9 (s, Ar*C*), 127.9 (d, $J = 9$ Hz, Ar*C*), 127.4 (s, Ar*C*), 126.1 (s, *m*-*C* of BPh_4), 122.1 (s, *p*-*C* of BPh_4), 109.0 (s, κ^2-Py*C*H), 106.0 (s, κ^1-Py*C*H), 49.7 (s, *C*H_2Ph), 47.4 (s, N*C*H_3), 43.8 (s, κ^1-N*C*H_2), 41.2 (s, κ^2-N*C*H_2), 34.9 (d, $J = 22.8$ Hz, κ^1-P*C*H_2), 25.7 (d, $J = 29.4$ Hz, κ^2-P*C*H_2), 15.7 (s, κ^2-C^3*C*H_3), 13.8 (s, κ^1-C^3*C*H_3), 12.6 (s, κ^2-C^5*C*H_3), 10.9 (s, κ^1-C^5*C*H_3) ppm. (*i*-*C* of PPh_2 were not observed). ESI-MS (DCM; *m*/*z* (%)): 901.1 (100) $[M]^+$, 781.1 (60) $[RuCl(Me_2PyP)_2(CO)]^+$.

[RuCl(κ^1*P*-Me$_2$PyP)(κ^2*P*,*N*-Me$_2$PyP)(κ^2*N*,*C*-(*N*′-phenylhydrazinyl)pentylcarbene)]BPh_4 (3). Yellow solid. Yield: 62%. Anal. Found: C, 70.16; H, 6.70; N, 6.36. Calcd for $C_{74}H_{80}BClN_6P_2Ru$: C, 70.39; H, 6.39; N, 6.66. ^1H NMR (500 MHz, $CDCl_3$): δ 10.84 (br s, 1H, N*H*H′), 7.63−6.98 (m, 37H, Ar*H*), 6.84 (t, $J = 7.2$ Hz, 4H, *p*-C*H* of BPh_4), 6.79 (apparent t, $J = 7.2$ Hz, 2H, Ar*H*), 6.45 (br d, $J = 3.9$ Hz, 1H, NH*H*′), 5.98 (s, 1H, Py*H*), 5.63−5.60 (m, 3H, Py*H* and Ar*H*), 3.62−3.55 (m, 2H, κ^1-NC*H*H′ and κ^2-NC*H*H′), 3.39−3.37 (m, 1H, C*H*H′(*n*-Bu)), 3.14−3.12 (m, 1H, CH*H*′(*n*-Bu)), 2.92−2.89 (m, 1H, κ^1-NCH*H*′), 2.76−2.72 (m, 1H, κ^1-PCH*H*′), 2.59−2.53 (m, 3H, κ^2-PCH_2 and κ^1-PC*H*H′), 2.27 (s, 3H, κ^2-C^{3}CH_3), 1.99 (s, 3H, CH_3), 1.84 (s, 3H, CH_3) 1.78−1.71 (m, 4H, κ^2-NCH*H*′ and CH_3), 0.76−0.48 (m, 9H, CH_2CH_2CH_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 38.9 (d, $^2J_{P-P} = 33.1$ Hz), 34.7 (d, $^2J_{P-P} = 33.1$ Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 263.9 (m, Ru=*C*), 164.2 (q, $J = 49.1$ Hz, B−*C*), 151.7 (s, PyC_q), 142.7 (s, ArC_q), 142.2 (s, PyC_q), 139.0 (s, PyC_q), 136.2 (s, *o*-*C* of BPh_4), 135.2 (m, *i*-*C* of PPh_2), 135.0 (m, *i*-*C* of PPh_2), 133.3−133.1 (m, 2 × Ar*C*H), 132.7 (d, $J = 10.3$ Hz, Ar*C*H), 131.9 (s, Ar*C*H), 131.3−131.2 (m, 2 × Ar*C*H), 130.3 (d, $J = 8.4$ Hz, Ar*C*H), 129.8 (s, Ar*C*H), 129.7 (s, Ar*C*H), 128.9 (d, $J = 9.6$ Hz, Ar*C*H), 128.6 (d, $J = 9.5$ Hz, Ar*C*H), 128.2 (s, Ar*C*H), 127.9−127.8 (m, 2 × Ar*C*H), 125.4−125.3 (m, *m*-*C* of BPh_4), 124.2 (s, Ar*C*H), 121.5 (s, *p*-*C* of BPh_4), 109.2 (s, Py*C*H), 105.3 (s, Py*C*H), 46.1 (s, *C*H_2(*n*-Bu)), 42.8 (s, N*C*H_2), 40.1 (s, N*C*H_2), 36.4 (d, $J = 22.1$ Hz, κ^1-P*C*H_2), 31.7 (s, −(*C*H_2)$_3$−), 24.8 (d, $J = 28.91$ Hz, κ^2-P*C*H_2), 23.4 (s, −(*C*H_2)$_3$−), 21.2 (s, −(*C*H_2)$_3$−), 15.0 (s, κ^2-C^3*C*H_3), 13.5 (s, (CH$_2$)$_3$*C*H_3), 12.8 (s, *C*H_3), 12.1 (s, *C*H_3), 10.2 (s, *C*H_3) ppm. ESI-MS (DCM; *m*/*z* (%)): 944.2 (100) $[M]^+$, 781.1 (70) $[RuCl(Me_2PyP)_2(CO)]^+$.

[RuCl(κ^1*P*-Me$_2$PyP)(κ^2*P*,*N*-Me$_2$PyP)(κ^2*N*,*C*-(*N*′-methylhydrazinyl)pentylcarbene)]BPh_4 (4). Yellow solid. Yield: 50%. ^1H NMR (500 MHz, $CDCl_3$): δ 9.94 (br s, 1H, N*H*H′), 7.58−6.76 (m, 38H, BC_6H_5 and PC_6H_5), 5.94 (s, 1H, 6.41 κ^2-Py*H*), 5.74−5.71 (m, 2H, NH*H*′ and κ^1-Py*H*), 5.60 (br s, 2H, Ar*H*), 3.62−3.52 (m, 1H, κ^2-NC*H*H′), 3.41−3.36 (m, 2H, κ^1-NCH*H*′ and =CC*H*H′−), 3.17 (s, 3H, NCH_3), 2.92−2.88 (m, 1H, κ^1-NC*H*H′), 2.75−2.68 (m, 2H, κ^1-PCH*H*′ and =CCH*H*′−), 2.51 (m, 3H, κ^1-PC*H*H′ and κ^2-PCH_2) 2.25 (s, 3H, κ^2-C^{3}CH_3), 2.20 (s, 3H, κ^1-C^{3}CH_3), 1.97 (s, 3H, κ^2-C^{5}CH_3), 1.79−1.72 (m, 4H, κ^2-NCH*H*′ and κ^1-C^{5}CH_3) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 39.6 (d, $^2J_{P-P} = 33.5$ Hz), 35.0 (d, $^2J_{P-P} = 33.5$ Hz) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 256.3 (m, Ru=*C*), 164.1 (q, $J = 49.0$ Hz, B−*C*), 151.5 (s, C_q), 148.3 (s, C_q), 141.7 (s, C_q), 139.3 (s, C_q), 136.1 (s, *o*-*C* of BPh_4), 133.2- 133.1 (m, 2 × Ar*C*H), 133.5 (d, $J = 10.1$ Hz, Ar*C*H), 131.5 (s, Ar*C*H), 131.2 (d, $J = 7.7$ Hz, Ar*C*H), 131.1 (s, Ar*C*H), 129.6 (s, 2 × Ar*C*H), 128.9 (d, $J = 9.3$ Hz, Ar*C*H), 128.4 (d, $J = 9.1$ Hz, Ar*C*H), 127.8 (m, 2 × Ar*C*H), (s, *m*-*C* of BPh_4), 121.6 (s, *p*-*C* of BPh_4), 109.0 (s, κ^2-Py*C*H), 105.6 (s, κ^1-Py*C*H), 45.3 (s, =C*C*H$_2$−), 44.2 (s, N*C*H_3), 43.0 (s, κ^1-N*C*H_2), 40.1 (s, κ^2-N*C*H_2), 36.1 (d, $J = 22.4$ Hz, κ^1-P*C*H_2), 32.2 (s, =C(*C*H$_2$)$_4$−), 24.7 (d, $J = 29.0$ Hz, κ^2-P*C*H_2), 23.6 (s, =C(*C*H$_2$)$_4$−), 21.9 (s, =C(*C*H$_2$)$_4$−), 14.8 (s, 15.0 κ^2-C^3*C*H_3), 13.9 (s, (CH$_2$)$_4$*C*H$_3$), 13.2 (s, κ^1-C^3*C*H_3), 12.0 (s, κ^2-C^5*C*H_3), 10.2 (s, κ^1-C^5*C*H_3) ppm (*i*-*C* of PPh_2 was not observed). ESI-MS (DCM; *m*/*z* (%)): 881.2 (100) $[M]^+$, 781.1 (60) $[RuCl(Me_2PyP)_2(CO)]^+$.

Procedure for in Situ Low-Temperature NMR Spectroscopy Reactions. CD_2Cl_2 (∼0.6 mL) was transferred to an NMR tube with a Young valve containing **1** (∼8 mg) via vacuum transfer on a high-vacuum line. The Young tap was replaced by a rubber septum in a N_2(g) glovebox, and the contents of the NMR tube were cooled to −80 °C in a EtOAc/N_2(l) slurry. Phenylhydrazine (excess) was syringed into the cooled NMR tube and the rubber septum replaced with a Young tap under a cone of Ar(g). The NMR tube was placed in a 300 MHz NMR spectrometer cooled to 190 K and gradually warmed to room temperature in the NMR machine.

This procedure was repeated with aniline, *n*-propylamine, and 1,1-dimethylhydrazine in place of phenylhydrazine.

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Supporting Information Available: CIF files giving crystallographic data for complexes **1**, **3**, and **4** and text describing simultaneous deposition of the data at the Cambridge Crystallographic Database. This material is available free of charge via the Internet at http://pubs.acs.org.

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