

Communication

Reactivity of Amido Ligands on a Dinuclear Ru(II) Center: Formation of Imido Complexes and C–N Coupling Reaction with Alkyne

Shin Takemoto, Tomoharu Kobayashi, and Hiroyuki Matsuzaka

J. Am. Chem. Soc., **2004**, 126 (35), 10802-10803 • DOI: 10.1021/ja047920s • Publication Date (Web): 14 August 2004

Downloaded from <http://pubs.acs.org> on April 1, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 4 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Reactivity of Amido Ligands on a Dinuclear Ru(II) Center: Formation of Imido Complexes and C–N Coupling Reaction with Alkyne

Shin Takemoto,[†] Tomoharu Kobayashi,[†] and Hiroyuki Matsuzaka^{*,†,‡}

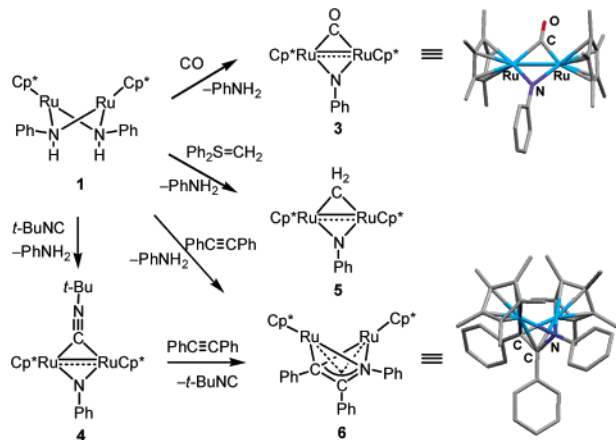
Department of Chemistry, Faculty of Arts and Sciences, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan, and Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

Received April 10, 2004; E-mail: matuzaka@ms.cias.osakafu-u.ac.jp

Amido and imido complexes of low-valent late transition metals have received considerable study recently,¹ primarily because of their implication in many important catalytic processes.^{2,3} Extensive studies on isolable amido and imido complexes of group 8–10 metals have revealed diverse reactivities of such M–N bonds, including insertion and metacyclization with unsaturated C–C and C–X bonds,^{2c,4,5} C–N bond-forming reductive elimination,⁶ imido group transfer,⁷ and activation of H–H and C–H bonds.^{8,9} Still, relatively little is known about how such ligands are incorporated into chemical reactions when they are bound to multimetallic centers,¹⁰ even though such polynuclear amido- and imidometal species have been invoked in certain catalytic systems³ and offer considerable prospect for new reaction sequences. In this context, the dimeric Ru(II) anilido complex $[\text{Cp}^*\text{Ru}(\mu_2\text{-NHPh})_2]$ (**1**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$)¹¹ originally reported by Don Tilley et al. is of particular interest, since it contains two adjacent 16e Ru centers that are not stabilized by additional π -donation from the amido ligands as has been seen in many other 16e amido complexes¹² and, therefore, is expected to show exceptionally high reactivity. However, reactivity of **1** remains almost unexplored. Here we wish to describe reactions of **1** with CO, *t*-butyl isocyanide, a sulfur ylide $\text{Ph}_2\text{S}=\text{CH}_2$, and diphenylacetylene, which proceeded with an unexpected disproportionation of the μ_2 -anilido ligands to form free aniline and a series of new imidodiruthenium complexes. In the case of diphenylacetylene, the imido fragment underwent subsequent coupling reaction with the alkyne to produce an iminoalkenyl complex.

The chemistry we have observed is summarized in Scheme 1. Addition of 1.5 equiv of CO into a THF solution of **1** resulted in

Scheme 1



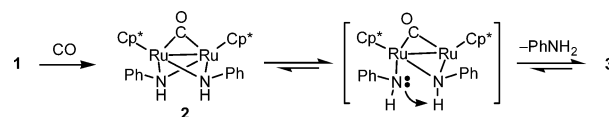
[†] Osaka Prefecture University.

[‡] Institute for Molecular Science.

the formation of the imido carbonyl complex **3** with elimination of 1 equiv of aniline. A small amount of Ru(I) carbonyl complex $[\text{Cp}^*\text{Ru}(\text{CO})_2]_2$ was also formed in this reaction. Complex **3** was isolated as red plates in 63% yield after recrystallization from hexanes and has been characterized by ¹H NMR and IR spectroscopy, elemental analysis, and single-crystal X-ray diffraction (Scheme 1). Noteworthy aspects of the structure include the presence of two five-coordinate Ru atoms, a very short Ru–Ru distance (2.6013(9) Å), and a μ_2 -imido moiety that is planar at nitrogen and exhibits very short Ru–N bond lengths (1.878 Å (mean)).¹³ Existence of a Ru–Ru multiple bond is suggested by electron counting and the short Ru–Ru distance that is close to those of some other compounds with Ru=Ru double bonds (2.417–2.629 Å).¹⁴ Orbital analysis of a DFT-B3PW91 optimized model compound $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-CO})(\mu_2\text{-NH})]$ (**3'**) has provided insights into the Ru–Ru bond in **3**. Although the first six of HOMOs of **3'** are predominantly metal-based orbitals and constitute a formally nonbonded $\sigma^2\sigma^{*2}\delta^4\delta^{*4}$ configuration, the multiple bond order between the Ru atoms can be rationalized by back-donation from the filled Ru–Ru σ^* orbital into a π^* orbital of the CO ligand,¹⁵ and by donation from the imido and CO ligands into empty Ru–Ru π -bonding orbitals.¹⁶

An intermediate in the above transformation was detected spectroscopically during the course of the reaction (Scheme 2). This

Scheme 2



species could not be isolated, but its formulation as a μ_2 -carbonyl adduct of **1**, $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-CO})(\mu_2\text{-NHPh})_2]$ (**2**), is supported by its ¹H and ¹³C{¹H} NMR, IR, and FAB-MS spectra. Complex **2** cleanly afforded **3** and aniline within 15 h at room temperature. The reverse reaction, addition of aniline to the imido complex **3**, did proceed and gave **2** although the conversion was very low (ca. 1% in the presence of 20 equiv of aniline). Since **2** is a coordinatively saturated species, dissociation of a Ru–N bond in **2** would be a facile process. This generates a basic terminal amido ligand capable of deprotonating the bridging amido ligand to form the imido complex **3** (Scheme 2). The disproportionation of amido ligands into amine and an imido ligand has been observed in some monomeric poly(amido) complexes and has been recognized as a useful method for the generation of reactive low-coordinate imidometal species.¹⁷ However, such a reaction is unprecedented for bridging amido systems.

Treatment of **1** with 1 equiv of *tert*-butyl isocyanide or a sulfur ylide $\text{Ph}_2\text{S}=\text{CH}_2$ ¹⁸ afforded analogous dinuclear imido complexes **4** (40%) and **5** (81%) containing μ_2 -isocyanide or μ_2 -methylene

ligands, respectively (Scheme 1), whose structures were also determined by X-ray crystallography. While complexes **3–5** show quite similar overall structures, the Ru–Ru distances vary in the order **5** (2.5728(11) Å) < **3** (2.6013(9) Å) < **4** (2.6594(5) Å),¹⁹ with decrease in the π -acceptor strength of the bridging ligands CH₂ > CO > *t*-BuNC. This trend is consistent with the above MO consideration, which concluded that back-bonding to the bridging π -acid ligands is crucial in the formation of the Ru–Ru bond. The methylene derivative **5** represents, to our knowledge, the first late transition-metal complex containing imido and carbene ligands.

The new imidodiruthenium fragment {(Cp*Ru)₂(μ_2 -NPh)} derived from **1** can not only bind various organic ligands as described above, but also induce subsequent transformation at the bimetallic center. Thus, treatment of the bis(amido) complex **1** with diphenylacetylene resulted in the formation of a dinuclear iminoalkenyl complex [(Cp*Ru)₂(μ_2 - η^3 : η^3 -PhNCPPhCPh)] (**6**) with elimination of 1 equiv of aniline (Scheme 1).²⁰ Complex **6** was isolated in 53% yield as dark red prisms and has been characterized by spectroscopic, analytical, and crystallographic methods. The molecule contains a crystallographic C₂ axis passing through the central iminoalkenyl carbon atom. This makes the terminal iminoalkenyl carbon and nitrogen atoms symmetrically related to each other, and the C–C and C–N bond lengths in the iminoalkenyl moiety are essentially identical (1.439(5) Å). The iminoalkenyl ligand is η^3 -bonded to each of the Ru atoms. The Ru–C bond length for the central carbon atom is 2.259(5) Å, which is longer than the Ru–C and Ru–N bond lengths for the terminal carbon and nitrogen atoms (2.016(3), 2.066(3) Å). Complex **6** was most likely formed by coupling of the imido and alkyne ligands via a transient μ_2 -imido μ_2 - η^2 : η^2 -alkyne complex [(Cp*Ru)₂(μ_2 -NPh)(μ_2 - η^2 : η^2 -PhCCPh)] (**6'**). This assumption is reinforced by the reaction of the isolated imido isocyanide complex **4** with diphenylacetylene, which also afforded **6** with liberation of the isocyanide ligand (Scheme 1). The coupling reaction between imido and alkyne ligands is relevant to catalytic hydroamination and has been well-established for mononuclear terminal imido derivatives of group 4 metals.²¹ However, such a reaction is uncommon for late transition-metal complexes^{5a} and has rarely been observed for polynuclear imido complexes where imido ligands tend to be stabilized by bridging coordination.^{10b}

In summary, we have demonstrated that the dimeric Ru(II) anilido complex **1** serves as an excellent precursor for a new dinuclear imidodiruthenium fragment {(Cp*Ru)₂(μ_2 -NPh)} that is capable of binding various organic ligands and promoting C–N bond formation with alkyne. The results disclosed here would broaden the scope of the reactions of bridging amido and imido complexes. Further studies on the reactivity of **1** and the new complexes **3–6** are now in progress.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan. We are also grateful to the Mitsubishi Foundation, the UBE Foundation, and The Japan Securities Scholarship Foundation for financial support.

Supporting Information Available: Experimental, crystallographic, and computational details (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239–482. (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175. (c) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163–1188. (d) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1–40. (e) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44–56.
- (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675–703. (b) Uchimar, Y. *Chem. Commun.* **1999**, 1133–1134. (c) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *J. Am. Chem. Soc.* **1988**, *110*, 6738–6744. (d) Brunet, J.-J.; Commenges, G.; Neibecker, D.; Philippot, K. *J. Organomet. Chem.* **1994**, *469*, 221–228. (e) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852–860. (f) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2001**, *219*, 131–209. (g) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40–73. (h) Watanabe, M.; Murata, K.; Ikariya, T. *J. Am. Chem. Soc.* **2003**, *125*, 7508–7509.
- (a) Alper, H.; Hashem, K. E. *J. Am. Chem. Soc.* **1981**, *103*, 6514–6515. (b) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7255–7259. (c) Bernhardt, W.; Von Schnering, C.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 381–381. (d) Holm, R. H.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239–2314.
- (a) Bryndza, H. E.; Fultz, W. C.; Tam, W. *Organometallics* **1985**, *4*, 939–940. (b) Joslin, F. L.; Johnson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781–2794. (c) Cowan, R. L.; Troglor, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750–4761.
- (a) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041–2054. (b) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hurthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 3771–3778.
- Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 8232–8245.
- (a) Waterman, R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2003**, *125*, 13350–13351. (b) Jenkins, D. M.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 11238–11239. (c) Leung, S. K.-Y.; Huang, J.-S.; Liang, J.-L.; Che, C.-M.; Zhou, Z.-Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 340–342.
- (a) Fryzuk, M. D.; Montgomery, C. D.; Rettig, S. J. *Organometallics* **1991**, *10*, 467–473. (b) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 15104–15118.
- (a) Fulton, J. R.; Sklenak, S.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 4722–4737. (b) Conner, D.; Jayaprakash, K. N.; Wells, M. B.; Manzer, S.; Gunnoe, T. B.; Boyle, P. D. *Inorg. Chem.* **2003**, *42*, 4759–4772. (c) Murata, K.; Konishi, H.; Ito, M.; Ikariya, T.; *Organometallics* **2002**, *21*, 253–255. (d) Thyagarajan, S.; Shay, D. T.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **2003**, *125*, 4440–4441.
- (a) Ge, Y.-W.; Sharp, P. R. *Organometallics* **1988**, *7*, 2234–2236. (b) Song, J.-S.; Han, S.-H.; Nguyen, S. T.; Geoffroy, G. L. *Organometallics* **1990**, *9*, 2386–2395. (c) Dobbs, D. A.; Bergman, R. G. *Organometallics* **1994**, *13*, 4594–4605. (d) Cabeza, J. A.; del Río, I.; García-Granda, S.; Moreno, M.; Riera, V.; Rosales-Hoz, M. d. J.; Suárez, M. *Eur. J. Inorg. Chem.* **2001**, 2899–2906. (e) Tejel, C.; Ciriano, M. A.; Bordonaba, M.; López, J. A.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **2002**, *41*, 2348–2355.
- Blake, R. E., Jr.; Heyn, R. H.; Tilley, T. D. *Polyhedron* **1992**, *11*, 709–710. For related amido-, alkoxo-, and thiolato-bridged diruthenium complexes, see: (a) Koelle, U. *Chem. Rev.* **1998**, *98*, 1313–1334. (b) Hiday, M.; Mizobe, Y.; Matsuzaka, H. *J. Organomet. Chem.* **1994**, *473*, 1–14. (c) Takemoto, S.; Oshio, S.; Kobayashi, T.; Matsuzaka, H.; Hoshi, M.; Okimura, H.; Yamashita, M.; Miyasaka, H.; Ishii, T.; Yamashita, M. *Organometallics* **2004**, *23*, 3587–3589.
- (a) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25–41. (b) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125–135.
- Examples of structurally characterized imidodiruthenium complexes: (a) Kee, T. P.; Park, L. Y.; Robbins, J.; Schrock, R. R. *J. Chem. Soc., Chem. Commun.* **1991**, 121–122. (b) Burrell, A. K.; Burrell, A. J. *Organometallics* **1997**, *16*, 1203–1208. (c) Nakajima, Y.; Suzuki, H. *Organometallics* **2003**, *22*, 959–969.
- (a) Cotton, F. A.; Feng, X. *J. Am. Chem. Soc.* **1997**, *119*, 7514–7520. (b) Lin, W.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 2309–2319. (c) Eisenberg, R.; Gaughan, A. P., Jr.; Pierpont, C. G.; Reed, J.; Shultz, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 6240–6241.
- A similar metal–metal bond has been proposed for Fe₂(CO)₉: Reinhold, J.; Hunstock, E. *New J. Chem.* **1994**, *18*, 465–471.
- See Supporting Information for details.
- (a) Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 251–253. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729–8731. (c) Zambrano, C. H.; Profflet, R. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1993**, *12*, 689–708. (d) Schaller, C. P.; Cummins, C. C.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 591–611.
- Gandelman, M.; Rytchinski, B.; Ashkenazi, N.; Gauvin, R. M.; Milstein, D. *J. Am. Chem. Soc.* **2001**, *123*, 5372–5373.
- This trend is reproduced in the DFT calculation of model complexes.
- The diruthenium complexes containing isoelectronic η^3 -amidinate ligands have been reported: Kondo, H.; Matsubara, K.; Nagashima, H. *J. Am. Chem. Soc.* **2002**, *124*, 534–535.
- (a) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708–1719. (b) Shi, L. Y.; Odom, A. L. *J. Am. Chem. Soc.* **2004**, *126*, 1794–1803. (c) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104–114.

JA047920S