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Synthesis of Tridentate 2,6-Bis(imino)pyridyl Ruthenium(II) Complexes with N-Heterocyclic Carbene Ligands: Activation of Imidazolium Salts

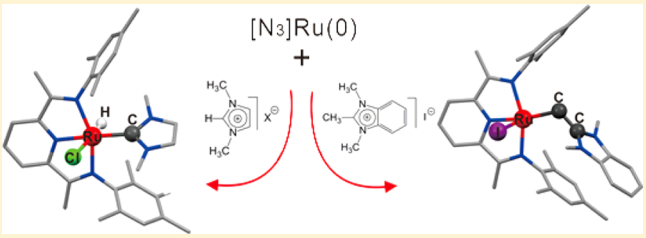
Hyojong Yoo*[,†] and Donald H. Berry[‡]

[†]Department of Chemistry, Hallym University, Chuncheon, Gangwon-do, 200-702, Republic of Korea

[‡]Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, United States

Supporting Information

ABSTRACT: Low-valent Ru(0) complexes, [η^2-N_3]Ru(η^6-Ar) (**1**) or {[N_3]Ru}$_2$(μ-N_2) (**2**), where Ar = C_6H_6 or C_6H_5Me, and [N_3] = 2,6-(2,4,6-$(CH_3)_3C_6H_2N{=}CCH_3)_2$-$C_5H_3N$, activate C−H bonds in imidazolium salts to produce bis(imino)pyridyl ruthenium−(imidazolidin-2-ylidene) complexes, [N_3]Ru(H)(X)(NHC) (**4**) (X = halides and tosylate). Formation of **4** is most likely to proceed via C−H oxidative addition, followed by anion coordination, which is expected to be a useful pathway in synthesizing new complexes with both N-heterocyclic carbene (NHC) and hydride ligands. A zwitterionic ruthenium complex with an ylidic ligand, bis(imino)pyridyl ruthenium−(2-methyleneimidazoline) complex, **7**, was also successfully isolated and fully characterized. The ^{1}H NMR spectra and the solid-state structure confirm that complex **7** is an ylidic transition-metal complex with both NHC and hydride ligands, which was formed through the activation of imidazolium salts.



INTRODUCTION

Highly nucleophilic N-heterocyclic carbenes (NHCs) are widely used as ligands in transition-metal-based catalysts for a variety of metal-catalyzed organic reactions.[1−3] NHC ligands in transition-metal complexes are formally neutral, two-electron donors with some properties similar to tertiary phosphines and can act as strong σ-donors and weak π-acceptors.[4] Transition-metal−NHC complexes are usually prepared through the direct complexation of free NHCs,[1−3] which can be generated by the deprotonation of azolium salts in strongly basic conditions,[5] by using weak bases,[6] by thermolysis,[7] etc. Transition-metal−NHC complexes can be also formed through the dissociation of dimers (involving the insertion of a metal into the C=C bond)[8] and transmetalation from silver−NHC complexes.[9] Salt metathesis and elimination reactions from azolium salts are widely used in the synthesis of NHC and transition-metal−NHC complexes.

Another useful synthetic method for transition-metal−NHC complexes is the oxidative addition of imidazolium salts to metal centers. Fürstner and co-workers demonstrated that oxidative addition of the C−Cl bonds in 2-chloro-1,3-disubstituted imidazolium salts to low-valent metals produced metal−imidazolidin-2-ylidene complexes.[10] Other C−X bond activations (X = CH_3, H, and I) of imidazolium salts leading to transition-metal−NHC complexes have been also reported.[11] The precursor imidazolium salts are easily prepared and have broad applicability.[12] In addition, the reaction for metal−NHC complexes can occur under mild conditions; therefore, the oxidative addition of imidazolium salts to metal centers is potentially useful for the design of new catalysts with N-heterocyclic carbenes.

Recently, the synthesis and characterization of novel zerovalent ruthenium complexes with a tridentate bis(imino)-pyridine ligand, [η^2-N_3]Ru(η^6-Ar) (**1**) and {[N_3]Ru}$_2$(μ-N_2) (**2**), where Ar = C_6H_6 or C_6H_5Me, and [N_3] = 2,6-(2,4,6-$(CH_3)_3C_6H_2N{=}CCH_3)_2C_5H_3N$, have been reported (Figure 1).[13−16,19] These complexes showed interesting reactivities toward Si−Cl bonds for the formation of ruthenium−silyl and

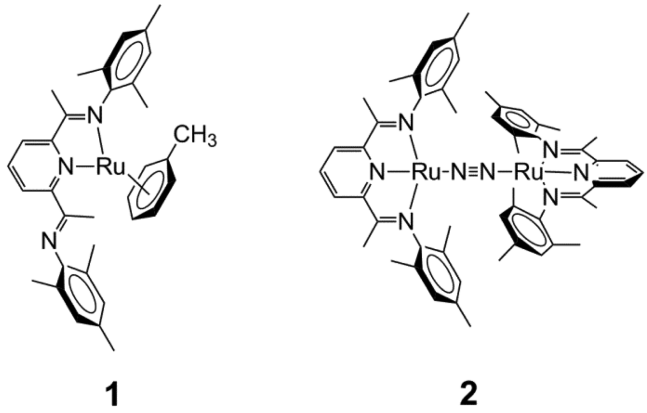


Figure 1. Low-valent ruthenium complexes with 2,6-bis(imino)-pyridine ligands.

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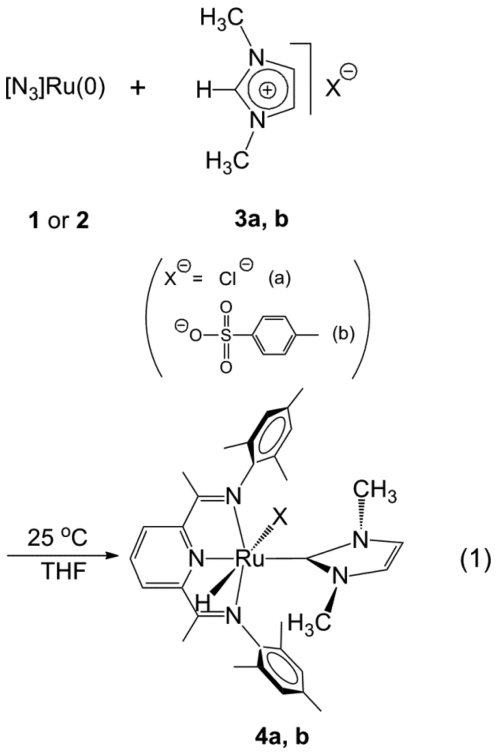
ruthenium−silylene complexes.[14,16] The coordination of electron-donating ligands to either complex **1** or **2** could generate a variety of [N_3]Ru(0) and [N_3]Ru(II) complexes.[13,15] These works have prompted us to describe our finding that ruthenium complexes, **1** and **2**, are capable of activating the C−H bond in 1,3-disubstituted imidazolium salts to give tridentate 2,6-bis(imino)pyridyl ruthenium(II) complexes with N-heterocyclic carbene ligands (ruthenium−NHC complexes).

Herein, we report the synthesis of noble ruthenium−NHC complexes, [N_3]Ru(H)(X)(NHC) (X = halides and tosylate), through the activation of imidazolium salts by either ruthenium complex **1** or **2**.[16] In particular, a zwitterionic metal complex with an ylidic ligand, bis(imino)pyridyl ruthenium−(2-methyleneimidazoline) complex, **7**, was successfully isolated and fully characterized. There are few reported examples of ylidic metal−NHC complexes,[17,18] but no previous examples of ylidic transition-metal complexes with both NHC and hydride ligands, which were formed through the activation of imidazolium salts. Formation mechanisms of these complexes are proposed and discussed.

RESULTS AND DISCUSSION

Synthesis and Structure of Ruthenium−(Imidazolidin-2-ylidene) Complexes [N_3]Ru(H)(X)(dmiy). Treatment of either [N_3]Ru(0) complex **1** or **2** with 1,3-dimethylimidazolium chloride salt, **3a** (X = Cl), in THF at room temperature led to the formation of [N_3]Ru(H)(Cl)(dmiy) (**4a**) (dmiy = 1,3-dimethylimidazolidin-2-ylidene) (eq 1).



(1)

Complex **4a** has been isolated with 54% yield, as a purple solid. The solid-state structure of **4a** was determined by a single-crystal X-ray diffraction study. As shown in Figure 2, **4a** exhibits a six coordinate, pseudooctahedral geometry with a *trans* arrangement of hydride and chloride ligands (H1−Ru1−Cl1 = 175.5(10)°), and a *cis* arrangement of the N-heterocyclic carbene (NHC) ligand to the chloride and hydride (H1−Ru1−N2 = 94.1(10)°, Cl1−Ru1−N2 = 82.38(6)°). The ruthenium−carbon bond distance of **4a** (Ru1−C28) is 2.100(2) Å, which is in the normal range of Ru−C bonds in other Ru−NHC complexes reported.[1−3]

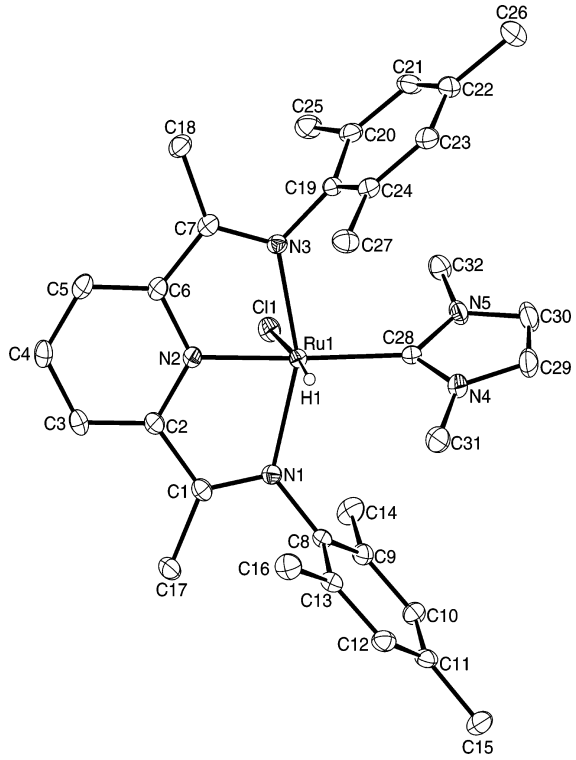


Figure 2. ORTEP drawing of [N_3]Ru(H)(Cl)(dmiy), **4a**, with 30% probability thermal ellipsoids.

The ^{1}H NMR spectrum of **4a** in solution shows four resonances determined as imine methyls, two pairs of *o*-mesityl methyls, and *p*-mesityl methyls, which is consistent with mirror symmetry from the solid-state structure. There is no mirror plane along the [N_3] ligand due to the *trans* hydride and chloride ligands. A single ^{1}H NMR resonance is observed for the ruthenium hydride (δ −21.18, singlet), and the upfield shift is consistent with those in other [N_3]Ru complexes with *trans* hydride−chloride arrangements.[13−16] Two singlet ^{1}H NMR resonances from inequivalent N−CH_3 groups and two singlets from inequivalent C−H in the −CH═CH− of the NHC ligand are observed below 360 K, indicating that rotation of NHC about the Ru−C bond is highly hindered in solution on the NMR time scale (Figure S1, Supporting Information).

Analogous reactivity of [N_3]Ru(0) complexes to other imidazolium salts could be observed. When either **1** or **2** was reacted with 1,3-dimethylimidazolium tosylate salt, **3b** (X = Ts, *p*-toluenesulfonate (tosylate)), in THF at room temperature, another ruthenium−imidazolidin-2-ylidene complex, [N_3]Ru(H)(Ts)(dmiy) (**4b**), was generated (eq 1). Complex **4b** has been successfully isolated as a purple solid (51% yield). The solid-state structure of **4b** (Figure 3) shows a six coordinate, pseudooctahedral geometry with the hydride *trans* to the tosylate ligand (H1−Ru1−O1 = 178.1(12)°) and the NHC *trans* to the pyridine (N2−Ru1−C28 = 179.34(10)°), similar to **4a**. The ruthenium−carbon bond distance (Ru1−C28) is 2.079(3) Å. The ^{1}H NMR spectrum of **4b** is consistent with the geometry found in the solid-state structure and exhibits an upfield shift for the Ru−H (δ −27.3, singlet, Figure S2, Supporting Information).

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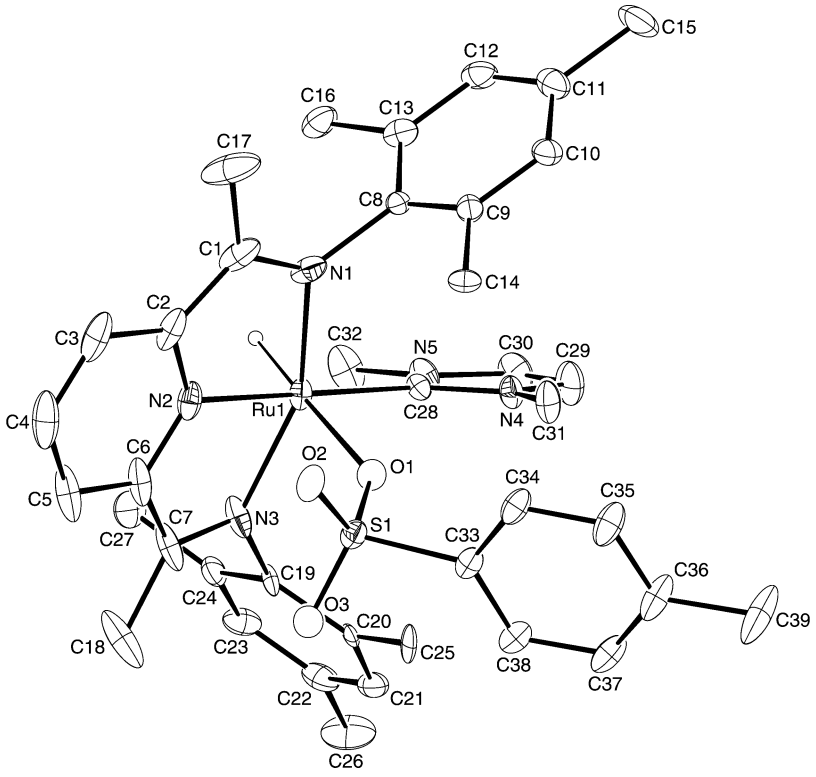
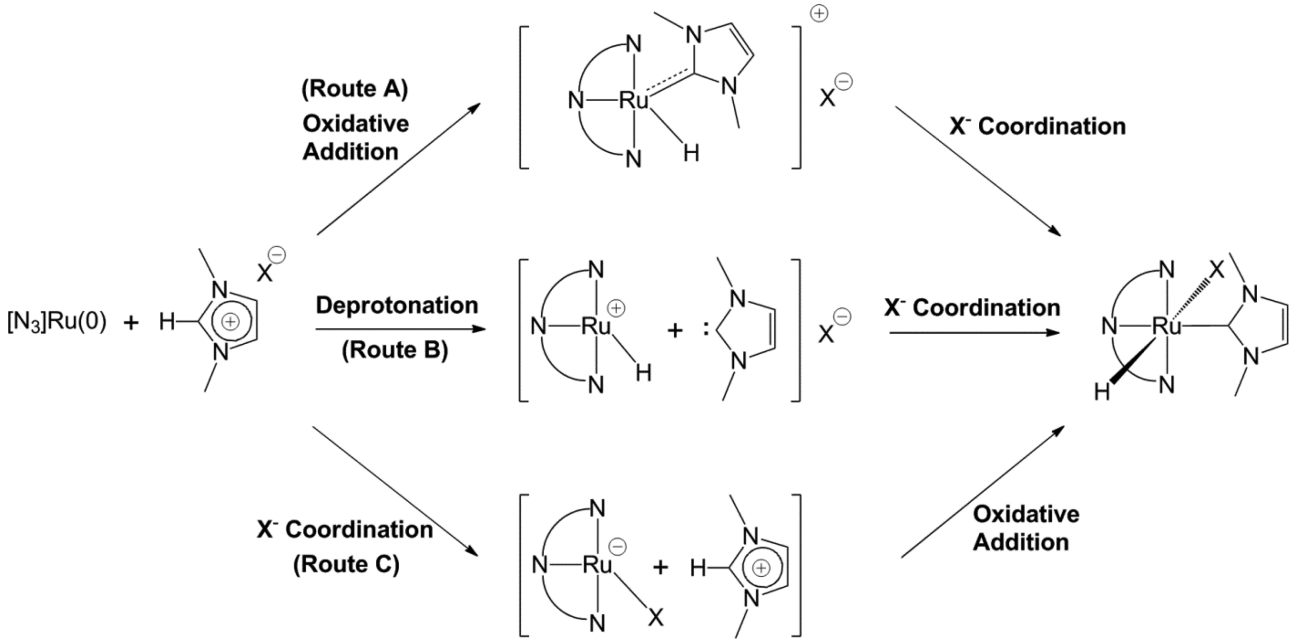


Figure 3. ORTEP drawing of $[N_3]Ru(H)(Ts)(dmiy)$, **4b**, with 30% probability thermal ellipsoids.

Scheme 1. Possible Formation Mechanisms of $[N_3]Ru(H)(X)(dmiy)$ Complexes, 4a and 4b



Reaction of **4a** with excess trimethylphosphine (PMe_3, 12 equiv, Me = methyl ($-CH_3$)) in benzene-d_6 (C_6D_6) or THF-d_8 led to the formation of $[N_3]Ru(PMe_3)_2$ (**8**)[20] with the concurrent formation of **3a**. The reaction did not occur at room temperature; however, it could be completed in 4 days at 45 °C. Formation of **8** is most likely the result of dissociation of a chloride and reductive elimination (or proton transfer) of **3a**, which are led by coordination of two PMe_3 ligands to the Ru center. No displacement reaction of the NHC ligand by PMe_3 has been observed.

$[N_3]Ru(H)(X)(dmiy)$, **4a** and **4b**, are possibly formed via C−H oxidative addition, followed by anion coordination (Route A in Scheme 1). A similar reaction pathway has been previously reported; Fürstner and co-workers reported the reaction of a 2-chloro-1,3-disubstituted imidazolium salt with $Pd(PPh_3)_4$ to give *trans*-$[Pd(PPh_3)_2(NHC)(Cl)]^+Y^-$ (Y = PF_6, BF_4, Cl; Ph = phenyl (C_6H_5)) via the oxidative addition of a C−Cl bond to the Pd(0) center and the loss of two phosphines.[10] We also reported the synthesis of low-valent bis(imino)pyridyl ruthenium complexes with amine hydro-

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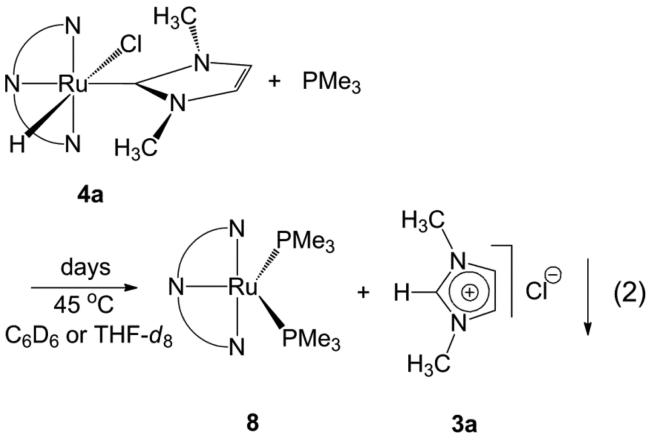
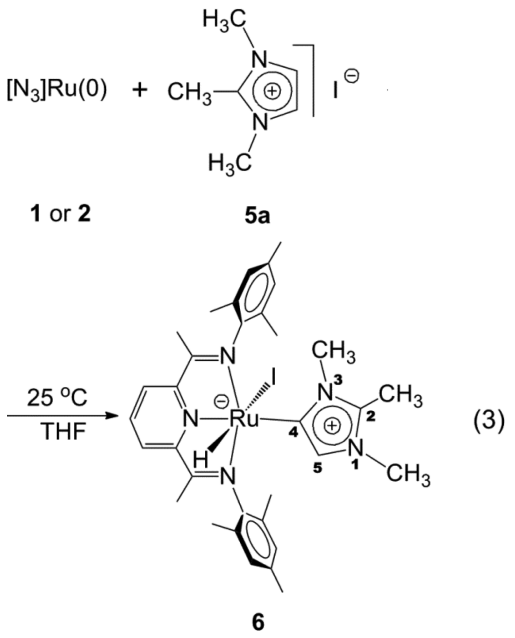
chlorides, $[N_3]Ru(H)(Cl)(amine)$, which were formed by the ionic oxidative addition of hydrochloride (HCl) from amine hydrochlorides and subsequent coordination of amine to the ruthenium centers.[15]

Other possible mechanisms could be also suggested. Deprotonation of imidazolium salts by the $[N_3]Ru(0)$ complexes, and subsequent addition of free carbene and anion to the Ru center, could lead to the Ru−NHC complexes (Route B). Prior anion coordination to the Ru center and C−H activation could also generate the same products (Route C) (Scheme 1). The formation of polar intermediates can be generally investigated through changes of the reaction rates in solvents with different polarities; however, due to the low solubility of imidazolium salts in nonpolar solvents such as benzene or pentane, the formation rates of **4** could not be compared. Both reactions of **4a** with PMe_3 in polar and nonpolar solvents (e.g., THF and benzene, eq 2) yielded $[N_3]Ru(PMe_3)_2$ (**8**) and white precipitates (assigned as **3a**) at 45 °C, and no solvent dependence of reaction rates was observed.

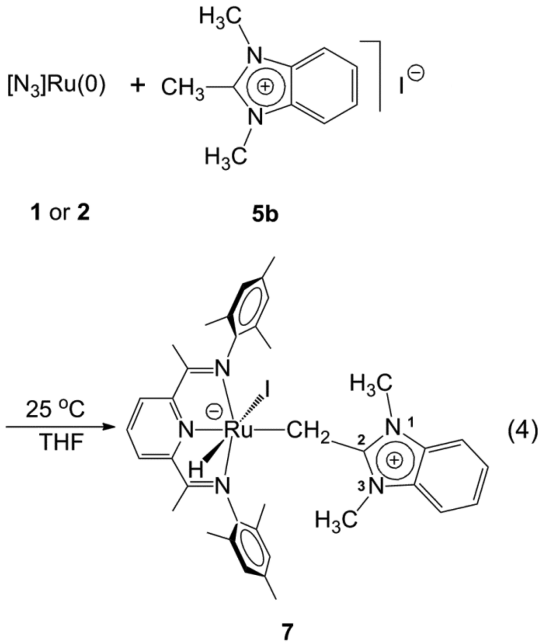


Reaction of $[N_3]Ru(0)$ Complexes with 1,2,3-Trimethylimidazolium Iodide, 5a. Treatment of either **1** or **2** with 1,2,3-trimethylimidazolium iodide, **5a**,[27] in THF at 25 °C led to the formation of an interesting ruthenium imidazolium complex, $[N_3]Ru(H)(I)(tmi)$ (**6**) (tmi = 1,2,3-trimethylimidazolium), by C(4)−H activation. Complex **6** has been isolated as a dark purple solid with 58% yield and characterized by multinuclear NMR spectroscopy (eq 3).

The ^1H NMR spectrum of **6** exhibits mirror symmetry in the plane bisecting the pyridine, but no mirror plane of the $[N_3]$ ligand. The single ^1H NMR resonance from the ruthenium hydride (δ −20.33, singlet) with a *trans* hydride−iodide arrangement, is similar to that of **4a** with a *trans* hydride−chloride arrangement. The ^1H NMR spectrum of the imidazolium ligand shows three inequivalent methyl groups and a singlet for the C(5)−H proton (δ 7.56, Figure S3, Supporting Information), which demonstrates that C−H bonds of three methyl groups (two N−CH_3's and one C−CH_3) in 1,2,3-trimethylimidazolium iodide were not activated by $[N_3]Ru(0)$ complexes. Complex **6** is likely a six coordinate, pseudooctahedral geometry with a *trans* arrangement of hydride and iodide ligands, based on the NMR experimental results. The similar examples of C−H bond activation at the "non-carbene sites" of imidazolium salts by transition-metal complexes have been reported previously.[21]



Reaction of $[N_3]Ru(0)$ Complexes with 1,2,3-Trimethylbenzimidazolium Iodide, 5b: Formation of an Ylidic Transition-Metal−Carbene Complex. Reaction of either **1** or **2** with 1,2,3-trimethylbenzimidazolium iodide, **5b**,[28] in THF at 25 °C led to the formation of $[N_3]Ru(H)(I)(dmmbi)$ (**7**) (dmmbi = 1,3-dimethyl-2-methylenebenzimidazoline) (eq 4).



Complex **7** has been isolated as a brown solid with 74% yield. The ^1H NMR spectrum of **7** shows four resonances from the imine methyls, two pairs of *o*-mesityl methyls, and *p*-mesityl methyls, indicating a geometry with mirror symmetry in the plane crossing the $[N_3]$ ligand. Only one resonance from the two N−CH_3 groups (6H) of the benzimidazoline ligand is observed at room temperature, indicating free rotation of this ligand around the Ru−$C_{methylene}$ bond or the $C_{methylene}$−C(2) bond in solution on the NMR time scale (Figure S4, Supporting Information). The single ^1H NMR resonance for

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the ruthenium hydride (δ −20.66, singlet) shows a *trans* hydride−iodide arrangement.[13−16] The coordinated methylene group (Ru−CH_2) is assigned by ^{1}H NMR (δ 3.86, s) and $^{13}C\{^1H\}$ NMR (δ 9.05). The solid-state structure of **7** was determined by a single-crystal X-ray diffraction study (Figure 4), although the hydrogen atom (hydride) on the ruthenium

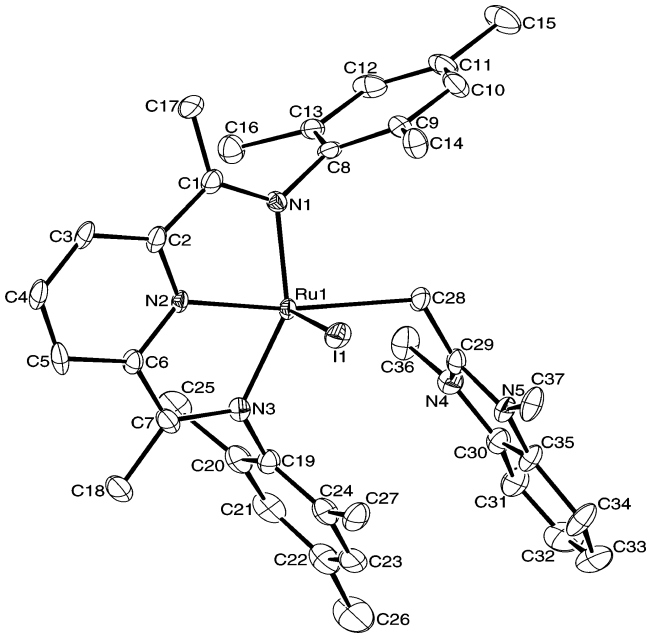
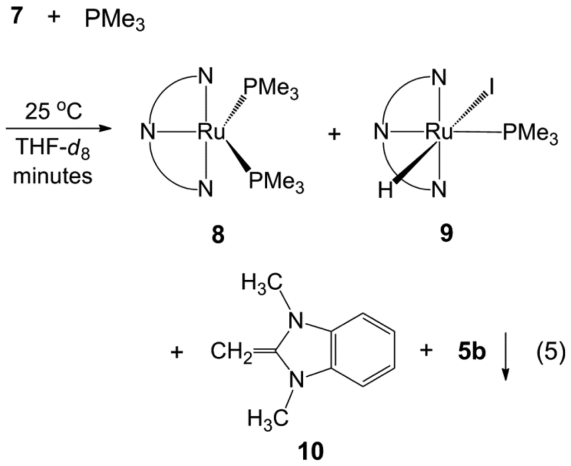


Figure 4. ORTEP drawing of $[N_3]Ru(H)(Cl)(dmmbi)$, **7**, with 30% probability thermal ellipsoids.

could not be completely refined. Compound **7** resulted from a crystal that was split or multiple. The data were processed as though it was a twin. The two components were related by a rotation of ~4°. This may explain the poor crystal quality. Because the crystal was twinned, SQUEEZE could not be used to account for those large solvent voids. However, although not of the highest quality, the solution serves to confirm the connectivity and geometry of compound **7**. Figure 4 shows that the ruthenium in **7** is directly bound to the carbon atom of the 1,2,3-trimethylbenzimidazolium ligand, which can also have the resonance structure showing the η^1-coordination of an ylidic olefin (1,3-dimethyl-2-methylenebenzimidazoline, **10**) to the ruthenium center (Scheme 2). There must be a hydride *trans* to the iodide (which is also confirmed by ^{1}H NMR), to account for a six coordinate distorted octahedral geometry around the ruthenium center. The CN_2C_2 ring of the benzimidazoline ligand lies almost parallel to the plane of one of the mesityl rings, and the bond angle of Ru1−$C28_{methylene}$−C29 is 116.3(3)°. Selected interesting distances are Ru1−C28 (2.255(4) Å), C28−C29 (1.443(7) Å), and the distance of the ruthenium and the ylidic carbon(C29) (3.169 Å). These spectroscopic and structural details indicate that complex **7** is a zwitterionic bis(imino)pyridyl hydroiodo ruthenium complex with an ylidic NHC ligand. There are very few reported examples of ylidic transition-metal−NHC complexes.[17,18] In particular, complex **7** is an unusual example of ylidic transition-metal complexes with both NHC and hydride ligands, which are generated through the activation of imidazolium salts.

Formation of **7** may be the result of the C−H oxidative addition of the methyl group (C(2)−CH_3) to the ruthenium center, followed by the coordination of iodide. Another possible pathway is the prior deprotonation of the imidazolium salt by the $[N_3]Ru(0)$ complex to give an ylidic 1,3-dimethyl-2-methylenebenzimidazoline, **10**, followed by the coordination of **10** and iodide to the ruthenium center (Scheme 2). An ylidic olefin, **10**, coordinates to the ruthenium center as an η^1-olefin to produce **7**, as shown in the solid-state structure. The η^1-coordination of olefins (by "end-on" mode) in transition-metal complexes is unusual.[17,18] Kuhn and co-workers reported the deprotonation of the pentamethylimidazolium ion by *tert*-butyllithium to give 1,3,4,5-tetramethyl-2-methyleneimidazoline, which showed interesting ylidic properties.[18a] In their work, the ylidic olefin coordinated to transition-metal complexes to generate a transition-metal−(1,3,4,5-tetramethyl-2-methyleneimidazoline) complex, which showed strong donor effects to the metal as an ylidic transition-metal−carbene complex.

The reaction of excess PMe_3 with **7** supports the two resonance structures in Scheme 2. Treatment of complex **7** with PMe_3 in THF-d_8 leads to the rapid formation (within 10 min) of $[N_3]Ru(H)(I)(PMe_3)$ (**9**) (ca. 80%)[20] and $[N_3]Ru(PMe_3)_2$ (**8**) (ca. 20%) at room temperature. Concurrent generation of complexes **10** and **5b** (as precipitates) was also observed (eq 5). This transformation might have resulted from two



competing pathways. In the first, dissociation of an iodide and reductive elimination (or proton transfer) of **7**, which are led by coordination of two PMe_3 ligands to the Ru center, could generate **8** and **5b**. This pathway would resemble the reverse of the formation process of **7**. The latter would involve dissociation of the coordinated olefin from **7** and trapping of the $[N_3]Ru(H)(I)$ species by PMe_3 to give **9** and **10**. The first pathway is essentially similar to that suggested for the reaction of the NHC complex **4a** with PMe_3.

■ CONCLUSION

In conclusion, low-valent bis(imino)pyridyl ruthenium complexes, $[\eta^2\text{-}N_3]Ru(\eta^6\text{-Ar})$ (**1**) or $\{[N_3]Ru\}_2(\mu\text{-}N_2)$ (**2**), activate C−H bonds in imidazolium salts to give bis(imino)pyridyl ruthenium−(imidazolidin-2-ylidene) complexes, $[N_3]Ru(H)(X)(NHC)$ (X = halides and tosylate, NHC = N-heterocyclic carbene). In particular, a zwitterionic metal complex of ylidic ligands, bis(imino)pyridyl ruthenium−(2-methyleneimidazoline) complex, **7**, was successfully isolated and fully characterized. Complex **7** is the first example of an ylidic transition-metal complex with both NHC and hydride ligands, which was formed through the activation of imidazolium salts.

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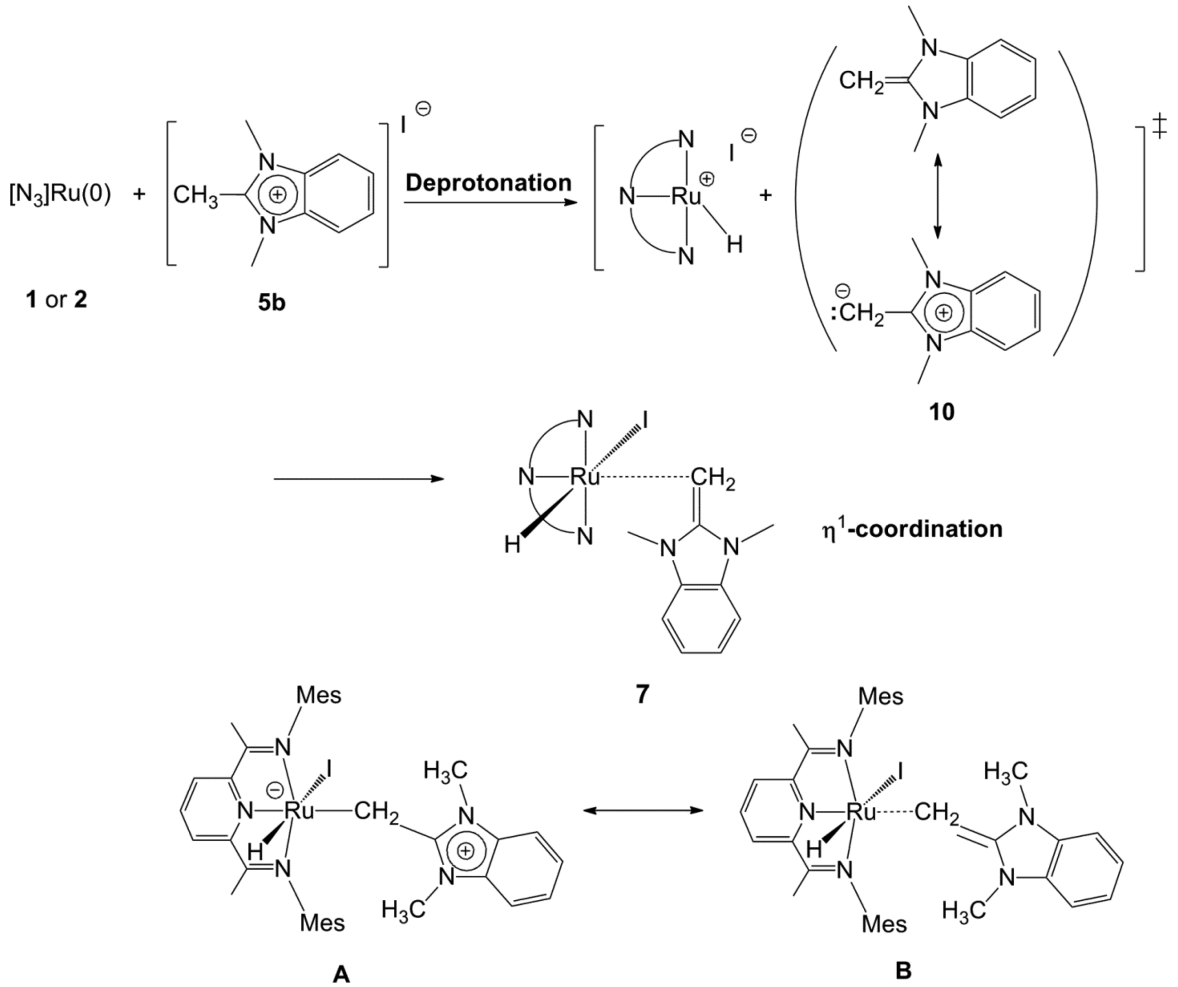
Scheme 2. Possible Formation Mechanism and Resonance Structures of $[N_3]Ru(H)(I)(dmmbi)$, 7



Transition-metal complexes with phosphorus ylides have been used for a variety of reactions, such as polymerization catalysis,[22] and study of the catalytic activities of the ylidic ruthenium−NHC complexes in the comparable transformations is currently underway.

EXPERIMENTAL SECTION

General Methods. All manipulations were performed in Schlenk-type glassware on a dual-manifold Schlenk line or in a nitrogen-filled vacuum atmospheres glovebox.[23] All glassware was oven-dried prior to use. ^{1}H NMR spectra were obtained at 300, 360 and 500 MHz on Bruker DMX-300, AM-360, and AMX-500 FT NMR spectrometers, respectively. ^{2}H NMR spectra were obtained at 76.8 MHz on a Bruker AM-500 spectrometer. ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded with broadband ^{1}H decoupling at 121.5 and 125.8 MHz, respectively, on Bruker DMX-300 (for ^{31}P{^{1}H}) and AMX-500 FT NMR (for ^{13}C{^{1}H}) spectrometers. All NMR spectra were recorded at 303 K unless stated otherwise. Chemical shifts are reported relative to tetramethylsilane for ^{1}H, ^{13}C and external 85% H_3PO_4 for ^{31}P resonances. Elemental analyses were performed by Robertson Laboratory, Inc. (Madison, NJ).

Materials. Hydrocarbon solvents were dried over Na/K alloy-benzophenone. Benzene-d_6, toluene-d_8, cyclohexane-d_{12}, and tetrahydrofuran-d_8 were dried over Na/K alloy. Chloroform-d was dried over molecular sieves. C_2H_4 (Airco) was used as received. Triethylsilane (Aldrich) was dried over Na prior to use. Ruthenium complexes $[\eta^2$-$N_3]Ru(\eta^6$-$MeC_6H_5)$ (**1**)[13] and $\{[N_3]Ru\}_2(\mu$-$N_2)$ (**2**)[13] and PMe_3[24] were synthesized according to the literature procedures. Imidazolium salts **3a**,[25] **3b**,[26] **5a**,[27] and **5b**[28] were prepared according to established literature procedures. Abbreviations used: $[N_3]$ = 2,6-(MesN=CMe)$_2C_5H_3N$; Mes = mesityl (−2,4,6-$(CH_3)_3C_6H_2$); Me = methyl ($-CH_3$); dmiy = 1,3-dimethylimidazolin-2-ylidene; tmi = 1,2,3-trimethylimidazolium; dmmbi = 1,3-dimethyl-2-methylenebenzimidazoline; Ts = *p*-toluenesulfonate (tosylate); NHC = N-heterocyclic carbenes.

Synthesis of $[N_3]Ru(H)(Cl)(dmiy)$, 4a (dmiy = 1,3-Dimethylimidazolin-2-ylidene). A THF solution (15 mL) of $[\eta^2$-$N_3]Ru(\eta^6$-$MeC_6H_5)$ (**1**) (52 mg, 0.088 mmol) and 1,3-dimethylimidazolium chloride, **3a** (30 mg, 0.224 mmol), was stirred under nitrogen for 1 day at 25 °C. The reaction mixture was filtered under N_2 at −78 °C to filter out excess **3a** as a white solid and then reduced in volume to approximately 0.5 mL in vacuo. The product was recrystallized from pentane/THF, yielding 30 mg of purple **4a** (54% yield). ^{1}H NMR (benzene-d_6): δ 7.25 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Py−H_m), 7.04 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Py−H_p), 6.67 and 6.57 (s, each 2H, Mes−H_m), 6.12 and 6.02 (d, $^3J_{HH}$ = 1.8 Hz, each 1H, NC*H*=C*H*N), 4.10 and 2.79 (s, each 3H, NCH_3), 2.52, 2.09, 1.89, and 1.87 (s, each 6H, Mes−$Me_{o,p}$, Im−*Me*), −21.18 (s, 1H, Ru−*H*). ^{13}C{^{1}H} NMR (benzene-d_6): δ 194.33 (s, NCN), δ 166.75 (s, C=N), 160.38 (s, Py−C_0), 150.06 (s, Mes−*C*−N), 133.91, 132.30, 129.36, 128.53, 128.29, 125.53, and 118.63 (s, aryl *C*), 121.80 and 120.67 (s, NCH=CHN), 39.49 and 37.36 (s, NCH_3), 20.80, 20.07, 18.03, and 16.78 (s, Mes−$Me_{o,p}$ and Im−*Me*). Anal. Calcd for $C_{32}H_{40}N_5Cl_2SiRu$ ($[N_3]Ru(H)(Cl)$(dmiy), **4a**): C, 60.89; H, 6.39, N, 11.09. Found: C, 61.22; H, 6.53; N, 9.53. No changes in ^{1}H NMR spectrum were observed below 360 K. $\{[N_3]Ru\}_2(\mu$-$N_2)$ (**2**) showed almost the same reactivity to **3a** to produce **4a**.

Reaction of 4a with PMe_3. An NMR tube was loaded with a benzene-d_6 solution (0.3 mL) of **4a** (6 mg, 0.0095 mmol), and the

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Table 1. Crystallographic Data for 4a, 4b, and 7

	4a	4b	7
formula	$C_{38}H_{46}N_5ClRu$	$C_{39}H_{47}N_5SO_3Ru$	$C_{37}H_{43}N_5IRu$
formula weight	709.32	766.95	785.73
crystal class	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	2	2	2
cell constants			
a (Å)	8.0362(5)	10.2854(8)	11.9653(6)
b (Å)	13.8659(5)	12.4186(11)	12.7276(7)
c (Å)	17.5403(9)	15.7211(13)	15.6224(8)
α (deg)	67.466(4)	78.672(6)	82.814(3)
β (deg)	87.847(5)	75.450(6)	74.997(2)
γ (deg)	77.184(4)	77.123(6)	63.955(2)
V (Å^3)	1757.9(2)	1873.7(3)	2064.5(2)
μ (cm^{-1})	5.55	5.17	11.55
crystal size (mm)	0.22 × 0.08 × 0.05	0.34 × 0.22 × 0.12	0.42 × 0.25 × 0.05
D_{calc} (g/cm^3)	1.340	1.359	1.264
$F(000)$	740	800	794
radiation	Mo−Kα (λ = 0.71069 Å)	Mo−Kα (λ = 0.71069 Å)	Mo−Kα (λ = 0.71069 Å)
diffractometer	Rigaku Mercury CCD	Rigaku Mercury CCD	Rigaku Mercury CCD
scan type	ϕ and ω rotations	ϕ and ω rotations	ϕ and ω rotations
rotation width (deg)	0.5	0.5	0.5
exposure (s)	60	30	30
total number of images	682	862	1210
2θ range (deg)	5.2−54.96	5.42−54.92	5.22−55.12
hkl collected	$-8 \le h \le 10$; $-17 \le k \le 17$; $-22 \le l \le 22$	$-13 \le h \le 13$; $-13 \le k \le 16$; $-19 \le l \le 19$	$-14 \le h \le 13$; $-16 \le k \le 15$; $-20 \le l \le 19$
No. reflections measured	16849	22546	46952
No. unique reflections	7704 (R_{int} = 0.0270)	8267 (R_{int} = 0.0269)	46952 (R_{int} = 0.0000)
No. observed reflections	6648 ($F > 4\sigma$)	7274 ($F > 4\sigma$)	40782 ($F > 4\sigma$)
No. reflections used in refinement	7704	8267	46952
No. parameters[34]	421	609	399
weighting scheme	$w = 1/[\sigma^2(F) + 0.0449P^2 + 0.9501P]$ $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F) + 0.608P^2 + 2.7621P]$ $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F) + 0.2000P^2 + 0.0000P]$ $P = (F_o^2 + 2F_c^2)/3$
R indices ($F > 4\sigma$)s	R_1 = 0.0392 wR_2 = 0.0908	R_1 = 0.0489 wR_2 = 0.1182	R_1 = 0.1216 wR_2 = 0.3744
R indices (all data)	R_1 = 0.0479 wR_2 = 0.0976	R_1 = 0.0565 wR_2 = 0.1250	R_1 = 0.1365 wR_2 = 0.4116
GOF	1.077	1.067	1.973
final difference peaks, e/Å^3	+1.702, −0.537	+1.614, −0.963	+6.522, −3.093

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solution was degassed in vacuo. At −196 °C, PMe_3 (0.11 mmol) was added, and the NMR tube was sealed. The reaction was monitored via ^1H NMR. No reaction was observed at room temperature. After 1 day at 45 °C, ca. 15% of **4a** changed to $[N_3]Ru(PMe_3)_2$ (**8**)[13,20] with concurrent formation of **3a**. After 4 days at 45 °C, all of **4a** was consumed and converted to **8** with **3a** as a solid.

Synthesis of $[N_3]$Ru(H)(Ts)(dmiy), 4b (dmiy = 1,3-Dimethylimidazolin-2-ylidene, Ts = *p*-Toluenesulfonate (Tosylate)). A THF solution (15 mL) of $[\eta^2\text{-}N_3]Ru(\eta^6\text{-}MeC_6H_5)$ (**1**) (58 mg, 0.098 mmol) and 1,3-dimethylimidazolium tosylate, **3b** (45 mg, 0.168 mmol), was stirred under nitrogen for 1 day at 25 °C. The reaction mixture was filtered under N_2 at −78 °C to filter out excess **3b** as a white solid and then reduced in volume to approximately 0.5 mL in vacuo. The product was recrystallized from pentane/THF at −78 °C, yielding 38 mg of purple **6** (~50.6% yield). Although multiple recrystallizations were conducted for elemental analysis, and complete removal of contaminants was not successful. ^1H NMR (benzene-d_6): δ 7.78 and 6.86 (d, $^3J_{HH}$ = 6.9 Hz, each 2H, phenyl in *tosylate*), 7.33 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Py−H_m), 7.20 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Py−H_p), 6.66 and 6.55 (s, each 2H, Mes−H_m), 5.99 and 5.93 (s, each 1H, NC*H*=C*H*N), 3.51 and 2.68 (s, each 3H, NCH_3), 2.41, 2.07, 2.02, and 1.83 (s, each 6H, Mes−$Me_{o,p}$, Im−*Me*), 2.00 (s, 3H, CH_3 in *tosylate*), −26.66 (s, 1H, Ru−*H*). ^1H NMR (THF-d_8), 7.48 (d, $^3J_{HH}$ = 8.7 Hz, 2H, Py−H_m), 7.30 (t, $^3J_{HH}$ = 8.7 Hz, 1H, Py−H_p), 6.91 and 6.62 (d, $^3J_{HH}$ = 7.6 Hz, each 2H, phenyl in *tosylate*), 6.38 and 6.31 (s, each 2H, Mes−H_m), 6.36 and 6.31 (s, NC*H*=C*H*N), 3.11 and 2.42 (s, each 3H, NCH_3), 1.89, 1.74, and 1.49 (s, Mes−$Me_{o,p}$, Im−*Me*), 1.95 (s, 3H, CH_3 in *tosylate*), −27.34 (s, 1H, Ru−*H*). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 195.63 (s, NCN), 170.67 (s, C=N), 162.47 (s, Py−C_0), 149.65 (s, Mes−*C*−N), 137.89, 133.97, 131.82, 129.33, 129.27, 128.57, 127.54, 126.44, 121.74, 120.73, and 120.51 (s, aryl *C* in $[N_3]$ ligand and *tosylate*, NCH=CHN), 37.60 and 36.78 (s, NCH_3), 21.09 (s, CH_3 in *tosylate*), 20.78, 19.06, 17.86, and 16.88 (s, Mes−$Me_{o,p}$ and Im−*Me*). $\{[N_3]Ru\}_2(\mu\text{-}N_2)$ (**2**) showed almost the same reactivity to **3b** to produce **4b**.

Synthesis of $[N_3]$Ru(H)(I)(tmi), 6 (tmi = 1,2,3-Trimethylimidazolium). A THF solution (15 mL) of $[\eta^2\text{-}N_3]Ru(\eta^6\text{-}MeC_6H_5)$ (**1**) (76 mg, 0.129 mmol) and 1,2,3-trimethylimidazolium iodide, **5a** (63 mg, 0.265 mmol) was stirred under nitrogen for 1 day at 25 °C. The reaction mixture was filtered under N_2 at −78 °C to filter out excess **5a** as a white solid and then reduced in volume to approximately 0.5 mL in vacuo. The product was recrystallized from pentane/THF at −78 °C, yielding 54 mg of purple solid. (57.7% yield). ^1H NMR (benzene-d_6): δ 7.56 (s, 1H, C=C*H*−N), 7.53 (d, $^3J_{HH}$ = 7.8 Hz, 2H, Py−H_m), 7.10 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Py−H_p), 6.66 and 6.57 (s, each 2H, Mes−H_m), 2.74 and 2.33 (s, each 3H, N−CH_3), 2.80, 2.03, 1.94, and 1.79 (s, each 6H, Mes−$Me_{o,p}$, Im−*Me*), 0.86 (s, each 3H, NNC−CH_3), −20.33 (s, 1H, Ru−*H*). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 163.97 (s, *C*=N), 160.47 (s, Py−C_0), 150.98 (s, Mes−*C*−N), 136.85, 132.80, 131.90, 131.76, 128.91, 128.78, 128.52, 124.17, and 117.50 (s, aryl *C* in $[N_3]$ ligand and −*C(5)*N=*C(4)*H−N), 35.59 and 32.13 (s, NCH_3), 8.74 (s, NCN−CH_3), 23.13, 20.71, 17.70, and 16.70 (s, Mes−$Me_{o,p}$ and Im−*Me*).

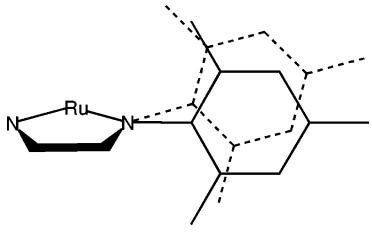
Synthesis of $[N_3]$Ru(H)(I)(dmmbi), 7 (dmmbi = 1,3-Dimethyl-2-methylenebenzimidazoline. A THF solution (15 mL) of $[\eta^2\text{-}N_3]Ru(\eta^6\text{-}MeC_6H_5)$ (**1**) (55 mg, 0.093 mmol) and 1,2,3-trimethylbenzimidazolium iodide, **5b** (40 mg, 0.146 mmol) was stirred under nitrogen for 1 day at 25 °C. The reaction mixture was filtered under N_2 at −78 °C to filter out excess **5b** as a white solid and then reduced in volume to approximately 0.5 mL in vacuo. The product was recrystallized from pentane/THF at −78 °C, yielding 53 mg of purple 7. (~73.6% yield). Although multiple recrystallizations were conducted for elemental analysis, complete removal of contaminants was not successful. ^1H NMR (THF-d_8): 7.90 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Py−H_m), 7.34 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Py−H_p), 7.09 and 6.95 (m, each 2H, phenyl), 6.58 and 6.35 (s, each 2H, Mes−H_m), 3.86 (s, 2H, −CH_2−CNN), 3.25 (s, 6H, NC*H*), 2.38, 2.09, 2.05, and 1.54 (s, each 6H, Mes−$Me_{o,p}$, Im−*Me*), −20.66 (s, 1H, Ru−*H*). $^{13}C\{^1H\}$ NMR (THF-d_8): δ 174.83 (s, C=N), 165.31 (s, Py−C_0), 161.54 (s, Mes−*C*−N), 134.29, 133.78, 131.57, 129.75, 129.51, 129.29, 122.46, and 122.01 (s, aryl *C* in $[N_3]$ ligand, and NCN), 149.29, 119.22, and 109.05 (s, benzyl *C*), 34.90 (s, 2C, −N−*Me*), 22.74, 21.31, 17.77, and 16.78 (s, Mes−$Me_{o,p}$, Im−*Me*), 9.05 (s, 1C, Ru−CH_2).

Reaction of 7 with PMe_3. An NMR tube was loaded with a benzene-d_6 solution (0.3 mL) of 7 (6 mg, 0.0077 mmol), and the solution was degassed in vacuo. At −196 °C, PMe_3 (0.08 mmol) was added, and the NMR tube was sealed. The reaction mixture was then warmed to room temperature, and the reaction was monitored via ^1H NMR spectroscopy. After 10 min at 25 °C, all of 7 was consumed, and the mixture of $[N_3]Ru(H)(I)(PMe_3)$ (**9b**) (ca. 80%),[13,20] $[N_3]Ru(PMe_3)_2$ (**8**) (ca. 20%), 1,3-dimethyl-2-methylenebenzimidazoline, **10**, and **5b** (as a solid) were observed. ^1H NMR of $[N_3]Ru(H)(I)(PMe_3)$ (**9b**) (benzene-d_6): δ 7.23 (d, $^3J_{HH}$ = 7.9 Hz, 2H, Py−H_m), 6.92 (t, $^3J_{HH}$ = 7.9 Hz, 1H, Py−H_0), 6.77 and 6.69 (s, each 2H, Mes−H_m), 2.65, 2.12, 1.88, and 1.81 (s, each 6H, Mes−$Me_{o,p}$, Im−*Me*), 1.06 (d, $^2J_{PH}$ = 8.1 Hz, 9H, PMe_3), −18.46 (d, $^2J_{HP}$ = 42.5 Hz, 1H, Ru−H). ^1H NMR of **10** (benzene-d_6): δ 6.29 (m, 4H, phenyl), 2.98 (s, 2H, CH_2), 2.59 (s, 6H, NCH_3).

Single-Crystal X-ray Diffraction Analysis: General Procedures. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo−Kα radiation (λ = 0.71069 Å) at a temperature of 143 K. Preliminary indexing was performed from a series of twelve 0.5° rotation images with exposures of 30 s. Oscillation images were processed using CrystalClear,[29] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed to the CrystalStructure[30] program package for further processing and structure solution on a Dell Pentium III computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB. The structure was solved by direct methods (SIR97).[31] Refinement was conducted by full-matrix least-squares based on F^2 using SHELXL-97.[32] All reflections were used during refinement (F^2's that were experimentally negative were replaced by F^2 = 0). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a "riding" model, except hydride hydrogen atoms, which were refined isotropically. Table 1 lists cell information, data collection parameters, and refinement data.

*$[N_3]$Ru(H)(Cl)(dmiy) (**4a**).* Suitable X-ray quality crystals of **4a** were grown from benzene/pentane. Tables S1 and S2 (Supporting Information) list bond distances and bond angles. Figure 2 is an ORTEP[33] representation of the molecule with 30% probability thermal ellipsoids displayed.

*$[N_3]$Ru(H)(Ts)(dmiy) (**4b**).* Suitable X-ray quality crystals of **4b** were grown from benzene/pentane. The mesityl groups are disordered by a slight twisting of the N−C bond out of planarity, as shown below for one of the mesityl rings:



The mesityl groups were refined with atomic fractional populations of 0.50. Tables S3 and S4 (Supporting Information) list bond distances and bond angles. Figure 3 is an ORTEP[33] representation of the molecule with 30% probability thermal ellipsoids displayed.

*$[N_3]$Ru(H)(I)(dmmbi) (**7**).* Suitable X-ray quality crystals of 7 were grown from THF. It became apparent during data reduction that there were extraneous reflections that did not fit the orientation matrix. The Twinsolve module of CrystalClear was used to calculate F^2 data for the two twin components. The two components were related by a rotation of 3.92° about the $\bar{1}$ 0 $\bar{1}$ plane. Tables S5 and S6 (Supporting Information) list bond distances and bond angles. Figure 4 is an ORTEP[33] representation of the molecule with 30% probability thermal ellipsoids displayed.

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■ ASSOCIATED CONTENT

Supporting Information

Details of ^{1}H NMR spectroscopic data, and X-ray crystallographic data for **4a**, **4b**, and **7** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hyojong@hallym.ac.kr (H.Y.).

Notes

The authors declare no competing financial interest.

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(34)

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$$

$$GOF = \{\sum w(F_o^2 - F_c^2)^2 / (n - p)\}^{1/2}$$

where n = the number of reflections and p = the number of parameters refined.