Synthesis and Reactivity of a Ruthenium(III) Bis(anilide) Dimer by Oxidative Addition of an N,N′-Disubstituted Hydrazine

Jessica M. Hoover, Antonio DiPasquale,† James M. Mayer,* and Forrest E. Michael*

Department of Chemistry, Campus Box 351700, University of Washington, Seattle, Washington 98195-1700

Received January 17, 2007

The Ru^{III} bis(anilide) dimer [Cp*RuCl(μ-NHPh)]$_2$ (**1a**) is formed upon reaction of (Cp*RuCl)$_4$ with 1,2-diphenylhydrazine in benzene. An X-ray crystal structure shows a centrosymmetric (C_i) dimer with a planar Ru_2N_2 core. Reaction of (Cp*RuCl)$_4$ with a mixture of PhNHNHPh and TolNHNHTol gives only the homodimers **1a** and [Cp*RuCl(μ-NHTol)]$_2$ (Tol = *p*-tolyl). The lack of crossover indicates that cleavage of the hydrazine N−N bond is an intramolecular process. In polar solvents such as acetonitrile, the C_i dimer **1a** isomerizes to the C_{2v} isomer **1b**, in which the anilido substituents are cis across the Ru_2N_2 core. Both isomers appear to be kinetic products of the synthesis, but **1b** isomerizes to **1a** in the benzene solvent. In the presence of **1a**, 1,2-diphenylhydrazine disproportionates into azobenzene and aniline, and labeling studies show that this occurs without participation of the anilido ligands of **1a**. Complex **1a** shows slow exchange of the anilide ligands with toluidine (H_2NTol) by NMR spectroscopy and is unreactive toward methanol, triethylphosphine, styrene, and phenylacetylene. The addition of silver triflate and phenylacetylene to **1a** leads to a new species, assigned as the acetylene complex [{Cp*Ru(μ-NHPh)}$_2$(μ-η^2:η^2-PhC≡CH)](OTf)$_2$ (**6a**).

Introduction

The development of new C−N bond forming reactions has attracted much attention. Most interest lies in the catalytic hydroamination and diamination of unsaturated hydrocarbons, since these methods could provide efficient and atom-economic routes to a variety of amines.[1] The hydroamination of alkynes, allenes, and alkenes catalyzed by early-transition-metal systems have been studied in detail.[2] Late metals are also known to catalyze intra-[3] and intermolecular[4] hydroamination reactions, including rhodium,[5] iridium,[6] and ruthenium complexes.[7] The addition of an amine N−H bond to an olefin gives a substituted amine, without a change in the oxidation state of the substrate.[8] Oxidative amination, with a stoichiometric oxidant, can yield enamines, imines,[9] or nitrogen heterocycles.[10]

Diamination reactions of alkenes and alkynes are also oxidative processes.[11] Early reports of vicinal diamination reactions involve a stoichiometric transition-metal promoter, such as the palladium-promoted process described by Bäckvall[12] and the stoichiometric addition of two ^{t}BuNH groups to alkenes by osmium,[13] among others.[14] Recently, palladium-catalyzed diamination reactions with sacrificial oxidants have been

* To whom correspondence should be addressed. E-mail: mayer@chem.washington.edu (J.M.M.); michael@chem.washington.edu (F.E.M.).

† University of Washington X-ray Crystallography facility.

(1) Beller, M.; Breindl, C.; Eichberger, M.; Hartung, C. G.; Seayad, J.; Thiel, O. R.; Tillack, A.; Trauthwein, H. *Synlett* **2002**, 1579−1594.

(2) (a) Haak, E.; Bytschkov, I.; Doye, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3389−3391. (b) Pohlki, F.; Doye, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2305−2308. (c) Straub, B. F.; Bergman, R. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 4632−4635. (d) Johnson, J. S.; Bergman, R. G. *J. Am. Chem. Soc.* **2001**, *123*, 2923−2924. (e) Cao, C.; Ciszewski, J. Y.; Odom, A. L. *Organometallics* **2001**, *20*, 5011−5013. (f) Shi, Y.; Ciszewski, J. T.; Odom, A. L. *Organometallics* **2001**, *20*, 3967−3969. (g) Shi, Y.; Hall, C.; Ciszewski, J. T.; Cao, C.; Odom, A. L. *Chem. Commun.* **2003**, 586−587. (h) Thomson, R. K.; Bexrud, J. A.; Schafer, L. L *Organometallics* **2006**, *25*, 4069−4071. (i) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, *68*, 935−946. (j) Ackermann, L.; Bergman, R. G.; Loy, R. N. *J. Am. Chem. Soc.* **2003**, *125*, 11956−11963.

(3) (a) Bajracharya, G. B.; Huo, Z.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 4883−4886. (b) Beccalli, E.; Broggini, G.; Martinelli, M.; Paladino, G. *Synlett* **2006**, *1*, 73−76. (c) Siriwardana, A. I.; Kamada, M.; Nakamura, I.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 5932−5937. (d) Krogstad, D. A.; Cho, J.; DeBoer, A. J.; Klitzke, J. A.; Sanow, W. R.; Williams, H. A.; Halfen, J. A. *Inorg. Chim. Acta* **2006**, *359*, 136−148. (e) Michael, F. E.; Cochran, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 4246−4247. (f) Müller, T. E.; Pleier, A.-K. *J. Chem. Soc., Dalton Trans.* **1999**, 583−587. (g) Campi, E. M.; Jackson, W. R. *J. Organomet. Chem.* **1996**, *523*, 205−209.

(4) (a) Li, K.; Horton, P. N.; Hursthouse, M. B.; Hii, K. K. *J. Organomet. Chem.* **2003**, *665*, 250−257. (b) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 12640−12646. (c) Kadota, I.; Shibuya, A.; Lutete, L. M.; Yamamoto, Y. *J. Org. Chem.* **1999**, *64*, 4570−4571.

(5) Burling, S.; Field, L. D.; Messerle, B. A. *Organometallics* **2000**, *19*, 87−90. Coulson, D. R. *Tetrahedron Lett.* **1971**, *12*, 429−430.

(6) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738−6744.

(7) (a) Tokunaga, M.; Eckert, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3222−3225. (b) Klein, D. P.; Ellern, A.; Angelici, R. J. *Organometallics* **2004**, *23*, 5662−5670. (c) Takaya, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5756−5757. (d) Kondo, T.; Okada, T.; Suzuki, T.; Mitsudo, T. *J. Organomet. Chem.* **2001**, *622*, 149−154. (e) Tokunaga, M.; Eckert, M.; Wakatsuki, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3222−3225.

(8) (a) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104−114. (b) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368−3398.

(9) (a) Beller, M.; Eichberger, M.; Trauthwein, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2225−2227. (b) Brice, J. L.; Harang, J. E.; Timokhin, V. I.; Anastasi, N. R.; Stahl, S. S. *J. Am. Chem. Soc.* **2005**, *127*, 2868−2869. (c) Brunet, J. J.; Neibecker, D.; Philippot, K. *Tetrahedron Lett.* **1993**, *34*, 3877−3880.

(10) (a) Kondo, T.; Okada, T.; Mitsudo, T. *J. Am. Chem. Soc.* **2002**, *124*, 186−187. (b) Rogers, M. M.; Wendlandt, J. E.; Guzei, I. A.; Stahl, S. S. *Org. Lett.* **2006**, *8*, 2257−2260. (c) Fix, S. R.; Brice, J. L.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 164−166.

(11) Lucet, D.; Le Gall, T.; Mioskowski, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 2580−2627.

(12) Bäckvall, J-E. *Tetrahedron Lett.* **1978**, *19*, 163−166.

(13) (a) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420−3426. (b) Corey, E. J.; Jardine, P. D.; Virgil, S.; Yuen, P.-W.; Connell, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 9243−9244.

(14) Zabawa, T. P.; Kasi, D.; Chemler, S. R. *J. Am. Chem. Soc.* **2005**, *127*, 11250−11251.

10.1021/om0700462 CCC: $37.00
Publication on Web 06/01/2007

developed.[15] A direct analogy to the hydroamination reaction would be the direct addition of an N−N bond across a C−C multiple bond. Such a process can be envisioned to occur by oxidative addition of a hydrazine to a metal center to make an oxidizing amide complex, followed by addition of the amido ligands to an alkene with a two-electron reduction of the metal center. An interesting example is the recently reported Pd-catalyzed diamination of dienes with di-*tert*-butylaziridinone, which may proceed through an oxidative addition pathway.[16]

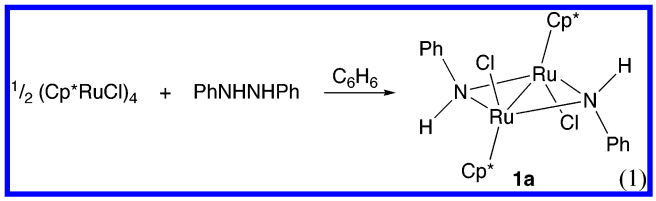
Few studies have addressed the fundamental reactivity of hydrazines with metal centers,[17] except as models for the cleavage of N−N bonds by nitrogenase enzymes.[18] The reductive cleavage of hydrazines is accomplished by a number of systems,[19] and a few catalyze the disproportionation of hydrazine into ammonia and dinitrogen.[20] Schrock and co-workers have proposed oxidative addition of a hydrazine to be on the pathway to imido formation in their molybdenum and tungsten systems.[19a] A recent publication reports the addition of 1,2-diphenylhydrazine to an iron(II) monomer to yield a dimeric iron(III) bis(imido) complex in a multistep process.[21] To our knowledge, there have been no direct observations of a simple oxidative addition of a hydrazine N−N bond.

The Cp*Ru system (Cp* = C_5Me_5) is a promising candidate for hydrazine oxidative addition, since related oxidative additions are known for disulfides, alkyl halides,[22] allyl halides,[23] Si−H bonds,[24] and others.[25] Oxidative addition of a hydrazine to a Ru^{II} center would form a Ru^{IV} bis(amido) species, similar to Che's $[L_2Ru(NHCMe_2CMe_2NH_2)_2]^{2+}$ complexes.[26] The Cp*Ru moiety has been shown to stabilize Ru(IV) species.[27] Cp*Ru complexes are also known to react with C−C multiple bonds,[28] including a Cp^*Ru^{II}−bis(amido) dimer which inserts diphenylacetylene into a Ru−N bond[29] and a Cp^*Ru^{III}−bis(thiolate) dimer which oxidizes alkenes to vicinal dithioethers.[30]

This paper reports the formation of the new ruthenium(III)−bis(amido) complex $[Cp^*RuCl(\mu\text{-NHPh})]_2$ by oxidative addition of 1,2-diphenylhydrazine to $(Cp^*Ru^{II}Cl)_4$. The reactivity of this complex toward hydrazines, amines, and terminal alkynes is described.

Results

***C*$_i$-[Cp*RuCl(μ-NHPh)]$_2$ (1a)**. The reaction of $(Cp^*Ru^{II}Cl)_4$ with an excess of 1,2-diphenylhydrazine (PhNHNHPh) in C_6H_6 forms the anilide-bridged ruthenium dimer *C*$_i$-$[Cp^*Ru^{III}Cl(\mu\text{-NHPh})]_2$ (**1a**; eq 1). After 3 days at room temperature followed



by 20 h at 50 °C, **1a** was precipitated from solution with pentane and isolated in 76% yield (see below). Complex **1a** is also formed on reaction of unsaturated $Cp^*Ru^{II}Cl(PCy_3)$[31] with PhNHNHPh, with loss of PCy_3, but it is not generated upon reaction of $[Cp^*Ru^{III}Cl(\mu\text{-Cl})]_2$ with aniline.

The structure of **1a** was established by single-crystal X-ray diffraction to contain dimeric molecules in which the halves are related by an inversion center (Figure 1, Tables 1 and 2). The Ru−Ru distance of 2.7134(7) Å is typical of Ru−Ru single

(15) (a) Bar, G. L. J.; Lloyd-Jones, G. C.; Brooker-Milburn, K. I. *J. Am. Chem. Soc.* **2005**, *127*, 7308−7309. (b) Steuff, J.; Hövelmann, C. H.; Nieger, M.; Muñiz, K. *J. Am. Chem. Soc.* **2005**, *127*, 14586−14587.
(16) Du, H.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2007**, *129*, 762−763.
(17) Barkley, J. V.; Heaton, B. T.; Jacob, C.; Mageswaran, R.; Sampanthar, J. T. *J. Chem. Soc., Dalton Trans.* **1998**, 697−701.
(18) (a) Bernskoetter, W. H.; Pool, J. A.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 7901−7911. (b) Bernskoetter, W. H.; Lobkovsky, E.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 14051−14061. (c) Zhang, Q.-F.; Zheng, H.; Wong, W.-Y.; Wong, W.-T.; Leung, W.-H. *Inorg. Chem.* **2000**, *39*, 5255−5264. (d) Frédéric, B. *Coord. Chem. Rev.* **2003**, *236*, 71−89.
(19) (a) Schrock, R. R.; Glassman, T. E.; Vale, M. G. *J. Am. Chem. Soc*. **1991**, *113*, 725−726. (b) Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc*. **1993**, *115*, 1760−1772. (c) Vale, M. G.; Schrock, R. R. *Inorg. Chem.* **1993**, *32*, 2767−2772. (d) Prakash, R.; Ramachandraiah, G. *J. Mol. Catal. A: Chem*. **2000**, *151*, 193−204. (e) Nakajima, Y.; Suzuki, H. *Organometallics* **2003**, *22*, 959−969. (f) Nakajima, Y.; Inagaki, A.; Suzuki, H. *Organometallics* **2004**, *23*, 4040−4046. (g) Nakajima, Y.; Suzuki, H. *Organometallics* **2005**, *24*, 1860−1866. (h) Shaver, M.; Fryzuk, M. D. *J. Am. Chem. Soc.* **2005**, *127*, 500−501. (i) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1989**, 425−430.
(20) (a) Kuwata, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1994**, *33*, 3619−3620. (b) Hitchcock, P. B.; Hughes, D. L.; Maguire, M. J.; Marjani, K.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1997**, 4747−4752. (c) Takei, I.; Dohki, K.; Kobayashi, K.; Suzuki, T.; Hidai, M. *Inorg. Chem.* **2005**, *44*, 3768−3770.
(21) Ohki, Y.; Takikawa, Y.; Hatanaka, T.; Tatsumi, K. *Organometallics* **2006**, *25*, 3111−3113.
(22) (a) Hubbard, J. L.; Morneau, A.; Burns, R. M.; Zoch, C. R. *J. Am. Chem. Soc.* **1991**, *113*, 9176−9180. (b) Takahashi, A.; Mizobe, Y.; Matsuzaka, H.; Dev, S.; Hidai, M. *J. Organomet. Chem.* **1993**, *456*, 243−253.
(23) (a) Nagashima, H.; Mukai, K.; Itoh, K. *Organometallics* **1984**, *3*, 1314−1315. (b) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1987**, *6*, 2347−2354. (c) Nagashijma, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799. (d) Kondo, H.; Kageyama, A.; Yamaguchi, Y.; Haga, M.; Kirchner, K.; Nagashima, H. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1927−1937.
(24) (a) Johnson, T. J.; Coan, P. S.; Caulton, K. G. *Inorg. Chem.* **1993**, *32*, 4594−4599. (b) Lemke, F. R.; Chaitheerapapkul, C. *Polyhedron* **1996**, *15*, 2559−2565.
(25) Kuhlman, R.; Folting, K.; Caulton, K. G. *Organometallics* **1995**, *14*, 3188−3195. Navarro Clemente, M. E.; Juarez Saavedra, P.; Cervantes Vasquez, M.; Paz-Sandoval, M. A.; Arif, A. M.; Ernst, R. D. *Organometallics* **2002**, *21*, 592−605.
(26) Chiu, W.-H.; Peng, S.-M.; Che, C.-M. *Inorg. Chem.* **1996**, *35*, 3369−3374.
(27) Arliguie, T.; Chaudret, B. *Chem. Commun.* **1986**, *13*, 985−986. Nagashima, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.-I.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799−807. Beach, N. B.; Jenkins, H. A.; Spivak, G. J. *Organometallics* **2003**, *22*, 5179−5181. Beach, N. J.; Williamson, A. E.; Spivak, G. J. *J. Organomet. Chem.* **2005**, *690*, 4640−4647. Fernández, I.; Pregosin, P. *Organometallics* **2006**, *25*, 4520−4529. Bruneau, C.; Renaud, J.-L.; Demerseman, B. *Chem. Eur. J.* **2006**, *12*, 5178−5187.
(28) (a) Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K. *Organometallics* **1993**, *12*, 2221−2226. (b) de los Ríos, I.; Tenorio, M. J.; Puerta, C. M.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529−6538. (c) Dérien, S.; Dixeneuf, P. H. *J. Organomet. Chem.* **2004**, *689*, 1382−1392. (d) Koelle, U.; Kang, B.-S.; Thewalt, U. *Organometallics* **1992**, *11*, 2893−2899. (e) Carreno, R.; Chaudret, B.; Labroue, D.; Sabo-Etienne, S. *Organometallics* **1993**, *12*, 13−14. (f) Takemori, T.; Inagaki, A; Suzuki, H. *J. Am. Chem. Soc.* **2001**, *123*, 1762−1763. (g) Tutusaus, O.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Núñez, R.; Viñas, C.; Teixidor, F. *Tetrahedron Lett.* **2002**, *43*, 983−987. (h) Kawanami, Y.; Sonoda, Y.; Mori, T.; Yamamoto, K. *Org. Lett.* **2002**, *4*, 2825−2827. (i) Oe, Y.; Ohta, T.; Ito, Y. *Chem. Commun.* **2004**, 1620−1621. Fukuyama, T.; Yamaura, R.; Higashibeppu, Y.; Okamura, T.; Ryu, I.; Kondo, T.; Mitsudo, T. *Org. Lett.* **2005**, *26*, 5781−5783. (j) Inada, Y.; Yoshikawa, M.; Milton, M. D.; Nishibayashi, Y.; Uemura, S. *Eur. J. Org. Chem.* **2006**, 881−890. (k) Jia, G.; Lau, C. P. *J. Organomet. Chem.* **1998**, *565*, 37−48. (l) Itoh, K.; Masuda, K.; Fukahori, T.; Nakano, K.; Aoki, K.; Nagashima, H. *Organometallics* **1994**, *13*, 1020−1029. (m) Yi, C. S.; Liu, N. *J. Organomet. Chem.* **1998**, *553*, 157−161.
(29) Takemoto, S.; Kobayashi, T.; Matsuzaka, H. *J. Am. Chem. Soc.* **2004**, *126*, 10802−10803.
(30) Kondo, T.; Uenoyama, S.; Fujita, K.; Mitsudo, T. *J. Am. Chem. Soc.* **1999**, *121*, 482−483.
(31) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1998**, 278−280. Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308−1314.

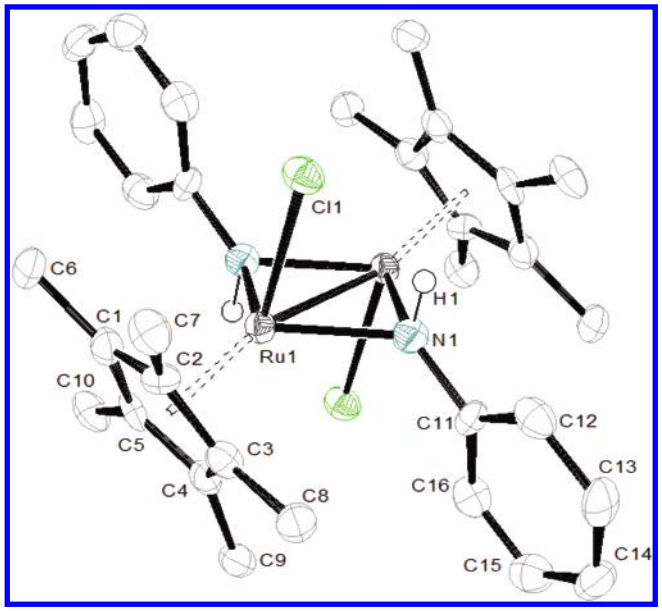


Figure 1. ORTEP drawing of $[Cp^*RuCl(\mu\text{-NHPh})]_2$ (**1a**) showing 50% probability ellipsoids.

Table 1. Selected Bond Distances (Å) and Angles (deg) in 1a

Ru1−Ru1′	2.7134(7)	Ru1−Cl1	2.4919(11)
Ru1−N1	2.072(4)	C11−N1	1.429(6)
Ru1−N1′	2.085(4)		
Ru1−N1−Ru1′	81.50(14)	Ru1−N1−C11	128.0(3)
N1−Ru1−N1′	98.50(14)	Ru1′−N1−C11	128.6(3)

Table 2. Crystallographic Data for 1a

formula	$C_{32}H_{42}Cl_2N_2Ru_2$
formula wt	727.72
space group	$P\bar{1}$
cryst syst	triclinic
cryst color	brown
cryst dimens (mm)	0.24 × 0.07 × 0.07
a (Å)	9.361(5)
b (Å)	9.382(5)
c (Å)	10.278(5)
α (deg)	63.061(5)
β (deg)	82.784(5)
γ (deg)	68.665(5)
V (Å^3)	748.7(7)
Z	1
d_{calcd} (Mg m^{-3})	1.614
μ_{calc} (mm^{-1})	1.211
F(000)	370
no. of unique rflns	3554
no. of data used	3554
no. of params refined	180
R^a	0.0537
$R_w{}^b$	0.1186
GOF^c	1.009

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. [c] GOF $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

bonds[32,35] and is significantly shorter than that found in the divalent analogue $[Cp^*Ru^{II}(\mu\text{-NHPh})]_2$ (2.945(4) Å), which lacks a Ru−Ru bond.[33] The Ru−Ru distance in **1a** is similar to those in related thiolate- and selenolate-bridged Ru(III) dimers $[Cp^*Ru^{III}Cl(\mu\text{-ER})]_2$: *d*(Ru−Ru) = 2.8354(7)−2.847(1) Å for E = S, 2.898(1)−2.9258(7) Å for E = Se; R = Me, Et, Ph.[34,35] The Ru−N distances in **1a** (2.072(4), 2.085(4) Å) are also shorter than those in $[Cp^*Ru^{II}(\mu\text{-NHPh})]_2$ (2.101(8), 2.117(7) Å). The anilido phenyl rings in **1a** are oriented nearly perpendicular to the Ru_2N_2 plane, with the torsional angle Ru1−N1−C11−C16 = 68.9(6)°. The rings are on opposite sides of the Ru_2N_2 plane (anti), with the ipso carbons (C11) angled 35.04° out of the plane. In contrast, the thiolate-bridged dimers most often have C_{2v} structures with syn thiolate substituents.[36] The amide hydrogens (H1, H1′) in **1a** were located in the Fourier difference map.

The ^{1}H NMR spectrum of **1a** shows a single Cp* resonance, a single N*H* resonance, and five inequivalent aryl resonances. Similarly, the ^{13}C NMR spectrum shows one kind of Cp* and six unique aryl resonances. The equivalence of the two Cp* ligands and the two anilide ligands is consistent with the C_i symmetry seen in the crystal structure. The spectra indicate that **1a** is diamagnetic, again supporting the presence of a Ru−Ru bond. The resonance at δ 11.0 was assigned as N*H* by its disappearance in the ^{1}H NMR spectrum of **1a-*d*$_2$** made from $(Cp^*RuCl)_4$ and PhNDNDPh. This assignment was confirmed by ^{2}H NMR analysis. The ESI-MS of **1a** shows a parent ion (*m*/*z* 693.3) and isotope distribution characteristic of dimeric **1a**. Thus, the spectroscopy shows that **1a** has the same structure in solution as observed in the solid state.

The ^{1}H and ^{13}C{^{1}H} NMR spectra show that rotation of the anilide phenyl rings is slow on the NMR time scale at room temperature. The aryl resonances do not broaden upon heating to 353 K. However, 2D EXSY experiments[37] show exchange cross-peaks between the two ortho resonances (δ 8.62, 7.33) and give a rate constant for rotation about the $N_{amido}-C_{phenyl}$ bond of 1.0 ± 0.2 s^{-1} at 298 K ($\Delta G^{\ddagger}_{298}$ = 17 ± 2 kcal mol^{-1}). An Eyring plot over a limited temperature range (*T* = 285−320 K) gives $\Delta H^{\ddagger}$ = 10 ± 1 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −23 ± 3 cal mol^{-1} K^{-1} (see the Supporting Information). The barrier for this rotation is larger than the barriers to phenyl rotation in related $TpRu^{II}L_2(NHPh)$ monomers: $\Delta G^{\ddagger}$ = 12.8 kcal mol^{-1} at 0 °C for L = PMe_3, $\Delta G^{\ddagger}$ < 9.5 kcal/mol at −20 °C for L = $P(OMe)_3$.[38] In the monomers, hindered rotation is in part due to donation from the N lone pair into the phenyl π system.[38] In the case of **1a**, however, the barrier results from steric factors, since no nitrogen lone pair is available for donation into the phenyl ring.

To evaluate the scope of the hydrazine cleavage reaction, $(Cp^*Ru^{II}Cl)_4$ was reacted with several other hydrazines. 1,2-Di-*p*-tolylhydrazine (TolNHNHTol) rapidly reacts with $(Cp^*RuCl)_4$, forming the toluidide dimer $[Cp^*RuCl(\mu\text{-NHTol})]_2$ (**2**). Analogous to **1a**, the ^{1}H NMR spectrum of **2** shows one Cp*, one NH, one tolyl methyl, and four aryl resonances. The electron-deficient phenyl(trifluoroacetyl)hydrazine (PhNHNHCOCF$_3$) reacts more slowly with $(Cp^*RuCl)_4$, and cleavage of the hydrazine N−N bond is not observed. Instead, $[Cp^*Ru(\eta^6\text{-PhNHNHCOCF}_3)]Cl$ is formed by simple η^6 coordination of the arene ring, a very common reaction of $(Cp^*RuCl)_4$.[59,39] Dimethyl hydrazine-1,2-dicarboxylate ($MeO_2CNHNHCO_2Me$),

(32) Ferrence, G. M.; Fanwich, P. E.; Kubiak, C. P.; Haines, R. J. *Polyhedron* **1997**, *16*, 1453−1459. Kuncheria, J.; Mirza, H. A.; Jenkins, H. A.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1998**, 285−290. Gao, Y.; Jennings, M. C.; Puddephatt, R. J. *Organometallics* **2001**, *20*, 3500−3509.

(33) Blake, R. E.; Heyn, R. H.; Tilley, T. D. *Polyhedron* **1992**, *11*, 709−710.

(34) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 5100−5103.

(35) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 26−30.

(36) Nishibayashi, Y.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2003**, *22*, 873−876.

(37) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935−967.

(38) Conner, D.; Jayaprakash, K. N.; Gunnoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2002**, *41*, 3042−3049.

(39) Arene coordination has been observed by ^{1}H NMR and ESI-MS and in some cases by X-ray crystallography.

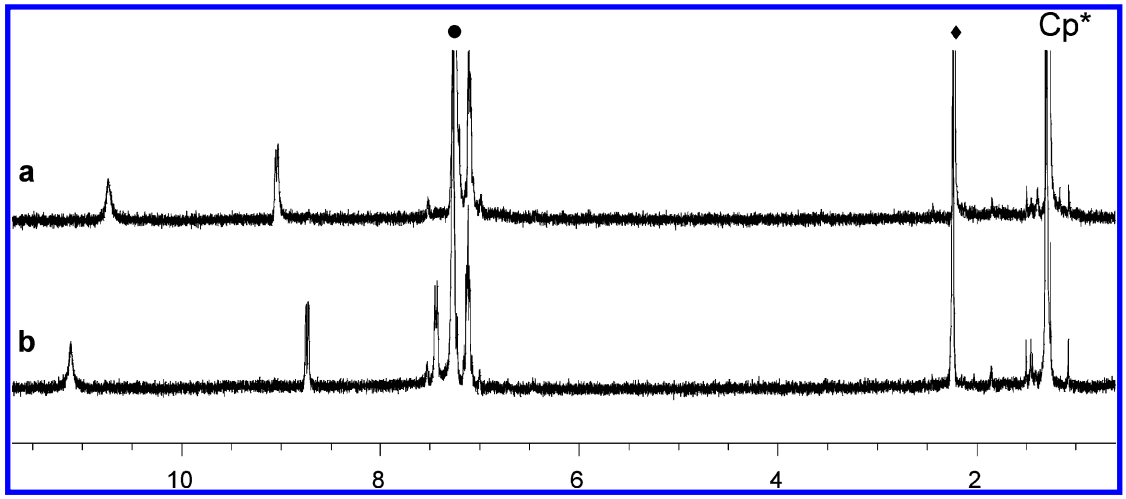
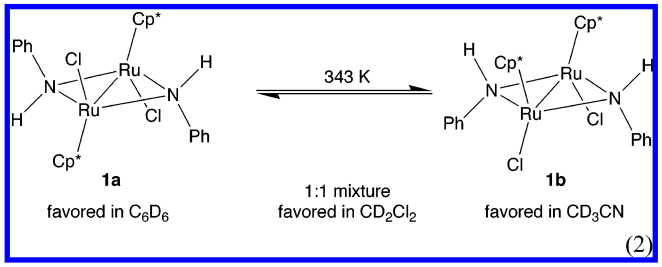


Figure 2. ^{1}H NMR spectra of one sample of [Cp*RuCl(μ-NHPh)]$_2$ in C_6D_6 (●) and with a C_6Me_6 internal standard (◆): (a) the initial C_{2v} isomer **1b**; (b) the C_i isomer **1a** after isomerization.

which has no arene to coordinate, reacts so slowly with (Cp*RuCl)$_4$ in C_6D_6 solution that coordination of the benzene solvent leads to precipitation of ([Cp*Ru(C_6D_6)]Cl) within 1 day. In CD_2Cl_2, $MeO_2CNHNHCO_2Me$ converts (Cp*RuCl)$_4$ to a new Cp*-containing ruthenium species over the course of 5 days. This species has not yet been characterized but does not appear to be [Cp*Ru(MeO_2CNH)Cl]$_2$, the bis(amido) product analogous to **1a**. The electron-rich, terminal 1,2-dimethylhydrazine reacts rapidly with (Cp*RuCl)$_4$ to give new Cp*-containing products that are not analogous to **1a** and **2** and are the subject of ongoing studies. Thus, it appears that the cleavage of the N−N bond to form the bis(amido) dimer is specific to 1,2-diarylhydrazines.

***C*$_{2v}$-[Cp*RuCl(μ-NHPh)]$_2$ (1b)**. Monitoring the reaction of (Cp*RuCl)$_4$ with excess PhNHNHPh by ^{1}H NMR spectroscopy in C_6D_6 shows that the ruthenium starting material is completely consumed within 3 min and at least three new Cp*-containing species can be distinguished: **1a**, **1b**, and one or two reaction intermediates. The reaction of Cp*RuCl(PCy_3) with excess PhNHNHPh shows the same set of ^{1}H NMR resonances, indicating formation of **1a**, **1b**, and the same intermediate(s) as observed with (Cp*RuCl)$_4$. After 70 min, the intermediate(s) convert to **1a** and **1b.** After 5 h, **1b** isomerizes to **1a**. Isomerization is observed in the other direction when isolated **1a** is heated in CD_3CN at 343 K for 21 h, quantitatively forming **1b** (by ^{1}H NMR integration, eq 2). Complex **1b** is stable in



CD_3CN at 298 K and can be observed by ^{1}H NMR spectroscopy in C_6D_6 at 298 K. Complex **1b** converts quantitatively back to **1a** upon heating in C_6D_6 for 18 h at 343 K. Heating either **1a** or **1b** in CD_2Cl_2 at 343 K for a day results in a 1:1 mixture of the two isomers. Isomerization of **1b** to **1a** in the initial reaction mixture (eq 1) appears to be faster than isomerization of isolated **1b** in C_6D_6, perhaps indicating that interconversion is catalyzed by a reaction intermediate in solution.

In CD_3CN, C_6D_6, or CD_2Cl_2, the ^{1}H NMR resonances for **1b** are distinct from those of **1a** but show the same pattern: a single Cp*, a single NH, and five inequivalent aryl resonances (Figure 2). As with **1a**, the $^{13}C\{^1H\}$ NMR spectrum of **1b** in CD_3CN shows six unique aryl resonances consistent with equivalent, nonrotating phenyl rings. The ESI-MS analysis of **1b** shows an *m*/*z* value (693) and a fragmentation pattern identical with that of **1a**. When **1b** is formed in CH_3CN, isolated, and then converted back to **1a** by heating in C_6D_6, ^{1}H NMR spectra do not show any free CH_3CN. This eliminates the possibility that **1b** could contain bound CH_3CN. The data indicate that complex **1b** is an isomer of **1a** with C_{2v} symmetry in which the Cp* ligands, the chloride ligands, and the anilido substituents are all oriented cis with respect to the Ru_2N_2 plane.

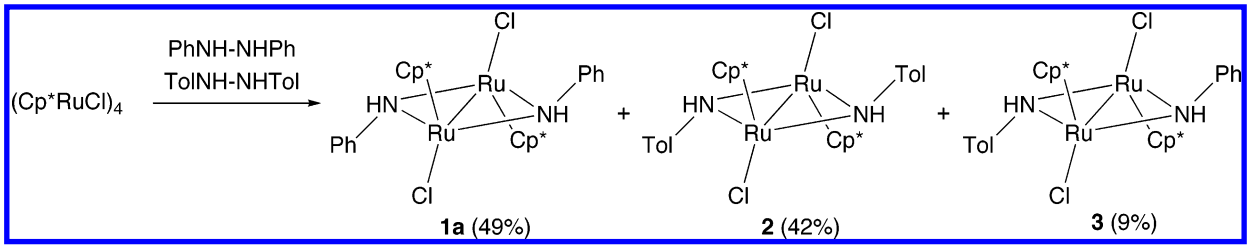
Disproportionation of 1,2-Disubstituted Hydrazines by [Cp*RuCl(μ-NHPh)]$_2$. Monitoring the reaction of (Cp*RuCl)$_4$ with excess PhNHNHPh (4 equiv) shows that the remaining 2 equiv of PhNHNHPh are slowly but completely converted into azobenzene (PhN=NPh) and aniline ($PhNH_2$). Similarly, the addition of 2 equiv of PhNHNHPh to isolated **1a** results in complete disproportionation (eq 3). The time required for

$$2ArNHNHAr \xrightarrow{\mathbf{1a}} ArN{=}NAr + 2ArNH_2 \qquad (3)$$

disproportionation varies from sample to sample, in some cases requiring 1 month at 50 °C. In larger scale preparations of **1a**, heating for 1 day at 50 °C is sufficient to ensure both the conversion of **1b** to **1a** and complete disproportionation of PhNHNHPh. This is done to avoid coprecipitation of the hydrazine with **1a** upon addition of pentane. The catalytic disproportionation of hydrazines has been seen in several other systems, all containing sulfur-ligated metal centers: [Cp*RuSR]$_2$ (R = ^{i}Pr, 2,6-$Me_2C_6H_3$),[20a] [MoH($SC_6H_2{}^iPr_3$)$_3$($PMePh_2$),[20b] and several $RuMo_3$ cubane clusters ([Cp*Mo]$_3$(μ_3-S)$_4$RuH_2(PR_3)]-[PF_6]; R = Ph, Cy).[20c]

To explore the disproportionation reaction, isolated **1a** was added to solutions of di-*p*-tolylhydrazine (3 equiv) in C_6D_6. This reaction results in a similar complete hydrazine disproportionation over 2 days to azotoluene (TolN=NTol) and toluidine ($TolNH_2$) in a 1:2 ratio. To our surprise, **1a** remains unchanged in this reaction, with no formation of either the toluamide dimer **2** or the mixed dimer [Cp*$_2$Ru$_2$Cl$_2$(μ-NHPh)(μ-NHTol)] (**3**; see below). $PhNH_2$, PhN=NTol, and PhN=NPh were also not observed by ^{1}H NMR. Thus, the hydrazine is not being

Scheme 1



incorporated into **1a** and the anilide ligands of **1a** do not appear to be involved in the disproportionation.

The lack of involvement of the anilide ligands raised the issue of the role of **1a** in the disproportionation reaction. A set of reactions at 50 °C with 4.3 mM PhNHNHPh and different concentrations of **1a** (0.31, 1.04, 2.5, 5.2 mM) were monitored by ^{1}H NMR spectroscopy. All the reactions showed first-order decay of the hydrazine with no apparent dependence on the concentration of **1a** ($k_{obs} = 0.011 \pm 0.002$ s^{-1}). When performed in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (2 equiv) or 9,10-dihydroanthracene (1 equiv), the disproportionation reaction proceeds without a reduction in rate. Similarly, the radical initiator AIBN (0.4 equiv) does not promote the disproportionation of PhNHNHPh in the absence or the presence of **1a** (0.2 equiv) at 75 °C over the course of 12 days. It appears that the disproportionation reaction does not involve an acid-promoted or a radical-initiated mechanism. Although **1a** is a necessary component in the disproportionation of PhNHNHPh, its role is not yet understood. It is possible that an impurity in **1a** is responsible for this reactivity, although isolated crystals of **1a** have also been shown to be catalytically active.

Crossover Experiment. To determine whether both anilide bridges of **1a** and **1b** arise from the same molecule of hydrazine, a crossover experiment was performed using diphenyl- and di-*p*-tolylhydrazines. $(Cp^*RuCl)_4$ was added to an equimolar mixture of the hydrazines, both in excess, in C_6D_6. Monitoring by ^{1}H NMR spectroscopy at room temperature over 1 day showed predominant formation of the symmetric complexes **1a** (49%) and **2** (42%), with smaller amounts of the asymmetric compound $[Cp^*_2Ru_2Cl_2(\mu\text{-NHPh})(\mu\text{-NHTol})]$ (**3**; 9%) (Scheme 1). Compounds **1a**, **2**, and **3** were identified by their distinct Cp* resonances (see below); the aryl resonances for **3** are the same as those for **1a** and **2**. ESI/MS confirms the formation of **1a** (*m*/*z* 693, $[Cp^*_2Ru_2(\mu\text{-NHPh})_2Cl]^+$) and **2** (*m*/*z* 721, $[Cp^*_2Ru_2(\mu\text{-NHTol})_2Cl]^+$) as the dominant species with small amounts of **3** (*m*/*z* 707, $[Cp^*_2Ru_2(\mu\text{-NHPh})(\mu\text{-NHTol})Cl]^+$). Both ^{1}H NMR spectroscopy and GC-MS analyses of the organic products show both azobenzene and azotoluene, but the mixed PhN═NTol was not observed.

To confirm the identity and stability of the unsymmetric dimer **3**, $(Cp^*RuCl)_4$ was reacted in C_6D_6 with a mixture of the three symmetrical and unsymmetrical hydrazines: PhNHNHPh, TolNHNHTol, and PhNHNHTol. The mixture of hydrazines was made by reduction of a mixture of nitrobenzene and nitrotoluene and shown by GC-MS and ^{1}H NMR to have a 1:0.60:1.17 ratio of the PhPh, TolTol, and PhTol derivatives. Reaction with $(Cp^*RuCl)_4$ gives **1a**, **2**, and **3** in a 1:3.3:2.3 ratio, as determined by integration of the Cp* resonances of the ^{1}H NMR spectrum and confirmed by ESI-MS analysis. This experiment not only serves as a control for the crossover experiment but also shows that the more electron rich tolylhydrazines are more reactive with $(Cp^*RuCl)_4$.

The origin of the small amount of the mixed dimer **3** has been explored, specifically whether it could be derived from an exchange process. Aniline and toluidine are present in the reaction mixture from the disproportionation of the hydrazines that is concurrent with formation of **1a** and **2**. Independent experiments show that **1a** is unreactive with toluidine (see below), and **2** is unreactive with aniline under these room-temperature conditions. Similarly, neither amine reacts with $(Cp^*RuCl)_4$. Even though neither the starting material nor the product reacts with arylamines, the reaction of $(Cp^*RuCl)_4$ with 5 equiv of PhNHNHPh in the presence of 18 equiv of toluidine in C_6D_6 at room temperature does show incorporation of tolyl substituents. Complexes **1a**, **2**, and **3** are observed after 25 h of reaction, in a 1:1:0.7 ratio (by ^{1}H NMR spectroscopy and confirmed by ESI-MS). This surprising result indicates that there is an intermediate that exchanges with $ArNH_2$. This exchange process is likely the origin of the small amount of **3** found in the crossover experiment.

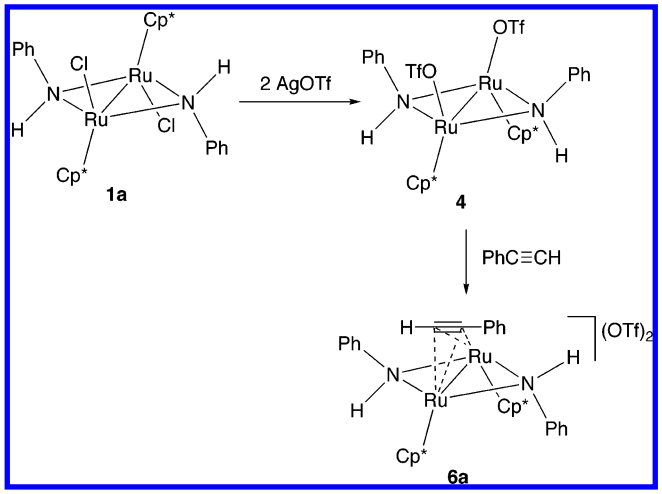
Reactivity of 1a. The anilide ligands in **1a** do not exchange with 8 equiv of toluidine ($TolNH_2$) in C_6D_6 or CD_3CN at room temperature or after 1 day at 80 °C by ^{1}H NMR. After days at 80 °C, however, a small amount of the mixed dimer **3** is seen (**1a**:**3** = 1:0.16). The analogous addition of aniline (10 equiv) to the bis(toluidide) complex **2** shows the presence of complexes **1a**, **2**, and **3**, in a 1:0.14:0.46 ratio after 5 days at 80 °C.

Complex **1a** is unreactive with alkenes and alkynes, such as norbornene, styrene, PhC≡CPh and PhC≡CH. Reactions were run in C_6D_6 or CD_3CN at room temperature with excess substrate and were monitored by ^{1}H NMR. The reactions in CD_3CN showed only slow isomerization of **1a** to **1b**. Heating a mixture of **1a** with styrene (1.5 equiv), norbornene (12 equiv), or phenylacetylene (20 equiv) in toluene-d_8 at 100 °C for 3 days gave no reaction. Complex **1a** is also unreactive with triethylphosphine (50 equiv) over 1 day at 50 °C in either C_6D_6 or in CD_2Cl_2 (by ^{1}H NMR) and with 5 equiv of MeOH in C_6D_6 at 100 °C for 3 days.

Chloride Abstraction from 1a and Reaction with Terminal Alkynes. Silver triflate reacts rapidly with **1a** in C_6D_6 at room temperature to remove the chloride ligands and form the bis(triflate) complex $[Cp^*Ru(\mu\text{-NHPh})(OTf)]_2$ (**4**). The ^{1}H NMR spectrum of **4** has a single Cp* resonance, a single N*H* resonance, and five distinct aryl resonances, two of which are overlapping. The $^{13}C\{^1H\}$ NMR spectrum shows six different aryl carbons, indicating that the aryl rings are not rotating. The ^{19}F NMR spectrum shows a single peak at −78.1 ppm in C_6D_6, which indicates equivalent triflate anions covalently bonded to the ruthenium.[40] Addition of degassed water to a solution of **4** in C_6D_6 results in a shift of all resonances in the ^{1}H NMR spectrum, and after a few hours, complex **5** crystallized out of solution. A single-crystal X-ray diffraction study was problematic, because of low crystal quality and disorder, but suggested that **5** is the monoaquo complex C_{2v}-$[Cp^*Ru(\mu\text{-NHPh})_2RuCp^*(OH_2)](OTf)_2$ (on the basis of this, **4** is assumed to also have

(40) Jones, V. A.; Sriprang, S.; Thronton-Pett, M.; Kee, T. P. *J. Organomet. Chem.* **1998**, *567*, 199−218.

Scheme 2



the cis structure). ^{1}H NMR spectra of the mother liquor show a single product with a single set of Cp* and anilido resonances, indicating either that the material in solution is the diaquo complex or that the unsymmetrical monoaquo seen in the crystal is fluxional on the NMR time scale. The ^{19}F NMR resonance for **5** indicates ionic triflate (δ −79.2 in C_6D_6; δ −79.7 in CD_2Cl_2).

Addition of an excess of phenylacetylene (PhC≡CH) to **4** (generated in situ from **1a** and 2 AgOTf) in C_6D_6 leads to precipitation of a dark green solid, assigned as the acetylene complex [{Cp*Ru(μ-NHPh)}$_2$(μ-η^2:η^2-PhC≡CH)](OTf)$_2$ (**6a**) (Scheme 2). The more easily isolated PF_6^- salt [{Cp*Ru(μ-NHPh)}$_2$(μ-η^2:η^2-PhC≡CH)](PF$_6$)$_2$ (**6b**) was prepared similarly from **1a**, $AgPF_6$, and PhC≡CH in 51% yield. ESI-MS analyses of both **6a** and **6b** show ions with one acetylene added to the dimeric ruthenium unit, for instance [Cp*$_2$Ru$_2$(NHPh)$_2$(PhC≡CH)OTf]$^+$ from **6a** (*m*/*z* 909). Isolating this *m*/*z* 909 ion in an ion trap mass spectrometer and fragmenting it with helium atoms proceeds with loss of HOTf ([Cp*$_2$Ru$_2$(NPh)(NHPh)(PhC≡CH)]$^+$; *m*/*z* 759) and PhC≡CH ([Cp*$_2$Ru$_2$(NPh)(NHPh)]$^+$; *m*/*z* 657).

The ^{1}H NMR spectra of **6a** and **6b** in CD_2Cl_2 are only slightly different, indicating the same basic structure in solution (the values given are for **6a** unless otherwise indicated). The ^{1}H NMR spectra show a single peak for two equivalent Cp* ligands (30 H), which are also equivalent in the ^{13}C{^{1}H} NMR. However, all of the other groups in the cation are inequivalent, as there are two distinct N*H* protons (4.4 and 6.8 ppm for **6a**) and eight aryl resonances in the ratio 1:1:3:3:2:1:2:2, as well as a characteristic downfield singlet (δ(CD_2Cl_2) 9.3). A 2D COSY analysis indicates three distinct aryl rings, two of which do not rotate on the NMR time scale, while the third does. The more downfield of the nonrotating rings was assigned as the phenyl of the acetylene, through the in situ synthesis of the *p*-TolC≡CH and *p*-^{t}BuC$_6$H$_4$C≡CH analogues. The assignment of the N*H* resonances was confirmed by the synthesis of **6-(N*D*)$_2$** from [Cp*RuCl(μ-NDPh)]$_2$ (**1a-*d*$_2$**), AgOTf, and PhC≡CH. The downfield singlet was similarly shown to originate from the acetylene by the addition of PhC≡CD to **1a** and AgOTf to form [{Cp*Ru(μ-NHPh)}$_2$(μ-η^2:η^2-PhC≡CD)](OTf)$_2$ (**6-PhCC*D***). Derivatives of **6** with different counterions (from different silver salts as reactants) show that this resonance shifts further downfield with more hydrogen bonding counterions: δ 9.29 (OTf^-), 9.02 (ClO_4^-), 8.83 (BF_4^-), and 8.45 (PF_6^-) in CD_2Cl_2.[41] This shift is consistent with hydrogen bonding between the triflate anion and the acetylenic hydrogen.[42,43] The ^{19}F NMR of **6a** shows one triflate resonance at −79.5 ppm, consistent with noncoordinating counterions.[40]

The ^{1}H NMR spectra indicate dimeric molecules with C_s symmetry, in which the mirror plane relates the two Cp*Ru fragments and contains all of the other atoms. Three kinds of structures are consistent with this data: a vinylidene complex, a product from insertion of the alkyne into the Ru−N bond, or an alkyne complex. The nature of the acetylene unit in **6a** was probed by preparing it with Ph^{13}C≡^{13}CH. The ^{13}C{^{1}H} NMR spectrum of **6a-$^{13}C_2$** shows two acetylenic carbons (95.80 and 92.94 ppm) with a coupling constant of $^1J_{CC}$ = 52 Hz. The similarity of the ^{13}C chemical shifts, only 3 ppm apart, argues against a vinylidene complex or a structure in which PhC≡CH has coupled with an anilide ligand. A vinylidene complex can also be eliminated, due to the absence of the characteristic carbon resonance between 300 and 400 ppm.[44]

2D HMQC and HMBC experiments are consistent with an alkyne-coordinated species (see the Supporting Information). The 2D HMQC spectrum of **6a-$^{13}C_2$** confirms that the downfield proton (9.3 ppm) is coupled to both acetylene carbons ($^1J_{HC}$ = 235 Hz, $^2J_{HC}$ = 16 Hz). In addition, the HMBC experiment shows coupling between the ortho protons of PhC≡CH and C$_\beta$, showing that the acetylene proton and the acetylene phenyl ring remain on adjacent carbons, again eliminating a vinylidene species as a possible structure. Coupling of a PhC≡CH unit with an anilide is unlikely, because the NH protons do not show any coupling to ^{13}C. Thus, the phenylacetylene is intact within **6a**, and the C−C multiple bond has alkene character. In addition, ESI/MS of **6a** and **6b** show fragmentation that involves loss of the acetylene without loss of the anilide ligands, arguing against the presence of a C−N bond.

All of the data support the assignment of **6** as an alkyne complex. The coupling constants ($^1J_{CC}$ = 52 Hz, $^1J_{HC}$ = 235 Hz, $^2J_{HC}$ = 16 Hz) suggest a μ-η^2:η^2-bound alkyne in **6a** because they are close to those observed for the μ-η^2:η^2 complex [(CO)$_3$Co(μ-η^2:η^2-HC≡CH)Co(CO)$_3$], which has $^1J_{CC}$ = 55.9 Hz, $^1J_{HC}$ = 209.8 Hz, and $^2J_{HC}$ = 15.7 Hz.[45] The orientations of the substituents were determined by phase-sensitive NOESY experiments (see the Supporting Information). These show an NOE between the upfield N*H* resonance (4.4 ppm) and the ortho protons of the rotating phenyl ring, and an NOE between the downfield N*H* resonance (6.8 ppm) and both ortho protons of the acetylene phenyl ring (Figure 3). This indicates that the rotating phenyl ring and the acetylene phenyl ring lie on opposite sides of the Ru−Ru bond. The data taken together show that **6a** and **6b** are the μ-η^2:η^2-alkyne complexes shown in Scheme 2.

Diphenylacetylene does not react with **4** under the same conditions, perhaps due to unfavorable steric interactions. Steric

(41) Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1025−1027.
(42) DeLaat, A. M.; Ault, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 4232−4236. Steiner, T. *J. Mol. Struct.* **1998**, *443*, 149−153. Scheiner, S.; Grabowski, S. J.; Kar, T. *J. Phys. Chem. A* **2001**, *105*, 10607−10612. Domagala, M.; Grabowski, S. J. *J. Phys. Chem. A* **2005**, *109*, 5683−5688. Alkorta, I.; Zborowski, K.; Elguero, J. *J. Phys. Chem. A* **2006**, *110*, 10279−10286.
(43) Solà, J.; Riera, A.; Verdaguer, X.; Maestro, M. A. *Organometallics* **2006**, *25*, 5795−5799.
(44) Stüer, W.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **2002**, 203−207. Pavlik, S.; Mereiter, K.; Puchberger, M.; Kirchner, K. *J. Organomet. Chem.* **2005**, *690*, 5497−5507. Sun, Y.; Chan, H.-S.; Dixneuf, P.; Xie, Z. *Organometallics* **2006**, *25*, 2719−2721. Kopf, H.; Pietraszuk, C.; Hübner, E.; Burzlaff, N. *Organometallics* **2006**, *25*, 2533−2546. Beach, N.; Walker, J.; Jenkins, H.; Spivak, G. *J. Organomet. Chem.* **2006**, *691*, 4147−4152.
(45) Aime, S.; Osella, D.; Giamello, E.; Granozzi, G. *J. Organomet. Chem.* **1984**, *262*, C1−4.

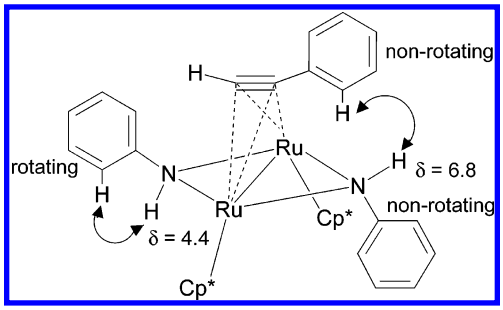


Figure 3. Cationic fragment of **6**, $[\{Cp^*Ru(\mu\text{-}NHPh)\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}PhC{\equiv}CH)]^{2+}$, with key NOE interactions indicated by curved arrows.

crowding in **6** is suggested by hindered rotation of two of the phenyl rings.

Discussion

Anilide Dimers. $[Cp^*RuCl(\mu\text{-}NHPh)]_2$ (**1a** and **1b**) are additions to the family of known Cp*Ru dimers. They are Ru^{III} analogues of the Ru^{II}−anilido dimer $[Cp^*Ru^{II}(\mu\text{-}NHPh)]_2$ and the more studied methoxide analogue $[Cp^*Ru^{II}(\mu\text{-}OMe)]_2$ that have been reported by Tilley and co-workers.[33,46] Analogous sulfide and selenide dimers $[Cp^*RuCl(\mu\text{-}ER)]_2$ have also been described.[34−36] With these good bridging ligands, NHR and SR, the dimers are diamagnetic with short Ru^{III}−Ru^{III} distances (2.71−2.94 Å), implying metal−metal bonds and 18-electron configurations. The analogous chloride dimer $[Cp^*Ru^{III}Cl(\mu\text{-}Cl)]_2$ is paramagnetic and crystallizes with two quite different molecules in the unit cell, one with a Ru−Ru bond and one without, $d(Ru^{III}{-}Ru^{III})$ = 2.930(1), 3.752(1) Å,[47] suggesting a metal−metal interaction weaker than that found in **1a**.

$[Cp^*Ru^{III}Cl(\mu\text{-}X)]_2$ dimers have anti (C_i) or syn (C_{2v}) structures, depending on the distribution of the Cp* and Cl groups about the central Ru_2X_2 unit. $[Cp^*Ru^{III}Cl(\mu\text{-}Cl)]_2$, which has the anti structure,[47] is reported to react with 1-phenylethanethiol to yield a 1:1 mixture of the syn and anti isomers of $[Cp^*RuCl(\mu\text{-}SCHPhMe)]_2$, which do not interconvert.[48] Formation of these thiolate-bridged dimers by oxidative addition of disulfides to $(Cp^*RuCl)_4$, however, yields only *syn*-$[Cp^*RuCl(\mu\text{-}SR)]_2$.[34−36] The anilide dimers in this work also exist in both C_i (**1a**) and C_{2v} (**1b**) forms, and slow isomerization between the forms is observed. The isomers are close enough in energy that the polarity of the solvent shifts the equilibrium position, with the C_i isomer **1a** that has no dipole moment favored in nonpolar solvents such as benzene and the C_{2v} isomer **1b** favored in the more polar acetonitrile solvent. In dichloromethane, a solvent of intermediate polarity, an equimolar mixture of the two isomers is observed.

Formation of 1. The addition of PhNHNHPh to $(Cp^*Ru^{II}Cl)_4$ to give **1** is a formal oxidative addition of the hydrazine N−N bond. The reaction appears to be faster with the more electron rich TolNHNHTol, while more electron-deficient hydrazines such as $PhNHNHCOCF_3$ and $MeO_2CNHNHCO_2Me$ are unreactive. This pattern is opposite to what would be expected from consideration of the hydrazine as an oxidant. It may be that initial hydrazine coordination is playing an important role.

Formally, the anilido dimers **1** could be formed by direct addition of PhNHNHPh to a diruthenium unit of the tetrameric $(Cp^*RuCl)_4$. The trinuclear Ru^{II} hydride $(Cp^*Ru)_3(\mu_2\text{-}H)(\mu_3\text{-}H)_2$ has similarly been reported to add the monosubstituted hydrazine $RNHNH_2$ (R = Me, Ph) to give the bis(imido) complex $(Cp^*Ru)_3(\mu_3\text{-}NR)(\mu_3\text{-}NH)(\mu_2\text{-}H)$.[49] However, direct formation of **1** from $(Cp^*RuCl)_4$ plus PhNHNHPh is ruled out by the toluidine exchange experiments. $TolNH_2$ is incorporated into the product of PhNHNHPh + $(Cp^*RuCl)_4$, forming $[Cp^*_2Ru_2Cl_2(\mu\text{-}NHPh)_x(\mu\text{-}NHTol)_{2-x}]$ (**2**, **3**), but it does not exchange with either $(Cp^*RuCl)_4$ or **1a** under these conditions. This requires that there be an intermediate along the pathway with sufficient lifetime to undergo anilide exchange. In addition, **1** is also formed from PhNHNHPh and monomeric $Cp^*RuCl(PCy_3)$, and the $(Cp^*RuCl)_4$, tetramer is known to be readily cleaved into monomers.[50,59] Thus, the reactions could also proceed by oxidative addition of PhNHNHPh to a single metal center to give a transient Ru(IV) bis(anilide) complex, which could exchange with $TolNH_2$ or be trapped by a source of "Cp*RuCl". Hydrazine oxidative addition to form a monomeric bis(amido) metal complex has not yet, to our knowledge, been reported. $TolNH_2$ exchange could also occur in a dimeric intermediate, similar to the reaction of $[Cp^*Ru^{III}Cl(\mu\text{-}Cl)]_2$ with a thiol to give $[Cp^*RuCl(\mu_2\text{-}SR)]_2$.[36] However, the analogous addition of aniline to $[Cp^*Ru^{III}Cl(\mu\text{-}Cl)]_2$ does not form **1a** or **1b**. The crossover experiment showing that both anilide ligands in **1** arise from the same hydrazine is consistent with either mononuclear or binuclear oxidative addition mechanisms. Similarly, either path could rationalize the formation of a nonthermodynamic 1:1 ratio of C_i (**1a**) and C_{2v} (**1b**) isomers from PhNHNHPh plus $(Cp^*RuCl)_4$, which may simply reflect the twisted hydrazine geometry.

Reactivity of 1a. Complex **1a** is not very reactive, being inert to alkenes and alkynes even upon heating. This is in contrast to the analogous thiolate-bridged complexes which oxidize alkenes to dithioethers.[30] Substitution of the bridging NHPh ligands by NHTol occurs only upon heating to 70 °C for 1 day. No reaction is observed with methanol, even though a methoxy-bridged dimer such as "$[Cp^*Ru^{III}Cl(\mu\text{-}OMe)]_2$" would seem to be a reasonable product.[46] Triethylphosphine does not react with **1a** at 50 °C, either to reduce it or to cleave the dimer into monomeric complexes (which would be somewhat analogous to $Cp^*Ru^{II}Cl(py)(PCy_3)$).[51] In general, the Ru_2N_2 core appears to be quite stable both thermodynamically and kinetically. Opening of the Ru_2N_2 ring is most likely involved in the isomerization between **1a** and **1b** and in the slow exchange with $TolNH_2$, but the opened form is not easily trapped by other reagents.

The propensity of the amido ligand to form strong bridges presents a challenge in the pursuit of a reactive bis(amido) monomer that will accomplish diamination. Oxidative addition of a hydrazine requires an intermediate with an open coordination site, and such an unsaturated species could add to the bis(amido) desired product to form an amido-bridged compound. Sterically bulky ligands could be used to prevent dimerization but are also likely to inhibit reactivity with substrates. Electron-deficient amide ligands could reduce the tendency to bridge and

(46) Loren, S. D.; Campion, B. L.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712−4718.
(47) Kölle, U.; Kossakowski, J.; Klaff, N.; Wesemann, L.; Englert, U.; Heberich, G. E. *Angew. Chem., Int. Ed.* **1991**, *30*, 690−691.
(48) Nishibayashi, Y.; Onodera, G.; Inada, Y.; Hidai. M.; Uemura, S. *Organometallics* **2003**, *22*, 873−876.
(49) Nakajima, Y.; Suzuki, H. *Organometallics* **2003**, *22*, 959−969.
(50) Luo, L.; Nolan, S. P. *Organometallics* **1994**, *13*, 4781−4786. Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322−4326. Cokoja, M.; Gemel, C.; Seinke, T.; Schröder, F.; Fischer, R. A. *Dalton Trans.* **2005**, 44−54.
(51) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278−280.

enhance reactivity with electrophiles such as alkenes, and these will be a focus of future studies.

Chloride Abstraction and Subsequent Reaction with PhC≡CH. Removal of the chloride ligands from **1a** with silver salts generates reactive dinuclear complexes. Use of AgOTf gives a triflate-coordinated dimer, according to ^{19}F NMR spectra, but the extent of anion coordination is not known for the PF_6^-, BF_4^-, and ClO_4^- derivatives. Addition of PhC≡CH gives a C_s-symmetric dimer in which the acetylene is perpendicular to the Ru−Ru bond. This binding mode is uncommon for ruthenium dimers, which tend to incorporate a terminal alkyne either as a vinylidene ligand[52] or through insertion into the Ru−N bond, such as in the [Cp*Ru^{II}(μ_2-NHPh)]$_2$ system.[29,53] The thiolate dimers [Cp*RuCl(μ-SR)]$_2$ react with RC≡CH and 1 equiv of Ag^+ to give vinylidene[54] and allenylidene[35,55] complexes. Complex **1a**, however, remains unreactive toward PhC≡CH in the presence of 1 equiv of AgOTf. A μ-η^2:η^2-bound acetylene is found in the Ru^I−carbonyl dimer [Cp$_2$Ru$_2$(CO)$_2$(μ-η^2:η^2-HC≡CH)],[56] and this binding mode is common for other transition metals.[57]

Conclusion

The Ru^{III}−bis(amido) species [Cp*RuCl(μ-NHPh)]$_2$ (**1**) is easily accessed from the oxidative addition of 1,2-diphenylhydrazine to (Cp*RuCl)$_4$. This complex shows solvent-dependent interconversion between the C_i (**1a**) and C_{2v} (**1b**) isomers and promotes the disproportionation of PhNHNHPh into azobenzene and aniline. Formation of these dimers involves oxidative addition of the hydrazine N−N bond, which is a rare process. Complex **1a** has limited reactivity, in part because of the stability of the Ru$_2$(μ-NHPh)$_2$ core. The strength of the bridging anilide ligands inhibits the reactivity of **1a** with unsaturated hydrocarbons. Abstraction of the chloride ligands gives a more reactive species that adds phenylacetylene to give a complex with a μ-η^2:η^2-PhC≡CH ligand, an uncommon binding mode for a diruthenium compound. The disproportionation of hydrazine and the propensity of the amido ligands to bridge may be some of the challenges associated with the use of hydrazines in amination reactions.

Experimental Section

General Considerations. All manipulations were performed under N_2 using standard high-vacuum-line or inert-atmosphere glovebox techniques, unless otherwise noted. Protio (Fisher Scientific) and deuterio (Cambridge Isotope) solvents were dried before use (pentane, THF, THF-d_8, C_6H_6 using sodium/benzophenone; C_6D_6, CD_2Cl_2, CH_2Cl_2 using CaH_2; CD_3CN using CaH_2/P_2O_5/CaH_2). CH_3OD was used as received. [Cp*RuCl$_2$]$_2$,[58] (Cp*RuCl)$_4$,[59] 1,2-di-*p*-tolylhydrazine,[60] and phenyacetylene-*d*[61] were prepared according to literature methods. Pentamethylcyclopentadiene (Strem) and $RuCl_3 \cdot 3H_2O$ (Pressure Chemical) were used as received. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker Avance 300 (^{1}H) and 500 MHz (^{1}H, ^{13}C, and ^{19}F) spectrometers and referenced to the residual solvent signal (^{1}H and ^{13}C) or an external CF_3COOH standard (−78.5 ppm);[62] all coupling constants are reported in Hz. Assignments of the ^{13}C NMR resonances were made using 2D HMQC and HMBC experiments. Mass spectra were recorded from CH_3CN solutions on a Bruker Esquire ion trap electrospray ionization mass spectrometer. GC-MS analyses used a Hewlett-Packard 5971A GC-MS with an Agilent DB-5MS column (25 m × 200 μm i.d. × 0.33 μm phase thickness): 70 °C, 20 °C/min, 210 °C. Elemental analyses were performed by Atlantic Microlab, Inc.

***C$_i$*-[Cp*RuCl(μ-NHPh)]$_2$ (1a).** A mixture of 1,2-diphenylhydrazine (700 mg, 3.8 mmol) and (Cp*RuCl)$_4$ (1.196 g, 1.1 mmol) was stirred in 50 mL of C_6H_6 for 3 days at room temperature and then heated to 50 °C for ∼20 h. The volume was then reduced to ∼25 mL, and pentane (∼20 mL) was added to precipitate out a dark brown solid. The mixture was filtered and the solid washed with pentane (2 × 10 mL) to give 1.23 g of **1a** (1.69 mmol, 77%). ^{1}H NMR (C_6D_6, 500 MHz): δ 11.01 (s, 2H, N*H*), 8.62 (d, J = 7.5, 2H, *o*), 7.33 (d, J = 6.5, 2H, *o*), 7.13 (2H, *m*), 7.01 (m, 4H, *m*, *p*), 1.19 (s, 30H, Cp*). ^{13}C{^{1}H} NMR (C_6D_6): δ 130.62 (*i*), 130.27 (*m*), 128 (*p*), 126.22 (*o*), 123.48 (*m*), 122.62 (*o*), 94.11 ($C_5(CH_3)_5$), 9.00 ($C_5(CH_3)_5$). ESI/MS (CH_3CN): *m*/*z* 693 ([Cp*$_2$Ru$_2$(NHPh)$_2$-Cl]$^+$). Anal. Calcd for $C_{32}H_{42}Cl_2N_2Ru_2$: C, 52.81; H, 5.82; N, 3.85. Found: C, 52.59; H, 5.89; N, 3.96.

***C$_i$*-[Cp*RuCl(μ-NDPh)]$_2$ (1a-*d*$_2$).** A J. Young tube was charged with a solution of PhNDNDPh (96% ^{2}H, prepared from exchange with MeOD; 13 mg, 7 mmol) in C_6D_6. (Cp*RuCl)$_4$ (2 mg, 1.8 mmol) was added, and after 3 days at room temperature, ^{2}H and ^{1}H NMR show 94% ^{2}H.

***C$_{2v}$*-[Cp*RuCl(μ-NHPh)]$_2$ (1b).** A J. Young NMR tube was charged with **1a** (2 mg, 2.7 mmol) and CD_3CN and the mixture heated to 70 °C for 21 h. ^{1}H NMR (CD_3CN, 500 MHz): δ 9.85 (s, 2H, NH), 7.77 (d, J = 7, 2H, *o*), 7.37 (m, 4H, *m*), 7.25 (t, 2H, *p*), 6.54 (d, J = 6.5, 2H, *o*), 1.16 (s, 30H, Cp*). ^{13}C{^{1}H} NMR (C_6D_6): δ 158.36 (*i*), 130.97 (*m*), 128.59 (*m*), 127.38 (*o*), 126.72 (*p*), 123.03 (*o*), 94.58 ($C_5(CH_3)_5$), 8.40 ($C_5(CH_3)_5$) ppm. ESI/MS (CH_3CN): *m*/*z* 693 ([Cp*$_2$Ru$_2$(NHPh)$_2$Cl]$^+$). Similar heating of **1a** in CD_2Cl_2 showed an equal mixture of **1a** and **1b**. ^{1}H NMR of **1b** (CD_2Cl_2, 500 MHz): δ 9.66 (s, 1H, NH), 7.74 (d, 1H, *o*), 7.38 (m, 2H), 7.27 (m, 1H), 6.45 (d, 1H, *o*), 1.191 (s, 15H, Cp*).

[Cp*RuCl(μ-NH-*p*-tol)]$_2$ (2). A C_6D_6 solution of di-*p*-tolylhydrazine (1 mg, 5 μmol) and (Cp*RuCl)$_4$ (2 mg, 1.8 μmol) was allowed to react for 2 days in a J. Young NMR tube. The solvent was removed under vacuum, and the remaining brown solids were washed with pentane and dried to give a dark brown solid. ^{1}H NMR (C_6D_6, 500 MHz): δ 11.09 (s, 1H, NH), 8.57 (d, J = 8.5, 1H, *o*), 7.33 (d, J = 8, 1H, *o*), 6.98 (d, J = 8.5, 1H, *m*), 6.89 (d, J = 7.5, 1H, *o*), 2.04 (s, 3H, *p*-methyl), 1.25 (s, 15H, Cp*). ESI/MS (CH_3CN): *m*/*z* 721 ([Cp*$_2$Ru$_2$(NHTol)$_2$Cl]$^+$).

Reaction of (Cp*RuCl)$_4$ with Diphenylhydrazine and Di-*p*-tolylhydrazine. (Cp*RuCl)$_4$ (2.5 mg, 2.3 μmol) was added to a

(52) (a) Matsuzaka, H.; Takagi, Y.; Hidai, M. *Organometallics* **1994**, *13*, 13−15. (b) Takagi, Y.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *Organometallics* **1997**, *16*, 4445−4452. (c) Puerta, M. C.; Valerga, P. *Coord. Chem. Rev.* **1999**, *193*−*5*, 977−1025. (d) Dragutan, V.; Dragutan, I. *Platinum Met. Rev.* **2004**, *48*, 148−153.

(53) Insertion into Ru−N bonds: (a) Standfest-Hauser, C. M.; Mereiter, K.; Schmid, R.; Kirchner, K. *Dalton Trans.* **2003**, 2329−2334. (b) Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. *J. Organomet. Chem.* **2006**, *291*, 2424−2439. (c) Sun, Y.; Chan, H.-S.; Xie, Z. *Organometallics* **2006**, *25*, 3447−3453.

(54) Takagi, Y.; Matsuzaka, H.; Ishi, Y.; Hidai, M. *Organometallics* **1997**, *16*, 4445−4452.

(55) Nishibayashi, Y.; Waskiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019−11020.

(56) Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1989**, 1799−1805. Cooke, M.; Davies, D. L.; Guerchais, J. E.; Knox, S. A. R.; Mead, K. A.; Roué, J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 862−864.

(57) (a) George, B. S. A.; McDonald, R.; Cowie, M. *Can. J. Chem.* **1996**, *74*, 2289−2303. (b) Zhang, Y.-H.; Lao, W.-J.; Liu, Y.-Q.; Yin, Y.-Q.; Wu, J.-J.; Huanh, Z.-H. *Polyhedron* **2001**, *20*, 1108−1113. (c) Chen, X.-N.; Zhang, J.; Yin, Y.-Q.; Huang, X.-Y. *Organometallics* **1999**, *18*, 3164−3169.

(58) Koelle, U.; Kossakowski, J. *Inorg. Synth.* **1992**, *29*, 225−227.

(59) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698−1719.

(60) Khurana, J. M.; Singh, S. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1893−1895.

(61) Gronheid, R.; Zuilhof, H.; Hellings, M. G.; Cornelisse, J. Lodder, G. *J. Org. Chem.* **2003**, *68*, 3205−3215.

(62) Walstrom, A.; Pink, M.; Tsvetkov, N. P.; Fan, H.; Ingleson, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2005**, *127*, 16780−16781.

C_6D_6 solution of PhNHNHPh (1.5 mg, 8 μmol) and di-*p*-tolylhydrazine (1.5 mg, 7 μmol) in a J. Young ^{1}H NMR tube. The reaction was monitored by ^{1}H NMR spectroscopy. After ~1 day the reaction mixture was dried and washed with pentane. The washings were analyzed by GC-MS and separated with retention times of 18.2 min (*m*/*z* 182; PhN═NPh) and 21.9 min (*m*/*z* 210; TolN═NTol). No PhN═NTol was observed.

Mixture of TolNHNHTol, *p*-TolNHNHPh, and PhNHNHPh. This mixture was synthesized by following a modification of a literature procedure.[60] A solution of nitrobenzene (0.77 g, 6.3 mmol), nitrotoluene (2.765 g, 19.5 mmol), and aluminum powder (1.4 g, 52 mmol) in methanol (14 mL) was treated with KOH (8.3 g, 148 mmol). The mixture was stirred for 20 min, and then aliquots of Al, KOH, and MeOH were added at 10 min intervals until no azo compound was seen by TLC. The reaction was quenched, and the product was extracted according to literature procedures and recrystallized from hexanes. The ^{1}H NMR spectrum of the hydrazine mixture showed a 1:0.7 ratio of Ph and Tol groups, but the unsymmetrical hydrazine could not be separately quantified because its resonances are coincident with those of the symmetric hydrazines. GC-MS analysis of the mixture (as an ether solution) shows separate peaks for the corresponding azo compounds, allowing for the indirect detection of the mixed hydrazine. The ratio from GC-MS, 1.68:1:1.97 PhPh, TolTol, and PhTol (azo derivative retention times 18.7, 21.7, and 20.2 min, respectively), is in agreement with the Ph to Tol ratio obtained from integration of the ^{1}H NMR spectrum.

[Cp*Ru(μ-NHPh)(OTf)]$_2$ (4) AgOTf (2.4 mg, 9 μmol) and **1a** (3.2 mg, 4.5 μmol) were dissolved in C_6D_6 in a J. Young tube. The solution turned dark brown with the precipitation of AgCl. ^{1}H NMR (C_6D_6, 500 MHz): δ 12.35 (s, 1H, N*H*), 8.01 (d, 1H, *o*), 7.07 (m, 1H, *m*), 6.93 (m, 2H, *o*, *p*), 6.43 (d, 1H, *m*), 0.976 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (C_6D_6): δ 156.12 (*i*), 131.80, 130.16, 128.60, 126.23, 125.88, 121.864, 96.12 ($C_5(CH_3)_5$), 8.48 ($C_5(CH_3)_5$). ^{19}F NMR (C_6D_6): δ −78.1.

[Cp*Ru(μ-NHPh)$_2$RuCp*(H$_2$O)](OTf)$_2$ (5). AgOTf (50 mg, 0.349 mmol) and **1a** (40 mg, 0.110 mmol) were combined in C_6H_6 (10 mL) and stirred for 30 min before filtration of the AgCl solids. Degassed, wet C_6H_6 (2 mL) was added to the resulting solution, and the mixture was stirred for 20 h. The resulting dark solids were filtered, washed with C_6H_6 (1 mL) and pentane (2 × 1 mL), and dried to give 28 mg (0.058 mmol, 53%). ^{1}H NMR (C_6D_6, 200 MHz): δ 11.77 (s, 1H, NH), 8.56 (d, J = 7, 1H, *o*), 7.06 (t, J = 7, 1H), 6.82 (t, J = 8, 1H), 6.66 (t, J = 8, 1H), 5.91 (d, J = 8, 1H, *o*), 0.83 (s, 15H, Cp*). ^{19}F NMR (C_6D_6): δ −79.2. ^{19}F NMR (CD_2Cl_2): δ −79.1. The product was recrystalized from CH_2Cl_2/pentane at −78 °C and analyzed. Anal. Found: C, 39.67; H, 4.27; N, 2.74. These values are low for **5** (calcd for $C_{68}H_{86}F_{12}N_4O_{13}Ru_4S_4AgCl$: C, 41.97; H, 4.56; N, 2.88) but are consistent with a 1:1 mixture of **5** and **4·AgCl** (calcd for $C_{34}H_{43}AgClF_{12}N_4O_{13}Ru_4S_4$: C, 39.43; H, 4.18; N, 2.70). The presence of some residual AgCl in recrystallized **5** is indicated by solutions of this material becoming cloudy with a gray-white solid overy time. Attempts to remove the residual AgCl by filtration through Celite have been unsuccessful.

[Cp*$_2$Ru$_2$(μ-NHPh)$_2$(μ-η^2:η^2-PhC≡CH)](OTf)$_2$ (6a). An excess (3.6 mg, 14.0 μmol) of AgOTF was added to a solution of **1a** (2.3 mg, 3.2 μmol) and PhC≡CH (19 μmol) in C_6D_6 in a J. Young NMR tube. The solution was decanted after the formation of dark precipitates, which were then dried under vacuum. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.29 (s, 1H, PhC≡C*H*), 8.20 (d, J = 6, 1H, *o*-*Ph*C≡CH), 8.02 (d, J = 8, 1H, *o*-*Ph*C≡CH), 7.78 (t, J = 6, 1H, *m*-*Ph*C≡CH), 7.63 (m, 3H), 7.47 (m, 3H), 7.32 (m, 2H), 7.26 (t, J = 5, 1H, *m*-*Ph*NH), 7.03 (d, J = 5, 2H, *o*-*Ph*NH), 6.77 (s, 1H, N*H*), 6.71 (d, J = 4, 1H, *o*-*Ph*NH), 4.40 (s, 1H, N*H*), 1.53 (s, 15H, Cp*). ^{13}C NMR (CD_2Cl_2): δ 108.2 (Cp*), 95.8 (J_{CC} = 52.5, Ph^{13}*C*≡^{13}CH), 92.9 (J_{CC} = 52.5, J_{HC} = 235, Ph^{13}C≡^{13}*C*H), 9.9 (Cp*). ^{19}F NMR (CD_2Cl_2): δ −79.5 (C*F*$_3$SO$_3$). ESI/MS (CH_3CN): *m*/*z* 909 ([Cp*$_2$Ru$_2$(NHPh)$_2$(PhCCH)OTf]$^+$).

[Cp*$_2$Ru$_2$(μ-NHPh)$_2$(μ-η^2:η^2-PhC≡CH)](PF$_6$)$_2$ (6b). To a solution of **1a** (74.6 mg, 102.6 μmol) and $AgPF_6$ (66 mg, 260 μmol) in C_6H_6 (15 mL) was added an excess of phenylacetylene (40 μL, 363 μmol). The dark green precipitate was isolated by filtration, extracted with CH_2Cl_2, reprecipitated with pentane, washed with pentane, and dried to give **6** (60.3 mg, 52.4 μmol, 51%). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.45 (s, 1H, PhC≡C*H*), 7.92 (d, 1H, *o*-*Ph*C≡CH), 7.79 (t, 1H, *m*-*Ph*C≡CH), 7.70 (m, 2H), 7.63 (m, 2H), 7.53 (t, 2H, *m*-*Ph*NH), 7.41 (t, 1H, *p*-*Ph*NH), 7.37 (t, 1H, *p*-*Ph*NH), 7.31 (t, 1H, *m*-*Ph*NH), 7.21 (d, 1H, *o*-*Ph*NH), 6.91 (d, 2H, *o*-*Ph*NH), 6.78 (d, 1H, *o*-*Ph*NH), 6.00 (s, br, 1H, N*H*), 4.70 (s, br, 1H, N*H*), 1.516 (s, 30H, Cp*). ESI/MS (CH_3CN): *m*/*z* 905 ([Cp*$_2$Ru$_2$(NHPh)$_2$(PhCCH)PF$_6$]$^+$). Two independent samples were analyzed. Anal. Found: C, 39.89; H, 3.83; N, 2.14. Found: C, 40.76; H, 4.24; N, 2.30; Cl, 0.55. These values are low for **6b** (calcd for $C_{40}H_{48}F_{12}N_2P_2Ru_2$: C, 45.8; H, 4.61; N, 2.67) but are consistent with **6b·AgCl** (calcd for $C_{40}H_{48}AgClF_{12}N_2P_2Ru_2$: C, 40.30; H, 4.06; N, 2.35; Cl, 2.97), except for the low Cl. Dissolving these samples in C_6H_6 gave solutions that slowly deposited white solids, consistent with AgCl as a contaminant.

Acknowledgment. We are grateful to the University of Washington and the National Science Foundation (Grant No. CHE-0513023) for support of this work.

Supporting Information Available: Figures giving an Eyring plot for phenyl rotation in **1a**, 2D HMQC and HMBC spectra of **6a-^{13}C$_2$**, NOESY of **6a**, and ^{1}H NMR spectra of **2**, **4**, **5**, and **6b** and a CIF file for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0700462