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ARTICLE

A thermally robust ruthenium phosphonium alkylidene catalyst — the effect of more bulky *N*-heterocyclic carbene ligands on catalyst performance in olefin metathesis reactions

Erin M. Leitao, Warren E. Piers, and Masood Parvez

Abstract: Three new ruthenium phosphonium alkylidene complexes incorporating *N*-heterocyclic carbene ligands with bulky *N*-aryl groups (2,6-diethyl, L = 1,3-bis(2,6-diethylphenyl)imidazolin-2-ylidene (H_2IDEP) and 2,6-diisopropyl, L = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (H_2ID-*i*-PP)) were synthesized and characterized. The H_2ID-*i*-PP supported complex was found to exhibit excellent thermal stabilities relative to the parent *N*-mesityl (*N*-Mes) complexes as well as the H_2IDEP supported complexes. All three phosphonium alkylidenes were evaluated in comparison to the *N*-Mes derivative and Grubbs second generation catalyst using standard olefin metathesis reactions and conditions. The complex containing the bulky H_2ID-*i*-PP ligand was found to have excellent activity and longevity in comparison to the other catalysts. Although initiation rates were slow for this sterically bulky precatalyst, its superior activity led to the best overall efficiency in test reactions.

Key words: olefin metathesis, ruthenium, catalysis, ligand design, decomposition.

Résumé : On a synthétisé et caractérisé trois nouveau complexes ruthénium phosphonium alkylidène dans lesquels sont intégrés des ligands carbènes *N*-hétérocycliques contenant des groupements *N*-aryles volumineux (2,6-diéthyle, L = 1,3-bis(2,6-diéthylphényl) imidazolin-2-ylidene (H_2IDEP) et 2,6-diisopropyle, L = 1,3-bis(2,6-diisopropylphényl)imidazolin-2-ylidene (H_2ID*i*PP)). On a constaté que les complexes supportés par H_2ID-*i*-PP présentaient une excellente stabilité thermique comparativement aux complexes *N*-mesityl (*N*-Mes) parents, ainsi qu'aux complexes supportés par H_2IDEP. On a évalué les trois phosphonium-alkylidènes comparativement au dérivé *N*-Mes et au catalyseur de Grubbs de deuxième génération en utilisant des réactions et des conditions classiques de métathèse des oléfines. L'activité et la longévité du complexe contenant le volumineux ligand H_2ID-*i*-PP se sont avérées excellentes comparativement aux autres catalyseurs. Même si les vitesses d'initiation de ce précatalyseur stériquement volumineux étaient faibles, son activité supérieure a donné lieu à la meilleure efficacité globale dans les réactions de test. [Traduit par la Rédaction]

Mots-clés : métathèse des oléfines, ruthénium, catalyse, conception de ligands, décomposition.

Introduction

Ruthenium-based olefin metathesis catalysts that combine high activity (turn over frequency) with high thermal stability (turn over number) are of interest for the continued development and application of this important technology. Since these two attributes tend to work against each other, imparting both can be a challenge, one that is met mainly through catalyst modification via ligand design. Using the catalyst platforms known as the first and second generation Grubbs complexes[1] or the Grubbs–Hoveyda complexes[2] (Chart 1: **I**, **II** and **III**, **IV**, respectively), impressive strides have been made in improving the longevity of these highly active catalysts. Further efforts have focused on substituting the chloride ligands for other anionic ligands,[3–14] and a wide variety of alkylidene ligands have also been employed.[15–29] Another approach has involved extensive modification of *N*-heterocyclic carbene (NHC) ligands[1,30–45] on the generally more active second generation ruthenium olefin metathesis catalysts. These investigations have unearthed a number of systematic variations that can lead to improvements in activity and thermal stability, but rarely both. The advances in this field have been summarized in recent reviews.[46,47]

The activity of catalysts **I–IV** is to a large degree related to the facility with which they dissociate the phosphine ligand trans to L and this dissociated phosphine can lead to catalyst decomposition.[48] The phosphonium alkylidene catalysts exemplified by **V** and **1-R_3-A** in Chart 1 eliminate L from the catalyst altogether, resulting in very rapidly initiating[49] and highly active[50] catalysts. These four-coordinate catalysts are accessed by protonating the terminal carbide ligand formed in stoichiometric metathesis reactions between **I** or **II** with Feist's ester.[51] However, as a consequence of this high activity, they tend to suffer from poor longevity,[52] particularly at higher temperatures or low concentrations of substrate. We have demonstrated that the dominant degradation pathway for these compounds involves reversible C–H addition from the *o*-methyl group on the aryl substituent of the NHC ligand across the phosphonium alkylidene double bond. (Scheme 1). Irreversible elimination of the methyl phosphonium salt forms a highly reactive chelating alkylidene that may be trapped with normally reticent substrates like 1,1-dichloroethene. Based on these observations,[52] we set out to stymie the initial C–H activation by modification of the ortho substitutents on the *N*-aryl groups.[30,35] In particular, we increased their steric bulk, incorporating ethyl and *iso*-propyl groups as shown in Chart 1. The idea being that this would increase the barriers required to attain the transition state for C–H addition across the Ru=C bond.[53] Examples of catalyst precursors **2-R_3-A** and **3-R_3-A** (Chart 1) were readily prepared and their performance evaluated against the previously

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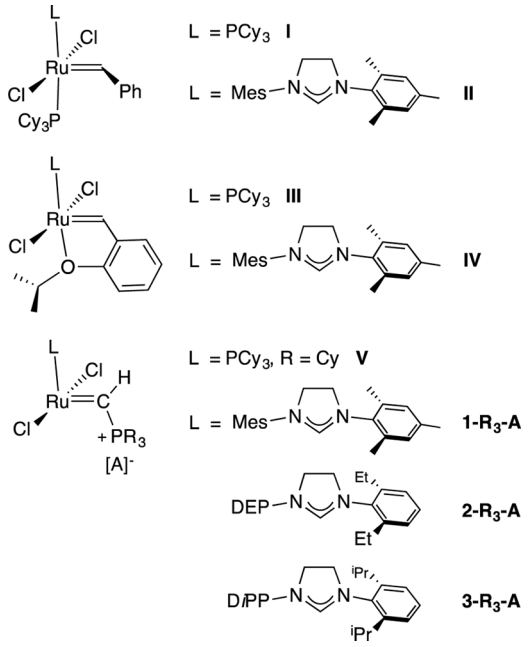
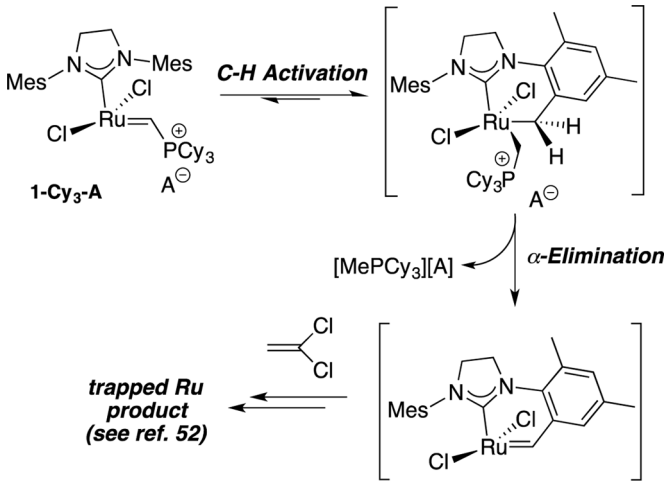
Chart 1.



Scheme 1.



studied compounds **II** and **1-R$_3$-ClB(C$_6$F$_5$)$_3$** in several standard metathesis applications.[38]

Results and discussion

Synthesis

The syntheses of the imidazolinium salts of 1,3-bis(2,6-diethylphenyl)imidazolin-2-ylidene (H$_2$IDEP·HCl) and 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (H$_2$ID-*i*-PP·HCl) are straightforward;[54,55] deprotonation with potassium hexamethyldisilazane (KHMDS) in tetrahydrofuran (THF), followed by recrystallization from hot hexanes gave the free carbenes. These ligands were installed onto ruthenium by substitution reactions using **I** (Chart 1) to afford the second generation type catalysts in moderate yields (59%–80%) upon workup. The standard methodology for preparing the phosphonium alkylidenes (Scheme 2), involving conversion to the terminal carbides using Feist's ester[51] followed by protonation with gaseous HCl in CH_2Cl_2, worked well with these ligands to afford compounds **2-Cy$_3$-Cl** (incorporating H$_2$IDEP, 57% yield) and **3-Cy$_3$-Cl** (incorporating H$_2$ID-*i*-PP, 77% yield). The triisopropylphosphonium derivative **2-iPr$_3$-Cl** was prepared in an 87% yield using a slightly different starting complex, namely the *bis*-pyridine adduct (H$_2$IDEP)(py)$_2$RuCl$_2$=C(H)Ph[12] prepared using methodology developed in our lab.[50,56] Attempts to prepare the missing compound in the series (i.e., **3-*i*-Pr$_3$-Cl**) were not successful (see the Supplementary material section for details on these attempts). These zwitterionic chloride salts were used as catalyst precursors due to their superior stability in the solid state, and easily lead to the highly active, four-coordinate catalysts ***n*-R$_3$-ClB(C$_6$F$_5$)$_3$** by treatment in situ with the strong, chloride abstracting Lewis acid B(C$_6$F$_5$)$_3$.[57–60]

The greater steric bulk of the NHC ligands in compounds **2-R$_3$-Cl** and **3-Cy$_3$-Cl** is manifest in their ^{1}H NMR spectra, as compared to that of the parent second generation phosphonium alkylidene catalyst precursor **1-Cy$_3$-Cl**. Sharp, time averaged signals for the *N*-mesityl (*N*-Mes) groups in **1-Cy$_3$-Cl** indicate that rotation about the Ru–NHC carbon bond is rapid on the NMR timescale in this species. For **2-Cy$_3$-Cl**, the ^{1}H NMR spectrum exhibits broadened resonances for both the *N*-aryl protons and the NHC backbone protons that decoalesce at low temperatures, a behavior consistent with restricted rotation about the NHC carbon–ruthenium bond that renders the *N*-aryl groups diastereotopic in the lower temperature regime. This behavior is not accounted for by exclusive restricted rotation about the *N*-aryl N–C bond.[61] For the bulkiest system, **3-Cy$_3$-Cl**, this rotation is slow enough at room temperature that sharp signals for two diastereotopic *N*-aryl groups are observable in the ^{1}H NMR spectra under these conditions.

Crystals suitable for X-ray diffraction of both **2-*i*-Pr$_3$-Cl** and **2-Cy$_3$-Cl** were grown by slow diffusion of pentane into a dichloromethane solution of zwitterions; the molecular structures are shown in Fig. 1, while selected metrical data appear in Table 1, along with analogous data for the corresponding mesityl substituted compounds **1-*i*-Pr$_3$-Cl**[56] and **1-Cy$_3$-Cl**[62] for comparison.

The geometry about the ruthenium center for these complexes is best described as distorted square pyramidal with the phosphonium alkylidene carbon C(1) occupying the apical position. Due to the greater steric bulk of the ortho groups in compounds **2-R$_3$-Cl**, the Ru(1)–C(1) distances of 1.83 Å are slightly elongated in comparison to the *N*-Mes analogs **1-R$_3$-Cl**, but otherwise the metrical parameters in the two new complexes are very similar to those in the previously reported *N*-Mes derivatives. Following the trend for other complexes containing three anionic chloride ligands, the chloride ligand trans to the NHC ligand has an elongated Ru(1)–Cl(3) bond relative to the others by ~0.12 Å.[50] In all four structures, the isopropyl and cyclohexyl substituents are rotated away from Cl(3) to minimize steric interactions. The C(2)–Ru(1)–C(1)–P(1) dihedral angles of 157.5(2)°–159.5(3)° were relatively consistent for the complexes, except for the bulkiest of the series, **2-Cy$_3$-Cl**, in which this dihedral angle is about 8° greater at 165.5(3)°.

Thermal stability

Previously, we have examined the thermal stability of catalysts **1-R$_3$-ClB(C$_6$F$_5$)$_3$** by heating in the presence of 1,1-dichloroethene (Scheme 1), establishing decomposition rate profiles.[52] For comparison, identical conditions were used to examine the thermal stability of the new compounds **2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$**, **2-Cy$_3$-ClB(C$_6$F$_5$)$_3$**, and **3-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$**; these derivatives were generated in situ by treating the chloride zwitterions with B(C$_6$F$_5$)$_3$. The progress of the decomposition of these compounds was monitored by following their disappearance, as well as the appearance of the [MePR$_3$][A] byproduct (Scheme 1), by ^{1}H NMR spectroscopy.

At 323 K, the thermal decomposition profile for **1-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$** exhibits clean first-order behavior,[52] but under the same conditions that of **2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$** deviates from an exponential decay curve (Fig. 2, top). The approximate half-life for the thermal degradation of **2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$** was found to be ≈120 min (Table 2), shorter than the *N*-Mes derivative **1-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$** whose half-life was ~200 min. We attribute this ap-

Scheme 2.

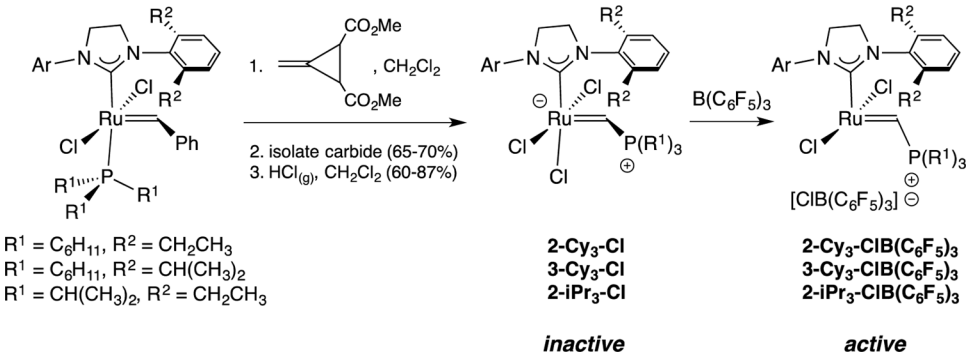
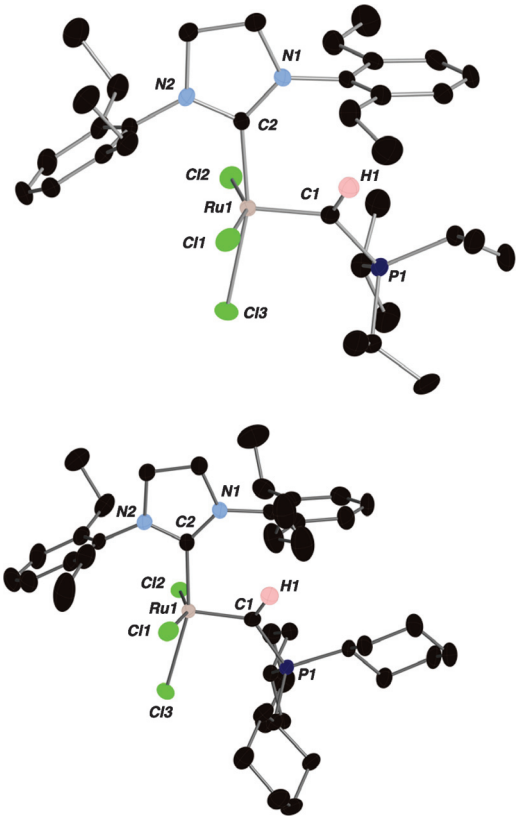


Fig. 1. Thermal ellipsoid diagrams of **2-*i*-Pr$_3$-Cl** (top) and **2-Cy$_3$-Cl** (bottom) (50% probability ellipsoids, solvent molecules and all hydrogens, except H1A, are omitted for clarity). Selected metrical data appear in Table 1.



proximately two-fold decrease in stability upon replacement of ortho methyl groups with ethyl substituents (and the nonexponential decay curve) to the operation of a second, competing decomposition pathway during the thermal degradation of **2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$.** ESI-MS analysis of the two reactions showed that both samples predominantly contain [MeP-*i*-Pr$_3$]$^+$ at *m*/*z* 175.3, which is the byproduct from unimolecular C–H activation of the ortho substituent on the *N*-aryl ring. In addition, both decomposition mixtures exhibit a small amount of their respective protonated NHC ligand at *m*/*z* 307.3 (H$_2$IMes·H$^+$) and *m*/*z* 333.2 (H$_2$IDEP·H$^+$). However, in the spectrum for **2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$**, a third species with a peak at *m*/*z* 187.2 was observed; this mass is consistent with the vinyltriisopropylphosphonium ion, suggesting that one of the ortho ethyl groups may undergo facile dehydrogenation to form an ortho vinyl group capable of undergoing intramolecular metathesis.[52] It is also possible that the greater number of accessible C–H bonds in the ortho ethyl groups of **2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$** results in more rapid C–H activation (see Scheme 1). Ultimately, the more rapid decomposition of this compound relative to the parent *N*-Mes derivative discouraged further exploration of its decomposition processes.

Similar decomposition profiles were obtained for the tricyclohexylphosphonium alkylidene complexes ***n*-Cy$_3$-ClB(C$_6$F$_5$)$_3$** at 343 K; each of these decompositions can be fitted to first-order behavior (Fig. 2, bottom). An analysis of the thermal decomposition mixtures by ESI-MS showed very simple spectra for **1-Cy$_3$-ClB(C$_6$F$_5$)$_3$** and **3-Cy$_3$-ClB(C$_6$F$_5$)$_3$**, where only the phosphonium salt byproduct [CH$_3$PCy$_3$]$^+$ at *m*/*z* 295.3 and very small amounts of H$_2$IMes·H$^+$ (*m*/*z* 307.2) or of H$_2$IDiPP·H$^+$ (*m*/*z* 389.4) were observed. Again, the mass spectrum observed for the ethyl substituted catalyst **2-Cy$_3$-ClB(C$_6$F$_5$)$_3$** was somewhat more complex, exhibiting peaks for these two species in addition to significant amounts of higher molecular weight (MW) peaks in a region indicative of dimeric and trimeric ruthenium containing species (*m*/*z* 800–1200). It is clear from this data that there are significant differences in the thermal stability of each of the precatalysts. The ethyl substituted derivative was again more rapidly consumed in comparison to the parent *N*-Mes compound, but the catalyst with isopropyl groups in the ortho positions of the *N*-aryl ring was much more stable towards degradation with a half-life of over 2000 min, which is two orders of magnitude better than the other two catalysts (Table 2).

The ~40-fold increase in stability associated with the precatalyst **3-Cy$_3$-ClB(C$_6$F$_5$)$_3$** is further evidence that the rotation about the Ru–NHC (and *N*-aryl N–C) bonds are significantly hindered by the ortho isopropyl groups. It appears that this higher rigidity discourages C–H activation of the ortho groups; since [CH$_3$PCy$_3$]$^+$is the major product of this degradation, we presume that C–H activation remains the primary initial step in this catalyst's decomposition path. Thus, while introducing ethyl groups instead of methyl groups appears to result in more facile catalyst decomposition, the use of isopropyl groups has the opposite effect and gives a much more thermally stable catalyst platform.

Olefin metathesis reactions

Grubbs and co-workers[38] have proposed standardized olefin metathesis reactions and conditions to be used for comparative evaluation of catalysts. These transformations include ring closing metathesis (RCM) and cross metathesis (CM) reactions and a ring opening metathesis polymerization (ROMP) process. Typical conditions for the metathesis reactions with the phosphonium alkylidene complexes entail 0.1–5 mol% catalyst loading, CD_2Cl_2 as solvent, hexamethyldisiloxane as the internal standard, and temperatures between 263 and 298 K. The temperature was reduced for most reactions relative to the standard conditions (T = 298 K) reported by Grubbs and co-workers[38] since the phosphonium alkylidene complexes are rapidly initiating and required lower temperatures for convenient spectroscopic monitoring of these re-

Table 1. Selected metrical parameters for complexes **2-R$_3$-Cl** and **1-R$_3$-Cl**.

Parameter[a]	**2-*i*-Pr$_3$-Cl**	**1-*i*-Pr$_3$-Cl**[b]	**2-Cy$_3$-Cl**	**1-Cy$_3$-Cl**[c]
Ru(1)–C(1)	1.830(2)	1.820(3)	1.831(4)	1.815(6)
Ru(1)–C(2)	2.032(2)	2.036(3)	2.032(4)	2.021(5)
Ru(1)–Cl(1)	2.3344(6)	2.3332(13)	2.3310(10)	2.3590(15)
Ru(1)–Cl(2)	2.3299(6)	2.3353(12)	2.3353(10)	2.3991(15)
Ru(1)–Cl(3)	2.4560(6)	2.4619(9)	2.4608(10)	2.4038(14)
C(1)–Ru(1)–C(2)	96.99(10)	96.58(13)	97.39(16)	97.4(2)
Ru(1)–C(2)–N(1)	133.75(18)	131.9(2)	134.7(3)	133.0(4)
Ru(1)–C(2)–N(2)	119.87(17)	120.4(2)	118.2(3)	119.3(4)
C(2)–Ru(1)–Cl(3)	164.75(7)	165.04(9)	163.23(11)	155.79(16)
Cl(1)–Ru(1)–Cl(2)	159.74(2)	158.61(3)	159.64(4)	168.57(6)
Ru(1)–C(1)–P(1)	128.01(14)	126.96(18)	126.9(2)	129.3(3)
C(2)–Ru(1)–C(1)–P(1)	157.82(17)	157.5(2)	165.5 (3)	150.7(4)

[a]Distances given in Å, angles and dihedrals given in °.
[b]Data taken from ref. 56.
[c]Data taken from ref. 62.

Fig. 2. Exponentially fitted first-order plots for the disappearance of ***n*-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$** at 323 K (top) and ***n*-Cy$_3$-ClB(C$_6$F$_5$)$_3$** at 343 K (bottom) with [Ru]$_o$ = 33.8 mmol/L at 323 K in $(CDCl_2)_2$, monitored by ^{1}H NMR spectroscopy.

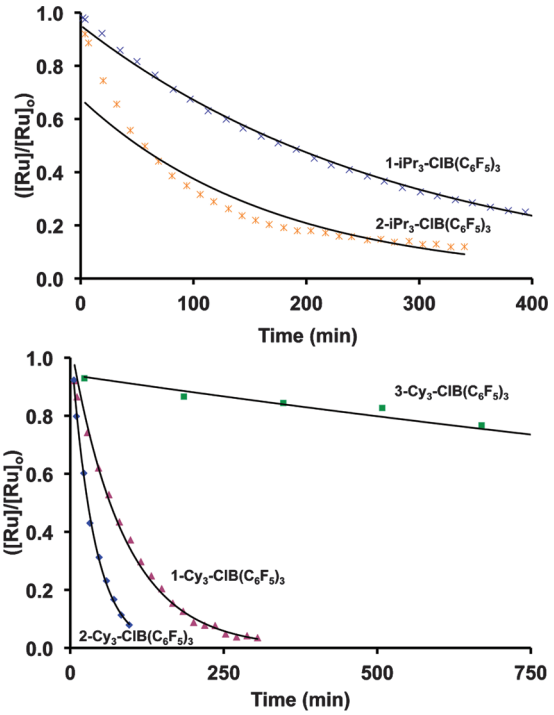


Table 2. Rate constants and half-lives for the decomposition of ***n*-R$_3$-ClB(C$_6$F$_5$)$_3$** with [Ru]$_o$ = 33.8 mmol/L in $(CDCl_2)$ determined by ^{1}H NMR spectroscopy.

Compound	Temperature (K)	Rate constant (k, s^{-1})	Half-life ($t_{1/2}$, min)
1-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$	323	$5.9(2) \times 10^{-5}$	200
2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$	323		120
1-Cy$_3$-ClB(C$_6$F$_5$)$_3$	343	$1.9(2) \times 10^{-4}$	60
2-Cy$_3$-ClB(C$_6$F$_5$)$_3$	343	$4.5(2) \times 10^{-4}$	26
3-Cy$_3$-ClB(C$_6$F$_5$)$_3$	343	$5.5(2) \times 10^{-6}$	2100

actions (Scheme 3). In this way, a series of five precatalysts were compared: the benchmark second generation Grubbs complex (**II**), the well-studied phosphonium alkylidene derivative **1-Cy$_3$-ClB(C$_6$F$_5$)$_3$**,[49,50] and the three new catalysts **2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$**, **2-Cy$_3$-ClB(C$_6$F$_5$)$_3$**, and **3-Cy$_3$-ClB(C$_6$F$_5$)$_3$**. For the phosphonium alkylidenes, the catalyst was generated by mixing stock solutions of ***n*-R$_3$-Cl** and B(C$_6$F$_5$)$_3$, while for **II**, a measured amount of a stock solution was loaded into an NMR tube and placed in a dry ice/acetone bath (at –78 °C). Substrate stock solution was subsequently added via syringe prior to placing in the temperature equilibrated NMR spectrometer probe. Spectra were acquired at regular intervals, and integration of the substrate proton signals were typically used to monitor the conversion to product.

The first standard reaction performed was the RCM of the substrate 4,4-dicarbethyoxy-1,6-heptadiene (Scheme 3*a*). Under these conditions, all of the phosphonium alkylidene complexes tested in this reaction catalyzed the transformation to completion with no sign of precatalyst decomposition (Fig. 3, top). Notably, the performance of the Grubbs second generation catalyst (**II**) was comparably inferior under these conditions. Although the differences in the overall efficiencies in the series of phosphonium alkylidene catalysts for this transformation are minimal, subtle differences in the sigmoidal curve shapes are notable (see also Fig. SI-1 in the Supplementary data), particularly that observed for **3-Cy$_3$-ClB(C$_6$F$_5$)$_3$**, which exhibits a significant period of minimal activity at the beginning of the reaction, followed by very rapid conversion of substrate to product. We have previously shown that this initiation behavior is related to the rate at which ethene is generated, since ethene more rapidly reacts with the precatalysts to generate the highly active species that results upon loss of the phosphonium alkylidene.[50] Using this knowledge, we subsequently demonstrated that adding ethene to the reaction results in a much shorter induction period for the catalyst for **3-Cy$_3$-ClB(C$_6$F$_5$)$_3$** (Fig. 3, bottom). The metathesis event that liberates the phosphonium alkylidene as a vinylphosphonium salt requires that the phosphonium alkylidene ligand rotate about the Ru=C bond to allow for proper approach of the substrate olefinic functionality. This process becomes more difficult as the alkyl group on the phosphorus get larger; the comparative behavior of catalysts **1–3** suggest that the bulk of the ortho substituent on the *N*-aryl group also has a significant impact in raising the barrier to this process (Scheme 4). Ethene catalyzes the initiation reaction because of its much smaller size as compared to monosubstituted substrates, resulting in lowered steric interactions in this initial metathesis reaction. However, when both the phosphorus alkyls and the ortho *N*-aryl groups are large, as in **3-Cy$_3$-ClB(C$_6$F$_5$)$_3$**, even the reaction with ethene is slow enough to result in a measurable sigmoidal reaction profile (Fig. 3, bottom). It is the greater stability imparted to the active species (vide supra) that leads to greater overall performance by this catalyst.

A benchmarking cross metathesis[63] reaction to form the product (*E*)-methyl-7-(ethanoyloxy)hepta-2-enoate was performed using methyl acrylate and 5-hexenyl acetate[38] (Scheme 3*b*). To drive the reaction forward, ethene was removed by purging the atmosphere above the reaction solution with an argon flow. As the

Scheme 3.

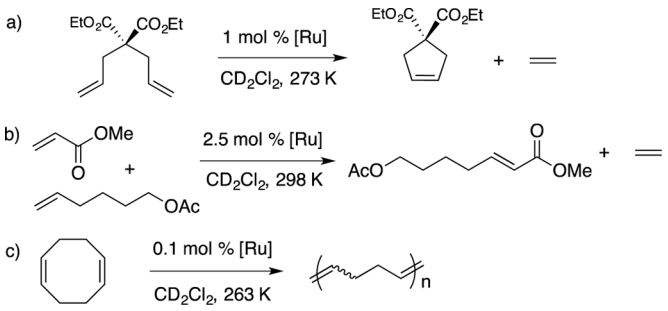
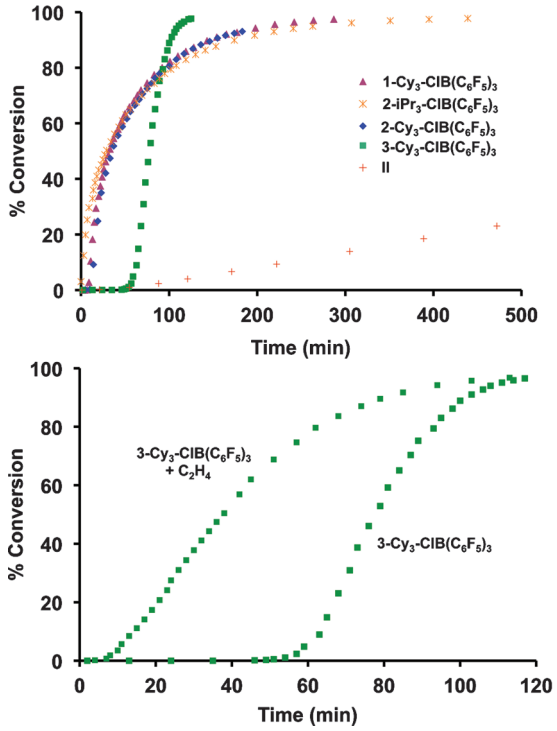
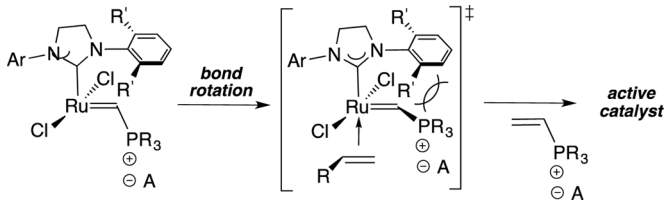


Fig. 3. Reaction profiles depicting the catalysis of the RCM reaction of 4,4-dicarbethoxy-1,6-heptadiene at 273 K with phosphonium alkylidene catalysts and **II** (top) and the RCM reaction of 4,4-dicarbethoxy-1,6-heptadiene at 273 K with and without added ethene (bottom).



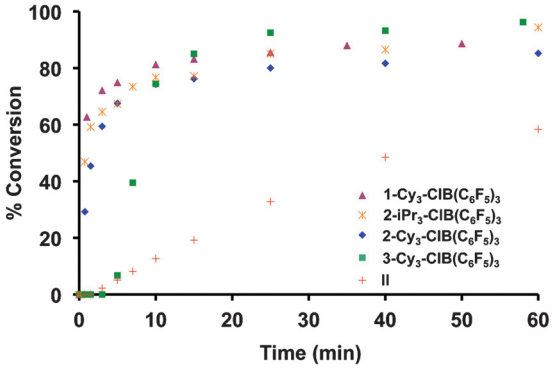
Scheme 4.



reaction profiles in Fig. 4 show, each phosphonium alkylidene catalyst was effective in this reaction, achieving >80% conversion in under 30 min. In comparison, the Grubbs second generation catalyst (**II**), while effective, catalyzed the reaction at about half the rate. Again, sigmoidal reaction profiles were observed for the ***n*-R$_3$-ClB(C$_6$F$_5$)$_3$** catalysts, reflecting the slow initiation rates and the catalyst with the fastest optimal conversion rate, but the longest initiation period was the bulky **3-Cy$_3$-ClB(C$_6$F$_5$)$_3$**.

Finally, the catalysts were compared in a ring opening metathesis polymerization (ROMP) of *cis*,*cis*-1,5-cyclooctadiene. This is a

Fig. 4. Reaction profiles depicting the catalysis of the CM reaction of methyl acrylate and 5-hexenyl acetate at 298 K.

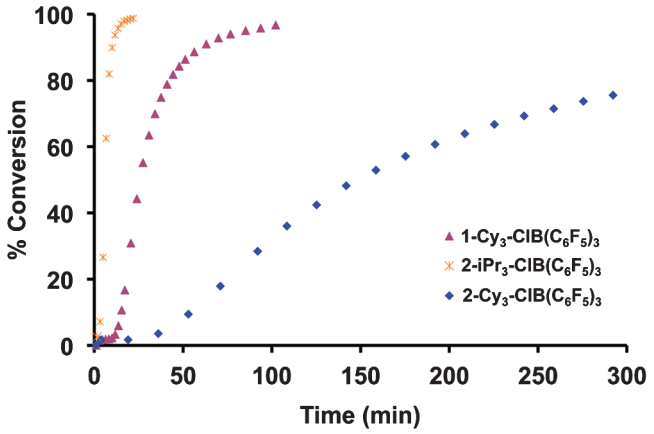


facile reaction and so both the catalyst loading and the temperature were drastically decreased relative to the other transformations (Scheme 3*c*). Reaction profiles are given in Fig. 5. Under these conditions, Grubbs complex **II** and **3-Cy$_3$-ClB(C$_6$F$_5$)$_3$** were not effective catalysts for ROMP of cyclooctadiene and are thus not shown in the Fig. 5; however, they were found to be more reactive at higher temperatures. In contrast, **2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$** showed excellent activity in this transformation, reaching 100% conversion within only 20 min, while its cyclohexyl substituted congener **2-Cy$_3$-ClB(C$_6$F$_5$)$_3$** was notably less effective. These observations suggest the right balance between the ability to effectively initiate and the stability of the propagating species is embodied in **2-iPr$_3$-ClB(C$_6$F$_5$)$_3$** for this transformation under these conditions.

Conclusions

This study has examined the effect of changing the ortho substituents on the *N*-aryl groups of the NHC ligand in fast initiating phosphonium alkylidene olefin metathesis catalysts. By increasing the steric bulk of these groups from methyl (in the parent complexes) to ethyl and isopropyl groups, dramatic changes to the thermal stability of the precatalysts and the stability of the propagating species in a series of test metathesis reactions were noted. Furthermore, the efficiency of initiation was significantly impacted. In terms of the thermal stability of the precatalysts, those supported by ethyl substituted ligand H$_2$IDEP underwent a more rapid thermal decomposition (accelerated by ~2 fold), while those incorporating the isopropyl substituted donor H$_2$ID-*i*-PP were remarkably resistant to thermal decomposition (decelerated by ~40 fold) in comparison to their H$_2$IMes congeners. Moreover, the bulky NHC stabilized system **3-Cy$_3$-ClB(C$_6$F$_5$)$_3$** gave propagating species that were more stable relative to those of the other catalysts probed, resulting in high turnover numbers in several standard metathesis reactions (for example, >6200 for the RCM of 4,4-dicarbethyoxy-1,6-heptadiene). On the other hand, the bulkier NHC substituents made these catalysts slower to initiate due to the steric interactions triggered in the initial metathesis event. As

Fig. 5. Reaction profiles depicting the catalysis of ROMP of *cis*,*cis*-1,5-cyclooctadiene at 263 K in CD_2Cl_2 as monitored by ^1H NMR spectroscopy.



a result, the characteristic sigmoidal shape of the metathesis reaction profile was more pronounced for catalysts **3** versus those of catalysts **1** and **2**. Indeed, even the ethene-catalyzed initiation[50] of these catalysts was significantly slower for the bulkier catalysts **3**. Nonetheless, since the peak efficiency of the propagating species stabilized by this ligand was superior to those attained by the less bulky catalysts, the performance of catalysts **3** in the test reactions was excellent.

Experimental section

For general experimental methods, see the Supplementary material section.

Synthesis of 2-Cy_3-Cl

In a 25 mL round-bottom flask, equipped with a stir bar, $(H_2IDEP)(PCy_3)(Cl)_2Ru{\equiv}C$ (168 mg, 0.209 mmol) was added. On the vacuum line, 20 mL CH_2Cl_2 was vacuum transferred into the flask (at −78 °C). The solution was allowed to warm to room temperature to dissolve the solids and then gaseous hydrochloric acid was added (at −78 °C). The green solution became red within 30 s. The flask was left at this temperature for 20 min and then allowed to warm to room temperature overnight (18 h) under an atmosphere of gaseous hydrochloric acid. The volatiles were removed in vacuo. The green residue was slurried several times in 10 mL portions of pentane, sonicated, and then dried in vacuo. The crude solids were purified by dissolving in dichloromethane and layering with pentane to yield green crystals (0.100 g, 0.120 mmol, 57.3%). ^1H NMR (CD_2Cl_2, 400.2 MHz, 300 K) δ: 19.68 (d, $^2J_{HP}$ = 50 Hz, 1H, Ru=C(*H*)PCy$_3$), 7.43 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar *o*-*CH*), 7.25 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar *p*-*CH*), 4.04 (br s, 4H, CH_2CH_2), 3.14–2.85 (m, 11H, overlapping Cy *CH* and CH_2CH_3), 1.70–1.28 (m, 42H, overlapping and Cy CH_2 and CH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 300 K) δ: 270.4 (br s, Ru=*C*(H)PCy$_3$), 203.7 (s, Ru-*C*(N)$_2$), 143.5 (very br s, quaternary *C*), 129.3 (s, Ar *p*-*CH*), 126.3 (s, Ar *o*-*CH*), 53.8 (br s, CH_2CH_2), 34.1 (d, $^1J_{CP}$ = 40 Hz, Cy *CH*), 27.4, 27.3, 26.6, 25.7 (m, all Cy CH_2), 26.8 (very br s, CH_2CH_3), 14.4 (very br s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162.0 MHz, 297 K) δ: 32.1 (s). The ethyl groups are very fluxional as determined by the broad signals. Anal. calcd. for $C_{42}H_{64}Cl_3N_2PRu$: C 60.39, H 7.72, N 3.35; found: C 60.13, H 7.51, N 3.27.

Synthesis of 2-*i*-Pr_3-Cl

In a 50 mL round-bottom flask, equipped with a stir bar, $(H_2IDEP)(P\text{-}i\text{-}Pr_3)(Cl)_2Ru{\equiv}C$ (100 mg, 0.169 mmol) was added. On the vacuum line, 25 mL CH_2Cl_2 was vacuum transferred into the flask (at −78 °C). The solution was allowed to warm to room temperature to dissolve the solids and then gaseous hydrochloric acid was added (at −78 °C). The green solution became red within 30 s. The flask was left at this temperature for 120 min and then allowed to warm to room temperature overnight (18 h) under an atmosphere of gaseous hydrochloric acid. The volatiles were removed in vacuo. The green residue was slurried several times in 10 mL portions of pentane, sonicated, and then dried in vacuo. The crude solids were purified by dissolving in dichloromethane and layering with pentane to yield green crystals (0.092 g, 0.15 mmol, 87%). ^1H NMR (CD_2Cl_2, 400.2 MHz, 300 K) δ: 19.63 (d, $^2J_{HP}$ = 51 Hz, 1H, Ru=C(*H*)P-*i*-Pr$_3$), 7.44 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Ar *o*-*CH*), 7.29 (d, $^3J_{HH}$ = 7.6 Hz, 4H, Ar *p*-*CH*), 4.08 (br s, 4H, CH_2CH_2), 3.31–2.83 (m, 11H, overlapping *i*-Pr *CH* and CH_2CH_3), 1.29 (t, 12H, CH_2CH_3), 1.17 (d, $^3J_{HP}$ = 17 Hz, 18H, *i*-Pr CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 300 K) δ: 270.3 (br s, Ru=*C*(H)P-*i*-Pr$_3$), 203.4 (s, Ru-*C*(N)$_2$), 144.9, 143.1, 141.4, 129.0 (very br s, quaternary *C*), 127.4 (s, Ar *p*-*CH*), 126.4 (s, Ar *o*-*CH*), 53.8 (br s, CH_2CH_2), 25.2 (very br s, CH_2CH_3), 24.4 (d, $^1J_{CP}$ = 37 Hz, *i*-Pr *CH*), 17.6 (d, $^2J_{CP}$ = 3 Hz, *i*-Pr CH_3), 14.5 (very br s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162.0 MHz, 300 K) δ: 42.8 (s). The ethyl groups are very fluxional as determined by the broad signals. Anal. calcd. for $C_{33}H_{52}Cl_3N_2PRu$: C 55.42, H 7.33, N 3.92; found: C 55.48, H 7.45, N 3.67.

Synthesis of 3-Cy_3-Cl

In a 100 mL round-bottom flask, equipped with a stir bar, $(H_2ID\text{-}i\text{-}PP)(PCy_3)(Cl)_2Ru{\equiv}C$ (250 mg, 0.294 mmol) was added. On the vacuum line, dichloromethane (50 mL) was vacuum transferred into the flask (at −78 °C). The solution was allowed to warm to room temperature to dissolve the solids and then gaseous hydrochloric acid was added (at −78 °C). The green solution became red within 90 s. The flask was left at this temperature for 20 min and then allowed to warm to room temperature overnight (18 h) under an atmosphere of gaseous hydrochloric acid. The volatiles were removed in vacuo. The green residue was slurried several times in 10 mL portions of pentane, sonicated, and then dried in vacuo. Crude solids were purified by dissolving in dichloromethane and layering with pentane to yield green flakes (0.202 g, 0.227 mmol, 77.3%). ^1H NMR (CD_2Cl_2, 400.2 MHz, 300 K) δ: 19.62 (d, $^2J_{HP}$ = 52 Hz, 1H, Ru=C(*H*)PCy$_3$), 7.49, 7.41 (both t, $^3J_{HH}$ = 7.6 Hz, 1H each, Ar *o*-*CH*), 7.32, 7.26 (both d, $^3J_{HH}$ = 7.6 Hz, 2H each, Ar *p*-*CH*), 4.16–3.95 (m, 4H, CH_2CH_2), 3.73, 3.58 (m, 4H *i*-Pr *CH*), 3.54 (m, 3H, Cy *CH*), 1.68–0.89 (m, 54H, overlapping Cy CH_2 and *i*-Pr CH_3 signals). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 298 K) δ: 268.4 (br s, Ru=*C*(H)PCy$_3$), 204.9 (s, Ru-*C*(N)$_2$), 148.6, 148.3, 137.0, 136.3 (all s, quaternary *C*), 129.6, 129.3 (s, Ar *p*-*CH*), 124.8, 124.0 (s, Ar *o*-*CH*), 55.2, 54.0 (both s, CH_2CH_2), 34.8 (d, $^1J_{CP}$ = 35 Hz, Cy *CH*), 28.8, 27.1, 26.9, 26.0 (m, Cy CH_2), 28.0, 27.7, 26.6, 25.7 (m, *i*-Pr *CH*), 23.7 (d, $^2J_{CP}$ = 7 Hz, *i*-Pr CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162.0 MHz, 300 K) δ: 33.5 (s). Notice that the aromatic rings and NHC backbone protons are inequivalent suggesting that the *i*-Pr groups are too bulky to allow fast rotation about the Ru–NHC bond. Anal. calcd. for $C_{46}H_{72}Cl_3N_2PRu{\cdot}CH_2Cl_2$: C 57.81, H 7.64, N 2.87; found: C 57.80, H 7.45, N 2.80.

Generation of 2-Cy_3-$ClB(C_6F_5)_3$

In an NMR tube, $(H_2IDEP)(Cl)_3Ru{=}C(H)PCy_3$ (25 mg, 0.030 mmol) and $B(C_6F_5)_3$ (17 mg, 33 μmol) were combined in CD_2Cl_2 (0.5 mL). The NMR tube was immediately placed in a dry ice/acetone bath (−78 °C) and inserted into a precooled NMR probe (243 K) to acquire spectra without the compound decomposing at all overnight. ^1H NMR (CD_2Cl_2, 399.3 MHz, 243 K) δ: 17.52 (d, $^2J_{HP}$ = 36 Hz, 1H, Ru=C(*H*)PCy$_3$), 7.52 (br s, 2H, Ar *o*-*CH*), 7.34 (br s, 4H, Ar *p*-*CH*), 4.23 (s, 4H, CH_2CH_2), 3.21–2.71 (m, 8H, CH_2CH_3), 2.67 (m, 3H, Cy *CH*), 1.74–0.94 (m, $^3J_{HH}$ = 7.6 Hz, 42H, overlapping and Cy CH_2 and CH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz, 243 K) δ: 262.0 (d, $^1J_{CP}$ = 10 Hz, Ru=*C*(H)PCy$_3$), 188.2 (s, Ru-*C*(N)$_2$), 149.3, 146.8, 138.2, 135.7, 118.3 (very br s, quaternary *C*), 130.6 (s, Ar *o*-*CH*), 127.0 (s, Ar *p*-*CH*), 54.0 (br s, CH_2CH_2), 29.6 (d, $^1J_{CP}$ = 39 Hz, Cy *CH*), 27.6, 26.0, 25.8, 24.7 (m, all Cy CH_2) 23.6 (very br s, CH_2CH_3), 15.3, 13.5 (very br s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162.0 MHz, 243 K) δ: 54.7 (s).

Generation of 2-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$

In an NMR tube, (H$_2$IDEP)(Cl)$_3$Ru=C(H)P-*i*-Pr$_3$ (25 mg, 39 μmol) and B(C$_6$F$_5$)$_3$ (22 mg, 43 μmol) were combined in CD_2Cl_2 (0.5 mL). The NMR tube was immediately placed in a dry ice/acetone bath (–78 °C) and inserted into a precooled NMR probe (243 K) to acquire spectra without the compound decomposing at all overnight. ^{1}H NMR (CD_2Cl_2, 399.3 MHz, 243 K) δ: 17.46 (d, $^2J_{HP}$ = 36 Hz, 1H, Ru=C(*H*)P-*i*-Pr$_3$), 7.49 (br s, 2H, Ar *o*-C*H*), 7.35 (br s, 4H, Ar *p*-C*H*), 4.29 (s, 4H, CH_2CH_2), 3.21–3.18 (br s, 11H, overlapping *i*-Pr C*H* and CH_2CH_3), 1.26 (br s, 12H, CH$_2$CH_3), 0.93 (br d, $^3J_{HP}$ = 16 Hz, 18H, *i*-Pr CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.4 MHz, 243 K) δ: 260.3 (br s, Ru=*C*(H)P-*i*-Pr$_3$), 187.3 (s, Ru-*C*(N)$_2$), 149.1, 146.9, 141.6, 138.8, 138.0, 135.5 (br s, quaternary *C*), 130.8 (s, Ar *p*-CH), 127.1 (s, Ar *o*-CH), 53.8 (br s, CH_2CH$_2$), 24.7 (very br s, CH_2CH$_3$), 20.5 (d, $^1J_{CP}$ = 39 Hz, *i*-Pr C*H*), 17.5 (br s, *i*-Pr CH_3), 14.7 (very br s, CH$_2$CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz, 243 K) δ: 62.4 (s).

Generation of 3-Cy$_3$-ClB(C$_6$F$_5$)$_3$

In an NMR tube, (H$_2$ID-*i*-PP)(Cl)$_3$Ru=C(H)PCy$_3$ (25 mg, 28 μmol) and B(C$_6$F$_5$)$_3$ (16 mg, 31 μmol) were combined in CD_2Cl_2 (0.5 mL). The NMR tube was immediately placed in a dry ice/acetone bath (–78 °C) and inserted into a precooled NMR probe (243 K) to acquire spectra without the compound decomposing at all overnight. ^{1}H NMR (CD_2Cl_2, 399.3 MHz, 243 K) δ: 17.37 (d, $^2J_{HP}$ = 38 Hz, 1H, Ru=C(*H*)PCy$_3$), 7.43, 7.41 (both pt, $^3J_{HH}$ = 7.6 Hz, 1H each, Ar *o*-C*H*), 7.41, 7.25 (both pd, $^3J_{HH}$ = 7.9 Hz, 2H each, Ar *p*-C*H*), 4.26 (m, 4H, CH_2CH_2), 3.40, 3.25 (m, 2H, *i*-Pr C*H*), 2.21 (m, 3H, Cy C*H*), 1.72–0.95 (m, 54H, overlapping Cy CH_2 and *i*-Pr CH_3 signals). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.4 MHz, 243 K) δ: 257.1 (d, $^1J_{CP}$ = 10 Hz, Ru=*C*(H)PCy$_3$), 188.7 (s, Ru-*C*(N)$_2$), 149.2, 148.0, 147.9, 146.7, 142.3, 139.8, 138.1, 135.6, 135.4, 134.2 (all br s, quaternary *C*), 131.1, 130.5 (s, Ar *p*-CH), 125.7, 124.6 (s, Ar *o*-CH), 55.0 (s, CH_2CH$_2$), 29.8 (d, $^1J_{CP}$ = 38 Hz, Cy *C*H), 29.1, 28.6, 27.8, 26.3 (m, Cy CH_2), 26.0, 25.9, 25.8, 24.5 (m, *i*-Pr C*H*), 23.8, 23.3 (br s, *i*-Pr CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2, 161.6 MHz, 243 K) δ: 56.1 (s).

Thermal decomposition of catalysts *n*-R$_3$-ClB(C$_6$F$_5$)$_3$

In an NMR tube, L(Cl)$_3$Ru=C(H)PR$_3$ (32 μmol) and B(C$_6$F$_5$)$_3$ (25 mg, 54 μmol) were combined along with 1,1-dichloroethene (0.50 mL), (CDCl$_2$)$_2$ (0.4 mL), and an internal standard (0.004 mmol hexamethyldisiloxane). The tube was placed in an acetone/dry ice bath (–78 °C) for transport to the NMR spectrometer and then placed in the prewarmed NMR probe (323 or 343 K). Proton cycling experiments were used to acquire spectra at various intervals during the decomposition and integration of the methyl doublet of doublets (on the P-*i*-Pr$_3$ group) in the starting material was monitored against the decomposition product for complexes ***n*-*i*-Pr$_3$-ClB(C$_6$F$_5$)$_3$** and the disappearance of the alkylidene proton at ~17.5 ppm was monitored for complexes ***n*-Cy$_3$-ClB(C$_6$F$_5$)$_3$**. All of the complexes showed at least the presence of a protonated NHC ligand and MePR$_3^+$ by ESI-MS.

X-ray crystallography

Single crystals of **2-*i*-Pr$_3$-Cl** and **2-Cy$_3$-Cl** were grown by diffusion of pentane into a dichloromethane solution of zwitterions. The crystals were coated with Paratone-N oil and measured on a Bruker D8/APEX II CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Further data collection and structure refinement details are given in Table S1 in the Supplementary data.

Supplementary material

Supplementary material (details on general methods, syntheses, and characterization of ligands and catalyst precursors and the procedures employed for the metathesis reactions and crystal and refinement data for the structures **2-Cy$_3$-Cl** and **2-*i*-Pr3-Cl**) is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0156. CCDC 933204 and 933205 contain the supplementary crystallographic data for the structures **2-Cy$_3$-Cl** and **2-*i*-Pr3-Cl**, respectively). These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK; fax: +44 1223 33603; or e-mail: deposit@ccdc.cam.ac.uk).

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