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Divalent Dirhodium Imido Complexes: Formation, Structure, and Alkyne Cycloaddition Reactivity

Shin Takemoto,* Shohei Otsuki, Yasuhiro Hashimoto, Ken Kamikawa, and Hiroyuki Matsuzaka*

Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Gakuen-cho 1-1, Naka-ku, Sakai, Osaka 599-8531, Japan

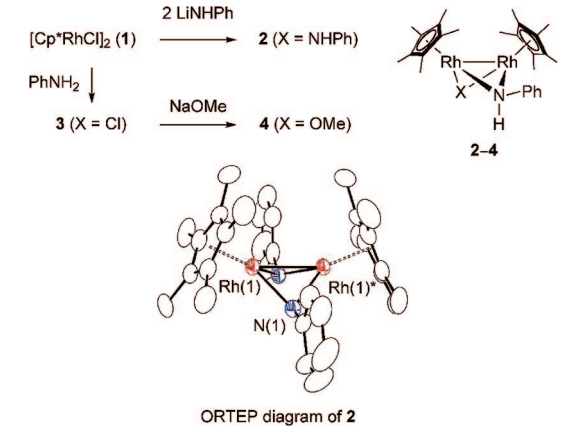
Received May 7, 2008; E-mail: takemoto@c.s.osakafu-u.ac.jp; matuzaka@c.s.osakafu-u.ac.jp

Utilization of transition metal imido complexes as reagents or catalysts in organic synthesis is a topic of broad current interest.[1–3] Among numerous reactivity patterns of multiple-bonded M=NR functionality,[1] the [2 + 2] cycloaddition with alkynes has received considerable attention as a crucial C−N bond forming step in the catalytic hydroamination of alkynes.[3–6] While certain monomeric imido complexes of group 4 and some neighboring metals have proven effective for this type of transformation,[4–6] few late transition metal imido complexes have exhibited comparable reactivity.[7] We previously described the formation of a dinuclear azametallacycle from the reaction of the 16-electron ruthenium amido complex $[Cp^*Ru(\mu_2\text{-}NHPh)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with diphenylacetylene, which likely proceeds via alkyne coordination and aniline elimination followed by imido-alkyne cycloaddition.[8] Exploring the scope of late transition metal imido complexes as reagents for C−N bond formation,[9] we here report the chemistry of corresponding Cp*Rh amido and imido complexes, including the synthesis of the divalent amido complex $[Cp^*Rh(\mu_2\text{-}NHPh)]_2$, generation and alkyne cycloaddition of a transient imido species $[Cp^*Rh(\mu_2\text{-}NPh)RhCp^*]$, and X-ray structure determination of a sterically protected imido complex $[Cp^*Rh(\mu_2\text{-}NAr)RhCp^*]$ (Ar = 2,6-diisopropylphenyl).

Amido[10] and imido[7a,11] derivatives of Cp*M (M = group 8−10 metals) fragments have been most commonly derived from the corresponding Cp*M halides by displacement reactions.[12] In this study, we employed the Rh(II) chloride $[Cp^*RhCl]_2$ (**1**), reported by Sharp and co-workers,[13] as a starting material and prepared the amido complexes **2**−**4** (Scheme 1) that can be used as precursors to imido complexes. The violet dimeric amide **2** was obtained in 74% yield upon treatment of **1** with 2 equiv of LiNHPh in THF. Heating the chloro dimer **1** with excess aniline in THF at 60 °C resulted in the selective monosubstitution of a chloride ligand to give the amido chloro complex **3** in 71% yield, which was then converted to the amide methoxide **4** in 72% yield upon treatment with NaOMe. Complexes **2**−**4** were isolated after extraction with hexanes and identified by standard spectroscopic and analytical methods; **2** was further defined by an X-ray diffraction which revealed the nonplanar M_2N_2 core and equatorial phenyl groups similar to those reported for $[Cp^*Ru(\mu_2\text{-}NHPh)]_2$.[10e] The Rh−Rh distance of 2.6097(9) Å is comparable to that of **1** (2.617(1) Å)[13] and is consistent with a single bond between the d^7 Rh(II) centers.

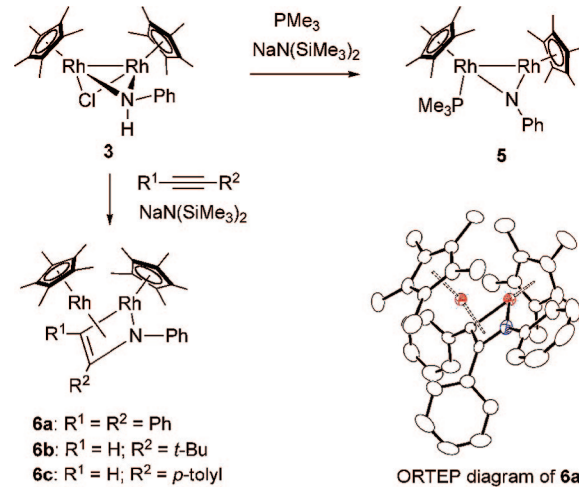
An initial evidence that an imido species can be generated from the amido complexes **2**−**4** was obtained by dehydrochlorination of **3** with $NaN(SiMe_3)_2$ in the presence of PMe_3 that afforded the imido complex $[Cp^*Rh(\mu_2\text{-}NPh)Rh(PMe_3)Cp^*]$ (**5**) in 80% yield (Scheme 2). This compound is an analogue of the iridium imido complex $[Cp^*Ir(\mu_2\text{-}NPh)Ir(PMe_3)Cp^*]$ reported by Dobbs and Bergman as a product of imido transfer reaction from $[Cp^*Ir(\mu_2\text{-}NPh)]_2$ to PMe_3.[11f] Analogous deprotonation of **3** in the presence of diphenylacetylene resulted in the formation of a dinuclear azametallacycle **6a** in 78% yield (Scheme 2). It seems likely that **6a** is formed by alkyne cycloaddition to a transiently generated imido species $[Cp^*Rh(\mu_2\text{-}NPh)RhCp^*]$, since **3** did not react with diphenylacetylene in the absence of the base under comparable reaction conditions (THF, 25 °C, 12 h). With terminal acetylenes, *tert*-butylacetylene and *para*-tolylacetylene, the cycloaddition proceeded regioselectively to give the Markovnikov adducts **6b** (85% yield) and **6c** (91% yield), respectively. The structure of **6a** has been determined by X-ray crystallography. Although terminal CPh and NPh groups in the bridging azapropenylidene ligand PhCCPh-NPh are disordered, solved structure clearly shows the unsymmetrical η^2:η^3 bonding, which markedly contrasts to the symmetrical η^3:η^3 bonded structure of the diruthenium complex $[(Cp^*Ru)_2(\mu_2\text{-}\eta^3\text{:}\eta^3\text{-}PhCCPhNPh)]$.[8] A fluxional behavior of the azametallacycles

Scheme 1. Synthesis of $[(Cp^*Rh)_2(\mu_2\text{-}NHPh)(\mu_2\text{-}X)]$ (**2**−**4**)



ORTEP diagram of **2**

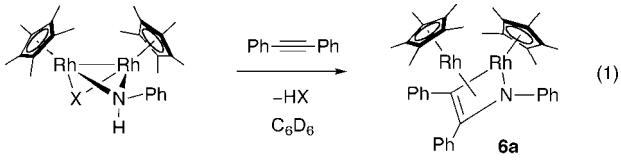
Scheme 2. Generation, PMe_3 Trapping, and Alkyne Cycloaddition of a Dirhodium Imido Species $[Cp^*Rh(\mu_2\text{-}NPh)RhCp^*]$



ORTEP diagram of **6a**

10.1021/ja8033922 CCC: $40.75

6a−**c** was suggested by their ^{1}H NMR spectra. For example, in THF-d_8 at −90 °C complex **6a** showed two inequivalent Cp* methyl resonances that coalesced into one sharp singlet as the temperature was raised. This can be accounted for by assuming a rapid flipping of the bridging azapropenylidene moiety between the two Rh centers.



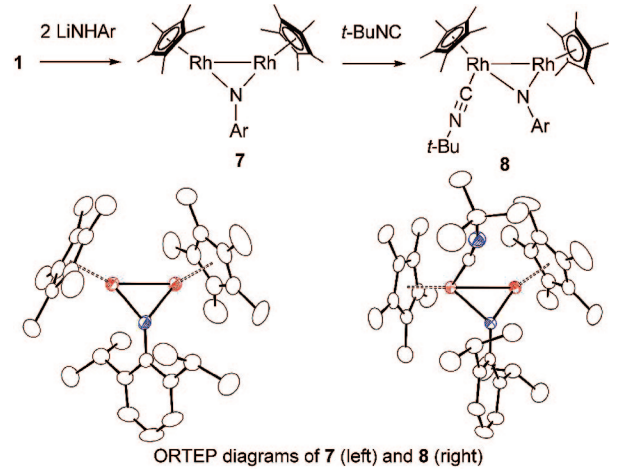
2 (X = NHPh)
4 (X = OMe)

47% from **2** (120 °C, 7 d)
98% from **4** (60 °C, 18 h)

The azametallacycle **6a** was also formed in 47% yield from the bis-amide **2** with elimination of 1 equiv of aniline when **2** was heated at 120 °C for 7 days in the presence of 10 equiv of diphenylacetylene (eq 1). The amide methoxide **4** more smoothly reacted with the same alkyne (1 equiv, 60 °C 18 h) to give **6a** in 98% yield. A preliminary kinetic estimation revealed that the rate of formation of **6a** is first order in the concentration of **4** with little dependence of k_{obs} values on the concentration of alkyne ($4.3 \pm 1.0 \times 10^{-5}$ s^{-1} in the presence of 10−30 equiv of alkyne in C_6D_6 at 50 °C), which again points to a dissociative pathway involving the imido intermediate [Cp*Rh(μ_2-NPh)RhCp*].

Use of a sterically hindered arylimido ligand allowed isolation of an unsaturated imido complex relevant to the above-postulated imido intermediate. Treatment of **1** with 2 equiv of LiNHAr (Ar = 2,6-diisopropylphenyl) afforded the singly bridged imido complex [Cp*Rh(μ_2-NAr)RhCp*] (**7**), which was isolated in 64% yield and crystallographically characterized (Scheme 3). The molecule contains a triangular Rh_2N core surrounded by the bulky Cp* and Ar groups. The planar arrangement around nitrogen and the short Rh−N distances (1.8946(18) and 1.8969(19) Å) indicate delocalized Rh−N multiple bonding interactions.[8,11] The Rh−Rh distance of 2.5190(7) Å is consistent with a Rh−Rh single bond with which each rhodium center would attain a formal 16-electron configuration. While **7** did not react with diphenylacetylene or *tert*-butylacetylene, it reacts instantaneously with *tert*-butyl isocyanide to give the adduct [Cp*Rh(*t*-BuNC)(μ_2-NAr)RhCp*] (**8**; 63% yield), in which the terminal isocyanide ligand rapidly migrates between the two Rh centers as evidenced by a single-crystal X-ray and variable temperature NMR studies.

Scheme 3. Synthesis and Structure of the Imido Complex **7**



ORTEP diagrams of **7** (left) and **8** (right)

In summary, the amido complexes **2**−**4** provided a chemistry attributable to a reactive imido species [Cp*Rh(μ_2-NPh)RhCp*] including a formal [2 + 2] cycloaddition reaction with unactivated alkynes. With the use of a sterically hindered arylimido ligand, a relevant coordinatively unsaturated imidodihodium complex was isolated and structurally characterized. Efforts will be directed toward detailed investigation of this system including catalytic alkyne hydroamination by an imido mechanism.[4]

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Supporting Information Available: Experimental procedure and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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