ORGANOMETALLICS

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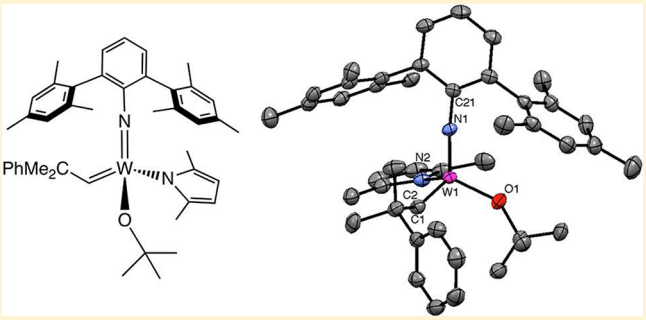
Molybdenum and Tungsten Monoalkoxide Pyrrolide (MAP) Alkylidene Complexes That Contain a 2,6-Dimesitylphenylimido Ligand

Laura C. H. Gerber, Richard R. Schrock,* and Peter Müller

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: Molybdenum and tungsten bispyrrolide alkylidene complexes that contain a 2,6-dimesitylphenylimido (NAr*) ligand have been prepared, in which the pyrrolide is the parent pyrrolide or 2,5-dimethylpyrrolide. Monoalkoxide pyrrolide (MAP) complexes were prepared through addition of 1 equiv of an alcohol to the bispyrrolide complexes. MAP compounds that contain the parent pyrrolide ($NC_4H_4^-$) are pyridine adducts, while those that contain 2,5-dimethylpyrrolide are pyridine free. Molybdenum and tungsten MAP 2,5-dimethylpyrrolide complexes that contain O-t-Bu, OCMe$(CF_3)_2$, or O-2,6-$Me_2C_6H_3$ ligands were found to have approximately equal amounts of *syn* and *anti* alkylidene isomers, which allowed a study of the interconversion of the two employing $^1H-^1H$ EXSY methods. The K_{eq} values ([*syn*]/[*anti*]) are all 2−3 orders of magnitude smaller than those observed for a large number of Mo bisalkoxide imido alkylidene complexes, as a consequence of the destabilization of the *syn* isomer by the sterically demanding NAr* ligand. The rates of interconversion of *syn* and *anti* isomers were found to be 1−2 orders of magnitude faster for W MAP complexes than for Mo MAP complexes.



INTRODUCTION

Bulky alkoxides and imido ligands in Mo- and W-based olefin metathesis catalysts of the type M(NR)(CHR′)$(OR'')_2$ slow or prevent intermolecular decomposition and/or ligand scrambling reactions, which allows the monomeric nature of these four-coordinate imido alkylidene complexes to be maintained.[1] Chiral versions that contain biphenolates or binaphtholates have been employed for enantioselective metathesis reactions (when the biphenolate or binaphtholate is enantiomerically pure)[2] or in order to control the structure of polymers prepared in ROMP reactions[3] (usually when the biphenolate or binaphtholate is racemic). The most recent development has been the synthesis of monoalkoxide (or monoaryloxide) pyrrolide (MAP) complexes of the type M(NR)(CHR′)(OR″)(Pyr), where Pyr is usually the parent pyrrolide or a 2,5-dimethylpyrrolide (Me_2Pyr).[1c] MAP complexes have proven to be more efficient in many olefin metathesis reactions in terms of higher turnover numbers, but more interestingly, they can provide high *Z* selectivities. *Z*-selective MAP catalysts have now been developed for ring-opening metathesis polymerization (ROMP),[4] homocoupling,[5] ring opening/cross metathesis,[6] ethenolysis,[7] and formation of natural products through ring-closing reactions.[8] *Z*-Selective reactions have been possible when one large OR″ ligand is present, e.g., a terphenoxide such as 2,6-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3O$ (HIPTO),[9] 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3O$ (HMTO),[10] or 2,6-$(C_6F_5)_2C_6H_3O$ (DFTO),[11] especially in combination with a relatively small imido ligand. The theory of metathesis by MAP complexes, which are members of the large class of four-coordinate stereogenic-at-metal (SAM) complexes, M(NR)(CHR′)(X)(Y), continues to be explored through theoretical calculations.[12] A large N-heterocyclic carbene and a stereogenic metal center also are found in *Z*-selective ruthenium catalysts.[13]

Although it has been established that the electronic and steric natures of the imido ligand play a significant role in determining the reactivity and selectivity of metathesis catalysts, no catalysts have been prepared in which the imido ligand is an analogue of a 2,6-terphenoxide. Anilines analogous to the large 2,6-terphenonols that we have employed have been prepared, namely 2,6-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3NH_2$ (2,6-$Trip_2C_6H_3NH_2$) and 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3NH_2$ (2,6-$Mes_2C_5H_3NH_2$ = Ar*NH_2), as have several transition-metal complexes that contain amido or imido derivatives of these large anilines.[14] In anticipation of an NAr* ligand being less sterically demanding than the 2,6-$Trip_2C_5H_3N$ ligand, we targeted NAr* imido alkylidene catalysts of Mo and W. The NAr* ligand is the approximate steric equivalent of the OHMT ligand. A shorter M═N bond as opposed to a M−O bond (M═N is expected to be ∼0.12 Å shorter) would suggest that the steric demand of a NAr* ligand may be greater than that of an OHMT ligand.

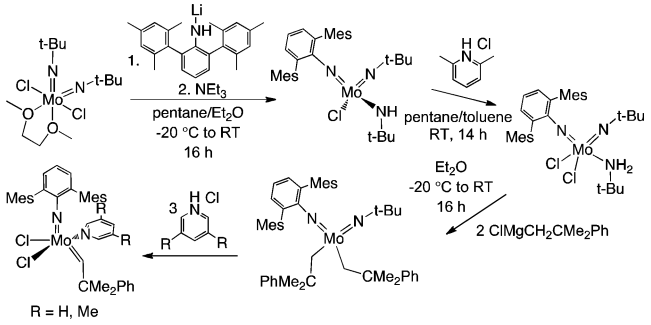
Received: January 30, 2013
Published: April 4, 2013

   dx.doi.org/10.1021/om4000693 | *Organometallics* 2013, 32, 2373−2378

However, this effect may be counteracted by an essentially linear M−N−C_{ipso} angle in most circumstances.

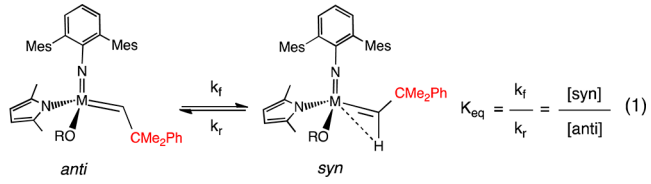
In our initial communication[15] we reported the synthesis of MoNAr* alkylidene complexes. A synthetic route had to be devised (Scheme 1) that did not require formation of

Scheme 1. Synthesis of Mo Alkylidenes That Contain the NAr* Ligand



$Mo(NAr^*)_2(CH_2R)_2$ precursors (R = t-Bu, CMe_2Ph) analogous to those employed for synthesizing virtually all imido alkylidene complexes of Mo and W to date. The synthetic route shown in Scheme 1 was inspired by observations published by Gibson.[16] $Mo(N\text{-}t\text{-}Bu)_2Cl_2(dme)$ was treated with LiNHAr* to give $Mo(N\text{-}t\text{-}Bu)_2(NHAr^*)Cl$, which was then transformed into Mo(N-t-Bu)(NAr*)(NH-t-Bu)Cl upon treatment with NEt_3. Addition of 2,6-lutidinium chloride to Mo(N-t-Bu)(NAr*)(NH-t-Bu)Cl yielded $Mo(N\text{-}t\text{-}Bu)(NAr^*)(NH_2\text{-}t\text{-}Bu)Cl_2$, which was then alkylated to give $Mo(N\text{-}t\text{-}Bu)(NAr^*)(CH_2CMe_2Ph)_2$. Upon addition of pyridinium chloride or 3,5-dimethylpyridinium chloride to $Mo(N\text{-}t\text{-}Bu)(NAr^*)(CH_2CMe_2Ph)_2$ the *tert*-butylimido group was protonated selectively and $Mo(NAr^*)(CHCMe_2Ph)Cl_2(L)$ complexes (L = pyridine, 3,5-dimethylpyridine) were isolated in high yield. This was the first time we were able to use a form of HCl instead of triflic acid to generate the alkylidene complex. Addition of triflic acid to $Mo(N\text{-}t\text{-}Bu)(NAr^*)(CH_2CMe_2Ph)_2$ in the presence of 1,2-dimethoxyethane led only to decomposition instead of formation of $Mo(NAr^*)(CHCMe_2Ph)(OTf)_2(dme)$.

The only Mo(NAr*) MAP compound that has been reported[15] is $Mo(NAr^*)(CHCMe_2Ph)(Me_2pyr)(O\text{-}t\text{-}Bu)$. It was synthesized either by treating $Mo(NAr^*)(CHCMe_2Ph)(Me_2pyr)_2$ ($\mathbf{2_{Mo}}$) with *tert*-butyl alcohol or by treating $Mo(NAr^*)(CHCMe_2Ph)Cl(O\text{-}t\text{-}Bu)(py)$ with $LiMe_2pyr$. $Mo(NAr^*)(CHCMe_2Ph)(Me_2pyr)(O\text{-}t\text{-}Bu)$ was found to have two alkylidene resonances in the proton NMR spectrum (at 11.861 and 11.695 ppm in C_6D_6) in approximately a 1:1 ratio. The $^1J_{CH}$ value for the downfield resonance (118 Hz) is consistent with it being a *syn* alkylidene and that for the upfield proton resonance (152 Hz) an *anti* alkylidene; the substituent on a *syn* alkylidene points toward the imido ligand, and the substituent on an *anti* alkylidene points away from the imido ligand (eq 1). The *syn* isomer is the only one observed in all

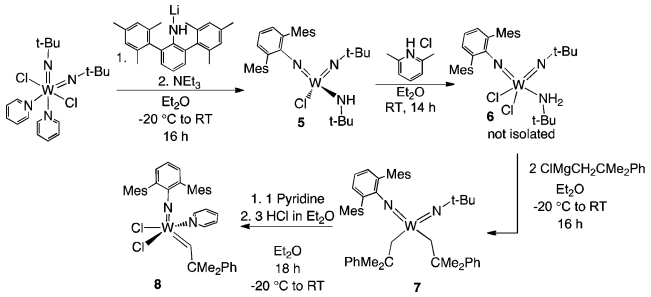


other MAP compounds except upon irradiation of *syn* isomers at low temperatures.[4b,d] Preliminary 2D $^1H-^1H$ EXSY experiments[15] suggested that the *syn* and *anti* forms of $Mo(NAr^*)(CHCMe_2Ph)(Me_2pyr)(O\text{-}t\text{-}Bu)$ interconvert at a rate of ~0.05 s^{-1} at 22 °C. Since the rate of interconversion of *syn* and *anti* isomers and the equilibrium between them is a crucial feature of many metathesis reactions with imido alkylidene complexes,[17] and since little is known about *syn* and *anti* isomers in MAP species,[4b] we set out to expand the chemistry of MoNAr* MAP species and to prepare WNAr* MAP complexes.

RESULTS AND DISCUSSION

Synthesis of W(NAr*) Compounds. We chose $W(N\text{-}t\text{-}Bu)_2Cl_2(py)_2$[18] as the starting point for expanding NAr* chemistry to tungsten. The approach (Scheme 2) is the same as

Scheme 2. Synthesis of W Complexes That Contain the NAr* Ligand



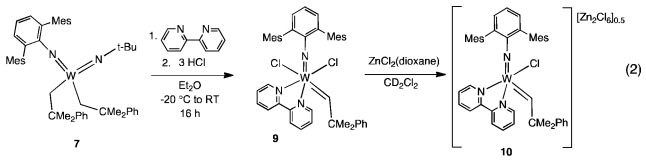
that employed to prepare the Mo(NAr*) species (Scheme 1). Upon addition of LiNHAr* to $W(N\text{-}t\text{-}Bu)_2Cl_2(py)_2$, $W(N\text{-}t\text{-}Bu)_2Cl(NHAr^*)$ is formed, which without isolation is treated with NEt_3 to give W(NAr*)(N-t-Bu)Cl(NH-t-Bu) (**5**) in 74% yield. $W(N\text{-}t\text{-}Bu)_2Cl_2(py)_2$ did not react with Ar^*NH_2 after 16 h at 80 °C. Attempts to use $[(t\text{-}BuN)_2WCl_2(NH_2\text{-}t\text{-}Bu)]_2$[19] instead of $W(N\text{-}t\text{-}Bu)_2Cl_2(py)_2$ as a starting material were also unsuccessful.

$W(NAr^*)(N\text{-}t\text{-}Bu)Cl_2(NH_2\text{-}t\text{-}Bu)$ (**6**) was synthesized through addition of 2,6-lutidine-HCl to **5** (Scheme 2). Rather than reduce the yield of **6** as a consequence of a lengthy purification, $W(NAr^*)(N\text{-}t\text{-}Bu)(CH_2CMe_2Ph)_2$ (**7**) was synthesized through the addition of 2 equiv of $MgClCH_2CMe_2Ph$ to crude **6**. $W(NAr^*)(N\text{-}t\text{-}Bu)(CH_2CMe_2Ph)_2$ was isolated in 68% yield.

Addition of 1 equiv of pyridine to **7** followed by 3 equiv of HCl in diethyl ether gave $W(NAr^*)(CHCMe_2Ph)Cl_2(py)$ (**8**) in 63% yield. Only the *anti* alkylidene isomer is visible in the ^1H NMR spectrum of **8** ($^1J_{CH}$ = 144 Hz). Compound **8** could *not* be prepared employing 3 equiv of pyridine-HCl. Employing HCl in diethyl ether or triflic acid also resulted in decomposition with little or no identifiable alkylidene species being observed in ^1H NMR spectra of the crude reaction product.

An alkylidene species, $W(NAr^*)(CHCMe_2Ph)Cl_2(bipy)$ (**9**), was also synthesized through a reaction between $W(NAr^*)(N\text{-}t\text{-}Bu)(CH_2CMe_2Ph)_2$ and 2,2′-bipyridine (bipy) followed by 3 equiv of HCl (eq 2). Compound **9** is insoluble in pentane, diethyl ether, benzene, and toluene. Its low solubility in CH_2Cl_2 allows $W(NAr^*)(CHCMe_2Ph)Cl_2(bipy)$ to be extracted and thereby separated from $t\text{-}BuNH_3Cl$. Bipy adducts have been employed as synthetic intermediates previously,[19,20] in part

dx.doi.org/10.1021/om4000693 | Organometallics 2013, 32, 2373−2378



because their low solubility allows them to be obtained readily in pure form.

$ZnCl_2$ or $ZnCl_2$(1,4-dioxane) can be employed to remove 2,2′-bipyridine or 1,10-phenanthroline from Mo imido alkylidene complexes.[19−21] When $ZnCl_2$(dioxane) is added to W(NAr*)($CHCMe_2Ph$)Cl_2(bipy) suspended in CD_2Cl_2, a new product and free dioxane are observed by ^1H NMR spectroscopy, but bipyridine resonances are still visible. An X-ray structure showed that the product is [W(NAr*)($CHCMe_2Ph$)Cl(bipy)][Zn_2Cl_6]$_{0.5}$ (**10**): i.e., $ZnCl_2$ abstracts a chloride ligand to form a cationic W bipyridine complex in which $[Zn_2Cl_6]^{2-}$ is the (di)anion (eq 2).

[W(NAr*)($CHCMe_2Ph$)Cl(bipy)][Zn_2Cl_6]$_{0.5}$ crystallizes in the space group $P\bar{1}$ with one [W(NAr*)($CHCMe_2Ph$)Cl(bipy)][Zn_2Cl_6]$_{0.5}$ unit and one toluene molecule per asymmetric unit (Figure 1). The alkylidene ligand is in the

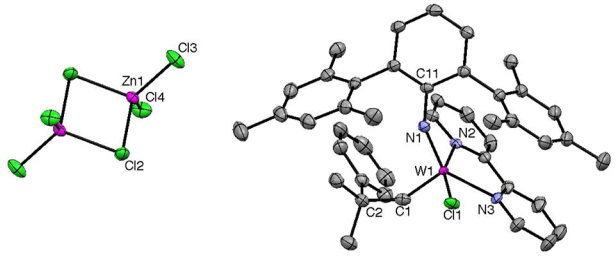


Figure 1. Crystal structure of [W(NAr*)($CHCMe_2Ph$)Cl(bipy)][Zn_2Cl_6]$_{0.5}$ in a thermal ellipsoid representation at the 50% probability level. Only half of the $Zn_2Cl_6^{2-}$ anion is present in the asymmetric unit, but the whole unit is pictured. Hydrogen atoms, the toluene solvent molecule, and a minor component of disorder are omitted for clarity. Selected bond angles (deg): C11−N1−W1 = 153.03(15), C2−C1−W1 = 148.42(17).

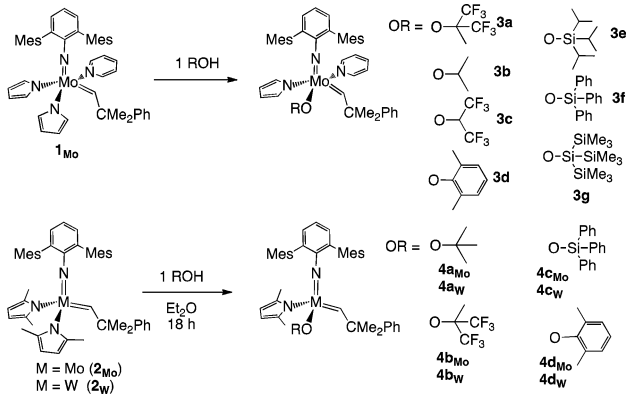
syn orientation. The bipyridine ligand is disordered over two positions. The geometry about W is best described as a distorted square pyramid (τ = 0.34, where τ = 0 for a perfect square pyramid[22]) with the alkylidene ligand at the apical site. The W1−N1−C11 angle (153.03(15)°) is relatively small compared to the 175−180° found in many other imido alkylidene complexes, possibly as a consequence of some attractive π interaction between one of the mesityl rings and the bipy ring system, but otherwise the bond lengths and angles (see the Supporting Information) are those expected for W imido alkylidene complexes. The coordination geometry around each zinc is a slightly distorted tetrahedron, as expected.

Since bipyridine could not be removed easily from W(NAr*)($CHCMe_2Ph$)Cl_2(bipy), possibly in part because of the π interaction noted above, further syntheses focused on W(NAr*)($CHCMe_2Ph$)Cl_2(py) as a starting material. W(NAr*)($CHCMe_2Ph$)(Pyr)$_2$(py) (**1$_W$**) can be synthesized through addition of excess LiC_4H_4 to a solution of **8** in diethyl ether. Addition of $LiMe_2C_4H_2$ to **8** gives W(NAr*)($CHCMe_2Ph$)(Me_2pyr)$_2$ (**2$_W$**). Proton NMR spectra of **2$_W$** show free pyridine unless the product is left under a good vacuum for several hours. The resonances in the ^1H NMR spectrum of **2$_W$** are broad at room temperature. A proton NMR spectrum at −40 °C reveals that all pyrrolide protons and methyl groups are inequivalent. A $^1J_{CH}$ value of 126 Hz, which can be observed at −40 °C, suggests that the alkylidene is in the *syn* orientation. (The $^1J_{CH}$ value for Mo(NAr*)($CHCMe_2Ph$)(Me_2pyr)$_2$ (**2$_{Mo}$**) is 130 Hz.[15]) We do not know whether one pyrrolide ligand is bound in an η^1 fashion and the other in an η^5 fashion in both **2$_W$** and **2$_{Mo}$** or both pyrrolides are bound in an η^1 fashion. In either case, restricted rotations of ligands at −40 °C could result in the observed lack of symmetry for **2$_W$** at that temperature.

Synthesis of M(NAr*) MAP Compounds. Addition of 2 equiv of LiPyr to Mo(NAr*)($CHCMe_2Ph$)Cl_2(py) led to formation of Mo(NAr*)($CHCMe_2Ph$)(Pyr)$_2$(py) (**1$_{Mo}$**) in good yield. Pyridine is retained in the coordination sphere in **1$_{Mo}$** simply for steric reasons. The synthesis of **1$_{Mo}$** completes the syntheses of M(NAr*)($CHCMe_2Ph$)(Pyr)$_2$(py) (M = Mo (**1$_{Mo}$**), W (**1$_W$**)) and M(NAr*)($CHCMe_2Ph$)(Me_2Pyr)$_2$ (M = Mo (**2$_{Mo}$**), W (**2$_W$**)) and sets the stage for the synthesis of MAP complexes.

Complexes **3a−g** are formed upon addition of 1 equiv of alcohol to **1$_{Mo}$** (Scheme 3). The pyridine ligand remains bound

Scheme 3. Synthesis of Mo and W MAP Complexes from Bispyrrolides



to the metal in **3a−g**. In all cases in solution, according to ^1H NMR spectroscopy, the alkylidene is in the *anti* form. This is unusual for Mo or W imido alkylidene complexes in general if they are four-coordinate, but less so when the complex is five-coordinate. Several five-coordinate NAr* monochloride monoalkoxide species reported previously were also *anti* alkylidenes in solution.[15] Other *anti* group 6 imido alkylidenes that are base-stabilized species have been known for some time.[23]

Since pyridine essentially blocks a coordination site and thereby reaction of the alkylidene complex with olefins, Lewis acids were employed with the goal of removing pyridine and isolating base-free alkylidene complexes. It was found that upon addition of 1 equiv of $B(C_6F_5)_3$ to **3a−g**, $B(C_6F_5)_3(NC_5H_5)$ formed immediately, according to ^1H and ^{19}F NMR spectra. Unfortunately, the similar solubilities of any base-free species and $B(C_6F_5)_3(NC_5H_5)$ prevented isolation of the base-free alkylidene complexes in pure form. Also, clean conversion to one base-free alkylidene species, which we expected to have two alkylidene resonances, was not observed when $B(C_6F_5)_3$ was added to **3a−e**; thus, further characterization of the target MAP species in situ did not seem feasible. However, only two alkylidene resonances are observed in ^1H NMR spectra of base-free **3f,g** (**3f′,g′**, respectively). In each case the two resonances were confirmed as being those of *syn* and *anti* alkylidenes on

dx.doi.org/10.1021/om4000693 | Organometallics 2013, 32, 2373−2378

the basis of the $^1J_{CH}$ values. For **3f′** K_{eq} = 2.0, and for **3g′** K_{eq} = 2.3 (where K_{eq} = [*syn*]/[*anti*]).

In order to isolate pyridine-free MAP compounds, attention shifted toward pyridine-free $\mathbf{2_{Mo}}$ as a precursor. Four representative alcohols were chosen in order to prepare MAP species. The MAP complexes Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-t-Bu) ($\mathbf{4a_{Mo}}$), Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)[OCMe(CF$_3$)$_2$] ($\mathbf{4b_{Mo}}$), Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OSiPh$_3$) ($\mathbf{4c_{Mo}}$), and Mo(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OAr′) ($\mathbf{4d_{Mo}}$) (Ar′ = 2,6-Me$_2$C$_6$H$_3$) could all be synthesized through addition of 1 equiv of the appropriate alcohol to $\mathbf{2_{Mo}}$ (Scheme 3). Like many MAP complexes, $\mathbf{4a_{Mo}}$–$\mathbf{d_{Mo}}$ were all found to be extremely soluble in solvents that have previously been employed for recrystallization (e.g., pentane or diethyl ether) and therefore not isolable in crystalline form from such solvents. However, $\mathbf{4a_{Mo}}$–$\mathbf{d_{Mo}}$ could be isolated in pure crystalline form from acetonitrile and isolated as acetonitrile-free species; there was no evidence for any reaction between the MAP species and acetonitrile at room temperature. Compounds $\mathbf{4a_{Mo}}$–$\mathbf{d_{Mo}}$ are all mixtures of *syn* and *anti* alkylidene isomers, according to ^{1}H NMR studies.

Addition of 1 equiv of an alcohol to W(NAr*)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ ($\mathbf{2_W}$) led to W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-t-Bu) ($\mathbf{4a_W}$), W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)[OCMe(CF$_3$)$_2$] ($\mathbf{4b_W}$), W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OSiPh$_3$) ($\mathbf{4c_W}$), and W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(OAr′) ($\mathbf{4d_W}$) (Scheme 3). All could be isolated in pure form through crystallization from acetonitrile.

An X-ray study of W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-t-Bu) ($\mathbf{4a_W}$) revealed a whole molecule disorder, with the major component representing approximately 90% of the electron density (Figure 2). The alkylidene ligand in the major component is in the *syn* orientation and is slightly twisted with an N1–W1–C1–C2 dihedral angle of 12.25°. The W1–C1 bond length is 1.875(2) Å, the W1–N1–C21 angle is 173.4(3)°, and the C2–C1–W1 angle is 147.33(19)°, all typical of group 6 MAP complexes. When the molecule is viewed along the C21–N1–W1 axis, one mesityl group of the NAr* ligand is seen to be located over the alkoxide, while the other mesityl group falls between the pyrrolide and alkylidene ligands.

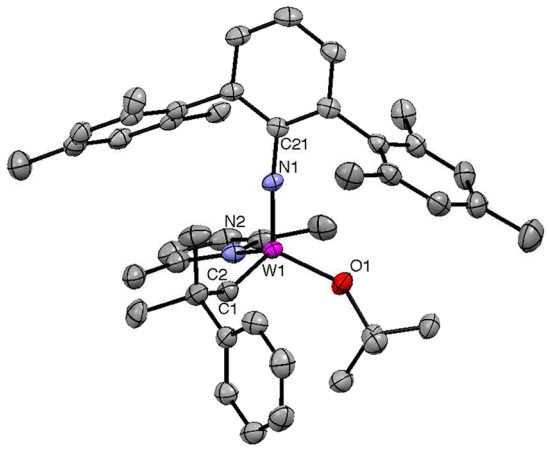


Figure 2. Crystal structure of W(NAr*)(CHCMe$_2$Ph)(Me$_2$pyr)(O-t-Bu) ($\mathbf{4a_w}$) in a thermal ellipsoid representation at the 50% probability level. Hydrogen atoms and a minor disorder component are omitted for clarity. Selected bond lengths (Å): C1–W1 = 1.875(2), W1–N1 = 1.750(2), W1–O1 = 1.8682(19), W1–N2 = 2.033(2). Selected bond angles (deg): C2–C1–W1 = 147.33(19), N1–W1–O1 = 115.59(14), N1–W1–C1 = 106.04(16), O1–W1–C1 = 109.35(10), N1–W1–N2 = 111.05(13), O1–W1–N2 = 110.03(10), C1–W1–N2 = 104.07(11), C21–N1–W1 = 173.4(3).

Study of Alkylidene Rotation. Compounds **4a–d** for Mo and W (Table 1) are a mixture of *syn* and *anti* alkylidene isomers (eq 1) in C$_6$D$_6$ solution, according to ^{1}H NMR studies. The *syn* isomer is often the major isomer in imido alkylidene complexes of Mo and W, due to an agostic interaction that stabilizes it relative to the *anti* isomer. Significant additional factors include the counteracting steric demands of the alkylidene, imido, and other ligands. Compounds similar to those reported here, but with a relatively smaller 2,6-diisopropylphenyl imido ligand, such as Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)(OCMe$_3$) and Mo(NAr)(CHCMe$_2$Ph)(Me$_2$pyr)[OCMe(CF$_3$)$_2$], only show the *syn* isomer in solution.[24]

Table 1. Rate and Equilibrium Constants for MAP Species at 21 °C for Mo and W M(NAr*)(CHCMe$_2$Ph)(Me$_2$Pyr)(OR) ("M(OR)") Compounds

compd	K_{eq}	k_f (s^{-1})	k_r (s^{-1})
Mo(O-t-Bu) ($\mathbf{4a_{Mo}}$)	0.9	0.05(0.01)	0.06(0.01)
Mo[OCMe(CF$_3$)$_2$] ($\mathbf{4b_{Mo}}$)	2.7	0.029(0.006)	0.011(0.004)
Mo(OSiPh$_3$) ($\mathbf{4c_{Mo}}$)	26	~0.5	~0.02
Mo(O-2,6-C$_6$H$_3$) ($\mathbf{4d_{Mo}}$)	2.2	0.10(0.02)	0.05(0.01)
W(O-t-Bu) ($\mathbf{4a_W}$)	1.8	1.4(0.6)	0.8(0.4)
W[OCMe(CF$_3$)$_2$] ($\mathbf{4b_W}$)	12	1.8(1.1)	0.15(0.2)
W(OSiPh$_3$) ($\mathbf{4c_W}$)	100	~50	~0.5
W(O-2,6-C$_6$H$_3$) ($\mathbf{4d_W}$)	5.6	2(2)	0.4(0.4)

The K_{eq} values in Table 1 are all 2–3 orders of magnitude smaller than those observed for a large number of Mo bisalkoxide imido alkylidene complexes in benzene or toluene.[17] K_{eq} values in Mo bisalkoxide complexes[17] are approximately the same order of magnitude as those given in Table 1 when data are obtained in THF-d_8, as a consequence of THF binding more strongly to the *anti* form and therefore shifting the equilibrium in that direction. We propose that the "low" K_{eq} values in Table 1 are simply a consequence of the demanding steric bulk of the NAr* ligand and therefore destabilization of the *syn* isomer relative to the *anti* isomer. The values for K_{eq} for Mo(OSiPh$_3$) ($\mathbf{4c_{Mo}}$) and W(OSiPh$_3$) ($\mathbf{4c_W}$) (26 and 100, respectively) are consistent with the greater steric demand of the OSiPh$_3$ ligand in comparison with the three other OR ligands.

^{1}H–^{1}H EXSY studies were conducted to obtain the rate constants for alkylidene rotation for **4a,b,d** for Mo and W (Table 1).[25] The relatively large values of K_{eq} for Mo(OSiPh$_3$) ($\mathbf{4c_{Mo}}$) and W(OSiPh$_3$) ($\mathbf{4c_W}$) (26 and 100, respectively) did not allow us to obtain rate constants for interconversion of *syn* and *anti* isomers using the ^{1}H–^{1}H EXSY method. Therefore, $\mathbf{4c_{Mo}}$ and $\mathbf{4c_W}$ were photolyzed[17] at 350 nm at −78 °C to generate a greater proportion of the *anti* isomer. Rate constants were obtained over a 20 °C range (−20 to −40 °C for $\mathbf{4c_{Mo}}$ and −40 to −60 °C for $\mathbf{4c_W}$) for the rotation of the *anti* alkylidene to the *syn* form, and the data were extrapolated to give k_f at 21 °C. Because rate constants can only be obtained over a small temperature range, k_f at 21 °C is not highly accurate and is therefore given with only one significant figure in Table 1.

The values for k_f for the four Mo complexes ($\mathbf{4a_{Mo}}$, $\mathbf{4b_{Mo}}$, $\mathbf{4c_{Mo}}$, and $\mathbf{4d_{Mo}}$) vary from 0.029 to 0.10, while the values for k_r

dx.doi.org/10.1021/om4000693 | *Organometallics* 2013, 32, 2373–2378

vary from 0.011 to 0.06. For comparison, k_f for Mo(NAr)(CHCMe$_2$Ph)(OTPP)(Pyr) (OTPP = 2,3,5,6-tetraphenylphenoxide) at 21 °C has been found to be 0.67 s^{-1},[4b] roughly an order of magnitude larger. Another example is k_f for Mo(NAd)(CHCMe$_2$Ph)(OHIPT)(Pyr) (Ad = 1-adamantyl) at 298 K, which is 0.96 s^{-1}.[4d] For Mo(NAd)(CHCMe$_2$Ph)(OHIPT)(Pyr) the equilibrium constant is estimated to be on the order of 4000 or more and the value for k_r therefore is 2.5 × 10^{-4} s^{-1} or less. Although few data are available, we can tentatively draw the conclusion that the NAr* ligand not only destabilizes the *syn* isomer but also restricts the rate of *anti* to *syn* alkylidene rotation. Both are consistent with the unusually large steric demand of the NAr* ligand.

The data in Table 1 can be compared to data for Mo(NAr)(CHR)(OR′)$_2$ complexes.[17] For Mo(NAr)(CHCMe$_2$Ph)(OR)$_2$ complexes in toluene the k_f values at 298 K for OR = O-t-Bu, OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, OC(CF$_3$)$_3$ are ∼500 (estimated), 6.8, 0.10, and 0.0015 s^{-1}, respectively. This is a dramatic trend that spans approximately 5 orders of magnitude. Since the K_{eq} values for this series of bisalkoxides (in toluene at 298 K) are 1200, 1800, 1400, and 190, the k_r values are 2−3 orders of magnitude smaller than k_f. The most obvious reason why the rates of interconversion vary more dramatically in bisalkoxides than in the MAP species in Table 1 is that MAP species contain only one alkoxide; therefore, the "alkoxide effect" is diluted in MAP species. Another possibility is that in a MAP species, in which the metal is a stereogenic center, the alkylidene might rotate in only one direction, one that is regulated largely by the pyrrolide ligand, which is the same in all the MAP species in Table 1. The "alkoxide effect" would again be diluted, perhaps dramatically. Finally, it should be noted that a "bending" of the NAr* ligand in bisalkoxide complexes[17] was proposed to stabilize the intermediate alkylidene that has rotated by 90°. One might expect that the NAr* ligand would not bend as readily as (e.g.) the 2,6-diisopropylphenyl ligand, which also could contribute to a less dramatic variation in the MAP species than in the bisalkoxide complexes. What is required are k_f data for Mo(NR)(CHR′)(Me$_2$Pyr)(OR″) species in which OR″ is varied widely and R is constant. Currently, we know k_f at 298 K only for Mo(NAr)(CHCMe$_2$Ph)(OTPP)(Pyr) (0.67 s^{-1})[4b] and Mo(NAd)(CHCMe$_2$Ph)(OHIPT)(Pyr) (0.96 s^{-1}).[4d]

Another important feature of the data in Table 1 is that the values for k_f are 1−2 orders of magnitude larger for W than for analogous Mo compounds. This result is consistent with reported data for k_f for M(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ (M = Mo, W) complexes.[17] Values for k_f for W(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ over a range of temperatures extrapolated to −27.4 °C gave k_f = 153 × 10^{-4} s^{-1}, while k_f for Mo(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$ at −27.4 °C was found to be 2.26 × 10^{-4} s^{-1}. The value for W is 68 times that for Mo. For the complexes given in Table 1, k_f values are larger for W by factors of 28 (for O-t-Bu), 62 (for OCMe(CF$_3$)$_2$), ∼100 (for OSiPh$_3$), and 20 (for O-2,6-Me$_2$C$_6$H$_3$) at 21 °C. A similar trend was observed for rotation of a methylidene ligand in W complexes versus that in Mo complexes.[26] The rate of methylidene rotation in W(NAr)(CH$_2$)(OTPP)(Me$_2$Pyr) at 20 °C was 90 s^{-1}, while in Mo(NAr)(CH$_2$)(OHIPT)(Me$_2$Pyr) the rate was <0.2 s^{-1}. Although the quantity of data is again relatively small and direct comparisons are few, the trend is clearly toward a more rapid interconversion of alkylidenes for W versus Mo.

CONCLUSIONS

Molybdenum and tungsten alkylidene compounds that contain the 2,6-dimesitylphenylimido (NAr*) ligand have been synthesized and several MAP species for both Mo and W prepared. The demanding steric bulk of the NAr* ligand is reflected in the relatively low K_{eq} values ([*syn*]/[*anti*]) along with a slower rate of conversion of the *anti* to the *syn* alkylidene isomers in NAr* complexes relative to complexes that contain a smaller imido ligand, even NAr. Alkylidene rotation in four-coordinate MAP species was found to be at least an order of magnitude larger in W(NAr*) complexes than in Mo(NAr*) complexes. It remains to be seen how the steric bulk of the NAr* ligand will effect the reactivity of M(NAr*) MAP species, the stability of metallacyclobutanes, and the performance of M(NAr*) MAP species in a variety of olefin metathesis reactions.

ASSOCIATED CONTENT

Supporting Information

Text and figures giving experimental details for the synthesis of all compounds and characterization data, along with tables and CIF files that provide crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for R.R.S.: rrs@mit.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Science Foundation (CHE-1111133 to R.R.S.) for supporting this research. The Department of Chemistry thanks the NSF for funds to purchase a Varian 500 NMR instrument (CHE-9808061) and an X-ray diffractometer (CHE-0946721).

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