

# Olefin metathesis for metal incorporation: Preparation of conjugated ruthenium-containing complexes and polymers

Sarah L. Bolton, Danielle E. Schuehler, Xiang Niu<sup>1</sup>, Lakshmi Gopal<sup>2</sup>, Michael B. Sponsler<sup>\*</sup>

*Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100, USA*

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## Abstract

Olefin Metathesis for Metal Incorporation (OMMI) was used for the stoichiometric attachment of ruthenium to both small and large polyenes. The dinuclear complexes  $(\text{PCy}_3)_2\text{C}_1\text{Ru}=\text{CH}(\text{CH}=\text{CH})_n\text{CH}=\text{Ru}(\text{PCy}_3)_2\text{Cl}_2$  ( $n = 1, 2$ ), were prepared by reacting 2 equiv. of the Grubbs first-generation catalyst  $(\text{PCy}_3)_2\text{C}_1\text{Ru}=(\text{CHPh})$  with 1 equiv. of the appropriate polyene (1,3,5-hexatriene for  $n = 1$  and 1,3,5,7-octatetraene for  $n = 2$ ). Use of excess hexatriene led to the formation of the monoruthenium complex  $(\text{PCy}_3)_2\text{C}_1\text{Ru}=\text{CHCH}=\text{CHCH}=\text{CH}_2$ . The mono- and di-ruthenium complexes exhibited marked differences in their spectroscopic and electrochemical properties, in addition to their *Z-E* isomerization rates. Nucleophilic attack of  $\text{PCy}_3$  on the end  $\text{CH}_2$  of the mono complex was observed, leading to both isomerization and phosphonium products. Extending the OMMI strategy to the second-generation catalyst was also done, despite the reduced initiation rate. The more reactive catalyst  $(\text{H}_2\text{IMes})\text{RuCl}_2=(\text{CHPh})(3\text{-bromopyridine})_2$  allowed for ruthenium incorporation into polyacetylene, leading to the formation of polymers and oligomers with high ruthenium content.  
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**Keywords:** Olefin metathesis; Ruthenium; Alkylidene

## 1. Introduction

For the purpose of preparing new ruthenium containing complexes and materials, we have explored a stoichiometric variation of olefin metathesis in which the catalytic cycle [1] is effectively stopped following the first cycloreversion. In this method, which we will call olefin metathesis for metal incorporation (OMMI), the “catalyst” acts as a stoichiometric reagent and is incorporated into the product as shown in Fig. 1. This method can be used to synthesize both mono- and di-nuclear ruthenium complexes, depending on the number of metathesis sites the olefinic ligand contains and the stoichiometry employed.

The OMMI process, though not by that name, has been used for over a decade to prepare several early (including

Ta [2], Cr [3,4], Mo [3–5], W [3,4,6], and Re [7]) and late (mainly Ru) transition metal catalysts. Derivatives of the Grubbs first-generation catalyst  $(\text{PCy}_3)_2\text{C}_1\text{Ru}=(\text{CHPh})$ , **G1** including the Hoveyda–Grubbs catalyst [8], heterobimetallic complexes [9], and several different alkylidene complexes [10,11] have been prepared using this strategy. OMMI has also been reported in sulfur-rich Ru complexes [12] and on ruthenium surfaces [13]. Our efforts have been directed specifically at preparing conjugated complexes for the study of electronic properties and potential application in molecular electronics. Complexes with metal centers linked by  $\pi$ -conjugated bridges have potential as molecular wires [14], molecular switches [15], and NLO chromophores [16], and olefin metathesis is a convenient way to make such molecules.

In 2000, we reported the preparation of diruthenium **1** and monoruthenium **2** from the reaction of **G1** with 1,3,5-hexatriene in different ratios (Scheme 1) [17]. That report focused on the *Z-E* isomerization of these and related complexes, including experimental and computa-

<sup>\*</sup> Corresponding author. Tel.: +1 315 443 4880; fax: +1 315 443 4070.  
E-mail address: [sponsler@syr.edu](mailto:sponsler@syr.edu) (M.B. Sponsler).

<sup>1</sup> Currently with Eisai Research Institute, Andover, MA.

<sup>2</sup> Currently with Materials Modification Inc., Fairfax, VA.

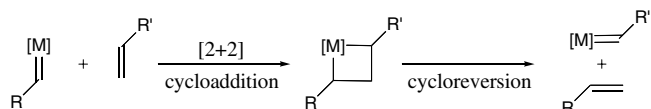
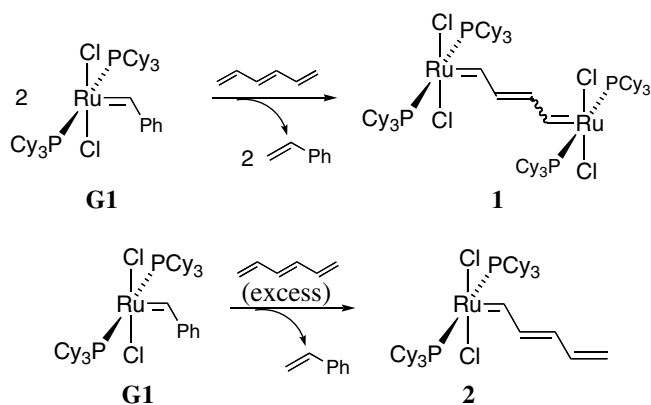


Fig. 1. In Olefin Metathesis for Metal Incorporation (OMMI) the incoming alkylidene (=CHR') replaces the original alkylidene (=CHR) generating a new organometallic complex in stoichiometric amounts.



Scheme 1.

tional analyses of mechanisms. This contribution, while adding some insights into isomerization mechanisms, is meant to present our work using OMMI in a number of contexts, illustrating some of the ways this method might be useful in the preparation of ruthenium containing molecules and materials.

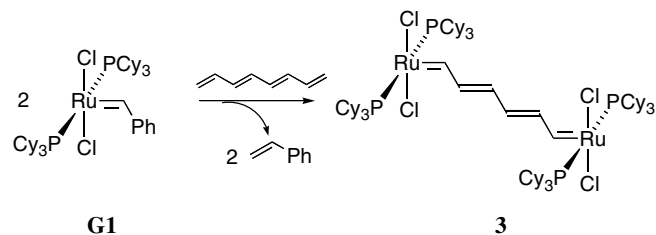
## 2. Results and discussion

### 2.1. Incorporation of the first-generation Grubbs catalyst

When a purple  $\text{CH}_2\text{Cl}_2$  solution of **G1** (2 equiv.) was treated with 1 equiv. of hexatriene, the color changed immediately to red, the color of **1** in solution (Scheme 1) [17]. Synthesis of mononuclear **2** was done identically except that excess hexatriene was used. The stereochemical details for **1** and **2** were very different [17]. Complex **1** was obtained as a 10:1 mixture of the *E* and *Z* isomers (**1E** and **1Z**) regardless of whether *E*- or *Z*-hexatriene (or a mixture) was used in the synthesis. Signals for both **1E** and **1Z** were visible in the  $^1\text{H}$  NMR spectrum, but coalescence occurred above  $100^\circ\text{C}$ . By extrapolation, the room temperature isomerization rate of **1** was found to have a half-life of 11 s. In contrast, separated *E* and *Z* isomers of **2** were readily prepared from *E*- or *Z*-hexatriene. Isomerization of **2Z**–**2E** proceeded in  $\text{CH}_2\text{Cl}_2$  solution with an 8 h half-life at room temperature. Also different was the dependence of the isomerization rates on additives; for example, added  $\text{PCy}_3$  had no effect on the isomerization of **1** but dramatically accelerated the isomerization of **2** (see Section 2.3).

In analogous fashion, OMMI was used to prepare the  $(\text{CH})_6$ -bridged complex **3** by using *E,E*-1,3,5,7-octatetraene

(Scheme 2). The  $^1\text{H}$  NMR spectrum of **3** shows an AA'BB'XX' pattern for the bridge hydrogens with coupling constants of  $J_{\alpha\beta} = 10.8$ ,  $J_{\beta\gamma} = 14.7$ ,  $J_{\gamma\gamma'} = 11.8$ ,  $J_{\alpha\gamma} = -0.6$ , and  $J_{\beta\gamma'} = -0.9$  Hz (Fig. 2).



Scheme 2.

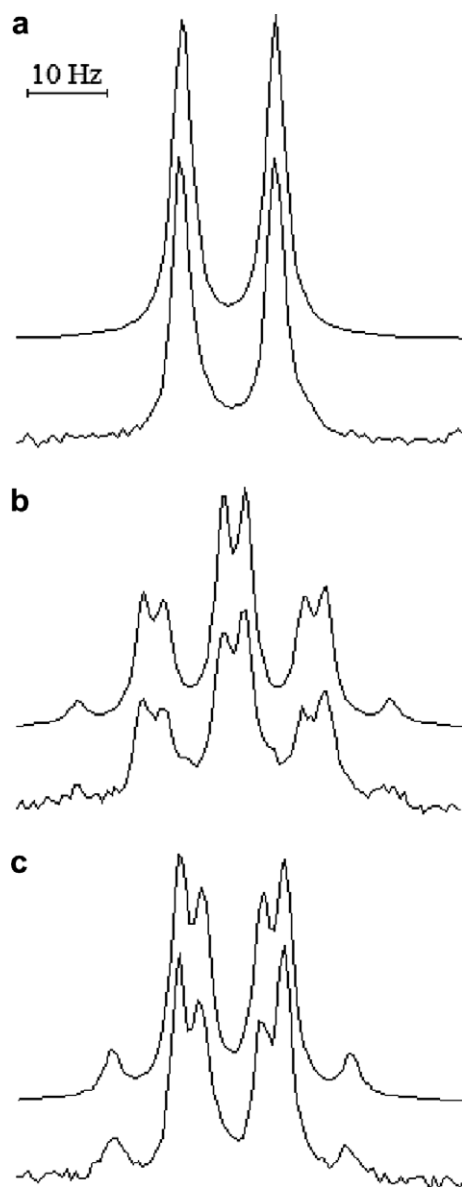
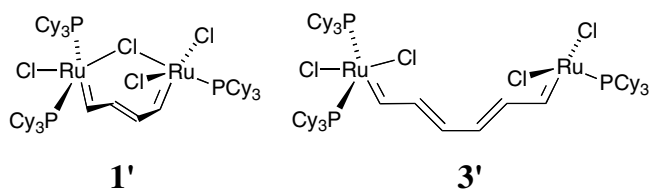


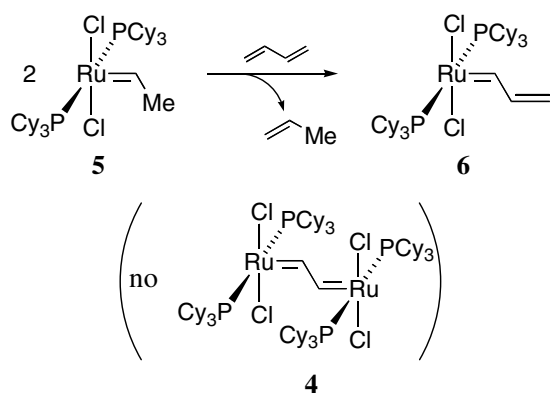
Fig. 2. Simulated (top) and experimental (bottom)  $^1\text{H}$  NMR signals for (a)  $\text{H}_\alpha$ , (b)  $\text{H}_\beta$ , and (c)  $\text{H}_\gamma$  in **3**. Each signal represents part of an AA'BB'XX' pattern at 300 MHz.

In contrast to **1**, only one  $H_z$  peak was observed for complex **3**, implying that only one isomer was formed. The coupling constants are consistent with the *E,E* isomer. An alternative explanation is that the isomerization is much faster for **3**, such that the observed signals represent averaged *E–Z* signals. We prefer the opposite explanation: that isomerization is much slower for **3**, and that the *E,Z* and *Z,Z* isomers are not observed because they are unstable, perhaps reacting through cyclization processes. Complex **3** is less stable in solution than **1**, decomposing on a several-hour time frame. That isomerization would be slower in **3** is consistent with the primary isomerization mechanism proposed for **1**: a metathesis-like electrocyclic closure to a ruthenacyclobutene followed by reopening [17]. The fast isomerization of **1** was proposed to result from a seven-membered ring Cl-bridge chelation that can occur in the phosphine-loss intermediates of both isomers (*E* shown as **1'**), stabilizing the isomerization intermediates and transition states. A similar nine-membered chelation would be impossible in the isomerization of the *E,E* isomer of **3** (shown as **3'**).

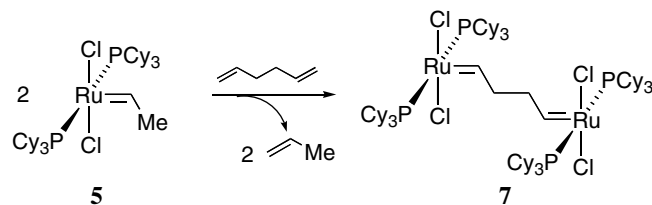


1,3-Butadiene was used in an attempt to prepare the shorter bridged complex **4** (Scheme 3). Molecular mechanics calculations suggest that **4** is a potentially stable complex, with the  $PCy_3$  ligands on one ruthenium nesting between those on the other. The monoruthenium complex **6** [10b] was observed as the only ruthenium product from the reaction of butadiene with even the exceptionally reactive ethylidene analog **5** [10b] (2 equiv.). Reaction of isolated **6** with **5** also failed to produce the bridged complex **4**.

The use of OMMI for preparation of complexes **1**, **2**, and **3** is aided by metathesis equilibria that favor these



Scheme 3.



Scheme 4.

products, an apparent consequence of the conjugation present in the products. Indeed, OMMI using **G1** and 1,5-hexadiene was unsuccessful for the synthesis of the diruthenium complex **7**, due to an unfavorable metathesis equilibrium. When **5** was used in place of **G1** (Scheme 4), the equilibrium was more favorable, and the reaction was driven to completion by removal of the propene byproduct.

Complexes **1** and **2** might be expected to exhibit interesting properties due to electronic delocalization across the bridge. Polyene segments can provide for long-distance electronic coupling through  $\pi$  interactions. One consequence of such coupling is the differentiation of first and second oxidation or reduction potentials as observed in a cyclic voltammogram (CV). The CV of **1** at  $-78^\circ C$ , shown in Fig. 3, shows two oxidation waves and two reduction waves, indicating the existence of five oxidation states. The observed potentials for **1**, **2**, **5**, and **7** are given in Table 1. These results show that conjugation has little effect on oxidations in these complexes but very marked effects on reductions. This is in agreement with DFT calculations on the  $PH_3$  analog of **1** [17], which shows that the HOMO is not associated with the bridge  $\pi$  system, while the LUMOs are associated with the  $\pi$  system. Attempts were made to collect electrochemical data also from **3**. Complex **3** exhibited redox activity similar to that of **1**, however due to the apparent decreased stability of the oxidized and reduced forms of **3**, meaningful potentials could not be obtained. Methods of stabilization for the bridged complexes are currently being explored.

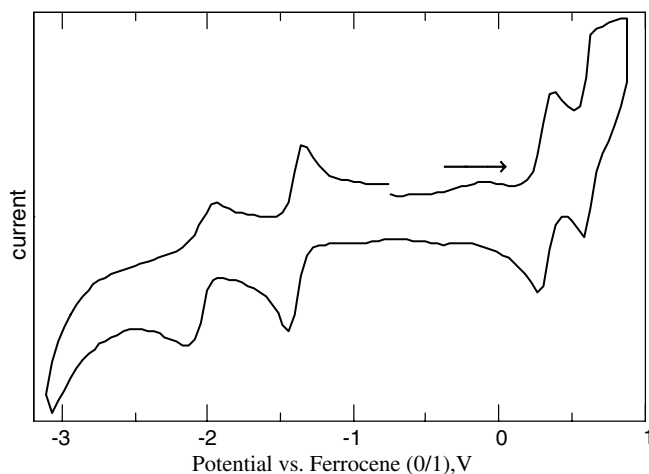
Fig. 3. Cyclic voltammogram of **1** in THF.

Table 1  
Cyclic voltammetry (THF) and UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>) data

Compound	$E'_0(V)$	$E''_0(V)$	$E'_0(V)$	$E''_0(V)$	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (M <sup>-1</sup> cm <sup>-1</sup> )
<b>1</b>	-2.04	-1.39	0.31	0.66	438	17000
<b>2</b>		-2.0 (irrev.)	0.25		343	9600
<b>3<sup>a</sup></b>					450	23000
<b>5</b>			0.4			
<b>7</b>			0.40	0.69	Tail	

<sup>a</sup> The CV data for complex **3** did not provide meaningful potentials.

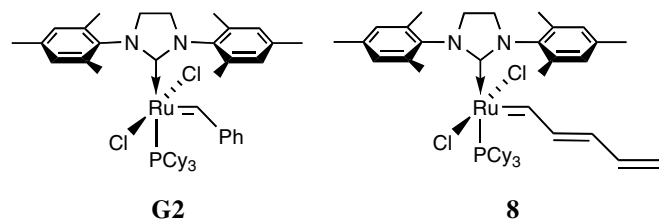
A molecular mechanics calculation [18] on **1** indicates that the phosphine ligands on the two ruthenium centers are in close proximity. This steric crowding does not lead to appreciable strain but does provide a shield around the bridge. The lower degree of ligand shielding in complex **3**, due to the lengthening of the bridge may account for the decreased stability. Complexes **1** and **3** were observed to be metathesis active, as excess hexatriene or octatetraene could be used to convert these complexes to the corresponding monoruthenium complexes [19].

The UV–Vis spectra of **1–3** and **7** (Fig. 4 and Table 1) are suggestive of strong conjugation in **1** and **3**. Both **1** and **3** show strongly red-shifted ( $\geq 95$  nm) and much more intense absorptions relative to the mononuclear **2** and the non-conjugated **7**. For comparison, the visible absorption of the Ru(II)–Ru(II) oxidation state of the Creutz-Taube ion, [(NH<sub>3</sub>)<sub>5</sub>Ru(pyrazine)Ru(NH<sub>3</sub>)<sub>5</sub>]<sup>4+</sup> (547 nm), is red-shifted by 75 nm relative to that of the mononuclear [(NH<sub>3</sub>)<sub>5</sub>Ru(pyrazine)]<sup>2+</sup> (472 nm) [20].

## 2.2. OMMI in the second generation

Though Grubbs' second-generation catalyst ((H<sub>2</sub>IMes)–RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>), **G2**) is a more active metathesis catalyst than the first-generation catalyst (**G1**), it is a less reactive reagent for OMMI. This is easily understood based upon mechanistic data reported by Grubbs and coworkers that show that the activity of **G2** comes in spite of a significantly slower initiation step, corresponding to the loss of PCy<sub>3</sub> from the complex [21]. In other words, the catalysis done by **G2** is typically the result of a small

portion of the catalyst that initiates through the loss of PCy<sub>3</sub> to form a highly active intermediate. The activity of this intermediate partly derives from its strong preference to bind olefins rather than PCy<sub>3</sub>. For a stoichiometric reaction like OMMI, the initiation step is all-important: the entire sample is needed for reaction, not just an active portion.



The consequence of the slower initiation of **G2** is that OMMI reactions take 6–10 h rather than <5 min for **G1**. Reaction of **G2** with excess hexatriene cleanly produced the anticipated monoruthenium complex **8** after 10 h as determined by <sup>1</sup>H NMR spectroscopy.

Faster-initiating analogues to **G2** have appeared in the catalysis literature. A popular alternative is the 3-bromopyridine complex **G2B** [22]. With this complex, preparation of **8** was accomplished very quickly: reaction of **G2B** with excess hexatriene for a few minutes, followed by addition of PCy<sub>3</sub>. We recently reported that the alkylidenes **9** (R = Me, Et, Pr) also offer faster initiation [11]. While the first-generation ethylidene **5** offers advantages for OMMI based on metathesis equilibrium and volatile propene byproduct (see above), the analogous second-generation complexes are also of value for their faster dissociation of PCy<sub>3</sub>. OMMI reactions of these complexes are generally complete in less than an hour.

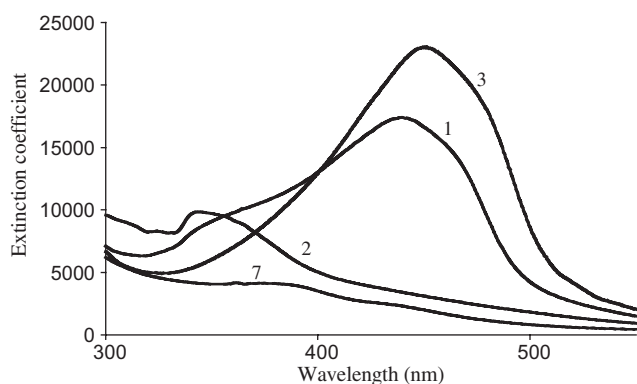
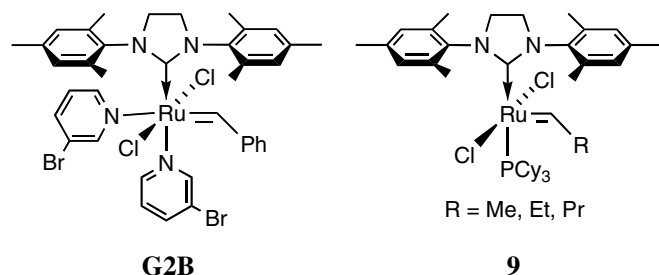


Fig. 4. UV–Vis spectra (CH<sub>2</sub>Cl<sub>2</sub>).

Another difference between the first- and second-generation complexes is the greater steric bulk of the H<sub>2</sub>IMes ligand. This was demonstrated by attempts to prepare the diruthenium complex by reaction of 2 equiv. **G2** (or the more reactive **G2B** followed by PCy<sub>3</sub>) and 1 equiv. hexatriene: only the monoruthenium **8** was formed, presumably because the short four-carbon bridge would draw the ligands into prohibitive steric contact. Reactions with octatetraene successfully produced both the mono- and diruthenium complexes.

### 2.3. Isomerization by nucleophilic attack

During our investigation of **1** and **2**, the isomerization of **2Z**–**2E** was found to be accelerated by PCy<sub>3</sub>, apparently through a nucleophilic conjugate addition-elimination mechanism. Nucleophilic attack on unsaturated organic ligands coordinated to transition metals has been a powerful method in organic and organometallic synthesis [23]. In ruthenium metathesis catalysts, similar nucleophilic attack at the carbene carbon has been shown to account for catalyst decomposition [24]. As monosubstituted complexes are either targets or intermediates of OMMI, we sought to better understand the consequences of such nucleophilic reactions in complex **2**.

When **2Z** was treated with 1–2 equiv. PCy<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>, isomerization to **2E** was observed along with the formation of two new phosphonium products (**10** and **11**) in an approximate 1:1 ratio (Scheme 5) [17]. These products were apparently formed through trapping of the zwitterionic addition intermediate **12** by addition of H<sup>+</sup> and abstraction of H<sup>−</sup>, respectively. The proton source was determined to be CH<sub>2</sub>Cl<sub>2</sub> by using CD<sub>2</sub>Cl<sub>2</sub> and observing the deuterated form of **10** by <sup>1</sup>H and <sup>2</sup>H NMR. The carbenoid formed from deprotonation of CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>2</sub><sup>−</sup> is known to effect abstraction of hydride (presumably through the carbene, CHCl) [25]. This mechanistic explanation also accounts for the observed 1:1 ratio of **10** and **11**. The observed isomerization suggests that rotation about the C<sub>β</sub>–C<sub>γ</sub> bond is fast in **12** and that elimination of PCy<sub>3</sub> from **12** is competitive with protonation. To further support the mechanism, the addition of an acid, *i*Pr<sub>2</sub>NH<sup>+</sup>PF<sub>6</sub><sup>−</sup>, led to the formation of only **10** and the use of a base strong enough to deprotonate CH<sub>2</sub>Cl<sub>2</sub>, LDA, or *n*BuLi, showed a preference for the formation of **11**.

In benzene, a less polar solvent, the rate of isomerization of **2Z** in the presence of PCy<sub>3</sub> was slower than in CH<sub>2</sub>Cl<sub>2</sub>, consistent with the weaker solvation of the zwitterionic **12**. Nonetheless, isomerization of **2Z** in benzene was accelerated about six times by the addition of 0.5 equiv. of PCy<sub>3</sub>, suggesting that **12** was still formed. Starting with **2E**, the minor extent of the reverse isomerization to **2Z**

was also observable; the equilibrium constant ([**2E**]/[**2Z**]) was observed to be approximately 15. As expected, **10** and **11** were not observed as products in benzene.

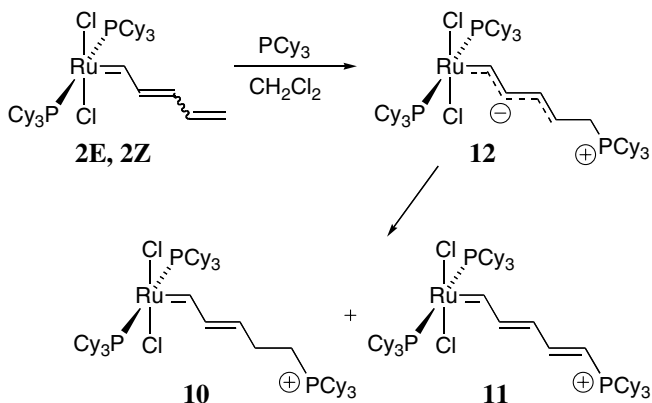
Diisopropylamine, dimethylsulfide, and tetraethylammonium chloride were all ineffective nucleophiles for either isomerization of **2Z** or production of analogous nucleophilic attack products. Additionally, nucleophilic attack products were not observed with the addition of PCy<sub>3</sub> to **8**.

### 2.4. Metal-incorporated polyacetylene (MIPA)

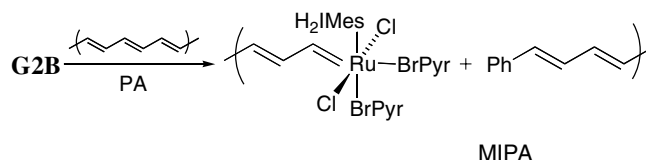
Metal-incorporated polyacetylene (MIPA) is a metalla-polyene material prepared following the OMMI strategy. Freshly prepared, high surface area polyacetylene (PA) underwent a metathesis reaction with **G2B** leading to the incorporation of up to 72% **G2B** by mass into the polymer [26], producing MIPA (Scheme 6). Efficient reaction with the disubstituted olefinic bonds of polyacetylene required the more highly reactive **G2B**; neither **G1** nor **G2** led to extensive OMMI. The MIPA produced had properties distinct from PA and attributable to the Ru centers. In addition to producing an interesting material, this work joins the subjects of two recent Nobel Prizes, namely olefin metathesis (2005) [27] and polyacetylene (2000) [28].

Our initial attempts to produce MIPA, using two known forms of PA, were only marginally successful. PA films were prepared by the methods of Grubbs (ring-opening metathesis polymerization of cyclooctatetraene with **G2** [29]) and Shirakawa (polymerization of acetylene with a Zeigler-Natta catalyst [30]), and these films were treated with concentrated solutions of **G1**, **G2**, and **G2B**. The films noticeably gained mass only when treated with **G2B**, but the increases were small (≤6%). Since both types of PA films are densely packed, we suspected that the inefficient OMMI was due to the low surface area of the polymer.

We recently reported that **G2B** is an efficient catalyst for the polymerization of acetylene [31]. When a concentrated **G2B** solution was added to spongy samples of freshly polymerized PA from the reaction of dilute **G2B** and acetylene, high levels of ruthenium incorporation into the washed polymer were observed (up to 72% by mass, corresponding to one **G2B** center for every 24 acetylene units). The efficient OMMI reaction was presumably a direct result of the open morphology and high surface area of this type of PA. The effectiveness of OMMI in the case of PA is notable, given that there are remarkably few examples of



Scheme 5.



Scheme 6.

post polymerization chemical reactions of PA, excluding redox doping, due to the insolubility of the material [32]. When the surface area was reduced by compression (by filtration, for example), irreversibly forming densely packed PA films, the ruthenium incorporation (6%) was very similar to that observed for the PA films formed by the other methods.

MIPA samples have been characterized by a variety of methods [33]; however, our goal in this report is primarily to establish that the [Ru] centers are covalently attached to the polymer. Electronic spectroscopy offers suggestive evidence: the visible absorption observed at 645 nm for PA was red-shifted to 676 nm, with a shoulder at 780 nm, for a sample of MIPA. This red-shift is consistent with the incorporation of ruthenium centers, based upon our results for **1** and **2**.

The most direct evidence that [Ru] centers were covalently attached in the MIPA samples relates to metathesis activity. For example, when samples of MIPA (20 and 26% [Ru], having been washed until the washings were colorless) were treated with 1-octene, washings were then orange. After drying, the polymer masses decreased by approximately the calculated amount of [Ru] in the polymer. This indicates that the [Ru] in MIPA was covalently attached and was cleaved from the polymer by metathesis. Also, when a sample of MIPA (33% [Ru] by mass) was suspended in  $\text{CHCl}_3$  and acetylene was bubbled through the mixture for 1 h, the sample increased in mass by 40%, indicating that more of the monomer was incorporated.

The incorporation of redox-active metal centers into PA could potentially affect the conductivity in either direction, but we have observed no signs of significant conductivity in the MIPA samples either before or after redox doping. Doping with iodine, a procedure that yielded metallic conductivities with PA [34], did not increase the conductivity of MIPA samples. Chemical single-electron redox agents likewise did not produce conducting samples.

A striking result is that the visual appearance and the polymer handling properties of MIPA samples with as much as 72% [Ru] are remarkably similar to the properties of PA. Both are black, insoluble powders that can be pressed into sturdy, shiny films (silver for PA, light gold for MIPA).

### 3. Experimental

#### 3.1. General

All reactions were performed under nitrogen using standard Schlenk techniques or in an inert atmosphere glovebox (MBraun MB 150 M). All solvents (benzene, dichloromethane, pentane, THF) were distilled under nitrogen from calcium hydride. Deuterated solvents ( $\text{CD}_2\text{Cl}_2$ ,  $\text{CDCl}_3$ , and  $\text{C}_6\text{D}_6$ ) were vacuum transferred from calcium hydride after standing for 2 days. All reagents were obtained from common commercial sources unless other-

wise stated and were used as received. 1,3,5,7-Octatetraene was prepared according to the literature procedures [35] and stored under nitrogen at  $-25^\circ\text{C}$ . The molarity of the 1,3,5,7-octatetraene was found by comparison to an internal standard of dichloroethane or benzene.  $i\text{Pr}_2\text{NH}_2^+\text{PF}_6^-$  was prepared by mixing equimolar amounts of  $\text{NH}_4^+\text{PF}_6^-$  and  $i\text{Pr}_2\text{NH}$  in  $\text{CH}_2\text{Cl}_2$  and removing solvent and  $\text{NH}_3$  by vacuum. The Grubbs first generation catalyst (**G1**) was purchased, purified by precipitation of a  $\text{CH}_2\text{Cl}_2$  solution into methanol, and stored under nitrogen. All  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{C}_6\text{D}_6$ ,  $\text{CD}_2\text{Cl}_2$ , or  $\text{CDCl}_3$  on a 300 MHz Bruker-300 spectrometer or 600 MHz DRX-600 spectrometer. All  $^{31}\text{P}$  NMR spectra were collected in  $\text{C}_6\text{D}_6$  using a 500 MHz Bruker-500 spectrometer or 600 MHz DRX-600 spectrometer. All chemical shifts are referenced to TMS by using known shifts of residual proton or carbon solvent signals or to external 85% phosphoric acid ( $^{31}\text{P}$  NMR). NMR simulation of the AA'XX'YY' patterns for **2** was done using SwaN-MR. UV/Vis spectra were recorded on a Cary 50 spectrophotometer. Mass spectrometry was done using a Shimadzu LCMS-2010A. Elemental analysis was performed by E & R Microanalysis Co., Parsippany, NJ.

Conductivity values were measured using a Signatone four-point probe (SP4-40045OFS) and an Abtech Independently Addressable Microband Electrode with 5  $\mu\text{m}$  spacings. Lower limit values ( $\leq 10^{-8}$  S/cm) were obtained by using two probe points connected to an electrometer. Higher values were obtained by the standard four-point probe method. Iodine doping was performed by placing a film under vacuum on a vacuum line and then exposing it to iodine vapor for 1 h and then vacuum for 1 h.

#### 3.2. Electrochemical experiments

Cyclic voltammograms were recorded by using a Pine AFRDE4 potentiostat with computer data collection. A single-chambered cell was used with Pt disk working electrodes and a silver wire as pseudoreference. All reported measurements were done at  $-78^\circ\text{C}$  under nitrogen with  $5 \times 10^{-4}$  M analyte, 0.1 M  $\text{Bu}_4\text{NPF}_6$  as electrolyte, and THF as solvent. 1,1'-Dimethylferrocene was added at the end of each experiment as an internal reference. Separate measurements showed that the potential of this reference is  $-0.10$  V relative to the ferrocene/ferrocenium couple, the reference relative to which all potentials are reported. Each compound was studied with scan rates from 50 to 800 mV/s. In general, results were not significantly dependent on scan rate.

#### 3.3. $[(\text{Cy})_3\text{P}_2\text{Cl}_2\text{Ru}]_2(\mu\text{-CHCH=CHCH=CHCH})$ (**3**)

To a solution of  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (72 mg, 87  $\mu\text{mol}$ ) in benzene (2 mL) was added 41  $\mu\text{l}$  (36  $\mu\text{mol}$ ) of 0.089 M 1,3,5,7-octatetraene. The mixture was stirred at room temperature for 2 min; the solvent was removed by freeze-drying under vacuum. The stoichiometry was

confirmed by using  $^1\text{H}$  NMR integration and adjusted if necessary. The resulting residue was repeatedly washed with pentane until the washings became almost colorless. The residue was again freeze-dried under vacuum for 3 h. An orange–brown microcrystalline solid was obtained. In some cases **3** was recovered from the pentane layer and purified by passing through 3–5 cm of silica in a pipette with benzene. Yield: 16.4 mg (34%). The compound was soluble in benzene but began to precipitate after 2 h, was soluble in  $\text{CH}_2\text{Cl}_2$ , and was partially soluble in pentane. The compound was indefinitely stable in the solid state under nitrogen at room temperature, was stable in benzene solution for over 48 h, and in  $\text{CH}_2\text{Cl}_2$  solution for up to 5 h at room temperature.  $^1\text{H}$  NMR:  $\delta$  20.04 (A part of AA'XX'YY',  $J_{\alpha\beta} = 10.8$  Hz,  $J_{\beta\gamma} = 14.7$  Hz,  $J_{\gamma\gamma'} = 11.8$ ,  $J_{\alpha\gamma} = -0.6$  Hz,  $J_{\beta\gamma'} = -0.9$  Hz, 2H,  $\text{H}_\alpha$ ), 8.82 (X part of AA'XX'YY', 2H,  $\text{H}_\beta$ ), 6.68 (Y part of AA'XX'YY', 2H,  $\text{H}_\gamma$ ), 2.84, 2.03, 1.82, 1.56, 1.30 (all m,  $\text{PCy}_3$ , 132H).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  37.5.  $^{13}\text{C}$  NMR could not be obtained due to the insolubility or instability of the complex in NMR solvents. Anal. Calc. for  $\text{C}_{78}\text{H}_{138}\text{Cl}_4\text{P}_4\text{Ru}_2$ : C, 60.68; H, 9.01. Found C, 60.56; H, 8.93%.

### 3.4. $[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}]_2(\mu - \text{CHCH}_2\text{CH}_2\text{CH})$ (**7**)

To a solution of  $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHMe}$  (**5**, 174 mg, 228  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (6 mL) was added 13.5  $\mu\text{L}$  (114  $\mu\text{mol}$ ) 1,5-hexadiene at room temperature. The mixture was stirred for 6 min. The solution was concentrated under vacuum to half its original volume.  $\text{CH}_2\text{Cl}_2$  (3 mL) was added, and the mixture was stirred for 3 min. The solution was concentrated to half of its volume, 3 mL  $\text{CH}_2\text{Cl}_2$  was again added, and the mixture was stirred for 3 min. The solvent was removed under vacuum. The residue was washed with pentane ( $5 \times 3$  mL), then dried under vacuum for several hours. A grey microcrystalline solid was obtained. Yield 94 mg (54%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  19.09 (bs, 2H,  $\text{H}_\alpha$ ), 3.30 (bs, 4H,  $\text{H}_\beta$ ), 2.55, 1.83, 1.72, 1.52, 1.25 (all m, 132H,  $\text{PCy}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  316.5 ( $\text{C}_\alpha$ ); 58.1 (s,  $\text{C}_\beta$ ); 32.3 (pseudo-t,  $J_{\text{app}} = 9.4$  Hz,  $\text{C}_1$  of Cy); 30.0 (s,  $\text{C}_3$  of Cy); 28.4 (pseudo-t,  $J_{\text{app}} = 5.0$  Hz,  $\text{C}_2$  of Cy); 27.0 (s,  $\text{C}_4$  of Cy).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  38.7 (s). Anal. Calc. for  $\text{C}_{76}\text{H}_{138}\text{Ru}_2\text{Cl}_4\text{P}_4$ : C, 60.06; H, 9.15. Found: C, 59.67; H, 9.49%.

### 3.5. $[(\text{H}_2\text{IMes})(\text{PCy}_3\text{Cl}_2\text{Ru}=\text{CHCH}=\text{CHCH}=\text{CH}_2)$ (**8**)

To a solution of **G2B** (6.7 mg, 7.8  $\mu\text{mol}$ ) in  $\text{CD}_2\text{Cl}_2$  (0.6 mL) was added 1.3  $\mu\text{L}$  (12.0  $\mu\text{mol}$ ) 1,3,5-hexatriene at room temperature. The mixture was stirred for 10 min when the color changed from green to bright red. The solution was transferred to a vial charged with  $\text{PCy}_3$  (2.0 mg, 7.1  $\mu\text{mol}$ ), producing a brown solution.  $^1\text{H}$  NMR:  $\delta$  18.11 (d,  $J = 10.9$  Hz, 1H,  $\text{H}_\alpha$ ), 7.30 (dd,  $J = 13.9$ , 10.9 Hz, 1H,  $\text{H}_\beta$ ), 6.97 (s, 2H, Mes), 6.74 (s, 2H, Mes), 6.05 (m, 2H,  $\text{H}_\gamma$  and  $\text{H}_\delta$ ), 5.8 (two overlapping d,

$J = 13.9$ , 8.8 Hz, 2H,  $\text{H}_\epsilon$ ), 2.57 (s, 6H, *o*- $\text{CH}_3$ ), 2.35 (s, 6H, *o*- $\text{CH}_3$ ), 2.29 (s, 3H, *p*- $\text{CH}_3$ ), 2.12 (s, 3H, *p*- $\text{CH}_3$ ), 0.19–1.85 (all m,  $\text{PCy}_3$ , 33H).

### 3.6. $E-[(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}=\text{CHCH}=\text{CHCH}_2\text{CH}_2\text{PCy}_3]^+$ ( $\text{PF}_6^-$ ) (**10**)

A solution of **2E** (58 mg, 73  $\mu\text{mol}$ ),  $i\text{Pr}_2\text{NH}_2^+\text{PF}_6^-$  (23 mg, 93  $\mu\text{mol}$ ) and  $\text{PCy}_3$  (50 mg, 179  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was stirred for 4 h, and the solvent was removed under vacuum. The residue was washed with pentane and dried under vacuum for several hours. The resulting **10** (>80% by NMR) obtained was contaminated with  $i\text{Pr}_2\text{NH}_2^+\text{PF}_6^-$  and a small amount of residual  $\text{PCy}_3$ . Purification by column chromatography (pentane/ethyl acetate) produced samples clean by NMR, but combustion analysis results were unsatisfactory.  $^1\text{H}$  NMR:  $\delta$  19.02 (d,  $J_{\alpha\beta} = 10.5$  Hz, 1H,  $\text{H}_\alpha$ ), 8.11 (dd,  $J_{\beta\gamma} = 15.3$  Hz,  $J_{\alpha\beta} = 10.5$  Hz, 1H,  $\text{H}_\beta$ ), 6.62 (dt,  $J_{\beta\gamma} = 15.3$  Hz,  $J_{\gamma\delta} = 6.3$  Hz, 1H,  $\text{H}_\gamma$ ), 2.58 (m, 6H,  $\text{H}_1$  of  $\text{PCy}_3$ ), 2.4 (br q,  $J_{\text{H-P}} \approx J_{1-2\text{ax}} \approx 10.8$  Hz, 3H,  $\text{H}_1$  of  $^+\text{PCy}_3$ ), 2.2 (AA BB X,  $J_{\text{H-P(Ax)}} \approx J_{\text{AB}} \approx 12.4$  Hz,  $J_{\text{AB}'} \approx 4$  Hz,  $J_{\text{AA}'} \approx J_{\text{BB}'} \approx -13$  Hz,  $\Delta\nu = 0.22$  ppm, 2H,  $\text{H}_\epsilon$ ), 2.0–1.2 (m, 92H,  $\text{H}_2\text{--H}_4$  of  $\text{PCy}_3$  and  $^+\text{PCy}_3$ ,  $\text{H}_\delta$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  292.2 (t,  $J = 7$  Hz,  $\text{C}_\alpha$ ), 150.0 (s,  $\text{C}_\beta$ ), 131.1 (d,  $J = 14$  Hz,  $\text{C}_\gamma$ ), 32.3 (pseudo-t,  $J_{\text{app}} = 9.5$  Hz,  $\text{C}_1$  of  $\text{PCy}_3$ ), 31.7 (d,  $J = 12.0$  Hz,  $\text{C}_\delta$ ), 30.5 (d,  $J = 39.5$  Hz,  $\text{C}_1$  of  $^+\text{PCy}_3$ ), 30.0 (s,  $\text{C}_3$  of  $\text{PCy}_3$ ,  $^+\text{PCy}_3$ ), 28.3 ( $\text{C}_2$  of  $\text{PCy}_3$ ), 27.5 ( $\text{C}_2$  of  $^+\text{PCy}_3$ ), 27.0 (s,  $\text{C}_4$  of  $\text{PCy}_3$ ), 26.9 (s,  $\text{C}_4$  of  $^+\text{PCy}_3$ ), 13.0 (d,  $J = 42.2$  Hz,  $\text{C}_\epsilon$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  37.6 (s,  $\text{PCy}_3$ ), 32.5 (s,  $^+\text{PCy}_3$ ). MS (APCI)  $m/z$  799, s [ $\text{M}^+ - \text{PCy}_3$ ], 745, w [ $\text{M}^+ - \text{CHCHCH}_2\text{CH}_2\text{PCy}_3$ ]; expected isotopic patterns observed for both fragments.

### 3.7. Reaction of **2Z**, **2E** with $\text{PCy}_3$ and LDA in $\text{CH}_2\text{Cl}_2$

To 1.0 mL of ether, 6 mg diisopropylamine (60  $\mu\text{mol}$ ) and 11 mg  $\text{PCy}_3$  (39  $\mu\text{mol}$ ) were added. The solution was cooled to  $-78^\circ\text{C}$ . After 15 min, 11  $\mu\text{L}$  2.5 M *n*-butyllithium (28  $\mu\text{mol}$ ) in hexane were added. The reaction mixture was stirred under nitrogen for 25 min before being warmed to  $0^\circ\text{C}$  for 5 min. This mixture was then added by syringe to solution of **2** (15.8 mg, 19.8  $\mu\text{mol}$ ) in 1.4 mL of  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ . The reaction was stirred for 45 min at  $-78^\circ\text{C}$  and 1 h at  $0^\circ\text{C}$ . The solvent was removed by vacuum. Complex **11** was the major product by NMR:  $^1\text{H}$  NMR:  $\delta$  19.98 (d,  $J_{\alpha\beta} = 10.5$  Hz, 1H,  $\text{H}_\alpha$ ), 7.96 (dd,  $J_{\beta\gamma} = 15.0$  Hz,  $J_{\alpha\beta} = 10.5$  Hz, 1H,  $\text{H}_\beta$ ), 7.9 (t,  $^2J_{\text{H-P}} = J_{\delta\epsilon} = 16.5$  Hz, 1H,  $\text{H}_\epsilon$ ), 7.41 (dt,  $J_{\beta\gamma} = 15.0$  Hz,  $J_{\gamma\delta} = 10.7$  Hz, 1H,  $\text{H}_\gamma$ ), 6.81 (td,  $^3J_{\text{H-P}} = J_{\delta\epsilon} = 16.5$  Hz,  $J_{\gamma\delta} = 10.7$  Hz, 1H,  $\text{H}_\delta$ ), 2.56 (m, 6H,  $\text{H}_1$  of  $\text{PCy}_3$ ), 2.35 (m, 3H,  $\text{H}_1$  of  $^+\text{PCy}_3$ ), 2.09–0.92 (m, 92H,  $\text{H}_2 - \text{H}_4$  of  $\text{PCy}_3$  and  $^+\text{PCy}_3$ ,  $\text{H}_\delta$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  285.9 (t, 7 Hz,  $\text{C}_\alpha$ ), 156.3 (s,  $\text{C}_\delta$ ), 151.6 (s,  $\text{C}_\beta$ ), 124.6 (d,  $J = 20$  Hz,  $\text{C}_\gamma$ ), 109.7 (d,  $J = 72$  Hz,  $\text{C}_\epsilon$ ), 30.4 (d,  $J = 42.8$  Hz,  $\text{C}_1$  of  $^+\text{PCy}_3$ ), other  $\text{PCy}_3$  and  $^+\text{PCy}_3$  signals not resolved from those of other complexes present.  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  39.0

(s, PCy<sub>3</sub>), 30.5 (s, <sup>+</sup>PCy<sub>3</sub>). MS (APCI) *m/z* 797, s [M<sup>+</sup> – PCy<sub>3</sub>]; expected isotopic pattern observed.

### 3.8. Experimental procedure for formation of MIPA

**G2B** (4.5 mg, 5.3 μmol) was dissolved in 3 mL CHCl<sub>3</sub> under nitrogen in a septum-capped vial. Acetylene gas (99.6%) was bubbled through the solution at a rate fast enough to allow easy observation of the bubbles but slow enough that the solvent would last for 1 h (approximately 0.1 mL/s). The color changed in a few seconds from light green through red to black, after which black solid was observed [31]. After 1 h of bubbling, the spongy material was taken in a vial into a N<sub>2</sub>-filled glovebox, and **G2B** (30.5 mg, 36.0 μmol) was added in 0.5 mL CHCl<sub>3</sub>. The color of the solvent immediately changed from green to bright red when high levels of doping were achieved. The **G2B** remained on the polymer for 5 h. The MIPA was dried under high vacuum to give a black, fibrous powder (70.1 mg). The solid, insoluble material was transferred into a pipet with a glass wool plug and washed with copious amounts CHCl<sub>3</sub> (1 mL, 20–40 times) until several consecutive washes were clear and colorless to give a black, insoluble solid (56.9 mg). The dried weight of the washings (red in color) was 13.0 mg. Films were formed by pressing the powder in an IR KBr pellet press. Anal. Calc. for C<sub>154</sub>H<sub>157</sub>Br<sub>2</sub>Cl<sub>2</sub>N<sub>4</sub>Ru: C, 77.23; H, 6.16. Found: C, 77.23; H, 6.56%.

## 4. Conclusion

OMMI is a robust strategy for incorporating metal centers into olefins and has been used to produce mono- and di-ruthenium complexes containing conjugated and non-conjugated carbene ligands. It is useful both for homogeneous solution phase synthesis and for heterogeneous incorporation of metal centers into insoluble polymers [33].

The complexes obtained through OMMI exhibit interesting structural, electronic, and reaction properties. The CV data and UV–Vis spectra strongly indicate the ability of conjugated bridges of **1** and **2** to promote intermetal communication. Methods to prevent isomerization and to increase stability of OMMI products are currently under investigation [36].

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## References

[1] R.H. Grubbs, *Tetrahedron* 60 (2004) 7117.

[2] K.C. Wallace, A.H. Liu, J.C. Dewan, R.R. Schrock, *J. Am. Chem. Soc.* 110 (1988) 4964.

- [3] J. Barluenga, F. Aznar, A. Martin, *Organometallics* 14 (1995) 1429.
- [4] H. Dialer, K. Polborn, W. Beck, *J. Organomet. Chem.* 589 (1999) 21.
- [5] R.R. Schrock, A.J. Gabert, R. Singh, A.S. Hock, *Organometallics* 24 (2005) 5058.
- [6] R.R. Schrock, R.T. DePue, J. Feldman, K.B. Yap, D.C. Yang, W.M. Davis, L. Park, M. DiMare, M. Schofield, *Organometallics* 9 (1990) 2262.
- [7] (a) A.M. LaPointe, R.R. Schrock, *Organometallics* 14 (1995) 1875; (b) R. Toreki, R.R. Schrock, *J. Am. Chem. Soc.* 112 (1990) 2448.
- [8] J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus Jr., A.H. Hoveyda, *J. Am. Chem. Soc.* 121 (1999) 791.
- [9] T.K. Maishal, B. Mondal, V.G. Puranik, P.P. Wadgaonkar, G.K. Lahiri, A. Sarkar, *J. Organomet. Chem.* 690 (2005) 1018.
- [10] (a) P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 2039; (b) P. Schwab, R.H. Grubbs, J.W. Ziller, *J. Am. Chem. Soc.* 118 (1996) 100.
- [11] J.E. Williams, M.J. Harner, M.B. Sponsler, *Organometallics* 24 (2005) 2013.
- [12] W.-H. Leung, K.-K. Lau, Q.-f. Zhang, W.-T. Wong, B. Tang, *Organometallics* 19 (2000) 2084.
- [13] G.S. Tulevski, M.B. Myers, M.S. Hybertsen, M.L. Steigerwald, C. Nuckolls, *Science* 309 (2005) 591.
- [14] A. Cecon, S. Santi, L. Orian, A. Bisello, *Coord. Chem. Rev.* 248 (2004) 683.
- [15] L. Fabbrizzi, M. Licchelli, P. Pallavicini, *Acc. Chem. Res.* 32 (1999) 846.
- [16] H. Xia, T.B. Wen, Q.Y. Hu, X. Wang, X. Chen, L.Y. Shek, I.D. Williams, K.S. Wong, G.K.L. Wong, G. Jia, *Organometallics* 24 (2005) 562.
- [17] X. Niu, L. Gopal, M.P. Masingale, D.A. Braden, B.S. Hudson, M.B. Sponsler, *Organometallics* 19 (2000) 649.
- [18] X. Niu, Ph.D. dissertation, Syracuse University, 2000.
- [19] Complex **3** was converted to the monoruthenium complex only for the purpose of adjusting the stoichiometry of the reactants; this monoruthenium complex was not isolated.
- [20] C. Creutz, H. Taube, *J. Am. Chem. Soc.* 95 (1973) 1086.
- [21] M. Scholl, T.M. Trnka, J.P. Morgan, R.H. Grubbs, *Tetrahedron Lett.* 40 (1999) 2247.
- [22] J.A. Love, J.P. Morgan, T.M. Trnka, R.H. Grubbs, *Angew. Chem., Int. Ed. Engl.* 41 (2002) 4035.
- [23] (a) J.P. Collman, L. Hegedus, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, California, 1980 (Chapter 7); (b) C.P. Casey, W.R. Brunsvold, D.M. Scheck, *Inorg. Chem.* 16 (1977) 3059; (c) D.W. Macomber, M.H. Hung, A.G. Verma, R.D. Rogers, *Organometallics* 7 (1988) 2072; (d) G. Cardaci, *J. Chem. Soc., Dalton Trans.* (1984) 815.
- [24] S.H. Hong, M.W. Day, R.H. Grubbs, *J. Am. Chem. Soc.* 126 (2004) 7414.
- [25] (a) A. Oku, T. Harada, K. Hattori, Y. Nozaki, Y. Yamaura, *J. Org. Chem.* 53 (1988) 3089; (b) A. Oku, Y. Yamaura, T. Harada, *J. Org. Chem.* 51 (1986) 3730; (c) T. Harada, H. Maeda, A. Oku, *Tetrahedron Lett.* 26 (1985) 6489; (d) T. Harada, Y. Nozaki, Y. Yamaura, A. Oku, *J. Am. Chem. Soc.* 107 (1985) 2189.
- [26] Ruthenium incorporation was computed as % [Ru], where [Ru] represents **G2B**; the mass of the washings was subtracted from the initial mass of the **G2B** used and divided by the total mass of the polymer to obtain % [Ru]. The % [Ru] incorporation determined through this mass balance method was in good agreement with elemental analysis measurements.
- [27] (a) R.H. Grubbs, *Angew. Chem. Int. Ed. Engl.* 45 (2006) 3760; (b) K. Harries-Rees, Y. Chauvin, R. Grubbs, R. Schrock, *Chem. World* 2 (2005) 42.
- [28] H. Shirakawa, A. MacDiarmid, A. Heeger, *Chem. Commun.* (2003) 1.



- [29] (a) O.A. Scherman, R.H. Grubbs, *Polym. Mater. Sci. Eng.* 84 (2001) 603;  
(b) O.A. Scherman, I.M. Rutenberg, R.H. Grubbs, *J. Am. Chem. Soc.* 125 (2003) 8515.
- [30] T. Ito, H. Shirakawa, S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.* 12 (1974) 11.
- [31] D.E. Schuehler, J.E. Williams, M.B. Sponsler, *Macromolecules* 37 (2004) 6255.
- [32] (a) R. Cosmo, H. Naarmann, *Mol. Cryst. Liq. Cryst.* 185 (1990) 89;  
(b) Y.M. Tsai, F.J. Boerio, W.J. Van Ooij, D.K. Kim, *J. Adhesion* 62 (1997) 127;
- (c) H. Shirakawa, M. Sato, A. Hamano, S. Kawakami, K. Soga, S. Ikeda, *Macromolecules* 13 (1980) 457.
- [33] D.E. Schuehler, J.E. Williams, M.B. Sponsler, in preparation.
- [34] O.A. Scherman, R.H. Grubbs, *Polym. Mater. Sci. Eng.* 84 (2001) 605.
- [35] (a) K.L. D'Amico, C. Manos, R.L. Christensen, *J. Am. Chem. Soc.* 102 (1980) 1777–1782;  
(b) H. Yoshida, M. Tasumi, *J. Chem. Phys.* 89 (1988) 2803–2809.
- [36] S.L. Bolton, J.E. Williams, M.B. Sponsler, in preparation.