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Syntheses and Reactivity of Analogues of Grubbs' Second Generation Metathesis Catalyst with Fluorous Phosphines: A New Phase-Transfer Strategy for Catalyst Activation

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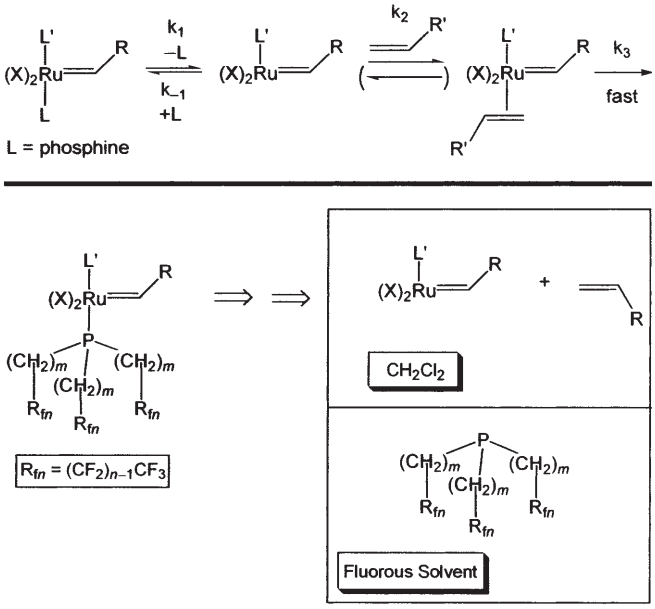
Abstract: Reactions of the bis(pyridine) complex $(H_2IMes)(Py)_2(Cl)_2Ru(=CHPh)$, ($H_2IMes$ = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) and the highly fluorophilic phosphines $[R_{fn}(CH_2)_m]_3P$ [**1**; m/n = **a**, 2/6; **b**, 2/8; **c**, 2/10; **d**, 3/8; $R_{fn} = CF_3(CF_2)_{n-1}$] give $(H_2IMes)\{[R_{fn}(CH_2)_m]_3P\}(Cl)_2Ru(=CHPh)$ (**4a**–**d**, 64–78%), which are analogues of Grubbs' second generation alkene metathesis catalyst. Complexes **4a**,**b** are effective catalysts for conversions of 1,6-dienes to cyclopentenes under monophasic and biphasic conditions in CH_2Cl_2 and CH_2Cl_2/fluorous solvent mixtures. The latter generally exhibit rate accelerations, which are believed to arise from phase transfer of the dissociated fluorous phosphine, allowing the substrate to better compete for the fourteen valence-electron intermediate. Only modest effects are observed when Grubbs' second generation catalyst is similarly reacted. The most fluorophilic catalyst, **4c**, can be recycled by extracting the reaction mixtures with perfluoro(methylcyclohexane).

Keywords: alkene metathesis; fluorous; Grubbs' catalyst; phase transfer; phosphines; recycling

Introduction

Fluorous catalysts most commonly feature ponytails of the formulae $R_{fn}(CH_2)_m$ [$R_{fn} = CF_3(CF_2)_{n-1}$, $n \geq 6$], and exhibit moderate to marked affinities for fluorous liquid and solid phases.[1] As such, they can easily be recovered and reused. However, it seemed to us that fluorous methodologies also present intriguing opportunities for catalyst *activation*. For example, there are many transition metal-based catalyst precursors from which a ligand must first dissociate before the catalytic cycle can be entered. The reverse process can slow the overall rate. Thus, if the ligand could be efficiently scavenged, faster reactions should often occur. Most scavenging strategies involve chemical derivatization.[2] However, we wondered whether phase transfer of a fluorous ligand into a fluorous phase might also be exploited.

A case in point would be the ruthenium alkene metathesis catalysts developed by Grubbs.[3] As summarized in Scheme 1 (top), the dissociation of a phosphine (k_1 or initiation step) can be followed either by unproductive recoordination (k_{-1} step) or productive alkene binding (k_2 step). Under conditions where the product of k_2 and the alkene concentration is much greater than that of k_{-1} and the phosphine concentration (k_2[alkene] $\gg$ k_{-1}[phosphine]), phosphine dissociation is rate-determining and scavengers should have



Scheme 1. Initiation sequence for a Grubbs-type ruthenium alkene metathesis catalyst.

little or no effect. However, kinetics studies have identified many catalysts, including the commercially available first and second generation systems, for which $k_{-1} \geq k_2$, even with very reactive alkenes (e.g., ethyl vinyl ether).[3]

We wondered whether rate enhancements might be realized when similar metathesis catalysts bearing fluorous phosphines were employed under organic/fluorous liquid/liquid biphase conditions. As illustrated in Scheme 1 (bottom), fluorous phosphines can have high thermodynamic affinities for fluorous phases, whereas the active catalyst and alkenes would have high thermodynamic affinities for organic phases. For example, even the non-polar alkene 1-decene shows a marked preference (95:5) to partition into toluene versus perfluoro(methylcyclohexane) ($CF_3C_6F_{11}$).[4] This bias should be even more pronounced for functionalized alkenes and the more polar solvents commonly used for alkene metathesis. To the extent that the less fluorous catalyst precursor partitions into the fluorous phase, some counteracting rate loss would be expected.

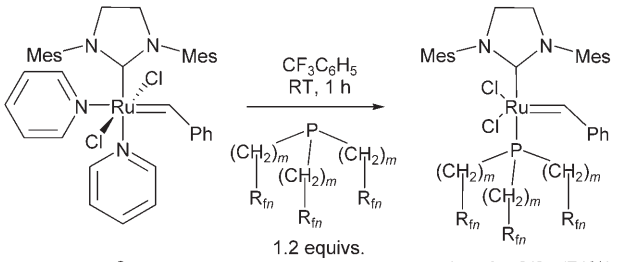
As depicted in Figure 1, several fluorous versions of Grubbs' catalysts have been reported.[5–7] Other catalysts that contain two- or three-carbon perfluoroalkyl segments,[8] or $(CF_3)_3CO$ ligands,[9] are known. However, the fluorinated moieties in all of these systems are located in either non-dissociating spectator ligands or "boomerang" carbene ligands. To our knowledge, only one metathesis catalyst with a fluoroalkylated phosphine, $(p\text{-}CF_3C_6H_4)_3P$,[3b] has ever been reported. Accordingly, we set out to prepare and evaluate catalysts containing the highly fluorophilic aliphatic phosphines $[R_{fn}(CH_2)_m]_3P$ (**1**; *m*/*n* = **a**, 2/6; **b**, 2/8; **c**, 2/10; **d**, 3/8),[10] which offer a spectrum of phase properties. Due to the short $(CH_2)_m$ spacer segments, **1a–d** are much less basic and nucleophilic than tri(*n*-alkyl)phosphines.[11]

In this paper, we report (1) the facile synthesis of a family of fluorous phosphine analogues of Grubbs' second generation catalyst $(H_2IMes)(Cy_3P)(Cl)_2Ru(=CHPh)$ (**2**; H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene); (2) applications in alkene metatheses under monophasic and biphasic conditions in CH_2Cl_2 and CH_2Cl_2/fluorous solvent mixtures; (3) substantial rate accelerations under the latter conditions, and (4) successful recycling experiments. A portion of this work has been communicated,[12] and additional details are supplied elsewhere.[13]

Results

Synthesis and Characterization of New Metathesis Catalysts

As shown in Scheme 2, the bis(pyridine) benzylidene complex $(H_2IMes)(Py)_2(Cl)_2Ru(=CHPh)$ (**3**)[14] and



Scheme 2. Syntheses of fluorous Grubbs' catalysts **4a–d**.

fluorous phosphines **1a–d** were reacted under homogeneous conditions in the amphiphilic solvent trifluoromethylbenzene ($CF_3C_6H_5$). Work-ups gave the target complexes **4a–d** as analytically pure pink solids in 64–78% yields. They were characterized by NMR spectroscopy (^1H, ^{13}C, ^{31}P, ^{19}F) and mass spectrometry, as summarized in the Experimental Section. Most data were routine, combining features previously observed with Grubbs' second generation catalyst **2** and metal complexes of **1a–d**.

Complexes **4a–d** were air-stable as solids for extended periods, as well as overnight in solution. However, crystallization attempts did afford an unusual oxidation product, a ruthenium(III) species described

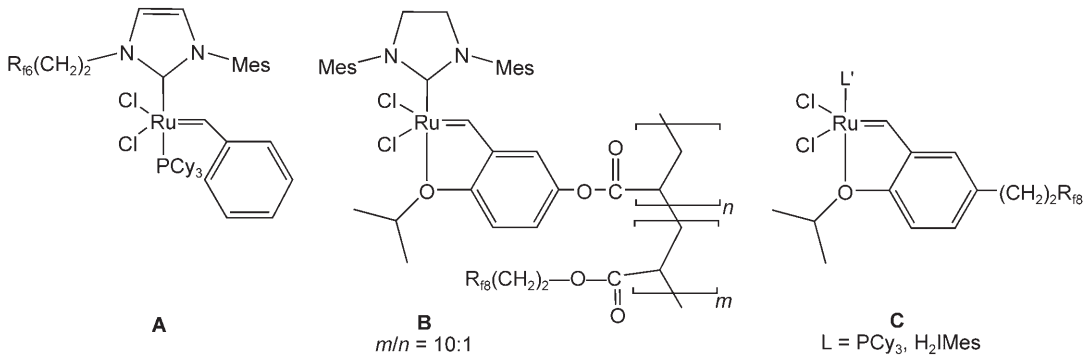


Figure 1. Previously reported fluorous alkene metathesis catalysts.

elsewhere.[15] Complexes **4a–d** melted without decomposition at temperatures ranging from 101 to 118 °C. No other phase transitions were noted by DSC. Exotherms were observed 20–65 °C above the melting points, accompanied by slight mass losses (2.9–4.5 %; TGA). Complexes **4a**,**b**,**d** were soluble in CH_2Cl_2, benzene, and hexane. However, **4c** was much less soluble, paralleling the effect of the R_{fn} length in the free phosphines **1a–c**. Interestingly, all complexes were soluble in the more polar solvent methanol.

The $CF_3C_6F_{11}$/toluene partition coefficients of **4a–d** were measured by HPLC as described in the Experimental Section. The data are summarized in Table 1,

Table 1. Partition coefficients ($CF_3C_6F_{11}$/toluene, 25 °C) for fluorous phosphines and new fluorous metathesis catalysts.

Fluorous Phosphine	Partition Coefficient[10]	Fluorous Catalyst	Partition Coefficient
1a	98.8:1.2	**4a**	13.2: 86.8
1b	>99.7:<0.3	**4b**	39.6:60.4
1c	>99.7:<0.3	**4c**	77.6:22.4
1d	98.8:1.2	**4d**	11.5:88.5

together with values for the corresponding phosphines.[4,10] The values for **4a–c** followed the expected trend, with **4a** predominantly lipophilic (13.2:86.8) and **4c** significantly fluorophilic (77.6:22.4). The additional methylene group in each ponytail of **4d** as compared to **4b** significantly enhances lipophilicity (11.5:88.5 *vs.* 39.6:60.4). When toluene is replaced by a solvent of greater polarity (e.g., CH_2Cl_2), the proportions of **4a**,**b**,**d** in the non-fluorous phase should increase.

Metatheses with 4b: Monophasic and Biphasic Conditions

Initial experiments focused on the moderately fluorophilic complex **4b**. The ring-closing metathesis of diethyl diallylmalonate (**5**)[16] was investigated under the conditions depicted in Figure 2. Two reactions were conducted under N_2 using CH_2Cl_2 that was 0.048–0.051 M in **5** (default diene concentration for all experiments) and 0.0012–0.0013 M in **4b** (2.5 mol %), and contained an internal standard. In one case, $CF_3C_6F_{11}$ was added, corresponding to 50 % of the CH_2Cl_2 volume. As noted above, this should not significantly affect the concentration of **5** in the CH_2Cl_2 phase. The concentration of **4b** should be reduced by less than 20 % (i.e., the 39.6 % that would be extracted with a 1:1 volume ratio divided by two; this would be further decreased due to the substitution of toluene by CH_2Cl_2). Visually, all of the catalyst color remained in the CH_2Cl_2 phase.

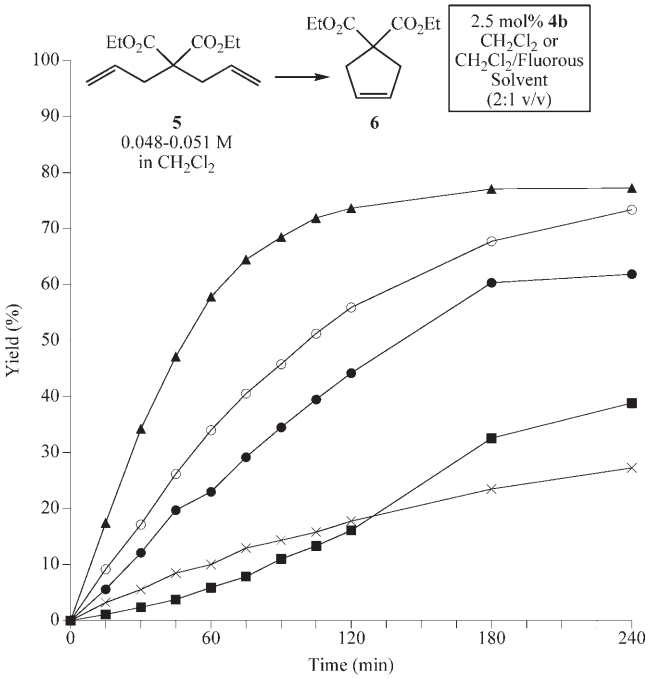


Figure 2. Rates of formation of **6** (room temperature). Solvent systems: ▲ $CH_2Cl_2/C_8F_{16}O$ (2.2 mL/1.1 mL); ○ $CH_2Cl_2/CF_3C_6F_{11}$ (4.0 mL/2.0 mL); ● $CH_2Cl_2/CF_3C_6F_{11}$ (5.0 mL/2.5 mL); × $CH_2Cl_2/CF_3(CF_2)_5CH_2OH$ (2.2 mL/1.1 mL); ■ CH_2Cl_2 (3.1 mL).

The samples were rapidly stirred, dispersing the fluorous phase. The formation of cyclopentene **6** was monitored by GC, and yields were calculated with respect to the internal standard. The initial rate was significantly enhanced in the presence of $CF_3C_6F_{11}$. After 1 and 2 h the yields of **6** were 23 % and 44 % (●), as opposed to 6 % and 16 % in CH_2Cl_2 alone (■). The effect was reproducible, with yields of 34 % and 56 % in a similar run (○); these traces represent the maximum deviation observed in duplicate experiments in the course of this study. An analogous experiment was conducted using perfluoro(2-butyltetrahydrofuran) ($C_8F_{16}O$). This solvent is somewhat less viscous than $CF_3C_6F_{11}$,[17] which we imagined might aid phosphine diffusion across the phase boundary. Interestingly, the rate was much faster, with 58 % and 74 % yields of **6** after 1 and 2 h (▲).

Analogous experiments with perfluorohexane (C_6F_{14}) were complicated by some solvent volatilization, and are detailed elsewhere.[13] However, the rate was not as fast as with $C_8F_{16}O$, with 36 % and 47 % yields of **6** after 1 and 2 h. The fluorous alcohol 1H,1H-perfluoroheptanol [$CF_3(CF_2)_5CH_2OH$] was also evaluated. Although we are not aware of any quantitative viscosity data for this compound, qualitatively it can be judged to be much higher. As depicted in Figure 2, only a very slight initial rate enhancement

was observed, with 10% and 18% yields of **6** after 1 and 2 h (×).

For the most effective solvent system in Figure 2 ($CH_2Cl_2/C_8F_{16}O$), the catalyst loading (2.5%) was varied. As shown in Figure 3, when the loading was

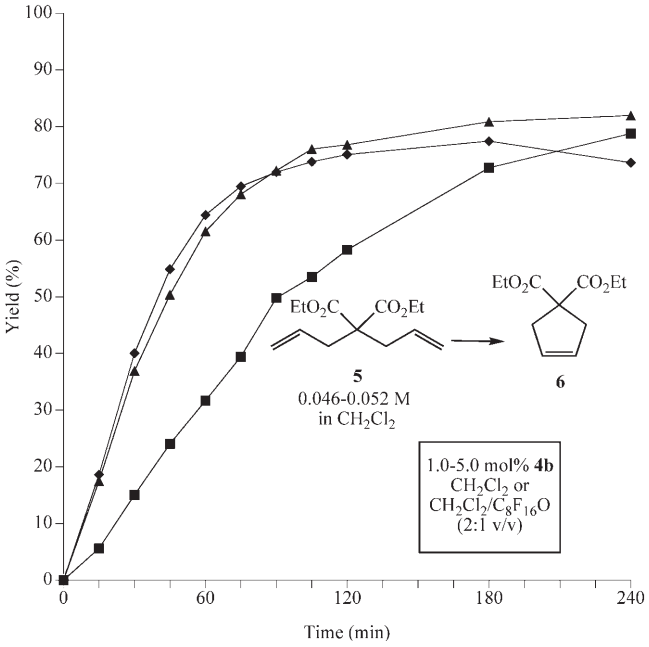


Figure 3. Rates of formation of **6** (room temperature) in 2:1 v/v $CH_2Cl_2/C_8F_{16}O$ with different catalyst loadings: ◆ 5.0 mol% (1.2 mL/0.6 mL); ▲ 2.5 mol% (2.2 mL/1.1 mL); ■ 1.0 mol% (5.2 mL/2.6 mL).

decreased to 1.0 mol%, metathesis became somewhat slower, with 32% and 58% yields of **6** after 1 and 2 h (■). However, reaction remained at least as fast as that in $CH_2Cl_2/CF_3C_6F_{11}$ with 2.5 mol% **4b** (Figure 2). In contrast, when the catalyst loading was increased to 5.0%, little effect was observed (◆). The amount of fluorous solvent was also varied, keeping the CH_2Cl_2 volume and concentrations of **6** (0.048–0.049 M) and **4b** (2.5 mol%) constant. Interestingly, the results with 5.0:2.5 v/v (● in Figure 2) and 5.0:1.0 v/v $CH_2Cl_2/CF_3C_6F_{11}$ (not depicted) differed very little, with 12% *vs.* 10%, 23% *vs.* 24%, and 35% *vs.* 36% yields of **6** after 0.5, 1.0, and 1.5 h.

We sought to confirm that these phenomena were not unique to a single substrate. Figure 4 summarizes results obtained with diethyl 2-allyl-2-methallylmalonate (**7**) under standard conditions in CH_2Cl_2 (0.051–0.052 M in **7** and 0.0013 M in **4b**). In the presence of $CF_3C_6F_{11}$, the formation of cyclopentene (**8**)[18] was again significantly faster. After 1 and 2 h, the yields of **8** were 47% and 73% (●), as opposed to 20% and 51% in CH_2Cl_2 alone (■). In contrast, there was little or no effect in the presence of $C_8F_{16}O$, which represents the only reaction involving a fluorous solvent

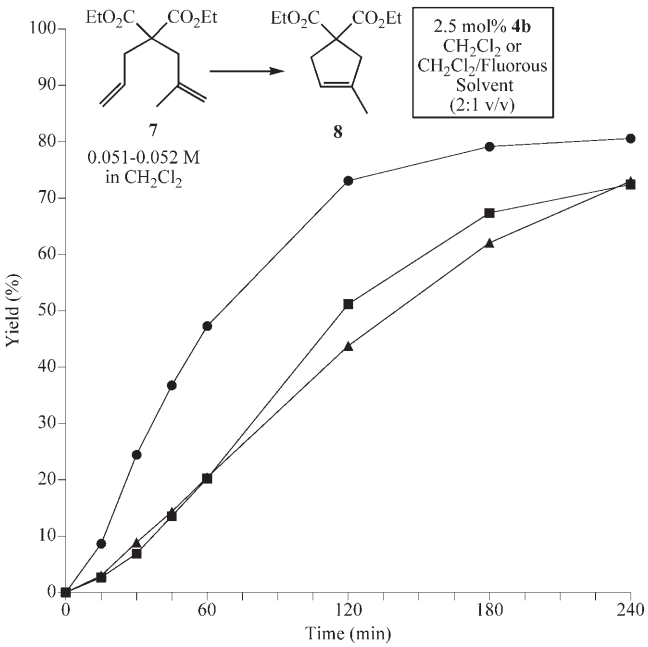


Figure 4. Rates of formation of **8** (room temperature). Solvent systems: ● $CH_2Cl_2/CF_3C_6F_{11}$ (4.0 mL/2.0 mL); ■ CH_2Cl_2 (4.0 mL); ▲ $CH_2Cl_2/C_8F_{16}O$ (4.6 mL/2.3 mL).

and catalyst in this study for which no rate acceleration was observed. However, as shown in Figure 5, $C_8F_{16}O$ gave a dramatic effect with *N,N*-diallyltosylamide (**9**). The yields of cyclopentene **10**[6] were 58% and 91% after 1 and 2 h (◆), as compared to 1–2% and 3–4% with CH_2Cl_2 alone (two runs, ■ and ▲).

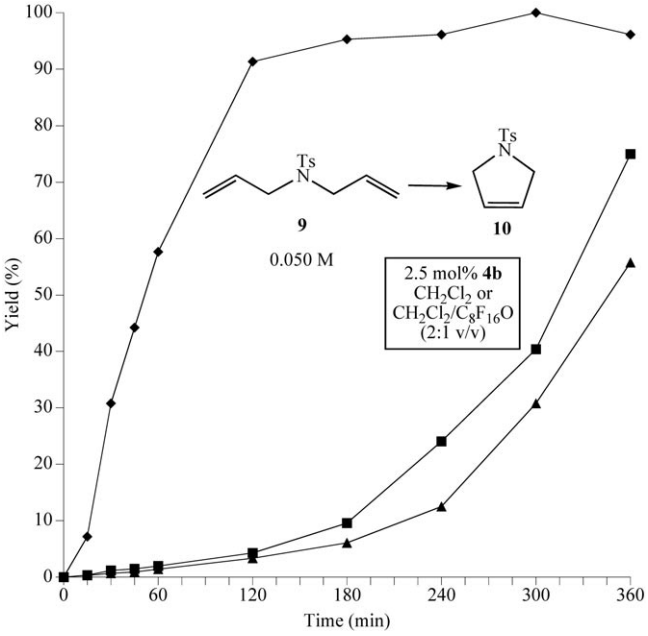


Figure 5. Rates of formation of **10** (room temperature). Solvent systems: ◆ $CH_2Cl_2/C_8F_{16}O$ (2.0 mL/1.0 mL); ■ CH_2Cl_2 (2.0 mL); ▲ CH_2Cl_2 (2.0 mL; duplicate run).

Metatheses with Other Catalysts

As shown in Figure 6, the metathesis of **7** was also studied with the less fluorophilic R_{f6} catalyst **4a**.

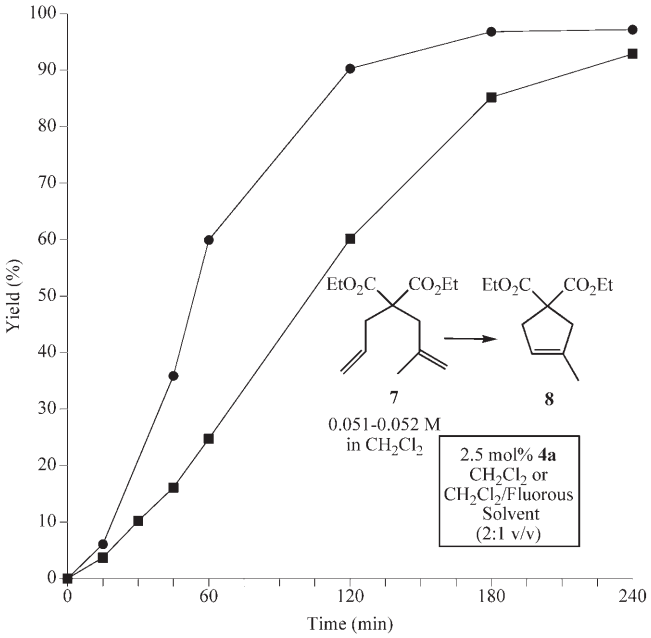


Figure 6. Rates of formation of **8** (room temperature). Solvent systems: ● $CH_2Cl_2/CF_3C_6F_{11}$ (4.0 mL/2.0 mL); ■ CH_2Cl_2 (4.0 mL).

Under conditions analogous to those in Figure 4, similar rate enhancements were observed using 2:1 v/v $CH_2Cl_2/CF_3C_6F_{11}$ (●) as compared to CH_2Cl_2 (■). The yields of **8** were 60% *vs.* 25% and 90% *vs.* 60% after 1 and 2 h. In both solvent systems, reactions were slightly faster than with **4b** (Figure 4). Two experiments were also conducted with *N*-allyl-*N*-methallyltosylamide (**11**). As shown in Figure 7, the cyclopentene **12**[6] formed slightly faster in $CH_2Cl_2/C_8F_{16}O$ (▲) than CH_2Cl_2 (■), with conversions of 79% *vs.* 59% after 1 h.

The appreciably fluorophilic R_{f10} catalyst **4c** could not be studied under identical conditions due to its much lower solubility in CH_2Cl_2. Accordingly, solutions that were 0.049–0.050 M in **7** and 0.00046–0.00051 M in **4c** (1.0 mol%) were employed, giving homogeneous reaction conditions. Reactions of **7** conducted with 2:1 v/v $CH_2Cl_2/CF_3C_6F_{11}$ were now *slower* than those in CH_2Cl_2. Yields of **8** were 3% *vs.* 5%, 12% *vs.* 18%, and 21% *vs.* 40% after 1, 2, and 3 h. The $CF_3C_6F_{11}$ phase was distinctly more colored than the CH_2Cl_2 phase, suggesting inhibition *via* phase transfer of the catalyst precursor.

In organic/fluorous biphase systems, small amounts of the fluorous solvent typically partition into the organic solvent, and *vice-versa*.[19] Therefore, there remains some possibility that the preceding trends might in part represent solvent effects.[20] Hence, control experiments were conducted with a related nonfluorous metathesis catalyst, Grubbs' second generation complex **2**. Identical substrate concentrations and catalyst loadings were employed, and the data are presented in Figure 8 and Figure 9. Note that the reaction times are much shorter than with **4b** (Figure 2 and Figure 5), indicating **2** to be a more active catalyst.

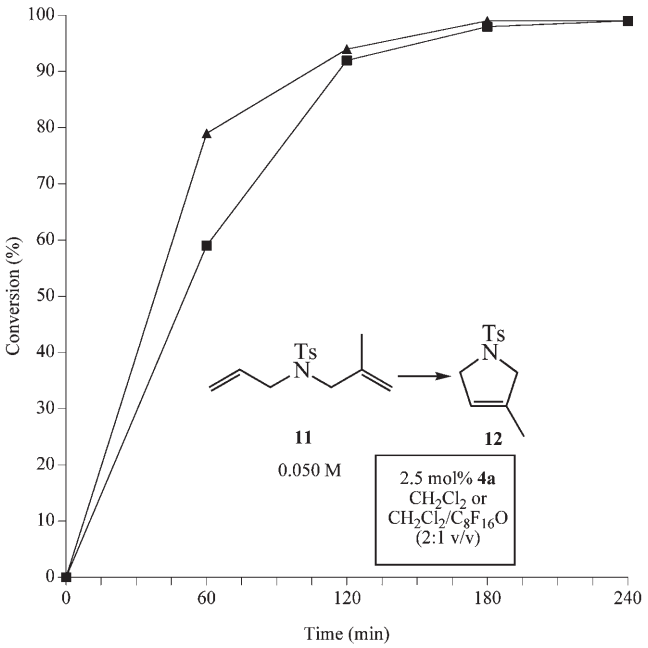


Figure 7. Rates of formation of **12** (room temperature). Solvent systems: ▲ $CH_2Cl_2/C_8F_{16}O$ (2.4 mL/1.2 mL); ■ CH_2Cl_2 (2.4 mL).

Figure 8 shows that the initial rates of formation of cyclopentene **6** were virtually identical in CH_2Cl_2 (■) and $CH_2Cl_2/C_8F_{16}O$ (●), with yields of 50% vs. 49% and 74% vs. 78% after 15 and 30 min. Moderate differences were observed with CH_2Cl_2 (▲) and $CH_2Cl_2/CF_3C_6F_{11}$ (×). Yields of **6** were 44% *vs.* 62% and 65% *vs.* 78% after 15 and 30 min. The metathesis of **9** was also checked in CH_2Cl_2 (■) and $CH_2Cl_2/C_8F_{16}O$ (◆). As shown in Figure 9, the yield of **10** was 49% *vs.* 53% after 15 min. Hence, we conclude that there is no appreciable fluorous solvent effect with non-fluorous metathesis catalysts.

Catalyst Recycling

Apart from the applications above, there is the obvious question whether **4a–d** might have utility as recyclable metathesis catalysts, as demonstrated earlier by Yao and Curran with **B** and **C** in Figure 1.[6,7] Since **4a–d** can be purified *via* silica gel chromatography, we

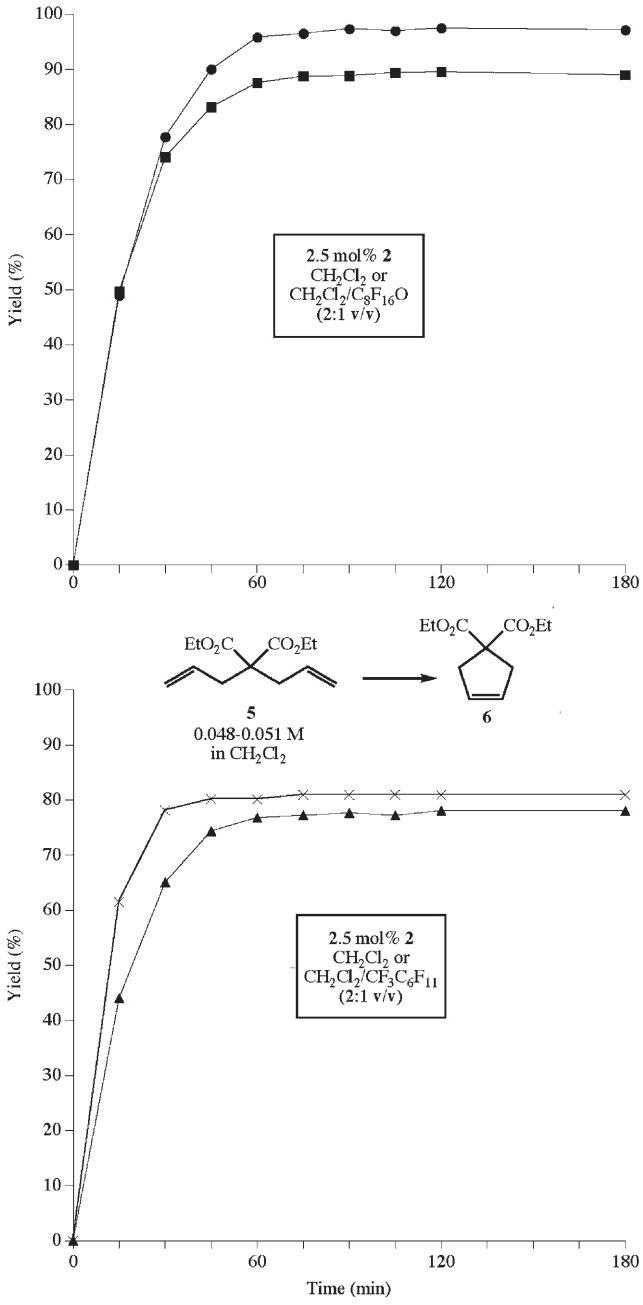


Figure 8. Rates of formation of **6** (room temperature). Solvent systems: ● $CH_2Cl_2/C_8F_{16}O$ (5.0 mL/2.5 mL); ■ CH_2Cl_2 (5.0 mL); × $CH_2Cl_2/CF_3C_6F_{11}$ (5.0 mL/2.5 mL); ▲ CH_2Cl_2 (5.0 mL).

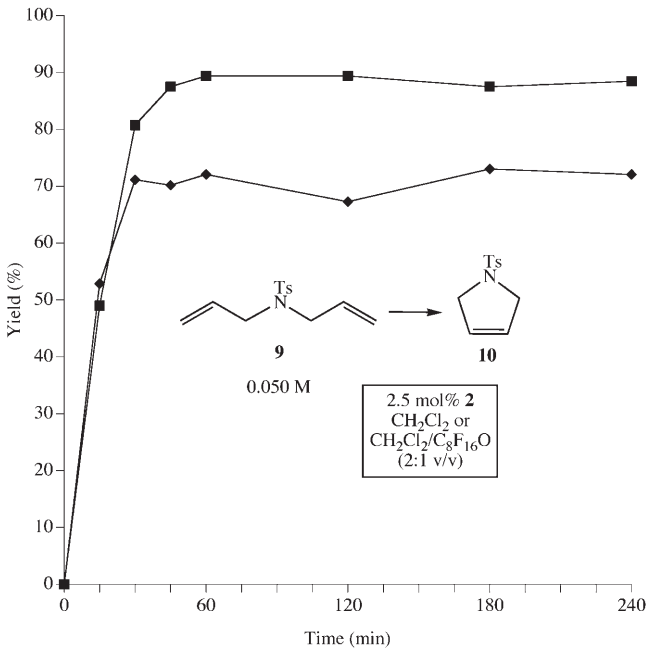
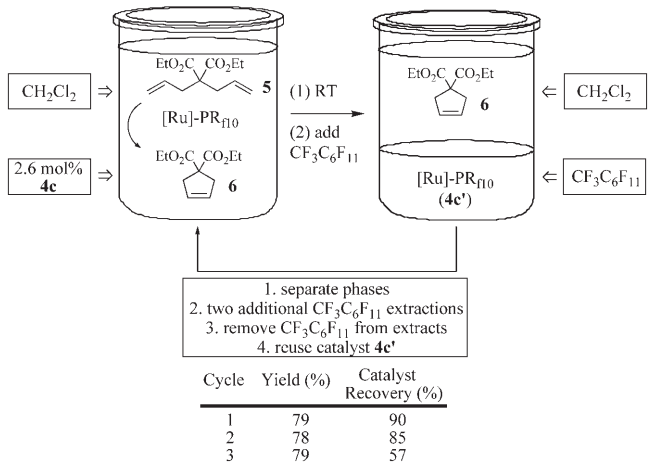


Figure 9. Rates of formation of **10** (room temperature). Solvent systems: ◆ $CH_2Cl_2/C_8F_{16}O$ (2.0 mL/1.0 mL); ■ CH_2Cl_2 (2.0 mL).



Cycle	Yield (%)	Catalyst Recovery (%)
1	79	90
2	78	85
3	79	57

Figure 10. Fluorous/organic liquid/liquid biphase recycling of metathesis catalyst **4c** ([Ru]-PR_{f10}).

presumed that they could be recovered with fluorous silica gel as employed by Curran. We therefore focused on fluorous/organic liquid/liquid biphase methods, using the most fluorophilic catalyst **4c**. Note that although **4c** has a benzylidene ligand, the recovered catalyst (**4c′**) will contain a different, educt-derived alkylidene ligand.

The recycling protocol sketched in Figure 10 was investigated, using a CH_2Cl_2 solution (10.7 mL) that was 0.050 M in the diene **5** and contained a GC standard. The initial charge of **4c** (0.0307 g, 2.6 mol%) would only be partially soluble in this quantity of CH_2Cl_2, but completely dissolved in the presence of the additives. As shown in Figure 11, the yield of **6** was 74% after 10 min, and increased only slightly thereafter. After 1 h, the mixture was extracted with $CF_3C_6F_{11}$ (3×2 mL). Solvent removal from the fluorous phase gave *ca.* 90% recovery of **4c′** (0.0275 g; 90% if **4c′** and **4c** have identical formula weights). The CH_2Cl_2 phase still carried a residual color.

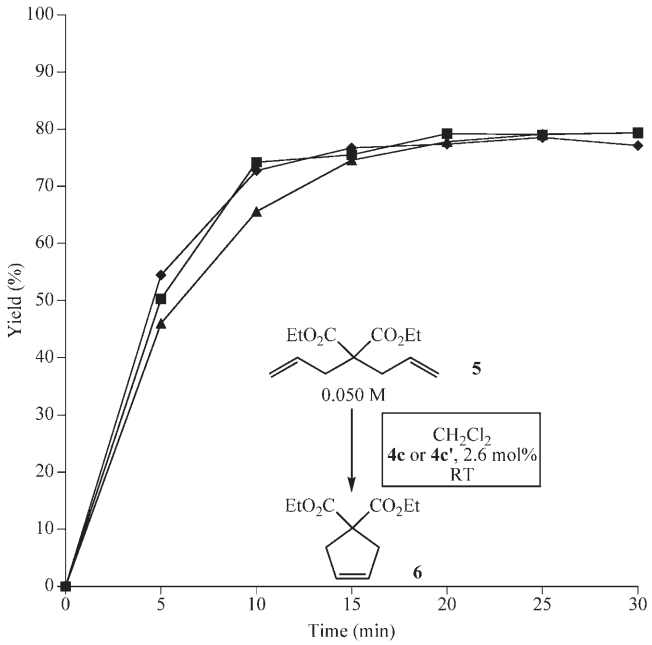


Figure 11. Rates of formation of **6** (room temperature) under the conditions of Figure 10; ■ first cycle; ◆ second cycle; ▲ third cycle.

A second cycle was conducted with **4c′** and a 0.049 M CH_2Cl_2 solution of **5**, with the quantity reduced slightly to preserve a 2.6 mol% loading with the decreased amount of catalyst. As shown in Figure 11, comparable results were obtained, with a 73% yield of **6** after 10 min. Approximately 85% of the charge of **4c′** was recovered. The rate of formation of **6** during the third cycle was comparable (66% after 10 min), but less **4c′** (57%) could be recovered. A parallel sequence conducted in air gave similar results up to this cycle, when the rate slowed somewhat (40% and 61% after 10 and 20 min; 60% recovery of **4c′**).[21] A fourth cycle gave significantly poorer results. Nonetheless, these data show that the new catalyst family can be recycled by fluorous/organic liquid/liquid biphase techniques.

Discussion

The data presented above are consistent with what we believe is a new mechanism of catalyst activation, sketched for alkene metathesis in Scheme 1, that in theory can be (1) applied to many catalyst precursors from which a ligand must dissociate in a pre-equilibrium step before the catalyst cycle can be entered, and (2) extended to other phases, for example a highly polar ligand that would preferentially partition into water. Ideally, the catalyst precursor should have a very high affinity for the reaction phase, and the dissociated ligand a very high affinity for the orthogonal phase. The fluorophilicity of our lead catalyst **4b** is likely somewhat greater than optimum, but could easily be attenuated by modification of the non-fluorous ligands. The reactivity trends have been confirmed in many additional experiments employing non-standard catalyst concentrations or solvent ratios.

Although only a few of the metatheses in Figures 2–11 attain yields of $>90\%$, this is not unusual for ruthenium-based catalysts. Deactivation can occur, and under preparative conditions it is common to add multiple charges, for example 2×2.5 mol%. However, in most cases the starting diene was completely consumed. In order to maintain the integrities of the solvent mixtures, no attempts were made to surmount possible equilibrium constraints by aspirating the volatile ethylene coproduct. Note that despite the *ca.* 75% yields in Figure 11, the recovered catalysts retain their activities. Hence, the non-quantitative yields in these cases cannot be ascribed to catalyst deactivation.

In all of the above metatheses with **4a–c**, the fourteen valence-electron methylidene intermediate $(H_2IMes)(Cl)_2Ru(=CH_2)$ is generated in the cyclopentene-forming steps. The same intermediate is obtained when starting with the second generation catalyst **2**, and Grubbs has shown that if it combines with the dissociated Cy_3P, it is essentially incapable of reentering the catalytic cycle.[3a] The dissociated Cy_3P is also intimately involved in the decomposition of **2** to non-alkylidene species.[22] Therefore, another advantage of the phase transfer activation strategy can be longer-lived catalysts.

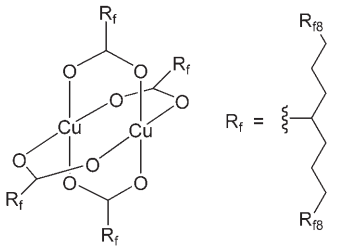
Detailed kinetic measurements, which would be complicated by the partial partitioning of catalyst precursors **4a–c** into the fluorous phases, are beyond the scope of this initial feasibility study. However, previous investigations involving a variety of ruthenium catalysts have established that there is no simple relationship between the rate of phosphine dissociation (k_1; Scheme 1) and the k_{-1}/k_2 ratio.[3] Triarylphosphine ligands with electron-withdrawing substituents give greater k_1 values, in accord with their weaker Brønsted basicities and therefore enhanced leaving group abilities.[3b] Hence, **4a–d** would be expected to be faster initiating catalysts than isosteric analogues with more basic tri(*n*-alkyl)phosphines. Indeed, (H_2IMes)-$[(n\text{-}Bu)_3P](Cl)_2Ru(=CHPh)$ gives a very low k_1 value and has never seen practical application.[3b]

Nonetheless, comparison of Figure 8 and 9 with Figure 2 and Figure 5 shows that Grubbs' second generation catalyst **2** is much more active than **4b**, despite the much stronger Brønsted basicity of the phosphine Cy_3P compared to **1b**.[11] Presumably steric factors, which could affect the relative k_{-1} values, are also at work. An interesting extension of this study would involve catalysts with fluorous versions of Cy_3P, perhaps with two R_{fn} groups attached to the 4-position of each

ring. Finally, it should be emphasized that any catalyst/substrate combination for which ligand dissociation is a rate-determining as opposed to a pre-equilibrium step would not be a candidate for phase transfer activation.

Other approaches to inhibiting the k_{-1} step in Scheme 1 have been investigated. Grubbs,[23] Nolan,[24] and Blechert[25] have studied various types of copper species and Lewis or Brønsted acids that are believed to bind the dissociated phosphine. Rate accelerations have been observed in certain cases, but are sometimes accompanied by earlier catalyst deactivation. Phenol additives can have positive effects, but other mechanisms are thought to be involved.[26] Highly unsaturated catalyst precursors that *lack* any ligand L have also been developed, but since there are concurrent changes in the ancillary ligands these are not automatically more active.[9b,27]

A possible enhancement of our methodology would involve the addition of a fluorous scavenger for the phosphines **1a–d**. This would shift the phase equilibrium beyond what can be achieved *via* partition coefficients alone. In this regard, Vincent has reported the highly fluorous dicopper tetracarboxylate $Cu_2[O_2CCH(CH_2CH_2CH_2R_{f8})_2]_4$ (**13**).[28] Complex **13** efficiently extracts non-fluorous pyridines into fluorous phases, including C_{60} derivatives. As detailed elsewhere, we have studied reactions of the bis(pyridine) metathesis catalyst **3** (Scheme 2) in fluorous/organic liquid/liquid biphase mixtures containing **13**.[13] However, only rapid catalyst deactivation was observed.



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A final point concerns ligand transport across the phase boundary, which of course must be rapid on the time scale of the catalytic reaction for a rate enhancement to be possible. This issue underlies all phase-transfer catalysis and has been extensively studied.[29] To our knowledge, there are no quantitative data involving heavy fluorous species. However, colored fluorous compounds rapidly equilibrate across stirred phase boundaries, and we presume that phosphines **1a–d** behave similarly. Given the extremely high fluorophilicities of **1a–d**, we have tentatively attributed the rate differences with various fluorous solvents not to equilibrium effects but rather to transport rates. One parameter that can affect transport rates is viscosity, but there are others and the origin of these effects will require further study.[30]

Conclusions

In summary, the data in this paper are consistent with a new catalyst activation mechanism featuring phase transfer to fluorous media for the removal of dissociated ligands that can compete with substrate molecules for binding to a reactive metal center. This strategy is potentially extendible to a wide variety of orthogonal phase combinations and ligand phase tags, and defines a very promising new frontier for future catalyst design.

Experimental Section

General Remarks

All reactions were conducted under N_2 unless noted. Chemicals were treated as follows: ether, toluene, hexanes, distilled from Na/benzophenone; perfluoro(methylcyclohexane) ($CF_3C_6F_{11}$; ABCR), $CF_3C_6H_5$ (ABCR), distilled from CaH_2; diethyl diallylmalonate (**5**; Lancaster), tridecane (Aldrich), perfluoro(2-butyltetrahydrofuran) ($C_8F_{16}O$; Apollo), perfluorohexane (C_6F_{14}; Fluorochem), 1H,1H-perfluoroheptanol ($CF_3(CF_2)_5CH_2OH$; ABCR), CD_2Cl_2 (Cambridge Isotope or Aldrich) and other solvents, used as received. Diethyl 2-allyl-2-methallylmalonate (**7**),[31] *N,N*-diallyltosylamide (**9**)[32] and *N*-allyl-*N*-methallyltosylamide (**11**)[6] were synthesized by literature procedures.

NMR spectra were recorded on 400 MHz spectrometers at ambient probe temperatures and referenced to residual internal $CHDCl_2$ (^1H, $\delta = 5.32$), internal CD_2Cl_2 (^{13}C, $\delta = 53.23$ ppm), internal C_6F_6 (^{19}F, $\delta = -162.0$ ppm) or external H_3PO_4 (^{31}P, $\delta = 0.00$ ppm). IR spectra were measured on an ASI React-IR spectrometer. GC data were acquired using a ThermoQuest Trace GC 2000 instrument fitted with a capillary column (OPTIMA 5–0.25 μm; 25 m × 0.32 mm). HPLC data were acquired using a Thermoquest instrument package (pump/autosampler/detector P4000/AS3000/UV6000 LP). DSC and TGA data were recorded with a Mettler-Toledo DSC821 instrument and treated by standard methods.[33] Elemental analyses were conducted with a Carlo Erba EA1110 instrument.

$(H_2IMes)[(R_{f6}CH_2CH_2)_3P](Cl)_2Ru(=CHPh)$ (4a)

A Schlenk flask was charged with $(H_2IMes)(Py)_2(Cl)_2Ru(=CHPh)$ (**3**;[14] 0.0924 g, 0.127 mmol), $P(CH_2CH_2R_{f6})_3$ (**1a**;[10] 0.1524 g, 0.142 mmol), and $CF_3C_6H_5$ (3.0 mL). The mixture was stirred (1 h). The solvent was removed by oil pump vacuum to give a brownish pink residue that was passed through a silica gel plug (4 × 2 cm) using hexanes and then hexanes/ether (10:1 v/v). The solvent was removed from the filtrate by rotary evaporation and oil pump vacuum to give **4a** as a pink solid; yield: 0.1482 g

(0.090 mmol, 71%): mp 113–118 °C (capillary). DSC: $T_i/T_e/T_p/T_c/T_f$ 83.8/114.3/123.7/128.0/129.3 °C (endotherm), 129.4/134.6/146.8/154.0/159.5 °C (exotherm). TGA: onset of first and second mass loss regimes (T_e), 127.7 (3.4%) and 171.3 °C. Anal. calcd. (%) for $C_{52}H_{45}Cl_2F_{39}N_2PRu$ (1641.8): C 38.04, H 2.76, N 1.71; found: C 37.85, H 2.83, N 1.67. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 18.91 (s, 1H, Ru=CH), 7.83 (d, J = 7.6 Hz, 2H of Ph), 7.51 (t, J = 7.7 Hz, 1H of Ph), 7.18 (t, J = 7.8 Hz, 2H of Ph), 6.99 (s, 2H of 2Mes), 6.37 (s, 2H of 2Mes), 4.20–3.90 (4H, NCH_2CH_2N), 2.59 (s, 6H, $2CH_3$), 2.28 (s, 3H, CH_3), 2.23 (s, 6H, $2CH_3$), 1.94 (s, 3H, CH_3), 1.90–1.60 [br m, 12H, $P(CH_2)_2$]; ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, partial): δ = 217.8 [d, J = 90.2 Hz, $RuC(N)_2$], 150.9 (d, J = 1.6 Hz), 139.6, 139.3, 138.4, 137.1, 136.9, 134.3, 130.8, 130.6, 129.8, 129.5, 129.2, 128.8, 52.2 (d, J = 3.4 Hz), 51.8 (d, J = 1.6 Hz), 25.4 (t, J = 22.7 Hz), 20.9, 20.8, 20.2, 18.4, 12.3 (d, J = 21.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 19.96 (s); ^{19}F NMR (282 MHz, CD_2Cl_2, partial): δ = −81.64 (t, J = 9.3, CF_3). MS (FAB, 3-NBA): m/z (%) = 1640 (5) $[M-H]^+$, 1605 (2.5) $[M-Cl]^+$, 1073 (2.5) $[P(CH_2CH_2R_{f6})_3+H]^+$.

$(H_2IMes)((R_{f8}CH_2CH_2)_3P)(Cl)_2Ru(=CHPh)$ (4b)

Complex **3** (0.1201 g, 0.165 mmol),[14] $P(CH_2CH_2R_{f8})_3$ (**1b**;[10] 0.1524 g, 0.142 mmol), and $CF_3C_6H_5$ (4.0 mL) were combined in a procedure analogous to that for **4a**. An identical workup gave **4b** as a pink solid; yield: 0.2050 g (0.106 mmol, 64%); mp 113–115 °C (capillary). DSC: $T_i/T_e/T_p/T_c/T_f$, 96.6/112.4/117.1/120.0/130.3 °C (endotherm), 159.5/175.7/178.8/180.0/186.8 °C (exotherm). TGA: onset of first and second mass loss regimes (T_e), 154.8 (4.5%) and 198.2 °C. Anal. calcd (%) for $C_{58}H_{45}Cl_2F_{51}N_2PRu$ (1941.9): C 35.87, H 2.34, N 1.44; found: C 35.31, H 2.38, N 1.31; ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 18.90 (s, 1H, Ru=CH), 7.83 (d, J = 7.7 Hz, 2H of Ph), 7.50 (t, J = 7.3 Hz, 1H of Ph), 7.18 (t, J = 7.7 Hz, 2H of Ph), 6.99 (s, 2H of 2Mes), 6.40 (s, 2H of 2Mes), 4.20–4.90 (dm, J = 36.6 Hz, 4H, NCH_2CH_2N), 2.59 (s, 6H, $2CH_3$), 2.27 (s, 3H, CH_3), 2.23 (s, 6H, $2CH_3$), 1.93 (s, 3H, CH_3), 1.90–1.60 [br m, 12H, $P(CH_2)_2$]; ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, partial): δ = 218.4 [d, J = 90.5 Hz, $RuC(N)_2$], 150.9, 139.6, 139.3, 138.4, 137.0, 136.9, 134.2, 130.7, 130.6, 129.7, 129.4, 128.7, 52.2 (d, J = 3.7 Hz), 51.7 (d, J = 2.8 Hz), 25.4 (t, J = 22.9 Hz), 20.9, 20.8, 20.2, 18.4, 12.2 (d, J = 21.1 Hz); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 20.17 (s); ^{19}F NMR (282 MHz, CD_2Cl_2, partial): δ = −81.74 (t, J = 10.0 Hz, CF_3); MS (FAB, 2-nitrophenyl octyl ether): m/z (%) = 1940 (90) $[M-H]^+$, 1905 (40) $[M-Cl]^+$, 1373 (100) $[P(CH_2CH_2R_{f8})_3+H]^+$, 568 (75) $[M-P(CH_2CH_2R_{f8})_3]^+$, 532 (85) $[M-P(CH_2CH_2R_{f8})_3-Cl]^+$.

$(H_2IMes)[(R_{f10}CH_2CH_2)_3P](Cl)_2Ru(=CHPh)$ (4c)

Complex **3** (0.0800 g, 0.110 mmol),[14] $P(CH_2CH_2R_{f10})_3$ (**1c**;[10] 0.1840 g, 0.110 mmol), and $CF_3C_6H_5$ (3.0 mL) were combined in a procedure analogous to that for **4a**. An identical work-up gave **4c** as a pink solid; yield: 0.1806 g (0.081 mmol, 73%); mp 111–114 °C (capillary). DSC: $T_i/T_e/T_p/T_c/T_f$ 98.8/114.6/116.8/118.6/126.2 °C (endotherm), 153.6/167.3/173.3/176.8/189.8 °C (exotherm). TGA: onset of first and second mass loss regimes (T_e), 173.4 (2.9%) and 198.0 °C. Anal. calcd. (%) for $C_{64}H_{45}Cl_2F_{63}N_2PRu$ (2241.9): C 34.29, H 2.02, N 1.25; found: C 34.31, H 2.00, N 1.21. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 18.90 (s, 1H, Ru=CH), 7.83 (d, J = 7.6 Hz, 2H of Ph), 7.49 (t, J = 6.4 Hz, 1H of Ph), 7.17 (t, J = 7.8 Hz, 2H of Ph), 6.98 (s, 2H of 2Mes), 6.36 (s, 2H of 2Mes), 4.12–3.90 (2 m, 4H, NCH_2CH_2N), 2.59 (s, 6H, $2CH_3$), 2.27 (s, 3H, CH_3), 2.22 (s, 6H, $2CH_3$), 1.93 (s, 3H, CH_3), 1.90–1.50 (br m, 12H, $P[CH_2)_2]$; ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 20.24 (s); ^{19}F NMR (282 MHz, CD_2Cl_2, partial): δ = −81.80 (t, J = 10.0 Hz, CF_3); MS (FAB, 3-NBA): m/z (%) = 2240 (28) $[M-H]^+$, 2204 (12) $[M-Cl]^+$, 1673 (17) $[P(CH_2CH_2R_{f10})_3+H]^+$, 568 (32) $[M-P(CH_2CH_2R_{f10})_3]^+$, 532 (55) $[M-P(CH_2CH_2R_{f10})_3-Cl]^+$.

$(H_2IMes)[(R_{f8}CH_2CH_2CH_2)_3P](Cl)_2Ru(=CHPh)$ (4d)

Complex **3** (0.0790 g, 0.109 mmol),[14] $P(CH_2CH_2CH_2R_{f8})_3$ (**1d**;[10] 0,1700 g, 0.120 mmol), and $CF_3C_6H_5$ (3.0 mL) were combined in a procedure analogous to that for **4a**. An identical work-up gave **4d** as a pink solid; yield: 0.1695 g (0.086 mmol, 78%); mp 101–103 °C (capillary). DSC: $T_i/T_e/T_p/T_c/T_f$ 102.6/106.6/109.4/111.4/117.8 °C (endotherm), 153.6/167.3/173.3/176.8/189.8 °C (exotherm). TGA: onset of first and second mass loss regimes (T_e), 142.8 (3.9%) and 188.8 °C. Anal. calcd. (%) for $C_{61}H_{51}Cl_2F_{51}N_2PRu$ (1983.9): C 36.93, H 2.59, N 1.41; found: C 36.74, H 2.51, N 1.35. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 18.88 (s, 1H, Ru=CH), 7.88 (d, J = 7.8 Hz, 2H of Ph), 7.50 (t, J = 7.4 Hz, 1H of Ph), 7.15 (t, J = 7.8 Hz, 2H of Ph), 6.98 (s, 2H of 2Mes), 6.34 (s, 2H of 2Mes), 4.12–3.85 (2 m, J = 40.9 Hz, 4H, NCH_2CH_2N), 2.61 (s, 6H, $2CH_3$), 2.29 (s, 3H, CH_3), 2.22 (s, 6H, $2CH_3$), 1.93 (overlapping s, 3H, CH_3), 1.99–1.80, 1.60–1.44 and 1.25–1.10 [overlapping m, m, and m, 6H, 6H, 6H, $P(CH_2)_3$]; ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, partial): δ = 218.4 [d, J = 90.6 Hz, $RuC(N)_2$], 150.9, 139.6, 139.3, 138.4, 137.0, 136.9, 134.2, 130.7, 130.6, 129.7, 129.5, 128.8, 66.0, 52.2 (d, J = 3.7 Hz), 51.7, 25.4 (t, J = 22.9 Hz), 20.9, 20.8, 20.2, 18.4, 12.3 (d, J = 23.3 Hz); ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ = 22.37; ^{19}F NMR (282 MHz, CD_2Cl_2, partial): δ = −81.64 (t, J = 9.9 Hz, CF_3). MS (FAB, 3-NBA): m/z (%) = 1982 (65) $[M-H]^+$, 1947 (25) $[M-Cl]^+$, 1415 (100) $[P(CH_2CH_2R_{f8})_3+H]^+$, 568 (10) $[M-P(CH_2CH_2CH_2R_{f8})_3]^+$, 532 (20) $[M-P(CH_2CH_2CH_2R_{f8})_3-Cl]^+$.

Experiments in Figure 2

(A): A two-neck flask was charged with **5** (0.0381 g, 0.159 mmol) and tridecane (0.0248 g, 0.135 mmol), and flushed with nitrogen. Freshly distilled CH_2Cl_2 was added (3.1 mL, giving a 0.051 M solution). The solution was stirred and **4b** (0.0075 g, 0.0039 mmol, 2.5 mol%) was added against a stream of nitrogen. Samples were periodically removed by syringe for GC analyses.[34]

(B): A two-neck flask was similarly charged with **5** (0.0574 g, 0.239 mmol) and tridecane (0.0481 g, 0.261 mmol), and flushed with nitrogen. Freshly distilled CH_2Cl_2 (5.0 mL, giving a 0.048 M solution) and $CF_3C_6F_{11}$ (2.5 mL) were added. The biphasic mixture was stirred and **4b** (0.0116 g, 0.00598 mmol, 2.5 mol%) was added against a stream of nitrogen.

(B′): A two-neck flask was similarly charged with **5** (0.0490 g, 0.204 mmol), tridecane (0.0590 g, 0.320 mmol; GC standard), freshly distilled CH_2Cl_2 (4.0 mL, giving a 0.051 M solution), $CF_3C_6F_{11}$ (2.0 mL), and **4b** (0.0097 g, 0.0050 mmol, 2.5 mol%).

(C): A two-neck flask was similarly charged with **5** (0.0260 g, 0.108 mmol), tridecane (0.0212 g, 0.115 mmol), freshly distilled CH_2Cl_2 (2.2 mL, giving a 0.049 M solution), $C_8F_{16}O$ (1.1 mL), and **4b** (0.0052 g, 0.0027 mmol, 2.5 mol %).

(D): A two-neck flask was similarly charged with **5** (0.0275 g, 0.114 mmol), tridecane (0.0194 g, 0.105 mmol), freshly distilled CH_2Cl_2 (2.2 mL, giving a 0.052 M solution), $CF_3(CF_2)_5CH_2OH$ (1.1 mL), and **4b** (0.0057 g, 0.0029 mmol, 2.5 mol %).

Experiments in Figure 3

One experiment is identical to C in Figure 2 and the others were conducted analogously.

(A): A two-neck flask was similarly charged with **5** (0.0133 g, 0.055 mmol), tridecane (0.0093 g, 0.050 mmol), freshly distilled CH_2Cl_2 (1.2 mL, giving a 0.046 M solution), $C_8F_{16}O$ (0.6 mL), and **4b** (0.0053 g, 0.0027 mmol, 5.0 mol %).

(B): A two-neck flask was similarly charged with **5** (0.0644 g, 0.268 mmol), tridecane (0.0482 g, 0.261 mmol), freshly distilled CH_2Cl_2 (5.2 mL, giving a 0.052 M solution), $C_8F_{16}O$ (2.6 mL), and **4b** (0.0052 g, 0.0027 mmol, 1.0 mol %).

Experiments in Figure 4

(A): A two-neck flask was charged with **7** (0.0524 g, 0.206 mmol)[31] and hexadecane (0.0530 g, 0.234 mmol), and flushed with nitrogen. Freshly distilled CH_2Cl_2 was added (4.0 mL, giving a 0.052 M solution). The solution was stirred and **4b** (0.0100 g, 0.00516 mmol, 2.5 mol %) was added against a stream of nitrogen. Samples were periodically removed by syringe for GC analyses.[34]

(B): A two-neck flask was similarly charged with **7** (0.0531 g, 0.209 mmol), hexadecane (0.0530 g, 0.234 mmol), and freshly distilled CH_2Cl_2 (4.0 mL, giving a 0.052 M solution), $CF_3C_6F_{11}$ (2.0 mL) and **4b** (0.0100 g, 0.00516 mmol, 2.5 mol %).

(C): A two-neck flask was similarly charged with **7** (0.0600 g, 0.236 mmol), hexadecane (0.0510 g, 0.225 mmol), freshly distilled CH_2Cl_2 (4.6 mL, giving a 0.051 M solution), $C_8F_{16}O$ (2.3 mL), and **4b** (0.0113 g, 0.00582 mmol, 2.5 mol %).

Experiments in Figure 5

(A): A two-neck flask was charged with **9** (0.0260 g, 0.104 mmol)[32] and octadecane (0.0212 g, 0.083 mmol), and flushed with nitrogen. Freshly distilled CH_2Cl_2 was added (2.0 mL, giving a 0.052 M solution). The solution was stirred and **4b** (0.0053 g, 0.0027 mmol, 2.5 mol %) was added against a stream of nitrogen. Samples were periodically removed by syringe for GC analysis.[34]

(A′): A two-neck flask was similarly charged with **9** (0.0260 g, 0.104 mmol), octadecane (0.0210 g, 0.083 mmol), freshly distilled CH_2Cl_2 (2.0 mL, giving a 0.052 M solution), and **4b** (0.0050 g, 0.0026 mmol, 2.5 mol %).

(B): A two-neck flask was similarly charged with **9** (0.0260 g, 0.104 mmol), octadecane (0.0212 g, 0.083 mmol), freshly distilled CH_2Cl_2 (2.0 mL, giving a 0.052 M solution), $C_8F_{16}O$ (1.0 mL), and **4b** (0.0052 g, 0.0027 mmol, 2.5 mol %).

Experiments in Figure 6

(A): A two-neck flask was charged with **7** (0.0510 g, 0.201 mmol) and hexadecane (0.0459 g, 0.203 mmol) and flushed with nitrogen. Freshly distilled CH_2Cl_2 was added (4.0 mL, giving a 0.050 M solution). The solution was stirred and **4a** (0.0085 g, 0.0052 mmol, 2.5 mol %) was added against a stream of nitrogen. Samples were periodically removed by syringe for GC analysis.[34]

(B): A two-neck flask was similarly charged with **7** (0.0524 g, 0.206 mmol), hexadecane (0.0471 g, 0.208 mmol), freshly distilled CH_2Cl_2 (4.0 mL, giving a 0.052 M solution), $CF_3C_6F_{11}$ (2.0 mL), and **4a** (0.0085 g, 0.00518 mmol, 2.5 mol %).

Experiments in Figure 7

(A): A two-neck flask was charged with **11** (0.0325 g, 0.123 mmol)[6] and hexadecane (0.0301 g, 0.133 mmol), and flushed with nitrogen. Freshly distilled CH_2Cl_2 was added (2.4 mL, giving a 0.051 M solution). The solution was stirred and **4a** (0.0050 g, 0.00305 mmol, 2.5 mol %) was added against a stream of nitrogen. Samples were periodically removed by syringe for GC analysis.[34] Due to a technical problem, conversions of **11** to **12** are plotted.

(B): A two-neck flask was similarly charged with **11** (0.0328 g, 0.124 mmol), hexadecane (0.0316 g, 0.140 mmol), freshly distilled CH_2Cl_2 (2.4 mL, giving a 0.052 M solution), $C_8F_{16}O$ (1.2 mL), and **4a** (0.0050 g, 0.00305 mmol, 2.5 mol %).

Experiments in Figure 8

(A): A two-neck flask was charged with **5** (0.0603 g, 0.251 mmol) and tridecane (0.0424 g, 0.230 mmol), and flushed with nitrogen. Freshly distilled CH_2Cl_2 was added (5.0 mL, giving a 0.050 M solution). The solution was stirred and **2** (0.0052 g, 0.00612 mmol, 2.5 mol %) was added against a stream of nitrogen. Samples were periodically removed by syringe for GC analysis.[34]

(B): A two-neck flask was similarly charged with **5** (0.0600 g, 0.250 mmol), tridecane (0.0440 g, 0.239 mmol), freshly distilled CH_2Cl_2 (5.0 mL, giving a 0.050 M solution), $C_8F_{16}O$ (2.5 mL), and **2** (0.0100 g, 0.00516 mmol, 2.5 mol %).

(C): A two-neck flask was similarly charged with **5** (0.0590 g, 0.246 mmol), tridecane (0.0451 g, 0.245 mmol), freshly distilled CH_2Cl_2 (5.0 mL, giving a 0.049 M solution), and **2** (0.0053 g, 0.00624 mmol, 2.5 mol %).

(D): A two-neck flask was similarly charged with **5** (0.0593 g, 0.247 mmol), tridecane (0.0460 g, 0.250 mmol), freshly distilled CH_2Cl_2 (5.0 mL, giving a 0.049 M solution), $CF_3C_6F_{11}$ (2.5 mL), and **2** (0.0053 g, 0.00625 mmol, 2.5 mol %) was added against a stream of nitrogen.

Experiments in Figure 9.

(A): A two-neck flask was charged with **9** (0.0260 g, 0.104 mmol) and octadecane (0.0211 g, 0.083 mmol), and flushed with nitrogen. Freshly distilled CH_2Cl_2 was added (2.0 mL, giving a 0.050 M solution). The solution was stirred and **2** (0.0022 g, 0.00259 mmol, 2.5 mol %) was added against a stream of nitrogen. Samples were periodically removed by syringe for GC analysis.[34]

(B): A two-neck flask was similarly charged with **9** (0.0260 g, 0.104 mmol), octadecane (0.0213 g, 0.084 mmol), freshly distilled CH_2Cl_2 (2.0 mL, giving a 0.050 M solution), $C_8F_{16}O$ (1.0 mL), and **2** (0.0022 g, 0.0026 mmol, 2.5 mol %).

Experiments in Figure 10 and Figure 11

(A): A two-neck flask was charged with **5** (0.1295 g, 0.539 mmol) and tridecane (0.1000 g, 0.542 mmol), and flushed with nitrogen. Freshly distilled CH_2Cl_2 was added (10.7 mL, giving a 0.050 M solution). The solution was stirred and **4c** (0.0305 g, 0.0136 mmol, 2.6 mol %) was added against a stream of nitrogen. Samples were periodically taken by syringe for GC analyses. After 1 h, the sample was extracted with degassed $CF_3C_6F_{11}$ (3×2.0 mL) under nitrogen. The fluorous phases were combined in a two-neck flask. The solvent was removed by oil pump vacuum to give **4c′** as a pinkish residue; yield: 0.0275 g (0.0123 mmol, 90 %).

(B): The two-neck flask from cycle A was similarly charged with **5** (0.1200 g, 0.499 mmol), tridecane (0.0900 g, 0.488 mmol), and CH_2Cl_2 (10.0 mL, giving a 0.049 M solution). An identical reaction and workup gave **4c′** as a pinkish residue; yield: 0.0258 g (0.0115 mmol, 85 %).

(C) The two-neck flask from cycle B was similarly charged with **5** (0.1117 g, 0.465 mmol), tridecane (0.0871 g, 0.472 mmol), and CH_2Cl_2 (10.0 mL, giving a 0.047 M solution). An identical reaction and workup gave **4c′** as a pinkish residue; yield: 0.0172 g (0.00767 mmol, 57 %).

Partition Coefficients

The following is representative, and other data are given elsewhere.[13] A 10-mL vial was charged with **4a** (0.0106 g, 6.46×10^{-3} mmol), $CF_3C_6F_{11}$ (2.000 mL) and toluene (2.000 mL), fitted with a mininert valve, and vigorously shaken (2 min). After 2 h (24 °C), a 0.500 mL aliquot of each phase was removed. The solvents were evaporated and the residues dried by oil pump vacuum (2 h). Each residue was taken up in MeOH (1.000 mL) and analyzed by HPLC (average of 5 injections, 200×4 mm Nucleosil 100–5 column, UV/visible detector). The relative peak intensities were 13.2:86.8

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