**ABSTRACT:** In the interest of preparing molybdenum and tungsten alkylidene complexes for olefin metathesis that are longer-lived at high temperatures (≥150 °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-Pr3C6H2 (Trip) in the other ortho position ([MesON]− or [TripON]−, respectively). The alkylidene (neophylidene) complexes that were prepared include W(O)(CHCMe2Ph)(Me2Pyr)(RON) (R = Mes or Trip), Mo(NC6F5)(CHCMe2Ph)(RON)Cl, Mo(N-t-Bu)(CHCMe2Ph)(RON)Cl, and M(N-2,6-i-Pr2C6H3)(CHCMe2Ph)(TripON)(OTf) (M = Mo or W). The reaction between Mo(NAr)(CHCMe2Ph)(TripON)(OTf) and ethylene yielded an ethylene complex, Mo(NAr)(C2H4)(TripON)(OTf)(ether). All neophylidene complexes were essentially unreactive toward terminal olefins at 22 °C and showed modest homocoupling activity (at 80 or 100 °C) and alkane metathesis activity (at 150 and 200 °C). W(O)(CHCMe2Ph)(Me2Pyr)(MesON) also stereoselectively polymerized several substituted norbornadienes at 100 °C.

**INTRODUCTION**

The synthesis of olefin metathesis catalysts that are relatively stable and active above 150 °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. 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; 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 pyridyl donor is likely to be necessary for reaction with an olefin. We found that a six-coordinate metallacyclobutane complex, Mo(NC6F5)(CH2CH2CH2)(ONO), which is formed from Mo(NC6F5)(CHCMe2Ph)(ONO) upon reaction with ethylene, is 5 or more orders of magnitude more stable toward loss of ethylene than typical 14e TBP metallacycles. A tungsten-based oxo metallacyclobutane complex, W(O)(CH2CH2CH2)(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 (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 °C or greater. To this end, we prepared two such bidentate ligands which we call [MesON]− (2′,4′,5′,6′-tetramethyl-3-(pyridin-2-yl)-[1,1′-biphenyl]-2-olate) and [TripON]− (2′,4′,6′-triisopropyl-5-methyl-3-(pyridin-2-yl)-[1,1′-biphenyl]-2-olate; Figure 1). These bidentate ligands could allow the required TBP metallacycle structure to form through dissociation of the pyridyl donor, unlike the tridentate [ONO]2− 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.

**Supporting Information**

**Figure 1.** [MesON]− and [TripON]− ligands.
RESULTS AND DISCUSSION

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

Addition of H[MesON] or H[TripON] to W(O)(CHC-Me2Ph)(Me2Pyr)(PPhMe2) (where Me2Pyr is 2,5-dimethylpyrrolide), yielded two new tungsten oxo MAP (monoaryl-oxide pyrrolide) complexes as a consequence of protonation of one of the pyrrolide ligands, as shown in eq 1. The reaction employing H[MesON] proceeded several times faster than the reaction employing H[TripON] (~16 h), as one might expect on the basis of the larger size of H[TripON]. W(O)(CHC-Me2Ph)(Me2Pyr)(MesON) (1(MesON)) and W(O)(CHC-Me2Ph)(Me2Pyr)(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 C1 symmetry.

On the basis of the fact that H2[ONO] (Figure 2) will protonate imido groups in bisimido dialkyl precursors to give alkylidene complexes, we proposed that protonated forms of H[MesON] and H[TripON] might lead directly from dineophyl to neophylidene complexes. Alkylidene formation is the result of an irreversible α abstraction reaction after double protonation of an imido ligand and loss of the aniline. Treatment of H[MesON] and H[TripON] with an excess of HCl in ether gave the HCl adducts, H2[MesON]Cl and H2[TripON]Cl, respectively, as white powders in >90% yields. Reactions between H2[MesON]Cl or H2[TripON]Cl and Mo(NC6F5)2(CH2CMe2Ph)2 proceeded smoothly to give Mo(NC6F5)(CHCMe2Ph)(MesON)Cl (2(MesON)) and Mo(NC6F5)(CHCMe2Ph)(TripON)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 (JCH = 148 Hz, anti) and 13.31 (JCH = 147 Hz, syn) ppm for 2(MesON), and 14.52 (JCH = 127 Hz, syn) and 13.39 (JCH = 127 Hz, anti) ppm for 2(TripON).

An X-ray study of 2(MesON) shows that its structure is close to a distorted square pyramid structure (r = 0.12°) with the

Figure 2. [ONO]2− ligand.
alkylidene ligand in the apical position (Figure 3). The complex crystallizes as the syn isomer, in which Mo(1)−C(1)−C(2) = 142.8(6)°. The imido and phenoxide ligands are trans to one another with N(2)−Mo(1)−O(1) = 150.4(2)°, while Cl(1)−Mo(1)−N(1) = 157.6(2)°.

Attempts to extend the reactions shown in eq 2 to aryl- and alkylimido precursors Mo(NArMe)2(CH2CMe2Ph)2 and Mo(N-t-Bu)2(CH2CMe2Ph)2 (where NArMe = 2,6-dimethylphenylimido) led to only ∼50% conversion of the starting material and formation of a colorless precipitate in each case. The problem was traced to a deprotonation of H2[MesON]Cl or H2[TripON]Cl by the ArMeNH2 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 H2[MesON]Cl or H2[TripON]Cl.

In this manner, Mo(NArMe)(CHCMe2Ph)(MesON)Cl (3(MesON)), Mo(NArMe)(CHCMe2Ph)(TripON)Cl (3(TripON)), Mo(N-t-Bu)(CHCMe2Ph)(MesON)Cl (4(MesON)), and Mo(N-t-Bu)(CHCMe2Ph)(TripON)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 (JCH = 146 Hz, anti) and 14.35 ppm (JCH = 146 Hz), respectively, whereas 4(MesON) and 4(TripON) were found to be syn isomers with alkylidene resonances at 13.30 ppm (JCH = 125 Hz) and 13.31 ppm (JCH = 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 (τ = 0.43). The complex crystallizes as the anti isomer with Mo(1)−C(1)−C(2) = 127.6(3)°. The imido ligand is found trans to the phenoxide with a N(1)−Mo(1)−O(1) bond angle of 141.4(2)°, while the chloride ligand is trans to the pyridyl donor with a Cl(1)−Mo(1)−N(2) bond angle of 166.3(1)°.

Treatment of H[TripON] with n-BuLi in ether/hexanes yielded Li(ether)[TripON] in 80% yield. Reactions between Li(ether)[TripON] and W(NAr)(CHCMe2Ph)(DME)(OTf)2 (Ar is 2,6-diisopropylphenylimido) or Mo(NAr)(CHCMe2Ph)(DME)(OTf)2 gave the mono triflate complexes, W(NAr)(CHCMe2Ph)(TripON)(OTf) (5(TripON)) and Mo(NAr)(CHCMe2Ph)(TripON)(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 Ha resonances at 12.75 ppm (JCH = 144 Hz, anti) and 10.52 ppm (JCH = 114 Hz, syn), while, in 6(TripON), the alkylidene is predominantly syn with Ha resonances at 14.94 (JCH = 147 Hz, anti) and 13.29 (JCH = 119 Hz, syn) ppm.

A reaction between 6(TripON) and ethylene in diethyl ether yielded the ethylene complex, Mo(NAr)(C2H4)(TripON)(OTf)(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 Mo(1)−C(1) and Mo(1)−C(2) bond lengths (2.200(6) and 2.193(6) Å, respectively) and C(1)−C(2) bond length (1.40(1) Å) are similar to those in other molybdenum imido ethylene complexes of this general type.4
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 C7 and C16 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)\(^1\) with Ir(t-BuPOCOP)(C,H\(_5\)) where t-BuPOCOP is \((\text{Me}_2\text{Pyr})\text{POC}_6\text{H}_3\text{OP(CMe}_3)_2\)) 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 C7 to C14 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).\(^8\)

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 W(O)(CHCM,eP)OHMT(Me,Pyr) or W(O)(CHCMe,P)OHMT(Me,Pyr)(PMe3,P) 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 [RON]\(^{1-}\) ligand (R = Mes or Trip) have been prepared and isolated. In several cases, the alkylidene can be prepared in a reaction between the dialkyl bisimido precursor and H\(_2\)[RON]Cl. Complexes that contain the [RON]\(^{1-}\) ligand reported here are more active in metathesis than compounds previously published with the same electron count that contain the [ONO]\(^{2-}\) ligand.\(^3\) 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 ROP can be stereoselective with [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 deoxygenized 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.

**Synthesis of 3-iodo-2′,4′,6′-trisopropyl-5 methyl-[1,1′-bi-phenyl]-2-ol (H[TripON]).** To a solution of 9.1 g of 3-iodo-2′,4′,6′-trisopropyl-5-methyl-[1,1′-bi-phenyl]-2-ol (1 equiv, 20.8 mmol) and 9.2 g of 2-(triphenylstannyl)pyridine (1 equiv, 20.8 mmol) in 100 mL of toluene was added 1.2 g of Pd(PPh₃)₄ (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 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. Calc. for C₉₆H₇₂ClO: C, 83.68; H, 8.58; N, 3.61. Found: C, 83.29; H, 8.87; N, 3.41.

**Synthesis of H₂[MesON]Cl.** A round-bottom flask was charged with 0.425 g of H[MesON] (1 equiv, 1.40 mmol) and suspended in 5 mL of ether with stirring. 2.5 mL of 1 M 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. Calc. for C₅H₁₀ClO: C, 74.22; H, 6.52; N, 4.12. Found: C, 74.63; H, 6.69; N, 4.12.

**Synthesis of H₃[TripON].** 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. Calc. for C₆₂H₅₀ClO₃: 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 °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. Calc. for C₆₂H₅₀ClO₃: 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)((CHMe2Ph)2(Me2Pyr))(PhMe) (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. Calcld for [C43H52N2O2W]: C, 63.55; H, 6.45; N, 5.26; W, 15.73. Found: C, 65.98; H, 5.72; N, 5.15.

Synthesis of 1(TripON). A vial was charged with 0.0849 g of W(O)((CHMe2Ph)2(Me2Pyr))(PhMe) (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. Calcld for [C43H52N2O2W]: C, 63.55; H, 6.45; N, 5.26. Found: C, 66.30; H, 6.18; N, 5.41.

Synthesis of 2(MesON). A vial was charged with 0.100 g of 2(MesON)Cl (1 equiv, 0.247 mmol) and a suspension of 0.100 g of Mo(NArMe)2(CH2Me2Ph)2 (1 equiv, 0.247 mmol) in 10 mL of benzene was slowly 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 0.1223 g (59.49%). Anal. Calcld for C39H41ClMoN2O: 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)(CHCMe2Ph)(DME)(OTf)2 (1 equiv, 0.214 mmol), and a solution of 0.100 g of H[TripON] (1 equiv, 0.247 mmol) in 5 mL of benzene was slowly added. The solution was stirred for 4 h, and a suspension of 0.0485 g of Ph3NH2Cl (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 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 °C, and left at ~30 °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. Calcld for C39H41ClMoN2O: C, 70.25; H, 6.34; N, 3.63. 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(CH2CMe2Ph)2 (1 equiv, 0.247 mmol), and a suspension of 0.100 g of H[MesON]Cl (1 equiv, 0.247 mmol) in 5 mL of benzene was added. The solution was stirred for 4 h, and a suspension of 0.0605 g of Ph3NH2Cl (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 °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 °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. Calcld for C39H41ClMoN2O: 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)(CHCMe2Ph)(DME)(OTf)2 (1 equiv, 0.214 mmol), and a solution of 0.100 g of H[TripON] (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 Ph3NH2Cl (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 dissolved in ~40 mL of pentane. The solution was filtered and cooled to ~30 °C for 2 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. Calcld for C39H41ClMoN2O: 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)(CHCMe2Ph)(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 °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. Calcld for C39H41ClMoN2O: C, 70.25; H, 6.34; N, 3.63. Found: C, 70.10; H, 6.98; N, 3.63.

Synthesis of 6(TripON). A vial was charged with 0.1693 g of Mo(NAr)(CHCMe2Ph)(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 30 min Lo f
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%). 

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 °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%).

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-d₈. IR and NMR spectra can be found in the Supporting Information.

ASSOCIATED CONTENT

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

AUTHOR INFORMATION

Corresponding Author
*E-mail: rrs@mit.edu.

Notes
The authors declare no competing financial interest.

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AUTHOR INFORMATION

Corresponding Author
*E-mail: rrs@mit.edu.

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Supporting Information
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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)