Synthesis, Structure, and Olefin Metathesis Activity of Two Ruthenium Monofluoromethylidene Complexes

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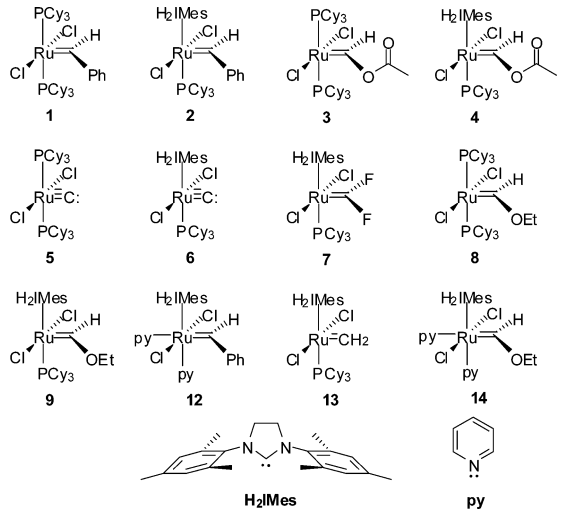
*Summary: The monofluoromethylidene complexes Ru(═CHF)(H$_2$IMes)(PCy$_3$)Cl$_2$ (**10**) and Ru(═CHF)(H$_2$IMes)(py)$_2$Cl$_2$ (**11**) have been synthesized from Ru(═CHPh)(H$_2$IMes)(PCy$_3$)Cl$_2$ and Ru(═CHPh)(H$_2$IMes)(py)$_2$Cl$_2$ via reaction with β-fluorostyrene. Both **10** and **11** catalyze ring-closing metathesis and cross-metathesis with activity comparable to that of Ru(═CHOEt)(H$_2$IMes)(PCy$_3$)Cl$_2$.*

Olefin metathesis has had an enormous impact on organic and polymer synthesis.[1] Over the past two decades, Ru-based catalysts have been developed to tolerate a wide assortment of important functional groups while retaining excellent activity.[1,2] However, some key functional groups are incompatible with Ru-based catalysts in cross-metathesis (CM) reactions. Alkenyl halides are very important building blocks in transition-metal-catalyzed syntheses, particularly palladium-catalyzed coupling reactions.[3] Nevertheless, attempted CM reactions of vinyl halides using Ru-based catalysts such as Ru(═CHPh)(L)(PCy$_3$)Cl$_2$ (L = PCy$_3$, **1**; L = H$_2$IMes, **2**; Chart 1) fail. However, this does not indicate an inability of the vinyl halide moiety to participate in metathesis reactions, as a number of examples of catalytic ring-closing metathesis (RCM) reactions involving α-chloro-α,ω-dienes[4,5] and α-fluoro-α,ω-dienes have been reported.[6−8] Given what is known about the metathesis mechanism,[9] these RCM results indicate that β-haloruthenacyclobutanes are competent intermediates. However, these results do not address the stability of α-halocarbenes, as they are not obligate intermediates in these cases.

In contrast, we have recently shown that acyloxycarbenes such as **3** and **4** (Chart 1) are unstable with respect to expulsion of acetic acid, forming the corresponding terminal carbide complexes **5** and **6** (Chart 1) cleanly.[10] This observation suggested that the instability of complexes of the form Ru(═CHX)(L)(PCy$_3$)Cl$_2$ (L = PCy$_3$, H$_2$IMes; X = halogen) with respect to formation of terminal carbides or related compounds might be responsible for the failure of vinyl halides to undergo productive CM reactions. Certainly, monohalomethylidene complexes are exceptionally rare: there is a single report of four closely related complexes of the form Os(═CHF)(P-*t*-Bu$_2$Me)$_2$(CO)(X)(Y) (X, Y = F, O$_3$SCF$_3$; two isomers for X ≠ Y), which were characterized spectroscopically in fluid solution but apparently not isolated.[11] Carbide formation is not the only mode of Fischer carbene decomposition in the Grubbs system, however. For example, Ru(═CHX)(PCy$_3$)$_2$Cl$_2$ (X = OEt, SEt, SPh, N[carbazole], N[pyrrolidinone]) decompose as well, though the decomposition products are in general not known except in the case of Ru(CHOEt)(PCy$_3$)$_2$Cl$_2$, which forms Ru(H)(CO)(PCy$_3$)$_2$Cl via a first-order reaction with a half-life of 3 h in benzene at 80 °C.[12]

Chart 1. Important Carbene and Carbide Complexes



Alternatively, stabilization of the monohalocarbene complex Ru(═CHX)(L)(PCy$_3$)Cl$_2$ with respect to PCy$_3$ dissociation would also interrupt catalysis. This possibility is suggested by the enhanced stability of the difluorocarbene complex **7**[13] (Chart 1) and the ethoxycarbene complexes **8** and **9**[12] (Chart 1) with respect to loss of PCy$_3$. Indeed, ethyl vinyl ether is frequently used to terminate ring-opening metathesis polymerization (ROMP) reactions.[1] Likewise, **7** displays almost no metathesis activity.[13] However, unlike **7** and Fischer carbene complexes containing single N, S, or O atoms in the α-position,[12] the corresponding monohalocarbene complexes have not been accessible.

Accordingly, we set out to synthesize monohalomethylidene complexes in order to test their stability and activity in CM

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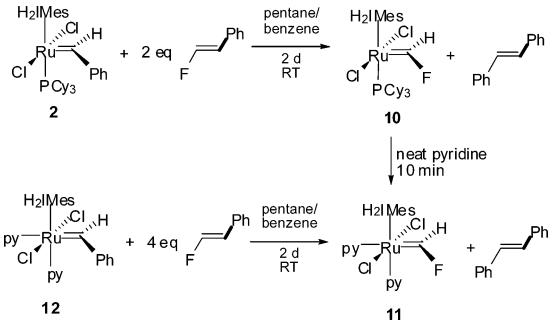
Scheme 1. Syntheses of 10 and 11



reactions. Reasoning that a monofluoromethylidene complex was the monohalomethylidene species most likely to be stable, we investigated potential syntheses of Ru(=CHF)(H_2IMes)(PCy_3)Cl_2 (**10**) and Ru(=CHF)(H_2IMes)(py)$_2Cl_2$ (**11**). Herein, we report the synthesis, metathesis activity, and some decomposition reactions of these, the first isolated monofluoromethylidene complexes.

Metathesis of **2** with β-fluorostyrene[14] in pentane/benzene affords **10** in 77% isolated yield after 2 days; stilbene is the byproduct (Scheme 1). A shorter reaction time can be achieved with a greater excess of β-fluorostyrene, but obtaining large quantities of this reagent presents synthetic challenges.

Complex **10** is unambiguously identifiable by NMR spectroscopy. The carbene α-proton is clearly visible as a doublet at 13.1 ppm ($^2J_{HF}$ = 106 Hz) in the ^{1}H NMR spectrum. Coupling to ^{31}P is not observed, which suggests that the CHF fragment lies in a plane approximately perpendicular to the Ru−P bond.[12,15,16] The CHF fragment gives rise to a doublet at 283 ppm in the ^{13}C{^{1}H} NMR spectrum ($^1J_{CF}$ = 416 Hz). These ^{1}H and ^{13}C NMR signals occur at chemical shifts very similar to those in **9**,[12] respectively 6 and 11 ppm upfield of their counterparts in **2**. The resonance at 32.6 ppm in the ^{31}P{^{1}H} NMR spectrum is a poorly resolved doublet due to coupling to ^{19}F. The latter nucleus gives rise to a doublet at 113.7 ppm in the ^{19}F NMR spectrum ($^2J_{HF}$ = 106 Hz); the P−F coupling is again poorly resolved. Although the ^{19}F NMR chemical shift and $^2J_{CF}$ values of **10** are similar to those in difluorocarbene **7** (δ 133; 432 Hz), the corresponding ^{13}C{^{1}H} NMR signal in **7** (δ 218) occurs well upfield of that in **10**.[13]

Single-crystal X-ray diffraction confirmed this assignment (Figure 1). Orange **10** is the first crystallographically characterized terminal monohalomethylidene complex. The Ru=C distance in **10** is statistically indistinguishable from that of **7**[13] but is shorter than that of **2**.[17] The CHF unit lies in the Cl−Ru−Cl plane; unfortunately, disorder of the CHF moiety precludes precise determination of the C−F bond length and Ru−C−F angle.

Compound **11** was synthesized in two ways (Scheme 1). Dissolution of **10** in pyridine afforded rapid conversion to **11** in 91% isolated yield. Alternatively, Ru(=CHPh)(H_2IMes)(py)$_2Cl_2$ (**12**) was treated with 4 equiv of β-fluorostyrene, affording **11** in 75% isolated yield. Doublets at 13.3 ($^2J_{HF}$ = 95 Hz), 298.3 ($^1J_{CF}$ = 409 Hz), and 130.3 ppm ($^2J_{FH}$ = 91 Hz)

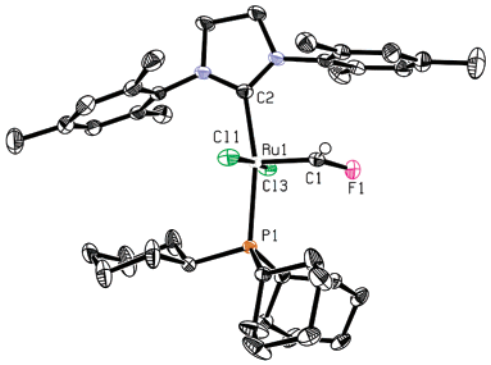


Figure 1. Thermal ellipsoid plot of **10** (50% probability level; CHF disorder not shown). Selected bond distances (Å) and angles (deg): Ru1−C1, 1.783(2); Ru1−C2, 2.0872(19); Ru1−P1, 2.4238(5); Ru1−Cl1, 2.3853(5); Ru1−Cl3, 2.3901(5); C1−Ru1−C2, 97.36(8); C1−Ru1−P1, 95.52(6); C1−Ru1−Cl1, 95.63(8); C1−Ru1−Cl3, 93.71(8); C2−Ru1−P1, 167.08(6); Cl1−Ru1−Cl3, 170.63(2).

in the ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra, respectively, are diagnostic of the CHF ligand in this complex, which retains two pyridine ligands that are equivalent on the ^{1}H NMR time scale at 23 °C.

Both **10** and **11** exhibit olefin metathesis activity. Complex **10** effects complete RCM of the benchmark substrate diethyl diallylmalonate within 3 h, only slightly more rapidly than does sluggish **9**[12] under the same conditions (0.10 M substrate, 3 mol % catalyst, C_6D_6, 60 °C). We attribute the low RCM activity of **9** and **10** to slow initiation in both cases. An alternative explanation involves a thermodynamic preference for Ru=CHX (X = OEt, F) compared to Ru=CH_2 ligation, which would also account for the formation of only a small quantity of the active RCM catalyst, Ru(=CH_2)(H_2IMes)(PCy_3)$_2Cl_2$ (**13**). Although this may also contribute to the relatively slow RCM rate, a ^{31}P NMR magnetization transfer experiment reveals that PCy_3 dissociation from **10** is so slow that no exchange with free PCy_3 is observed, even at 80 °C under standard conditions[9] in toluene. Thus, initiation via loss of PCy_3 is clearly problematic for **10**. However, it is apparently not nearly as difficult as in **7**, as indicated by ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD). Under conditions (0.005 M catalyst, 300 equiv of COD in CD_2Cl_2, 25 °C, 1.25 h) in which **7** effects the ROMP of COD to the extent of only 9%,[13] ROMP was complete with **10**. Note that, unlike **13**,[9] **10** was stable for 1 h at 80 °C, showing no sign of decomposition during this time.

RCM of diethyl diallylmalonate with **11** was initially more rapid than with **10** but ceased after 2 h, due to catalyst decomposition at this temperature. Self-cross-metathesis of 1-hexene, a type I substrate in this system,[18] occurs with both **10** and **11** (0.10 M substrate, 3 mol % catalyst, C_6D_6, 23 °C), the latter being more rapid, although both are slow compared to **2**. Under these conditions of lower temperature compared to the RCM reaction, **11** remains active even after 76 h. It is important to note that **11** decomposes much more rapidly under the conditions of significantly higher concentration required for ^{13}C NMR spectrum acquisition. This suggests that at least one decomposition mechanism is at least second order in [**11**]. No new alkylidene complexes are observed by ^{1}H NMR at any time, which again indicates either that there is slow initiation to form a small quantity of highly active catalyst or that **10** and **11** are

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thermodynamically favored relative to the other possible alkylidene complexes. In agreement with the slow initiation posited for **10**, no fluorinated olefins (vinyl fluoride, 1-fluoro-1-hexene) were observed in the reactions involving **10**. However, a very small quantity (too small for accurate integration) of vinyl fluoride appeared over time in the latter reaction of **11**. This quantity of vinyl fluoride can be accounted for in two ways. Equilibrium formation of small quantities of vinyl fluoride and Ru(=CH-*n*-Bu)(H_2IMes)($py)_2Cl_2$ upon reaction of **11** with 1-hexene is one explanation. A second possibility that can account for vinyl fluoride generation is bimolecular decomposition[19] of **11** with Ru(=CH_2)(H_2IMes)($py)_2Cl_2$, which must be present at least in low concentration. At present, we cannot rule out either possibility, although we reiterate that no other alkylidene complexes are observed at any time in the reaction mixture. Interestingly, when it is treated with 2 equiv of ethyl vinyl ether (EVE), **11** undergoes conversion to ≥95% Ru(=CHOEt)(H_2IMes)($py)_2Cl_2$ (**14**) within hours at room temperature, with concomitant liberation of vinyl fluoride. In contrast, conversion of **10** to **9** is not seen even after 3 days at 23 °C (10 equiv of EVE used). We propose that the apparent dichotomy in the reactions of **10** and **11** with EVE is due to the aforementioned slow initiation of **10** under these conditions rather than a change in the relative stability of monofluoromethylidene vs ethoxymethylidene ligation as a result of the change in ancillary ligand set. We are currently working to test this assertion.

These reactions bear directly on the stability of α-fluororuthenacyclobutane intermediates. Formation of **10** and **11** in good yields from **2** and **12** require that the α-fluoro-β,γ-diphenylruthenacyclobutane intermediate must decompose (if at all) slowly compared to the rate at which it undergoes cycloreversion to these products. The successful RCM and 1-hexene self-CM reactions involving both **10** and **11** require that at least some other alkylidene complexes are formed from **10** and **11**. This in turn requires that the intermediate α-fluororuthenacyclobutane complexes must have at least enough stability to permit the formation of some alkylidene complex. The essentially quantitative reaction of EVE with **11** further requires that the α-fluoro-γ-ethoxyruthenacyclobutane intermediate must not decompose rapidly compared to the rate of ring fragmentation to yield **14** and vinyl fluoride.

Although **10** is stable in the solid state and is relatively stable in THF solution (90% remains after 28 days at 23 °C), it eventually undergoes conversion to the terminal carbide complex **6** under other conditions. As measured by ^{1}H and ^{31}P NMR, conversion to **6** is complete after 16 h in CD_2Cl_2. This transformation also occurs in benzene or toluene, but with a long and variable induction period. In one case, the **10** → **6** conversion required 5 days in C_6D_6; in toluene solution, it occurred after heating to 80 °C for 1 h, but in another case only 3% conversion to **6** was noted after being subjected to temperatures of 80 °C for 1 h followed by 55 °C for 4 h and finally 23 °C for 7 days. Unlike the related formation of **5** from **3**,[10,20] this reaction does not display simple first-order kinetics but evinces a long induction period, during which time no **6** is observed, followed abruptly by relatively rapid formation of **6**. We propose that this is due to the slow formation of Lewis or Brønsted acidic species that initiate the **10** → **6** decomposition. In order to test the competence of Brønsted and Lewis acids to mediate this process, we examined reactions of **10** with HCl and with Me_3SiCl. In the former case, we find that 1 equiv of ethereal HCl consumes **10** in C_6D_6 quantitatively, affording 89% **6** and 11% of an unidentified side product within 1 h. Treatment of **10** with 2 equiv of Me_3SiCl in CD_2Cl_2 yields quantitative formation of **6** within 30 min, along with 1 equiv of Me_3SiF. Thus, suitable Lewis or Brønsted acids are competent to promote the **10** → **6** conversion process.

In summary, olefin metathesis reactions of **2** and **12** with β-fluorostyrene afford the first two isolated monofluoromethylidene complexes, **10** and **11**, both of which catalyze RCM and CM of benchmark alkenes. Thus, failure to form the monofluoroalkylidene complex is ruled out as an explanation for the failure of CM reactions of vinyl fluoride. Likewise, irreversible trapping of the active 14-electron intermediate by one or more labile neutral ligands to form inactive 16- or 18-electron complexes is ruled out, at least in the case of pyridine. Quantitative formation of **10** and **11** upon reaction of **2** and **12** with β-fluorostyrene does indicate a thermodynamic preference for the monofluoromethylidene ligand relative to the benzylidene moiety. However, the CHF ligand in **11** is replaced quantitatively by CHOEt upon reaction with EVE. Complex **11** is the more rapidly initiating catalyst but suffers from the rapid decomposition typical of the Grubbs-type bis(pyridine) catalysts. In contrast, **10** decomposes much more slowly, by a different route, eventually forming the stable terminal carbide complex **6**. Brønsted and Lewis acids facilitate carbide formation. Given that C−F bond cleavage can occur even in **10**, formation of carbides (or products derived therefrom) in attempted CM reactions involving vinyl halides is a likely mode of catalyst deactivation. We are currently investigating this possibility, with the aim of developing complexes that are resistant to this decomposition mode in order to render vinyl halides compatible with Ru-based olefin metathesis catalysts in CM reactions.

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Supporting Information Available: Text, figures, and tables giving details of the syntheses and characterization data for new compounds, X-ray structural data for **10**, and conditions for reactions of **10** and **11** with substrates; X-ray data for **10** are also given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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