Olefin Metathesis

Rapidly Initiating Ruthenium Olefin-Metathesis Catalysts[**]

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Olefin metathesis is arguably the most powerful carbon–carbon bond breaking and making reaction in chemical synthesis.[1] Depending on the nature of the reacting partners, olefin metathesis can be used for ring-opening polymerization (ROMP),[2] to create advanced polymeric materials,[3] transformation of acyclic diene substrates into complex cyclic organic molecules (in ring-closing metathesis (RCM))[4] or polymers (in acyclic diene metathesis (ADMET))[5] or in cross metathesis (CM) to generate unsymmetrical olefins.[6,7] Although olefin metathesis is fully reversible, RCM, ADMET, and CM rely on the elimination of ethylene, the simplest olefin, as a thermodynamic driving force. Used by itself or in tandem with other synthetic transformations,[8,9] olefin metathesis is a versatile method for the modern synthetic chemist.

It is generally acknowledged that a metal carbene species, $\{L_nM{=}CRR'\}$, is required and that interaction with an olefin substrate leads to four-membered metallacyclobutane intermediates or transition states, $\{L_nM(CRR')_3\}$, by a 2+2 cycloaddition; cleavage of this intermediate in the opposite sense by which it was formed leads to olefin metathesis, creating a new carbon–carbon double bond and regenerating an active metal carbene. Metal carbenes are generally classified as being nucleophilic (electron rich) or electrophilic (electron poor) in character at the carbene carbon atom, but an effective olefin-metathesis catalyst exhibits behavior between these two extremes. Two carefully tuned classes of mediator have evolved into the catalysts of choice for olefin metathesis. Schrock catalysts[10,11] are molybdenum- or tungsten-based alkylidenes with a fairly specific ligand set designed to modulate the properties of the carbene (Figure 1). These catalysts display high activities and stabilities, but are sensitive to ambient air and moisture and are relatively intolerant of polar functionalities. The Grubbs-catalyst portfolio[12] consists of a variety of ruthenium-based systems of general formula $[Cl_2(L)(L')Ru{=}C(H)R]$ (compounds **1**) which are significantly more functional-group tolerant, but do not exhibit the same levels of activity or longevity as the Schrock catalysts.

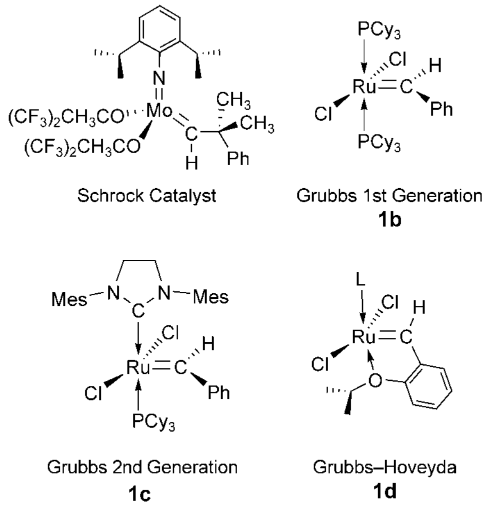

Figure 1. Commercially available olefin-metathesis catalysts. Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl.

The root of the lower activities of the Grubbs systems lies in their mode of initiation and the accessibility of the reactive species, which has been shown experimentally[13,14] and computationally[15,16] to be the 14-electron alkylidene $[Cl_2(L)Ru{=}C(H)R]$ formed upon reversible dissociation of L′. The reaction temperatures required to overcome this initiation step can lead to decreased catalyst lifetimes. Successful improvements to the "Grubbs first-generation" catalyst $[Cl_2(PCy_3)_2Ru{=}C(H)Ph]$ (**1b**) are modifications that either encourage loss of L′[17] or reduce the tendency of $[Cl_2(L)Ru = C(H)R]$ to re-capture the liberated L′,[18] which competes with the olefin substrate for the unsaturated metal center in $[Cl_2(L)Ru{=}C(H)R]$. Alternatively, Hoveyda and co-workers have developed catalysts **1d**, in which L′ is incorporated into a loosely chelating group associated with the carbene ligand that is removed upon the first metathesis event.[19,20] Fast-initiating improvements on this motif have been devised by Blechert and Wakamatsu.[21]

Herein we report a surprising twist on the Grubbs-catalyst motif that improves the kinetics of initiation dramatically by circumventing the initiation step in commercially available Grubbs catalysts completely, thus providing direct access to the reactive 14-electron catalyst species with no free L′ present to interfere with the operation of the catalyst. This new generation catalyst precursor is easily prepared from existing Grubbs catalysts and brings their activity into the realm of the Schrock family, while retaining the favorable functional-group tolerance associated with the ruthenium systems.

Recently, Heppert and co-workers reported a stoichiometric metathesis reaction between catalyst precursors **1b** and **1c** and a methylene cyclopropane olefin known as Feist's ester.[22] Metathesis and elimination of diethyl fumarate provides the unusual ruthenium carbides **2a–c** (Scheme 1).

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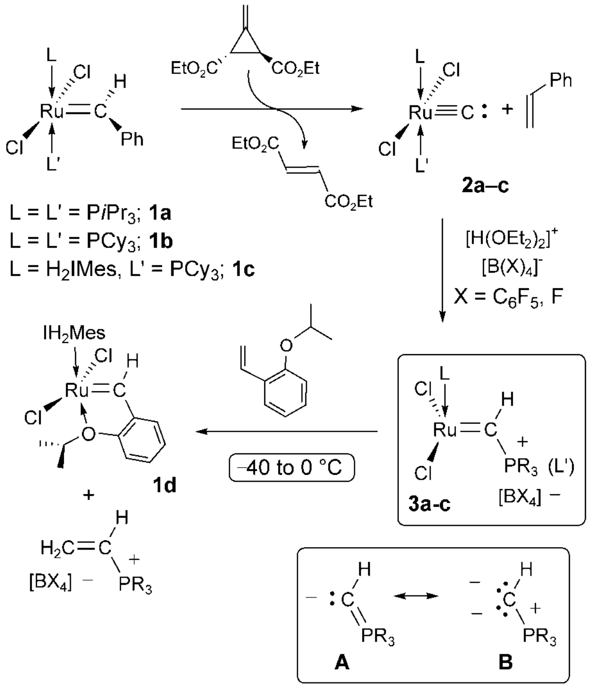


Scheme 1. Synthesis of rapidly initiating metathesis catalysts **3**; H_2IMes = N-heterocyclic carbene ligand.

Heppert and co-workers reported the preparation of carbides **2b** and **2c** in low yields; we have found this to be fairly a general reaction and a variety of carbides containing other combinations of L and L′ can be prepared in improved yields (90–96 %) from **2b** and **2c**. We became interested in the reactivity of these carbides with electrophiles and discovered that protonation with $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$, Jutzi's acid,[23] leads to the cationic four-coordinate, 14-electron phosphonium alkylidenes **3a**–**c** by transfer of a trialkylphosphine ligand (that is, L′, Scheme 1) to the protonated carbide carbon atom in high yields (87–95 %).[24]

Evidently, protonation of the carbide carbon atom switches it from being electron rich to electron poor; the electrophilicity of the protonated carbide carbon atom is quenched by transfer of the phosphine (L′) from the metal center, generating the observed phosphonium alkylidenes. For **3a** and **3b** (L = PR_3, R = *i*Pr or Cy), the signal for the alkylidene proton appears as a distinctive doublet of doublets in the proton NMR spectrum at $\delta = 17.35$ ppm for **3a** and 17.46 ppm for **3b** ($^2J_{H,P} = 36$ Hz; $^3J_{H,P} = 1.5 \pm 3$ Hz). In **3c**, where L = H_2IMes, the three-bond hydrogen–phosphorus coupling is lost and the alkylidene hydrogen resonance signal appears as a doublet at $\delta = 17.70$ ($^2J_{H,P} = 36$ Hz). In the $^{31}P\{^1H\}$ NMR spectra, the signals for the phosphonium phosphorus atoms appear in the region around $\delta = 54$–58 ppm, while those of the phosphorus nuclei bonded to ruthenium appear at $\delta = 97.6$ (**3a**) and 88.7 ppm (**3b**). These latter resonance signals, while shifted about 60 ppm downfield relative to those found for **1b** and **1c**, are similar to that observed for the four coordinate complex $[(t\text{BuO})_2(\text{PCy}_3)\text{Ru=C(H)Ph}]$ prepared by Grubbs and co-workers.[25] In **3c**, rotation of the IH_2Mes ligand about the Ru-C2 bond (see Figure 2) is fast on the NMR timescale, with a free energy barrier of 11.5(5) kcal mol^{-1} at 236 K calculated from the coalescence behavior of the NMR signals arising from the inequivalent mesityl groups at low temperature. This contrasts with the behavior for the parent compound **1c**, which exhibits slow rotation with a barrier of 21.8 kcal mol^{-1}.[26] Remarkably, when solutions of **3c** are exposed to the atmosphere, the NMR spectra remain unchanged for several hours, which indicates that the compound is stable to oxygen and ambient moisture. Indeed, introduction of water into these samples results only in minor perturbations to the spectra, owing to reversible coordination of H_2O to the ruthenium center. The compounds are thermally stable indefinitely in the solid state at room temperature and can be heated under refluxing CD_2Cl_2 (45 °C, sealed tube) for several hours with no evidence of decomposition. Heating at 75 °C in C_6D_5Br results in clean decomposition to an unidentified species ($^{31}P\{^1H\}$ NMR $\delta = 37$ ppm) with a half-life of approximately 5 h; the nature of this process is under investigation.[27] Preliminary studies show that the carbides can be converted into more economically viable BF_4 salts of cations **3a**–**c** by protonation with $[H(Et_2O)_x]^+[BF_4]^-$ with little change in the behavior of the compounds.

The precise structure of **3c** was determined by X-ray crystallography (Figure 2).[28] Compounds **3** represent the closest structural models for the proposed four-coordinate, 14-electron active species in the Grubbs-catalyst family; the only other structurally characterized example, the *bis-tert*-butoxide derivative $[(t\text{BuO})_2(\text{PCy}_3)\text{Ru=C(H)Ph}]$,[25] relies on the replacement of the chloride ligands with sterically bulky groups for kinetic stabilization, but is essentially inactive as an olefin metathesis catalyst. As in the *bis-tert*-butoxide complex, the geometry about the ruthenium center in **3c** is a distorted trigonal pyramid with the H_2IMes ligand occupying the apex; however, the Cl1-Ru-Cl2 angle is at 150.51(2)° substantially larger than the O1-Ru-O2 angle of 133.19(6)° in

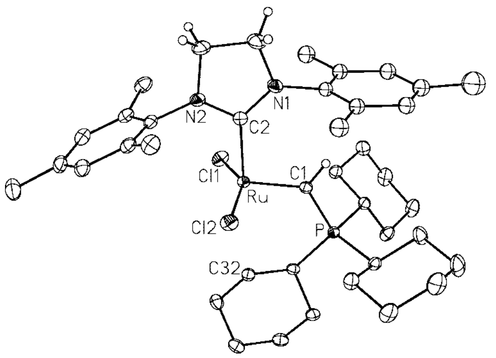


Figure 2. ORTEP diagram of **3c** (thermal ellipsoids set at 50 % probability; counteranion and hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru-C1 1.817(2), Ru-C2 1.988(2), Ru-Cl1 2.2951(5), Ru-Cl2 2.2809(5), P-C1, 1.805(2); C1-Ru-C2 100.07(7), Cl1-Ru-Cl2 150.51(2), Cl1-Ru-C1 103.15(6), Cl2-Ru-C1 102.79(6), Cl1-Ru-C2 96.14(5), Cl2-Ru-C2 92.90(5). Selected torsion angle [°]: C2-Ru-C1-P, −175.06(11).

[$(t\mathrm{BuO})_2(\mathrm{PCy_3})\mathrm{Ru{=}C(H)Ph}$]. The Ru-C1 and Ru-C2 bonds of 1.817(2) and 1.988(2) Å, are slightly shorter than those in **1c**,[17] a difference accounted for by the reduced coordination number in **3c**. The phosphonium alkylidene unit is oriented such that the PCy_3 group is pointing away from the IH_2Mes ligand. Angles and separations are normal within this part of the molecule and although C32 is positioned near a vacant ruthenium coordination site, any stabilization of the ruthenium center from the C–H sigma bonds of C32 is weak (Ru···C32 3.001 Å). No evidence for a C–H agostic interaction is observed in the proton NMR spectra, nor are low-frequency C–H vibrations apparent in the IR spectra of compounds **3**, which would be expected if any of the C–H bonds were donating electron density to the unsaturated ruthenium center.[29] Four-coordinate ruthenium complexes not stabilized by C–H agostic interactions are rare;[30] thus, apart from being models for the 14-electron active species in olefin metathesis, compounds **3** are unusual coordination compounds.

Metal carbenes are classified according to the donor qualities of the atoms directly bonded to the carbene carbon atom. Fischer carbenes incorporate π-donating groups (OR, NR_2), while the nucleophilic Schrock carbenes have π-neutral groups, such as H or alkyl substituents.[1] The phosphonium substituted carbenes of compounds **3** are a less common third class since the $[PR_3]^+$ group is a π acceptor.[31] Formally, this $CHPR_3$ ligand can be viewed as a deprotonated phosphorus ylid species (ylene resonance structure **A**, inset Scheme 1), but according to experimental[32] and computational[33] studies and the parameters for **3c** discussed above, a more realistic depiction is the dicarbanionic ylid resonance structure **B**. The ruthenium centers in compounds **3** may thus be viewed as formally Ru^{IV} with the carbene ligand functioning as a four-electron donor.

The electron-withdrawing nature of the phosphonium substituent in the carbene ligands of compounds **3** does not impede their ability to conduct olefin metathesis; they are exceptionally active RCM catalysts in comparison to catalyst precursors **1**. Using the RCM of diallyldiethylmalonate as a benchmark reaction, catalysts **1c** (Grubbs 2nd Generation), Schrock's molybdenum-based catalyst (Figure 1), the fast-initiating Grubbs catalyst [$(\mathrm{IH_2Mes})\mathrm{Cl_2}(3\text{-Br-py})_2\mathrm{Ru{=}CHPh}$],[34] and compounds **3b** and **3c** were compared at 0 °C by monitoring reaction progress to the cyclized product (Figure 3). At 0 °C **1c** is a poor initiator[18] and only reaches approximately 25 % conversion after 4 h. Compound **3b** fares somewhat better, providing about 90 % conversion after 4 h, while Schrock's catalyst mediates the reaction to a similar point in this time. The sigmoidal shape of the curve for **3b** is reflective of the different activities of initiating versus propagating species at 0 °C for this catalyst.[13] The transformation is very rapid for compound **3c**, however, which brings the reaction to > 90 % conversion after only 2 h at 0 °C, twice as fast as the Schrock catalyst under these conditions and, significantly, it out-performs the fast-initiating Grubbs catalyst incorporating more labile 3-bromopyridine ligands. Furthermore, the rate of RCM for **3c** is qualitatively similar to the best Blechert catalyst,[21b] a less conveniently available metathesis catalyst.

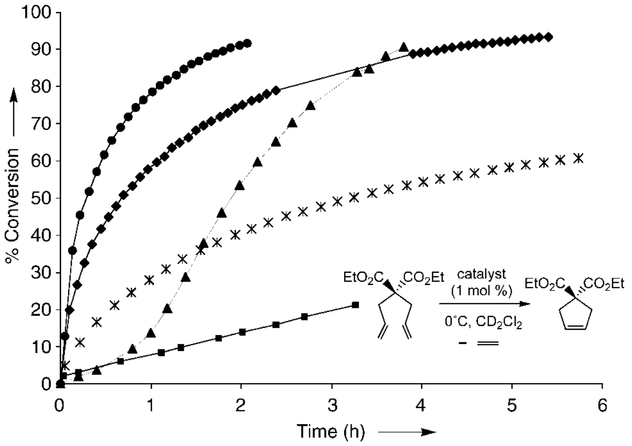
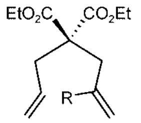
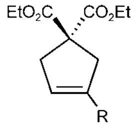
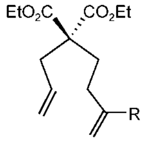
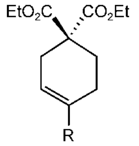
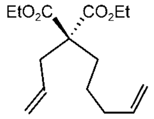
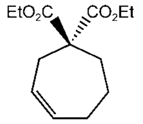


Figure 3. Relative rates of conversion for RCM of diethyldiallylmalonate at 273 K by (■) **1c**, (◆) Schrock's molybdenum alkylidene, (✱) the Grubbs fast-initiating catalyst [$(\mathrm{IH_2Mes})\mathrm{Cl_2}(3\text{-Br-py})_2\mathrm{Ru{=}CHPh}$], (▲) **3b**, and (●) **3c**.

We have also explored additional substrates for the RCM process with catalyst **3c** and initial results are summarized in Table 1. The reactions are completed within 2–60 min at room temperature (1 % mol catalyst loading, except entry 2 and 6). Diethyldiallylmalonate (entry 1) is ring-closed in under 2 min, this is determined as an upper limit since the reaction time is too fast to be accurately measured at room temperature. Using 0.1 % mol catalyst loading, a 100 % conversion is reached within 30 min (entry 2). Similar results are found in the formation of a six-membered ring (entry 4 and 5), while higher catalyst loadings are required to push the closing of a seven-membered ring to acceptable conversions (entry 6). Notably, the closing of trisubstituted olefins proceeds to high conversion, under very mild conditions (entries 3 and 5). In particular, formation of the trisubstituted cyclopentene is complete in less than 10 min (entry 3); this particular substrate allows a more direct comparison with Blechert's catalyst, which accomplished this conversion in 40 min, under otherwise identical conditions.[21]

The reason **3c** is so active is that the need to dissociate a ligand for the ruthenium complex to enter the catalytic cycle[13,18] has been completely obviated and initiation is now the much more energetically favorable binding of the substrate C=C bond to the ruthenium center. Rate constants for this process have been measured by monitoring the reaction of **3c** with varying excesses of *ortho*-isopropoxy styrene (10–40 equiv) at −30 to 0 °C by proton NMR spectroscopy. This substrate was chosen since it produces the Grubbs–Hoveyda catalyst **1d** (Figure 1), which is inactive towards further metathesis reactions at the temperatures used; the other product is [$(\mathrm{CH_2{=}CH})\mathrm{PCy_3}$][$\mathrm{B(C_6F_5)_4}$], which was identified by separate synthesis and comparison of ^1H and ^{31}P NMR spectroscopy data. Use of this less-active substrate slows the reaction down, but also avoids complications in the kinetics arising from the presence of multiple active species in the reaction.[35] These studies indicate that the reaction is second order, first order in each of [**3c**] and [styrene]

Table 1: Ring-closing metathesis using **3c**[a] at room temperature.

Entry	Substrate	Product	R	CL[b]	*t* [min]	Conversion [%][c]
1			H	1.0	<2	100
2			H	0.1	30	100
3			Me	1.0	<10	100
4			H	1.0	<10	100
5			Me	1.0	60	98
6			–	5.0	<10	85

[a] Conditions: room temperature, toluene, [diene] = 0.23 M. [b] Catalyst loading. [c] Conversions determined by ^{1}H NMR spectroscopy.

substrate, with a second order rate constant of $5.9 \pm 0.3 \times 10^{-4}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at −10 °C.[36] By evaluating this rate constant as a function of temperature (30 equiv of styrene), the thermodynamic activation parameters of the reaction were measured as $\Delta H^{\ddagger} = 8.6(4)\,\mathrm{kcal\,mol^{-1}}$ and $\Delta S^{\ddagger} = -55(6)$ eu. The large, negative activation entropy is consistent with a bimolecular initiation step, which supports the notion that the measured barrier corresponds to rate-limiting olefin binding. Nevertheless, even for this very unreactive substrate,[20] the magnitude of the second-order rate constant at −10 °C is comparable to the initiation rate of $4.6 \pm 0.4 \times 10^{-4}\,\mathrm{s}^{-1}$ measured at 35 °C for the widely used Grubbs second-generation catalyst **1c**.[18]

These results are an advance in the evolution of ruthenium-based olefin-metathesis catalysis. Slow initiation has been a limiting factor for the existing Grubbs-catalyst portfolio and the phosphonium alkylidene compounds disclosed herein circumvent this problem by effectively eliminating the phosphine-dissociation initiation step altogether. In essence, all of the ruthenium added is actually operating as a catalyst in these reactions as compared to the traditional Grubbs catalysts, where the majority of ruthenium is tied up as the non-active **1c**. In compounds **3**, initiation consists of the much lower barrier olefin-binding event; subsequent metathesis to liberate $[(\mathrm{CH_2{=}CH})\mathrm{PR_3}][\mathrm{B(C_6F_5)_4}]$ provides rapid and direct access to the propagating 14-electron ruthenium alkylidene complexes without any free phosphine present to drain the catalyst pool of active ruthenium.

The benefits of fast-initiating catalysts for a variety of metathesis applications are many. Lower catalyst loadings can be achieved which improves the economics and the environmental impact associated with use of these catalysts. Reactions can be performed at much lower temperatures, potentially providing greater enantioselectivity in asymmetric RCM reactions[37] and better chemoselectivity in commercially important CM processes.[38] In ROMP applications, rapid initiation leads to polymer products with narrower molecular-weight distributions.[39] Finally, the new compounds provide an opportunity to probe the mechanism of the propagating steps in the olefin metathesis reaction without the problem of excess phosphine in the reaction medium, as well as catalyst decomposition processes that do not involve the dissociated phosphine ligand of catalysts **1**.[40]

Experimental Section

Complete experimental details, including synthesis and characterization of all the new compounds, can be found in the Supporting Information.

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[28] Crystal data for **3c**: $C_{64}H_{60}BCl_2F_{20}N_2PRu$, $M_r = 1450.89$, triclinic, $P\bar{1}$, $a = 12.0671(6)$ Å, $b = 16.4448(9)$ Å, $c = 17.6951(9)$ Å, $\alpha = 102.1701(8)°$, $\beta = 108.1299(8)°$, $\gamma = 102.6938(9)°$, $V = 3104.4(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.552$ g cm^{-3}, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = -80$ °C, 23973 measured reflections, 12683 unique ($R_{int} = 0.0168$), 11455 reflections with $I_{net} > 2.0(I_{net})$, $\mu = 0.467$ mm^{-1}, min/max transmission = 0.7732 and 0.8803, $R1$ ($I > 2\sigma$) = 0.0310, $wR2$ 0.0822, GoF = 1.037, No. of parameters = 820, final difference map within $+0.686$ and -0.392 e Å^3. CCDC-243766 (**3c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[35] Attempts to determine rate constants by monitoring the ring closing of diallyldiethylmalonate gave nonlinear plots because, even at −60 °C, the alkylidene product of initiation was active for turning the reaction over, as evidenced by the slow build-up of ethylene in the sample over time.

[36] The pseudo first-order plots from which the rate constants were obtained are linear for the duration of the reaction after a region of curvature at the beginning of the reaction (see Supporting Information). The origins of this kinetic behavior are not currently understood; further investigations are underway.

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