Catalytic Synthesis of \( n \)-Alkyl Arenes through Alkyl Group Cross Metathesis

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ABSTRACT: \( n \)-Alkyl arenes can be prepared in a one-pot tandem dehydrogenation/olefin-metathesis/hydrogenation sequence directly from alkanes and ethylbenzene. Excellent selectivity is observed when \( ^{11} \text{B} \text{PCP} \text{IrH}_2 \) is paired with W monoaaryl oxide pyrrolide complexes such as W(NAr)(C\(_2\)H\(_5\))(pyr)(OHIPT) (1a) (NAr = 2,6-i-Pr\(_2\)C\(_6\)H\(_3\); pyr = pyrrolide; OHIPT = O-2,6-(2,4,6-i-Pr\(_3\)C\(_6\)H\(_3\))\(_2\)C\(_6\)H\(_3\)). Complex 1a is also especially active in \( n \)-octane self metathesis, providing the highest product concentrations yet reported. The thermal stability of selected olefin metathesis catalysts allows elevated temperatures and extended reaction times to be employed.

Selective functionalizations of C-H bonds are highly sought due to the abundance of hydrocarbon feedstocks.\(^1\) \( n \)-Alkyl arenes would be ideal starting materials in many reactions if C-H bond activation in an alkane were possible. One goal could be the synthesis of \( n \)-alkyl arenes (e.g., 1-phenyloctane), which are precursors for surfactants with high detersive power at elevated temperatures and low concentrations.\(^7\) The largest group of linear alkyl benzenes, produced on a million-ton scale per year for the synthesis of surfactants,\(^7\) are typically branched alkyl arenes (e.g., 2-phenyloctane) generated by Friedel-Crafts alkylation of benzene with olefins.\(^6\) \( n \)-Alkyl arenes cannot be produced in this fashion, and while the anti-Markownikov arylation of olefins\(^5\) is a potential catalytic method for their synthesis, a more efficient route would proceed directly from an abundant alkane as a starting material. Dehydroaromatization is one strategy for the synthesis of specific \( n \)-alkyl arenes from \( n \)-alkanes in a single step,\(^6\) although dehydroaromatization requires a stoichiometric amount of an olefin to serve as a hydrogen acceptor.

An Ir dehydrogenation/hydrogenation catalyst and a W or Mo complex competent for olefin metathesis have been shown to work in tandem to generate a broad distribution of \( n \)-alkanes from a single \( n \)-alkane.\(^7\) We have been exploring the possibility of what could be called alkyl group cross metathesis (AGCM) to generate \( n \)-alkyl arenes from ethylbenzene and an alkane (Scheme 1). (Only terminal olefins are shown in Scheme 1.) While ethylbenzene has never been used previously in an alkane metathesis reaction, the (PCP)Ir catalyzed dehydrogenation of ethylbenzene has been reported.\(^9\) In alkane metathesis, the overall distribution of products is influenced by several factors, including the terminal selectivity of the alkane dehydrogenation step,\(^10\) and the rate at which intermediate olefins are isomerized, either by Ir complexes\(^11\) or by the products of Mo or W decomposition.\(^12a\) Competitive metathesis homocoupling of intermediate olefins could compete with cross metathesis and further increase the number of products.

Scheme 1. The alkyl group cross metathesis reaction.

Catalyst longevity is another major challenge towards developing a practical alkane metathesis protocol. The high temperatures (at least 125 °C) and multi-day reaction times required for alkane metathesis deactivate Mo and W olefin metathesis catalysts more rapidly than Ir pincer complexes. We now find that certain Mo and W Monoaryloxide Pyrrolide (MAP) complexes, previously studied in the context of Z-selective metathesis reactions,\(^13,15\) are thermally quite stable. In concert with Ir pincer complexes, they provide high total product concentrations in the metathesis of \( n \)-octane. These MAP complexes are also robust catalysts for the alkyl group cross metathesis of alkanes and ethylbenzene, as we describe here.

A previous screen of Mo and W alkylidene complexes identified several active catalysts for \( n \)-octane metathesis, and established that tungsten complexes provide higher total product concentrations than the analogous molybdenum species.\(^16\) Unfortunately, the thermal stability of the most active complexes at 150 °C was poor. Therefore, we turned to complexes that contain sterically demanding phenoxide ligands, which we hypothesized may slow decomposition by discouraging bimolecular decomposition.\(^17\)

The results of an evaluation of olefin metathesis catalysts for the metathesis of \( n \)-octane are shown in Table 1. The most encouraging results were obtained with complexes that incorporate the O-2,6-(2,4,6-i-Pr\(_3\)C\(_6\)H\(_3\))\(_2\)C\(_6\)H\(_3\) (OHIPT)
ligand. The OHIPT-containing compounds 1a,15 1b,14 and W(N-tr-Bu)(CH-tr-Bu)(pyr)(OHIPT)16 are superior catalysts. W(O)(CH-tr-Bu)(MePyr)(OHIPT),19 W(NC5F5)(CH-tr-Bu)(MePyr)(OHIPT), and W(NAr)(CH-tr-Bu)(Me2Pyr)(OHMT) are essentially inactive. Surprisingly, W(NC5F5)(CH-tr-Bu)(Me2Pyr)(OHMT) (Me2Pyr = 2,5-dimethylpyrrole; OHMT = O-2,6-(2,4,6-Me3C6H2)2C6H4) is an excellent catalyst for the metathesis of n-octane at 125 °C, in contrast to W(NC5F5)(CH-tr-Bu)(Me2Pyr)(OHIPT). We previously found that W and Mo bisalkoxide complexes containing the pentafluorophenylimido (NC5F5) group are poor catalysts for alkane metathesis.20

![Image](323x579 to 563x742)

**Figure 1.** GC trace of the alkane metathesis of 1:4 v:v n-octane:ethylbenzene, 150 °C, 2 days, 16 mM 1a, 10 mM (117POCOP)Ir(C2H4).

With thermally robust olefin metathesis catalysts in hand, we began to investigate the metathesis of n-octane in ethylbenzene (1:4 v:v). A broad distribution of n-alkylbenzenes (1-phenylpropane, PhC3, to 1-phenyloctane, PhC8) is obtained with 1a and (117POCOP)Ir(C2H4) at 150 °C over 2 days (Figure 1). Various n-alkanes are also formed as side products (up to tetradecane, C14). Alkylbenzenes are the major products in the C10-C14 range when (117POCOP)Ir(C2H4) is employed, but despite the high selectivity for alkylbenzenes over alkanes, there is no selectivity for specific alkylbenzenes with this Ir catalyst. In addition, a large fraction of the alkanes are in the range C5-C7. Other Ir complexes produce more PhC8, even when the reaction temperature is increased to 180 °C (Table 2). The (117PCP)IrH2 complex provides 240 mM of 1-phenyloctane (PhC8) in the cross metathesis of n-octane and ethylbenzene over 24h (Scheme 2). The selectivity for alkylbenzenes over alkanes is maintained even when only a slight excess of ethylbenzene is used (3:4 v:v n-octane:ethylbenzene). After 1-phenyloctane (PhC8), 1-phenylethane (PhC7) is the next major n-alkylarene product in the C10-C14 range (60 mM). Additionally, 20 mM of tetradecane (C14) is generated. Because the AGCM reactions described here proceed only to low conversion (relative to ethyl benzene), only traces of diphenyl Ph(CH2)3Ph products, formed by cross metathesis on both termini of one alkane, are produced.

![Image](250x250)

**Scheme 2.** Major products in the alkane metathesis of a 3:4 v:v n-octane:ethylbenzene mixture.

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**Table 1.** Total product concentration (mM) obtained in the metathesis of n-octane (4d, 125 °C).*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Total product (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(NAr)(C6H5)(pyr)(OHIPT) (1a)</td>
<td>3920, 4910b</td>
</tr>
<tr>
<td>W(NAr')(C6H5)(pyr)(OHIPT) (1b)</td>
<td>2400</td>
</tr>
<tr>
<td>Mo(NAr)(C6H5)(pyr)(OHIPT)</td>
<td>2450</td>
</tr>
<tr>
<td>W(NC5F5)(CH-tr-Bu)(Me2Pyr)(OHMT)</td>
<td>3660, 3750b</td>
</tr>
<tr>
<td>W(NC5F5)(CH-tr-Bu)(Me2Pyr)(OHMT)</td>
<td>~0</td>
</tr>
<tr>
<td>W(N-tr-Bu)(CH-tr-Bu)(pyr)(OHIPT)</td>
<td>2790</td>
</tr>
<tr>
<td>W(O)(CH-tr-Bu)(OHMT)2</td>
<td>1600</td>
</tr>
<tr>
<td>W(NAr)(CHCMe2Ph)[OC(CF3)3]2</td>
<td>2260</td>
</tr>
<tr>
<td>W(NAr')(CHCMe2Ph)[OSiPh3]2</td>
<td>2770, 1420b</td>
</tr>
<tr>
<td>W(O)(CH-tr-Bu)(MePyr)(OHIPT)</td>
<td>~0</td>
</tr>
<tr>
<td>W(NAr)(CH-tr-Bu)(MePyr)(OHMT)</td>
<td>~0</td>
</tr>
</tbody>
</table>

*a* Conditions: 125 °C, 4 days in J. Young tubes; 16 mM metathesis catalyst, 10 mM (117POCOP)Ir(C2H4), and 28.8 mM mesitylene (internal standard). See SI for details. (Ar = 2,6-i-Pr3C6H2; Ar' = 2,6-Me3C6H2; pyr = pyrrole; MePyr = 2,5-dimethylpyrrole; OHMT = O-2,6-(2,4,6-Me3C6H2)2C6H4; OHIPT = O-2,6-(2,4,6-i-Pr3C6H2)2C6H4). b 150 °C, 2 days.

The activity of 1a at various temperatures and reaction times was explored further. A higher total product concentration is obtained upon increasing the reaction temperature from 125 °C to 150 °C and decreasing the reaction time from 4 days to 2 days (Table 1). Higher efficiency at higher temperatures is not a general phenomenon; for example, W(NAr)(CHCMe2Ph)(OSiPh3)2 provides lower product concentrations at higher reaction temperatures (2770 mM at 125 °C, 4d vs. 1420 mM at 2d, 150 °C). W(NC5F5)(CH-tr-Bu)(Me2Pyr)(OHMT) also shows good stability at higher temperatures, generating 3750 mM of total product at 150 °C over two days.
Various olefin metathesis catalysts were screened using (\textsuperscript{1b}PCOP)IrH\textsubscript{2} as the dehydrogenation catalyst (Table 3). W(NAr)(C\textsubscript{6}H\textsubscript{5})(pyr)(OHIMT) (1b) provides the highest conversion to 1-phenyloctane (PhC\textsubscript{8}) under these conditions (350 mM), corresponding to a W TON of 31 and an Ir TON of 50. Complex 1b also provides the highest selectivity for n-alkyl arene versus tetradecape (C14) (~17:1 PhC\textsubscript{8}: C14). While bisalkoxide complexes are also active for alkyl group cross metathesis, they generate more n-alkane side products. However, Mo(NAr)(CHCM\textsubscript{e}Ph)(OR\textsubscript{6})\textsubscript{2} (OR\textsubscript{6} = OC(CF\textsubscript{3})\textsubscript{2}CH\textsubscript{3}) demonstrates the greatest selectivity for PhC\textsubscript{8} versus PhC\textsubscript{7} of any catalyst (12:1). This result is consistent with the high levels of C14 selectivity previously observed using Mo(NAr)(CHCM\textsubscript{e}Ph)(OR\textsubscript{6})\textsubscript{2} for the metathesis of n-octane.\textsuperscript{8}

Branched alkanes, which are less prone to isomerization or dehydrogenation at internal positions, can also undergo AGCM reactions. The substrates shown in Table 4 react with ethylbenzene 180 °C in the presence of \textsuperscript{1b}PCOP)Ir(C\textsubscript{2}H\textsubscript{4}) and 1a. Bibenzyl is the only major byproduct of these reactions as a consequence of homoolane metathesis of ethylbenzene. Only trace amounts of products derived from isomerization are observed with the substrates in Table 4. Less hindered alkanes prone to isomerization lead to broader distributions of products. For example, n-propyltrimethylsilane in ethylbenzene affords trimethyl(3-phenylpropyl)silane in 24% yield over 2 days at 180 °C, with only bibenzyl as a side product. If n-butyltrimethylsilane is employed, trimethyl(3-phenylpropyl)silane, n-propylbenzene, and n-propyltrimethylsilane are all formed, along with trace amounts of trimethyl(4-phenylbutyl)silane according to GC-MS analysis (Scheme 3).

### Table 2. Total concentration (mM) of 1-phenyloctane (PhC\textsubscript{8}), 1-phenylethane (PhC\textsubscript{7}), and tetradecape (C14) obtained in AGCM (24 h, 180 °C, 11 mM 1a).\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>C14</th>
<th>PhC8</th>
<th>PhC7</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\textsuperscript{1b}PCOP)IrH\textsubscript{2}</td>
<td>60</td>
<td>230</td>
<td>150</td>
</tr>
<tr>
<td>(\textsuperscript{1b}Bu\textsubscript{3}PCP)IrH\textsubscript{2}</td>
<td>40</td>
<td>210</td>
<td>140</td>
</tr>
<tr>
<td>(\textsuperscript{1b}PCOP)Ir(C\textsubscript{2}H\textsubscript{4})</td>
<td>20</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>(\textsuperscript{1b}PCP)Ir(C\textsubscript{2}H\textsubscript{4})</td>
<td>10</td>
<td>190</td>
<td>80</td>
</tr>
<tr>
<td>(\textsuperscript{1b}Bu\textsubscript{3}PCOP)Ir(C\textsubscript{2}H\textsubscript{4})</td>
<td>20</td>
<td>70</td>
<td>100</td>
</tr>
<tr>
<td>(\textsuperscript{1b}Bu\textsubscript{3}PCP)IrH\textsubscript{2}</td>
<td>20</td>
<td>240</td>
<td>60</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conditions: J. Young tubes; 0.3 mL n-octane, 0.4 mL ethylbenzene, 11 mM metathesis catalyst, 7 mM Ir catalyst, and mesitylene (internal standard). See SI for details.

### Table 3. Total concentration (mM) of 1-phenyloctane (PhC\textsubscript{8}), 1-phenylethane (PhC\textsubscript{7}), and tetradecape (C14) obtained in AGCM (24 h, 180 °C, (\textsuperscript{1b}PCOP)IrH\textsubscript{2}).\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>C14</th>
<th>PhC8</th>
<th>PhC7</th>
</tr>
</thead>
<tbody>
<tr>
<td>W(NAr)(C\textsubscript{6}H\textsubscript{5})(pyr)(OHIMT) (1a)</td>
<td>20</td>
<td>240</td>
<td>60</td>
</tr>
<tr>
<td>W(NAr)(C\textsubscript{6}H\textsubscript{5})(pyr)(OHIMT) (1b)</td>
<td>20</td>
<td>350</td>
<td>100</td>
</tr>
<tr>
<td>Mo(NAr)(C\textsubscript{6}H\textsubscript{5})(pyr)(OHIMT)</td>
<td>20</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>W(NC\textsubscript{6}F\textsubscript{5})(CH\textsubscript{2}Bu)(Me\textsubscript{2}Pyr)(OHIMT)</td>
<td>&lt;10</td>
<td>160</td>
<td>40</td>
</tr>
<tr>
<td>W(N-C\textsubscript{6}Bu)(CH\textsubscript{2}Bu)(pyr)(OHIMT)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Mo(NAr)(CHCM\textsubscript{e}Ph)(OR\textsubscript{6})\textsubscript{2}</td>
<td>50</td>
<td>240</td>
<td>20</td>
</tr>
<tr>
<td>W(NAr)(CHCM\textsubscript{e}Ph)(OC(CF\textsubscript{3})\textsubscript{2}CH\textsubscript{3})</td>
<td>&lt;10</td>
<td>30</td>
<td>&lt;10</td>
</tr>
<tr>
<td>W(NAr)(CHCM\textsubscript{e}Ph)(OSiPh\textsubscript{3})</td>
<td>50</td>
<td>220</td>
<td>60</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conditions: J. Young tubes; 0.3 mL n-octane, 0.4 mL ethylbenzene, 11 mM metathesis catalyst, 7 mM (PCP)IrH\textsubscript{2}, and mesitylene (internal standard). See SI for details. (OR\textsubscript{6} = OC(CF\textsubscript{3})\textsubscript{2}CH\textsubscript{3}) b 22 mM metathesis catalyst.

### Table 4. Branched substrates for alkyl group cross metathesis with ethylbenzene.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Yield (Conc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiMe\textsubscript{3}</td>
<td>PhSiMe\textsubscript{3}</td>
<td>25% (400 mM)</td>
</tr>
<tr>
<td>SiEt\textsubscript{3}</td>
<td>PhSiEt\textsubscript{3}</td>
<td>11% (180 mM)</td>
</tr>
<tr>
<td>Ph</td>
<td>Ph</td>
<td>18% (290 mM)</td>
</tr>
<tr>
<td>Ph</td>
<td>6% (100 mM)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conditions: J. Young tubes; 16 mM 1a, 10 mM (\textsuperscript{1b}PCOP)Ir(C\textsubscript{2}H\textsubscript{4}), mesitylene (internal standard), 2d, 180 °C.

### Scheme 3. Alkyl group cross metathesis of n-butyltrimethylsilane and ethylbenzene.

Substrates that contain a heteroatom, e.g., methyl propionate and n-propyl(trimethoxysilyl)silane, deactivate one or both catalysts. Ir complexes are known to be deactivated in the presence of CO\textsubscript{2}, CX\textsubscript{2}, and CF\textsubscript{3} bonds. However, these bond cleavages may be reversible under some conditions. The known reversible activation of arene C-H bonds by (PCP)Ir\textsubscript{24} clearly does not inhibit AGCM.

Although the conditions required for appreciable conver-
sion in alkyl group cross metathesis are relatively harsh. W alkylidenes can be observed in the residue remaining after two days in a 180 °C reaction. A proton NMR spectrum of the non-volatile components of a completed catalytic reaction reveals two 1H NMR resonances in the alkylidene region. One integrates as 25% of the original W catalyst loading (versus an internal standard) and is assigned to W(NAr)(CHPh)(pyr)(OHIPPT) (δ CHPh = 10.25, δCD3 = 0.2 ppm) on the basis of comparison with the alkylidene complex formed through addition of styrene to 1a. The identity of the other alkylidene (δ CHR = 10.61 ppm; 0.2 μmol, or 2.5% of the original W catalyst) is currently not known.

We conclude that certain W and Mo complexes catalyze alkyl group cross metathesis reactions at relatively high temperatures. Sterically demanding aryloxide ligands appear to make complexes more thermally stable. These robust catalysts can be employed in alkyl group cross metathesis to provide n-alkyl arenes directly from ethylbenzene and alkanes in a one-pot process that is relatively selective for formation of alkylarenes over alkanes. Beyond providing a new route to n-alkyl arenes, this work more broadly demonstrates that a dehydrogenation/olefin metathesis sequence can provide alkyl group cross metathesis products with good selectivity, even between alkyl chains in different substrates. An understanding of the inherent biases of each catalyst towards alkyl group cross metathesis variations to be designed.

ASSOCIATED CONTENT
Experimental details for all metal complexes, substrates, and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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REFERENCES


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\[
R - \overset{+}{\text{Ph}} \xrightarrow{180 ^\circ \text{C}, 24-48h} R' - \overset{\text{Ph}}{\text{Ph}} + \text{C}_2\text{H}_6
\]
Supporting Information for

Catalytic Synthesis of \( n \)-Alkyl Arenes through Alkyl Group Cross Metathesis

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General Details.

All manipulations were conducted under a nitrogen or argon atmosphere in a Vacuum Atmospheres drybox or using Schlenk techniques unless otherwise specified. All glassware was oven-dried prior to use. Acetonitrile, pentane, toluene, and benzene were degassed and passed through activated alumina columns under nitrogen or argon. All dried and deoxygenated solvents were stored over molecular sieves in a nitrogen or argon-filled glovebox. NMR spectra were recorded on a Bruker or Varian 300 MHz, 400 MHz, 500 MHz or 600 MHz spectrometer at room temperature unless otherwise specified. Chemical shifts for 1H spectra were referenced to the residual resonances of the deuterated solvent and are reported as parts per million relative to tetramethylsilane. Removal of solvent was achieved by evaporation at room temperature unless otherwise specified. The residue was extracted with toluene.

Analytical data were obtained from the CENTC Elemental Analysis Facility at the University of Rochester, funded by NSF CHE-0650456. N-butyltrimethylsilane was prepared by a known procedure.\(^1\) W(O)(CH-t-Bu)(OHMT)\(_2\),\(^2\) WO(CH-t-Bu)(Me,Pyr)(OHIPT),\(^3\) W(NAr)(C\(_2\)H\(_2\))(pyr)(OHIPT),\(^4\) Mo(NAr)(C\(_2\)H\(_2\))(pyr)(OHIPT),\(^5\) W(NAr')(C\(_4\)H\(_6\))(pyr)(OHIPT),\(^6\) W(N-t-Bu)(CH-t-Bu)(pyr)(OHIPT),\(^7\) W(NAr)(CHMe\(_2\)Ph)[OC(CF\(_3\))\(_2\)]\(_2\),\(^8\) and W(NAr)(CHMe\(_2\)Ph)(OSiPh\(_3\))\(_2\) were prepared through previously reported procedures. \(^{i}{\text{Bu}}\text{PCP}\)IrH\(_2\), \(^{i}{\text{Bu}}\text{POCOP}\)Ir(C\(_2\)H\(_4\)), \(^{P}\text{PCP}\)Ir(C\(_2\)H\(_4\)), and \(^{i}{\text{Bu}}\text{MoPCP}\)IrH\(_2\) were prepared through previously reported procedures. All other compounds were obtained from commercial suppliers. \(^{P}\text{PCP}\)Ir(C\(_2\)H\(_4\)) was synthesized from \(^{P}\text{PCP}\)IrH\(_4\), prepared in analogy with the procedure reported for the para-methoxy derivative (p-MeO-\(^{P}\text{PCP}\)IrH\(_4\)), followed by treatment with ethylene gas.

Synthesis of W alkylidene complexes.

**W(NAr)(CH-t-Bu)(Me,Pyr)(OHMT).** A vessel containing a suspension of W(NAr)(CH-t-Bu)(Me,Pyr)\(_2\) (217.0 mg, 0.352 mmol) and 2,6-bis(2,4,6-trimethylphenyl)phenol\(^{15}\) (116.1 mg, 0.352 mmol) was placed in a sonicator bath for 3 hours. Volatiles were removed in vacuo to obtain a yellow solid. Recrystallization in pentane (-20 °C) afforded the product as yellow crystals (219.7 mg, 73% yield). 1H NMR (400 MHz, C\(_6\)D\(_6\), 25°C) δ 8.61 – 8.49 (br s, 1H, W=CHR), 7.06 – 6.89 (m, 3H, Ar), 6.89 – 6.86 (m, 3H, Ar), 6.84 (s, 2H, Ar), 6.81 (s, 2H, Ar), 6.09 (br s, 1H, Ar), 5.85 (br s, 1H, Ar), 3.14 (br s, 2H, CH(CH\(_2\))\(_2\)), 2.26 (s, 3H, pyr -CH\(_3\)), 2.18 (s, 12H, OHMT -CH\(_3\)), 2.05 (s, 6H, OHMT –CH\(_3\)), 1.96 (s, 3H, pyr -CH\(_3\)), 1.48-0.60 (m, 21H, CH(CH\(_3\))\(_3\), \(^{1}\text{Bu}).^{13}\text{C}(^{1}\text{H})\) NMR (125 MHz, C\(_6\)D\(_6\), 25°C) δ 266.42 (W=CHR, \(^{1}\text{J}_{CW} = 187.5\) Hz), 158.69, 152.18, 136.99, 136.77, 136.75, 135.83, 132.36, 131.13, 129.55, 128.90, 126.71, 123.24, 122.97 (br s), 110.44, 110.02, 47.66, 33.39, 28.21 (br s), 24.18 (br s), 23.64 (br s), 21.55, 21.34, 20.45, 19.53, 15.84. Anal. Calcd. for C\(_{42}\)H\(_{60}\)N\(_2\)OW: C, 66.19; H, 7.09; N, 3.28. Found: C, 66.27; H, 7.15; N, 3.17.

**W(NC\(_5\)F\(_3\))(CH-t-Bu)(Me,Pyr)\(_2\).** W(NC\(_5\)F\(_3\))(CH-t-Bu)(DME)(OTf)\(_2\) (1.5 mg, 1.82 mmol) was suspended in THF/Et\(_2\)O (1mL/5mL). Li-Me,Pyr (405.0 mg, 4 mmol) was added at -30 °C. The mixture turned to dark in 5 min. After 30min, the solvent was removed to give dark oil/solid product. The residue was extracted with toluene. Removal of solvent gave dark solid. The solid was recrystallized from Et\(_2\)O to give brown yellow solid. Washing
with cold Et₂O gave yellow solid (478 mg, 50%). Washing the brown solid to yellow solid reduced the yield. \(^1\)H NMR (500 MHz, C₆D₆, 20 °C) δ 10.88 (s, 1H, W=CH), 5.97 (br, 4H, Me₂Pyr), 2.20 (br, 12H, Me₂Pyr), 1.18 (s, 9H, \(^1\)Bu). \(^{19}\)F NMR (282 MHz, C₆D₆, 20 °C) δ -148.7 (d, 18 Hz, 2F), -158.8 (m, 1F), -163.3 (m, 2F). \(^{13}\)C\(^{1}\)H NMR (125 MHz, C₆D₆) δ 288.2 (W=CH), 143.7 (d, \(^1\)J CF = 250 Hz, Ar-F), 138.8 (d, \(^1\)J CF = 247 Hz, Ar-F), 137.9 (d, \(^1\)J CF = 248 Hz, Ar-F), 131.9, 107.9, 47.9, 34, 38. Anal. Calcd. for C₂₃H₂₆F₅N₃W: C, 44.32; H, 4.20; N, 6.74. Found: C, 44.03; H, 4.30; N, 6.43.

W(NC₆F₅(CH-t-Bu)(Me₂Pyr)(OHMT). W(NC₆F₅(CH-t-Bu)(Me₂Pyr)₂ (100 mg, 0.16 mmol) and 2,6-bis(2,4,6-trimethylphenyl)phenol\(^{15}\) (53 mg, 0.176 mmol) were dissolved in benzene (5 mL). After heating at 80 °C for 1 day, the solvent was removed by vacuum and the residue was recrystallized from THF/pentane to give yellow solid (112 mg, 76%). \(^1\)H NMR (500 MHz, C₆D₆, 20 °C) δ 8.10 (s, 1H, W=CH), 6.92 (s, 2H), 6.74 (s, 2H), 6.65 (s, 2H), 6.05 (s, 2H), 5.59 (m, 1H), 2.05 (12H), 1.94 (12H), 1.18 (9H). \(^{19}\)F NMR (282 MHz, C₆D₆, 20 °C) δ -148.4 (d, 27 Hz, 2F), -162.5 (m, 1F), -165.0 (m, 2F). Anal. Calcd. for C₄₅H₄₇F₅N₂O₂W: C, 58.32; H, 5.11; N, 3.02. Found: C, 58.08; H, 5.30; N, 3.12.

W(NC₆F₅(CH-t-Bu)(Me₂Pyr)(OHIP). W(NC₆F₅(CH-t-Bu)(Me₂Pyr)₂ (100 mg, 0.16 mmol) and 2,6-bis(2,4,6-triisopropylphenyl)phenol\(^{17}\) (80 mg, 0.16 mmol) were dissolved in toluene (1 mL). After heating at 100 °C for 2 days, the solvent was removed by vacuum to give a dark oil. MeCN (0.5 mL) was added and stirred for 1 hour to give yellow precipitate. After cooling at -30 °C for overnight, the mixture was filtered to yellow solid (86 mg, 52%). \(^1\)H NMR (500 MHz, C₆D₆, 20 °C) δ 9.42 (s, 1H, W=CH), 7.23 (s, 2H), 7.18 (s, 2H), 6.96 (d, 8Hz, 2H), 6.81 (t, 8Hz, 1H), 5.95 (2H), 3.02 (sept, 2H), 2.86 (sept, 4H), 1.96 (m, 9H), 1.33-1.05 (m, 42H). \(^{19}\)F NMR (282 MHz, C₆D₆, 20 °C) δ -147.9 (d, 20Hz, 2F), -159.1 (m, 1F), -164.1 (m, 2F). Anal. Calcd. for C₅₃H₆₇F₅N₂OW: C, 61.99; H, 6.58; N, 2.73. Found: C, 61.92; H, 6.57; N, 2.94.
Synthesis of \(^{18}P\)COP)Ir complexes.

\(\text{3-(tert-butylphosphinomethyl)phenol.}\) A mixture of 3-(bromomethyl)phenol (4.003 g, 21.40 mmol) and di-tert-butylphosphine (3.161 g, 21.62 mmol) in degassed acetone (30 mL) was heated to reflux for 12 h and then stirred at room temperature overnight. The mother liquor was decanted from the white waxy precipitate that formed and the precipitate was dried under vacuum. The precipitate was treated with saturated solution of aqueous NaHCO\(_3\) (40 mL) and stirred at 80 °C for 6 h. After cooling down to room temperature, the mother liquor was cannulated out and the white precipitate was dried under vacuum. Product was extracted with Et\(_2\)O (30 mL x 3) and the combined solution was evaporated under vacuum to obtained waxy orange colored products. Yield: 4.807 g, 19.05 mmol, 89%. (NMR \(\delta\), CDCl\(_3\)): \(^1H\): 7.01 (t, \(J_{HH} = 7.8\) Hz, 1H, Ar-\(H\)), 6.82 (d, \(J_{HH} = 7.5\) Hz, 1H, Ar-\(H\)), 6.75 (s, 1H, Ar-\(H\)), 6.47 (d, \(J_{HH} = 8.0\) Hz, 1H, Ar-\(H\)), 4.66 (s, 1H, OH), 2.71 (d, \(J_{PH} = 3.5\) Hz, 2H, CH\(_2\)), 1.06 (d, \(J_{PH} = 11.0\) Hz, 18H, 2 C(CH\(_3\))\(_3\)). \(^{13}C\{^1H\}: 155.8 (s, Ar-C), 143.8 (d, \(J_{PC} = 12.4\) Hz, Ar-C), 129.7 (s, Ar-C), 122.3 (d, \(J_{PC} = 8.0\) Hz, Ar-C), 116.7 (d, \(J_{PC} = 9.2\) Hz, Ar-C), 112.7 (d, \(J_{PC} = 2.1\) Hz, Ar-C), 30.1 (d, \(J_{PC} = 13.1\) Hz, 6C, C(CH\(_3\))\(_3\)), 28.6 (d, \(J_{PC} = 23.2\) Hz, 2C, C(CH\(_3\))\(_3\)).

\(^{18}P\)COP ligand. A solution of 3-(tert-butylphosphinomethyl)phenol (2.657 g, 10.53 mmol) in THF (40 mL) was added dropwise to the suspension of NaH (0.2779 mg, 11.58 mmol) in THF (20 mL) and the reaction mixture was heated to reflux for 1.5 h. After cooling down to room temperature, a solution of di-tert-butylchlorophosphine (2.00 mL, 10.50 mmol) in THF (10 mL) was added dropwise through a cannula and the resultant reaction mixture was heated to reflux for 2 h. The solvent was then removed under vacuum and the product was extracted with pentane (20 mL x 2). The combined pentane solution was removed under vacuum to obtain a pale yellow viscous liquid product. Yield: 3.514 g, 8.862 mmol, 84%. (NMR, \(\delta\), C\(_6\)D\(_6\) \(^1H\): 7.62 (s, 1H, Ar-Hipso), 7.10-7.18 (m, 3 H, Ar-H), 2.80 (d, \(^2J_{PH} = 2.25\) Hz, 2H, CH\(_2\)), 1.21 (d, \(^2J_{PH} = 11.6\) Hz, 18 H, C(CH\(_3\))\(_3\)), 1.11 (d, \(^3J_{PH} = 10.5\) Hz, 18H, C(CH\(_3\))\(_3\)). \(^{13}C\{^1H\}: 160.3 (d, \(^3J_{PC} = 9.4\) Hz, Ar-Cipso), 143.7 (dd, \(J_{PC} = 12.7\) Hz, \(J_{PC} = 0.7\) Hz, Ar-C), 129.5 (s, Ar-C), 123.3 (dd, \(J_{PC} = 8.7\) Hz, \(J_{PC} = 1.2\) Hz, Ar-C), 120.1 (dd, \(J_{PC} = 11.3\) Hz, \(J_{PC} = 9.1\) Hz, Ar-C), 115.9 (dd, \(J_{PC} = 10.5\) Hz, \(J_{PC} = 1.9\) Hz, Ar-C), 35.7 (d, \(^1J_{PC} = 26.8\) Hz, CH\(_2\)), 31.8 (d, \(^1J_{PC} = 24.5\), C(CH\(_3\))\(_3\)), 30.0 (d, \(^2J_{PC} = 13.5\) Hz,
C(CH$_3$)$_3$, 29.2 (d, $^1J_{PC} = 25.8$ Hz, C(CH$_3$)$_3$), 27.6 (d, $^2J_{PC} = 15.8$ Hz, C(CH$_3$)$_3$). $^{31}$P{${^1}$H}: 152.7 (s, O-P), 34.1 (s, CH$_2$-P).

($^{18}$BuPCOP)IrCl$_2$. A mixture of $^{18}$BuPCOP ligand (3.0 mL of 0.367 M solution in toluene, 1.1 mmol) and [Ir(COD)Cl]$_2$ (0.335 g, 0.499 mmol) in toluene (15 mL) was heated to reflux for 72 h at 110 °C under H$_2$ atmosphere. After cooling the reaction mixture to room temperature, the mother liquor was evaporated under vacuum. The product was extracted with pentane (60 mL x 3) and the combined pentane solution was evaporated to obtain an orange-red crystalline product. Yield: 0.470 g, 0.753 mmol, 68%. (NMR, δ, C$_6$D$_6$) $^1$H: 6.93-6.83 (m, 3H, Ar-H), 3.10 (dd, $^2J_{HH} = 17.6$ Hz, $^2J_{PH} = 9.5$ Hz, 1H, CH$_2$), 3.00 (dd, $^1J_{HH} = 17.6$ Hz, $^2J_{PH} = 8.9$ Hz, 1H, CH$_2$), 1.34 (d, $^3J_{PH} = 14.0$ Hz, 9H, C(CH$_3$)$_3$), 1.29 (d, $^3J_{PH} = 14.2$ Hz, 9H, C(CH$_3$)$_3$), 1.22 (d, $^3J_{PH} = 13.0$ Hz, 9H, C(CH$_3$)$_3$), 1.19 (d, $^3J_{PH} = 13.4$ Hz, 9H, C(CH$_3$)$_3$), -41.38 (dd, $^2J_{PH} = 13.3$ Hz, $^2J_{PH} = 12.3$ Hz). $^{13}$C{${^1}$H}: 168.1 (apparent t, $^3J_{PC} = 6.1$ Hz, Ar-Cipso), 152.0 (dd, $^3J_{PC} = 11.3$ Hz, $^2J_{PC} = 5.5$ Hz, Ar-C), 132.2 (dd, $^3J_{PC} = 5.6$ Hz, $^2J_{PC} = 3.0$ Hz Ar-C), 124.6 (s, Ar-C), 118.1 (d, $^3J_{PC} = 15.5$ Hz, Ar-C), 108.5 (d, $^3J_{PC} = 11.7$ Hz, Ar-C), 43.6 (dd, $^1J_{PC} = 19.3$ Hz, $^3J_{PC} = 4.9$ Hz, C(CH$_3$)$_3$), 39.4 (dd, $^1J_{PC} = 20.9$ Hz, $^3J_{PC} = 5.9$ Hz, C(CH$_3$)$_3$), 37.5 (dd, $^1J_{PC} = 15.9$ Hz, $^3J_{PC} = 3.2$ Hz, C(CH$_3$)$_3$), 35.3 (dd, $^1J_{PC} = 29.8$ Hz, $^3J_{PC} = 1.0$ Hz, CH$_2$), 35.0 (dd, $^1J_{PC} = 17.7$ Hz, $^3J_{PC} = 3.3$ Hz, C(CH$_3$)$_3$), 29.9 (dd, $^2J_{PC} = 3.8$ Hz, $^4J_{PC} = 1.3$ Hz C(CH$_3$)$_3$), 29.3 (dd, $^2J_{PC} = 3.8$ Hz, $^4J_{PC} = 1.3$ Hz C(CH$_3$)$_3$), 27.8 (d, $^3J_{PC} = 4.9$ Hz, C(CH$_3$)$_3$), 27.7 (dd, $^2J_{PC} = 4.9$ Hz, $^4J_{PC} = 1.0$ Hz, C(CH$_3$)$_3$). $^{31}$P{$^1$H}: 168.6 (dd, $^2J_{pp} = 345.0$ Hz, $^2J_{PH} = 12.3$ Hz O-P), 70.6 (dd, $^2J_{pp} = 345.0$ Hz, $^2J_{PH} = 11.0$ Hz, CH$_2$-P).

($^{18}$BuPCOP)IrH$_2$. ($^{18}$BuPCOP)IrHCl (0.150 g, 0.247 mmol) was dissolved in pentane (60 mL) and 1.0 M solution (in THF) of LiBEt$_3$H (0.25 mL, 0.25 mmol) was added dropwise via syringe under a hydrogen atmosphere, causing the orange solution to turn a pale yellow color and resulting in the precipitation of lithium chloride. The reaction mixture was stirred for 30 min and filtered by cannula. The pentane solution was evaporated under vacuum to obtain a red crystalline solid. Yield: 0.136 g, 0.231 mmol, 93%. (NMR, δ, C$_6$D$_6$) $^1$H: 7.23 – 7.13 (m, 3H, Ar-H), 3.50 (d, $^2J_{PH} = 8.5$ Hz, 2H, CH$_2$), 1.34 (d, $^3J_{PH} = 13.8$ Hz, 18H, C(CH$_3$)$_3$), 1.19 (d, $^3J_{PH} = 12.9$ Hz, 18H, C(CH$_3$)$_3$), -18.12 (apparent t, $^3J_{PH} = 8.6$ Hz, 2H, IrH$_2$). $^{13}$C{${^1}$H}: 171.0 (dd, $^3J_{PC} = 5.7$ Hz, $^3J_{PC} = 3.1$ Hz, Ar-Cipso) 170.7 (dd, $^3J_{PC} = 8.5$ Hz, $^3J_{PC} = 7.0$ Hz, Ar-C), 157.6 (dd, $^3J_{PC} = 14.2$ Hz, $^3J_{PC} = 5.8$ Hz, Ar-C), 129.5 (dd, $^3J_{PC} = 0.6$ Hz, Ar-C), 116.3 (d, $^3J_{PC} = 16.1$ Hz, Ar-C), 107.7 (d, $^3J_{PC} = 12.5$ Hz, Ar-C), 40.3 (d, $^3J_{PC} = 28.6$ Hz, CH$_2$), 40.1 (dd, $^3J_{PC} = 20.7$ Hz, $^3J_{PC} = 4.6$ Hz, C(CH$_3$)$_3$), 35.1 (dd, $^1J_{PC} = 17.6$ Hz, $^3J_{PC} = 2.4$ Hz, C(CH$_3$)$_3$), 29.9 (dd, $^2J_{PC} = 5.3$ Hz, $^4J_{PC} = 0.8$ Hz, C(CH$_3$)$_3$), 29.0 (d, $^2J_{PC} = 6.3$ Hz, C(CH$_3$)$_3$). $^{31}$P{$^1$H}: 200.3 (d, $^2J_{pp} = 330$ Hz, O-P), 87.3 (d, $^2J_{pp} = 330$ Hz, CH$_2$-P).
**n-octane metathesis procedure.** The catalytic runs were performed using a modification of our previous procedure. An Ir stock solution of $(\text{Ir}^{\text{III}}\text{POCOP})\text{Ir}(\text{C}_2\text{H}_4)$ (10 mM), n-octane, and mesitylene (28.8 mM; internal standard) was prepared under an argon atmosphere. To a 7” J. Young type NMR tube charged with the respective Mo or W olefin metathesis catalyst (typically 8 µmol) was added 500 µL of the Ir stock solution. The tube was frozen in liquid nitrogen; the headspace was evacuated, and the Teflon valve was closed. Samples were placed in an oil bath such that the liquid mixture was completely submerged. Once the reaction was complete, the mixture was passed through basic alumina and the resulting solution was subjected to GC analysis using the method of Goldman et al. The peaks were integrated with respect to the mesitylene internal standard. GC response factors were calculated with C7-C15 standards. Integrations were totaled for all alkanes and normalized to 6154 mM (corresponding to 500 µL of n-octane).

**Representative procedure for n-octane/ethylbenzene metathesis.** To a vial containing the respective Mo or W olefin metathesis catalyst (typically 8 µmol) was added $(\text{Ir}^{\text{III}}\text{PCP})\text{Ir}(\text{C}_2\text{H}_4)$ (3.1 mg, 5.3 umol), 400 µL ethylbenzene, 300 µL n-octane, mesitylene (internal standard) and t-butyl ethylene (10 uL, 78 umol). The mixture was added to a 7” J. Young type NMR tube and frozen in liquid nitrogen; the headspace was evacuated, and the Teflon valve was closed. Samples were placed in a 180 °C oil bath for 24 hours such that the liquid mixture was completely submerged. The resulting solution was subjected to GC analysis. The peaks were integrated with respect to the mesitylene internal standard, and GC response factors were calculated using 1-phenylheptane, tetradecane and 1-phenyloctane reference standards (commercially available from Sigma-Aldrich).

**Representative procedure for hindered alkane/ethylbenzene metathesis.** An Ir stock solution of $(\text{Ir}^{\text{III}}\text{POCOP})\text{Ir}(\text{C}_2\text{H}_4)$ (10 mM) and mesitylene (internal standard) in ethylbenzene was prepared under an argon atmosphere. To a vial containing W(NAr)(C$_3$H$_6$)(pyr)(OHIPT) (7.7 mg, 8 µmol) was added 500 µL of the Ir stock solution, followed by 0.80 mmol of the hindered alkane substrate. The mixture was added to a 7” J. Young type NMR tube and frozen in liquid nitrogen; the headspace was evacuated, and the Teflon valve was closed. Samples were placed in a 180 °C oil bath for 48 hours such that the liquid mixture was completely submerged. Once the reaction was complete, the mixture was passed through basic alumina. The reaction yields were determined by $^1$H NMR analysis of a reaction aliquot in CDCl$_3$ ($n$-propyltrimethylsilane, $n$-propyltriethysilane) or in C$_6$D$_6$ (2-methyl-2-phenyl-pentane, 2,2-dimethylpentane).

**Observation of W alkylidenes in a crude reaction mixture.** A reaction of $n$-propyltrimethylsilane (0.80 mmol) and ethylbenzene was prepared as described above. After two days, the volatiles were removed in vacuo. To the remaining residue was added a ferrocene internal standard (4.0 mg, 0.022 mmol) and C$_6$D$_6$ (0.5 mL). $^1$H NMR of the mixture showed two alkylidene peaks at δ 10.25 (W(NAr)(CHPh)(pyr)(OHIPPT), 2.0 µmol) and δ 10.61 (unknown, 0.2 µmol). W(NAr)(CHPh)(pyr)(OHIPPT) was independently observed by addition of 14 mg styrene to a J. Young NMR tube containing 6.0 mg W(NAr)(C$_3$H$_6$)(pyr)(OHIPT) and 0.7 mL C$_6$D$_6$, which was freeze pump thawed three
times. 60% of the original W(NAr)(C₅H₆)(pyr)(OHIPT) was converted to W(NAr)(CHPh)(pyr)(OHIPT) according to the integration of the product alkylidene peak (δ 10.25) relative to the starting material resonances.

**Thermal stability of W(NAr)(CH-t-Bu)(pyr)(OHIPT).** To a J. Young NMR tube was added 4.0 mg W(NAr)(CH-t-Bu)(pyr)(OHIPT) (4.0 mg, 4 µmol), 0.5 mL C₆D₆, and mesitylene as an internal standard. The tube was freeze pump thawed and heated in a 150 °C oil bath. After two days, the proton resonance corresponding to the alkylidene proton (W=CHR) of W(NAr)(CH-t-Bu)(pyr)(OHIPT) (δ 9.56) was 83% of its original integration relative to the mesitylene internal standard.

**Thermal stability of W(NAr)(C₅H₆)(pyr)(OHIPT) in the presence of olefin.** To a J. Young NMR tube was added 4.0 mg W(NAr)(C₅H₆)(pyr)(OHIPT) (4.0 mg, 4 µmol), 0.5 mL toluene-d₈ and 1-octene (90 mg, 0.80 mmol). The tube was freeze pump thawed and heated in a 175 °C oil bath for 36 hours. The crude reaction mixture was passed through basic alumina and subjected to GC analysis.

**Olefin cross metathesis competition experiment.** Styrene (1.6 mg, 0.159 mmol), 1-octene (3.6 mg, 0.032 mmol) and trans-2-octene (3.6 mg, 0.032 mmol) were added to a C₆D₆ solution of W(NAr)(C₅H₆)(pyr)(OHIPT) (2.5 mg, 2.6 µmol) at room temperature. The reaction was run in a small uncapped vial within a larger, capped 20 mL scintillation vial, providing additional headspace for any generated ethylene. Within 24 hours, isomers of 7-tetradecane and oct-1-en-1-ylbenzene can be observed by GC-MS.
Synthesis of alkane metathesis substrates.

\[ \text{SiMe}_3 \]

\textit{n-propytrimethylsilane}. This known compound was prepared using the method of Whitmore et al.\textsuperscript{18} A THF solution of trimethylchlorosilane (19.5 mL, 0.154 mol) was added via cannula to a THF solution of \textit{n}-propyl magnesium bromide, freshly prepared from magnesium (5.48g) and \textit{n}-propyl bromide (18.2 mL, 0.200 mol). The solution was heated to reflux for 16 hours. The reaction was quenched with water and extracted into diethyl ether. The organic layer was washed three times with water and once with brine, and dried over magnesium sulfate. Fractional distillation provided a mixture of the product with THF; this mixture was repeatedly washed with cold \textit{H}_2\textit{O} until the THF was completely removed. The product was dried over \textit{CaH}_2. Yield 4.64g (26%). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ 1.42 – 1.26 (m, 2H, \textit{R}-\textit{C}_\text{H}_2-\text{Me}), 0.95 (t, \textit{J} = 7.3 Hz, 3H, \textit{R}-\text{CH}_3), 0.57 – 0.42 (m, 2H, Et-\text{CH}_2-Si), -0.03 (s, 9H, -\text{Si}(\text{CH}_3)_3). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) δ 19.52, 18.49, 17.57, -1.44.

\[ \text{SiEt}_3 \]

\textit{n-propytriethylsilane}. This known compound was prepared using the method of Whitmore et al.\textsuperscript{18} A 2-methyl THF solution of \textit{n}-propyl magnesium bromide (1.0M, 50 mL) was added to a solution of triethylchlorosilane (7.6 mL, 0.045 mmol) in THF. The solution was refluxed for 48 hours. The reaction was quenched with water and extracted into diethyl ether. The organic layer was washed three times with water and once with brine, and dried over magnesium sulfate. Volatiles were removed in vacuo. The resulting residue was dissolved in pentane, and passed through a silica plug. Volatiles were removed in vacuo to afford the product. Yield 1.80g (25%). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ 1.37 – 1.29 (m, 2H, \textit{R}-\text{CH}_2-\text{Me}), 0.99 – 0.91 (m, 12H, \textit{R}-\text{CH}_3), 0.55 – 0.47 (m, 8H, Si-\text{CH}_2-R). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) δ 18.83, 17.59, 14.28, 7.63, 3.51.

\[ \text{Ph} \]

\textit{2-methyl-2-phenylpentane}. This known compound was prepared using a procedure modified from Pines et al.\textsuperscript{19} A solution of neophyl magnesium chloride (0.5 M in Et\textsubscript{2}O) was added dropwise to a THF solution of ethyl iodide cooled to 0 °C. The reaction was allowed to warm to room temperature. After 1 hour, the reaction was quenched with water and extracted into diethyl ether. The organic layer was washed three times with water and once with brine, and dried over magnesium sulfate. Volatiles were removed in vacuo. The resulting residue was dissolved in pentane, and passed through a silica plug. Vacuum distillation afforded the pure product. Yield 750 mg (13%). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ 7.36 – 7.28 (m, 4H, Ar), 7.17 (t, \textit{J} = 7.2 Hz, 1H, Ar), 1.64 – 1.53 (m, 2H, R-\text{CH}_2-Et), 1.30 (s, 6H, R_2C(CH_3)_2), 1.12 – 1.02 (m, 2H, R-\text{CH}_2-Me), 0.82 (t, \textit{J} = 7.3 Hz, 3H, R-\text{CH}_3). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) δ 149.87, 128.09, 125.94, 125.41, 47.26, 37.86, 29.09, 18.13, 14.93.
Synthesis of authentic samples of alkane cross metathesis products.

**trimethyl(3-phenylpropyl)silane.** This known compound\(^{20}\) was prepared by addition of trimethylsilyl chloride (380 µL) to a THF solution of 3-phenylpropyl magnesium bromide (0.2 M, 10 mL). The solution was refluxed for 48 hours. The reaction was quenched with water and extracted into diethyl ether. The organic layer was washed three times with water and once with brine, and dried over magnesium sulfate. Volatiles were removed in vacuo. The resulting residue was dissolved in pentane, and passed through a silica plug. Volatiles were removed in vacuo to afford the product. Yield 79.5 mg (21 %). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.31 – 7.26 (m, 2H, Ar), 7.21 – 7.16 (m, 3H, Ar), 2.62 (t, \(J = 7.9\) Hz, 2H, Ph-CH\(_2\)), 1.66 – 1.58 (m, 2H, -CH\(_2\)-), 0.59 – 0.51 (m, 2H, -CH\(_2\)-SiR\(_3\)), -0.02 (s, 9H, -Si(CH\(_3\))\(_3\)). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) δ 142.94, 128.62, 128.35, 125.74, 40.10, 26.31, 16.75, -1.52.

**triethyl(3-phenylpropyl)silane.** This known compound\(^{21}\) was prepared by addition of triethylsilyl chloride (500 µL) to a THF solution of 3-phenylpropyl magnesium bromide (0.2 M, 10 mL). The solution was refluxed for 48 hours. The reaction was quenched with water and extracted into diethyl ether. The organic layer was washed three times with water and once with brine, and dried over magnesium sulfate. Volatiles were removed in vacuo. The resulting residue was dissolved in pentane, and passed through a silica plug. Volatiles were removed in vacuo to afford the product. Yield 61.2 mg (13 %). \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.31 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 2.62 (d, \(J = 7.8\) Hz, 2H), 1.66 – 1.57 (m, 2H), 0.91 (t, \(J = 7.9\) Hz, 9H), 0.61 – 0.53 (m, 2H), 0.49 (q, \(J = 7.9\) Hz, 6H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ 142.91, 128.58, 128.34, 125.72, 40.40, 26.26, 11.46, 7.62, 3.40.

**(4-methylpentane-1,4-diyl)dibenzene.** This known compound\(^{22}\) was prepared by addition of neophyl magnesium chloride (14 mL, 0.5 M in Et\(_2\)O) to a solution of 2-iodoethyl benzene (1.60g, 6.91 mmol) in THF. The solution was allowed to stir for 4 hours at room temperature. The reaction was quenched with water and extracted into diethyl ether. The organic layer was washed three times with water and once with brine, and dried over magnesium sulfate. Volatiles were removed in vacuo. The resulting residue was dissolved in pentane, and passed through a silica plug. Remaining 2-iodoethyl benzene starting material was removed through a short-path distillation (60 mTorr, 100 °C) to provide pure product. Yield 754 mg (46%). \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 7.30 – 7.02 (m, 10H), 2.48 (t, \(J = 7.7\) Hz, 2H), 1.68 – 1.57 (m, 2H), 1.41 – 1.31 (m, 2H), 1.25 (s, 6H). \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)) δ 7.23 – 7.18 (m, 4H), 7.13 (t, \(J = 7.5\) Hz, 2H), 7.10 – 7.02 (m, 2H), 6.97 (d, \(J = 7.4\) Hz, 2H), 2.38 (t, \(J = 7.6\) Hz, 2H), 1.57 – 1.51 (m, 2H), 1.41 – 1.33 (m, 2H), 1.17 (s, 6H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ 149.53, 142.70, 128.49, 128.31, 128.13, 125.91, 125.72, 125.47, 37.76, 36.60, 29.09, 26.71.
(4,4-dimethylpentyl)benzene. This known compound was prepared by addition of neopentyl magnesium chloride (30 mL, 0.28 M in Et₂O) to a solution of 2-iodoethyl benzene (1.60g, 6.91 mmol) in THF. The solution was allowed to stir for 4 hours at room temperature. The reaction was quenched with water and extracted into diethyl ether. The organic layer was washed three times with water and once with brine, and dried over magnesium sulfate. Volatiles were removed in vacuo. The resulting residue was dissolved in pentane, and passed through a silica plug. Yield 698 mg (57%). ¹H NMR (600 MHz, CDCl₃) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.16 (m, 3H), 2.63 – 2.54 (m, 2H), 1.67 – 1.54 (m, 2H), 1.29 – 1.19 (m, 2H), 0.87 (s, 9H). ¹H NMR (600 MHz, C₆D₆) δ 7.23 – 7.18 (m, 2H), 7.12 – 7.07 (m, 3H), 2.47 (t, J = 7.7 Hz, 2H), 1.63 – 1.44 (m, 2H), 1.27 – 1.09 (m, 2H), 0.83 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 143.13, 128.51, 128.37, 125.71, 44.08, 37.02, 30.46, 29.54, 26.89.
References