

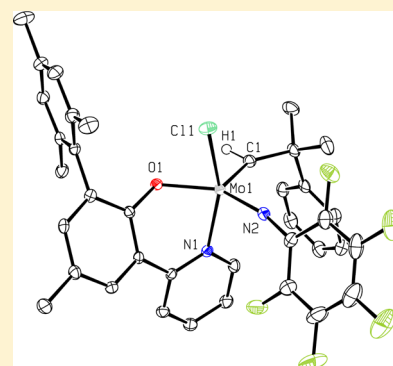
# Molybdenum and Tungsten Alkylidene Complexes That Contain a 2-Pyridyl-Substituted Phenoxide Ligand

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## Supporting Information

**ABSTRACT:** In the interest of preparing molybdenum and tungsten alkylidene complexes for olefin metathesis that are longer-lived at high temperatures ( $\sim 150^\circ\text{C}$  or above), we synthesized complexes that contain a phenoxide ligand with a 2-pyridyl in one *ortho* position and a mesityl (Mes) or 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (Trip) in the other *ortho* position ([MesON]<sup>−</sup> or [TripON]<sup>−</sup>, respectively). The alkylidene (neophylidene) complexes that were prepared include W(O)(CHCMe<sub>2</sub>Ph)(Me<sub>2</sub>Pyr)(RON) (R = Mes or Trip), Mo(NC<sub>6</sub>F<sub>5</sub>)(CHCMe<sub>2</sub>Ph)(RON)Cl, Mo(N-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(CHCMe<sub>2</sub>Ph)(RON)Cl, Mo(N-*t*-Bu)(CHCMe<sub>2</sub>Ph)(RON)Cl, and M(N-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(CHCMe<sub>2</sub>Ph)(TripON)(OTf) (M = Mo or W). The reaction between Mo(NAr)(CHCMe<sub>2</sub>Ph)(TripON)(OTf) and ethylene yielded an ethylene complex, Mo(NAr)(C<sub>2</sub>H<sub>4</sub>)(TripON)(OTf)(ether). All neophylidene complexes were essentially unreactive toward terminal olefins at  $22^\circ\text{C}$  and showed modest homocoupling activity (at  $80$  or  $100^\circ\text{C}$ ) and alkane metathesis activity (at  $150$  and  $200^\circ\text{C}$ ). W(O)(CHCMe<sub>2</sub>Ph)(Me<sub>2</sub>Pyr)(MesON) also stereoselectively polymerized several substituted norbornadienes at  $100^\circ\text{C}$ .



## INTRODUCTION

The synthesis of olefin metathesis catalysts that are relatively stable and active above  $150^\circ\text{C}$  would be potentially beneficial for alkane metathesis, a catalytic reaction that employs an iridium dehydrogenation/hydrogenation catalyst and an olefin metathesis catalyst in tandem.<sup>1</sup> The reason is that catalytic activity is limited by decomposition of the metathesis catalyst, not the iridium catalyst. In order to test whether 16e molybdenum-based imido alkylidene complexes could be active for metathesis at elevated temperatures, we synthesized complexes that contain a dianionic pincer-type ligand (made first by Bercaw;<sup>2</sup> Figure 2); we proposed that the pyridine donor might block one or more decomposition pathways (e.g., metallacycle rearrangement to an olefin), even though dissociation of the pyridine donor is likely to be necessary for reaction with an olefin.<sup>3</sup> We found that a six-coordinate metallacyclobutane complex, Mo(NC<sub>6</sub>F<sub>5</sub>)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(ONO), which is formed from Mo(NC<sub>6</sub>F<sub>5</sub>)(CHCMe<sub>2</sub>Ph)(ONO) upon reaction with ethylene, is 5 or more orders of magnitude more stable toward loss of ethylene than typical 14e trigonal bipyramidal metallacycles.<sup>4</sup> A tungsten-based oxo metallacyclobutane complex, W(O)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)(ONO), was similarly stable toward loss of ethylene. We concluded that an olefin can be lost readily only from a 14e TBP metallacycle, not a 16e pseudo-octahedral metallacycle. The reason why this is the case, we propose, is that an alkylidene/olefin intermediate with an electron count two higher than that for the metallacyclobutane complex (and arguably a higher coordination number by one) must be an intermediate or transition state on the path toward loss of olefin.

We decided to test whether 16e alkylidene complexes that contain a *bidentate* ligand in which a pyridine donor is in one *ortho* position in a sterically demanding terphenoxide ligand would allow metathesis to proceed and also would extend catalyst life at  $150^\circ\text{C}$  or greater. To this end, we prepared two such bidentate ligands which we call [MesON]<sup>1−</sup> (2',4',5,6'-tetramethyl-3-(pyridin-2-yl)-[1,1'-biphenyl]-2-olate) and [TripON]<sup>1−</sup> (2',4',6'-triisopropyl-5-methyl-3-(pyridin-2-yl)-[1,1'-biphenyl]-2-olate; Figure 1). These bidentate ligands could allow the required

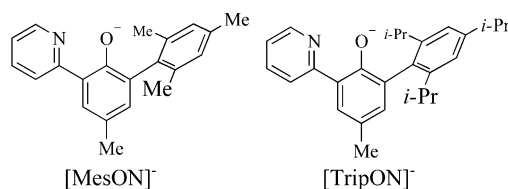
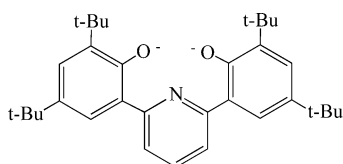


Figure 1. [MesON]<sup>−</sup> and [TripON]<sup>−</sup> ligands.

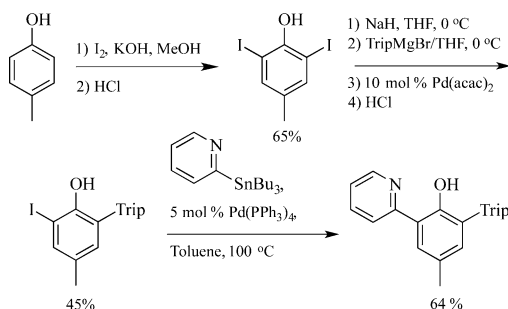
TBP metallacycle structure to form through dissociation of the pyridyl donor, unlike the tridentate [ONO]<sup>2−</sup> ligand shown in Figure 2. Here, we report syntheses of the MesON or TripON ligands and several tungsten and molybdenum alkylidene complexes that contain them, along with a brief exploration of representative olefin metathesis reactions.

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Figure 2.  $[\text{ONO}]^{2-}$  ligand.

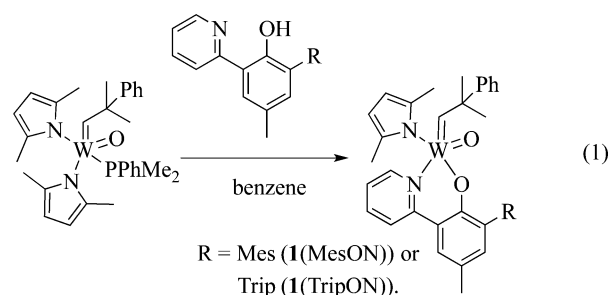
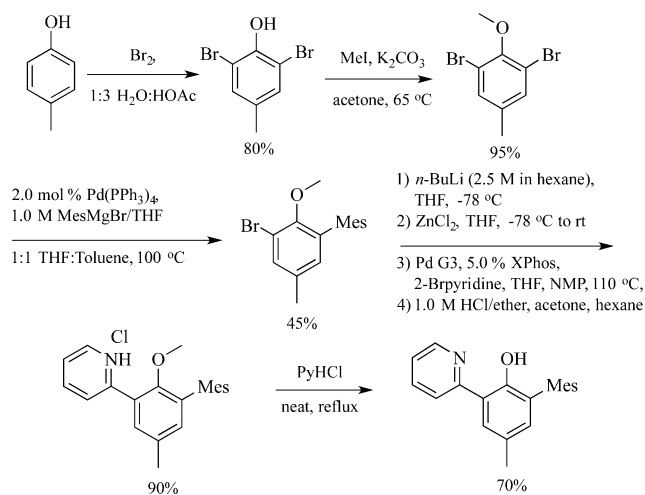
## RESULTS AND DISCUSSION

The two ligands were prepared by different routes. The synthesis of  $\text{H}[\text{TripON}]$  starts with *para*-cresol, as shown in Scheme 1. Modest selectivity for the desired mono-Trip

Scheme 1. Synthesis of  $\text{H}[\text{TripON}]$ 

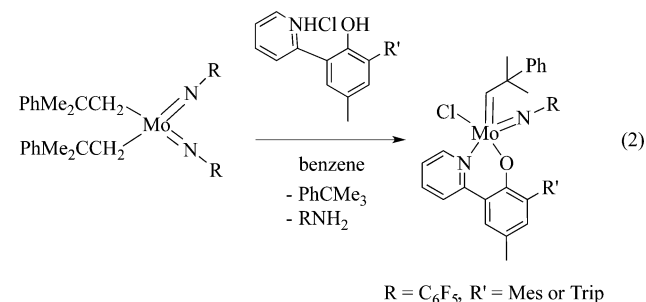
product was found upon coupling the diiodide with the Grignard, but a significant amount of the disubstituted side product and the diiodide starting material were present in the crude reaction mixture. The pyridyl group was then installed employing a Stille coupling with 2-(tributylstannyl)pyridine. The Stille reaction did not proceed in good yield with an analogous bromide.

A different approach had to be used to prepare  $\text{H}[\text{MesON}]$  because the Kumada coupling between a mesityl Grignard and the diiodo starting material shown in Scheme 1 gave largely the undesired disubstituted product. The dibromide was prepared from *para*-cresol, and the hydroxyl was converted to a methoxy, as shown in Scheme 2. In this way, the mono mesityl product could be prepared in modest yield (45%). The pyridyl group was added in a high yielding Negishi coupling, followed by deprotection with pyridinium chloride.

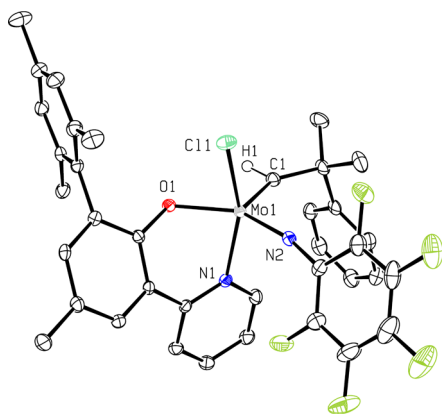
Scheme 2. Synthesis of  $\text{H}[\text{MesON}]$ 

Addition of  $\text{H}[\text{MesON}]$  or  $\text{H}[\text{TripON}]$  to  $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})_2(\text{PPhMe}_2)$  (where  $\text{Me}_2\text{Pyr}$  is 2,5-dimethylpyrrolide),<sup>5</sup> yielded two new tungsten oxo MAP (monoaryloxide pyrrolide) complexes as a consequence of protonation of one of the pyrrolide ligands, as shown in eq 1. The reaction employing  $\text{H}[\text{MesON}]$  proceeded several times faster than the reaction employing  $\text{H}[\text{TripON}]$  (~16 h), as one might expect on the basis of the larger size of  $\text{H}[\text{TripON}]$ .  $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{MesON})$  (**1(MesON)**) and  $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{TripON})$  (**1(TripON)**) were isolated in moderate yields (~50%) as bright yellow powders. NMR spectra suggest that the alkylidene is in the *syn* orientation in both **1(MesON)** and **1(TripON)** and the pyridyl is bound strongly to the metal on the NMR time scale; both compounds have  $C_1$  symmetry.

On the basis of the fact that  $\text{H}_2[\text{ONO}]$  (Figure 2) will protonate imido groups in bisimido dialkyl precursors to give alkylidene complexes,<sup>3</sup> we proposed that protonated forms of  $\text{H}[\text{MesON}]$  and  $\text{H}[\text{TripON}]$  might lead directly from dineophyl to neophylidene complexes. Alkylidene formation is the result of an irreversible  $\alpha$  abstraction reaction after double protonation of an imido ligand and loss of the aniline. Treatment of  $\text{H}[\text{MesON}]$  and  $\text{H}[\text{TripON}]$  with an excess of  $\text{HCl}$  in ether gave the  $\text{HCl}$  adducts,  $\text{H}_2[\text{MesON}]\text{Cl}$  and  $\text{H}_2[\text{TripON}]\text{Cl}$ , respectively, as white powders in >90% yields. Reactions between  $\text{H}_2[\text{MesON}]\text{Cl}$  or  $\text{H}_2[\text{TripON}]\text{Cl}$  and  $\text{Mo}(\text{NC}_6\text{F}_5)_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$  proceeded smoothly to give  $\text{Mo}(\text{NC}_6\text{F}_5)(\text{CHCMe}_2\text{Ph})(\text{MesON})\text{Cl}$  (**2(MesON)**) and  $\text{Mo}(\text{NC}_6\text{F}_5)(\text{CHCMe}_2\text{Ph})(\text{TripON})\text{Cl}$  (**2(TripON)**) in moderate yields (62–75%) as yellow/brown powders (eq 2). As found for **1(MesON)** and **1(TripON)** (*vide supra*), the NMR spectra of **2(MesON)** and **2(TripON)** reveal that these complexes have no symmetry. In contrast to **1(MesON)** and **1(TripON)**, **2(MesON)** and **2(TripON)** were present as mixtures of *syn* and *anti* isomers (predominantly *syn*) in solution with alkylidene resonances at 14.48 ( $J_{\text{CH}} = 148$  Hz, *anti*) and 13.31 (s, 1H,  $\text{Mo}=\text{CH}$ ,  $J_{\text{CH}} = 127$  Hz, *syn*) ppm for **2(MesON)**, and 14.52 ( $J_{\text{CH}} = 147$  Hz, *anti*) and 13.39 ( $J_{\text{CH}} = 127$  Hz, *syn*) ppm for **2(TripON)**.



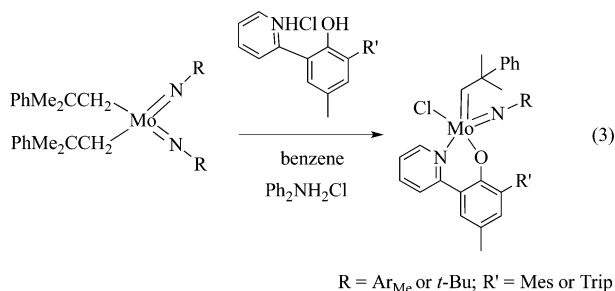
An X-ray study of **2(MesON)** shows that its structure is close to a distorted square pyramid structure ( $\tau = 0.12^6$ ) with the



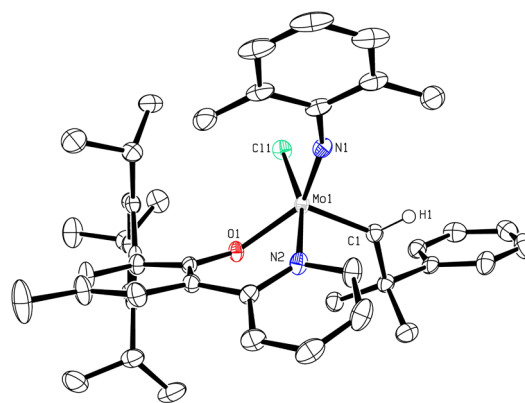
**Figure 3.** Thermal ellipsoid drawing (50% probability) of 2(MesON). The solvent and most of the hydrogen atoms were removed for clarity.

alkylidene ligand in the apical position (Figure 3). The complex crystallizes as the *syn* isomer, in which  $\text{Mo}(1)\text{--C}(1)\text{--C}(2) = 142.8(6)^\circ$ . The imido and phenoxide ligands are *trans* to one another with  $\text{N}(2)\text{--Mo}(1)\text{--O}(1) = 150.4(2)^\circ$ , while  $\text{Cl}(1)\text{--Mo}(1)\text{--N}(1) = 157.6(2)^\circ$ .

Attempts to extend the reactions shown in eq 2 to aryl- and alkylimido precursors  $\text{Mo}(\text{NAr}_{\text{Me}})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$  and  $\text{Mo}(\text{N-}t\text{-Bu})_2(\text{CH}_2\text{CMe}_2\text{Ph})_2$  (where  $\text{NAr}_{\text{Me}} = 2,6\text{-dimethylphenyl-imido}$ ) led to only  $\sim 50\%$  conversion of the starting material and formation of a colorless precipitate in each case. The problem was traced to a deprotonation of  $\text{H}_2[\text{MesON}]\text{Cl}$  or  $\text{H}_2[\text{TripON}]\text{Cl}$  by the  $\text{Ar}_{\text{Me}}\text{NH}_2$  or *t*-butylamine product as they are formed along with the metal-containing product in each circumstance, thereby limiting conversion to 50%. The problem was solved by employing 1 equiv of diphenylammonium chloride along with  $\text{H}_2[\text{MesON}]\text{Cl}$  or  $\text{H}_2[\text{TripON}]\text{Cl}$ . In this manner,  $\text{Mo}(\text{NAr}_{\text{Me}})(\text{CHCMe}_2\text{Ph})(\text{MesON})\text{Cl}$  (3(MesON)),  $\text{Mo}(\text{NAr}_{\text{Me}})(\text{CHCMe}_2\text{Ph})(\text{TripON})\text{Cl}$  (3(TripON)),  $\text{Mo}(\text{N-}t\text{-Bu})(\text{CHCMe}_2\text{Ph})(\text{MesON})\text{Cl}$  (4(MesON)), and  $\text{Mo}(\text{N-}t\text{-Bu})(\text{CHCMe}_2\text{Ph})(\text{TripON})\text{Cl}$  (4(TripON)) could be prepared, although in relatively poor yields (25–30%; eq 3). NMR spectra of all four again are characteristic of compounds that have no symmetry. Compounds 3(MesON) and 3(TripON) were found to be *anti* isomers in solution with alkylidene resonances at 14.33 ppm ( $J_{\text{CH}} = 146$  Hz) and 14.35 ppm ( $J_{\text{CH}} = 146$  Hz), respectively, whereas 4(MesON) and 4(TripON) were found to be *syn* isomers with alkylidene resonances at 13.30 ppm ( $J_{\text{CH}} = 125$  Hz) and 13.31 ppm ( $J_{\text{CH}} = 125$  Hz).



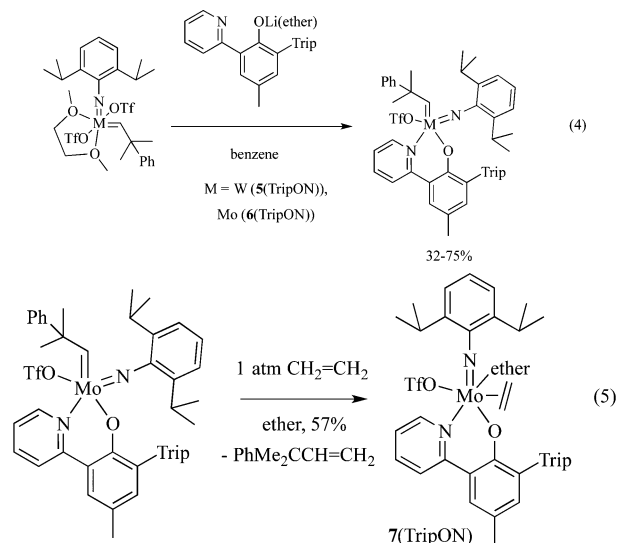
An X-ray structure of 3(TripON) (Figure 4) shows that the metal center adopts a highly distorted structure approximately halfway between a square pyramid and a trigonal bipyramid ( $\tau = 0.43$ ). The complex crystallizes as the *anti* isomer with  $\text{Mo}(1)\text{--C}(1)\text{--C}(2) = 127.6(3)^\circ$ . The imido ligand is found *trans* to the phenoxide with a  $\text{N}(1)\text{--Mo}(1)\text{--O}(1)$  bond angle of  $141.4(2)^\circ$ , while the chloride ligand is *trans* to



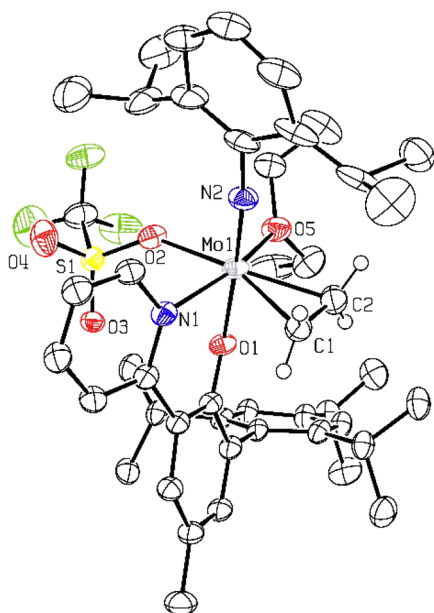
**Figure 4.** Thermal ellipsoid drawing (50% probability) of 3(TripON). The solvent and most of the hydrogen atoms were removed for clarity.

the pyridyl donor with a  $\text{Cl}(1)\text{--Mo}(1)\text{--N}(2)$  bond angle of  $166.3(1)^\circ$ .

Treatment of  $\text{H}[\text{TripON}]$  with *n*-BuLi in ether/hexanes yielded  $\text{Li}(\text{ether})[\text{TripON}]$  in 80% yield. Reactions between  $\text{Li}(\text{ether})[\text{TripON}]$  and  $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{DME})(\text{OTf})_2$  (Ar is 2,6-diisopropylphenylimido) or  $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{DME})(\text{OTf})_2$  gave the monotriflate complexes,  $\text{W}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{TripON})(\text{OTf})$  (5(TripON)) and  $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{TripON})(\text{OTf})$  (6(TripON)), in poor to moderate yields (32–75%; eq 4). NMR spectra showed that both 5(TripON) and 6(TripON) are unsymmetric and mixtures of *syn* and *anti* isomers. In 5(TripON), the alkylidene is predominantly in the *anti* orientation with  $H_\alpha$  resonances at 12.75 ppm ( $J_{\text{CH}} = 144$  Hz, *anti*) and 10.52 ppm ( $J_{\text{CH}} = 114$  Hz, *syn*), while, in 6(TripON), the alkylidene is predominantly *syn* with  $H_\alpha$  resonances at 14.94 ( $J_{\text{CH}} = 147$  Hz, *anti*) and 13.29 ( $J_{\text{CH}} = 119$  Hz, *syn*) ppm.



A reaction between 6(TripON) and ethylene in diethyl ether yielded the ethylene complex,  $\text{Mo}(\text{NAr})(\text{C}_2\text{H}_4)(\text{TripON})(\text{OTf})(\text{ether})$  (7(TripON); eq 5), which could be isolated in 57% yield. An X-ray structure of 7(TripON) (Figure 5) revealed that the molybdenum center adopts a pseudo-octahedral coordination geometry with the imido and phenoxide ligands *trans* to one another. The  $\text{Mo}(1)\text{--C}(1)$  and  $\text{Mo}(1)\text{--C}(2)$  bond lengths (2.200(6) and 2.193(6) Å, respectively) and  $\text{C}(1)\text{--C}(2)$  bond length (1.40(1) Å) are similar to those in other molybdenum imido ethylene complexes of this general type.<sup>4</sup>



**Figure 5.** Thermal ellipsoid drawing (50% probability) of 7(TripON). The solvent and most of the hydrogen atoms were removed for clarity.

The formation of 7(TripON) establishes that no metallacyclobutane complex that is relatively stable toward loss of ethylene is formed in this system, unlike the system that contains the  $[\text{ONO}]^{2-}$  ligand (Figure 2) described earlier. The metal is reduced either through bimolecular coupling of an intermediate methyldene complex to give ethylene or through rearrangement of the unsubstituted metallacyclobutane to propylene, which is then displaced by ethylene.

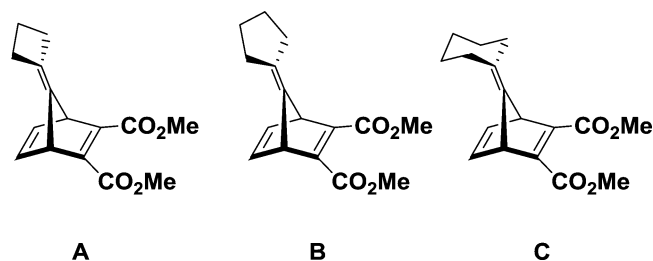
Crystalline samples of 7(TripON) all had essentially the same relatively complex NMR spectra consistent with 7(TripON) having no symmetry. However, the spectra were complicated further by the presence of another unsymmetric complex ( $\sim 60\%$  7(TripON')) formed through dissociation of ether from the metal in 7(TripON)). This proposal was confirmed through HSQC NMR spectroscopy (see the SI), where two sets of four ethylene proton resonances were identified for the two different species. One equivalent of free ether relative to 7(TripON') was also present in the NMR spectra.

Attempts to homocouple 1-hexene or 1-octene with complexes 1–6 revealed that they are all essentially inactive at room temperature. Homocoupling did proceed slowly at 80–120 °C to give roughly 1:1 mixtures of *cis* and *trans* homocoupled products (see the SI). However, some isomerization of the terminal olefins to internal olefins was also observed. Olefin isomerization is virtually unknown in metathesis reactions with Mo and W catalysts at room temperature. However, at temperatures above 100 °C, it has been shown that olefin complexes, which are plausible decomposition products of metathesis catalysts, can slowly catalytically isomerize olefins, presumably through allylic CH activation and allyl/hydride intermediates.<sup>7</sup> They also can convert olefins of a given chain length into a mixture of chain lengths through metathesis processes as a consequence of formation of traces of one or more alkylidene complexes from the olefin complexes in an as yet unknown manner. One possibility is that metallacyclobutanes can also form via an allyl hydride intermediate and then lose olefin to yield an alkylidene.

Reactions between 7(TripON) and 40 equiv of 1-octene at 100 °C showed that 1-octene was isomerized to 2-, 3-, and 4-octenes (according to GC). We also examined the reaction of 7(TripON) with neat 1-octene after 4 days at 150 °C; the reaction mixture was hydrogenated with 5% palladium on carbon and shown by GC to contain a distribution of alkanes between  $\text{C}_7$  and  $\text{C}_{14}$ , consistent with olefin metathesis in addition to olefin isomerization. (Details can be found in the Supporting Information.)

Complexes 1–6 were also tested for alkane metathesis (AM)<sup>1</sup> with  $\text{Ir}(t\text{-BuPOCOP})(\text{C}_2\text{H}_4)$  (where *t*-BuPOCOP is  $(\text{Me}_3\text{C})_2\text{POC}_6\text{H}_3\text{OP}(\text{CMe}_3)_2$ ) as the dehydrogenation/hydrogenation catalyst in a sealed J-Young tube in *n*-octane at 150 or 200 °C for 4 days. Only 1(MesON), 1(TripON), 4(TripON), 5(TripON), and 6(TripON) showed any (all modest) AM activity compared to reported activities with 14e initiators. (See the SI for details.) A distribution of alkane products was seen (from  $\text{C}_7$  to  $\text{C}_{14}$  chains) with essentially no selectivity for any given chain length.

Finally, we explored the polymerization of monomers A, B, and C (Figure 6; 50 equiv in toluene- $d_8$ ) with 1(MesON).<sup>8</sup>



**Figure 6.** Monomers polymerized by 1(MesON).

The polymerizations were extremely slow at 22 °C, but proceeded smoothly at 100 °C (see the SI) over a period of 1 h to give highly regular polymers in high yield according to their proton and carbon NMR spectra. IR spectra suggested that the polymers are not *trans*, and therefore, they must be *cis, isotactic*, or *cis, syndiotactic*. It is not possible to assign the tacticity with the data in hand. (See the SI.) We propose that dissociation of the pyridyl donor at 100 °C exposes the 14e core to attack by the monomer. Monomers A, B, and C were also polymerized by  $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{OHMT})(\text{Me}_2\text{Pyr})$  or  $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{OHMT})(\text{Me}_2\text{Pyr})(\text{PMe}_2\text{Ph})$  at 22 °C, but only polyA had a regularity comparable to that found when 1(MesON) was employed at 100 °C. The selectivity of these reactions eroded with increasing steric bulk of the ring in the 7-position of the three monomers (A–C).

## CONCLUSION

Complexes that contain an  $[\text{RON}]^{1-}$  ligand ( $\text{R} = \text{Mes}$  or  $\text{Trip}$ ) have been prepared and isolated. In several cases, the alkylidene can be prepared in a reaction between the dialkyl bisimido precursor and  $\text{H}_2[\text{RON}]\text{Cl}$ . Complexes that contain the  $[\text{RON}]^{1-}$  ligand reported here are more active in metathesis than compounds previously published with the same electron count that contain the  $[\text{ONO}]^{2-}$  ligand.<sup>3</sup> However, activity is still relatively low compared to catalysts with 14 electron counts. We conclude that coordination of the pyridyl group slows reactions to a significant degree and that metathesis appears to be limited by olefin isomerization at the high temperatures necessary for significant rates. The polymerizations of A, B, and C confirm



that ROMP can be stereoselective with  $[\text{RON}]^-$  complexes at 100 °C.

## ■ EXPERIMENTAL SECTION

**General Considerations.** All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk line and glovebox techniques unless stated otherwise. All glassware was oven-dried or flame-dried prior to use unless stated otherwise. Ether, pentane, toluene, dichloromethane, toluene, and benzene were degassed with dinitrogen and passed through activated alumina columns under nitrogen unless stated otherwise. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen-filled glovebox. Reagents were purchased from commercial sources and used without further purification unless stated otherwise. Deuterated solvents were purchased from Cambridge Isotope Laboratories. They were degassed and dried over activated molecular sieves prior to use. 2-(Tributylstannyl)pyridine,  $W(O)(CHCMe_2Ph)(Me_2Pyr)_2(PPhMe_2)$ ,  $W(O)(CHCMe_2Ph)(Me_2Pyr)(HMTTO)$ ,  $W(O)(CHCMe_2Ph)(Me_2Pyr)(HMTTO)(MeCN)$ ,  $W(O)(CHCMe_2Ph)(Me_2Pyr)(HMTTO)(PMe_2Ph)$ ,  $Mo(NAr)(CHCMe_2Ph)(DME)(OTf)_2$ ,  $W(NAr)(CHCMe_2Ph)(DME)(OTf)_2$ ,  $Mo(N-t-Bu)_2(DME)Cl_2$ ,  $Mo(NArMe)_2(CH_2CMe_2Ph)_2$ , and  $Mo(NC_6F_5)_2(CH_2CMe_2Ph)_2$  were synthesized according to literature procedures,<sup>3,5-9</sup> as were variations of the reported procedures for 2,6-dibromo-4-methylphenol,<sup>10</sup> 2,6-dibromo-4-methylanisole,<sup>11</sup> 3-bromo-2-methoxy-2',4',5,6'-tetramethyl-1,1'-biphenyl,<sup>12</sup> and 2,6-diiodo-4-methylphenol (see the SI).<sup>13</sup> NMR spectra were recorded on a Bruker 400 MHz spectrometer or a Varian 500 or 300 MHz spectrometer at ambient temperature. The  $^1H$  and  $^{13}C$  NMR spectra were measured relative to proton chemical shifts in partially deuterated NMR solvents, but are reported relative to tetramethylsilane. All  $^{19}F$  chemical shifts were measured relative to fluorobenzene ( $-113.15$  ppm) as an external reference. Elemental analyses were performed at the CENTC Elemental Analysis Facility at the University of Rochester with a PerkinElmer 2400 Series II CHN Analyzer.

**Synthesis of 2-(2-Methoxy-2',4',5,6'-tetramethyl-[1,1'-biphenyl]-3-yl)pyridinium Chloride.** The product was synthesized via a modified procedure reported by Yang et al.<sup>14</sup> A solution of 1.49 g of 2-bromopyridine (1.5 equiv, 9.40 mmol) in 10 mL of THF was cooled to  $-78^{\circ}\text{C}$ , and 4 mL of 2.5 M *n*-BuLi in hexanes (1.58 equiv, 10.0 mmol) was slowly added. The reaction was stirred at  $-78^{\circ}\text{C}$  for 1 h, and then anhydrous 1.37 g of  $\text{ZnCl}_2$  (1.58 equiv, 10.0 mmol) in 20 mL of THF was added. The reaction was warmed to room temperature, and solutions of 2.00 g of 3-bromo-2-methoxy-2',4',5,6'-tetramethyl-1,1'-biphenyl (1 equiv, 6.30 mmol) in 20.0 mL of THF and a 1:1 premixed solution of 0.149 g of XPhos (0.05 equiv, 0.31 mmol, CAS 564483-18-7) in 5 mL of THF and 0.265 g of XPhos Pd G3 (0.05 equiv, 0.31 mmol, CAS 1445085-55-1) in 5 mL of THF were added. An equivalent volume of anhydrous NMP was then added in one portion, and the reaction was heated at  $110^{\circ}\text{C}$  for 24 h. The reaction was cooled to room temperature, and the organic solvent was removed under high vacuum. The crude residue was taken up in 100 mL of  $\text{CH}_2\text{Cl}_2$  and washed with 50 mL of saturated  $\text{NH}_4\text{Cl}$  and 50 mL of brine. The organic layer was dried over anhydrous  $\text{MgSO}_4$ . The mixture was then filtered, and the solvent was removed from the filtrate using a rotary evaporator. The crude product was passed through a plug of silica. Residual impurities were removed through precipitation of the acidified product from an acetone–hexane mixture with excess 1.0 M HCl in ether; yield 2.0 g (90%). HRMS for  $\text{C}_{22}\text{H}_{24}\text{ClNO}$ : Theoretical  $[\text{M} - \text{Cl}]$ : 318.1852. Found  $[\text{M} - \text{Cl}]$ : 318.1850.

**Synthesis of 2',4',5,6'-Tetramethyl-3-(pyridin-2-yl)-[1,1'-biphenyl]-2-ol H[MesON].** A flask was charged with 2.0 g of 2-(2-methoxy-2',4',5,6'-tetramethyl-[1,1'-biphenyl]-3-yl)pyridinium chloride (1 equiv, 5.65 mmol) and excess pyridinium hydrochloride (~15 g). The mixture was then heated to reflux for 30 min. The reaction was allowed to cool to room temperature before dissolving the resulting residue in 200 mL of a 1:1 mixture of CH<sub>2</sub>Cl<sub>2</sub>:H<sub>2</sub>O. An additional 50 mL of CH<sub>2</sub>Cl<sub>2</sub> was added before separating the aqueous

layer, and washing the organic layer with 50 mL of saturated  $\text{NaHCO}_3$ , followed by 50 mL of brine. The organic layer was dried over anhydrous  $\text{MgSO}_4$ . After 30 min, the mixture was filtered and the solvent was removed from the filtrate using a rotary evaporator. The yellow residue was stirred in MeOH for several hours to afford an off-white solid; yield 0.7 g (56%). Anal. Calcd for  $[\text{C}_{21}\text{H}_{21}\text{NO}]$ : C, 83.13; H, 6.98; N, 4.62. Found: C, 82.77; H, 7.05; N, 4.51.

**Synthesis of 3-Iodo-2',4',6'-triisopropyl-5-methyl-[1,1'-bi-phenyl]-2-ol.** The product was synthesized via a modified procedure reported by Wu et al.<sup>15</sup> A suspension of 3.43 g of Mg (1.27 equiv, 0.141 mol) in 300 mL of THF was heated to reflux, and 40.00 g of 2-bromo-1,3,5-triisopropylbenzene (1.27 equiv, 0.141 mol) was added dropwise. The resulting mixture was refluxed for 1 h, and then cooled to room temperature. In another flask, a suspension of 2.81 g of 95% wt NaH (1 equiv, 0.111 mol) in 150 mL of THF was cooled to 0 °C. A solution of 40.00 g of 2,6-diiodo-4-methylphenol (1 equiv, 0.111 mmol) in 100 mL of THF was added slowly. The reaction was stirred at room temperature for 20 min, and the clear yellow solution was cooled to 0 °C. Pd(acac)<sub>2</sub> (3.38 g, 0.1 equiv, 0.012 mol) was added as a powder. The mixture was stirred for 5 min, and a solution of (2,4,6-triisopropylphenyl)magnesium bromide was added via cannula while maintaining the temperature at 0 °C. The resulting orange suspension was warmed to room temperature and stirred for 24 h. The solvent was removed, and 200 mL of water was added to the residue, followed by 12 mL of 35% wt aq. HCl (1.3 equiv, 0.144 mol). The aqueous solution was extracted with ethyl acetate (3 × 100 mL), and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was filtered, and the solvent was removed from the filtrate using a rotary evaporator. The product was recrystallized from MeOH at -20 °C to give a light gray powder; yield 21.8 g (45%). Anal. Calcd for C<sub>22</sub>H<sub>30</sub>IO: C, 60.55; H, 6.70. Found: C, 59.47; H, 6.67.

**Synthesis of 2',4',6'-Triisopropyl-5-methyl-3-(pyridin-2-yl)-[1,1'-biphenyl]-2-ol (H(TripON)).** To a solution of 9.1 g of 3-iodo-2',4',6'-triisopropyl-5-methyl-[1,1'-biphenyl]-2-ol (1 equiv, 20.8 mmol) and 9.2 g of 2-(tributylstannyl)pyridine (1 equiv, 20.8 mmol) in 100 mL of toluene was added 1.2 g of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 equiv, 1.04 mmol). The reaction mixture was refluxed for 36 h. The reaction was then cooled to room temperature, and the solvent was removed in vacuo. The residue was stirred in 50 mL of MeOH for 30 min, and the powder was filtered off and washed with cold MeOH. The filtrate was cooled to -20 °C and stood for several days. The product was filtered off and washed with cold MeOH. The yellow precipitates were combined and dried under high vacuum; yield 5.036 g (64%). Anal. Calcd for C<sub>27</sub>H<sub>33</sub>NO: C, 83.68; H, 8.58; N, 3.61. Found: C, 83.29; H, 8.87; N, 3.41.

**Synthesis of  $\text{H}_2[\text{MesON}]\text{Cl}$ .** A round-bottom flask was charged with 0.425 g of  $\text{H}[\text{MesON}]$  (1 equiv, 1.40 mmol) and suspended in 5 mL of ether with stirring. 2.5 mL of 1 M  $\text{HCl}$  in ether (1.8 equiv, 2.50 mmol) was added, and the resulting slurry was stirred for 45 min. The white precipitate was isolated by filtration, washed with cold ether, and dried under high vacuum to yield a white solid; yield 0.432 g (90.7%). Anal. Calcd for  $\text{C}_{21}\text{H}_{22}\text{ClNO}$ : C, 74.22; H, 6.52; N, 4.12. Found: C, 74.63; H, 6.69; N, 4.12.

**Synthesis of H<sub>2</sub>[TripON]Cl.** A round-bottom flask was charged with 0.477 g of H[TripON] (1 equiv, 1.23 mmol) and suspended in 5 mL of ether with stirring. 2.5 mL of 1 M HCl in ether (2 equiv, 2.50 mmol) was added, and the resulting slurry was stirred for 45 min. The white precipitate was isolated by filtration, washed with cold ether, and dried under high vacuum to yield a white solid; yield 0.495 g (94.9%). Anal. Calcd for C<sub>27</sub>H<sub>34</sub>ClNO: C, 76.48; H, 8.08; N, 3.30. Found: C, 76.78; H, 8.25; N, 3.28.

**Synthesis of Li[TripON].** A vial was charged with a solution of 0.300 g of H[TripON] (1 equiv, 0.77 mmol) in 3 mL of ether. The resulting yellow solution was cooled to  $-30\text{ }^{\circ}\text{C}$ . A cold solution of 0.31 mL of 2.5 M *n*-BuLi in *n*-hexane was added, and the resulting mixture was stirred at room temperature for 10 min. White precipitate formed. The precipitate was filtered off, washed with cold pentane, and dried under high vacuum to give the product as a white precipitate and an etherate salt; yield 0.247 g (80%). Anal. Calcd for  $\text{C}_{27}\text{H}_{34}\text{ClNO}\cdot\text{C}_4\text{H}_{10}\text{O}$ : C, 79.62; H, 9.05; N, 3.00. Found: C, 79.19; H, 9.05; N, 2.88.

**Synthesis of 1[MesON].** A vial was charged with 0.1085 g of  $W(O)(CHCMe_2Ph)(Me_2Pyr)_2(PPhMe_2)$  (1 equiv, 0.165 mmol), and a solution of 0.050 g of  $H[MesON]$  (1 equiv, 0.165 mmol) in 5 mL of benzene was added. The solution was stirred overnight, and the solvent was removed *in vacuo*. The resulting residue was stirred in ~6 mL of pentane for several hours, and the yellow powder was filtered off, washed with pentane, and dried under high vacuum; yield 0.0586 g (48.8%). Anal. Calcd for  $C_{43}H_{52}N_2O_2W$ : C, 61.00; H, 5.53; N, 3.85. Found: C, 60.78; H, 5.44; N, 3.72.

**Synthesis of 1[TripON].** A vial was charged with 0.0849 g of  $W(O)(CHCMe_2Ph)(Me_2Pyr)_2(PPhMe_2)$  (1 equiv, 0.129 mmol), and a solution of 0.050 g of  $H[TripON]$  (1 equiv, 0.129 mmol) in 5 mL of benzene was added. The solution was stirred overnight, and the solvent was removed *in vacuo*. The resulting residue was stirred in ~4 mL of pentane for several hours, and the yellow powder was filtered off, washed with pentane, and dried under high vacuum; yield 0.0507 g (48.4%). Anal. Calcd for  $[C_{43}H_{52}N_2O_2W]$ : C, 63.55; H, 6.45; N, 3.45. Found: C, 63.52; H, 6.41; N, 3.30.

**Synthesis of  $Mo(N-t-Bu)_2(CH_2CMe_2Ph)_2$ .** A suspension of 0.500 g of  $Mo(N-t-Bu)_2(DME)Cl_2$  (1 equiv, 1.25 mmol) in 12 mL of ether was cooled to  $-30^\circ C$ . To the chilled solution was added 5 mL of 0.5 M 2-methyl-2-phenylpropylmagnesium chloride in ether (2 equiv, 2.5 mmol) slowly. The reaction was allowed to warm to room temperature and left overnight. The reaction was filtered, and the solvent was removed under reduced pressure. The oily residue was dissolved in ~10 mL of pentane, and the solution was chilled to  $-30^\circ C$  overnight. The solution was filtered, and the solvent was removed *in vacuo*. The crude product was used without further purification; yield 0.5873 g (92.9%).

**Synthesis of 2(MesON).** A vial was charged with 0.100 g of  $2[MesON]Cl$  (1 equiv, 0.294 mmol), and a solution of 0.2132 g of  $Mo(NC_6F_5)_2(CH_2CMe_2Ph)_2$  (1 equiv, 0.294 mmol) in 7 mL of benzene was added. The solution was stirred for 4 h, and the solvent was removed *in vacuo*. The resulting residue was stirred in ~5 mL of pentane for several hours, and the yellow solid was filtered off, washed with pentane, and dried under high vacuum; yield 0.1648 g (75.0%). According to NMR data (see the SI), *syn* and *anti* isomers were present in a ratio of 94:6. Anal. Calcd for  $C_{37}H_{32}ClF_5MoN_2O$ : C, 59.49; H, 4.32; N, 3.75. Found: C, 59.33; H, 4.15; N, 3.64.

**Synthesis of 2(TripON).** A vial was charged with 0.100 g of  $H_2[TripON]Cl$  (1 equiv, 0.236 mmol), and a solution of 0.1709 g of  $Mo(NC_6F_5)_2(CH_2CMe_2Ph)_2$  (1 equiv, 0.236 mmol) in 7 mL of benzene was added. The solution was stirred for 4 h, and the solvent was removed *in vacuo*. The resulting residue was stirred in ~5 mL of pentane for several hours, filtered, washed with pentane, and dried under high vacuum to yield a yellow solid; yield 0.1223 g (62.4%). *Syn* and *anti* isomers were present in a ratio of 85:15. Anal. Calcd for  $C_{43}H_{44}ClF_3MoN_2O$ : C, 62.13; H, 5.34; N, 3.37. Found: C, 62.00; H, 5.26; N, 3.20.

**Synthesis of 3(MesON).** A vial was charged with 0.1485 g of  $Mo(NAr_{Me})_2(CH_2CMe_2Ph)_2$  (1 equiv, 0.247 mmol) and a suspension of 0.100 g of  $H_2[MesON]Cl$  (1 equiv, 0.247 mmol) in 5 mL of benzene was slowly added. The solution was stirred for 4 h, and a suspension of 0.0605 g of  $Ph_2NH_2Cl$  (1 equiv, 0.247 mmol) in 5 mL of benzene was added slowly. The solution was stirred for an additional 3 h and filtered. The solvent was removed under reduced pressure, and the dark residue was dissolved in ~1 mL of dichloromethane. The dichloromethane solution was layered with 15 mL of pentane and cooled to  $-30^\circ C$  for 2 days. The dark orange solution was decanted from the black oily residue and cooled to  $-30^\circ C$ . The dark residue was dissolved in ~3 mL of ether, and the mixture was stirred for 1 h. The yellow precipitate was isolated by filtration, washed with cold ether, and dried under high vacuum. The dark orange solution yielded a mixture of yellow precipitate and black crystalline solid after cooling for several days. The dark orange solution was decanted, and the mixture of solids was dried under reduced pressure. The solids were stirred in ~2 mL of ether for 1 h. The yellow precipitate was isolated by filtration, washed with cold ether, and dried under high vacuum. The two crops of precipitate were combined to give the desired product as a pale yellow powder; yield 0.0468 g

(27.7%). Anal. Calcd for  $C_{39}H_{41}ClMoN_2O$ : C, 68.37; H, 6.03; N, 4.09. Found: C, 68.74; H, 5.72; N, 4.59.

**Synthesis of 3(TripON).** A vial was charged with 0.1417 g of  $Mo(NAr_{Me})_2(CH_2CMe_2Ph)_2$  (1 equiv, 0.236 mmol), and a suspension of 0.100 g of  $H_2[MesON]Cl$  (1 equiv, 0.236 mmol) in 5 mL of benzene was slowly added. The solution was stirred for 4 h, and a suspension of 0.0485 g of  $Ph_2NH_2Cl$  (1 equiv, 0.236 mmol) in 5 mL of benzene was added slowly. The solution was stirred for an additional 3 h and filtered. The solvent was removed under reduced pressure, and the dark residue was triturated in ~6 mL of pentane for several hours. The orange precipitate was isolated by filtration, washed with pentane, and dried under high vacuum. The product was dissolved in ~5 mL of ether, and the solution was filtered. The filtrate was layered with 15 mL of pentane, cooled to  $-30^\circ C$ , and left at  $-30^\circ C$  for several days. The crystalline yellow product was isolated by filtration, washed with cold pentane, and dried *in vacuo*; yield 0.0487 g (26.8%). Anal. Calcd for  $C_{45}H_{53}ClMoN_2O$ : C, 70.25; H, 6.94; N, 3.64. Found: C, 70.10; H, 6.98; N, 3.63.

**Synthesis of 4(MesON).** A vial was charged with 0.1246 g of  $Mo(N-t-Bu)_2(CH_2CMe_2Ph)_2$  (1 equiv, 0.247 mmol), and a suspension of 0.100 g of  $H_2[MesON]Cl$  (1 equiv, 0.247 mmol) in 5 mL of benzene was slowly added. The solution was stirred for 4 h, and a suspension of 0.0605 g of  $Ph_2NH_2Cl$  (1 equiv, 0.247 mmol) in 5 mL of benzene was added slowly. The solution was stirred for an additional 3 h and filtered. The solvent was removed under reduced pressure, and the dark residue was dissolved in ~40 mL of pentane. The solution was filtered and cooled to  $-30^\circ C$  for 2 days. The light brown precipitate was isolated by filtration, washed with cold pentane, and dried *in vacuo*. Half the solvent was removed from the filtrate, and the solution was cooled to  $-30^\circ C$  for 2 days. The light brown precipitate was isolated by filtration, washed with cold pentane, dried under high vacuum, and combined with the previous crop to give a total yield of 0.0386 g (24.5%). Anal. Calcd for  $C_{35}H_{41}ClMoN_2O$ : C, 65.98; H, 6.49; N, 4.40. Found: C, 66.30; H, 6.18; N, 4.41.

**Synthesis of 4(TripON).** A vial was charged with 0.1417 g of  $Mo(NAr_{Me})_2(CH_2CMe_2Ph)_2$  (1 equiv, 0.236 mmol), and a suspension of 0.100 g of  $H_2[TripON]Cl$  (1 equiv, 0.236 mmol) in 5 mL of benzene was slowly added. The solution was stirred for 4 h, and a suspension of 0.0485 g of  $Ph_2NH_2Cl$  (1 equiv, 0.236 mmol) in 5 mL of benzene was added slowly. The solution was stirred for an additional 3 h and filtered. The solvent was removed under reduced pressure, and the dark residue was stirred in approximately 6 mL of pentane for several hours. The orange precipitate was isolated by filtration, washed with pentane, and dried under high vacuum. The product was dissolved in ~5 mL of ether and filtered. The filtrate was layered with 15 mL of pentane, cooled to  $-30^\circ C$ , and left for several days. The crystalline yellow product was isolated by filtration, washed with cold pentane, and dried under high vacuum; yield 0.0474 g (27.8%). Anal. Calcd for  $C_{45}H_{53}ClMoN_2O \cdot 2CH_3CN$ : C, 67.28; H, 7.40; N, 6.97. Found: C, 67.49; H, 7.53; N, 6.97.

**Synthesis of 5(TripON).** A Schlenk flask was charged with 0.1567 g of  $W(NAr)(CHCMe_2Ph)(DME)(OTf)_2$  (1 equiv, 0.178 mmol), and a solution of 0.100 g of  $Li[TripON]$  (1.2 equiv, 0.214 mmol) in 10 mL of benzene was added. The flask was sealed, and the solution was heated to  $60^\circ C$  for 16 h. The solution was cooled to room temperature and filtered through Celite, and the solvent was removed under reduced pressure. The orange solid was dissolved in approximately 4 mL of pentane and decanted from the insoluble oily residue. The solution was stirred for 1 h; the precipitate was isolated by filtration, washed with cold pentane, and dried under high vacuum to give the product as a pale orange powder; yield 0.0573 g (31.3%). *Syn* and *anti* isomers were present in a 74:26 ratio. Anal. Calcd for  $C_{50}H_{61}F_3N_2O_4SW$ : C, 58.48; H, 5.99; N, 2.73. Found: C, 58.21; H, 5.94; N, 2.62.

**Synthesis of 6(TripON).** A vial was charged with 0.1693 g of  $Mo(NAr)(CHCMe_2Ph)(DME)(OTf)_2$  (1 equiv, 0.214 mmol), and a solution of 0.120 g of  $Li[TripON]$  (1.2 equiv, 0.257 mmol) in 10 mL of benzene was added. The solution was stirred for 3 h and filtered through Celite, and the solvent was removed under reduced pressure. The dark residue was stirred in approximately 8 mL of pentane for

several hours; the precipitate was isolated by filtration, washed with pentane, and dried under vacuum. The yellow precipitate was dissolved in 5 mL of benzene and filtered through Celite, and the solvent was removed under reduced pressure. The residue was stirred in ~5 mL of pentane for 1 h; the precipitate was isolated by filtration, washed with pentane, and dried under high vacuum to give the product as a yellow powder; yield 0.144 g (71.7%). *Syn* and *anti* isomers were present in a 24:76 ratio. Anal. Calcd for  $C_{50}H_{61}F_3MoN_2O_4S$ : C, 63.95; H, 6.55; N, 2.98. Found: C, 63.77; H, 6.49; N, 2.92.

**Synthesis of 7(TripON).** A Schlenk flask was charged with a suspension of 0.100 g of 6[TripON] (1 equiv, 0.106 mmol) in 5 mL of ether and put under an atmosphere of ethylene. The solution was stirred for 16 h, and the orange precipitate was washed with cold pentane and dried under high vacuum. The filtrate was layered with 10 mL of pentane and cooled to  $-30\text{ }^{\circ}\text{C}$  for several days. The resulting orange crystals were isolated by filtration, washed with cold pentane, and dried under high vacuum. The orange precipitate and crystals were combined. In solution, the product is a mixture of the ether adduct and the ether-free complex in a 40:60 ratio; yield 0.0549 g (57.0%). Crystalline samples for elemental analysis consistently failed to give acceptable values, perhaps as a consequence of loss of ether in the solid state during shipping. Anal. Calcd for  $C_{46}H_{63}F_3MoN_2O_5S$ : C, 60.78; H, 6.99; N, 3.08. Found: C, 59.49; H, 6.78; N, 2.97.

**Polymerization of Monomers A, B, and C.** In a J-Young tube, 50 equiv of the monomer (52.1 mg of A, 54.9 mg of B, and 57.7 mg of C) was added to 0.5 mL of toluene- $d_8$ . A 0.5 mL solution of the initiator (2.8 mg, 4.0  $\mu\text{mol}$ ) in toluene- $d_8$  was then added. The tube was sealed and immersed into a preheated oil bath at  $100\text{ }^{\circ}\text{C}$  outside the glovebox, and the progress of the reaction was monitored by  $^1\text{H}$  NMR spectroscopy. After the monomer was consumed (1 h), the viscous solution was exposed to air and the solution was added dropwise to 35 mL of methanol. The polymer was isolated by centrifugation and dried *in vacuo*. IR and NMR spectra can be found in the SI. The rate of consumption of monomer was not zero, first, or second order in monomer.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00644.

Crystallographic data for all X-ray structures (CIF)  
Complete NMR data and spectra for all compounds, a description of the structural studies of 2(MesON), 3(TripON), and 7(TripON), and a description of the polymerization of A, B, and C (PDF)

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### Notes

The authors declare no competing financial interest.

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