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Ruthenium olefin metathesis catalysts with modified styrene ethers: influence of steric and electronic effects

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Abstract—A series of olefin metathesis catalysts with modified isopropoxybenzylidene ligands were synthesised, and the effects of ligands on the rate of metathesis investigated. Increased steric hinderance *ortho* to the isopropoxy group enhanced reaction rates. In the case of *N*-heterocyclic carbene complexes, decreasing electron density at both the chelating oxygen atom and the Ru=C bond accelerated reaction rates appreciably. Catalysts containing a tricyclohexylphosphane ligand, followed the same trend with regard to benzylidene electrophilicity, while higher electron density at oxygen enhanced reaction rates.
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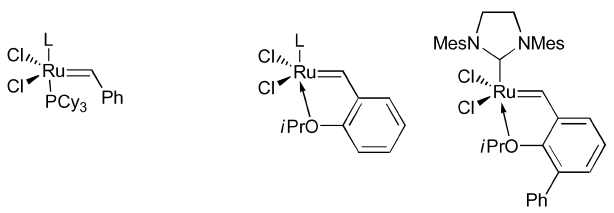
1. Introduction

Over the last decade, the olefin metathesis reaction has emerged from relative obscurity to become one of the most powerful carbon–carbon bond forming tools at the disposal of the contemporary organic chemist.[1] Much of this success can be attributed to the discovery by Grubbs of bis-phosphane catalyst **1**,[2] which combines excellent functional group tolerance with high catalytic activity, thus considerably broadening the scope of the olefin metathesis reaction. More recently, advances of comparable significance have come with the advent of ruthenium alkylidene catalysts (**2**[3] and **3**[4]) containing *N*-heterocyclic carbene (NHC) ligands.[5] It has been postulated that these non-labile ligands, which possess strong σ-donor and weak π-acceptor properties can stabilise both the 16-electron pre-catalysts and the highly electron deficient metathesis intermediates, which translates into catalysts with a similar or improved stability/functional group tolerance to **1**, while exhibiting much enhanced catalytic activity.[3,4,6,7] Catalysts bearing chelating isopropoxybenzylidene ligands (**4**[8] and **5**[9]) which can augment catalyst stability even further have also been introduced (Fig. 1).

Catalysts bearing these moieties can be readily purified by column chromatography; allowing for catalyst recycling after the reaction. Phosphane-free alkylidene **5** has been shown to perform relatively well in certain reactions involving challenging conditions or substrates,[10–15] i.e. in situations where catalyst decomposition is an important issue. A primary reason for our continued interest in these catalysts is the modifiability of the chelating ligand, which is considerably more amenable to practical structural attenuation than oxygen-sensitive trialkylphosphanes. Immobilisation of suitably substituted variants of **4** and **5** on solid support via the isopropoxybenzylidene ligand has been reported,[15,16] but it was the discovery of catalysts such as **6** which prompted us to further investigate the structure–reactivity relationship of these species. Catalysts such as **6**, which contain substituents other than hydrogen *ortho* to the isopropoxy group, show dramatically improved initiation rates across a wide range of olefin metathesis reactions.[17,18] It seems plausible that in the case of **6**, the increased steric



1 L = PCy_3

2 L = MesN NMes

3 L = MesN NMes

4 L = PCy_3

5 L = MesN NMes

6

Mes = 2,4,6-trimethylphenyl
Cy = cyclohexyl

Figure 1. Olefin metathesis catalysts.

Keywords: metathesis; ruthenium; carbene complex; catalysis.
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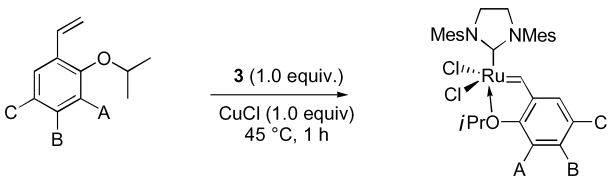


15 A = H, B = H, C = O*i*Pr
16 A = H, B = H, C = Me
17 A = H, B = H, C = CF_3
18 A = H, B = H, C = F
19 A = H, B = O*i*Pr, C = H
20 A = H, B = F, C = H
21 A = H, B = CN, C = H
22 A = OMe, B = H, C = H

7 A = H, B = H, C = O*i*Pr
8[a] A = H, B = H, C = Me
9 A = H, B = H, C = CF_3
10 A = H, B = H, C = F
11[a] A = H, B = O*i*Pr, C = H
12 A = H, B = F, C = H
13 A = H, B = CN, C = H
14[a] A = OMe, B = H, C = H

[a] 0.5 Equiv. **3** and 0.5 equiv CuCl required.

Scheme 1. Synthesis of substituted analogues of **5**.

Table 1. Analogues of **5**: catalyst yields

Entry	Styrene	Catalyst	Yield (%)[a]
1	**15**	**7**	63
2	**16**	**8**	82[b]
3	**17**	**9**	68
4	**18**	**10**	53
5	**19**	**11**	81[b]
6	**20**	**12**	63
7	**21**	**13**	21
8	**22**	**14**	81[b]

[a] Refers to isolated yields after chromatography.
[b] 2.0 equiv. styrene required.

bulk weakens the Ru–O chelate bond, thus facilitating faster ligand dissociation to form the catalytically active 14-electron[7] species whilst also hindering the catalyst-deactivating ligand reassociation step. Since initiation rates are closely linked to the strength of the Ru–O bond, it led us to postulate that they could be influenced by varying electron density at the isopropoxy group. An analogue of **5** with a nitro group *para* to the isopropoxy group has recently been synthesised, and initial RCM reactions show that this derivative is more active and stable than the parent complex.[19] It is clear that altering the steric and electronic environment of **5** can have a marked effect on the activity of the catalyst. This potential, along with the relatively straightforward synthesis of analogues of **5** have warranted further investigations. A systematic study into the effect of steric and electronic properties on the reaction rates on olefin metathesis catalysts bearing chelating isopropoxy-benzylidene ligands is reported.

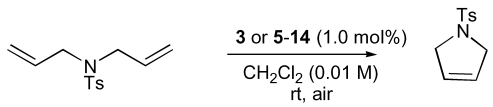
2. Results and discussion

A small library of analogues of **5** (**7**–**14**) was prepared from styrenes **15**–**22** (Scheme 1, Table 1).[9a] Even at this early stage it was evident that the more electron deficient catalysts were difficult to synthesise and purify in good yield, while those catalysts bearing electron-donating substituents were more readily prepared (Table 1).

The goal was to investigate the relative behaviour of catalysts **5**–**14** in ring-closing metathesis (RCM). Dienes **23** and **24** were chosen, to yield the 5- and 8-membered ring products **25** and **26**, respectively. Based on our experience with these types of precatalysts, an investigation of a large number of substrates was deemed unnecessary. All catalytic experiments were carried out in air to test the robustness of the catalysts in question. To limit reaction rate to a level useful for comparisons, relatively mild conditions (1 mol% catalyst, 22°C, 0.01 M CH_2Cl_2) were employed and the reactions were monitored by HPLC. The results of these experiments are outlined in Tables 2 and 3.

Analysis of the conversion rates yielded some interesting findings. The substrate half-life was arbitrarily chosen as an indicator of the initiation efficiency of each catalyst in the particular reaction under scrutiny. For the RCM of **23**, it was pleasing to find that this parameter varied widely depending not only on the steric, but also on the electronic properties of the catalyst. The order of catalyst activity in this reaction was found to be **6**>**13**>**14**,**3**,**9**>**10**,**12**>**5**>**7**⩾**8**⩾**11**. As we had expected, catalysts bearing electron withdrawing groups led to faster reaction rates than either the reference catalyst **5** or analogues substituted with electron donating groups. However, this view is somewhat simplistic and provides no information regarding the relative importance of electron density at either the benzylidene or isopropoxy group. These separate effects are more distinguishable when the results are interpreted with the aid of σ^+ values.[20] It is apparent that the rate of catalysis is largely but not entirely governed by electron density at the benzylidene moiety. For example, in the case of catalyst **7**, the non-chelating isopropoxy group would be expected to have a strong electron donating effect on its chelated counterpart while having little or no influence over benzylidene electrophilicity. Conversely, regioisomeric **11** possesses a relatively electron-rich Ru=C bond while the Ru–O bond should have similar electronic characteristics to the corresponding moiety of **5**. Therefore, the observation that **11** leads to slower reaction times than **7** strongly indicates that benzylidene electrophilicity is the dominant factor.[21] It is also interesting that **7** has a lower initial activity than **5**, taking 13 min longer to reach 50% conversion. Thus tighter Ru–O bonding due to increased electron density at the chelating isopropoxy group *does also influence activity*, albeit to a lesser extent. Catalyst **8** was somewhat unexpectedly and reproducibly sluggish in this and other

Table 2. RCM of **23** promoted by analogues of **5**



23 **25**

Entry	Catalyst	σ_m^+	σ_p^+	t (min) at 50% conversion[a]	Conversion (%)[a] after 4.5 h
1	**3**	–	–	23	98
2	**5**	0	0	50	91
3	**6**	0	–	9	78
4	**7**	0.05[b]	−0.78[b]	63	84
5	**8**	−0.06	−0.26	118	72
6	**9**	0.57	0.61	26	89
7	**10**	0.35	−0.07	32	93
8	**11**	0.05[b]	−0.78[b]	280	48[c]
9	**12**	0.35	−0.07	35	84
10	**13**	0.56	0.66	13	96
11	**14**	0.05	–	20	66

[a] Determined by HPLC.
[b] Based on value for OMe.
[c] Quantitative conversion after 24 h.

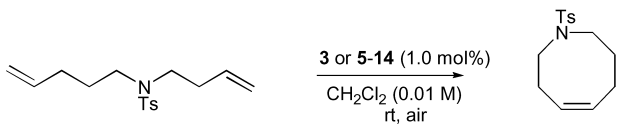
reactions, however this may still be explainable if one considers that the methyl substituent is the only one in this study which acts as an electron donor toward both the chelating atom and the benzylidene unit.

The fastest non-hindered variants of **5** are those which bear substituents capable of reducing electron density appreciably at both the *meta* and *para* positions. Nitrile-substituted catalyst **13** for example, even surpasses the hindered catalyst **14** in terms of initiation speed, while also converting the substrate to a greater extent. Catalyst **9**, which incorporates a powerfully electron withdrawing CF_3 substituent is also highly active, while **10** and **12**, which bear fluorine atoms in positions which allow them to withdraw electrons from either the benzylidene or the isopropoxy moiety (but not both) are less effective, although both are predictably faster than **5**.

Figures 2 and 3 show the reaction profile (RCM of **23**) for catalysts where electron density has been varied predominantly at the benzylidene or the isopropoxy group, respectively. For comparison both plots include one case where both moieties have been electronically modified by substituent effects (i.e. catalysts **9** and **13**). It is clear that although electron accepting groups accelerate the reaction in both cases, effects of greatest magnitude are possible through systematic variation of electron density at the benzylidene group, while the fastest catalysts are those with substituents of high σ_m^+ and σ_p^+ values.

It must be noted that with the exception of hindered catalysts **6** and **14** (which perform the RCM of **23** in excellent yield under anaerobic conditions),[17,18] conversion to **25** after prolonged reaction times was uniformly high regardless of the catalyst used. This is consistent with the

Table 3. RCM of **24** promoted by analogues of **5**



24 **26**

Entry	Catalyst	σ_m^+	σ_p^+	t (min) at 50% conversion[a]	Conversion (%)[a] after 4.5 h
1	**3**	–	–	26	89
2	**5**	0	0	28	87
3	**6**	0	–	2[b]	44
4	**7**	0.05[c]	−0.78[c]	25	84
5	**8**	−0.06	−0.26	33	80
6	**9**	0.57	0.61	11	88
7	**10**	0.35	−0.07	18	80
8	**11**	0.05[c]	−0.78[c]	107	69
9	**12**	0.35	−0.07	12	87
10	**13**	0.56	0.66	11	87
11	**14**	0.05	–	11	56

[a] Determined by HPLC.
[b] Time taken to reach 40% conversion.
[c] Based on value for OMe.

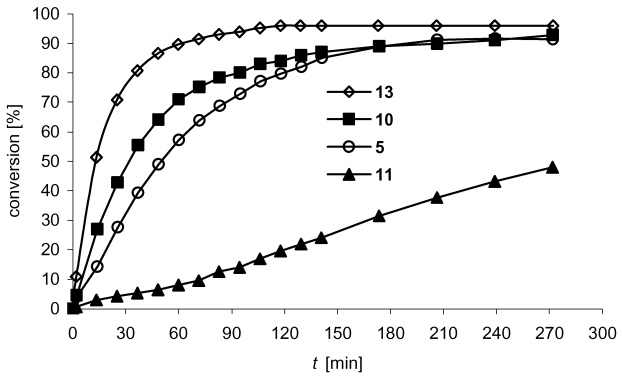


Figure 2. RCM of **23** promoted by analogues of **5**: variation of catalyst benzylidene moiety electrophilicity.

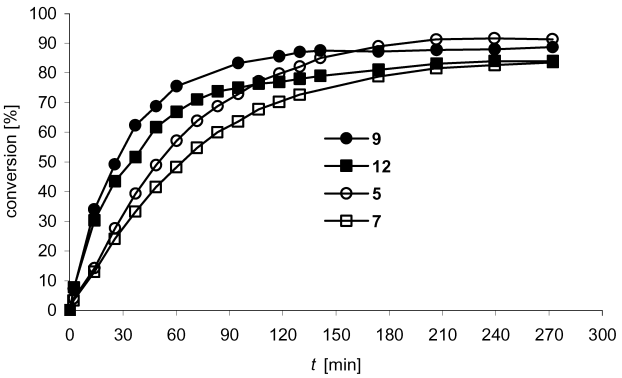
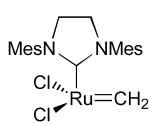


Figure 3. RCM of **23** promoted by analogues of **5**: variation of catalyst isopropoxy moiety electrophilicity.

presence of a common reactive intermediate, namely methylidene **27** (Fig. 4), in these reactions. It is the generation of this catalytically active species which is influenced by electronic and steric effects. In the studies involving the RCM of **23**, no evidence was found for the intermediacy of any other species which may explain the well documented[10–15] differences in activity between **3** and **5**.

The RCM of **24** promoted by analogues of **5** produced unexpected results. With the exception of phosphane-based initiator **3**, each RCM reaction to form the eight-membered ring product was faster than its five membered analogous transformation (**23**→**25**) when the same catalyst is used under identical conditions. Given that **26** is certainly more strained than **25** (and hence one would expect, more difficult to form), the relatively fast RCM of **24** observed is remarkable. There are three possible explanations for this counter-intuitive result: A) In the case where **23** is the substrate, the RCM reaction must involve intermediate **28a**,



27

Figure 4. The presumed active species during the RCM of **23** promoted by analogues of **5**.

where the ruthenium metal is attached to an allyl-*N*Ts moiety, the proximity of this electron withdrawing group both destabilises and inhibits the formation of **28a**, whereas in the RCM of **24**, the presumed alkylidene intermediate (**28b**) is further removed from the NTs moiety, meaning faster initial reaction and a more stable alkylidene. B) The formation of a 6-membered ring chelated intermediate **28c** (Fig. 5) is conceivable during the RCM of **23**, thereby trapping the catalyst in an inactive form. With **24** as the substrate, after the assumed initial reaction at the more electron rich olefin, formation of chelate **28d** (vide infra) would necessitate eight membered ring formation, and so would be expected to be considerably slower than the formation of **28c**. C) A combination of cases A and B contributes to the lower reactivity of **23** in the RCM reaction.

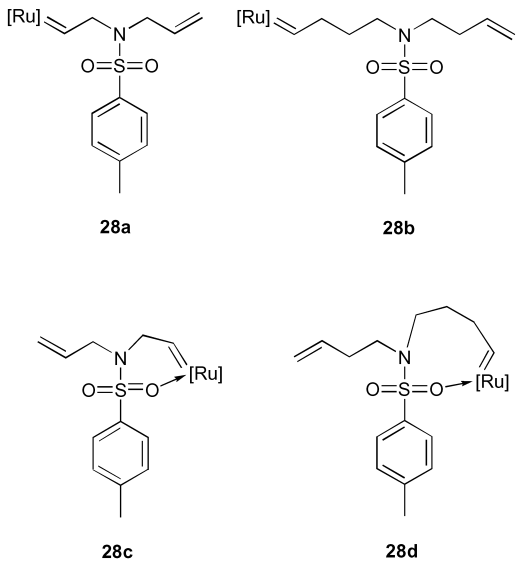


Figure 5. Possible intermediates in the RCM of **23** and **24**.

It was gratifying to find that the same catalyst activity order with isopropoxybenzylidene-based catalysts was found in the RCM of **24** as was observed with diene **23** (Table 3, Fig. 6). Figure 6 shows the trend where the electron density has been varied predominantly at the benzylidene unit. In comparison, the difference between the catalysts where the electron density was altered at the isopropoxy group was not as large, but the same trend was observed. However, the observation that the RCM of **24** catalysed by **3** was not faster than the analogous reaction involving **23** is intriguing. Repetition of the experiment did not alter this result, despite the fact that all of the phosphane-free catalysts ring-closed **24** faster than **23**. All that can be inferred at this juncture is that the intermediates in the RCM of **24** differ to some extent, depending on whether **3** or analogues of **5** are used as catalysts.

Encouraged by our results, it was decided to undertake a similar investigation of analogues of **4** (Scheme 2), which contain one trialkylphosphane and one isopropoxybenzylidene ligand. Catalysts **30**–**37** were readily prepared[8] using styrenes already in hand (Table 4). Once again the performance of these catalysts in the RCM of **23** and **24** was monitored by HPLC (Tables 5 and 6) under identical

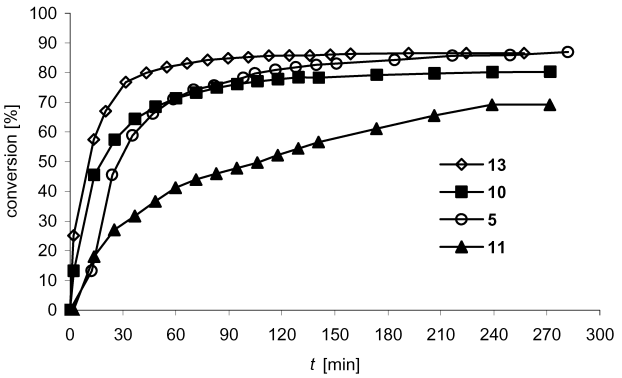
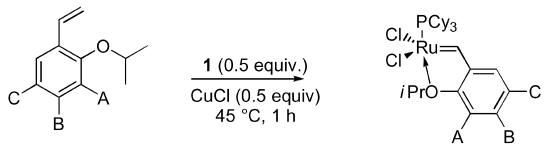


Figure 6. RCM of **24** promoted by analogues of **5**: variation of catalyst benzylidene moiety electrophilicity.



15 A = H, B = H, C = O*i*Pr
16 A = H, B = H, C = Me
17 A = H, B = H, C = CF_3
18 A = H, B = H, C = F
19 A = H, B = O*i*Pr, C = H
20 A = H, B = F, C = H
22 A = OMe, B = H, C = H
29 A = O*i*Pr, B = H, C = H

30 A = H, B = H, C = O*i*Pr
31 A = H, B = H, C = Me
32 A = H, B = H, C = CF_3
33 A = H, B = H, C = F
34 A = H, B = O*i*Pr, C = H
35 A = H, B = F, C = H
36 A = OMe, B = H, C = H
37 A = O*i*Pr, B = H, C = H

Scheme 2. Synthesis of substituted analogues of **4**.

Table 4. Analogues of **4**: catalyst yields

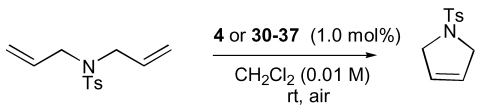
Entry	Styrene	Catalyst	Yield (%)[a]
1	**15**	**30**	66
2	**16**	**31**	80
3	**17**	**32**	74
4	**18**	**33**	90
5	**19**	**34**	87
6	**20**	**35**	86
7	**22**	**36**	60
8	**29**	**37**	36

[a] Refers to isolated yields after chromatography.

conditions to those to which the analogues of **5** were subjected.

Examination of the data from the RCM of **23** revealed a surprising result; hindered catalysts **36** and **37** aside (which resulted in the fastest reaction rates), alkylidene **30**, which is relatively electron-rich at the chelating oxygen atom, was the most efficient catalyst in this reaction. This was quite unexpected, and wholly inconsistent with results obtained using NHC-based catalysts. Furthermore, catalysts with substituents capable of reducing the Lewis-basicity at the isopropoxy group (**32** and **35**) were appreciably slower than anticipated (Table 5). The relative reaction rates indicated that as was the case with NHC-based catalysts, increasing the electrophilicity at the benzylidene moiety has an accelerating effect on catalysis. However, whereas with analogues of **5**, electron density at the oxygen atom was relatively unimportant, monophosphane catalysts **30**–**37** exhibited a strong sensitivity to electronic effects at this position. The data presented in Figures 7 and 8 are instructive. Figure 7 shows the reaction profile (RCM of **23**) using monophosphane catalysts with substituents which attenuate electron density mostly at the benzylidene moiety. The fastest catalyst here is **33**, and not **32**, which has the strongest electron-withdrawing properties and was clearly superior in terms of initiation in the NHC-based catalyst series. In fact, promotion of this reaction by **32** to 50% conversion requires almost exactly the same time as the reference catalyst **4**. As expected, *p*-, alkoxy-substituted alkylidene **34** was the slowest of all the catalysts tested. This trend indicates that while electrophilicity at the benzylidene unit contributes to overall catalytic rates in the expected way, if it is accompanied by concurrent reduction of Lewis-basicity at the adjacent oxygen atom, the beneficial effects on reaction speed are somewhat negated. In this regard it is interesting to note that the σ_m^+ and σ_p^+ values for the CF_3 group do not differ greatly, and that catalyst **32** behaves similarly to **4** in the RCM of **23**. While this should not be over-interpreted, this would seem to indicate that the effects of the CF_3 substituent on the benzylidene unit and chelating oxygen can cancel each other; pointing towards an almost equal but opposite contribution of electron density at both

Table 5. RCM of **23** promoted by analogues of **4**

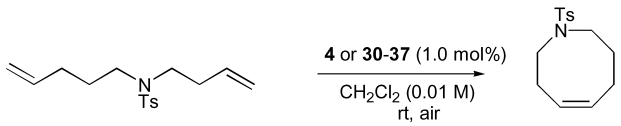


23 **25**

Entry	Catalyst	σ_m^+	σ_p^+	*t* (min) at 50% conversion[a]	Conversion (%)[a] after 4.5 h
1	**4**	0	0	50	89[b]
2	**30**	0.05[c]	−0.78[c]	29	89[b]
3	**31**	−0.06	−0.26	71	98
4	**32**	0.57	0.61	49	100
5	**33**	0.35	−0.07	33	94
6	**34**	0.05[c]	−0.78[c]	89	90
7	**35**	0.35	−0.07	63	99
8	**36**	0.05[c]	–	14	88[b]
9	**37**	0.05[c]	–	11	89[b]

[a] Determined by HPLC.
[b] After 140 min.
[c] Based on value for OMe.

Table 6. RCM of **24** promoted by analogues of **4**



24 **26**

Entry	Catalyst	σ_m^+	σ_p^+	t (min) at 50% conversion[a]	Conversion (%)[a] after 4.5 h
1	**4**	0	0	42	89[b]
2	**30**	0.05[c]	−0.78[c]	24	91
3	**31**	−0.06	−0.26	84	87
4	**32**	0.57	0.61	31	90
5	**33**	0.35	−0.07	32	91
6	**34**	0.05[c]	−0.78[c]	89	85
7	**35**	0.35	−0.07	34	91
8	**36**	0.05[c]	–	9	86
9	**37**	0.05[c]	–	7	88

[a] Determined by HPLC.
[b] After 140 min.
[c] Based on value for OMe.

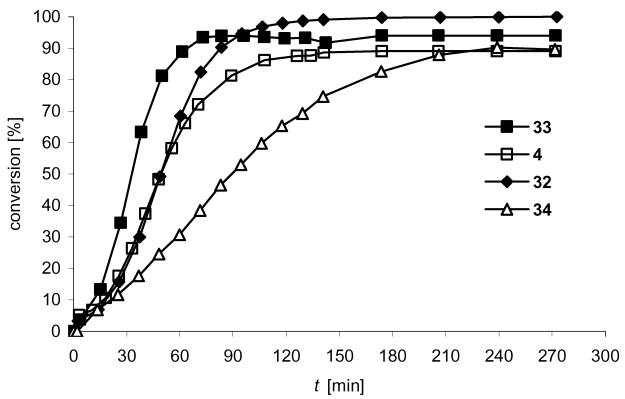


Figure 7. RCM of **23** promoted by analogues of **4**: variation of catalyst benzylidene moiety electrophilicity.

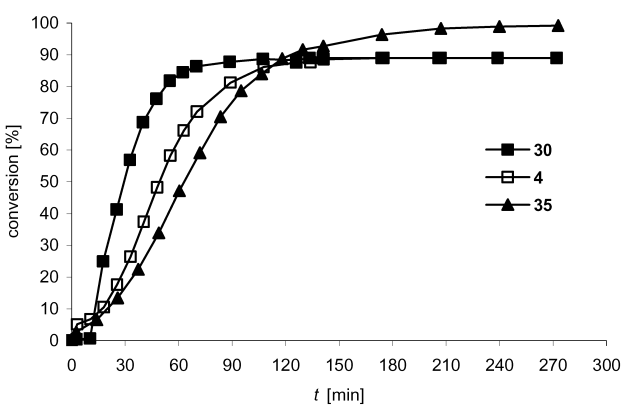


Figure 8. RCM of **23** promoted by analogues of **4**: variation of catalyst isopropoxy moiety electrophilicity.

moieties to overall initiation rates. This is supported by the observation of relatively fast catalysis using fluoro-substituted **33**, which would be expected to be more electrophilic at the Ru=C bond and more nucleophilic at the Ru–O bond than **4**.

When electron density is predominantly varied at the chelating oxygen, strong effects on reaction rates are observed (Fig. 8). Increased electron density at this position clearly results in faster catalysis. This greater significance of oxygen basicity in analogues of **4** can be seen on comparison of the efficacy (RCM of **23**) of fluoro-substituted alkylidenes (**10**, **12**) with **5**, and (**33**, **35**) with **4**. In the NHC based series, both **10** and **12** are faster than **5** (Table 2), while in the phosphane based series, **33** is faster than **4** while **35** (which is expected to be more electrophilic at oxygen) is markedly slower (Table 5). Again, it must be pointed out that over time conversions were excellent, regardless of the catalyst employed.

In the case of RCM of **24** catalysed by analogues of **4** (Table 6), the trends are not so clear-cut, although the same general activity order was observed (**32** being a conspicuous anomaly) and the reactions were all faster than the analogous 5-membered ring forming process.

These results pose an important question: Why does variation of the electron density at the chelating oxygen atom change catalytic rates in both magnitude and direction when the NHC ligand is replaced with tricyclohexyl-phosphane? Hoveyda et al. have proposed that the methylidene $Cl_2PCy_3Ru{=}CH_2$ (**38**) is the active species in reactions catalysed by **4**.[8b] However our experimental results strongly indicate that augmented coordinating ability of the isopropoxybenzylidene ligand has a beneficial effect on reaction speed. A possibility is that a mechanism is operating whereby this moiety, at least partly, remains attached to the ruthenium metal. Since ruthenium-catalysed metathesis reactions are assumed to proceed through 14-electron intermediates,[7] phosphane dissociation plays some role in metathesis reactions catalysed by analogues of **4**. As previously noted, NHCs possess negligible π-acceptor properties and are more σ-basic than trialkylphosphanes,[5] so it is plausible that electronic effects at the chelating oxygen atom could have more influence on the catalyst in the case of alkylidene **4** and related species than in **5**.

The RCM of **23** promoted by **4** was carried out in the presence of 1.2 equiv. (relative to the catalyst) of CuCl as a phosphane scavenger. This reaction was carried out in air as before, however vigorous stirring was employed to ensure mixing of the insoluble CuCl, and samples were taken and injected into the HPLC manually. Thus exposure of the solution to air is somewhat greater than in a non-stirred HPLC vial, leading to slower overall initiation rates for the blank (no additive) reaction than previously observed. Under these conditions an initial rate acceleration was observed compared to the same reaction without any additives under identical conditions (Fig. 9). This would be consistent with phosphane dissociation playing a role in metathesis reactions involving analogues of **4**. CuCl is known to react with phosphanes to form ill-defined complexes, but it is unclear whether the rate enhancement is as a result of phosphane dissociation or subsequent formation of bimetallic species.[22] It was found that when the same experiments were carried out using catalyst **5**, that CuCl had absolutely no effect, meaning that neither Cu–O nor CuCl chelation makes an observable contribution to catalyst initiation. These studies indicate that the mechanism involves phosphane dissociation, but what is clear is that a mechanism involving phosphane dissociation is not operating alone. This can be seen from the inhibition of catalyst initiation on addition of 1.2 equiv. (relative to the catalyst) of the isopropoxystyrene ligand (Fig. 9) to the RCM reaction of **23** catalysed by **4**, indicating that the concentration of this species in solution is also important. A mechanistic investigation with a view to determining the nature of the active species in these reactions is underway.

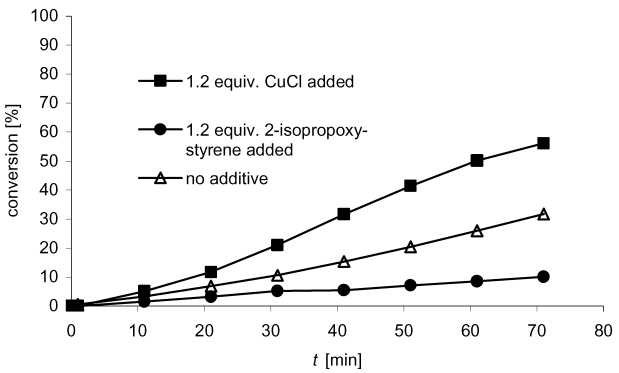


Figure 9. RCM of **23**: effect of added CuCl and ligand on the initiation activity of **4**.

3. Conclusions

We have shown that useful information regarding the factors that influence catalyst initiation in systems such as **4** and **5** can be obtained through systematic variation of electron density at either the benzylidene or the chelating isopropoxy group. For the data to be meaningful, interpretation with the aid of σ^+ values is critical, as they allow an approximation of the separate effects of a particular substituent on both the groups which are bound to ruthenium to be made. In the case of NHC-based catalysts (analogues of **5**), increased electrophilicity at either moiety leads to faster reaction rates, with the electronic character of the Ru=C bond being the dominant factor. RCM of **24** to form the eight-membered ring product **26** is faster than the RCM of **23** under identical conditions when isopropoxybenzylidene-based catalysts are employed. Possible explanations for this observation can be put forward based on the premise that the *N*-allylic moiety in **23** is less reactive towards metathesis catalysts due to either electronic or chelation effects. The exchange of a NHC for a tricyclohexylphosphane ligand (i.e. analogues of **4**) has an unexpected and profound effect on initiation trends. In these pre-catalysts, the effects of variation of electron density at the benzylidene moiety are the same as those in the NHC-based series, however, an increase in Lewis-basicity at the chelating oxygen atom leads to faster reaction rates, with a corresponding decrease in the rate of reaction when Lewis-basicity at this position is reduced. This suggests that phosphane dissociation plays some role in the catalytic cycle, a theory supported by the fact that RCM reactions catalysed by **4** in the presence of added phosphine scavenger reacted faster than in cases where no scavenger was used. These results show that care must be exercised in assigning a general mechanism based on isopropoxystyrene ligand dissociation to catalysts such as **4** and **5**.

4. Experimental

4.1. General

With the exception of RCM reactions, all manipulations were carried out under N_2 in pre-dried glassware using standard techniques. CH_2Cl_2 was dried by distillation over CaH_2, toluene over Na, THF over Na/benzophenone, and ether over Na. DMF was dried by distillation and was stored over molecular sieves (4 Å). ^1H and ^{13}C NMR spectra were recorded on Bruker DRX 500 (500 MHz) and AM 400 (400 MHz) instruments. Spectra are referenced relative to the chemical shift (δ) of $SiMe_4$. IR spectra were recorded on a Nicolet FT-750 spectrometer. Mass spectra were recorded using a Finnegan MAT 95 SQ (70 eV) instrument. Microanalysis were determined by the microanalytical laboratory, T. U. Berlin. HPLC was performed using a Waters system with a Waters 991 PDA detector. Flash chromatography (FC) was carried out using standard commercially available silica gel. All commercially available reagents were used without further purification

4.2. Catalyst synthesis

4.2.1. (4,5-DihydroIMes)Cl_2Ru=CH(2-O*i*Pr)(5-F)C_6H_3 (10). To a solution of **3** (46.7 mg, 0.055 mmol) and CuCl (6 mg, 0.057 mmol) in CH_2Cl_2 (1.1 mL) under N_2, was added a solution of **18** (10 mg, 0.055 mmol) in CH_2Cl_2 (1.1 mL). The reaction mixture was heated under reflux for 1 h, then allowed to cool to room temperature and concentrated in vacuo. The residue was dissolved in a minimum amount of a 1:1 pentane/CH_2Cl_2 mixture and the insoluble material filtered through a Pasteur pipette containing cotton wool. The solvent was concentrated again in vacuo, and the crude material was purified by FC (80:20 hexane/MTBE) to give the catalyst as a green solid (19 mg, 53%). ^1H NMR (500 MHz, C_6D_6): δ=16.47 (s, 1H), 6.89 (s, 4H), 6.80 (td, J=8 Hz, 2H), 6.02 (dd, J=8, 3.1 Hz, 1H), 4.33 (septet, J=6.0 Hz, 1H), 3.40 (s, 4H), 2.54 (s, 12H), 2.20 (s, 6H), 1.26 (d, J=6.0 Hz, 6H) ppm; IR (Nujol): ν=2966,

2919, 1482, 1419, 1257, 1213, 1133, 929 cm^{-1}; MS (70 eV, EI): *m/z* (%): 644 (17), 442 (12), 406 (18), 327 (12), 304 (100), 301 (18), 248 (28), 236 (34), 155 (19), 138 (50), 127 (57), 91 (69), 69 (46), 57 (96); HR-MS: calcd: 644.1304; found: 644.1316; elemental analysis calcd (%) for $C_{31}H_{37}N_2OFCl_2Ru$ (644.61): C 57.76, H 5.79, N 4.35; found: C 58.06, H 6.12, N 4.08.

4.2.2. (4,5-DihydroIMes)Cl_2Ru=CH(2-O*i*Pr)(5-Me)C_6H_3 (8). The procedure for the synthesis of catalyst **10** was followed using **3** (200 mg, 0.235 mmol), **16** (83 mg, 0.471 mmol) and CuCl (23.3 mg, 0.235 mmol) in CH_2Cl_2 (30 mL). FC (CH_2Cl_2/hexane 1:1) gave **8** as a green solid (123 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=16.50 (s, 1H), 7.28 (d, *J*=8.4 Hz, 1H), 7.07 (s, 4H), 6.69 (s, 1H), 6.66 (d, *J*=8.4 Hz, 1H), 4.84 (septet, *J*=6.0 Hz, 1H), 4.17 (s, 4H), 2.48 (bs, 12H), 2.41 (s, 6H), 2.34 (s, 3H), 1.25 (d, *J*=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2): δ=297.8, 211.8, 150.4, 145.4, 138.9, 131.5, 130.0, 129.5, 123.1, 112.6, 74.8, 51.6, 21.1, 20.1 ppm; IR (Nujol): ν=2974, 2918, 2857, 1701, 1486, 1419, 1260, 1221, 1135, 1104, 925, 853 cm^{-1}; MS (70 eV, EI): *m/z* (%): 640 (26), 526 (12), 507 (12), 478 (30), 442 (13), 406 (31), 395 (60), 377 (52), 341 (20), 307 (21), 304 (76), 287 (19), 250 (14), 210 (13), 171 (39), 147 (28), 134 (37), 121 (24), 91 (31), 73 (100), 57 (48); HR-MS: calcd: 640.1555; found: 640.1552; elemental analysis calcd (%) for $C_{32}H_{40}N_2OCl_2Ru$ (640.66): C 59.99, H 6.29, N 4.37; found: C 59.96, H 6.49, N 4.32.

4.2.3. (4,5-DihydroIMes)Cl_2Ru=CH(2,4-*bis*-O*i*Pr)C_6H_3 (11). The procedure for the synthesis of catalyst **10** was followed using **3** (200 mg, 0.235 mmol), **19** (104 mg, 0.472 mmol) and CuCl (23.3 mg, 0.235 mmol) in CH_2Cl_2 (30 mL). FC (CH_2Cl_2/hexane 1:1) gave **11** as a green solid (135 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=16.17 (s, 1H), 7.05 (s, 4H), 6.80 (d, *J*=8.5 Hz, 1H), 6.37 (dd, *J*=8.5, 1.8 Hz, 1H), 6.30 (s, 1H), 4.81 (septet, *J*=6.1 Hz, 1H), 4.51 (septet, *J*=6.1 Hz, 1H), 4.17 (s, 4H), 2.47 (bs, 12H), 2.39 (s, 6H), 1.28 (d, *J*=6.1 Hz, 6H), 1.26 (d, *J*=6.1 Hz, 6H) ppm; IR (Nujol): ν=2976, 2923, 2854, 1596, 1482, 1437, 1384, 1264, 1254, 1116, 1100, 842 cm^{-1}; MS (70 eV, EI): *m/z* (%): 684 (3), 510 (9), 412 (3), 312 (10), 304 (100), 289 (10), 250 (13), 215 (9), 171 (19), 136 (21), 91 (26), 57 (14); HR-MS: calcd: 684.1817; found: 684.1821; elemental analysis calcd (%) for $C_{34}H_{44}N_2Cl_2O_2Ru$ (684.72): C 59.64, H 6.48, N 4.09; found: C 59.34, H 6.85, N 3.51.

4.2.4. (4,5-DihydroIMes)Cl_2Ru=CH(2-O*i*Pr)(3-OMe)C_6H_3 (14). The procedure for the synthesis of catalyst **10** was followed using **3** (300 mg, 0.353 mmol), **22** (136 mg, 0.707 mmol) and CuCl (38.4 mg, 0.388 mmol) in CH_2Cl_2 (35 mL). FC (hexane/MTBE 2:1) gave **14** as a green solid (188 mg, 81%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ=16.51 (s, 1H), 7.15 (d, *J*=8.0 Hz, 1H), 7.09 (bs, 4H), 6.90 (dd, *J*=8.0, 7.5 Hz, 1H), 6.58 (d, *J*=7.5 Hz, 1H), 5.73 (septet, *J*=6.2 Hz, 1H), 4.13 (s, 4H), 3.79 (s, 3H), 2.45 (bs, 18H), 1.20 (d, *J*=6.2 Hz, 6H) ppm; ^{13}C NMR (125 MHz, CD_2Cl_2): δ=297.4, 210.7, 149.8, 147.7, 139.9, 139.7, 138.9, 138.8, 129.3, 123.6, 115.5, 114.2, 80.6, 56.4, 51.5, 21.6, 20.9, 20.2, 18.4 ppm; IR (Nujol): ν=3482, 1701, 1607, 1585, 1574, 1475, 1445, 1419, 1267, 1106 cm^{-1}; MS (70 eV, EI): *m/z* (%): 656 (2), 578 (6), 404 (10), 356 (9), 304 (15), 272 (29), 256 (10), 177 (10), 152 (27), 123 (21), 111 (28), 97 (44), 83 (62), 55 (100); HR-MS: calcd: 656.1504; found: 656.1519; elemental analysis calcd (%) for $C_{32}H_{40}O_2N_2Cl_2Ru$ (656.66): C 58.53, H 6.14, N 4.27; found: C 58.18, H 5.90, N 4.51.

4.2.5. (4,5-DihydroIMes)Cl_2Ru=CH(2-O*i*Pr)(4-F)C_6H_3 (12). The procedure for the synthesis of catalyst **10** was followed using **3** (100 mg, 0.118 mmol), **20** (21.2 mg, 0.118 mmol) and CuCl (11.7 mg, 0.118 mmol) in CH_2Cl_2 (2.4 mL). FC (hexane/EtOAc 7:1) gave **12** as a green solid (48 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=16.59 (s, 1H), 7.40 (d, *J*=8 Hz, 1H), 6.98 (s, 4H), 6.38 (td, *J*=8, 2.2 Hz, 1H), 6.21 (d, *J*=10.3 Hz, 1H), 4.23 (septet, *J*=6.0 Hz, 1H), 3.44 (s, 4H), 2.60 (bs, 12H), 2.26 (s, 6H), 1.25 (d, *J*=6.0 Hz, 6H) ppm; IR (Nujol): ν=3503, 2966, 2917, 2859, 1712, 1592, 1484, 1429, 1270, 1255, 1155, 1101, 990, 839 cm^{-1}; MS (70 eV, EI): *m/z* (%): 644 (14), 442 (12), 406 (20), 304 (100), 301 (20), 158 (20), 138 (18), 111 (22), 91 (49), 71 (52), 57 (83); HR-MS: calcd: 644.1304; found: 644.1315.

4.2.6. (4,5-DihydroIMes)Cl_2Ru=CH(2,5-O*i*Pr)C_6H_3 (7). The procedure for the synthesis of catalyst **10** was followed using **3** (189 mg, 0.222 mmol), **15** (48.4 mg, 0.222 mmol) and CuCl (21.8 mg, 0.222 mmol) in CH_2Cl_2 (4.0 mL). FC (CH_2Cl_2/hexane 1:1) gave **7** as a green solid (48 mg, 63%). ^{1}H NMR (500 MHz, C_6D_6): δ=16.61 (s, 1H), 7.20–6.90 (m, 5H), 6.76 (d, *J*=3.0 Hz, 1H), 6.29 (d, *J*=9.0 Hz, 1H), 4.50 (septet, *J*=6.0 Hz, 1H), 4.19 (septet, *J*=6.0 Hz, 1H), 3.49 (s, 4H), 2.62 (bs, 12H), 2.28 (s, 6H), 1.38 (d, *J*=6.0 Hz, 6H), 1.20 (d, *J*=6.0 Hz, 6H) ppm; IR (Nujol): ν=3485, 2976, 2920, 1701, 1607, 1579, 1485, 1419, 1257, 1215, 1137, 1104, 942 cm^{-1}; MS (70 eV, EI): *m/z* (%): 684 (42), 570 (14), 527 (13), 442 (13), 405 (48), 304 (100), 301 (44), 287 (20), 136 (56), 124 (37), 97 (29), 81 (43), 69 (91); HR-MS: calcd: 684.1817; found: 684.1819; elemental analysis calcd (%) for $C_{34}H_{44}N_2Cl_2O_2Ru$ (684.72): C 59.64, H 6.48, N 4.09; found: C 59.95, H 6.78, N 3.78.

4.2.7. (4,5-DihydroIMes)Cl_2Ru=CH(2-O*i*Pr)(5-CF_3)C_6H_3 (9). The procedure for the synthesis of catalyst **10** was followed using **3** (200 mg, 0.236 mmol), **17** (54.3 mg, 0.236 mmol) and CuCl (23.3 mg, 0.236 mmol) in CH_2Cl_2 (5.0 mL). FC (hexane/EtOAc 7:1) gave **9** as a green solid (111 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=16.46 (s, 1H), 7.77 (dd, *J*=9.0, 2.0 Hz, 1H), 7.18 (d, *J*=2.0 Hz, 1H), 7.04 (s, 4H), 6.97 (d, *J*=9.0 Hz, 1H), 4.97 (septet, *J*=6.0 Hz, 1H), 4.11 (s, 4H), 2.57 (s, 12H), 2.41 (s, 6H), 1.25 (d, *J*=6.0 Hz, 6H) ppm; IR (Nujol): ν=3493, 2976, 2920, 2863, 1705, 1599, 1492, 1483, 1421, 1331, 1282, 1263, 1212, 1166, 1130, 1101, 1072, 910, 854 cm^{-1}; MS (70 eV, EI): *m/z* (%): 694 (30), 442 (28), 406 (40), 348 (100), 304 (78), 301 (35), 215 (28), 188 (46), 176 (37), 91 (28), 57 (20); HR-MS: calcd: 694.1272; found: 694.1269.

4.2.8. (4,5-DihydroIMes)Cl_2Ru=CH(2-O*i*Pr)(4-CN)C_6H_3 (13). The procedure for the synthesis of catalyst **10** was followed using **3** (227 mg, 0.267 mmol), **21** (50.0 mg, 0.267 mmol) and CuCl (26.9 mg, 0.267 mmol) in CH_2Cl_2 (5.3 mL). FC (CH_2Cl_2/hexane 3:1) gave **13** as a green solid (36 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=16.63 (s, 1H), 7.21 (d, *J*=9.0 Hz, 1H), 7.05 (s, 4H),

7.03–6.99 (m, 2H), 4.86 (septet, 6.0 Hz, 1H), 4.19 (s, 4H), 2.45 (bs, 12H), 2.41 (s, 6H), 1.24 (d, J=6.0 Hz, 6H) ppm; IR (Nujol): ν=3493, 2974, 2921, 2856, 2227, 1858, 1700, 1606, 1556, 1482, 1417, 1262, 1117, 1099, 978, 853, 836 cm^{-1}; MS (70 eV, EI): m/z (%): 651 (>1), 163 (20), 147 (48), 131 (57), 103 (32), 84 (24), 69 (54), 56 (100); HR-MS: calcd: 651.1351; found: 651.1341.

4.2.9. (PCy_3)Cl_2Ru=CH(2-O*i*Pr)(5-F)C_6H_3 (33). To a solution of **1** (133 mg, 0.162 mmol) and CuCl (16.0 mg, 0.162 mmol) in CH_2Cl_2 (7.0 mL) under N_2, was added a solution of **18** (58.5 mg, 0.324 mmol) in CH_2Cl_2 (6.0 mL). The reaction mixture was stirred at ambient temperature for 12 h then concentrated in vacuo. The residue was dissolved in a minimum amount of a 1:1 pentane/CH_2Cl_2 mixture and the insoluble material filtered through a Pasteur pipette containing cotton wool. The solvent was concentrated again in vacuo, and the crude material was purified by FC (cyclohexane/EtOAc 9:1) to give the catalyst **33** as a brown solid (90 mg, 90%). ^{1}H NMR (500 MHz, C_6D_6): δ=17.09 (d, J=4.2 Hz, 1H), 6.99 (dd, J=7.6, 2.6 Hz, 1H), 6.93–6.86 (m, 1H), 6.26 (dd, J=8.6, 3.5 Hz, 1H), 4.59 (septet, J=5.8 Hz, 1H), 2.42–1.11 (series of multiplets, 33H), 1.69 (d, J=5.8 Hz, 6H) ppm; IR (Nujol): ν=2928, 2851, 1706, 1583, 1483, 1447, 1385, 1275, 1116, 1101, 929, 736 cm^{-1}; MS (70 eV, EI): m/z (%): 618 (44), 540 (4), 499 (2), 424 (6), 414 (10), 375 (22), 198 (32), 125 (38), 81 (52), 55 (100); HR-MS: calcd: 618.1528; found: 618.1522.

4.2.10. (PCy_3)Cl_2Ru=CH(2-O*i*Pr)(3-OMe)C_6H_3 (36). The procedure for the synthesis of catalyst **33** was followed using **1** (200 mg, 0.243 mmol), **22** (107 mg, 0.557 mmol) and CuCl (24.1 mg, 0.243 mmol) in CH_2Cl_2 (30 mL). FC (CH_2Cl_2/hexane 1:1) gave **36** as a brown solid (92 mg, 60%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=17.42 (d, J=4 Hz, 1H), 7.23 (d, J=6 Hz, 1H), 7.08–7.00 (m, 2H), 6.14 (septet, J=6 Hz, 1H), 3.88 (s, 3H), 2.40–1.00 (series of multiplets, 33H), 1.77 (d, J=6 Hz, 6H) ppm; IR (Nujol): ν=2927, 2850, 1839, 1690, 1574, 1473, 1445, 1270, 1106, 1079 cm^{-1}; MS (70 eV, EI): m/z (%): 630 (6), 552 (16), 434 (18), 356 (16), 314 (24), 279 (16), 272 (100), 198 (54), 177 (24), 138 (36), 117 (58), 83 (36), 55 (38); HR-MS: calcd: 630.1728; found: 630.1722.

4.2.11. (PCy_3)Cl_2Ru=CH(2,3-*bis*-O*i*Pr)C_6H_3 (37). The procedure for the synthesis of catalyst **33** was followed using **1** (500 mg, 0.608 mmol), **29** (161 mg, 0.729 mmol) and CuCl (60 mg, 0.608 mmol) in CH_2Cl_2 (20 mL).

FC (CH_2Cl_2/hexane 1:1) gave **37** as a brown solid (144 mg, 36%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=17.42 (d, J=4.1 Hz, 1H), 7.25 (d, J=6.7 Hz, 1H), 7.17 (d, J=8.0 Hz, 1H), 7.00 (dd, J=8.0, 6.7 Hz, 1H), 6.24 (septet, J=6.0 Hz, 1H), 4.58 (septet, J=6.0 Hz, 1H), 2.40–1.20 (series of multiplets, 33H), 1.76 (d, J=6.0 Hz, 6H), 1.38 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=282.4, 148.0, 147.1, 141.9, 123.8, 116.8, 116.2, 80.7, 71.4, 35.4, 35.7, 35.5, 30.2, 27.9, 27.8, 23.0, 21.9 ppm; IR (Nujol): ν=2972, 2926, 2850, 1466, 1444, 1383, 1268, 1114, 1104, 909 cm^{-1}; MS (70 eV, EI): m/z (%): 658 (13), 657 (8), 580 (20), 462 (16), 412 (14), 375 (22), 370 (35), 328 (18), 279 (22), 244 (100), 214 (13), 198 (39), 163 (18), 150 (25), 136 (52), 124 (80), 117 (44), 83 (30), 55 (45); HR-MS: calcd: 658.2041; found: 658.2044; elemental analysis calcd (%) for $C_{31}H_{51}Cl_2O_2PRu$ (658.68): C 56.53, H 7.80; found: C 56.31, H 7.77.

4.2.12. (PCy_3)Cl_2Ru=CH-(2,5-*bis*-O*i*Pr)C_3H_6 (30). The procedure for the synthesis of catalyst **33** was followed using **1** (100 mg, 0.146 mmol) **15** (32.1 mg, 0.146 mmol) and CuCl (14.5 mg, 0.146 mmol) in CH_2Cl_2 (3 mL).

FC (CH_2Cl_2) gave **30** as a brown solid (52.8 mg, 66%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=17.33 (d, J=4.4 Hz, 1H), 7.20–7.16 (m, 2H), 6.96 (d, J=8.4 Hz, 1H), 5.19 (septet, J=6.0 Hz, 1H), 4.50 (septet, J=6.0 Hz, 1H), 2.40–1.20 (series of multiplets, 33H), 1.78 (d, J=6.0 Hz, 6H), 1.35 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=279.1, 153.4, 147.1, 144.2, 117.6, 113.6, 109.9, 75.3, 71.4, 35.7, 35.5, 31.5, 27.8, 27.7, 26.9, 26.3, 22.1, 22.0 ppm; IR (Nujol): ν=2974, 2928, 2851, 1703, 1485, 1447, 1213, 1104, 941 cm^{-1}; MS (70 eV, EI): m/z (%): 658 (85), 657 (55), 541 (8), 464 (2), 462 (37), 412 (40), 375 (42), 373 (24), 281 (66), 259 (24), 211 (25), 198 (45), 124 (76), 117 (52), 97 (18), 83 (52), 55 (100); HR-MS: calcd: 658.2041; found: 658.2051; elemental analysis calcd (%) for $C_{31}H_{51}Cl_2O_2$-PRu (658.68): C 56.53, H 7.80; found: C 56.19, H 7.52.

4.2.13. (PCy_3)Cl_2Ru=CH-(2-O*i*Pr)(4-F)C_3H_6 (35). The procedure for the synthesis of catalyst **33** was followed using **1** (200 mg, 0.243 mmol), **20** (87.6 mg, 0.486 mmol) and CuCl (24.1 mg, 0.243 mmol) in CH_2Cl_2 (30 mL).

FC (CH_2Cl_2/hexane 1:1) gave **35** as a brown solid (129 mg, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ=17.30 (d, J=4.0 Hz, 1H), 7.63 (dd, J=9.0, 1.0 Hz, 1H), 6.89–6.74 (m, 2H), 5.21 (septet, J=6.0 Hz, 1H), 2.42–1.11 (series of multiplets, 33H), 1.84 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=278.0, 164.0, 162.0, 154.3, 154.2, 141.2, 141.1, 123.8, 123.7, 109.4, 109.2, 102.4, 102.2, 76.7, 36.4, 36.2, 35.8, 35.6, 30.4, 30.2, 30.1, 27.7, 26.2, 22.3, 22.0 ppm; IR (Nujol): ν=2928, 2851, 1703, 1292, 1447, 1262, 1157, 1102, 990, 910, 838 cm^{-1}; MS (70 eV, EI): m/z (%): 618 (40), 414 (16), 377 (23), 375 (25), 279 (38), 259 (14), 211 (18), 117 (24), 97 (18), 834 (28), 83 (52), 69 (63), 55 (100); HR-MS: calcd: 618.1528; found: 618.1527; elemental analysis calcd (%) for $C_{28}H_{44}Cl_2OPFRu$ (618.60): C 54.37, H 7.17; found: C 54.03, H 7.12.

4.2.14. (PCy_3)Cl_2Ru=CH-(2-O*i*Pr)(5-CF_3)C_3H_6 (32). The procedure for the synthesis of catalyst **33** was followed using **1** (200 mg, 0.243 mmol), **17** (80 mg, 0.347 mmol) and CuCl (24.1 mg, 0.243 mmol) in CH_2Cl_2 (30 mL).

FC (CH_2Cl_2/hexane 1:1) gave **32** as a brown solid (120 mg, 74%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=17.41 (d, J=4.2 Hz, 1H), 7.97 (s, 1H), 7.88 (d, J=8.4 Hz, 1H), 7.16 (d, J=8.4 Hz, 1H), 5.32 (septet, J=6.0 Hz, 1H), 2.39–1.21 (series of multiplets, 33H), 1.83 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=275.4, 154.8, 143.4, 126.1, 122.7, 119.8, 113.5, 76.9, 35.8, 35.6, 30.1, 27.8, 26.9, 22.1 ppm; IR (Nujol): ν=2929, 2852, 1711, 1601, 1447, 1331, 1284, 1213, 1166, 1131, 1075, 912 cm^{-1}; MS (70 eV, EI): m/z (%): 668 (14), 432 (14), 348 (48), 281 (10), 218 (16), 188 (16), 176 (100), 175 (36), 127 (18), 107 (34), 97

(16), 83 (27), 55 (38); HR-MS: calcd: 668.1496; found: 668.1502; elemental analysis calcd (%) for $C_{29}H_{44}Cl_2OPF_3Ru$ (668.61): C 52.10, H 6.63; found: C 52.39, H 6.67.

4.2.15. $(PCy_3)Cl_2Ru{=}CH\text{-}(2\text{-}O\textit{i}Pr)(5\text{-}Me)C_3H_6$ (31). The procedure for the synthesis of catalyst **33** was followed using **1** (200 mg, 0.243 mmol), **16** (77 mg, 0.437 mmol) and CuCl (23.1 mg, 0.243 mmol) in CH_2Cl_2 (30 mL).

FC (CH_2Cl_2/hexane 1:1) gave **31** as a brown solid (119 mg, 80%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=17.38 (d, J=4.1 Hz, 1H), 7.47 (s, 1H), 7.42 (d, J=8.3 Hz, 1H), 6.95 (d, J=8.3 Hz, 1H), 5.23 (septet, J=6.0 Hz, 1H), 2.46 (s, 3H), 2.44–1.26 (series of multiplets, 33H), 1.79 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=280.1, 150.9, 143.9, 131.8, 130.0, 128.17, 123.1, 113.0, 75.3, 35.7, 30.1, 27.8, 26.9, 22.7, 20.0 ppm; IR (Nujol): ν=2927, 2851, 1702, 1487, 1446, 1221, 1137, 1104, 926 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 614 (62), 418 (20), 412 (16), 377 (23), 307 (64), 281 (43), 259 (14), 198 (25), 117 (38), 97 (22), 83 (66), 69 (91), 55 (100); HR-MS: calcd: 614.1779; found: 614.1784; elemental analysis calcd (%) for $C_{29}H_{47}Cl_2OPRu$ (641.67): C 56.67, H 7.71; found: C 56.09, H 7.56.

4.2.16. $(PCy_3)Cl_2Ru{=}CH\text{-}(2,4\text{-}\textit{bis}\text{-}O\textit{i}Pr)C_3H_6$ (34). The procedure for the synthesis of catalyst **33** was followed using **1** (200 mg, 0.243 mmol), **19** (104 mg, 0.472 mmol) and CuCl (26.5 mg, 0.267 mmol) in CH_2Cl_2 (30 mL).

FC (CH_2Cl_2/hexane 1:1) gave **34** as a brown solid (139 mg, 87%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ=17.15 (d, J=4.2 Hz, 1H), 7.53 (d, J=8.3 Hz, 1H), 6.59–6.55 (m, 2H), 5.18 (septet, J=6.0 Hz, 1H), 4.63 (septet, J=6.0 Hz, 1H), 2.35–1.25 (series of multiplets, 33H), 1.81 (d, J=6.0 Hz, 6H), 1.40 (d, J=6.0 Hz, 6H) ppm; IR (Nujol): ν=2975, 2927, 2850, 1712, 1596, 1446, 1384, 1266, 1188, 1118, 1102, 1002, 940, 843 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 658 (10), 622 (30), 582 (30), 541 (16), 499 (9), 462 (32), 410 (100), 408 (88), 376 (68), 373 (43), 327 (16), 291 (25), 279 (30), 259 (35), 244 (38), 215 (32), 198 (76), 183 (30), 124 (34), 123 (100), 83 (49), 55 (70); HR-MS: calcd: 658.2041; found: 658.2047; elemental analysis calcd (%) for $C_{31}H_{51}Cl_2O_2PRu$ (658.68): C 56.53, H 7.80; found: C 56.99, H 7.96.

4.3. Ligand synthesis

4.3.1. 2-Isopropoxy-5-methylbenzaldehyde. A stirred mixture of 2-hydroxy-3-methylbenzaldehyde (2.2 g, 16.0 mmol), K_2CO_3 (4.4 g, 32.0 mmol) and KI (4.5 g, 27.2 mmol) in DMF (30 mL) was heated to 50°C. Isopropylbromide (3.0 mL, 32.0 mmol) was then added slowly dropwise. The reaction mixture was stirred for 12 h at 50°C, cooled and filtered. The organic layer was washed with saturated NH_4Cl solution (10 mL), brine (10 mL) and dried over $MgSO_4$. The organic extracts were concentrated in vacuo. The residue was purified by FC (MTBE/hexane 1:1) to afford the product (2.8 g, 97%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=10.46 (s, 1H), 7.63 (d, J=1.8 Hz, 1H), 7.32 (dd, J=8.5, 1.8 Hz, 1H), 6.90 (d, J=8.5 Hz, 1H), 4.63 (septet, J=6.0 Hz, 1H), 2.30 (s, 3H), 1.39 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=190.5, 158.8, 136.5, 130.0, 128.3, 125.6, 114.4, 71.4, 22.1, 20.3 ppm; IR (Nujol): ν=2963, 2906, 2858, 1684, 1491, 1259, 1090, 1017, 797 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 178 (16), 136 (100), 137 (8), 118 (10), 107 (16), 90 (7), 77 (14), 51 (6); HR-MS: calcd: 178.0994; found: 178.0991.

4.3.2. 1-Isopropoxy-2-vinyl-4-methylbenzene (16). Methyltriphenylphosphoniumbromide (16.8 g, 47.1 mmol) and KO*t*Bu (5.3 g, 47.1 mmol) were stirred in ether (150 mL) at 0°C for 1 h. A solution of 2-isopropoxy-3-methylbenzaldehyde (2.8 g, 15.7 mmol) in ether (20 mL) was then added and stirring continued for further 1 h at 0°C. The crude reaction mixture was filtered and concentrated in vacuo. The residue was purified by FC (hexane) to give **16** (2.6 g, 96%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.31 (d, J=1.5 Hz, 1H), 7.06 (dd, J=17.8, 11 Hz, 1H), 7.02 (dd, J=8.4, 1.5 Hz, 1H), 6.80 (d, J=8.4 Hz, 1H), 5.73 (dd, J=17.8, 1.2 Hz, 1H), 5.23 (dd, J=11, 1.2 Hz, 1H), 4.48 (septet, J=6.0 Hz, 1H), 2.31 (s, 3H), 1.35 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=153.1, 132.0, 129.9, 129.2, 127.8, 126.9, 114.8, 113.6, 71.2, 22.2, 20.6 ppm; IR (Nujol): ν=2976, 2963, 2928, 1714, 1362, 1221, 803 cm$^{-1;}$ MS (70 eV, EI): *m*/*z* (%): 176 (37), 134 (100), 133 (32), 105 (15), 91 (26), 77 (12), 65 (4), 51 (5); HR-MS: calcd: 176.1201; found: 176.1201.

4.3.3. 2,3-Diisopropoxybenzaldehyde. A stirred mixture of 2,3-dihydroxybenzaldehyde (2.0 g, 14.5 mmol), K_2CO_3 (8.0 g, 57.9 mmol) and KI (8.2 g, 49.2 mmol) in DMF (50 mL) was heated to 50°C. Isopropylbromide (5.5 mL, 57.9 mmol) was then added slowly dropwise. The reaction mixture was stirred for 12 h at 50°C then cooled and filtered. The organic layer was washed with saturated NH_4Cl solution (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by FC (MTBE/hexane1:9) to afford the product (3.0 g, 94%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=10.45 (s, 1H), 7.41 (dd, J=7.9, 1.3 Hz, 1H), 7.13 (dd, J=7.9, 1.3 Hz, 1H), 7.07 (t, J=7.9 Hz, 1H), 4.66 (septet, J=6.0 Hz, 1H), 4.57 (septet, J=6.0 Hz, 1H), 1.38 (d, J=6.0 Hz, 6H), 1.33 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=191.1, 151.9, 151.4, 123.6, 121.4, 119.2, 76.2, 71.4, 22.4, 22.1 ppm; IR (Nujol): ν=2977, 2933, 2869, 1688, 1593, 1581, 1475, 1381, 1374, 1261, 1248, 1220, 1104, 930 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 223 (14), 222 (82), 138 (100), 120 (8), 109 (14), 92 (8), 81 (23), 69 (8), 65 (12), 53 (8); HR-MS: calcd: 222.1256; found: 222.1249.

4.3.4. 1,2-Diisopropoxy-3-vinylbenzene (29). Methyltriphenylphosphoniumbromide (14.5 g, 40.5 mmol) and KO*t*Bu (4.5 g, 40.5 mmol) were stirred in ether (150 mL) at 0°C for 1 h. A solution of 2,3-diisopropoxy-benzaldehyde (3.0 g, 13.5 mmol) in ether (30 mL) was then added and stirring continued for further 1 h at 0°C. The crude reaction mixture was filtered and concentrated in vacuo. The residue was purified by FC (hexane) to give **29** (2.1 g, 70%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.15 (d, J=7.9 Hz, 1H), 7.12 (dd, J=17.8, 11.1 Hz, 1H), 6.98 (t, J=7.9 Hz, 1H), 6.83 (d, J=7.9 Hz, 1H), 5.71 (d, J=17.8 Hz, 1H), 5.25 (d, J=11.1 Hz, 1H), 4.55 (septet, J=6.0 Hz, 1H),

4.48 (septet, J=6.0 Hz, 1H), 1.36 (d, J=6.0 Hz, 6H), 1.31 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=151.2, 145.9, 132.9, 132.3, 123.2, 117.7, 115.2, 114.0, 75.2, 70.7, 22.5, 22.1 ppm; IR (Nujol): ν=2975, 2931, 2872, 1574, 1458, 1382, 1262, 1211, 1109, 1007, 937, 778 cm^{-1}; MS (70 eV, EI): m/z (%): 220 (16), 136 (100), 107 (14), 77 (8); HR-MS: calcd: 220.1466; found: 220.1463; elemental analysis calcd (%) for $C_{14}H_{20}O_2$ (220.31): C 76.33, H 9.15; found: C 76.15, H 9.10.

4.3.5. 2,4-Diisopropoxybenzaldehyde. A stirred mixture of 2,4-dihydroxybenzaldehyde (5.0 g, 36.2 mmol), K_2CO_3 (20.0 g, 145.0 mmol) and KI (20.4 g, 123 mmol) in DMF (100 mL) was heated to 50°C. Isopropylbromide (13.6 mL, 145.0 mmol) was then added slowly dropwise. The reaction mixture was stirred for 12 h at 50°C then cooled and filtered. The organic layer was washed with saturated NH_4Cl solution (30 mL), brine (30 mL) and dried over $MgSO_4$. The organic extracts were concentrated in vacuo. The residue was purified by FC (MTBE/hexane 1:1) to afford the product (8.0 g, 99%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=10.30 (s, 1H), 7.79 (d, J=8.6 Hz, 1H), 6.49 (dd, J=8.6, 1.5 Hz, 1H), 6.41 (d, J=1.5 Hz, 1H), 4.62 (m, 2H), 1.39 (d, J=6.0 Hz, 6H), 1.36 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=188.7, 164.5, 130.2, 119.6, 106.9, 101.3, 71.1, 70.3, 22.0 ppm; IR (Nujol): ν=2977, 2933, 2873, 1605, 1497, 1263, 1188, 1118, 1008 cm^{-1}; MS (70 eV, EI): m/z (%): 223 (14), 222 (80), 180 (36), 138 (100), 120 (9), 109 (14), 92 (8), 81 (23), 69 (8), 65 (12), 53 (8); HR-MS: calcd: 222.1256; found: 222.1249.

4.3.6. 2,4-Diisopropoxy-1-vinylbenzene (19). Methyltriphenylphosphoniumbromide (19.3 g, 54.0 mmol) and KO*t*Bu (6.1 g, 54.0 mmol) were stirred in ether (200 mL) at 0°C for 1 h. A solution of 2,4-diisopropoxybenzaldehyde (4.0 g, 18.0 mmol) in ether (30 mL) was then added and stirring continued for further 1 h at 0°C. The crude reaction mixture was filtered and concentrated in vacuo. The residue was purified by FC (hexane) to give **19** (2.6 g, 96%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.37 (d, J=8.5 Hz, 1H), 6.44 (dd, J=17.8, 11.2 Hz, 1H), 6.45 (dd, J=8.5, 2.1 Hz, 1H), 6.43 (d, J=2.1 Hz, 1H), 5.61 (dd, J=17.8 Hz, 1.3 Hz, 1H), 5.10 (dd, J=11.2, 1.3 Hz, 1H), 4.52 (m, 2H), 1.35 (d, J=6.0 Hz, 6H), 1.33 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=158.7, 156.3, 131.7, 127.2, 120.82, 111.7, 107.2, 103.0, 70.9, 70.0, 22.3, 22.2 ppm; IR (Nujol): ν=2977, 2932, 2874, 1605, 1497, 1383, 1372, 1287, 1263, 1188, 1118, 1008, 952 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{20}O_2$ (220.31): C 76.33, H 9.15; found: C 76.03, H 9.19.

4.3.7. 5-Fluoro-2-isopropoxybenzoic acid isopropyl ester. 5-Fluoro-2-hydroxybenzoic acid (1.0 g, 6.4 mmol), isopropylbromide (3.6 mL, 38.4 mmol) and K_2CO_3 (10.6 g, 76.8 mmol) were stirred in THF at 60°C for 12 h then cooled and water (20 mL) was added. The aqueous layer was separated and extracted with MTBE (3×10 mL). The combined organic layers were washed with water (3×10 mL) and brine (10 mL), dried over $MgSO_4$ and concentrated in vacuo to give the product (2.14 g, 72%) as a colourless oil, which was pure enough for further use without chromatography. ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.40 (dd, J=8, 4 Hz, 1H), 7.02–7.08 (m, 1H), 6.90 (dd, J=10, 4 Hz, 1H), 5.22 (septet, J=6 Hz, 1H), 4.49 (septet, J=6 Hz, 1H), 1.28 (d, J=6 Hz, 6H), 1.26 (d, J=6 Hz, 6H) ppm.

4.3.8. (5-Fluoro-2-isopropoxyphenyl)-methanol. To a stirred suspension of $LiAlH_4$ (0.68 g, 17.8 mmol) in ether (22 mL) under nitrogen was added a solution of 5-fluoro-2-isopropoxybenzoic acid isopropyl ester (2.14 g, 8.9 mmol) in ether (13.5 mL) slowly dropwise. The reaction mixture was heated at 24°C for 12 h, then cooled and quenched by the addition of water (20 mL). The aqueous layer was separated and extracted with MTBE (3×10 mL). The combined organic layers were washed with water (3×10 mL), brine (10 mL), dried over $MgSO_4$ and evaporated to afford the product (1.2 g, 74%) as a colourless oil, which was pure enough for further use without chromatography. ^{1}H NMR (200 MHz, $CDCl_3$): δ=7.01 (dd, J=8, 4 Hz, 1H), 6.84 (dd, J=8, 4 Hz, 1H), 6.80 (dd, J=10, 6 Hz, 1H), 4.61 (d, J=7 Hz, 2H), 4.46 (septet, J=6 Hz, 1H), 2.45 (t, J=7 Hz, 1H), 1.28 (d, J=6 Hz, 6H) ppm.

4.3.9. 5-Fluoro-2-isopropoxybenzaldehyde. (5-Fluoro-2-isopropoxyphenyl)-methanol (1.2 g, 6.5 mmol) was stirred in ether (12 mL) under nitrogen. To this was added manganese dioxide (6.1 g, 32.6 mmol) in one portion and the reaction mixture was stirred for 4 h at 24°C. The crude reaction mixture was then filtered through celite and concentrated in vacuo to give the product (1.2 g, 90%) as a colourless oil which was pure enough for further use without chromatography. ^{1}H NMR (200 MHz, $CDCl_3$): δ=10.40 (d, J=4 Hz, 1H), 7.48 (dd, J=8, 4 Hz, 1H), 7.07–7.14 (m, 1H), 6.96 (dd, J=10, 6 Hz, 1H), 4.62 (septet, J=6 Hz, 1H), 1.42 (d, J=6 Hz, 6H) ppm.

4.3.10. 4-Fluoro-1-isopropoxy-2-vinylbenzene (18). Methyltriphenylphosphoniumbromide (4.5 g, 12.7 mmol) and KO*t*Bu (1.4 g, 12.7 mmol) were stirred in ether (36 mL) at 0°C for 10 min. A solution of 5-fluoro-2-isopropoxybenzaldehyde (1.2 g, 6.4 mmol) in ether (24 mL) was then added and stirring continued for further 10 min at 0°C. The crude reaction mixture was quenched by the addition of saturated NH_4Cl solution (10 mL). The aqueous layer was separated and extracted with ether (3×10 mL). The combined organic layers were washed with water (3×10 mL) and brine (10 mL), dried over $MgSO_4$ and evaporated to afford **18** (1.0 g, 89%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.18 (dd, J=9.5, 2.5 Hz, 1H), 7.02 (dd, J=17.7, 11.1 Hz, 1H), 6.88 (dd, J=8.8, 1.6 Hz, 1H), 6.83 (dd, J=8.8, 4.7 Hz, 1H), 5.71 (d, J=17.7 Hz, 1H), 5.28 (d, J=11.1 Hz, 1H), 4.43 (septet, J=6.0 Hz, 1H), 1.33 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=151.3, 131.2, 129.8, 116.4, 115.0, 114.8, 112.6, 112.4, 72.2, 22.2 ppm; IR (Nujol): ν=2925, 1717, 1493, 1362, 1260, 1093, 1022, 800 cm$^{-1;}$ MS (70 eV, EI): m/z (%): 180 (12), 172 (1), 147 (10), 97 (100), 83 (8), 79 (14), 75 (16), 73 (24), 69 (16), 67 (12), 55 (58); HR-MS: calcd: 180.0950; found: 180.09510.

4.3.11. 2,5-Diisopropoxybenzaldehyde. A stirred mixture of 2,5-dihydroxybenzaldehyde (1.75 g, 12.7 mmol), K_2CO_3 (8.8 g, 63.4 mmol) and TBAI (0.5 g, 1.4 mmol) in DMF (100 mL) was heated to 50°C. Isopropylbromide (4.8 mL,

50.7 mmol) was then added slowly dropwise. The reaction mixture was stirred for 12 h at 50°C, cooled and filtered. The organic layer was washed with saturated NH_4Cl solution (30 mL), brine (30 mL), dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by FC (MTBE/hexane1:9) to afford the product (2.1 g, 76%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=10.45 (s, 1H), 7.35 (s, 1H), 7.08 (d, J=10.0 Hz, 1H), 6.93 (d, J=10 Hz, 1H), 4.56 (septet, J=6 Hz, 1H), 4.50 (septet, J=6 Hz, 1H), 1.37 (d, J=6 Hz, 6H), 1.31 (d, J=6 Hz, 6H) ppm.

4.3.12. 2,5-Diisopropoxy-1-vinylbenzene (15). A solution of methyltriphenylphosphoniumbromide (1.77 g, 5.0 mmol) in DMF (10 mL) was cooled to 0°C, BuLi (1.6 M in hexanes, 3.15 mL, 5.04 mmol) was added slowly dropwise and the reaction mixture stirred for further 10 min. Then 2,5-diisopropoxybenzaldehyde (1.0 g, 4.5 mmol) in THF (2 mL) was added dropwise and the reaction mixture stirred for 1 h at 24°C. The crude reaction mixture was quenched by the addition of water (5 mL). The aqueous layer was separated and extracted with MTBE (3×5 mL). The combined organic layers were dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by FC (hexane/CH_2Cl_2 4:1) to afford the product (806 g, 81%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.00–7.10 (m, 2H), 6.82 (d, J=8.9 Hz, 1H), 6.77 (dd, J=8.9, J=2.9 Hz, 1H), 5.71 (dd, J=17.8, 1.3 Hz, 1H), 5.24 (dd, J=11.1, 1.3 Hz, 1H), 4.46 (septet, J=6.0 Hz, 1H), 4.38 (septet, J=6.0 Hz, 1H), 1.35 (d, J=6.0 Hz, 6H), 1.33 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=152.0, 149.5, 131.9, 129.3, 116.8, 114.0, 114.0, 72.1, 70.7, 22.2, 22.1 ppm; IR (Nujol): ν=2976, 2933, 1487, 1383, 1371, 1281, 1210, 1137, 1113, 975, 956, 906 cm^{-1}; MS (70 eV, EI): m/z (%): 220 (25), 178 (8), 137 (11), 136 (100), 107 (14), 77 (7); HR-MS: calcd: 220.1463; found: 220.1461.

4.3.13. 1-Bromo-4-fluoro-2-isopropoxybenzene. The mixture of 2-bromo-5-fluorophenol (2.0 g, 10.5 mmol), isopropylbromide (5.9 mL, 62.8 mmol) and K_2CO_3 (2.9 g, 20.9 mmol) in DMF (25 mL) was heated to 50°C for 12 h, after which time water (5 mL) was added. The aqueous layer was separated and extracted with MTBE (3×5 mL). The combined organic layers were washed with brine and water, dried over $MgSO_4$ and evaporated. The residue was purified by FC (hexane) to afford the product (2.2 g, 88%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.46 (dd, J=8.4, 6.0 Hz, 1H), 6.66 (dd, J=11.0, 3.0 Hz, 1H), 6.56 (dt, J=8.4, 3.0 Hz, 1H), 4.54 (septet, J=6.0 Hz, 1H), 1.40 (d, J=6.0 Hz, 6H) ppm; IR (Nujol): ν=2981, 2935, 1715, 1601, 1579, 1479, 1417, 1282, 1184, 1114, 1105, 1039, 998, 918, 835, 795 cm^{-1}; MS (70 eV, EI): m/z (%): 232 (10), 190 (100), 161 (6), 112 (4), 83 (15), 82 (8), 57 (6); HR-MS: calcd: 231.9899; found: 231.9897.

4.3.14. 4-Fluoro-2-isopropoxy-1-vinylbenzene (20). $Pd(PPh_3)_4$ (485 mg, 0.42 mmol) and 1-bromo-4-fluoro-2-isopropoxybenzene (1.9 g, 8.4 mmol) were dissolved in toluene (50 mL) in a nitrogen-filled glovebox. Vinyltributyltin (2.7 mL, 9.2 mmol) was added slowly and the reaction mixture heated at 110°C for 12 h. After this time the reaction was allowed to cool and then filtered. The solvent was evaporated and the crude purified by FC (hexane) to give the product (900 mg, 60%) as a colourless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.41 (dd, J=8.3, 7.1 Hz, 1H), 6.96 (dd, J=17.8, 11.2 Hz, 1H), 6.57–6.62 (m, 2H), 5.66 (dd, J=17.8, 1 Hz, 1H), 5.19 (dd, J=11.2, 1 Hz, 1H), 4.50 (septet, J=6.0 Hz, 1H), 1.35 (d, J=6.0 Hz, 6H) ppm; IR (Nujol): ν=2957, 2922, 2872, 2854, 1464, 1457, 1377, 1075, 960 cm^{-1}; MS (70 eV, EI): m/z (%): 180 (20), 139 (8), 138 (100), 109 (76), 83 (16); HR-MS: calcd: 180.0950; found: 180.0951.

4.3.15. 2-Bromo-4-trifluoromethylphenol. To a solution of 4-trifluoromethylphenol (1.5 g, 9.3 mmol) in CH_2Cl_2 (10 mL) was added bromine (0.5 mL, 9.7 mmol) slowly dropwise. The reaction mixture was stirred for 12 h at 40°C, then cooled and quenched by the addition of a saturated $Na_2S_2O_3$ solution. The aqueous layer was separated and extracted with CH_2Cl_2 (100 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to afford 2-bromo-4-trifluoromethylphenol (2.23 g, 100%) as a yellow oil. No purification was required. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.77 (d, J=1.9 Hz, 1H), 7.48 (dd, J=8.3, 1.9 Hz, 1H), 7.09, (d, J=8.3 Hz, 1H), 5.84 (s, 1H) ppm; IR (Nujol): ν=3499, 2978, 2933, 1702, 1604, 1485, 1411, 1310, 1279, 1180, 1127, 1097, 884, 740, 652 cm^{-1}.

4.3.16. 2-Bromo-1-isopropoxy-4-trifluoromethylbenzene. 2-Bromo-4-trifluoromethylphenol (2.0 g, 8.3 mmol), isopropylbromide (6.2 mL, 66.4 mmol) and K_2CO_3 (4.6 g, 33.2 mmol) were dissolved in 25 mL DMF and the reaction mixture heated at 50°C for 12 h. After this time water (25 mL), and MTBE (50 mL) were added. The organic layer was separated and washed with water (3×25 mL) and dried over $MgSO_4$. The crude was purified by FC (hexane) to give 2.2 g, (92%) of the product as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.78 (d, J=2.2 Hz, 1H), 7.52 (dd, J=8.4, 2.2 Hz, 1H), 6.94 (d, J=8.4 Hz, 1H), 4.64 (septet, J=6.0 Hz, 1H), 1.42 (d, J=6.0 Hz, 6H) ppm.

4.3.17. 1-Isopropoxy-4-trifluoromethyl-2-vinylbenzene (17). $Pd(PPh_3)_4$ (197 mg, 0.17 mmol) and 2-bromo-1-isopropoxy-4-trifluoromethylbenzene (1.0 g, 3.4 mmol) were dissolved in toluene (20 mL) in a nitrogen-filled glovebox. Vinyltributyltin (1.0 mL, 3.4 mmol) was added slowly and the reaction mixture heated at 110°C for 12 h. After this time the reaction was allowed to cool and then filtered. The solvent was evaporated and the crude purified by FC (hexane) to give the product (554 mg, 73%) as a volatile colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.65 (d, J=2.2 Hz, 1H), 7.42 (dd, J=8.2, 2.2 Hz, 1H), 7.02 (dd, J=17.8, 11.2 Hz, 1H), 6.86 (d, J=8.2 Hz, 1H), 5.80 (dd, J=17.8, 1.0 Hz, 1H), 5.27 (dd, J=11.2, 1.0 Hz, 1H), 4.62 (septet, J=6.0 Hz, 1H), 1.29 (d, J=6.0 Hz, 6H) ppm.

4.3.18. 2-Isopropoxy-3-methoxybenzaldehyde. 2-Hydroxy-3-methoxybenzaldehyde (2.0 g, 13.14 mmol) was added to a suspension of NaH (631 mg, 15.77 mmol, 60%) in DMF (26 mL) at 0°C. After 20 min at room temperature, isopropylbromide (1.9 mL, 19.72 mmol) was added. This solution was stirred for 36 h at 50°C. Saturated NH_4Cl solution was added, and the aqueous phase was extracted with MTBE. The organic

layer was washed with water and brine, dried over Na_2SO_4 and concentrated in vacuo. The crude was purified by FC (MTBE/hexane 1:8) to afford 2-isopropoxy-3-methoxybenzaldehyde (1.70 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=10.45 (s, 1H), 7.42 (dd, J=7, 2 Hz, 1H), 7.14–7.07 (m, 2H), 4.63 (septet, J=6 Hz, 1H), 3.88 (s, 3H), 1.31 (d, J=6 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=190.9, 153.2, 150.6, 130.9, 123.6, 118.9, 117.8, 76.3, 56.0, 22.3 ppm; IR (Nujol): ν=3071, 2976, 2868, 1690, 1582, 1480, 1262 cm^{-1}; MS (70 eV, EI): m/z 194 (8), 152 (100), 122 (9), 106 (42); HR-MS: calcd: 194.0943; found: 194.0949.

4.3.19. 2-Isopropoxy-1-methoxy-3-vinylbenzene (22). To a mixture of KO*t*Bu (584 mg, 5.20 mmol) and methyltriphenylphosphoniumbromide (1.86 g, 5.20 mmol) was added ether (20 mL) at 0°C. This suspension was stirred for 10 min at the same temperature. To this mixture was added 2-isopropoxy-3-methoxybenzaldehyde (505 mg, 2.60 mmol) in ether (6 mL). The reaction mixture was stirred for 5 min at the same temperature. Saturated NH_4Cl solution was added, and the aqueous phase was extracted with MTBE (20 mL). The organic extracts were washed with saturated NH_4Cl solution, brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by FC (MTBE/hexane 1:40) to afford the product (487 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.14 (d, J=8 Hz, 1H), 7.09 (dd, J=18, 11 Hz, 1H), 7.00 (t, J=8 Hz, 1H), 6.82 (d, J=8 Hz, 1H), 5.71 (d, J=18 Hz, 1H), 5.26 (d, J=11 Hz, 1H), 4.42 (septet, J=6 Hz, 1H), 3.84 (s, 3H), 1.29 (d, J=6 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ=153.2, 144.6, 132.7, 132.2, 123.4, 117.6, 114.2, 111.5, 75.4, 55.7, 22.5 ppm; IR (Nujol): ν=3085, 2974, 1628, 1575, 1475, 1263 cm^{-1}; MS (70 eV, EI): m/z 192 (27), 150 (100), 135 (14), 121 (10), 107 (26), 77 (10); HR-MS: calcd: 192.1150; found: 192.1148.

4.3.20. 3-Methyl-4-isopropoxybenzonitrile. In a 50 mL flask, 3-methyl-4-hydroxybenzonitrile (700 mg, 5.26 mmol), was dissolved in DMF (15 mL) in the presence of K_2CO_3 (1.45 g, 10.5 mmol) and KI (1.48 g, 8.9 mmol). After 10 min at 50°C, isopropylbromide (1.29 g, 10.5 mmol) was added slowly dropwise and stirring continued for 10 h at 50°C. After cooling, water (25 mL) was added and the mixture was extracted with ether (6×10 mL). The organic layer was washed with saturated NH_4Cl solution (10 mL) and brine (10 mL) dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by bulb to bulb distillation yielding 3-methyl-4-isopropoxybenzonitrile (817 mg, 89%) as a colourless solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.15 (d, J=7.6 Hz, 1H), 7.08 (d, J=7.6 Hz, 1H), 6.98 (s, 1H), 4.48 (septet, J=6.0 Hz, 1H), 2.19 (s, 3H), 1.31 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ=156.2, 134.1, 131.4, 124.2, 119.4, 115.2, 110.1, 70.7, 22.0, 16.9 ppm.

4.3.21. 2-Isopropoxy-5-cyanobenzaldehyde. 3-Methyl-4-isopropoxybenzonitrile (139 mg, 7.94 mmol) was dissolved in tetrachloromethane (15 mL) in the presence of *N*-bromosuccinimide (3.22 g, 18.1 mmol). After heating at reflux temperature for 20 min, a small amount (ca. 10 mg) of dibenzoylperoxide was added. The mixture was maintained under reflux for 8 h. After cooling and filtration (to remove insoluble material), the NMR analysis of the crude product showed an incomplete reaction, thus the same procedure was then repeated until complete conversion was reached. This crude dibrominated compound was then dissolved in a MeOH/H_2O solvent mixture (70:30) and heated under reflux for 10 h. After cooling, the mixture was concentrated in vacuo, extracted with ether, dried over $MgSO_4$ and concentrated in vacuo. After purification by FC (CH_2Cl_2/hexane 9:1), the expected aldehyde was obtained (92.7 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=10.47 (s, 1H), 7.87 (d, J=8.2 Hz, 1H), 7.26 (d, J=8.2 Hz, 1H), 7.25 (s, 1H), 4.70 (septet, J=6.0 Hz, 1H), 1.43 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ=188.8, 160.0, 129.2, 128.3, 123.9, 118.4, 118.0, 117.4, 72.1, 21.9 ppm; IR (Nujol): ν=3357, 2984, 2939, 2870, 2231, 1684, 1603, 1566, 1488, 1417, 1387, 1278, 1261, 1112, 1099, 987, 839, 804 cm^{-1}; MS (70 eV, EI): m/z (%):189 (10), 147 (100), 146 (73), 129 (16), 119 (7), 63 (8); HR-MS: calcd: 189.0790; found: 189.0783.

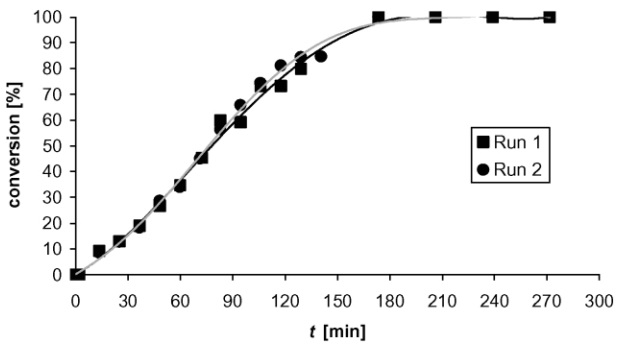
4.3.22. 3-Vinyl-4-isopropoxybenzonitrile (21). In a 25 mL flask under nitrogen, methyltriphenylphosphonium bromide (574.6 mg, 1.6 mmol), was suspended in ether (4 mL) at 0°C. After addition of KO*t*Bu (179.5 mg, 1.6 mmol) the yellow mixture was maintained at 0°C for 15 min. A solution of the above aldehyde (152 mg, 0.8 mmol) in ether (4 mL) was then added and stirring continued for 1 h at 0°C. After addition of hexane (6 mL), the mixture was filtered over celite to remove phosphane oxide and the crude product was purified by FC (CH_2Cl_2/hexane 2:1) yielding the expected styrene **21** (118 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.52 (d, J=7.9 Hz, 1H), 7.19 (d, J=7.9 Hz, 1H), 7.09 (s, 1H), 7.02 (dd, J=17.7, 11.2 Hz, 1H), 5.83 (d, J=17.7 Hz, 1H), 5.40 (d, J=11.2 Hz, 1H), 4.56 (septet, J=6.0 Hz, 1H), 1.35 (d, J=6.0 Hz, 6H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ=155.0, 132.6, 130.7, 127.2, 124.7, 119.1, 117.5, 116.6, 111.6, 71.4, 22.0 ppm; IR (Nujol): ν=2979, 2934, 2226, 1625, 1601, 1559, 1493, 1412, 1282, 1261, 1117, 989, 913, 827 cm^{-1}; MS (70 eV, EI): m/z (%):187 (26), 145 (100), 144 (16), 117 (8), 116 (21), 89 (10), 63 (5); HR-MS: calcd: 187.0997; found: 187.1004.

4.4. General procedure for RCM

In a 25 mL round bottomed flask 1 mg of the catalyst was added to a 0.01 M CH_2Cl_2 solution of **23** (or **24**) with stirring, such that the ratio of catalyst **23** was 1:100. After dissolution of the catalyst (ca. 10 s) a 1.5 mL aliquot was transferred via syringe to a HPLC vial under air and the progress of the reaction (conversion) was monitored periodically by a HPLC system fitted with an autosampler. Conditions: Waters RP-7 C-18 column (4 mm), particle size 7 μm; MeOH/H_2O 80:20; flow rate 1 mL min^{-1}, λ=254 nm. Retention times (min): 3.15 (**25**), 4.42 (**23**), 4.79 (**26**), 6.09 (**24**).

4.5. Reproducibility test

A test RCM reaction of **23** in air (constant stirring) using catalyst **4** (1.0 mol%) in CH_2Cl_2 (0.01 M) was carried out twice under identical conditions and monitored by HPLC. The following conversion vs time plots were obtained.



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