

Group-6 Imido Activation by a Ring-Strained Alkyne

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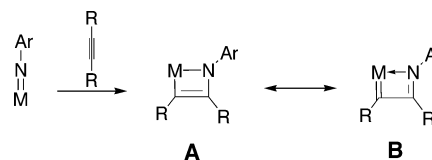
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Summary: Treatment of $M(\text{NAr})_2(\text{Cl})_2(\text{DME})$, where $\text{Ar} = 2,6\text{-diisopropylphenyl}$, with cyclooctyne results in the formation of $M(=\text{C}_8\text{H}_{12}=\text{C}_8\text{H}_{12}=\text{NAr})(\text{Cl})_2(\text{NAr})$, where $M = \text{Mo}$ (**1**) and W (**2**). The complexes have metrical and spectroscopic parameters that are most consistent with an alkylidene-imine formulation with some participation by the alkyl-amido resonance form. Thermolysis of metallacycles **1** and **2** generates a pyrrole elimination product, with the tungsten derivative being more thermally stable. In addition, the metallacycle is quite hydrolytically stable. Addition of 50% H_2SO_4 to a toluene solution of **2** protolytically cleaves all the ligands on the metal except those associated with the metallacycle, which are retained in the oxo product $[\text{W}(\text{O})(\mu\text{-O})(=\text{C}_8\text{H}_{12}=\text{C}_8\text{H}_{12}=\text{NAr})_2]$ (**3**). The metallacycles **1–3** will polymerize norbornene in the presence of AlCl_3 . Compounds **1–3** and the pyrrole were characterized by X-ray diffraction.

Mid- to high-oxidation-state transition metal alkylidenes, Schrock carbenes,¹ have made a tremendous and still expanding impact on organic synthesis.² Consequently, readily prepared alkylidenes are of interest, especially for stoichiometric but also for catalytic applications.³ We have been exploring the reactivity of titanium imido and hydrazido complexes in hydroamination^{4,5} and related processes⁶ that involve [2 + 2] cycloaddition of a $\text{Ti}=\text{N}$ substituent with an alkyne.⁷ The products of such cycloadditions are azametallacyclobutenes⁸ (form **A**, Scheme 1). Examining these intermediates, we were led to inquire if a different resonance form, the alkylidene-imine, might be favored under some circumstances (form **B**, Scheme 1).

This alkylidene-imine resonance form is most likely to be observed for metal complexes where converting the imido to an alkylidene gives a system known to have

Scheme 1. [2 + 2] Cycloaddition of an Alkyne with an Imido Substituent and Possible Resonance Forms



stable $\text{M}=\text{C}$ linkages. Since we are attempting to stabilize a multiple-bond over a two single-bond system, it would be advantageous to choose a metal center and oxidation state where $d\pi\text{-}p\pi$ bonding is prevalent. The most metal–ligand multiple-bond complexes are known for molybdenum.⁹ In addition, a multitude of stable imido alkylidene complexes of molybdenum have been reported by Schrock and co-workers.¹ Consequently, molybdenum imido alkylidenes are an excellent place to begin when trying to encourage alkylidene bonding.

The desired starting material to form a new molybdenum imido carbene is a bis(imido) molybdenum(VI) complex. Bis(imido) complexes $\text{Mo}(\text{NR})_2(\text{Cl})_2(\text{DME})$ can be prepared on large scales in a single step from H_2NR and ammonium molybdate,¹⁰ and reaction of these complexes with an alkyne would seem an ideal testing ground for resonance form **B** in Scheme 1. However, molybdenum(VI) bis(imido) complexes do not react with many typical alkynes under mild conditions where the alkylidene products would be expected to be stable. For example, treatment of $\text{Mo}(\text{NAr})_2(\text{Cl})_2(\text{DME})$, where $\text{Ar} = 2,6\text{-diisopropylphenyl}$, with a large excess of 3-hexyne at 75 °C overnight results in no reaction.

To encourage cycloaddition and activate the imido ligand, we examined treatment of $M(\text{NAr})_2(\text{Cl})_2(\text{dme})$, where $M = \text{Mo}$ and W , with a highly reactive, ring-strained¹¹ alkyne, cyclooctyne.¹² Treating solutions of $M(\text{NAr})_2(\text{Cl})_2(\text{DME})$ with 2.5 equiv of cyclooctyne results (Scheme 2) in formation of a yellow product; the product was identified as $M(=\text{C}_8\text{H}_{12}=\text{C}_8\text{H}_{12}=\text{NAr})(\text{NAr})\text{Cl}_2$, perhaps from [2 + 2] cycloaddition followed by insertion of alkyne into the four-membered metallacyclic intermediate (**A/B**, Scheme 1). The $M = \text{Mo}$ (**1**) and W (**2**) complexes were available in 90% and 93% yield, respectively, by this reaction.

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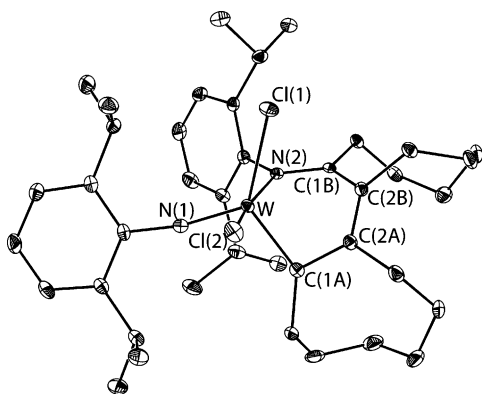
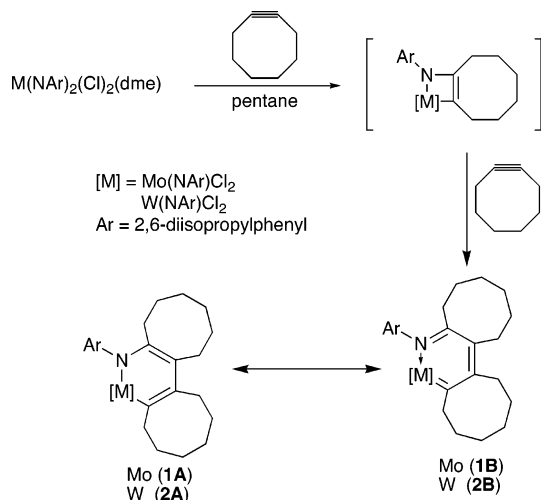


Figure 1. ORTEP diagram of **2** from X-ray diffraction.

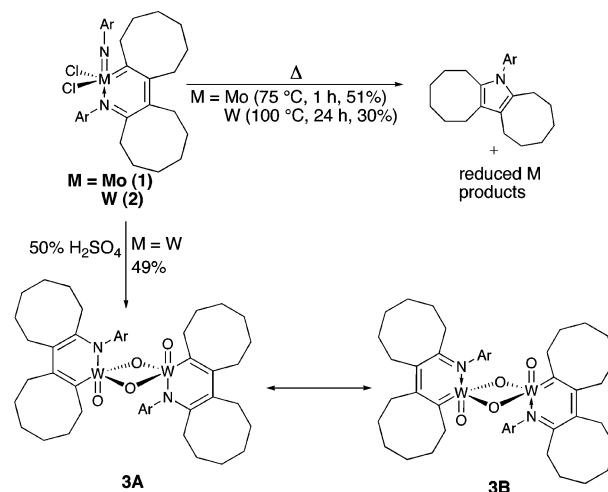
Scheme 2. Reactions of $M(\text{NAr})_2(\text{Cl})_2(\text{DME})$ with Cyclooctyne



Metallacycles **1** and **2** are identical within error by X-ray diffraction. The structure of **2** is shown in Figure 1. The metric parameters are more consistent with the carbene-imine resonance form (**1B/2B**, Scheme 2) than the potential alkyl-amido form (**1A/2A**, Scheme 2). However, the alkyl-amido form seems to participate. For example, the W=C distance in **2** is 1.944(4) Å compared with 1.878(9) Å in the PMe_3 adduct of Schrock's catalyst, $\text{Mo}(\text{NAr})[\text{C}(\text{H})\text{CMe}_2\text{Ph}][\text{OC}(\text{CF}_3)_2\text{Me}]_2(\text{PMe}_3)$,¹³ cf. the average Mo–C single bond distance of 2.128(5) Å in $\text{Mo}(\text{NAr})_2(\text{neophyl})_2$.¹⁰ For the carbene-imine resonance form **2B**, the C(2A)–C(2B) bond should have a bond order of 2; the bond length is 1.404(5) Å, slightly longer than the C=C distance of 1.336 Å in butadiene.¹⁴ The C(1A)–C(2A) and C(1B)–C(2B) distances average 1.449–(6) Å, and the C–C single-bond distance in butadiene is 1.465 Å.¹⁴ The W–N(2) distance in **2** is 2.120(3) Å.

In addition to the structural evidence, the ¹³C NMR spectroscopy is also indicative of alkylidene character. The resonance for C_α of **1** has a chemical shift of 309 ppm, which is similar to the shift in $\text{Mo}(\text{NAr})[\text{C}(\text{H})\text{CMe}_2\text{Ph}][\text{OC}(\text{CF}_3)_2\text{Me}]_2$ of 288 ppm.¹³ The analogous resonance for C_α in **2** has a chemical shift of 278 ppm, cf., the chemical shift of 254 ppm for the alkylidene carbon in $\text{W}(\text{NAr})[\text{C}(\text{H})\text{CMe}_2\text{Ph}][\text{OC}(\text{CF}_3)_2\text{Me}]_2$.¹⁵ Con-

Scheme 3. Thermolysis and Acid Hydrolysis of **1 and **2****



sequently, the reaction shown in Scheme 2 constitutes an unusual direct conversion of an imido to a ligand with alkylidene character.

The metallacycles have displayed several interesting reactions thus far. For example, **1** and **2** undergo an unusual decomposition reaction that results in the formation of a pyrrole (Scheme 3). The product formation may be regarded as reductive elimination from the alkyl-amido (**1A/2A**, Scheme 2) or intramolecular nucleophilic attack of the imine on the carbene in the alkylidene-imine (**1B/2B**, Scheme 2). As would be expected considering the process involves a net reduction of the metal center, decomposition of the tungsten derivative **2** occurs more slowly than for corresponding molybdenum-containing **1**.

While the complexes are thermally sensitive due to pyrrole elimination, they are quite chemically robust for molybdenum(VI) and tungsten(VI) complexes with alkylidene character, which is likely due to resonance stabilization of the metallacycle. For example, a toluene solution of **2** can be shaken in air with 50% aqueous H_2SO_4 , and the metallacycle is retained in the product! The reaction replaces all the ligands on tungsten except those associated with the metallacycle, which are retained in μ -oxo **3** (Scheme 3).

Tungsten μ -oxo **3** is apparently less alkylidene-like in its properties. The W–C(1A) distance increases from 1.944(4) Å in imido complex **2** to 2.010(4) Å in **3**. Indeed all the distances in the metallacycle are consistent with greater participation of the amido-alkyl resonance form (**3A**, Scheme 3) than in the imido derivative. For example, the W–N distance in the metallacycle of **3** shrinks to 2.021(3) Å from 2.120(3) Å in imido **2**, consistent with increased alkyl-amido resonance form participation. Also consistent with this assertion, the ¹³C NMR resonance for C_α is shielded significantly to 238 ppm in **3** from 278 ppm in **2**.

As can be seen by comparing the bond distances of the metallacycles in tungsten imido **2** and oxo **3**, the other ligands on the metal have a dramatic effect on the favored resonance form (Figure 2). While both reson-

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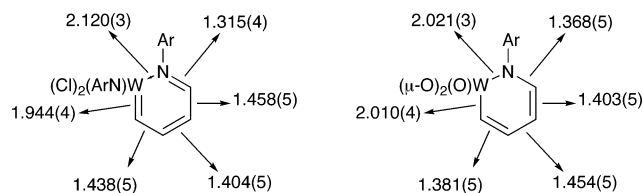


Figure 2. Simplified structure comparison between **2** (left) and **3** (right) illustrating the difference in bond alternation due to changing ligand sets.

ance forms undoubtedly participate in both complexes, changing the ligands on tungsten can affect whether the alkylidene-imine or alkyl-amido form is favored.

The isolated metallacycles **1–3** are not olefin metathesis active. However, addition of AlCl_3 to **1–3** results in mixtures that polymerize norbornene.¹⁶ It is hoped that through continued study of these metallacycles,

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this cyclooctyne activation of imido ligands may constitute a new, general route to reactive alkylidene complexes.

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Supporting Information Available: Data from the X-ray diffraction studies on **1–3**, the pyrrole, and $\text{Mo}(\text{neophyl})_2(\text{NAr})_2$. Synthesis and characterization data for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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