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Articles

Synthesis and Reactivity of Molybdenum Imido Diamido Metallacyclopentenes and Metallacyclopentadienes and the Mechanism of Ethylene Exchange with Metallacyclopentane Complexes

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In this paper the reactivity of the previously reported metallacyclopentane complex [Mo(NPh)(*o*-($Me_3SiN)_2C_6H_4)(CH_2)_4$] (**1**) is reported. Complex **1** reacts with acetylenes via ethylene exchange to form novel Mo imido metallacyclopentene complexes, [Mo(NPh)(*o*-($Me_3SiN)_2C_6H_4$)(CRCR′($CH_2)_2)_4$] (R = Ph, R′ = H, **4a**; R = H, R′ = Ph, **4b**; R, R′ = CO_2Et, **4c**). The kinetics of the formation of **4c** from **1**, in the presence of excess diethyl acetylenedicarboxylate (DEAC), was examined. The activation parameters for the formation of **4c** were found to be $\Delta H^\ddagger = 20.5(2.3)$ kcal mol^{-1} and $\Delta S^\ddagger = -14.8(6.6)$ cal (mol K)$^{-1}$. The metallacyclopentadiene complex [(NPh)Mo(C(Ph)CHCHC(Ph)){*o*-($Me_3SiN)_2C_6H_4$}] (**7**) was synthesized by the oxidative coupling of two phenylacetylene molecules. Compound **7** is active as a catalyst for the cyclotrimerization of phenylacetylene. X-ray crystal structures of **1**, **4b**, and **7** are reported.

Introduction

Metallacyclopentane complexes were originally observed in our laboratories as species that result from the deactivation of W(VI) alkylidenes during olefin metathesis reactions in which ethylene is formed.[1−3] Since these initial studies, we have been able to isolate and characterize metallacyclopentane complexes of W and Mo by more direct methods.[4,5] Group 6 imido metallacyclopentane complexes are rare, and our complexes are unusual in that their inherent stability toward decomposition by either β-hydrogen elimination/abstraction or β-carbon−carbon bond cleavage allows them to be readily isolated and characterized.

Schrock and co-workers have also observed group 6 imido metallacyclopentane complexes that resulted from the decompostion of alkylidene species.[6−17] These complexes, however, lacked the inherent stability of the molecules synthesized in our group and decompose via β-hydrogen transfer, resulting in the formation of butene. Our complexes differ from Schrock's in the nature of the chelating ancillary ligand. The diamide ligand {*o*-($Me_3SiN)_2C_6H_4$}$^{2-}$ is crucial in stabilizing the high oxidation state of the metal through π donation of the diamide lone pairs.[18−22] It appears that the alkoxide,[23,24] biphenolate, and binaphtholate ligands[7,8,12,14,16,17] in Schrock's metathesis catalysts

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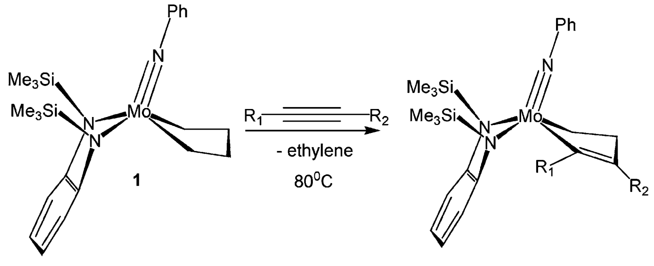
are not as effective at π donation and thus do not stabilize the high oxidation state of the metal.

Transition-metal metallacycles have been implicated as important species in many catalytic and stoichiometric conversions of organic fragments. One such process is the metal-mediated cyclooligomerization reaction of alkynes.[25−33] In the well-known mechanism for this reaction, metallacyclopentenes, metallacyclopentadienes, alkyne, and arene complexes have been cited as key intermediates.[27−29,33−43] Recent research in this field has focused on controlling the regioselectivity of the cyclooligimerization reaction. This has been achieved by developing ligand sets with steric properties that promote highly selective carbon−carbon bond forming reactions. In these reactions, low-valent transition metals mediate the formation of metallacycles from saturated organic substrates. Takahashi[44−54] and Ladipo[25,55,56] have utilized this chemistry in the synthesis of substituted arenes, pyridines, and other useful organic molecules. In Takahashi's work, the preparation of multisubstituted benzene and pyridine derivatives was achieved in a one-pot synthesis through the use of unsymmetrical metallacyclopentadienes obtained from the intermolecular cross-coupling reaction of two different alkynes and subsequent treatment with a third alkyne, or nitrile, in the presence of CuCl or $Ni(PPh_3)_2Cl_2$. The development of methodologies that would afford the stereoselective synthesis of metallacycles is an important area of research and warrants further study.

Scheme 1



4a. R_1= Ph R_2= H
4b. R_2 = H R_2= Ph
4c. R_1= CO_2Et R_2= CO_2Et

We have recently reported a method for the synthesis of group 6 imido diamido olefin complexes, $[(\eta^2\text{-olefin})Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)]$ (**3**: olefin = ethylene (**3a**), isobutylene (**3b**), styrene (**3c**), propene (**3d**)), from $[Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)Cl_2(THF)]$ (**2**).[4] In exploring the reactivity of these complexes, we became interested in developing the chemistry of group 6 metallacycles containing imido and bis(amido) chelating ligands because of the potential use of these compounds in organic synthesis.[31,33,44,52−54,57]

In this paper, we examine the chemistry of the metallacyclopentane complex $[Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)(CH_2)_4]$ (**1**). The synthesis of the metallacyclopentene complexes $[Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)(CHRCHR'(CH_2)_2)_4]$ (**4**) from **1** by the exchange of ethylene with an alkyne molecule is reported. We also examine the synthesis and reactivity of the novel metallacyclopentadiene complex $[Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)(C(Ph)(CH)_2(C(Ph))]$ (**7**) by the [2 + 2] cycloaddition reactions of two alkyne moieties. In addition, X-ray crystal structures of **1**, **4b**, and **7** are reported.

Results and Discussion

Synthesis of Metallacyclopentene Complexes. Heating a toluene solution of the metallacyclopentane complex **1** at 80 °C with 1 equiv of an alkyne results in the synthesis of the metallacyclopentene complex **4** (Scheme 1). The reaction with phenylacetylene results in a 1:4 mixture of the two regioisomers **4a** and **4b**. The phenyl substituent of the metallacycle in **4a** is in the α-position, while the phenyl substituent in **4b** is in the β-position.

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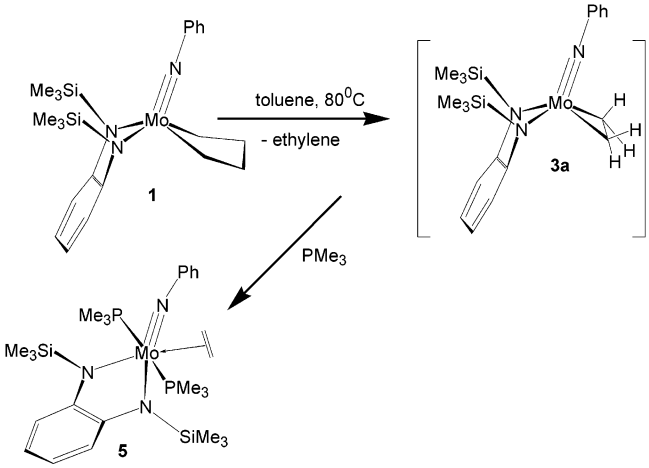
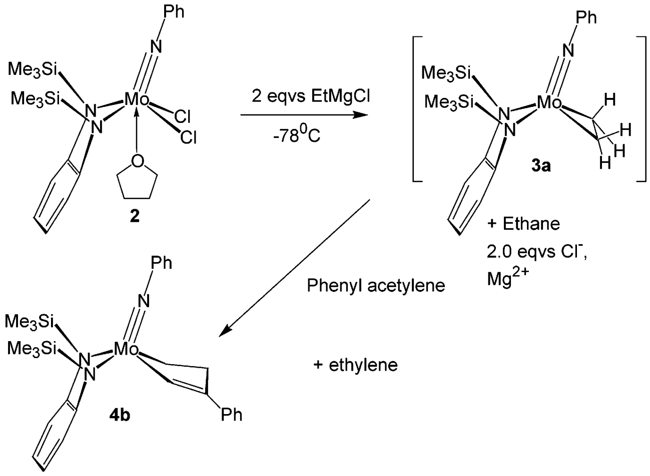
Scheme 2



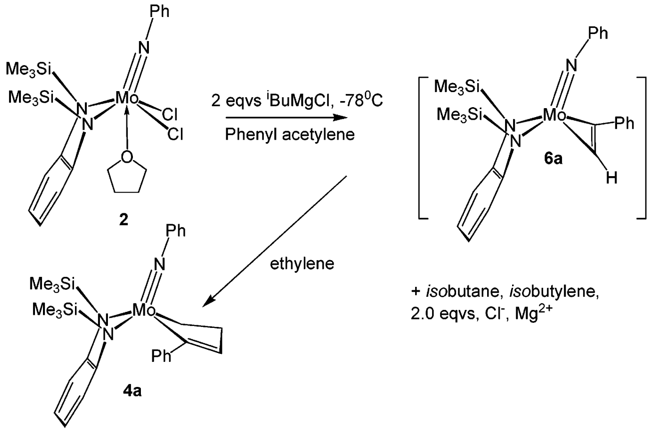
Scheme 3



The equilibrium between metallacyclopentanes and bis(ethylene) complexes has been extensively studied.[37−43] It has been demonstrated in our laboratories that heating **1** in the presence of a Lewis base (PMe_3) results in the formation of the ethylene complex **5** as a phosphine adduct (Scheme 2).[1,4] These results suggest that **1** is a precursor to the ethylene complex **3a** and that this complex can be trapped in the presence of Lewis bases.

Complex **3a** can also be generated from the dichloride complex **2** and ethylmagnesium chloride, as outlined in Scheme 3. We have successfully isolated olefin complexes using this method in the past.[58,59] This ethylene complex can be trapped in the presence of donor ligands such as PMe_3 and acetylenes. This strategy was employed to synthesize the metallacyclopentene complex **4b** as a single isomer. The resonances for the metallacycle fragment for this compound were observed as eight-line patterns at 3.70, 3.38 (2H overlapping), and 1.35 ppm in the ^1H NMR spectrum. The vinylic proton from the acetylene ligand was observed downfield at 8.47 ppm. In addition, two peaks were observed for the $SiMe_3$ resonances at 0.43 and 0.40 ppm. The strategy employed in Scheme 3 takes advantage of the steric environment around the metal center to promote the stereoselective formation of the metallacycle. Phenylacetylene adds to **3a** in a manner that minimizes the interaction between the phenyl substituent and the bulky $SiMe_3$ group. This results in the phenyl substituent of the acetylene ligand binding preferentially β to the Mo center.

Scheme 4



Similarly, complex **4a** can be isolated as a single isomer by taking advantage of the steric environment around the metal center. As outlined in Scheme 4, exposure of the phenylacetylene complex [(η^2-phenylacetylene)Mo(NPh)(*o*-($Me_3SiN)_2C_6H_4$)] (**6**), generated in situ from the isobutylene complex **3b**, to ethylene results in the isolation of **4a**. The resonances for the metallacycle fragment of **4a** are observed at 3.32, 3.06, 2.74, and 1.66 ppm in the ^1H NMR spectrum. The vinylic proton is observed as a broad singlet at 6.84 ppm. Resonances for the $SiMe_3$ protons are observed as singlets at −0.06 and 0.32 ppm. In this case, ethylene couples to the less sterically hindered side of the phenylacetylene ligand, resulting in the α orientation of the phenyl substituent in the metallacycle **4a**. Although **4a** and **4b** can be synthesized separately, we have not observed any tendency for interconversion of these two isomers at room temperature over long periods of time (months).

X-ray Crystal Structure of 4b. The identity of **4b** was also confirmed by X-ray diffraction analysis. X-ray-quality crystals were obtained by slow evaporation of a diethyl ether solution of **4b**. Figure 1 shows the thermal ellipsoid plot of **4b**. Complex

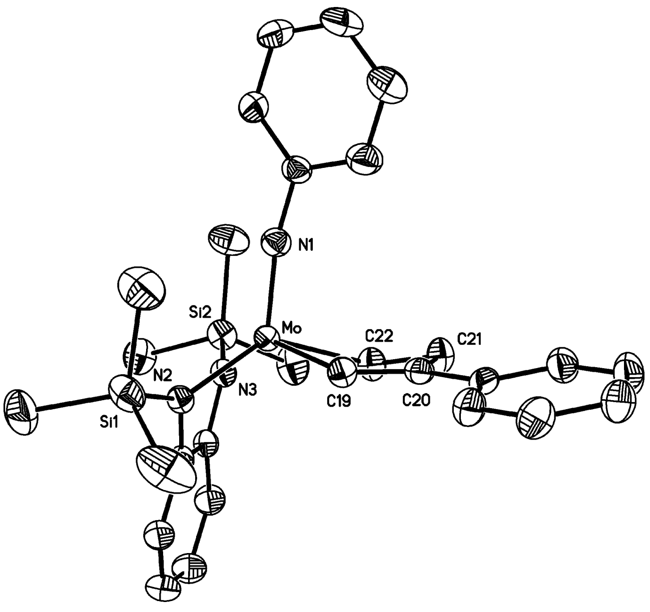


Figure 1. Thermal ellipsoid plot of **4b** (50% probability thermal ellipsoids). Selected bond lengths (Å): Mo−N(1) = 1.7305, Mo−C(19) = 2.1520(2), Mo−C(22) = 2.175(2), C(19)−C(20) = 1.344(3), C(20)−C(21) = 1.504(3), C(21)−C(22) = 1.531(3).

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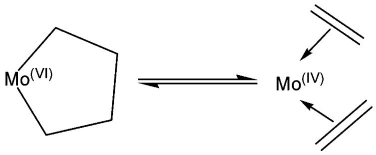
Scheme 5



4b exhibits a pseudo-square-pyramidal structure with the imido ligand occupying the apical position of the square pyramid. The Mo−N(1) bond length of 1.731(2) Å is comparable to Mo−N triple-bond lengths in the imido complexes seen in our group. The bond lengths in the metallacycle confirm the predicted arrangement of double and single bonds: i.e., the arrangement of two long C−C bonds (C(20)−C(21) = 1.504(3) Å and C(21)−C(22) = 1.531(3) Å) and one short C−C bond (C(19)−C(20) = 1.344(3) Å) confirms the metallacyclopentene description of this complex. As described for d^0 dialkyl complexes of this type, the diamide ligand is substantially folded (fold angle 135.6°); this has been attributed to donation of the diamide lone-pair electrons into a metal d orbital of appropriate symmetry. Complex **4b** represents the first example, to our knowledge, of a crystallographically characterized metallacyclopentene complex of Mo. In fact, the only other metallacyclopentene complexes that have been observed have occurred in our laboratories in the reaction of the styrene complex **3c** with diphenylacetylene.[60]

Kinetics and Mechanism of the Thermal Rerrangement of 1. The observation that heating the metallacyclopentane complex **1** can induce β-C−C bond cleavage of the metallacycle and the elimination of ethylene is consistent with the observation that metallacyclopentane complexes may exist in equilibrium with a bis(ethylene) species, as depicted in Scheme 5.

The reaction depicted in Scheme 5 represents a formal reduction of the Mo center by two electrons, as β-C−C bond cleavage reduces the metal center from Mo(VI) to Mo(IV). The syntheses of complexes **4** and **5** in Schemes 2 and 3 suggest that heat is required in order to induce β-C−C bond cleavage of the metallacyclopentane. This implies that the equilibrium depicted in Scheme 5 lies largely toward the metallacyclopentane species. To confirm the existence of this equilibrium, and to clarify the mechanism of ethylene exchange in the metallacyclopentane complex, we undertook kinetic studies for the reactions of **1** with diethyl acetylenedicarboxylate (DEAC).

The kinetics of the thermal disruption of the metallacycle of **1** in C_7D_8 were examined by following the disappearance of the $SiMe_3$ peaks of the starting material using ^{1}H NMR spectroscopy in the presence of excess DEAC. The data points were obtained by plotting the value of the integral for this peak with respect to time for more than 3 half-lives.

The temperature dependence for the conversion of **1** to **4c** was determined by following reactions of C_7D_8 solutions of **1** (0.020 M) with DEAC (1.40 M) in the NMR probe at temperatures between 335 and 356 K (three samples at each temperature). The disappearance of **1** follows first-order kinetics (Figure 2) with a rate constant at 342 K of $k = 3.3 \times 10^{-4}\ s^{-1}$ ($t_{1/2} = 2.1 \times 10^3$ s). The reaction rate is independent of the concentration of DEAC (Table 1) and the concentration of ethylene (Table 2). The energy of activation, $\Delta G^\ddagger$, corresponds to 17.5 kcal/mol at 342 K. Activation parameters (Figure 3) obtained from an Eyring plot ($\Delta S^\ddagger = R$[(intercept) − 23.76]; $\Delta H^\ddagger = -R$(slope)), for the formation of **4c** from **1** are $\Delta H^\ddagger$ = 20.5(2.3) kcal mol^{-1} and $\Delta S^\ddagger$ = −14.8(6.6) cal (mol K)$^{-1}$.

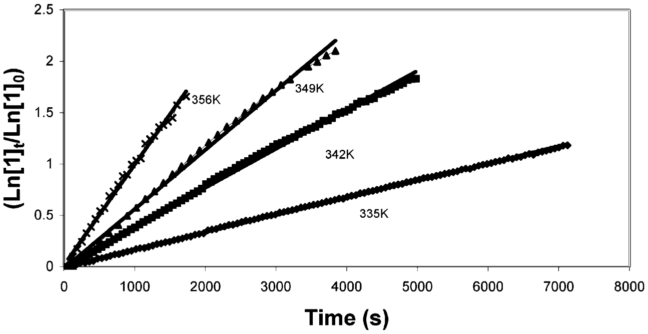


Figure 2. First-order kinetics for the formation of **4c**, where [**1**]$_t$ = concentration of **1** obtained from the value of the integral for the $SiMe_3$ peaks in the starting material at time = *t* seconds and [**1**]$_0$ = concentration of **1** obtained from the value of the integral for the $SiMe_3$ peaks of the starting material at time = 0 s.

Table 1. Dependence of DEAC on the Formation of 4c

[DEAC] (M)	rate *k* ($10^4\ s^{-1}$)	[DEAC] (M)	rate *k* ($10^4\ s^{-1}$)
0.974	3.19(4)	1.99	2.98(3)
1.44	2.86(8)	2.60	2.98(11)

Table 2. Dependence of Ethylene on the Formation of 4c

ethylene pressure (psi)	rate *k* ($10^4\ s^{-1}$)
0	2.78(8)
20	2.99(1)
30	3.06(3)

The mechanism and rate law depicted in Scheme 6 account for the observation that the formation of **4c** does not depend on the concentration of substrate (DEAC) or ethylene. The derived rate expression in Scheme 6 assumes steady-state concentrations of **1b** and **1c**. If k_3 is large and is not the rate-determining step of the reaction, then the reaction is first order in [**1**] and no dependence on [DEAC] should be observed.

The kinetic data are consistent with the proposed decomposition of the metallacyclopentane fragment via β-C−C bond cleavage to a bis(ethylene) species prior to the rate-determining step. The observed activation parameters are a combination of the elementary steps depicted in this mechanism. The negative entropy of activation, $\Delta S^\ddagger$, is consistent with the formation of a highly ordered transition state during the thermal rearrangement of **1** or the associative displacement of ethylene by solvent (C_7D_8) in the rate-determining step. The rate expression in Scheme 6 suggests there is no dependence on [DEAC] if k_3 is rapid. *Therefore, the incoming alkyne (DEAC) is not present in the rate-determining step of this reaction.*

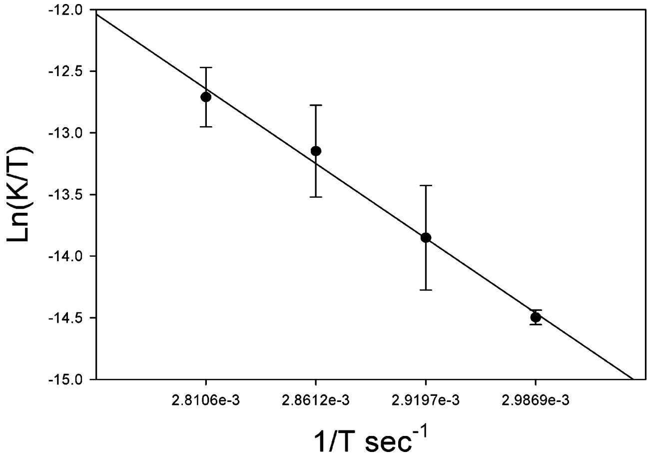


Figure 3. Eyring plot for the reaction of **1** with DEAC. Activation parameters: $\Delta H^\ddagger$ = 20.5 ± 2.3 kcal mol^{-1} and $\Delta S^\ddagger$ = −14.8 ± 6.6 cal (mol K)$^{-1}$.

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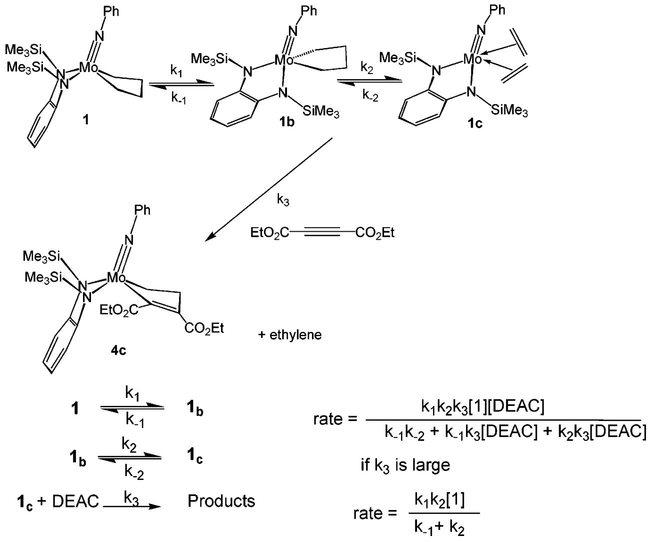
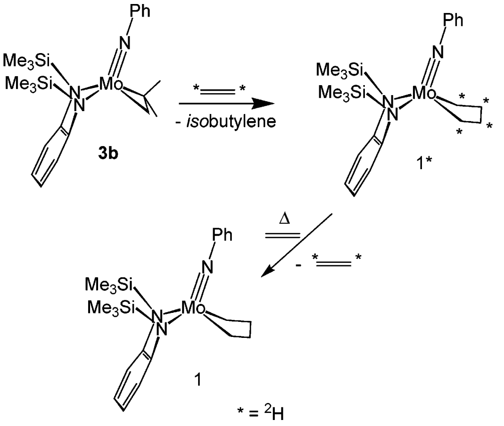
Scheme 6



Scheme 7



To probe the dependence of the reaction on substrate we examined the ethylene exchange in the metallacyclopentane complex **1***, where the metallacycle protons are fully deuterated. Complex **1*** was synthesized by methods similar to **1**, in that the isobutylene complex **3b** was treated with excess C_2D_4 (Scheme 7). The kinetics of ethylene exchange for this complex was examined by monitoring the appearance of the metallacycle ring protons in **1** over several half-lives.

We also examined the kinetics of ethylene exchange in the reaction of **1** with diphenylacetylene (DPA). As outlined in Scheme 8, heating C_7D_8 solutions of **1** (0.020 M) in the presence of excess DPA resulted in the formation of the previously reported diphenylacetylene complex [(η^2-diphenylacetylene)-Mo(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)] (**6b**) and the metallacyclopentene complex [Mo(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)(CH(Ph)CH(Ph)$(CH_2)_2$)$_4$] (**4d**). Complex **4d** was not isolated but was identified by the comparison of its ^{1}H NMR spectrum with the spectra of complexes **4a**−**c**. The kinetics of the formation of the mixture of **4d** and **6b** was observed by monitoring the disappearance of the $SiMe_3$ protons of **1** over several half-lives.

Activation parameters were also obtained for the exchange of ethylene with **1*** and the formation of **4d**/**6b** at temperatures between 335 and 356 K. As shown in Table 3, the rate constants and activation parameters for the formation of **1*** and **4d**/**6b** are similar to those found for the formation of **4c**. These data suggest that the kinetics of ethylene loss from **1** is independent of the nature of substrate and confirms the absence of substrate in the activated complex.

Scheme 8

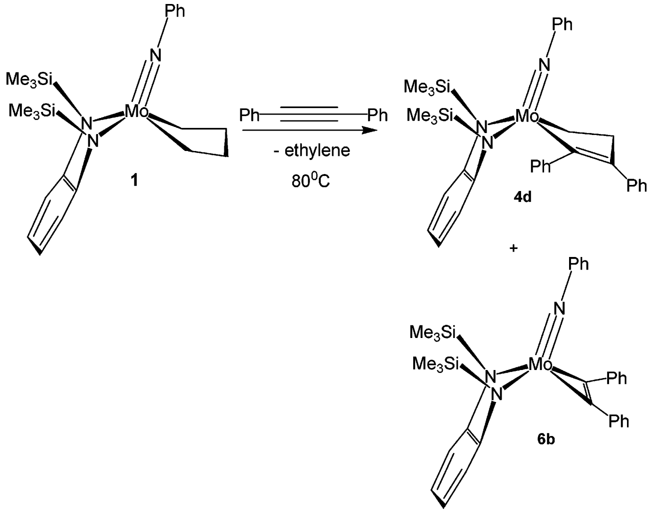


Table 3. Kinetics for the Formation of Metallacyclopentene Complexes

complex	$\Delta H^{\ddagger}$ (kcal mol^{-1})	error $\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal (mol K)$^{-1}$)	error $\Delta S^{\ddagger}$ (cal (mol K)$^{-1}$)	k(obsd) (10^4 s^{-1})
4c	20.5	2.3	−14.8	6.6	3.34
4d	18.2	1.8	−21.7	5.1	3.43
1*	18.4	2.8	−21.3	8.2	3.01

X-ray Crystal Structure of 1. The synthesis of the metallacyclopentane complex **1** has been reported;[58,59] however, X-ray structural studies on this compound were not performed at that time. An X-ray study was performed on a single crystal of **1** grown from a concentrated pentane solution at −30 °C. The thermal ellipsoid plot of **1** is depicted in Figure 4.

Complex **1** has a pseudo-square-pyramidal coordination geometry with the imido ligand occupying the apical position. The Mo−N(1) bond (1.728 Å) is within the normal range for a Mo−N triple bond. The Mo−diamide bonds Mo−N(2) and Mo−N(3) (2.010 and 2.015 Å) are also within the normal range for Mo−N single bonds. The Mo−C(13) and Mo−C(16) bonds (2.187 and 2.191 Å) are typical of Mo−C single bonds.

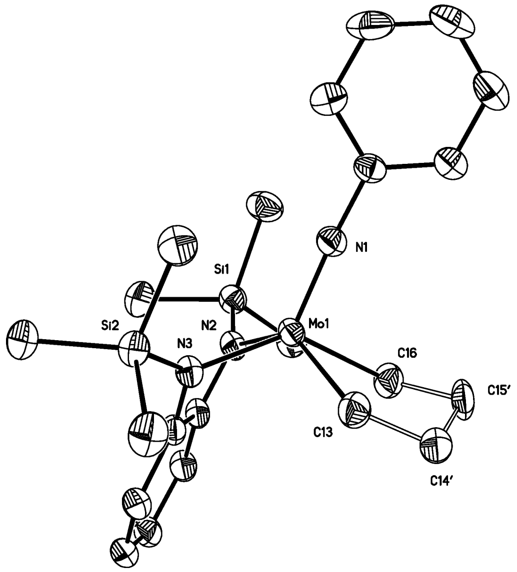
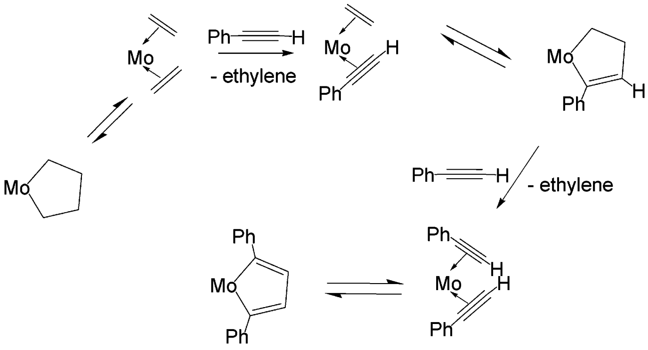
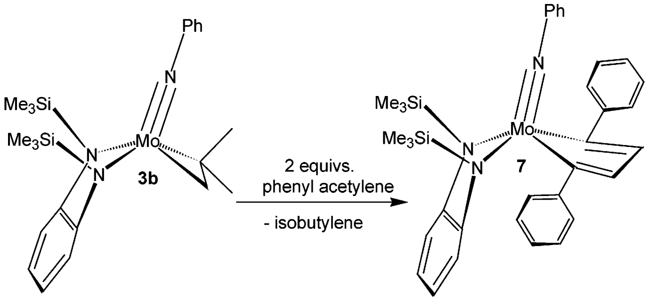


Figure 4. Thermal ellipsoid plot of **1** (50% probability thermal ellipsoids). Selected bond lengths (Å): Mo(1)−N(1) = 1.728(2), Mo(1)−N(2) = 2.010(2), Mo(1)−N(3) = 2.015(2), Mo(1)−C(13) = 2.187(2), Mo(1)−C(16) = 2.191(2).

Scheme 9



Scheme 10



Synthesis and Reactivity of a Metallacyclopentadiene Complex. Our success in synthesizing metallacyclopentenes inspired us to pursue the subsequent synthesis of metallacyclopentadiene complexes. One can envision the formation of metallacyclopentadienes from metallacyclopentenes by the sequential π ligand exchange of an ethylene molecule from a metallacyclopentene, as outlined in Scheme 9.[46] However, no β-C−C bond cleavage of the metallacyclopentenes was observed when **4** was heated at 80 °C in the presence of an alkyne for weeks.

Metallacyclopentadienes can be synthesized, however, from the [2 + 2] coupling reactions of terminal acetylenes. Thus, treatment of a pentane solution of the isobutylene complex **3b** with 2 equiv of phenylacetylene afforded the metallacyclopentadiene complex [(NPh)Mo(C(Ph)CHCHC(Ph)){*o*-($Me_3SiN)_2$-C_6H_4}] (**7**) in 40% yield (Scheme 10). The ^1H NMR spectrum of **7** showed a singlet (−0.07 ppm, 18H) for the $SiMe_3$ protons. A sharp singlet (6.46 ppm, 2H) assigned to the β-protons of the metallacycle characterizes the α,α′ orientation of the phenyl substituents. An examination of the reaction mixture revealed that small amounts of the α,β and β,β' isomers may also form during the course of this reaction. However, we were not able to isolate any of these isomers from the reaction mixture and the low yield of these complexes in this reaction prevented their complete spectroscopic characterization.

X-ray Crystal Structure of 7. Single crystals of **7** were obtained from slow evaporation of a concentrated diethyl ether solution (Figure 5). Complex **7** was found to have a pseudo-square-pyramidal geometry in which the imido group occupies an apical position. The Mo−N(1) bond length is 1.731 Å, consistent with a metal−nitrogen triple bond. The Mo−N(2) and Mo−N(3) bonds (2.008 and 2.004 Å) are consistent with Mo−N(diamide) bonds. The Mo−C(22) and Mo−C(19) bonds are within the range for Mo−C(sp^2) bonds. The bond lengths within the metallacycle reflect the localization expected for a metallacyclopentadiene fragment: i.e., two short C−C bonds (C(19)−C(20) = 1.335 Å and C(21)−C(22) = 1.339 Å) and one long C−C bond (C(20)−C(21) = 1.455 Å).

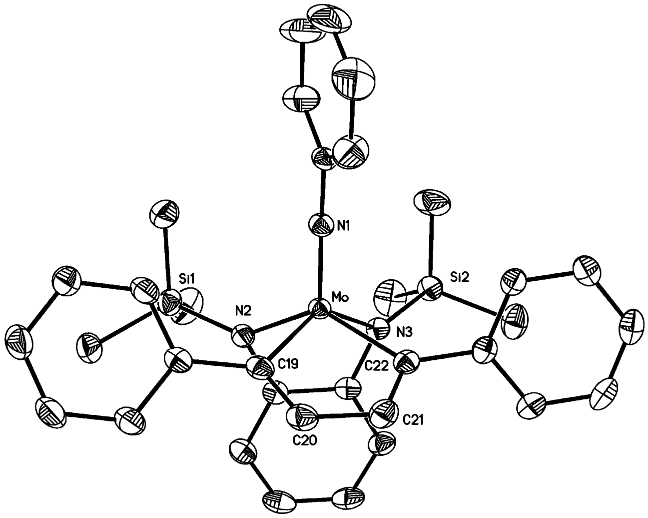
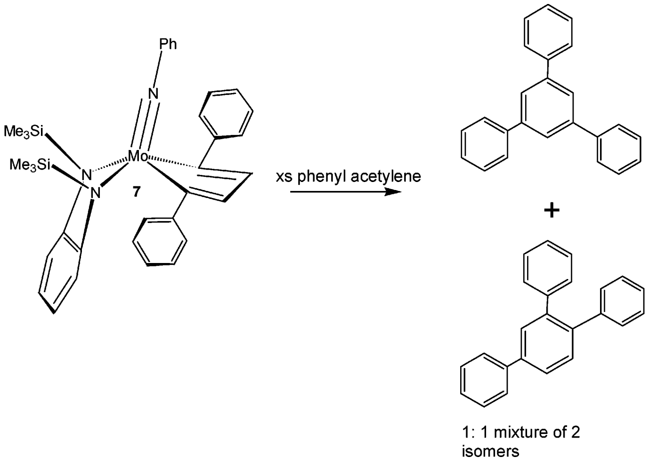


Figure 5. Thermal ellipsoid plot of **7** (50% probability thermal ellipsoids). Selected bond lengths (Å): Mo−N(1) = 1.731(2), Mo−N(2) = 2.008(2), Mo−N(3) = 2.002(2), Mo−C(19) = 2.197(3), Mo−C(22) = 2.188(3), C(19)−C(20) = 1.335(4), C(20)−C(21) = 1.455(4), C(21)−C(22) = 1.339(4).

Scheme 11



Metallacyclopentadiene complexes have been implicated as important intermediates in the cyclotrimerization of acetylenes.[12−33,57,61] When **7** (0.008 mmol) was allowed to react in an NMR tube with excess phenylacetylene (1.56 mmol) at 80 °C for 24 h, a 50:50 mixture of two cyclotrimerized products, 1,2,4-triphenylbenzene and 1,3,5-triphenylbenzene, was produced (Scheme 11; as identified by mass spectrometry). There is no evidence of the formation of poly(phenylacetylene) in this reaction. Thus, there is good chemoselectivity toward cyclotrimerization but essentially no regioselectivity of the benzene isomers that are formed. We are currently investigating the utility of **7** as a potential cyclotrimerization catalyst.

Summary and Conclusions

This work is a continuation of our studies on the effect of the ancillary ligand {*o*-($Me_3SiN)_2C_6H_4$}$^{2-}$ on the properties and reactivity of group 6 imido complexes. We have demonstrated again that diamide donation in these complexes has a profound effect on the reactivity and stability of this family of compounds. This allows us to access chemistry that is usually associated

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[61] Smith, D. P.; Strickler, J. R.; Gray, S. D.; Bruck, M. A.; Holmes, R. S.; Wigley, D. E. *Organometallics* **1992**, *11*(3), 1275−1288.

with late transition metals, as π donation by the ligands attenuates the high charge of the species encountered. Molybdenum metallacycles have been proposed as intermediates in olefin metathesis reactions, and specifically metallacyclopentane species have been observed as decomposition products of group 6 alkylidenes.[5,12] An understanding of the chemistry of these species is therefore important in the development of metathesis catalysis involving terminal olefins, where ethylene may form during the reaction.

Experimental Section

All operations were conducted under an inert atmosphere using standard Schlenk techniques or in a nitrogen-filled drybox. Diethyl ether, pentane, toluene, and tetrahydrofuran were distilled under nitrogen from sodium or sodium benzophenone ketyl, stored over molecular sieves, and degassed prior to use. Ethylene was predried by passing the gas through a column of molecular sieves. NMR spectra were recorded on Varian (300 MHz) Gemini300, VXR300, and Mercury300 instruments. Chemical shifts were referenced to the residual protons in the deuterated solvents and are reported in ppm relative to TMS. Elemental analyses were performed by Complete Analysis Laboratories Inc., Parsipanny, NJ.

[(NPh)Mo(C(Ph)C(H)CH$_2$CH$_2$)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)] (4a). In a sealed ampule, a pentane solution of **3a** (0.500 g, 1.013 mmol) was frozen and evacuated. The vessel was then cooled and the mixture thawed. The neck of the vessel was flushed with dry ethylene for 3 min. Ethylene gas was then added (15 psi) to the solution, and the mixture was stirred for 12 h. The volume was reduced in vacuo and the temperature lowered to −78 °C. Orange crystals of **4a** quickly precipitated from solution and were isolated in 80% yield. ^{1}H NMR (C$_6$D$_6$): δ −0.07 (s, 9H, SiMe$_3$), 0.33 (s, 9H, SiMe$_3$), 1.66 (dt, 1H, J = 11.8, 5.9 Hz), 2.74 (dddd, 1H, J = 17.9, 7.2, 5.1, 2.8), 3.05 (dddd, 1H, J = 17.6, 7.2, 6.6, 2.3 Hz), 3.32 (dddd, 1H, J = 11.7, 5.4, 2.7, 0.9 Hz), 6.84 (t, 1H, J = 2.4 Hz), 6.87−7.55 (aromatic), 7.24 (dd, 1H, phenyl ortho proton, J = 8.5, 1.5 Hz), 7.33 (dd, 1H, *o*-phenylenediamine proton, J = 8.0, 1.6 Hz), 7.37 (dd, 1H, *o*-phenylenediamine proton, J = 8.0, 1.6 Hz), 7.54 (dd, 1H, phenylimido ortho proton, J = 8.4, 1.3 Hz). ^{13}C NMR: δ 1.1, 1.5, 40.1, 56.5, 122.7, 125.0, 125.4, 122.8, 126.0, 126.5, 127.4, 129.4, 132.6, 135.1, 151.8, 157.2, 158.0, 188.6. Anal. Calcd for C$_{28}$H$_{37}$MoN$_3$Si$_2$: C, 59.24; H, 6.57; N, 7.40. Found: C, 58.97; H, 6.73; N, 7.65.

[(NPh)Mo(C(H)C(Ph)CH$_2$CH$_2$)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)] (4b). Method 1. A purple Et$_2$O solution of **2** (3.00 g, 5.17 mmol) was cooled to −78 °C and treated with 5.17 mL of EtMgCl$_2$ (2.0 M solution in Et$_2$O). An immediate color change from purple to red occurred, and the solution was stirred at −78 °C for 30 min. Phenylacetylene (0.52 mL, 6.20 mmol) was then added, and the solution was warmed to room temperature. The solution was stirred overnight, and the solvent was then removed in vacuo. Complex **4b** was then extracted with a toluene/pentane solution. The solvent was removed in vacuo, and a red solid was obtained. Washing this solid with cold pentane afforded **4b** in 40% yield.

Method 2. In a sealed ampule a toluene solution of **1** (0.50 g, 1.013 mmol) was heated for 12 h at 72 °C with phenylacetylene (0.27 mL, 1.21 mmol). The vessel was then cooled and the toluene removed in vacuo to afford an orange solid that consisted of a mixture of **4b** (20%) and **4a** (80%). The orange solid was then dissolved in pentane and recrystallized at −78 °C to afford **4b**. ^{1}H NMR (C$_6$D$_6$): δ 0.40 (s, 9H, SiMe$_3$), 0.43 (s, 9H, SiMe$_3$), 1.34 (dt, 1H, J = 12.2, 6.1 Hz), 3.35 (ddd, 1H, J = 11.9, 6.1, 1.2 Hz), 3.41 (ddd, 1H, J = 16.8, 7.2, 1.4 Hz), 3.70 (dddd, 1H, J = 17.1, 8.2, 6.0, 2.3 Hz), 6.82 (tt, 1H, phenylimido para proton, J = 7.4, 1.2 Hz), 6.99−7.14 (ov, mult, 7H), 7.36−7.46 (ov, mult, 4H), 7.54 (dt, 2H, phenylimido ortho proton, J = 7.2, 1.8 Hz), 8.47 (d, 1H, vinylic proton, 2.5 Hz). ^{13}C NMR (C$_7$D$_8$): δ 1.4, 42.8, 56.0, 122.8, 123.7, 125.9, 125.6, 126.0, 126.2, 126.4, 127.5, 129.2, 135.0, 135.2, 141.2, 147.8, 158.1, 168.5, 172.0. Anal. Calcd for C$_{30}$H$_{42}$MoO$_{0.5}$N$_3$Si$_2$: C, 59.58; H, 6.95; N, 6.95. Found (this molecule was isolated with $^1/_2$ molecule of diethyl ether): C, 60.68; H, 6.76; N, 6.93.

Table 4. Kinetic Analysis for the Reaction of DEAC with 1[a]

T (K)	k(run #1) (10^4 s^{-1})	k(run #1) (10^4 s^{-1})	k(run #1) (10^4 s^{-1})
355.8	9.81	10.6	11.9
349.5	5.78	7.02	7.72
342.5	3.79	3.49	2.73
334.8	1.67	1.67	1.74

[a] Eyring plot analysis: $\Delta S^{\ddagger} = -14.7 \pm 3.0$ cal (K mol)$^{-1}$; $\Delta H^{\ddagger} = 20.5 \pm 1.0$ kcal mol^{-1}.

[(NPh)Mo(C(CO$_2$Et)C(CO$_2$Et)CH$_2$CH$_2$)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)] (4c). A toluene solution of **1** (0.521 g, 1.06 mmol) was heated for 12 h at 72 °C with diethyl acetylenedicarboxylate (0.186 mL, 1.16 mmol) in a sealed ampule. The vessel was then cooled and the toluene removed in vacuo to afford an orange solid of **4c**. The orange solid was then dissolved in pentane and recrystallized at −78 °C to afford **4c** as an orange solid in 62% yield. ^{1}H NMR (C$_6$D$_6$): δ 0.30 (s, 9H, SiMe$_3$), 0.33 (s, 9H, SiMe$_3$), 0.87 (t, 3H, CH$_3$, J = 7.1 Hz), 1.17 (m, 1H, metallacycle proton), 1.27 (t, 3H, CH$_3$, J = 7.1 Hz), 3.09 (ddd, 1H, J = 15.8, 6.1, 3.8 Hz, metallacycle proton), 6.81 (m, 1H, phenylimido para proton), 7.00 (overlapping multiplets, 4H, *o*-pda protons and phenylimido meta protons), 7.20 (d, 1H, J = 7.9 Hz, *o*-pda proton), 7.58 (d, 1H, J = 7.4 Hz, phenylimido ortho proton), 7.67 (d, 1H, J = 8.2 Hz, *o*-pda proton). ^{13}C NMR (C$_7$D$_8$): δ 184.1, 176.1, 164.2, 157.9, 150.1, 134.3, 130.6, 128.2, 128.9, 127.8, 127.7, 126.4, 125.6, 122.0, 60.3, 60.1, 53.7, 41.2, 14.8, 14.5, 1.43. Anal. Calcd for C$_{28}$H$_{41}$MoN$_3$OSi$_2$: C, 52.9; H, 6.50; N, 6.61. Found: C, 52.86; H, 6.24; N, 6.90.

[(NPh)Mo(C(Ph)CHC(Ph))(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)] (7), Phenylacetylene (0.90 mL, 4.06 mmol) was added to a pentane solution of 1.00 g (2.03 mmol) of **3b**, with stirring. An immediate color change from green to yellowish brown occurred. The reaction mixture was stirred for $^1/_2$ h, after which the solution was concentrated by removal of the solvent in vacuo. Cooling to −78 °C resulted in the appearance of brown crystals of **7** in 40% yield. ^{1}H NMR (C$_6$D$_6$): δ −0.07 (s, 18H, SiMe$_3$), 6.48 (s, 2H, metallacycle), 6.85−7.78 (aromatic). ^{13}C NMR (C$_6$D$_6$): 1.3, 124.7, 125.9, 126.6, 127.4, 129.5, 130.7, 142.2, 154.2, 192.7. Anal. Calcd for C$_{34}$H$_{39}$MoN$_3$Si$_2$: C, 63.63; H, 6.12; N, 6.55. Found: C, 62.74; H, 6.24; N, 6.61.

Kinetic Studies. NMR tube samples were prepared by dissolving **1** (ca. 10 mg, 0.020 mmol) and mesitylene (13.88 μL), added as an internal standard, in 1.0 mL of C$_7$D$_8$ in the glovebox. Diethyl acetylenedicarboxylate was added to the NMR tube, and the tube was then capped. The concentration of DEAC was obtained by plotting the values of the integral for the DEAC ethyl group for known concentrations of DEAC versus the integrals for the CH$_3$ protons of mesitylene. The NMR probe was equilibrated to the desired temperature, and the sample was then loaded into the probe. Approximately 120 spectra were recorded over the duration of 3 half-lives. The value of the integral for the SiMe$_3$ protons of the starting material was recorded for each spectrum. The observed rate constants were obtained by plotting ln(integral) vs time. Three samples were performed at each temperature, and the rate constants reported were the average of three runs. Activation parameters were obtained by measuring the rate constants at four different temperatures. A plot of ln(k/T) vs 1/T (K), results in a line with a slope of $-\Delta H^{\ddagger}/R$ and an intercept of $\Delta S^{\ddagger}/R + 23.76$. Reported errors in the rate constants represent the standard deviation from the least-squares fit of the experimental data. Reported errors in the activation parameters are obtained from all experimental data (12 points in the Eyring plot), using 2σ. Data for these studies are given in Table 4.

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Supporting Information Available: Text giving full details for experimental procedures and crystallographic data for compounds **1**, **4b**, and **7** and CIF files giving tables of crystal data and data collection parameters, atomic coordinates, anisotropic displacement parameters, and all bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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