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# Molybdenum and Tungsten Alkylidene and Metallacyclobutane Complexes That Contain a Dianionic Biphenolate Pincer Ligand

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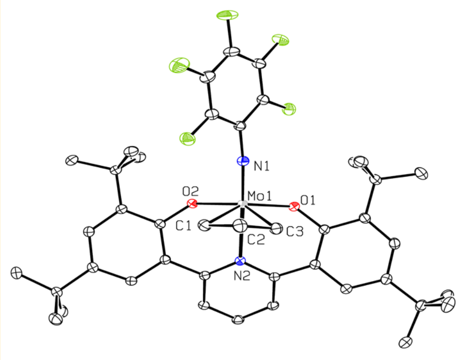
S *Supporting Information*

**ABSTRACT:** Molybdenum imido alkylidene and tungsten oxo alkylidene complexes that contain a tridentate "pincer" $[ONO]^{2-}$ ligand have been prepared and treated with ethylene to give unsubstituted metallacyclobutane complexes that have a 16e count. Both Mo and W metallacyclobutane complexes exchange $C_2D_4$ into the metallacyclobutane ring at 22 °C at a rate that is first order in metal and zero order in $C_2D_4$. These metallacycles lose ethylene at least $10^4$−$10^5$ times slower than reported 14e unsubstituted Mo and W metallacyclobutane complexes that have been explored in the literature that have a TBP geometry with the metallacyclobutane ring bound in the equatorial positions. Our studies suggest that breaking up the metallacyclobutane ring in these 16e $d^0$ Mo or W complexes is slow because a 14e TBP metallacyclobutane complex cannot be accessed readily.



Alkylidene complexes of molybdenum and tungsten with the formula M(Z)(CHR)(X)(Y), where X and Y are monodentate monoanionic ligands and Z is an imido (M = Mo, W) or oxo (M = W) ligand, have been explored extensively as initiators for the controlled metathesis of olefins.[1] If X and Y are not strong $\pi$-bonding ligands and Z (NR or O) is, then M(Z)(CHR)(X)(Y) complexes have a 14-electron count at the metal and 14e five-coordinate trigonal-bipyramidal metallacyclobutane complexes made from them upon addition of olefin are the key intermediates in the metathesis reaction.[1,2] In a recent investigation of $W(O)(CHR)(OAryl)_2(L)$ complexes (where L is a phosphine or acetonitrile) for ring-opening metathesis polymerization[3] it was found that 16e $W(O)(CHR)(OAryl)_2(L)$ complexes behave as initiators for ROMP to give polymers that are highly biased toward *cis,isotactic* structures, while 14e $W(O)(CHR)(OAryl)_2$ analogues yield polymers that are highly biased toward *cis,syndiotactic* structures. These results suggest that the presence of the 2e donor (L) changes the selectivity of the ROMP reaction. Fischer reported[4] that Mo alkylidyne complexes that contain the $[ONO]^{2-}$ "pincer" ligand shown in Figure 1[5] are efficient catalysts for the living ring-opening polymerization of cyclooctynes at 90 °C; the initiators are essentially inactive at 22 °C. In response to the above findings we became interested in preparing and exploring 16e imido alkylidene complexes that contain the $[ONO]^{2-}$ ligand shown in Figure 1. Coordination of the pyridyl nitrogen should essentially guarantee that a 16e count is maintained throughout the metathesis process.

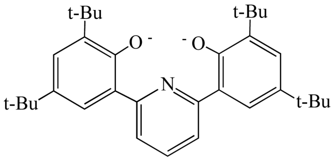
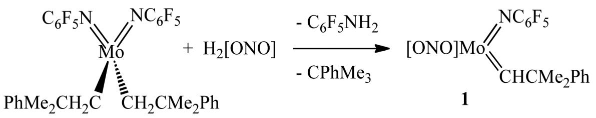


**Figure 1.** $[ONO]^{2-}$ ligand.

The reaction between $Mo(NC_6F_5)_2(CH_2CMe_2Ph)_2$ and $H_2[ONO]$ in benzene at 60 °C (12 h) led to the formation of $C_6F_5NH_2$, $CPhMe_3$, and $Mo(NC_6F_5)(CHCMe_2Ph)(ONO)$ (**1**) as the only products (eq 1), according to NMR data; **1** could be isolated in only ~30% yield starting with 0.30 g of $Mo(NC_6F_5)_2(CH_2CMe_2Ph)_2$, as a consequence of its relatively high solubility in pentane. This is the only example of forming an imido alkylidene complex employing a (bi)phenol as an acid whose p$K_a$ is not as low as that for $C_6F_5OH$. Pentafluorophenol has been employed to protonate the *tert*-butylimido ligand in $Mo(N\text{-}t\text{-}Bu)_2(CH_2CMe_3)_2$ to yield $Mo(N\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OC_6F_5)_2(NH_2\text{-}t\text{-}Bu)$ and neopentane,[6,7] but protonation of a pentafluorophenylimido nitrogen in compounds of this general type also was not known.



(1)

An X-ray structure of $Mo(NC_6F_5)(CHCMe_2Ph)(ONO)$ shows it to be essentially a square pyramid (Figure 2), in which the neophylidene ligand is in the apical position and in a *syn* orientation (in which the substituent points toward the imido nitrogen atom). The N−Mo−N2 angle is 140.86(7)°, the O−Mo−O angle is 153.38(5)°, and the Mo═N−C angle is

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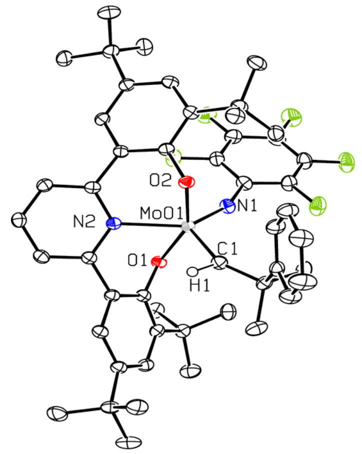


**Figure 2.** Thermal ellipsoid drawing (50% probability) of **1**. The solvent and all hydrogens except H1 were omitted for clarity.

159.10(16)°. The neophylidene ligand has a relatively large Mo−C1−C2 angle (150.68(15)°) and a small Mo−C1−H1 angle (96.1(5)°). The value for $^1J_{CH}$ (120 Hz) is typical for a syn alkylidene isomer.[1a,f,8]

An attempt to prepare **1** in a reaction between $Li_2ONO$ and $Mo(NC_6F_5)(CHCMe_2Ph)$(1,2-dimethoxyethane)$(OTf)_2$ led to formation of $Mo(NC_6F_5)(CHCMe_2Ph)(ONO)(OTf)(DME)(Li)$ (**1**(LiOTf)). An X-ray structural study shows **1**(LiOTf) to be essentially an octahedral complex in which triflate is bound to the metal and the lithium ion is coordinated to dimethoxyethane and the two $[ONO]^{2-}$ oxygen atoms (Figure 3). This circumstance forces the $[ONO]^{2-}$ ligand to be in an unusual *fac* configuration with the O1−Mo−O2 angle being 79.65(5)°. (The $[ONO]^{2-}$ ligand is close to a *mer* geometry in all previously reported octahedral complexes.[4,5]) The N1−Mo−O1 and N1−Mo−O2 bond angles are both 76.65(6) and 76.55(6)°, respectively, and the Mo−O1 and Mo−O2 bond lengths (2.2442(15) and 2.1175(14) Å, respectively) are significantly longer than the Mo−O bond distances (1.988 and 2.001 Å) found in the octahedral molybdenum alkylidyne complex reported by Fischer et al.[4] Recrystallization of **1**(LiOTf) from toluene and pentane multiple times yields **1**, which confirms that LiOTf is lost readily from **1**(LiOTf) in $C_6D_6$ at 22 °C.

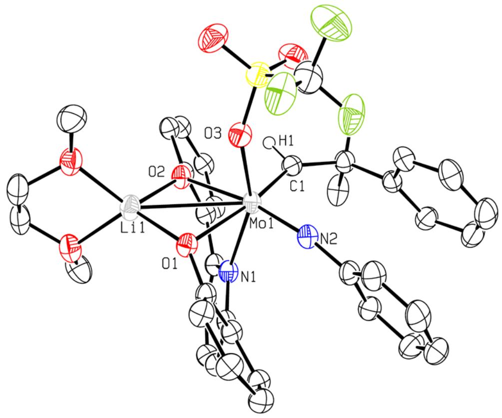


**Figure 3.** Thermal ellipsoid drawing (50% probability) of **1**(LiOTf). The solvent, several atoms, and several *tert*-butyl groups were omitted in order to reveal other details.

Compound **1** reacts slowly with ethylene (1 atm) over a period of 4 h at 22 °C to yield the six-coordinate unsubstituted metallacyclobutane complex $Mo(NC_6F_5)(CH_2CH_2CH_2)(ONO)$ (**2**) instead of the five-coordinate methylidene complex $Mo(NC_6F_5)(CH_2)(ONO)$ that we expected. An X-ray structure of **2** (Figure 4) showed that N1 and N2 are essentially *trans* to one another (178.40(5)°), the O1−Mo−O2 angle is 122.71(4)°, and the Mo−N2 distance is 2.3769(11) Å.

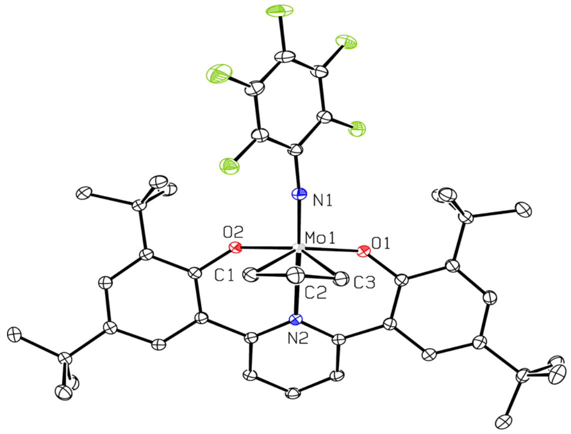


**Figure 4.** Thermal ellipsoid drawing (50% probability) of **2**. The solvent and all of the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−C(1) = 2.2037(14), Mo(1)−C(3) = 2.1948(14), C(1)−C(2) = 1.519(2), C(2)−C(3) = 1.517(2); O(1)−Mo(1)−O(2) = 122.71(4), N(1)−Mo(1)−N(2) = 178.40(5), C(1)−Mo(1)−C(3) = 62.14(5), C(1)−C(2)−C(3) = 96.77(11).

Complex **2** is one of four unsubstituted molybdacyclobutane complexes to be isolated; the other three are five-coordinate TBP complexes that contain the 2,6-diisopropylphenylimido ligand (NAr), and only one of the three, $Mo(NAr)(C_3H_6)(Me_2Pyr)(OBitetBr_2)$,[9] has been characterized in an X-ray study. As far as we are aware, the only other six-coordinate Mo or W metallacyclobutane complex in this family is $W[CH(t\text{-}Bu)CH_2CH(CO_2Me)](NAr)[OCMe_2(CF_3)]_2$,[10] in which the carbonyl oxygen in the carbomethoxy group is bound weakly to the metal *trans* to the imido nitrogen with the W−O distance being 2.37(6) Å (cf. Mo−N2 = 2.3769(11) Å in **2**). Other square-pyramidal metallacyclobutane complexes in this class of Mo or W complexes that have been characterized structurally include five-coordinate $W(NAr)[CH_2CH(t\text{-}Bu)CH_2][OCMe_2(CF_3)]_2$,[11] $W(O)(C_3H_6)(OHMT)[OSi(t\text{-}Bu)_3]$ (OHMT = O-2,6-$(2,4,6\text{-}Me_3C_6H_2)_2C_6H_3$),[12] and a trisubstituted metallacycle formed through addition of 5,6-bis(trifluoromethyl)norbornadiene to $W(NAr)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$.[13] The metallacyclobutane ring in **2** and in SP metallacycles are all somewhat bent with M−$C_\beta$ distances of ∼2.78 Å, and other angles and bond distances are distinctly different from what they are in TBP metallacycles (Figure 5).[1a,f,2] It has been proposed that five-coordinate TBP metallacycles are the crucial intermediates in metathesis reactions; the M−$C_\beta$ distances are relatively short (2.3−2.4 Å; see Figure 5), and the olefin is therefore able to be lost readily via what could be described as a transition state with a significant degree of olefin/alkylidene character.[2,14,15] One five-coordinate tungstacyclobutane complex has been observed in the solid state in which the distorted $WC_3$ ring spans apical and basal positions and appears to be on its way to losing ethylene.[16]

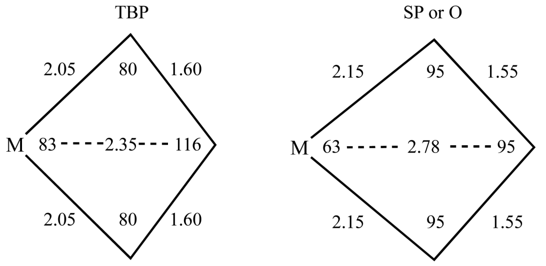
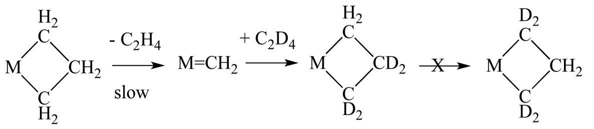


**Figure 5.** Approximate distances (Å) and angles (deg) in metallacyclobutane rings in TBP versus SP or octahedral complexes.

Compound **2** decomposes slowly in $C_6D_6$ at room temperature in the absence of ethylene to yield what we propose to be the ethylene complex $Mo(NC_6F_5)(CH_2CH_2)(ONO)$ (**3**) and free ethylene; no propylene, the product that would be formed through rearrangement of the metallacycle, is observed in the proton NMR spectrum. We propose that **2** loses ethylene slowly to give $Mo(NC_6F_5)(CH_2)(ONO)$. Bimolecular coupling of the methylidene ligands in $Mo(NC_6F_5)(CH_2)(ONO)$, possibly via a bis-$\mu$-methylidene bimetallic complex,[17] then leads to **3** in the presence of the 1 equiv of ethylene that was lost from **2**. Bimolecular decomposition of $d^0$ methylidene complexes, first observed in 18e $Cp_2Ta(CH_2)Me$,[18] is relatively common, although some 14e molybdenum and tungsten imido methylidene complexes are relatively stable and have been structurally characterized.[14,19] $Mo(NC_6F_5)(CH_2)(ONO)$ is not observed under the conditions where **2** decomposes, which suggests that bimolecular coupling is fast relative to the rate of loss of ethylene from **2**. Decomposition of **2** at elevated temperatures leads to mixtures that contain decomposition products other than **3** and, therefore, to significantly lower yields of **3**.

Exchange of $C_2D_4$ into **2** at 760 mmHg partial pressure in $C_6D_6$ at 22 °C can be observed by following the disappearance of one of the $H_\beta$ resonances in the proton NMR spectrum of **2**. The $H_\beta$ resonance in **2** in solution under 760 mm of Hg partial pressure of $C_2D_4$ disappears at a rate that depends to the first order on the concentration of **2** with $k = 8.8 \times 10^{-5}\ s^{-1}$. The result under 380 mmHg partial pressure of $C_2D_4$ is $7.5 \times 10^{-5}\ s^{-1}$, which suggests that the two rate constants are the same ($3\sigma = 1.9 \times 10^{-5}$) and that the rate-limiting step is loss of ethylene from **2** to give the intermediate $Mo(NC_6F_5)(CH_2)(ONO)$. The first-order disappearance of an $H_\beta$ resonance also suggests that **2**-$d_4$($\alpha$-$CH_2$) does not rearrange intramolecularly to give **2**-$d_4$($\beta$-$CH_2$) before $D_2C{=}CH_2$ is lost from **2**-$d_4$($\alpha$-$CH_2$) to give **2**-$d_6$ (eq 2) in the presence of $C_2D_4$. It is worth noting that the rate constant for loss of *tert*-butylethylene from square-pyramidal $W(NAr)[CH_2CH(t\text{-}Bu)CH_2][OCMe_2(CF_3)]_2$ at 23.7 °C is $7.6 \times 10^{-4}\ s^{-1}$,[20] which is 1 order of magnitude faster than loss of ethylene from **2**.



(2)

**2**-d4(α-CH2) **2**-d4(β-CH2)

We turned to tungsten oxo chemistry and encountered a second example of an unusually stable metallacyclobutane. The reaction between $Li_2[ONO]$ and tungsten oxo complexes of the type $W(O)(CHCMe_2Ph)L_2Cl_2$, where L = $PMePh_2$, $PMe_2Ph$, $PMe_3$, leads to complexes of the type $W(O)(CHCMe_2Ph)(ONO)(L)$ (**4**($PMePh_2$), **4**($PMe_2Ph$), and **4**($PMe_3$), respectively). The phosphine ligand in all three complexes rapidly dissociates to a significant extent in solution, and the alkylidene $CH_\alpha$ resonances at 22 °C consequently are relatively broad in the $^1H$ NMR spectrum and do not show resolved coupling to $^{31}P$. All **4** complexes also react readily with ethylene (1 atm) to give the phosphine-free metallacyclobutane complex $W(O)(CH_2CH_2CH_2)(ONO)$ (**5**), which can be isolated in 55−75% yield as a consequence of its relatively low solubility in pentane. Proton and carbon NMR spectra of **5** show the metallacyclobutane proton and carbon resonances in essentially the same positions as in **2**, which suggest that the structure of **5** is analogous to that of **2**.

The exchange of $C_2D_4$ into the metallacycle in **5** was also found to be first order in metal and zero order in $C_2D_4$ at 760 and 380 mmHg partial pressures of $C_2D_4$. However, the rate constants ($k = 8 \times 10^{-6}$ and $10 \times 10^{-6}\ s^{-1}$, respectively) are approximately one order of magnitude smaller in **5** than in **2**, and the half-life is approximately 21 h for exchange of $C_2D_4$ into **5** versus 2.4 h for exchange of $C_2D_4$ into **2**.

Loss of ethylene from 16e **2** and **5** is dramatically slower than the rate of loss of ethylene from 14e unsubstituted TBP metallacyclobutane complexes that have been explored through NMR methods.[14] Rate constants for loss of ethylene from molybdacyclobutane complexes are $>10\ s^{-1}$. The rate of loss of ethylene from **2** is at least $10^4$ times slower and the rate of loss of ethylene from **5** is at least $10^5$ times slower than loss of ethylene from observable TBP molybdacycles in the literature.[1a,f] There is some evidence from experimental studies,[14,15] but little from theoretical studies,[2] for an alkylidene/olefin transition state in forming a high-oxidation-state Mo or W metallacyclobutane complex or losing an olefin from a metallacyclobutane complex. The studies reported here provide convincing evidence that access to what is close to an alkylidene/olefin transition state is crucial to the olefin metathesis process and that 14e TBP intermediates are close to that transition state. An inability to access the 18e alkylidene/olefin state is a viable explanation as to why the metallacycles in **2** and **5** are not *destabilized* in the presence of the pyridine donor but in fact *stabilized* toward loss of olefin, which is contrary to what we expected. Because there is no evidence for rearrangement of **2**-$d_4$($\alpha$-$CH_2$) to **2**-$d_4$($\beta$-$CH_2$) in **2** and **5** (eq 2), ethylene must be lost faster than the metallacycle can re-form from any alkylidene/olefin intermediate. This circumstance has also been observed in NMR studies of TBP metallacycles where ethylene loss is fast.[14] Rearrangement of an SP complex to a TBP complex provides an *indirect* pathway for loss of olefin, but in six-coordinate **2** and **5** the metallacyclobutane ring is effectively "locked" in a pseudooctahedral form.

Preliminary experiments with **2** and **5** have shown that they are extremely slow catalysts for the metathesis of ordinary olefins and even polymerization of norbornene, at 22 °C, as one would expect on the basis of the ethylene exchange reactions that have been observed here. The room-temperature results did not eliminate the possibility that 16e complexes such as **2** and **5** could be useful for olefin metathesis at high temperatures, especially if both bimolecular decomposition and metallacyclobutane rearrangement to an olefin are slower relative to the rate of olefin metathesis. However, at loadings of 5 mol % of **2** homocoupling of 1-hexene progresses to only 28% conversion to 5-decene over 4 days at room temperature

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and to 24% conversion at 50 °C over 24 h. Catalyst **5** in similar experiments gives 20% conversion to 5-decene over 4 days at room temperature and 7% conversion at 50 °C over 24 h. Both catalysts also decompose in the 50 °C experiments.

The results presented here suggest that a 2e donor can block loss of an olefin from a metallacycle. An important remaining question then is as follows: how can a donor ligand dramatically alter the course of facile metathesis reactions?[3,21] A clue may lie in the finding that donor ligands also can catalyze rearrangement of four-coordinate alkylidene complexes through formation of five-coordinate adducts, as has been observed for diasteromers of four-coordinate imido alkylidene complexes that contain a stereogenic metal center.[22] Studies aimed toward answering questions concerning the role of donor ligands (including solvents) are being addressed.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00976.

Crystallographic data for **1** (CIF)
Crystallographic data for **1**(LiOTf) (CIF)
Crystallographic data for **2** (CIF)
Experimental details for the synthesis of all compounds and a description of the X-ray structural studies (PDF)

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### Notes

The authors declare no competing financial interest.

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