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Ruthenium Bisammine Complex and Its Reaction with Aryl Azides

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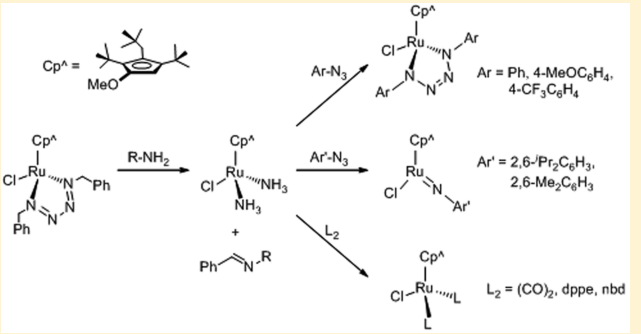
Supporting Information

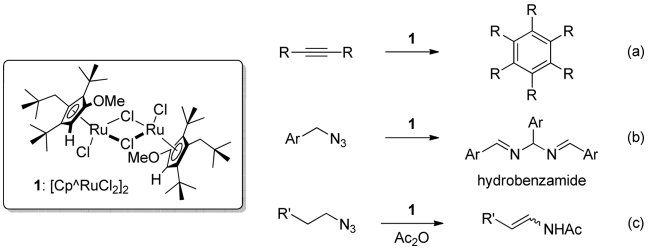
ABSTRACT: A ruthenium bisammine complex was formed in the reaction of ruthenium 1,4-dibenzyltetraazadiene complex with primary amines at room temperature, which was a versatile precursor for the synthesis of various Ru(II) complexes through ligand exchange reactions. In the reaction with azidobenzene, ruthenium 1,4-diphenyltetraaza-1,3-diene complex was formed, while ruthenium imido complexes were given in the reaction with bulky aryl azides such as 2-azido-1,3-dimethylbenzene and 2-azido-1,3-diisopropylbenzene. The ruthenium imido complexes showed high catalytic activity in the reaction of alkyl azides with primary amines to afford N-substituted imines.



INTRODUCTION

In 2007, Severin and co-workers reported a dimeric ruthenium half-sandwich complex $[Cp^{\wedge}RuCl_2]_2$ (**1**) (Cp^ = η^5-1-methoxy-2,4-di-*tert*-butyl-3-neopentylcyclopentadienyl) containing sterically demanding cyclopentadienyl ligand, which was formed in the simple reaction of Ru(III) chloride complex with *t*-butylacetylene in methanol.[1] They observed that the Cp^ ligand endows interesting catalytic activities to the ruthenium complex.[2,3] Arenes are produced from the reaction of alkynes (Scheme 1a),[2] while hydrobenzamides are formed in the

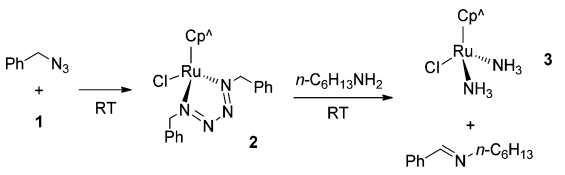
Scheme 1. Catalytic Reactions Using $[Cp^{\wedge}RuCl_2]_2$: (a) Reaction of Alkynes; (b) Reaction of Benzyl Azide; (c) Synthesis of Enamide



reaction of benzyl azide (Scheme 1b).[3] The catalytic activity of **1** for the transformation of benzyl azide attracted our attention, because N−H benzaldimine was proposed as the key intermediate.[3,4] In fact, we found that its catalytic activity is not only limited to the reaction with benzyl azides but also effective for that with alkyl azides to generate the corresponding N−H imines.[5] Various *N*-acetyl enamides can be synthesized by the catalytic transformation of alkyl azides in the presence of acetic anhydride (Scheme 1c).[5a]

Recently, we observed that the ruthenium complex **1** catalyzes the reaction of benzyl azide with *n*-hexylamine to give *N*-hexylbenzylideneimine at room temperature. This observation prompted us to carry out the stoichiometric reaction of *n*-hexylamine with the ruthenium dibenzyltetraazadiene complex **2** that is formed as the major product in the reaction of **1** with benzyl azide in the absence of *n*-hexylamine. In general, metal tetraazadiene complexes are quite stable, and there are few reports on the reactions of the reaction of metal tetraazadiene complexes.[6] Interestingly, we found that the complex **2** readily reacted with *n*-hexylamine to produce a new ruthenium complex along with *N*-hexylbenzylideneimine in quantitative yield at room temperature (Scheme 2). Herein we

Scheme 2. Formation of Ruthenium Bisammine Complex in the Reaction of Ruthenium Tetraazadiene Complex with *n*-Hexylamine



report that the new ruthenium complex is a ruthenium bisammine complex (**3**)[7] and that is an active precursor for the synthesis of various Cp^Ru(II) complexes (**4**−**6**) (Scheme 3). Notably, aryl azides reacted with **3** to give the corresponding ruthenium 1,4-diaryltetraazadiene complexes **7**.

RESULTS AND DISCUSSION

The ruthenium dibenzyltetraazadiene complex **2** did not react with benzyl azide at room temperature, but it acted as a catalyst for the reaction of benzyl azide with primary amines to give *N*-

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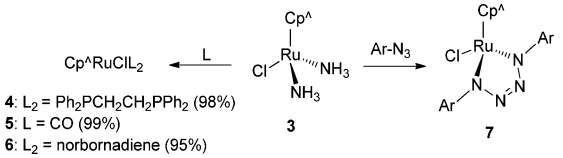
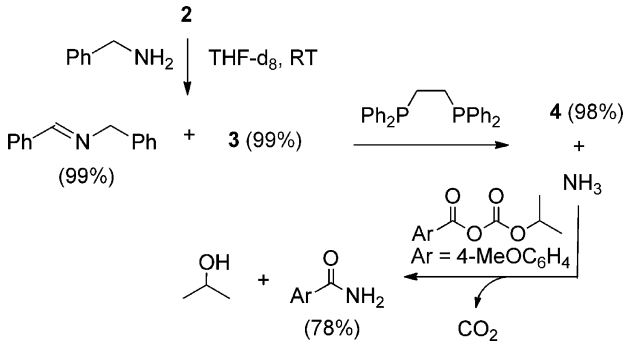
Organometallics XXXX, XXX, XXX−XXX

Scheme 3. Ligand Exchange Reactions of Ruthenium Bisammine Complex



benzylimines. In a stoichiometric reaction of **2** with benzylamine, 2 equivalents of benzylamine were consumed to produce *N*-benzylidene-1-phenylmethanamine and a new ruthenium complex quantitatively (Scheme 4). At first we

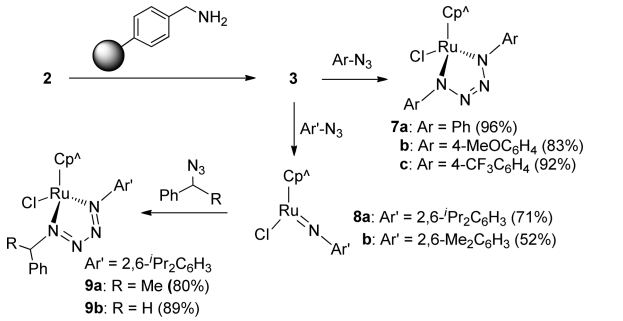
Scheme 4. Trapping of Ammonia Liberated in Ligand Exchange Reaction of the Ruthenium Bisammine Complex



thought that the ruthenium complex is [Cp^RuCl]$_2$,[8] but later we realized that it is monomeric and contains ammonia as ligands. The proton signal of the coordinated ammonia was observed as a broad peak at 2.4 ppm in the ^{1}H NMR spectrum[9] of the reaction mixture in tetrahydrofuran-d_8 (THF-d_8), in contrast to the free ammonia of which protons appear at 0.45 ppm (Figure S1 in the Supporting Information). The ligation of ammonia on the ruthenium center **3** was supported further by the formation of 4-methoxybenzamide in the reaction with (isopropyl carbonic) 4-methoxybenzoic anhydride after the ligand exchange reaction of **3** with 1,2-bis(diphenylphosphino)-ethane.

Then we tried to isolate the ruthenium bisammine complex **3** using polymer-bound benzylamine in the reaction with **2**. A solution of **3** was obtained successfully by simple filtration after the reaction, but **3** was decomposed during concentration. However, the solution was useful to obtain analytically pure products in the ligand exchange reactions. Furthermore, the addition of aryl azides to the solution provided ruthenium 1,4-diaryltetraazadiene complexes (**7a**−**c**). Although several ruthenium complexes containing imido ligands have been reported, which are coordinated to one or two ruthenium centers,[10,11] only one cyclopentadienyl ruthenium imido complex, [Cp^RuCl(NAd)] (Ad = adamantyl), has been reported by Severin and co-workers without reactivity investigation.[12] This result inspired us that the use of bulky aryl azides would give the ruthenium imido complexes, which are less sterically congested than the corresponding ruthenium tetraazadiene complexes. Actually, ruthenium imido complexes (**8a,b**) were formed in the reaction with bulky aryl azides such as 2-azido-1,3-diisopropylbenzene and 2-azido-1,3-dimethylbenzene (Scheme 5). The ruthenium imido complex **8a** reacted not only with benzyl azide but also with (1-azidoethyl)benzene to form unsymmetrical tetraazadiene

Scheme 5. Reaction of Ruthenium Bisammine Complex with Aryl Azides



complexes (**9**).[13] Interestingly, the reaction with (1-azidoethyl)-benzene to form **9a** was highly diastereoselective. The complexes **7a**−**c**, **8a,b**, and **9a,b** were characterized by NMR and high-resolution mass spectrometry. Fortunately, we succeeded in obtaining single crystals of **7a**, **8a**, and **9a** suitable for X-ray diffraction analysis (Figure 1). Selected bond distances of the complexes are listed in Table 1. The molecular structure of **7a** reveals that the tetraazadiene moiety exists as a dianionic resonance form to show short N2−N3 bond and longer N1−N2 and N3−N4 bonds.[14] In contrast, that of **9a** shows a highly distorted tetraazadiene moiety: N2−N3 bond is longer than the N1−N2 bond but shorter than the N3−N4 bond. The Ru−N bond (1.7459(19) Å) in **8a** is clearly shorter than those in the tetraazadiene complexes and comparable to that (1.718(3) Å) of an analogous ruthenium imido complex [Cp^RuCl(NAd)].[12] The coordination mode of the imido ligand in **8a** (Ru−N−C angle 168.76(16)°) is almost linear.

Then, ruthenium complexes (**1**−**3**, **7a**, and **8a**) were tested as catalysts for the reaction of benzyl azide with *n*-hexylamine (Table 2). *N*-Hexylbenzylideneimine was obtained in 83% yield using the dimeric ruthenium complex **1** at room temperature for 24 h (entry 1). The dibenzyltetraazadiene complex **2** showed a better reactivity (entry 2), while the ruthenium bisammine complex **3** was significantly less reactive (entry 3). The low reactivity of **3** is consistent with the predominant formation of **3** in the stoichiometric reaction of **2** and *n*-hexylamine as shown in Scheme 2. The diaryltetraazadiene complex **7a** was inactive, indicating that the formation of N−H imines from the corresponding tetraazadiene moiety is essential for the generation of active catalytic species (entry 4). The catalytic activity of the coordinatively unsaturated ruthenium imido complex **8a** was best (entry 5).

The scope of the catalytic reaction for the synthesis of N-substituted imines was investigated using **2** as the catalyst at 70 °C, which is more practical and convenient than **8a** for preparation and manipulation (Table 3). Generally, N-substituted imines (**10a**−**c**) were formed in high yields by the reaction of benzyl azide with a linear amine, branched one, and *t*-butylamine in 1 h. The reactions of (1-azidoethyl)-benzene with *n*-hexylamine and 2-butylamine were also successful to give the corresponding N-substituted imines (**10d,e**) in high yields, while 1-phenylethanimine was observed in the reaction using *t*-butylamine.[5a]

On the basis of the generation of N−H imines from benzyl azide and the transimination reaction of N−H imines with primary amines,[4a] a pathway for the formation of the ruthenium bisammine complex **3** in the reaction of **2** with an amine is proposed in Scheme 6. The ruthenium tetraazadiene complex **2**

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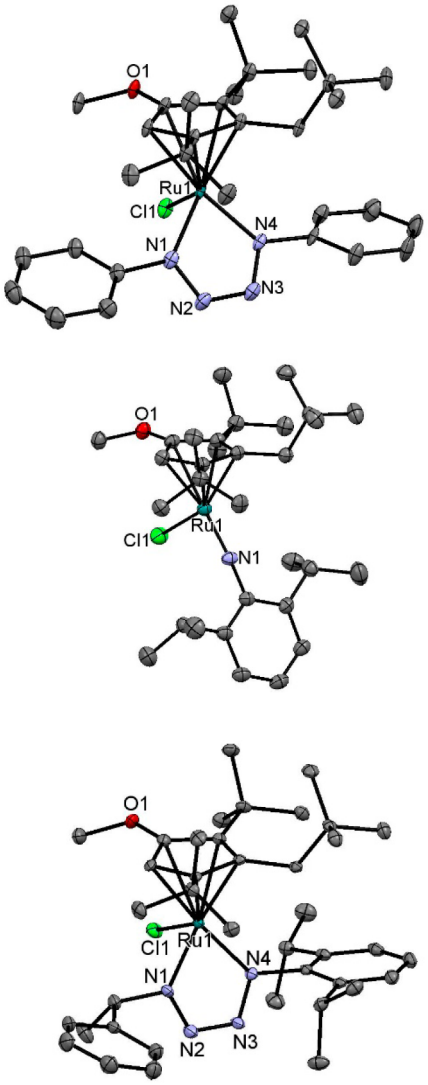


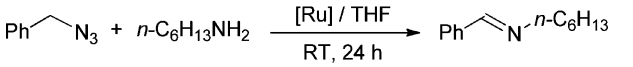
Figure 1. Graphical representation of the molecular structure of complex **7a** (top), **8a** (middle), and **9a** (bottom). Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) of Complexes 7a, 8a, and 9a

	7a	8a	9a
Ru1−N1	2.0027(18)	1.7459(19)	1.9924(18)
Ru1−N4	1.9618(16)	-	1.9741(19)
Ru1−Cl1	2.3674(8)	2.3626(8)	2.3677(7)
N1−N2	1.325(2)	-	1.308(3)
N2−N3	1.310(2)	-	1.323(3)
N3−N4	1.336(2)	-	1.341(2)

is in equilibrium with a ruthenium imido species (**B**), which is converted to a ruthenium N−H imine complex (**C**). Amine is reacted with the N−H imine to produce a benzylidene imine and a ruthenium species containing ammonia (**D**), from which another ruthenium imido species (**E**) is formed. Then, the nitrene moiety in **E** is converted to N−H imine, and the second reaction with amine gives the ruthenium bisammine complex **3**.

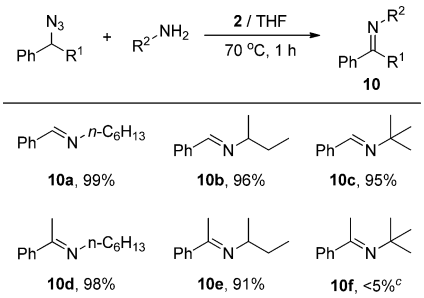
Table 2. Catalytic Activity Comparison in the Reaction of Benzyl Azide with *n*-Hexylamine[a]



entry	[Ru]	yield (%)
1	**1**	83[b]
2	**2**	91
3	**3**	62
4	**7a**	0
5	**8a**	95

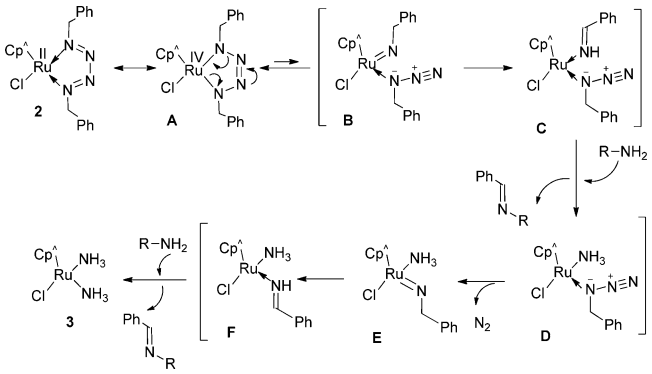
[a]A solution of azide (0.25 mmol), amine (1.2 equiv), and ruthenium catalyst (2.0 mol %) in THF (1.0 mL) was stirred. The yield was estimated by ^{1}H NMR using dibromomethane as an internal standard. [b]1.0 mol % of **1** was used.

Table 3. Catalytic Reaction of Alkyl Azides with Primary Amines[a,b]



[a]A solution of azide (0.25 mmol), amine (1.2 equiv) and **2** (2.0 mol %) in THF (1.0 mL) was stirred at 70 °C for 1 h. [b]The yields were estimated by ^{1}H NMR using dibromomethane as an internal standard. [c]1-Phenylethanimine was formed in >95% yield.

Scheme 6. Reaction Pathway for the Formation of Ruthenium Bisammine Complex



CONCLUSION

In summary, a new ruthenium bisammine complex was obtained in the reaction of a ruthenium dibenzyltetraazadiene complex with primary amines, which was utilized as an efficient precursor for the synthesis of various Ru(II) complexes containing a sterically demanding cyclopentadienyl ligand. Notably, its reactivity toward aryl azides provided novel ruthenium 1,4-diaryltetraaza-1,3-diene complexes and ruthenium imido complexes. In addition, we investigated the catalytic reaction of alkyl azides with various primary amines to synthesize N-substituted imines.

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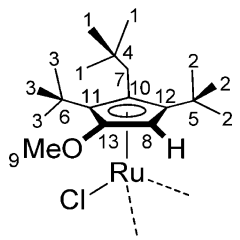
Organometallics XXXX, XXX, XXX−XXX

EXPERIMENTAL SECTION

General Procedures. Air-sensitive manipulations were carried out with standard Schlenk techniques under argon atmosphere. Commercial chemicals used without further purification. Flash column chromatography was carried out on silica gel (230−400 mesh) as the stationary phase. ^{1}H and ^{13}C NMR spectra were recorded with Bruker (300 MHz, 500, 600, and 850 MHz) spectrometer. ^{1}H NMR spectra were referenced to residual $CDCl_3$ (7.26 ppm), CD_2Cl_2 (5.32 ppm), THF-d_8 (3.58 ppm) and reported as follows; chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, and br = broad). Chemical shift of ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.23 ppm), CD_2Cl_2 (54.00 ppm), THF-d_8 (67.57 ppm). Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Elemental analyses were performed by the Korea Basic Science Institute (Busan) on a Vario-Micro Cube elemental analyzer. Ruthenium complexes **1**[1a] and **2**[3] were synthesized according to the literature procedure.



General Procedure for Synthesis of [Cp^RuCl(NH$_3$)$_2$] (3). *Method A: using benzylamine.* Benzylamine (46 μmol, 5.0 μL) was added to a solution of complex **2** (23 μmol, 15 mg) in THF (0.50 mL), and the mixture was stirred at ambient temperature for 1 h. The red solution was obtained.

Method B: using polymer-bound benzylamine. Polymer-bound benzylamine (50 μmol, 24 mg) was added to a solution of complex **2** (23 μmol, 15 mg) in THF-d_8 (0.80 mL), and the mixture was shaken at ambient temperature for 4 h. The resulting polymeric material was removed by filtration under argon atmosphere, and the red solution was obtained. ^{1}H NMR (300 MHz, THF-d_8): δ 3.71 (s, ^{1}H, Cp^-H), 3.64 (s, 3H, OCH_3), 2.74 (d, J = 16.0 Hz, 1H, Cp^-CH_2), 2.50 (d, J = 16.0 Hz, 1H, Cp^-CH_2), 2.44 (br, 6H, NH_3), 1.45 (s, 9H, *t*-Bu), 1.42 (s, 9H, *t*-Bu), 1.08 (s, 9H, *t*-Bu). ^{13}C NMR (125 MHz, THF-d_8): δ 124.3 (C13), 82.6, 72.9, 71.0 (C10, C11, C12), 57.1 (C9), 45.1 (C8), 39.0 (C7), 34.3, 33.5, 31.9 (C4, C5, C6), 32.9, 32.7, 32.4 (C1, C2, C3).

[Cp^RuCl(dppe)] (4).[1a] 1,2-Bis(diphenylphosphino)ethane (23 μmol, 9.2 mg) was added to a solution of complex **3** (23 μmol) in THF (0.80 mL), and the mixture was stirred at ambient temperature for 2 h. After the solvent was removed, the residue was dissolved with hexane and filtered by a Celite pad. The solution was concentrated and dried under vacuum to afford an orange solid (18 mg, 98%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.92−7.82 (m, 4H, Ph), 7.42−7.20 (m, 16H, Ph), 4.39 (s, 1H, Cp^-H), 3.14 (s, 3H, OCH_3), 2.90 (m, 2H, Cp^-CH_2), 2.62 (m, 2H, P-CH_2−CH_2−P), 2.28 (m, 2H, P-CH_2−CH_2−P), 1.21 (s, 9H, *t*-Bu), 1.15 (s, 9H, *t*-Bu), 0.98 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 142.3−127.4 (4 Ph), 132.1 (C13), 105.4, 93.5, 93.4 (C10, C11, C12), 57.5 (C9), 56.1 (C8), 39.4 (C7), 34.4, 34.0, 32.3 (C4, C5, C6), 33.5, 32.5, 32.2 (C1, C2, C3), 30.3 (dppe).

[Cp^RuCl(CO)$_2$] (5).[1b] A solution of complex **3** (23 μmol) in THF (0.80 mL) was stirred at ambient temperature under an atmosphere of CO (1 atm) for 2 h. After the solvent was removed, the residue was purified by flash chromatography on silica gel, using hexane/ethyl acetate as eluent. The product was isolated as a yellow solid (11 mg, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.84 (s, 1H, Cp^-H), 3.77 (s, 3H, OCH_3), 2.94 (d, J = 16.2 Hz, 1H, Cp^-CH_2), 2.38 (d, J = 16.2 Hz, 1H, Cp^-CH_2), 1.49 (s, 9H, *t*-Bu), 1.38 (s, 9H, *t*-Bu), 1.14 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.8, 198.4 (CO), 151.2 (C13), 111.4, 98.5, 95.9 (C10, C11, C12), 61.6 (C9), 58.4 (C8), 37.8 (C7), 34.5, 33.4 (C4, C5, C6), 32.5, 32.3 (C1, C2, C3).

[Cp^RuCl(nbd)] (6).[1a] Norbornadiene (35 μmol, 3.6 μL) was added to a solution of complex **3** (23 μmol) in THF (0.80 mL), and the mixture was stirred at ambient temperature for 18 h. After the solvent was removed, the residue was dissolved with hexane and filtered by a Celite pad. The solution was concentrated and dried under vacuum to afford an orange solid (11 mg, 95%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 5.18 (m, 1H, CH═CH, nbd), 4.82 (s, 1H, Cp^-H), 4.67 (m, 1H, CH═CH, nbd), 4.47 (m, 1H, CH═CH, nbd), 3.71 (s, 3H, OCH_3), 3.68−3.58 (m, 3H, CH═CH, nbd, CH bridge, nbd), 2.55 (d, J = 16.4 Hz, 1H, Cp^-CH_2), 2.35 (d, J = 16.4 Hz, 1H, Cp^-CH_2), 1.26 (m, 2H, CH_2, nbd), 1.19 (s, 9H, *t*-Bu), 1.16 (s, 9H, *t*-Bu), 1.14 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 85.4, 79.0, 78.5 (C10, C11, C12), 63.2, 60.2 (CH═CH, nbd), 56.8 (C9), 55.5 (bridging C, nbd), 50.7 (C8), 48.8 (CH_2, nbd), 38.3 (C7), 35.0, 33.9, 31.4 (C4, C5, C6), 33.2, 32.7, 31.3 (C1, C2, C3).

[Cp^RuCl(PhNNNNPh)] (7a). Azidobenzene (46 μmol, 5.5 mg) was added to a solution of complex **3** (23 μmol) in THF (0.80 mL), and the mixture was stirred at ambient temperature for 2 h. After the solvent was removed, the residue was purified by flash chromatography on silica gel, using hexane/ethyl acetate as eluent. The product was isolated as a red-yellow solid (14 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (d, J = 6.17 Hz, 2H, Ar), 7.90 (s, 2H, Ar), 7.48−7.39 (m, 6H, Ar), 4.78 (s, 1H, Cp^-H), 3.89 (s, 3H, OCH_3), 2.26 (d, J = 16.0 Hz, 1H, Cp^-CH_2), 1.25 (d, 1H, overlap, Cp^-CH_2), 1.22 (s, 9H, *t*-Bu), 0.95 (s, 9H, *t*-Bu), 0.71 (s, 9H, *t*-Bu). ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.1, 151.9, 129.3, 128.8, 128.5, 128.3, 124.9, 123.4 (Ar), 109.2, 101.8, 95.7 (C10, C11, C12), 65.4 (C8), 57.8 (C9), 38.9 (C7), 35.2, 32.4 (C4, C5, C6), 32.2, 31.3 (C1, C2, C3). HRMS (FAB) Calcd for $C_{31}H_{44}ClN_4ORu$ [M + H]$^+$ 625.2247, Found 625.2245. Anal. Calcd (%) for $C_{31}H_{43}ClN_4ORu$: C, 59.65; H, 6.94; N, 8.98. Found: C, 60.08; H, 6.88; N, 8.65. Single crystals were obtained from a CH_2Cl_2/hexane solution by slow evaporation.

[Cp^RuCl{(4-MeOC$_6$H$_4$)NNNN(4-MeOC$_6$H$_4$)}] (7b). 1-Azido-4-methoxybenzene (46 μmol, 6.9 mg) was added to a solution of complex **3** (23 μmol) in THF (0.80 mL), and the mixture was stirred at ambient temperature for 2 h. After the solvent was removed, the residue was purified by flash chromatography on silica gel, using hexane/ethyl acetate as eluent. The product was isolated as a red solid (14 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.55 (s, 2H, Ar), 7.86 (s, 2H, Ar), 6.99−6.91 (m, 4H, Ar), 4.77 (s, 1H, Cp^-H), 3.89 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 2.23 (d, J = 16.2 Hz, 1H, Cp^-CH_2), 1.30 (s, 9H, *t*-Bu), 1.25 (d, 1H, overlap, Cp^-H), 0.96 (s, 9H, *t*-Bu), 0.69 (s, 9H, *t*-Bu). ^{13}C NMR (213 MHz, $CDCl_3$): δ 160.1, 159.7, 150.7, 149.9, 126.3, 124.7, 114.3, 113.6 (Ar), 107.4, 101.3, 95.0 (C10, C11, C12), 64.8 (C8), 57.8 (C9), 56.0, 55.8 (OCH_3), 38.9 (C7), 35.1 (C4, C5, C6), 32.2, 31.7, 31.3 (C1, C2, C3). HRMS (FAB) Calcd for $C_{33}H_{48}ClN_4O_3Ru$ [M + H]$^+$ 685.2485, Found 685.2463. Anal. Calcd (%) for $C_{33}H_{47}ClN_4O_3Ru$: C, 58.57; H, 6.86; N, 7.70. Found: C, 57.92; H, 6.92; N, 8.19.

[Cp^RuCl{(4-CF$_3$C$_6$H$_4$)NNNN(4-CF$_3$C$_6$H$_4$)}] (7c). 1-Azido-4-(trifluoromethyl)benzene (46 μmol, 8.6 mg) was added to a solution of complex **3** (23 μmol) in THF (0.80 mL), and the mixture was stirred at ambient temperature for 2 h. After the solvent was removed, the residue was dissolved with hexane and filtered by a Celite pad. The solution was concentrated and dried under vacuum to afford a yellow solid (16 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.68 (d, J = 7.56 Hz, 2H, Ar), 7.99 (s, 2H, Ar), 7.78−7.68 (m, 4H, Ar), 4.83 (s, 1H, Cp^-H), 3.91 (s, 3H, OCH_3), 2.20 (d, J = 14.8 Hz, 1H, Cp^-CH_2), 1.25 (d, 1H, overlap, Cp^-CH_2), 1.22 (s, 9H, *t*-Bu), 0.96 (s, 9H, *t*-Bu), 0.72 (s, 9H, *t*-Bu). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 131.1, 130.9, 130.6, 129.9, 126.7, 125.8, 125.4, 123.5, 123.0 (Ar), 103.1, 96.8 (C10, C11, C12), 65.5 (C8), 58.1 (C9), 38.9 (C7), 35.3, 32.6 (C4, C5, C6), 32.1, 31.4 (C1, C2, C3). HRMS (FAB) Calcd for $C_{33}H_{42}ClF_6N_4ORu$ [M + H]$^+$ 761.1995, Found 761.1993. Anal. Calcd (%) for $C_{33}H_{41}ClF_6N_4ORu$: C, 52.14; H, 5.44; N, 7.37. Found: C, 52.07; H, 5.25; N, 7.21.

[Cp^RuCl{N(2,6-*i*Pr$_2$C$_6$H$_3$)}] (8a). 2-Azido-1,3-diisopropylbenzene (46 μmol, 9.3 mg) was added to a solution of complex **3** (23 μmol) in THF (0.80 mL), and the mixture was stirred at ambient temperature for 4 h. After the solvent was removed, the residue was purified by

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Organometallics XXXX, XXX, XXX−XXX

flash chromatography on silica gel, using hexane/ethyl acetate as eluent. The product was isolated as an orange solid (10 mg, 71%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.60 (t, J = 7.76 Hz, 1H, Ar), 7.01 (d, J = 7.76 Hz, 2H, Ar), 4.51 (s, 1H, Cp^-H), 4.10−3.96 (m, 2H, CH), 3.45 (s, 3H, OCH_3), 3.10 (d, J = 15.9 Hz, 1H, Cp^-CH_2), 2.44 (d, J = 15.9 Hz, 1H, Cp^-CH_2), 1.54 (s, 9H, t-Bu), 1.51 (s, 9H., t-Bu), 1.25−1.20 (m, 12H, i-Pr), 1.18 (s, 9H, t-Bu). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 158.4, 142.1, 139.7, 131.6, 125.3 (Ar, C13), 106.9, 97.4, 95.5 (C10, C11, C12), 69.9 (C9), 57.4 (C8), 39.6 (C7), 34.6, 33.9, 33.4 (C4, C5, C6), 32.9, 32.5, 32.4 (C1, C2, C3), 29.0 (CH), 24.0, 23.3 (i-Pr). HRMS (FAB) Calcd for $C_{31}H_{50}ClNORu$ $[M]^+$ 589.2624, Found 589.2627. Anal. Calcd (%) for $C_{31}H_{50}ClNORu$: C, 63.19; H, 8.55; N, 2.38. Found: C, 63.46; H, 8.14; N, 2.19. Single crystals were obtained from a diethyl ether by slow evaporation.

[Cp^RuCl{N(2,6-$Me_2C_6H_3$)}] (8b). 2-Azido-1,3-dimethylbenzene (46 μmol, 6.8 mg) was added to a solution of complex **3** (23 μmol) in THF (0.80 mL), and the mixture was stirred at ambient temperature for 2 h. After the solvent was removed, the residue was dissolved with hexane and filtered by a Celite pad. The solution was concentrated and dried under vacuum to afford an orange solid (6.4 mg, 52%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.42 (t, J = 7.57 Hz, 1H, Ar), 6.94 (d, J = 7.57 Hz, 2H, Ar), 4.53 (s, 1H, Cp^-H), 3.44 (s, 3H, OCH_3), 3.09 (d, J = 15.9 Hz, 1H, Cp^-CH_2), 2.46 (d, J = 15.9 Hz, 1H, Cp^-CH_2), 2.23 (s, 6H, CH_3), 1.53 (s, 9H, t-Bu), 1.51 (s, 9H, t-Bu), 1.18 (s, 9H, t-Bu). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 161.3, 140.0, 131.2, 130.5, 130.2 (Ar, C13), 106.6, 98.1, 95.9 (C10, C11, C12), 70.2 (C9), 57.4 (C8), 40.0 (C7), 34.4, 34.0, 33.6 (C4, C5, C6), 33.0, 32.6, 32.4 (C1, C2, C3), 20.6 (CH_3). HRMS (FAB) Calcd for $C_{27}H_{42}ClNORu$ [M]+ 533.1998, Found 533.2001. Anal. Calcd (%) for $C_{27}H_{42}ClNORu$: C, 60.82; H, 7.94; N, 2.63. Found: C, 60.56; H, 7.17; N, 2.83.

[Cp^RuCl{Ph(CH_3)CHNNNN(2,6-iPr$_2C_6H_3$)}] (9a). (1-Azidoethyl)benzene (44 μmol, 6.5 mg) was added to a solution of complex **5a** (22 μmol, 13 mg) in THF (1.0 mL), and the mixture was stirred at ambient temperature for 24 h. After the solvent was removed, the residue was purified by flash chromatography on silica gel, using hexane/ethyl acetate as eluent. The product was isolated as an pale green solid (13 mg, 80%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.63−7.61 (m, 2H, Ar), 7.39−7.18 (m, 6H, Ar), 6.13 (q, J = 6.81 Hz, 1H, N−CH), 4.69 (s, 1H, Cp^-H), 4.14 (m, 1H, CH), 3.56 (s, 3H, OCH_3), 2.08 (d, J = 6.75 Hz, 3H, CH_3), 2.09−2.03 (s, 1H, overlap, Cp^-CH_2), 1.84 (m, 1H, CH), 1.70 (d, J = 14.8 Hz, 1H, Cp^-CH_2), 1.31−1.28 (m, 6H, i-Pr), 1.13 (d, J = 6.67 Hz, 3H, i-Pr), 1.05 (s, 9H, t-Bu), 1.01 (s, 9H, t-Bu), 0.83 (s, 9H, t-Bu), 0.79 (d, J = 6.61 Hz, 3H, i-Pr). ^{13}C NMR (150 MHz, CD_2Cl_2): δ 152.3, 145.0, 144.4, 142.6, 129.0, 128.8, 127.5, 123.8, 123.0 (Ar), 99.4, 98.1 (C10, C11, C12), 79.1 (N−CH), 63.5 (C8), 58.2 (C9), 36.7 (C7), 34.9, 34.5, 32.7 (C4, C5, C6), 32.9, 32.1, 31.5 (C1, C2, C3), 28.7, 28.0 (CH), 27.2 (CH_3), 27.9, 26.4, 23.1, 21.9 (i-Pr). HRMS (FAB) Calcd for $C_{39}H_{60}ClN_4ORu$ $[M + H]^+$ 737.3499, Found 737.3497. Anal. Calcd (%) for $C_{39}H_{59}ClN_4ORu$: C, 63.61; H, 8.08; N, 7.61. Found: C, 63.20; H, 7.92; N, 6.97. Single crystals were obtained from a CH_2Cl_2/hexane solution by slow evaporation.

[Cp^RuCl{BnNNNN(2,6-iPr$_2C_6H_3$)}] (9b). Benzyl azide (22 μmol, 2.9 mg) was added to a solution of complex **5a** (22 μmol, 13 mg) in THF (1.0 mL), and the mixture was stirred at ambient temperature for 4 h. After the solvent was removed, the residue was purified by flash chromatography on silica gel, using hexane/ethyl acetate as eluent. The product was isolated as an pale green solid (14 mg, 89%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.58−7.56 (m, 2H, Ar), 7.42−7.16 (m, 6H, Ar), 5.66 (d, J = 16.0 Hz, 1H, N−CH_2), 5.44 (d, J = 16.0 Hz, 1H, N−CH_2), 4.76 (s, 1H, Cp^-H), 4.01 (m, 1H, CH), 3.72 (s, 3H, OCH_3), 2.00 (d, J = 15.3 Hz, 1H, Cp^-CH_2), 1.85 (m, 1H, CH), 1.63 (d, J = 16.1 Hz, 1H, Cp^-CH_2), 1.26 (d, J = 6.68 Hz, 3H, i-Pr), 1.19 (s, 9H, t-Bu), 1.19−1.13 (m, 6H, i-Pr), 1.13 (s, 9H, t-Bu), 1.02 (s, 9H, t-Bu), 0.71 (d, J = 6.61 Hz, 3H, i-Pr). ^{13}C NMR (213 MHz, CD_2Cl_2): δ 151.9, 144.9, 142.3, 137.6, 130.6, 128.8, 128.0, 123.6, 122.8 (Ar), 109.7, 102.7, 96.2 (C10, C11, C12), 72.3 (N−CH_2), 63.0 (C8), 58.4 (C9), 36.3 (C7), 35.0, 32.8 (C4, C5, C6), 32.8, 32.5, 31.6 (C1, C2, C3), 28.7, 27.9 (CH), 28.2, 26.3, 22.9, 21.8 (i-Pr). HRMS (FAB) Calcd for $C_{38}H_{58}ClN_4ORu$ $[M + H]^+$ 723.3343, Found 723.3340. Anal. Calcd (%) for $C_{38}H_{57}ClN_4ORu$: C, 63.18; H, 7.95; N, 7.76. Found: C, 63.36; H, 7.18; N, 7.50.

Trapping of Ammonia Liberated in Ligand Exchange Reaction of the Ruthenium Bisammine Complex. In an NMR tube filled with argon gas complex **2** (46 μmol, 30 mg) and benzylamine (92 μmol, 10 μL) were dissolved in THF-d_8 (1.0 mL), and the resulting solution was shaken at ambient temperature for 2 h. Then 1,2-bis(diphenylphosphino)ethane (46 μmol, 18 mg) was added to the solution, and the mixture was shaken at ambient temperature for 2 h. Then (isopropyl carbonic) 4-methoxybenzoic anhydride[15] (92 μmol, 22 mg) was added to the solution and the mixture was shaken at ambient temperature for 6 h. The yield of product was determined by ^{1}H NMR by using dibromomethane as an internal standard. After the solvent was removed, the residue was purified by flash chromatography on silica gel, using hexane/ethyl acetate as eluent. The 4-methoxybenzamide[16] was isolated as a white solid (11 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80−7.75 (m, 2H), 6.99−6.91 (m, 2H), 5.88 (br, 2H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 162.9, 129.5, 126.0, 114.1, 55.7.

General Procedure for Synthesis of N-Substituted Imines. Alkyl azide (0.25 mmol) and primary amine (0.30 mmol) was added to a solution of ruthenium complex **2** (2.0 mol %, 3.3 mg) in THF (1.0 mL), and the mixture was stirred at 70 °C for 1 h. After the solvent was removed, the yield of N-substituted imine was determined by ^{1}H NMR in $CDCl_3$ by using dibromomethane as an internal standard.

***N*-Hexylbenzylideneimine (10a).**[4a] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (s, 1H, N=CH), 7.75−7.71 (m, 2H, Ar), 7.41−7.39 (m, 3H, Ar), 3.61 (t, J = 7.0, 1.2 Hz, 2H, N−CH_2), 1.75−1.66 (m, 2H, N−CH_2−CH_2), 1.42−1.26 (m, 6H, $(CH_2)_3$-CH_3), 0.92−0.88 (m, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.8, 136.6, 130.6, 128.7, 128.2, 62.0, 31.8, 31.1, 27.2, 22.8, 14.2.

***N*-Benzylidenebutan-2-amine (10b).**[17] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (s, 1H, N=CH), 7.76−7.73 (m, 2H, Ar), 7.42−7.39 (m, 3H, Ar), 3.26−3.16 (m, 1H, CH), 1.68−1.58 (m, 2H, CH_2) 1.27 (d, J = 6.3 Hz, 3H, CH−CH_3), 0.86 (t, J = 7.4 Hz, 3H, CH_2−CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 136.8, 130.5, 128.7, 128.3, 68.4, 30.9, 22.4, 11.2.

***N*-Benzylidene-2-methylpropan-2-amine (10c).**[18] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (s, 1H, N=CH), 7.77−7.73 (m, 2H, Ar), 7.44−7.37 (m, 3H, Ar), 1.30 (s, 9H, t-Bu). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.4, 137.4, 130.4, 128.7, 128.1, 57.4, 29.9.

***N*-(1-Phenylethylidene)hexan-1-amine (10d).**[19] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79−7.76 (m, 2H, Ar), 7.39−7.36 (m, 3H, Ar), 3.48 (t, J = 7.1 Hz, 2H, N−CH_2), 2.23 (s, 3H, C−CH_3), 1.80−1.71 (m, 2H, N−CH_2−CH_2), 1.47−1.31 (m, 6H, $(CH_2)_3$-CH_3), 0.95−0.90 (m, 3H, CH_2−CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 141.7, 129.4, 128.3, 126.7, 52.4, 32.0, 31.1, 27.6, 22.8, 15.5, 14.2.

***N*-(1-Phenylethylidene)butan-2-amine (10e).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77−7.74 (m, 2H, Ar), 7.40−7.34 (m, 3H, Ar), 3.64−3.54 (m, 1H, N−CH), 2.24 (s, 3H, C−CH_3), 1.69−1.59 (m, 2H, CH_2), 1.18 (d, J = 6.3 Hz, 3H, CH−CH_3), 0.90 (t, J = 7.4 Hz, 3H, CH_2−CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.9, 142.2, 129.3, 128.3, 126.8, 57.5, 31.3, 21.3, 15.6, 11.4. HRMS (EI) Calcd for $C_{12}H_{17}N$ 175.1361, Found 175.1361.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00403.

Characterization including NMR spectroscopic data and X-ray crystallographic data (PDF)

XYZ coordinates of all structures (XYZ)

Accession Codes

CCDC 1552955−1552957 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by email-

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Organometallics XXXX, XXX, XXX−XXX

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Dutta, B.; Solari, E.; Gauthier, S.; Scopelliti, R.; Severin, K. *Organometallics* **2007**, *26*, 4791−4799. (b) Gauthier, S.; Solari, E.; Dutta, B.; Scopelliti, R.; Severin, K. *Chem. Commun.* **2007**, *0*, 1837−1839.

(2) Dutta, B.; Curchod, B. F. E.; Campomanes, P.; Solari, E.; Scopelliti, R.; Rothlisberger, U.; Severin, K. *Chem. - Eur. J.* **2010**, *16*, 8400−8409.

(3) Risse, J.; Scopelliti, R.; Severin, K. *Organometallics* **2011**, *30*, 3412−3418.

(4) A major research interest of our group is the catalytic generation of N−H imines from alkyl azides: (a) Lee, J. H.; Gupta, S.; Jeong, W.; Rhee, Y. H.; Park, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 10851−10855. (b) Han, J.; Rhee, Y. H.; Park, J. *Bull. Korean Chem. Soc.* **2014**, *35*, 3433−3436. (c) Jeong, W.; Lee, J. H.; Kim, J.; Lee, W. J.; Seong, J.-H.; Park, J.; Rhee, Y. H. *RSC Adv.* **2014**, *4*, 20632−20635. (d) Jeon, M.; Gupta, S.; Im, Y.-W.; Rhee, Y. H.; Park, J. *Asian J. Org. Chem.* **2015**, *4*, 316−319. (e) Kim, Y.; Rhee, Y. H.; Park, J. *Org. Biomol. Chem.* **2017**, *15*, 1636−1641. (f) Lee, W. J.; Jeong, W.; Park, J.; Rhee, Y. H. *Asian J. Org. Chem.* **2017**, *6*, 441−444.

(5) (a) Pak, H. K.; Han, J.; Jeon, M.; Kim, Y.; Kwon, Y.; Park, J. Y.; Rhee, Y. H.; Park, J. *ChemCatChem* **2015**, *7*, 4030−4034. (b) Kim, Y.; Pak, H. K.; Rhee, Y. H.; Park, J. *Chem. Commun.* **2016**, *52*, 6549−6552.

(6) (a) Obenhuber, A. H.; Gianetti, T. L.; Berrebi, X.; Bergman, R. G.; Arnold, J. *J. Am. Chem. Soc.* **2014**, *136*, 2994−2997. (b) Cramer, S. A.; Sánchez, R. H.; Brakhage, D. F.; Jenkins, D. M. *Chem. Commun.* **2014**, *50*, 13967−13970. (c) Gehrmann, T.; Fillol, J. L.; Wadepohl, H.; Gade, L. H. *Organometallics* **2012**, *31*, 4504−4515. (d) Lamberti, M.; Fortman, G. C.; Poater, A.; Broggi, J.; Slawin, A. M. Z.; Cavallo, L.; Nolan, S. P. *Organometallics* **2012**, *31*, 756−767. (e) Monillas, W. H.; Yap, G. P. A.; Theopold, K. H. *Inorg. Chim. Acta* **2011**, *369*, 103−119. (f) Gehrmann, T.; Fillol, J. L.; Wadepohl, H.; Gade, L. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 2152−2156. (g) Boren, B. C.; Narayan, S.; Rasmussen, L. K.; Zhang, L.; Zhao, H.; Lin, Z.; Jia, G.; Fokin, V. V. *J. Am. Chem. Soc.* **2008**, *130*, 8923−8930. (h) Meyer, K. E.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 974−985.

(7) As far as we know, the complex **3** is the first cyclopentadienyl ruthenium bisammine complex, while several cyclopentadienyl ruthenium monoammine complexes have been reported: (a) Miranda-Soto, V.; Grotjahn, D. B.; Cooksy, A. L.; Golen, J. A.; Moore, C. E.; Rheingold, A. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 631−635. (b) Rankin, M. A.; Schatte, G.; McDonald, R.; Stradiotto, M. *Organometallics* **2008**, *27*, 6286−6299. (c) Derrah, E. J.; Pantazis, D. A.; McDonald, R.; Rosenberg, L. *Organometallics* **2007**, *26*, 1473−1482. (d) Tsuno, T.; Brunner, H.; Katano, S.; Kinjyo, N.; Zabel, M. *J. Organomet. Chem.* **2006**, *691*, 2739−2747. (e) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 41−43. (f) Conroy-Lewis, F. M.; Simpson, S. J. *J. Organomet. Chem.* **1990**, *396*, 83−94.

(8) Dutta, B.; Scopelliti, R.; Severin, K. *Organometallics* **2008**, *27*, 423−429.

(9) We obtained ^{1}H NMR spectra of the complex **3** at various temperatures (Figure S3). Interesting fluxional behavior was observed due to the dynamic exchange of NH_3 and the restricted rotation of *t*-butyl groups and the Cp^ ring.

(10) (a) Singh, A. K.; Levine, B. G.; Staples, R. J.; Odom, A. L. *Chem. Commun.* **2013**, *49*, 10799−10801. (b) Takaoka, A.; Moret, M.-E.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, *134*, 6695−6706. (c) Intrieri, D.; Caselli, A.; Ragaini, F.; Macchi, P.; Casati, N.; Gallo, E. *Eur. J. Inorg. Chem.* **2012**, *2012*, 569−580. (d) Takaoka, A.; Gerber, L. C. H.; Peters, J. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 4088−4091. (e) Fantauzzi, S.; Gallo, E.; Caselli, A.; Ragaini, F.; Casati, N.; Macchi, P.; Cenini, S. *Chem. Commun.* **2009**, *0*, 3952−3954. (f) Walstrom, A. N.; Fullmer, B. C.; Fan, H.; Pink, M.; Buschhorn, D. T.; Caulton, K. G. *Inorg. Chem.* **2008**, *47*, 9002−9009. (g) Burrell, A. K.; Steedman, A. J. *Organometallics* **1997**, *16*, 1203−1208. (h) Burred, A. K.; Steedman, A. J. *J. Chem. Soc., Chem. Commun.* **1995**, *0*, 2109−2110. (i) Danopoulos, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1992**, *11*, 2961−2964.

(11) Takemoto, S.; Yamazaki, Y.; Yamano, T.; Mashima, D.; Matsuzaka, H. *J. Am. Chem. Soc.* **2012**, *134*, 17027−17035. (b) Takemoto, S.; Kobayashi, T.; Ito, T.; Inui, A.; Karitani, K.; Katagiri, S.; Masuhara, Y.; Matsuzaka, H. *Organometallics* **2011**, *30*, 2160−2172. (c) Kee, T. P.; Park, L. Y.; Robbins, J.; Schrock, R. R. *J. Chem. Soc., Chem. Commun.* **1991**, *0*, 121−122.

(12) Risse, J.; Dutta, B.; Solari, E.; Scopelliti, R.; Severin, K. *Z. Anorg. Allg. Chem.* **2014**, *640*, 1322−1329.

(13) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, *0*, 3771−3778.

(14) Cowley, R. E.; Bill, E.; Neese, F.; Brennessel, W. W.; Holland, P. L. *Inorg. Chem.* **2009**, *48*, 4828−4836.

(15) Dong, Z.; Wang, J.; Ren, Z.; Dong, G. *Angew. Chem., Int. Ed.* **2015**, *54*, 12664−12668.

(16) Tao, C.; Liu, F.; Zhu, Y.; Liu, W.; Cao, Z. *Org. Biomol. Chem.* **2013**, *11*, 3349−3354.

(17) Zhang, G.; Hanson, S. K. *Org. Lett.* **2013**, *15*, 650−653.

(18) Yuan, H.; Yoo, W.-J.; Miyamura, H.; Kobayashi, S. *J. Am. Chem. Soc.* **2012**, *134*, 13970−13973.

(19) Peeters, A.; Valvekens, P.; Ameloot, R.; Sankar, G.; Kirschhock, C. E. A.; De Vos, D. E. *ACS Catal.* **2013**, *3*, 597−607.

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Organometallics XXXX, XXX, XXX−XXX