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

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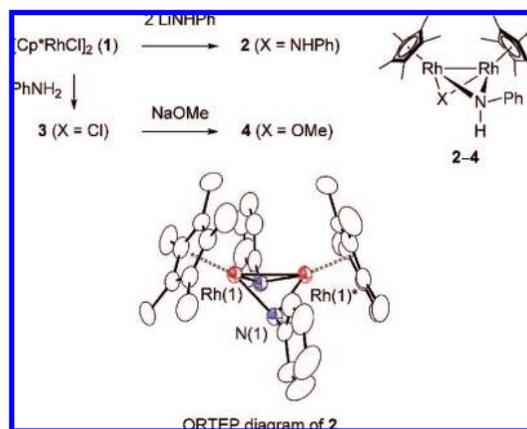
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Utilization of transition metal imido complexes as reagents or catalysts in organic synthesis is a topic of broad current interest.^{1–3} Among numerous reactivity patterns of multiple-bonded $M=NR$ functionality,¹ the [2 + 2] cycloaddition with alkynes 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 $[Cp^*Ru(\mu_2-NHPh)]_2$ ($Cp^* = \eta^5-C_5Me_5$) 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 $[Cp^*Rh(\mu_2-NHPh)]_2$, generation and alkyne cycloaddition of a transient imido species $[Cp^*Rh(\mu_2-NPh)RhCp^*]$, and X-ray structure determination of a sterically protected imido complex $[Cp^*Rh(\mu_2-NAr)RhCp^*]$ ($Ar = 2,6$ -diisopropylphenyl).

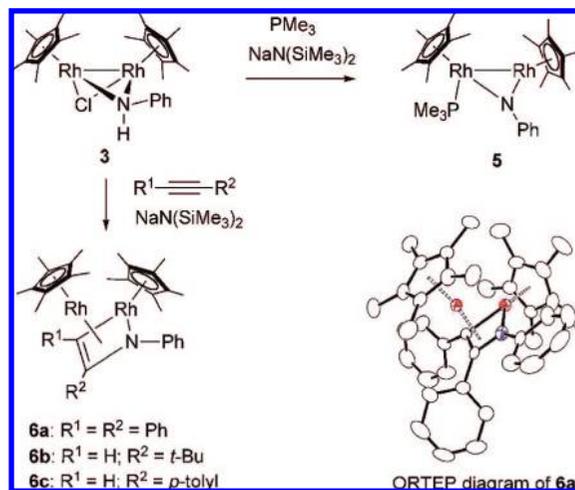
Amido¹⁰ and imido^{7a,11} derivatives of Cp^*M ($M =$ group 8–10 metals) fragments have been most commonly derived from the corresponding Cp^*M halides by displacement reactions.¹² In this study, we employed the Rh(II) chloride $[Cp^*RhCl]_2$ (**1**), reported by Sharp and co-workers,¹³ as a starting 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 $[Cp^*Ru(\mu_2-NHPh)]_2$.^{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 $[Cp^*Rh(\mu_2-NPh)Rh(PMe_3)Cp^*]$ (**5**) in 80% yield (Scheme 2). This compound is an analogue of the iridium imido complex $[Cp^*Ir(\mu_2-NPh)Ir(PMe_3)Cp^*]$ reported by Dobbs and Bergman as a product of imido transfer reaction from $[Cp^*Ir(\mu_2-NPh)]_2$ to PMe_3 .^{11f} Analogous deprotonation of **3** in the presence of diphenylacetylene resulted in the formation of a dinuclear

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

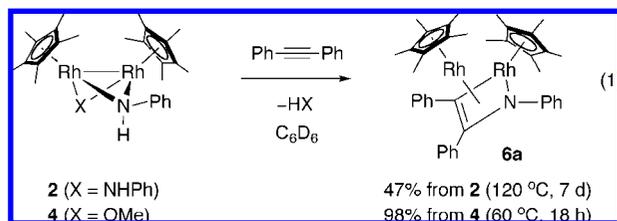


Scheme 2. Generation, PMe_3 Trapping, and Alkyne Cycloaddition of a Dirhodium Imido Species $[Cp^*Rh(\mu_2-NPh)RhCp^*]$



azametallacycle **6a** in 78% yield (Scheme 2). It seems likely that **6a** is formed by alkyne cycloaddition to a transiently generated imido species $[Cp^*Rh(\mu_2-NPh)RhCp^*]$, 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 PhCCPhNPh are disordered, solved structure clearly shows the unsymmetrical $\eta^2:\eta^3$ bonding, which markedly contrasts to the symmetrical $\eta^3:\eta^3$ bonded structure of the diruthenium complex $[(Cp^*Ru)_2(\mu_2-\eta^3:\eta^3-PhCCPhNPh)]$.⁸ A fluxional behavior of the azametallacycles

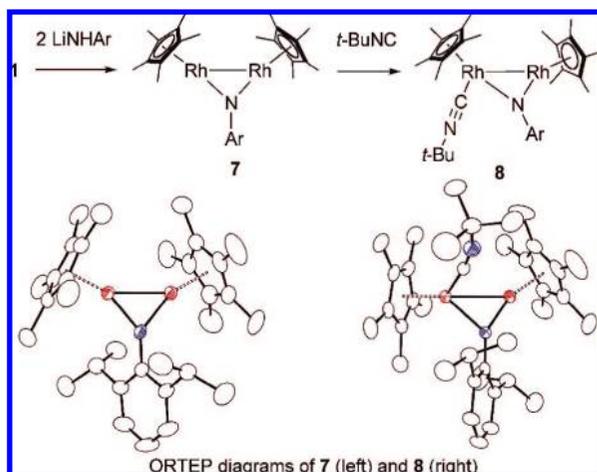
6a–c was suggested by their ^1H NMR spectra. For example, in THF-d_8 at -90°C complex **6a** showed two inequivalent Cp^* methyl resonances that coalesced into one sharp singlet as the temperature was raised. This can be accounted for by assuming a rapid flipping of the bridging azapropenyldiene moiety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



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 ($4.3 \pm 1.0 \times 10^{-5} \text{ s}^{-1}$ 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 $[\text{Cp}^*\text{Rh}(\mu_2\text{-NPh})\text{RhCp}^*]$.

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 ($\text{Ar} = 2,6\text{-diisopropylphenyl}$) afforded the singly bridged imido complex $[\text{Cp}^*\text{Rh}(\mu_2\text{-NAr})\text{RhCp}^*]$ (**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 $[\text{Cp}^*\text{Rh}(t\text{-BuNC})(\mu_2\text{-NAr})\text{RhCp}^*]$ (**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**



In summary, the amido complexes **2–4** provided a chemistry attributable to a reactive imido species $[\text{Cp}^*\text{Rh}(\mu_2\text{-NPh})\text{RhCp}^*]$ 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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