

Reactions of TpRu(CO)(NCMe)(Ph) with electron-rich olefins: examples of stoichiometric C–S, C–O and C–H bond cleavage†

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Stoichiometric reactions of TpRu(CO)(NCMe)(Ph) with electron-rich olefins result in metal-mediated cleavage of C–S and C–O bonds.

Metal-mediated activation of small molecules represents the foundation of homogeneous catalysis with discovery and understanding of bond cleavage processes central to the development of new synthetic methods. The catalytic activation of aromatic C–H bonds has recently gained substantial attention, and several new developments in the arena of aromatic functionalization have been reported.^{1–4} We have recently disclosed that TpRu(CO)(NCMe)(Ar) (Ar = aryl; Tp = hydridotris(pyrazolyl)borate) complexes catalyze the addition of aromatic C–H bonds (including arenes, furan and thiophene) across the C=C bonds of ethylene and simple α -olefins.^{5–7} Attempts to extend this chemistry to the hydroarylation of electron-deficient olefins resulted in radical polymerization reactions, and we have recently provided evidence that the polymerizations are likely initiated by oxidation of Ru^{II} to Ru^{III} followed by rapid Ru–C bond homolysis at the higher oxidation state.^{8,9} Herein, we report reactions of TpRu(CO)(NCMe)(Ph) (**1**) with the electron-rich olefins ethyl vinyl sulfide and 2,3-dihydrofuran that result in transformations that involve stoichiometric C–S and C–H/C–O bond cleavage, respectively.

Heating a homogeneous solution of complex **1** in neat ethyl vinyl sulfide at 100 °C for 2 hours leads to the isolation of the dimeric species [TpRu(CO)(μ -SEt)]₂ (**2**) (equation 1). NMR spectroscopy indicates that **2** is formed in ~ 80% yield (see below). The IR spectrum of **2** reveals $\nu_{\text{CO}} = 1929 \text{ cm}^{-1}$ ($\nu_{\text{CO}} = 1938 \text{ cm}^{-1}$ for **1**), and ¹H and ¹³C NMR spectra are consistent with the presence of a mirror plane of symmetry. A single-crystal X-ray diffraction study of **2** has confirmed its identity (Fig. 1).¹⁰ The structure reveals two pseudo-octahedral Ru^{II} fragments bridged by two μ -SEt fragments in which the two Ru moieties are symmetry equivalent. Other Ru binuclear species with similar bridging “SR” fragments have been reported.¹¹ In addition to **2**, analysis of crude reaction mixtures reveals the formation of a second uncharacterized product that is NMR silent but exhibits

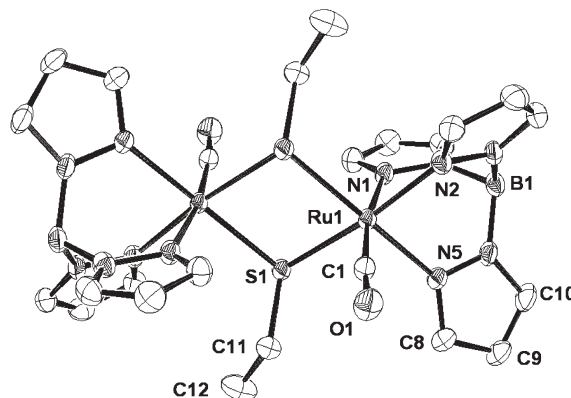
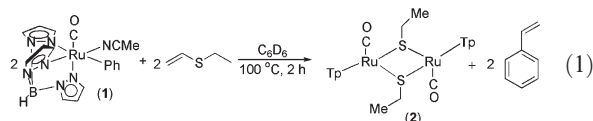


Fig. 1 ORTEP of [TpRu(CO)(μ -SEt)]₂ (**2**) (30% probability). Selected bond distances (Å): Ru1–S1 2.4148(9), Ru1–S1' 2.4129(9), Ru1–C1 1.813(4), S1–C11 1.836(4). Selected bond angles (°): Ru1–S1–Ru1' 98.73(3), S1–Ru1–S1' 81.27(3), S1–C11–C12 113.1(3), C1–Ru1–S1 94.2(1) {atoms marked with ' (e.g., S1') are at equivalent position (2 – x, – y, 1 – z)}.

$\nu_{\text{CO}} = 1964 \text{ cm}^{-1}$. Consistent with the ~ 80% yield of **2** (by ¹H NMR), the estimated yield of this uncharacterized complex based on IR spectroscopy is 15–20%. A qualitative Evans NMR experiment has confirmed the presence of paramagnetic material in the crude reaction mixture.



Monitoring the reaction of **1** and excess ethyl vinyl sulfide in C₆D₆ by ¹H NMR spectroscopy (80 °C for 18 hours) reveals that complex **2** is formed (approximately 80% yield) with styrene. The production of styrene reveals a metal-mediated C–C bond formation between the phenyl group of **1** and the vinyl group of ethyl vinyl sulfide and has been confirmed by both GC-FID and ¹H NMR spectroscopy including the addition of an authentic sample of styrene to the NMR solution.

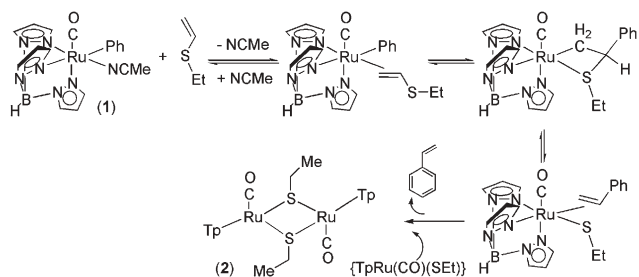
Due to its importance for hydrodesulfurization processes as well as for synthetic organic chemistry, there has been substantial interest in metal-mediated activation of C–S bonds.^{12–14} The activation of C–S bonds of heteroaromatic systems and allylic sulfides by several transition metal systems has been reported,^{14–19} however, observation of C–S bond activation of vinyl sulfides is less common.^{20–22} A possible mechanism for the formation of **2** includes coordination of the ethyl vinyl sulfide to the Ru^{II} center

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Scheme 1 Proposed pathway for the conversion of **1** and ethyl vinyl sulfide to complex **2**.

followed by olefin insertion, β -SEt elimination, and dissociation of styrene (Scheme 1). An alternative pathway is C–S oxidative addition to produce a Ru^{IV} intermediate and subsequent C–C reductive elimination of the vinyl and phenyl groups to produce styrene. Since the C–S bond cleavage is limited to vinyl sulfide (see below), we suggest that the former reaction pathway is most likely to be operative.

The scope of the Ru-mediated carbon–sulfur bond cleavage was probed by heating complex **1** with diethyl sulfide, ethyl phenyl sulfide or diphenyl sulfide in C₆D₆. These reactions lead to the formation of NMR silent ruthenium products with no apparent reaction with the sulfide reagents. It is likely that the paramagnetic ruthenium complex formed in these experiments is the product of the decomposition of **1** in the absence of the sulfide reagents.⁵ Thus, complex **1** fails to cleanly react with C–S bonds of alkyl or aryl substituents, and, in the absence of a vinyl–sulfur bond, complex **1** apparently does not react with the sulfide. These results indicate that the presence of an olefinic moiety is likely integral to the C–S bond cleavage to produce **2** and suggest that the mechanism shown in Scheme 1 is perhaps more viable than a pathway that invokes initial C–S oxidative addition. Although well-defined examples are limited, precedent for β -elimination of “XR” (X = O or S) groups exists.^{17,23–27}

Observation of C–S bond cleavage upon reaction of **1** with ethyl vinyl sulfide prompted us to study reactions with ethyl vinyl ether and 2,3-dihydrofuran. Reaction of **1** and ethyl vinyl ether results in an intractable mixture of products; however, heating a 2,3-dihydrofuran solution of **1** to 80 °C allows isolation of a complex characterized as TpRu(CO)(NCMe)(C≡CCH₂CH₂OH) (**3**). Complex **3** is isolated in 28% yield while monitoring the reaction by ¹H NMR spectroscopy suggests production of **3** in approximately 65% yield along with a second uncharacterized product. Diagnostic features in the ¹H NMR spectrum of **3** include a broad singlet at 6.13 ppm assigned to the hydroxy group ($\nu_{\text{OH}} = 3336 \text{ cm}^{-1}$ in the IR spectrum of **3**), doublet of doublets at 4.55 and 4.36 ppm (each 1H) due to the diastereotopic methylene group α to the hydroxy, and a multiplet at 2.38 ppm (2H) assigned as overlapping resonances due to the diastereotopic methylene group that is β to the hydroxy group. Homonuclear decoupling experiments confirm the assignment of the resonances due to the methylene groups (Fig. 2). Consistent with the assignment of the resonance at 6.13 ppm as a hydroxy, the addition of D₂O to **3** in C₆D₆ results in the disappearance of this resonance in the ¹H NMR spectrum after approximately 4 hours at room temperature. The ¹³C NMR spectrum of **3** reveals singlets at 236.8, 200.6 and 179.8 assigned as α -acetylide, CO and β -acetylide carbons,

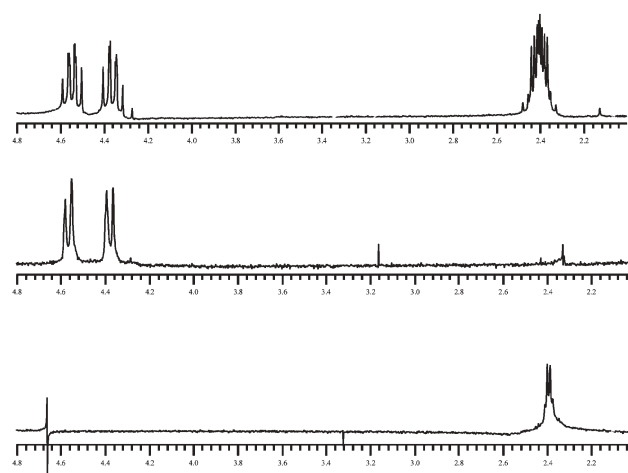
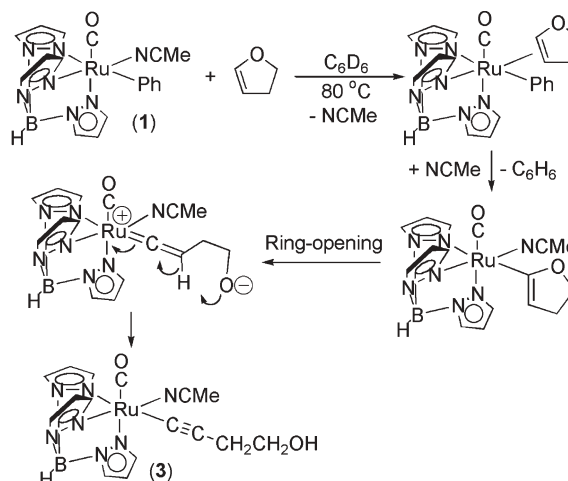


Fig. 2 Homonuclear decoupling experiments for TpRu(CO)(NCMe)(C≡CCH₂CH₂OH) (**3**). The top spectrum (2.2 to 4.8 ppm) shows the ¹H NMR spectrum of **3**. The middle spectrum shows the result of irradiation of the resonance at 2.38 ppm (resonances at 4.55 and 4.36 ppm are doublets). The bottom spectrum depicts the result of irradiation of the resonances at 4.55 and 4.36 ppm (the resonance at 2.38 ppm is an AB pattern).

respectively. In addition, triplets are observed at 76.9 ppm ($^1J_{\text{CH}} = 148 \text{ Hz}$) and 26.7 ppm ($^1J_{\text{CH}} = 132 \text{ Hz}$) due to the methylene carbons.

The production of benzene from the reaction of **1** and 2,3-dihydrofuran has been detected by NMR tube experiments, and a plausible reaction pathway is shown in Scheme 2. We suggest initial coordination of 2,3-dihydrofuran *via* ligand exchange with acetonitrile, net C–H activation at the 2-position of 2,3-dihydrofuran (based on ultimate coordination of the 2-position carbon of 2,3-dihydrofuran to Ru in the final product **3**), ring opening of the furyl intermediate to form a formally Ru(IV) allenylidene, and proton transfer to complete the formation of complex **3**. It is possible that an acid impurity (protic or Lewis acid) may coordinate to the 2,3-dihydrofuran oxygen and assist the C–O bond cleavage and ring opening of the heterocycle.



Scheme 2 Possible pathway for the production of TpRu(CO)(NCMe)(C≡CCH₂CH₂OH) (**3**).

We have previously reported that TpRu(CO)(NCMe)(R) systems can activate the C–H bonds of aromatic substrates such as benzene, furan and thiophene.^{5–7} We cannot, at this point, discount the possibility of C–H activation at the 3-position of 2,3-dihydrofuran followed by isomerization of Ru to the 2-position, a pathway which would be consistent with the regioselectivity of C–H activation of furan and thiophene by TpRu(CO)(NCMe)(Me) at the more electrophilic 2-position.⁷ Oxophilic zirconium has been reported to react with 2,3-dihydrofuran to initiate ring opening with the product being a zirconium alkoxide with a terminal olefinic group.²⁸ Caulton *et al.* have reported the ability of unsaturated Ru(II) systems to isomerize electron-rich olefins to carbene ligands.²⁹

Catalytic hydroarylation of olefins (and related substrates) requires that aromatic C–H activation and olefin insertion must be competitive with various possible side reactions. Extension of previously observed Ru^{II}-catalyzed hydroarylation of ethylene and α -olefins to electron-rich olefins is not possible, and the results reported herein provide a rationalization. For ethyl vinyl sulfide, apparently facile C–S bond cleavage competes with benzene C–H activation in a step that likely occurs after olefin insertion into the Ru–phenyl bond of complex **1**. For 2,3-dihydrofuran, C–H activation (likely at the 2-position) apparently competes with insertion of the C=C bond into the Ru–Ph bond. These results indicate that two closely related substrates (*i.e.*, olefins with π -electron donating groups) react in divergent pathways. Thus, the identity of the π -donating group (“SR” or “OR”) possibly alters the predilection toward olefin C–H activation *versus* olefin insertion. Future work will seek to understand these effects.

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