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Olefin Metathesis Reactions with Vinyl Halides: Formation, Observation, Interception, and Fate of the Ruthenium−Monohalomethylidene Moiety

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Over the past two decades, great progress has been made in the development of Ru-based catalysts that tolerate a wide assortment of important functional groups yet display excellent olefin metathesis activity.[1] This has had an enormous impact on organic and polymer synthesis.[1a] However, a few important functional groups are still incompatible with Ru-based catalysts in cross-metathesis (CM) reactions. In particular, catalysts such as **1** and **2** (Chart 1) fail to mediate CM of vinyl halides. This is unfortunate, given that alkenyl halides are key building blocks in transition-metal-catalyzed syntheses, particularly palladium-catalyzed coupling reactions.[2] Accordingly, we have begun to investigate how vinyl halides and other problematic substrates deactivate **1** and **2**. We recently reported that vinyl esters react stoichiometrically with **1** to afford the corresponding Fischer carbene complexes, which then transform cleanly into the terminal carbide complex **3**; **2** reacts analogously to form **4**.[3] Compounds **3** and **4** do not catalyze metathesis, but Piers showed that they can be converted into catalysts **5** and **6**.[4] We next established that the reaction of **2** with β-fluorostyrene similarly affords the exceptionally rare monofluoromethylidene complex **7**, which is an active, if sluggish, catalyst for both ring-closing metathesis (RCM) and CM, but which also ultimately converts into **4**.[5] Herein we report our investigations of reactions of **2** and its analogues with some other vinyl chlorides and bromides; monohalomethylidene intermediates are not observed at 22 °C.

Unlike the cases of other vinyl X reagents investigated earlier ($X = O_2CR$, O_2COR, F),[3,5] we did not observe the analogous Fischer carbene intermediate **8** upon reaction of **2** with vinyl chloride, although the styrene products of stoichiometric olefin metathesis were seen (Scheme 1). Furthermore, although **4** formed, it was not the major Ru-containing product. Instead, the remarkable new phosphoniomethylidene complex **9** formed in a 2−3:1 ratio with **4**. The ratio of compounds **4** and **9** remained constant over the reaction time. Reaction of **2** with vinyl bromides was more complicated because of halogen exchange not only among the Ru-containing species (as expected)[6] but also with the vinyl bromide and **2** (vinyl *chloride* was observed in the product mixture). We are now examining the latter halogen-exchange reaction. In order to simplify the reaction with vinyl bromide, we employed **10**, whereupon **11** and **12** formed in a 1:8−18 ratio along with some minor decomposition products that are not yet identified.

Single-crystal X-ray diffraction confirmed the structure of **9** (Figure 1).[7] The coordination geometry is best described as square pyramidal ($\tau = 0.213$)[8] with the phosphoniomethylidene ligand at the apex. Both the Ru1−C1 bond distance and the C1−Ru1−C20 bond angle are statistically indistinguishable from the corresponding parameters in **6**[$B(C_6F_5)_4$].[4] The Ru═C distance is in the usual range for “second-generation” Grubbs catalysts.[5,9]

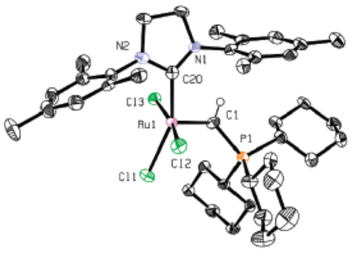
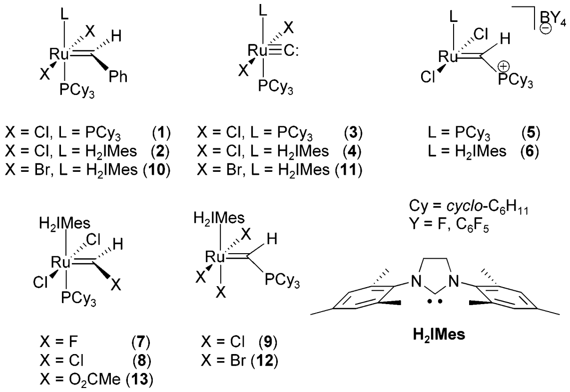
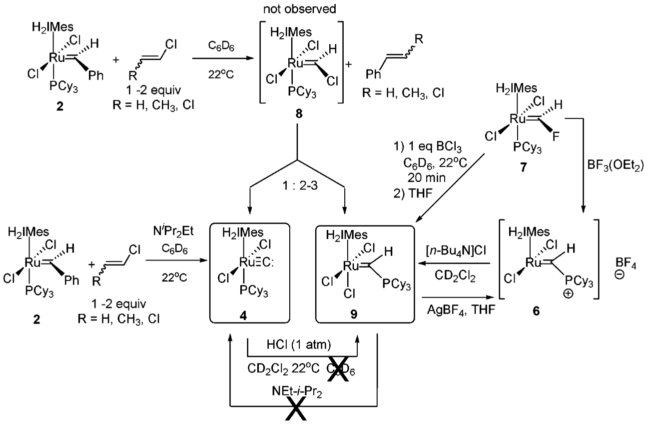


Figure 1. Plot of **9** (50% thermal ellipsoids). Selected bond distances (Å) and angles (°): Ru1−C1, 1.815(6); Ru1−C20, 2.021(5); C1−P1, 1.825(6); Ru1−Cl1, 2.4038(14); Ru1−Cl2, 2.3590(15); Ru1−Cl3, 2.3991(15); C1−Ru1−C20, 97.4(2); C1−Ru1−Cl1, 105.28(18); C1−Ru1−Cl2, 105.92(19); C1−Ru1−Cl3, 85.48(19); C20−Ru1−Cl1, 155.79(16); Cl2−Ru1−Cl3, 168.57(6); Ru1−C1−P1, 129.3(3). Selected dihedral angle: C20−Ru1−C1−P1, 150.7(4)°.

Chart 1. Important Carbene and Carbide Complexes



Scheme 1. Formation of Terminal Carbide and Phosphoniomethylidene Complexes



Formation of both **4** and **9** in reactions of **2** with vinyl chlorides implies loss of HCl. Accordingly, we investigated these reactions in the presence of NEt-*i*-Pr_2. Consumption of **2** occurred at a similar rate as in the absence of the base, but the product distribution changed: **4** formed quantitatively. Notably, NEt-*i*-Pr_2 fails to effect the conversion of **9** into **4** under these conditions. Thus, formation of **9** does not precede formation of **4** on the reaction pathway. It is

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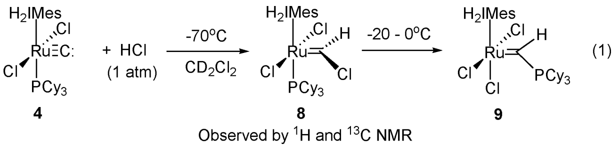
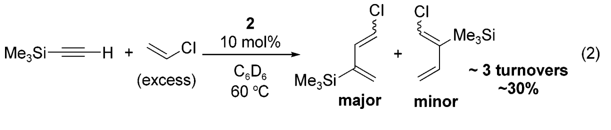
likely that both **4** and **9** form from a common intermediate such as a methylidyne complex of the form $[Ru(CH)(H_2IMes)(PCy_3)Cl_2]^+$ or $Ru(CH)(H_2IMes)(PCy_3)Cl_3$. Note, however, that neither of these putative intermediates has been observed in the Ru system, although we have prepared a closely related osmium complex, $[Os(CH)(PCy_3)_2Cl_2]OTf$.[10]

Complex **9**[11] is also formed upon reaction of ionic **6**$[BF_4]$ with $[n\text{-}Bu_4N]Cl$, as well as upon reaction of **4** at 22 °C with HCl in CD_2Cl_2 but not in C_6D_6 (Scheme 1). Given that BCl_3 has been used to convert difluorocarbene complexes into the corresponding dichlorocarbene species,[12] we examined the reaction of **7** with BCl_3 in benzene at 22 °C and in toluene at −40 °C. However, within 20 min, this afforded **6**$[BCl_{4-x}F_x]$ without observation of **8**. Upon addition of THF, conversion to **9** occurred (Scheme 1). Similarly, the reaction of **7** with $BF_3{\cdot}OEt_2$ produced **6**$[BF_4]$ directly in 70% isolated yield. In contrast, reaction of **7** with HCl or Me_3SiCl produces primarily **4**.[5] Although direct metathesis reaction at low temperature failed to produce **8**, addition of HCl (1 atm) to the headspace of a frozen solution of selectively ^{13}C-labeled **4**-^{13}C in CD_2Cl_2 followed by warming to −70 °C elicited a rapid color change from the pale yellow of **4** to red. Multinuclear NMR revealed complete consumption of **4**-^{13}C and formation of a single new complex (eq 1). Salient data for this compound include carbene resonances at δ 14.44 ($^1J_{HC} = 201$ Hz) and 268.1 in the ^1H and ^{13}C NMR spectra, respectively. On the basis of the similarity of these data to those for isolable **13** (Chart 1) and dissimilarity to cationic five-coordinate and neutral six-coordinate carbyne complexes,[7] we identify this compound as **8**-^{13}C. Upon increasing the temperature to −20 °C and then to 0 °C, **8** underwent conversion to **9** cleanly and quantitatively over ~2 h; no other species were observed (eq 1). In contrast, reaction of **4** with HO_3SCF_3 (HOTf) led directly to the formation of purple **6**[OTf] without any observable intermediate, even at −90 °C.



In order to demonstrate that a monochloromethylidene intermediate was being formed in the metathesis reactions as well, we sought to intercept it via enyne metathesis.[13] Addition of excess vinyl chloride to the headspace above a frozen C_6D_6 solution of **2** and 10 equiv of trimethylsilylacetylene[7] in a J. Young tube, followed by heating to 60 °C for 1 h, led to complete consumption of **2** and formation of a mixture of **4** and **9**. More importantly, GC−MS and ^1H NMR analysis revealed that a mixture of the products of enyne metathesis (eq 2) had formed in ~30% yield based on alkyne used, thus indicating three turnovers.



Styrene but no phenyl-containing butadiene compounds were observed, thus indicating that initiation occurred by reaction of vinyl chloride but not alkyne with **2**. This is consistent with the usual case, in which olefin metathesis is rapid and reversible, and it is the alkyne insertion that is slow, irreversible, and responsible for product selectivity.[14] The major diene product that we obtain is also best explained by alkyne insertion into the Ru═CHCl unit. Other paths that would lead to the same product are sterically disfavored, especially in the present case due to the presence of the bulky trimethylsilyl group.[14]

In summary, attempted CM of **2** with vinyl chloride yields styrene, the product of an initial metathesis cycle. However, the expected monochloromethylidene complex **8** is not observed. Instead, in the absence of added base, both the terminal carbide complex **4** and the phosphoniomethylidene complex **9** are formed; in the presence of NEt-*i*-Pr_2, only **4** is produced. However, NEt-*i*-Pr_2 does not convert **9** into **4**. Reaction of **2** with vinyl bromide is complicated by halogen exchange both among Ru complexes and with the vinyl halide itself, a result we are continuing to investigate. Nevertheless, complexes analogous to **4** and **9** are the major products in this case too. Attempted synthesis of **8** via reaction of the monofluoromethylidene complex **7** with BCl_3 instead produces **6** without observation of **8**. Low-temperature reaction of **4** with HCl in CD_2Cl_2 produces **8** as a thermally sensitive compound that undergoes conversion to **9** upon warming to −20 °C. We conclude that complex **8** is formed initially in CM but undergoes rapid conversion into **4** and **9**. Formation of these two complexes from unstable **8**, not failure to form **8**, accounts for the failure of attempted cross-metathesis reactions of vinyl chloride using catalysts such as **2**. We are currently investigating the reactions of 1,1-disubstituted monohaloolefins in order to identify reaction products when **4** and **9** cannot form. We are also probing the mechanisms of the **8** → **4** and **8** → **9** transformations in order to design more robust catalysts and to expand the scope of the enyne metathesis reaction.

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Supporting Information Available: Syntheses and characterization data for new compounds; X-ray structural data for **9**; conditions for reactions reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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