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Propellanes as Drop-In ROMP Initiators

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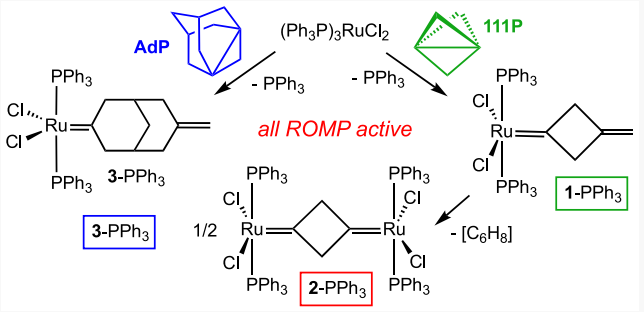
ABSTRACT: Addition of 1.1.1-propellane (**111P**) to $(Ph_3P)_3MCl_2$ (M = Ru, Os) afforded 3-*exo*-methylenecycloalkylidene complexes $(Ph_3P)_2Cl_2M{=}(^cC_4H_4){=}CH_2$ (M = Ru, **1**-PPh_3; M = Os, **4**-PPh_3) via electrophilic ring opening. When they were combined *in situ* or when they were isolated, both **1**-PPh_3 and **4**-PPh_3 were competent at the ROMP of norbornene. Phosphine substitution of **1**-PPh_3 with P^cHex_3 generated $(^cHex_3P)_2Cl_2Ru{=}(^cC_4H_4){=}CH_2$ (**1**-P^cHex_3), which was competent at norbornene ROMP and ring-closing metathesis. Similar *in situ* addition of tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane (i.e., 1,3-dehydroadamantane, **AdP**) to $(Ph_3P)_3RuCl_2$ yielded $(Ph_3P)_2Cl_2Ru{=}C\{C_9H_{14}\}$ (**3**-PPh_3), a cyclohexylidene derivative with related reactivity. Self-metathesis of **1**-PPh_3 produced $(Ph_3P)_2Cl_2Ru{=}(^cC_4H_4){=}RuCl_2(PPh_3)$ (**2**-PPh_3), which was structurally characterized. The use of ^{13}C-labeled **111P*** enabled identification of several alkylidene resonances in ^{13}C NMR spectra.



INTRODUCTION

Olefin metathesis, the swapping of the ends of olefins, and related polymerization reactions involving ring opening are critical reactions in the commodities and fine-chemical industries. The reactions are catalyzed by metal alkylidene complexes, $L_nM{=}CRR'$ (R is usually H, R′ is a hydrocarbyl), and Robert H. Grubbs, Richard R. Schrock, and Yves Chauvin were awarded the Nobel Prize in 2005 for understanding the process and catalyst development.[1−5]

Historically, organometallic chemistry has been advanced by a plethora of physical organic studies addressing the reactions of small molecules with labile metal species. Trapping cyclobutadiene,[6] benzyne,[7] etc. or activating cyclopropanes with metal fragments[8−10] has provided valuable insight into the development and mechanistic understanding of the field. Germane to the topic herein is the application of a special cyclopropane, 1.1.1-propellane (**111P**),[11−13] the simplest member of the propellane family, whose constituents possess rings—typically at least one being strained—cylindrically disposed about a central C−C bond. Early exposures of **111P** to transition metals generally resulted in rearrangements to 3-*exo*-methylenecyclobutene, dimers of the ring-opened carbene, and a trimer likely generated by cyclopropanation of the dimer, as shown in Scheme 1a.[14] Whether the products resulted from a transient metal alkylidene[15,16] or the free carbene was typically left in question.

A potentially practical application was recently reported by Aggarwal,[17] who thoroughly examined cyclopropanations with Ni(0) and **111P**. While styrenic substrates appear to be the most viable, the substrate scope was reasonable, and further elaboration of the *exo*-methylene constituent provided varied functionalities (Scheme 1b). While there is precedent for stable metal alkylidenes (carbenes and CPh_2 groups are excluded) in the late metals,[18−22] a treatise by Hoffmann et al. suggests that olefin metathesis can only be experienced in metals that are d^n ($n \leq 4$).[23] Since access to the corresponding formal oxidation states can only be reasonably achieved by ruthenium[1] and osmium,[24−29] their utility in olefin metathesis and related reactions is readily explained. Cyclopropanation reactivity is expected from late metals in other d counts, and the varied products in Scheme 1 are likely derived from the alkylidene or free carbene.[14−17]

In Scheme 2, two means of carbene formation are envisaged from **111P**: ring opening via metal nucleophiles on the σ^*_{CC} orbital and electrophilic attack at the σ^b_{CC} orbital. In either case, the protuberance of the σ^b_{CC} and σ^*_{CC} orbitals extending from the propellane framework provide ready access to the bridgehead carbon, allowing for cleavage of the central propellane bond and subsequent ring opening of a strained cyclobutane that neutralizes the opposing bridgehead charge. Herein we examine 1.1.1-propellane (**111P**) and tetracyclo-[3.3.1.1^{3,7}.0^{1,3}]decane (i.e., 1,3-dehydroadamantane, **AdP**)[30] as alkylidene precursors[31,32] in systems capable of ultimately conducting ROMP or olefin metathesis.

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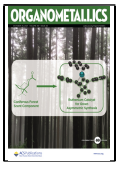

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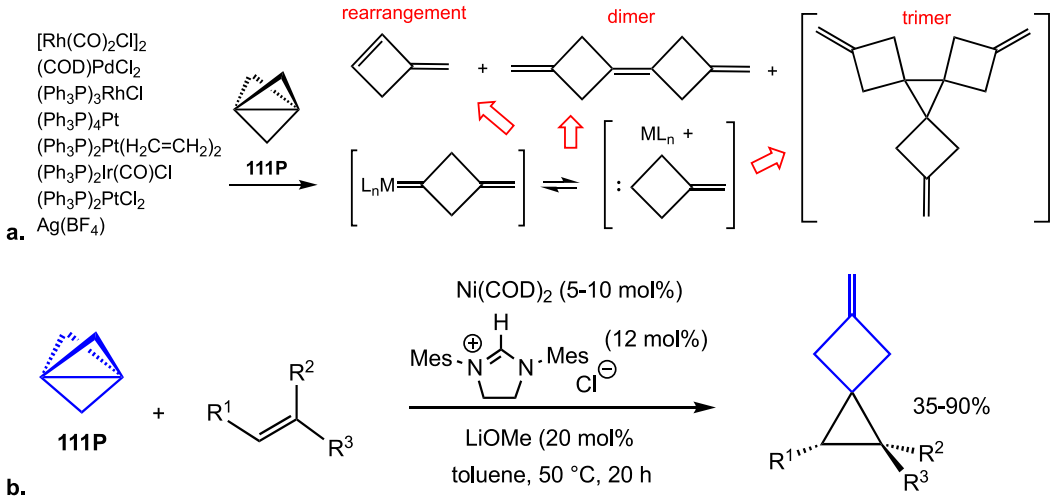
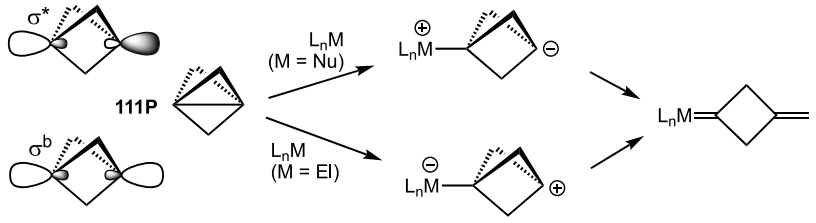
Scheme 1. (a) Initial Transition-Metal Studies with 1.1.1-Propellane Revealing Rearrangement and Aggregation Products and (b) Recent Practical Studies Showing Catalytic Cyclopropanations with Ni(0)



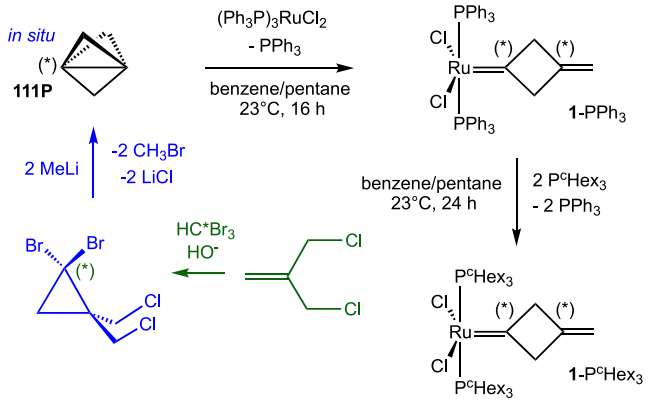
Scheme 2. Potenial Nucleophilic and Electrophilic Ring Openings of 1.1.1-Propellane (P111) Leading to a Strained 3-*exo*-Methylene Cyclobutenylidene



RESULTS AND DISCUSSION

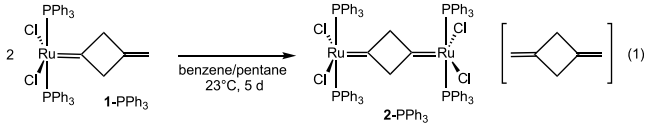
Synthesis of 1.1.1-Propellane-Derived Group 8 Alkylidenes. Treatment of a benzene solution of $(Ph_3P)_3RuCl_2$[33] with a pentane solution (~0.20 M) of excess 1.1.1-propellane (**111P**) generated $(Ph_3P)_2Cl_2Ru{=}(^cC_4H_4){=}CH_2$ (**1**-PPh_3) in 75% yield upon precipitation from benzene/pentane (Scheme 3). In all syntheses, **111P** was generated *in situ* using the method of Semmler, Szeimies, and Belzner,[34] which utilizes 1,1-dibromo-2,2-chloromethylcyclopropane and 2 equiv of MeLi. The ^1H NMR (C_6D_6) spectral signature for the strained 3-*exo*-methylenecyclobutanylidene is clear in the ^1H NMR spectrum of **1**-PPh_3 as two singlets at δ 3.30 and 4.65 in a ratio of 4H:2H, and the ^{31}P NMR spectrum of the complex manifests a singlet at δ 28.15. Without hydrogens on the alkylidene carbon, observation of its resonance in ^{13}C NMR spectra proved difficult. Fortunately, dibromocarbene can be generated from labeled bromoform ($H^{13}CBr_3$ = HC^*Br_3),[35] enabling labeling of the bridgehead carbons in **111P***. The alkylidene resonance was identified in the ^{13}C NMR spectrum at δ 326.39 with an 11.2 Hz coupling to the phosphines. Another first-generation Grubbs catalyst, $(^cHex_3P)_2Cl_2Ru{=}(^cC_4H_4){=}CH_2$ (**1**-P^cHex_3), was prepared via phosphine substitution, and a related, barely resolved signal was seen at δ 325.71 in its ^{13}C NMR spectrum along with a single ^{31}P NMR spectral resonance at δ 27.35. Both alkylidenes were modestly thermally sensitive, and efforts to obtain single crystals were hampered by remnants of PPh_3 and slow degradation.

Scheme 3. Syntheses of First-Generation Grubbs Catalysts Using 111P, Prepared *In Situ* Using the Procedure of Semmler, Szeimies, and Belzner[34,a]



[a]Shown in green, labeled $H^{13}CBr_3$ (HC^*Br_3) enables the synthesis of **111P*** with ^{13}C distributed between the bridgehead carbons.

Fortunately, the thermal stability of $(Ph_3P)_2Cl_2Ru{=}(^cC_4H_4){=}CH_2$ (**1**-PPh_3) provided a crystalline byproduct (52%) that is readily rationalized by its self-metathesis. As shown in eq 1, the dimer



$(Ph_3P)_2Cl_2Ru{=}(^cC_4H_4){=}RuCl_2(PPh_3)$ (**2**-PPh_3) was isolated from crystallization experiments, while the presumed

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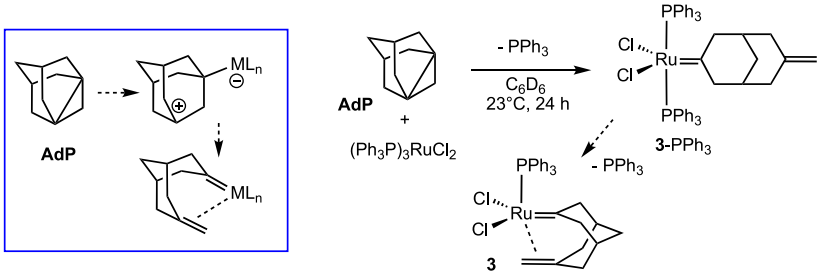
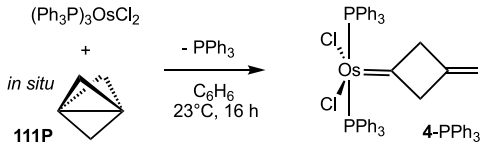
Scheme 4. Application of Tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane (i.e. 1,3-Dehydroadamantane, AdP) as an Alkylidene Precursor for Ru



initial organic byproduct, 1,3-di-*exo*-methylenecyclobutane, has not been identified and is unlikely to be stable in this environment. The ^{1}H NMR spectrum of **2**-PPh$_3$ lacks any olefinic signals, and its methylene singlet (δ 3.14) has half the integration of mononuclear **1**-PPh$_3$ relative to the phenyl resonances. The ^{31}P NMR spectral resonance at δ 27.44 is similar to that of **1**-PPh$_3$, and the alkylidene resonance is tentatively assigned at δ 325.71 in its ^{13}C NMR spectrum, although ^{31}P coupling could not be resolved. In this case structural confirmation of the compound was acquired by single-crystal X-ray crystallography.

The application of propellane substrates to group 8 alkylidene chemistry is not limited to 1.1.1-propellane (**111P**). As shown in Scheme 4, exposure of (Ph$_3$P)$_3$RuCl$_2$ to tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane, more commonly known as 1,3-dehydroadamantane (**AdP**),[30] provided the 3-alkylidene-6-*exo*-methylenetricyclo[3.3.1]decane ruthenium complex (Ph$_3$P)$_2$Cl$_2$Ru=C(C$_9$H$_{14}$) (**3**-PPh$_3$) in >90% yield on an NMR-tube scale. **AdP** was considered as a substrate due to its stability and the possibility that a labile PPh$_3$ might allow isolation of a highly labile *exo*-methylene isomer (**3**). Attempts toward the stoichiometric removal of PPh$_3$ from **3**-PPh$_3$ have not yet been fruitful. Elucidation of the ^{1}H NMR spectral signature of **3**-PPh$_3$ required multidimensional NMR experiments, which identified three diasterotopic CH$_2$ groups in a 4H:4H:2H ratio and an olefinic resonance at δ 4.86. The ^{31}P NMR spectrum of **3**-PPh$_3$ exhibits a singlet at δ 25.28, and a ^{13}C NMR resonance at δ 340.37 was tentatively assigned to the alkylidene carbon, although coupling to phosphorus was again not resolved. While **3**-PPh$_3$ was prepared rather cleanly on an NMR-tube scale, repeated efforts to isolate it were hampered by difficulties in removing free PPh$_3$ and (Ph$_3$P)$_3$RuCl$_2$ starting materials.

Related osmium derivatives of Grubbs catalysts have been prepared[24] but they have seen little utility due to increased expense, negligible performance advantages, and increased toxicity. Nonetheless, treatment of (Ph$_3$P)$_3$OsCl$_2$[36] with a pentane solution (~0.20 M) of 1.1.1-propellane (**111P**) generated (Ph$_3$P)$_2$Cl$_2$Os=(^{c}C$_4$H$_4$)=CH$_2$ (**4**-PPh$_3$) in 55% yield upon precipitation from pentane (eq 2). The NMR

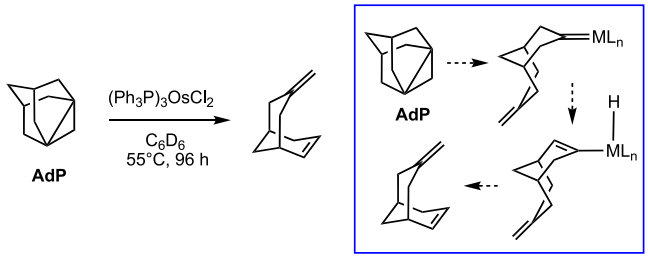


(2)

spectral signatures of **4**-PPh$_3$ resembled those of **1**-PPh$_3$, with ^{1}H singlet resonances at δ 3.59 (4H) and 4.63 (2H) reflecting the allylic and olefin *exo*-methylene cyclobutane hydrogens and a singlet in the ^{31}P NMR spectrum at δ 12.13. Unfortunately, the alkylidene resonance could not be identified in the ^{13}C NMR spectrum.

A related treatment of (Ph$_3$P)$_3$OsCl$_2$ with **AdP** failed to elilcit the desired alkylidene, instead producing 3-methylenebicyclo[3.3.1]non-6-ene in essentially quantitative yield, as illustrated in Scheme 5. Interestingly, this did not

Scheme 5. Rearrangement of AdP in the Presence of (Ph$_3$P)$_3$OsCl$_2$ and Likely Mechanism



preclude (Ph$_3$P)$_3$OsCl$_2$ and **AdP** from serving as a ROMP precatalyst combination (*vide infra*). As a consequence, it is possible that ring opening of **AdP** by osmium to render the alkylidene occurs but competing β-H-transfer from adjacent methylenes, and subsequent reductive elimination, leads to the rearrangement of **AdP**.

Structure of (Ph$_3$P)$_2$Cl$_2$Ru=(^{c}C$_4$H$_4$)=RuCl$_2$(PPh$_3$) (2-PPh$_3$). A single-crystal X-ray diffraction study was performed on (Ph$_3$P)$_2$Cl$_2$Ru=(^{c}C$_4$H$_4$)=RuCl$_2$(PPh$_3$) (**2**-PPh$_3$), and a molecular view is presented in Figure 1 with pertinent metric parameters listed in its caption. While there was some modest disorder, there is nothing extraordinary regarding bonding in the complex. There is an inversion center amidst the 1,3-diylidene-cyclobutane (internal angles of 90.3(3) and 89.7(3)°), and the Ru=C distance is 1.917(4) Å. According to metrics provided by the CCDC graphed in Figure 2, the double bond is clearly longer than average, perhaps as a result of the *syn*-PPh$_3$ groups that abut the bridging cyclobutanediyl group. Note that the orientation of the double bond is rotated 90° from those of typical first- and second-generation Grubbs catalysts[37,38] but is in accord with calculations of the model complex (PH$_3$)$_2$Cl$_2$Ru=CH$_2$,[39] which minimizes steric effects. If this is the more stable electronic alkylidene environment, perhaps the modest sterics of the cyclobutanediyl and the pocket formed by the four Ph groups surrounding the bridge allow it to maintain this orientation.

The Ru−Cl distances average 2.354(2) Å, and the phosphines show a bond distance difference of ~0.15 Å (2.451(2) vs 2.302(2) Å) that can be attributed to asymmetry

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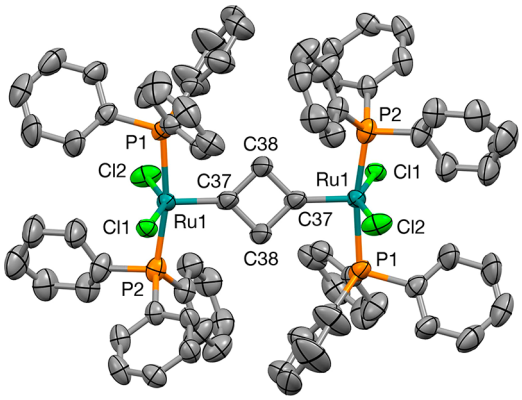


Figure 1. Molecular view of $(Ph_3P)_2Cl_2Ru{=}(^cC_4H_4){=}RuCl_2(PPh_3)_2$ (**2**-PPh_3), with selected interatomic distances (Å) and angles (deg) as follows: Ru−C37, 1.917(4); Ru−Cl1, 2.355(7); Ru−Cl2, 2.353(3); Ru−P1, 2.451(2); Ru−P2, 2.302(2); C37−C38, 1.510(4); C37−C38′, 1.528(5); P1−Ru−P2, 169.38(12); Cl1−Ru−Cl2, 149.18(19); C37−Ru−P1, 90.40(13); C37−Ru−P2, 100.20(14); C37−Ru−Cl1, 103.8(2); C37−Ru−Cl2, 107.01(16); P1−Ru−Cl1, 88.59(17); P1−Ru−Cl2, 90.25(9); P2−Ru−Cl1, 88.19(18); P2−Ru−Cl2, 87.35(9); Ru−C37−C38, 132.1(3); Ru−C37−C38′, 137.3(2); C37−C38−C37′, 89.7(3); C38−C37−C38′, 90.3(3).

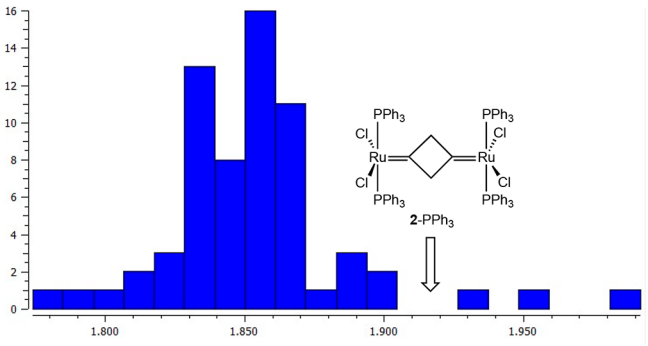


Figure 2. Distribution of 63 current d(Ru=C) values according to the Cambridge Crystallographic Data Center, revealing $(Ph_3P)_2Cl_2Ru{=}(^cC_4H_4){=}RuCl_2(PPh_3)$ (**2**-PPh_3) as containing uncommonly long distances.

derived from the mutual *trans* influence of the PPh_3 ligands. The core angles are closer to a square pyramid than a trigonal bipyramid, with an Addison[40] parameter of $\tau = 0.34$ based on the P1−Ru−P2 angle of 169.38(12)° and the Cl1−Ru−Cl2 angle of 149.18(19)°. The longer phosphine, P1, displays angles to the Cl atoms and alkylidene carbon averaging 89.8(10)°, while P2 exhibits greater variation, ranging from 107.01(16)° with the alkylidene carbon to an average of 87.8(6)° with the chlorines.

Drop-In ROMP Studies. Grubbs alkylidene catalysts of any generation are typically prepared beforehand, but there may be circumstances in which *in situ* synthesis of a catalyst could be useful. This application was reproducibly tested in norbornene polymerization, as indicated in Scheme 6. In addition, alkylidene preparation via 1.1.1-propellane (**111P**) is free of byproducts, making it different than most initiators, akin to the Binger reagent.[41,42] A caveat is that 1 equiv of PPh_3 is introduced upon *in situ* synthesis from standard precursors.

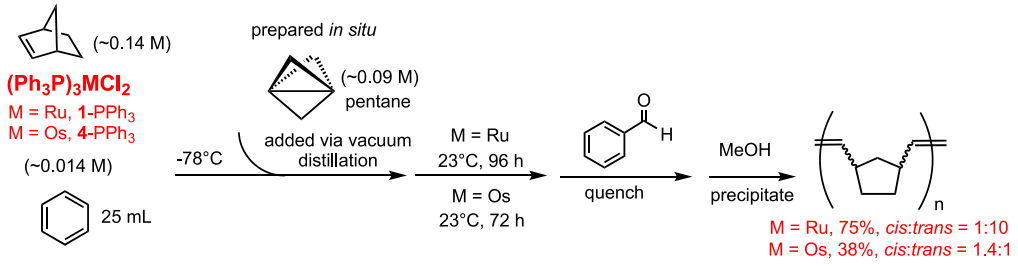
A benzene solution of group 8 precursor $(Ph_3P)_3Cl_2M$ (M = Ru, Os; 0.355 mmol) and norbornene (3.55 mmol) was frozen, and an ∼5 mL solution of **111P** (0.445 mmol, ∼ 0.09 M in pentane) was vacuum-distilled into the flask. Upon thawing to 23 °C, the mixture was stirred (Ru, 96 h; Os, 72 h), quenched with benzaldehyde, and harvested from MeOH. When M = Ru, a 75% yield of polynorbornene was obtained, and a ^{1}H NMR analysis of the product revealed a *cis*:*trans* ratio of 1:10, which matches previous reports on Grubbs first-generation catalysts.[42] For M = Os, the yield was lower (38%) and the *cis*:*trans* ratio of the polynorbornene was ∼1.4:1, consistent with osmium-based catalyses.[43]

Polymerizations with Cyclobutanylidene Complexes. Since the norbornene polymerizations[44] initiated with the propellanes below have the same propagation steps as in previous reports, with well-established spectral features, they were not studied in detail except to establish initiation viability.

Evidence that $L_2Cl_2Ru{=}(^cC_4H_4){=}CH_2$ (**1**-L; L = PPh_3, P^cHex_3) and $(PPh_3)_2Cl_2Os{=}(^cC_4H_4){=}CH_2$ (**4**-PPh_3) constituted the likely ROMP initiators was established by using the isolated complexes. First, as in the drop-in experiments above, **1**-PPh_3 was initially treated with 5 equiv norbornene, and the mixture was assessed by ^{1}H NMR spectroscopy after 12 h at 23 °C. Polymerization was evident, and less than 2% **1**-PPh_3 remained. Another 5 equiv of norbornene was added, and after 12 h complete conversion occurred, and no **1**-PPh_3 could be observed. This behavior is consistent with the expected living character of the propagating species,[42] and the trace of **1**-PPh_3 observed after only 5 equiv of norbornene addition suggests that the initiation (k_{init}) of polymerization is roughly similar to the propagation (k_{prop}).

As Figure 3 reveals, each 3-*exo*-methylenecyclobutanylidiene species was observed to polymerize 50−75 equiv of norbornene, with similar ^{1}H NMR spectral signatures and *cis*:*trans* ratios consistent with previously reported cases of ROMP and Scheme 6. Also, Ru=C*H* signals at δ ∼17.8 and end-group signals consistent with an *exo*-methylene-cyclobutanylidene group (from **1**-PPh_3, δ 4.94; from **1**-P^cHex_3, δ 4.95; from **4**-PPh_3, δ 4.94) were observed. Consumption of norbornene was swiftest with **1**-P^cHex_3 (≤45 min), followed by **1**-PPh_3 (≤3 h), with the osmium derivative **4**-PPh_3 proving

Scheme 6. General Procedure for "Drop-In" Initialization of Norbornene ROMP



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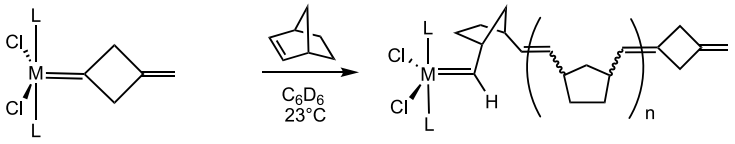
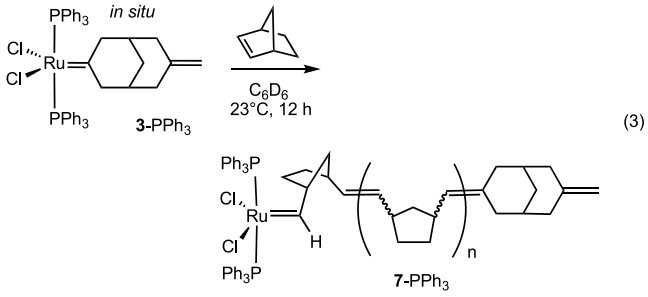


NBE polymerizations	t	NBE equiv
M = Ru, L = PPh_3 (**1**-PPh_3)	3 h	75
M = Ru, L = P^cHex_3 (**1**-$^cHex_3$)	45 min	50
M =Os, L = PPh_3 (**4**-PPh_3)	96 h	75

Figure 3. Bulk polymerizations using isolated cyclobutanylidene initiators.

somewhat sluggish (≤96 h), in line with prior work. While no **1**-P^cHex_3 initiator remained, traces of **1**-PPh_3 (<2%) and **4**-PPh_3 (<3%) were observed in those cases, again consistent with initiation rates comparable to propagation steps.

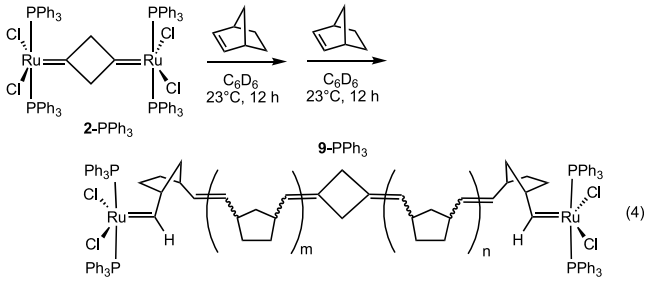
Application of the ring-opened 1,3-dehydroadamantane alkylidene $(Ph_3P)_2Cl_2Ru{=}C(C_9H_{14})$ (**3**-PPh_3) to the ROMP of norbornene was conducted in two ways. First, $(Ph_3P)_3RuCl_2$, **AdP**, and 50 equiv of norbornene were combined and heated at 55 °C, and complete consumption of norbornene was noted after 12 h. The ruthenium *cis*:*trans* ratio of 1:10 was again found, and no **3**-PPh_3 was detected, with the *exo*-methylene end group serving as an assayable ^1H NMR resonance (δ 4.66). A control run in which **AdP** was not included in the NMR tube yielded no polymer under the same conditions.[45,46] Premade **3**-PPh_3 (>95%), prepared *in situ*, was also subjected to 50 equiv of norbornene as in eq 3, and



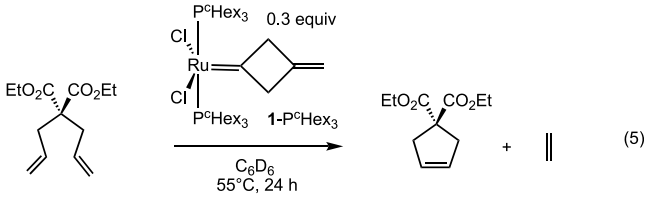
polymerization was complete within 7 h, with ∼3% **3**-PPh_3 remaining, suggesting that even this less strained, bulkier alkylidene possessed a k_{init} value close to that of k_{prop}.

Recall that the corresponding osmium alkyldene could not be isolated (Scheme 5), but subjecting $(Ph_3P)_3OsCl_2$ to **AdP** and 50 equiv of norbornene at 55 °C did afford polynorbornene over the course of 96 h. Its *cis*:*trans* ratio was 1.84:1, a slight change from osmium polymerization at 23 °C, and roughly 90% of the **AdP** was converted to 3-methylenebicyclo[3.3.1]non-6-ene. A plausible explanation is that $(Ph_3P)_2Cl_2Os{=}C\{C_9H_{14}\}$ (**8**-PPh_3), analogous to **3**-PPh_3, does form, but initiation unfavorably competes with rearrangement.

The dimer $[(Ph_3P)_2Cl_2Ru]_2(\mu\text{-}1,3\text{-}C_4H_4)$ (**2**-PPh_3) also served as a living catalyst for norbornene ROMP, as sequential additions of 5 equiv of norbornene were completely consumed, as eq 4 reveals. With 150 equiv of norbornene, no norbornene remained after 3 h, and ∼2% **2**-PPh_3 remained (eq 4). A rough integration of the alkylidene resonances (δ ∼17.9) relative to phosphine phenyl signals was consistent with ∼1.7 active ROMP centers; hence, the telechelic nature of **2**-PPh_3 is clear and its initiation events are again on par with propagation.

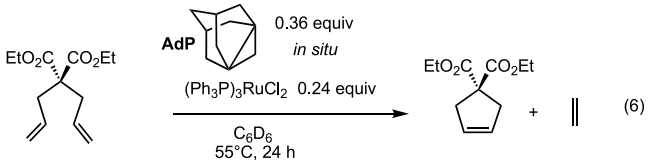


Olefin Metathesis with Cyclobutanylidene Complexes. Olefin metatheses with simple substrates such as ethylene and styrene proved difficult, but standard ring-closing metatheses (RCMs) were accomplished in NMR-tube-scale experiments in quantitative fashion. No attempt at optimization was made, as the complexes were tested simply to establish viability. In eq 5, the application of



$(^cHex_3P)_2Cl_2Ru{=}(^cC_4H_4){=}CH_2$ (**1**-P^cHex_3) to the RCM of diallylmalonic acid diester at 55 °C for 24 h in C_6D_6 afforded the cyclopentene in essentially quantitative yield, along with traces of ethylene. Roughly 8% of **1**-P^cHex_3 remains after diene consumption, indicating that the 3-*exo*-methylenecyclobutanylidene is quite competitive with the likely propagating ruthenium methylene.

Next, a related experiment was conducted where $(Ph_3P)_2Cl_2Ru{=}C(C_9H_{14})$ (**3**-PPh_3) was presumed to be generated *in situ* from **AdP** and $(Ph_3P)_3RuCl_2$ and applied to the RCM of diallylmalonic acid diester at 55 °C for 72 h (eq 6). Again, no diolefin starting material remained after this period; thus, quantitative conversion to 4,4-ethylcarboxylate-cyclopentene was realized and ∼12% of **3**-PPh_3 remained.



In eqs 5 and 6, it is important to note that control experiments without a metal complex or **AdP** failed to elicit the desired reactivity.[45,46]

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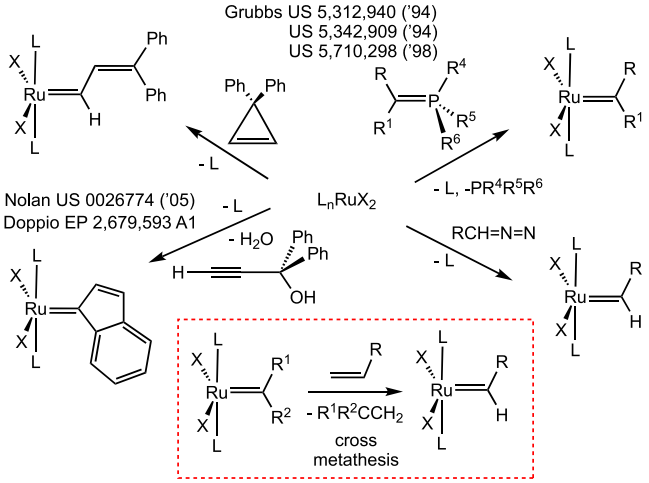
CONCLUSIONS

The application of 1.1.1-propellane (**111P**)[11−13,34] and tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane (i.e., 1,3-dehydroadamantane, **AdP**)[30] as alkylidene precursors may now be added to the pantheon of reagents used to initiate Grubbs-type catalysts. They are readily generated *in situ*, can be independently prepared, and possess excellent initiation rates relative to propagation, which should lead to low polydispersities for polynorbornene.[47]

A variety of the patented reactions used to prepare ruthenium alkylidenes is illustrated in Scheme 7. Diazoalkanes and related agents such as phosphoranes (i.e., $R^4R^5R^6P{=}CRR^1$) are among the most popular, as they permit the ready synthesis of neutral alkylidenes. $RR'CN_2$ species have two potential basic sites, and nitrogen binding can compete with carbene transfer.[48] Related transfer agents possess additional drawbacks. For example, the phosphine released ($R^4R^5R^6P$) upon use of the phosphorane can prove deleterious to subsequent reactions by inhibiting further RHC: transfer or inhibiting metathesis processes. In the case of 1,1-diphenyl-2-propynol, water is released, and while the ruthenium products are stable to small amounts, other transition-metal complexes might be subject to some form of hydrolysis. Only the Binger reagent (3,3-diphenylcyclopropene), which is substantially bulkier than **111P**, does not generate a byproduct.[32,33]

Scheme 7. Selection of Grubbs Catalyst Initiators



ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00398.

Experimental details on all procedures, spectroscopic data, and X-ray crystallographic information pertaining to **2**-PPh$_3$ (PDF)

Accession Codes

CCDC 2081299 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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