

A facile route to Ru-alkylidenes†

Q1 **Q2** Cite this: DOI: 10.1039/c3dt53525h Adam M. McKinty and Douglas W. Stephan*

Received 16th December 2013,
Accepted 17th December 2013

DOI: 10.1039/c3dt53525h

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Reactions of dithioacetal E(CH₂CH₂S)₂CHR (E = O, S, R = Ph, C₆F₅) and O(C₆H₄S)₂CHPh with either Ru(cod)(cot) or Ru(PPh₃)₃(H)₂ are used to prepare the Ru-alkylidene complexes E(CH₂CH₂S)₂RuCHPh(L), O(C₆H₄S)₂RuCHPh(L) (L = PCy₃, SIMes) in high yields.

Olefin metathesis as a synthetic strategy has impacted broadly on organic chemistry, polymer science and materials chemistry. Thus the discovery, mechanism and applications of this powerful methodology were recognized with the award of the Nobel Prize in 2005 to Chauvin, Grubbs and Schrock.¹ Despite recent advances,² the Schrock catalyst systems are generally perceived as more active although they are also more sensitive to functional groups. It is for this reason that the Ru-based catalysts of Grubbs', (Cy₃P)₂Cl₂RuCHPh and (Cy₃P)Cl₂RuCHPh (SIMes), are most commonly used.³ Nonetheless a variety of closely related derivatives have also been prepared and studied. A variety of derivatives of the Grubbs catalysts have also been probed. For example, a pendant oxygen atom donor on the arene of the benzylidene fragment is incorporated in the "Hoveyda-Grubbs" catalyst.⁴ On the other hand, Fogg and coworkers⁵ have developed active systems in which the halides are replaced with aryloxy ligands, while we have recently reported the dithiolate derivative of Grubbs catalyst (O(CH₂CH₂S)₂)(SIMes)RuCHPh.⁶ A variety of synthetic routes to the Ru-alkylidene (Cy₃P)₂Cl₂RuCHPh have also been explored. While use of cyclopropene was initially used to install the alkylidene fragment,⁷ sulfur-ylienes,⁸ dihalomethanes⁹ and diazomethanes¹⁰ provide synthetic alternatives and indeed the latter reagent is synthetically easier and thus more widely used to produce Grubbs' catalysts. Related complexes incorporating allenylidene, indenylidene,¹¹ vinylidene^{9c} or cumulenylidene¹² fragments have also been prepared from

reactions of Ru-synthons with alkynes, propargylchlorides,¹³ and propargylalcohols.¹⁴ Generally these latter compounds exhibit lower initiation efficiencies, however Dixneuf and co-workers^{11a} have shown that Ru-piano-stool complexes exhibit high metathesis activity.

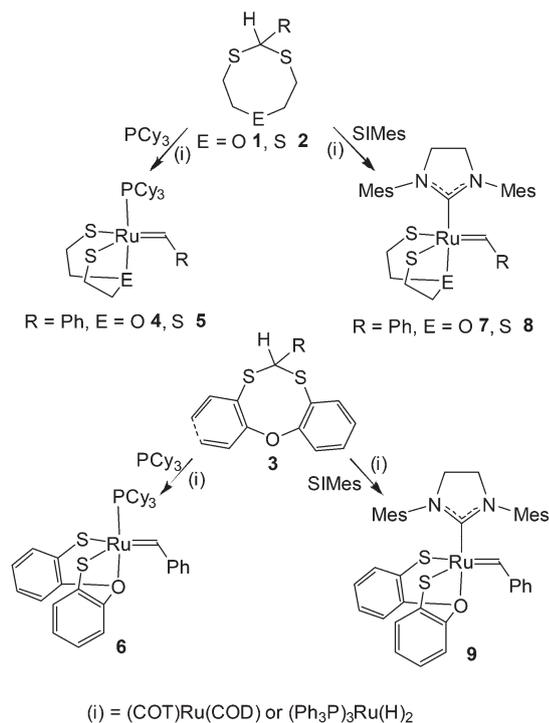
Despite these developments, the most commonly used and effective avenue to the installation of an alkylidene fragment remains the use of diazomethane. This methodology is however not without its problems as diazomethanes are unstable, potentially explosive, toxic and react with phosphine donors. Herein, we describe a new synthetic strategy to Ru-alkylidenes exploiting the reactivity of dithioacetals. This strategy offers a safe, low-cost, high yielding route which is readily adaptable to give a family of Ru-dithiolate alkylidene complexes. Moreover, these readily accessible compounds are shown to act as highly convenient synthons for Grubbs' catalysts.

The cyclic thioacetals were prepared employing a modification of the literature procedure described by Hu *et al.*¹⁵ Thus, to a solution of *p*-toluenesulfonic acid in MeOH heated to 55 °C, was added a mixture of 2-mercaptoethyl ether and benzaldehyde in a slow drop-wise fashion. Following stirring overnight at 55 °C, subsequent work-up afforded the cyclic thioacetal O(CH₂CH₂S)₂CHPh **1** in 95% isolated yield. ¹H NMR data for **1** and an X-ray structural determination confirmed the formation of cyclic species (see ESI†). This reaction proved amenable to variation and was adapted to give the species S(CH₂CH₂S)₂CHPh **2**¹⁵ and O(C₆H₄S)₂CHPh **3** each isolated in greater than 90% yield (Scheme 1).

The dithioacetal **1** was reacted with Ru(cod)(cot)¹⁶ in the presence of 1.1 equiv. of PCy₃ in C₆H₆ at 50 °C for 2 h. Cooling the solution afforded a red solid **4** in 73% yield. Compound **4** exhibits a single ³¹P{¹H} NMR signal at 65.6 ppm. The ¹H NMR spectrum was consistent with the presence of the dithiolate ligand and PCy₃ in a 1:1 ratio. In addition, a doublet resonance at 13.68 ppm with P-H coupling of 11.3 Hz was consistent with the presence of a ruthenium-alkylidene. This was further supported by the observation of the corresponding ¹³C{¹H} resonance at 208.0 ppm. Although compound **4**

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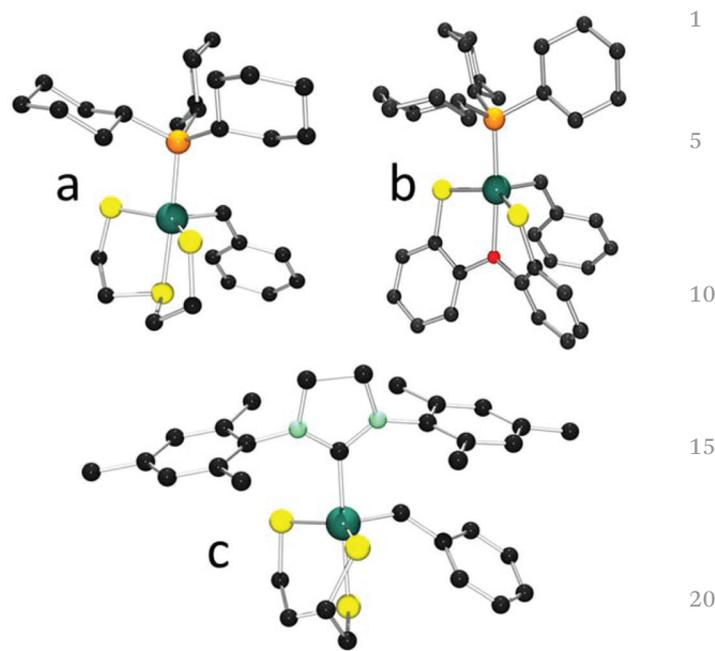
† Electronic supplementary information (ESI) available: Synthetic and spectroscopic data and spectra are deposited. Crystallographic data have been deposited in the Cambridge database. CCDC 971468–971470. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53525h



Scheme 1 Synthesis of 4–10.

could not be crystallographically characterized, these data infer the formulation as $\text{O}(\text{CH}_2\text{CH}_2\text{S})_2\text{RuCHPh}(\text{PCy}_3)$. This product is analogous to the recently reported species $\text{O}(\text{CH}_2\text{CH}_2\text{S})_2\text{RuCHPh}(\text{SIMes})$,⁶ prepared from reactions of the dilithiodithiolate ligand with $(\text{Cy}_3\text{P})\text{Cl}_2\text{RuCHPh}(\text{SIMes})$.

Seeking a more convenient Ru-synthon and thus an overall higher yielding pathway, the dithioacetal **1** was reacted with $\text{Ru}(\text{PPh}_3)_3(\text{H})_2$ ¹⁷ in the presence of PCy_3 . During heating to 50 °C for 2 h, the yellow solution became dark red with the evolution of gas. Subsequent work-up afforded **4** in 89% isolated yield. Following a similar process, the dithioacetals **2** and **3** were treated in a similar fashion with $\text{Ru}(\text{PPh}_3)_3(\text{H})_2$ in the presence of PCy_3 to give the species $\text{S}(\text{CH}_2\text{CH}_2\text{S})_2\text{RuCHPh}(\text{PCy}_3)$ **5** and $\text{O}(\text{C}_6\text{H}_4\text{S})_2\text{RuCHPh}(\text{PCy}_3)$ **6** in yields of 87, and 84%, respectively. The ³¹P resonance for these compounds were seen at 41.7 and 68.6 ppm respectively while the expected resonances from the alkylidenes giving rise to ¹H NMR signals at 13.48 ($J_{\text{P-H}} = 19$ Hz), 14.69 ($J_{\text{P-H}} = 15$ Hz) and the corresponding ¹³C signals at 235.2 and 192.2 ppm, respectively. X-ray structural data for **5** and **6** confirmed the above formulations (Fig. 1(a) and (b)) and demonstrate the distorted trigonal bipyramidal structures in which the two thiolate sulfur atoms and the alkylidene occupy the equatorial plane. The axial phosphine and thioether in **5** or ether in **6** donors complete the coordination sphere. The Ru–S(thiolate) and Ru–S(thioether) distances in **5** were found to be 2.2916(3) Å, 2.2981(3) Å and 2.3711(3) Å, respectively, while the Ru–S and Ru–O distances in **6** were 2.2870(8) Å, 2.3080(8) Å and 2.193(2) Å respectively. These Ru–S distances are similar to those observed in the structural analog we have previously reported. The Ru–C

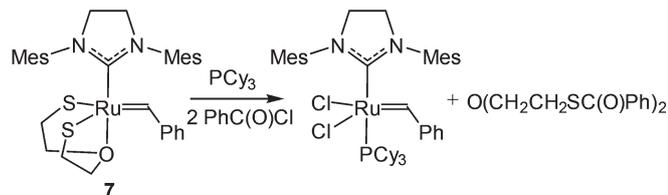
Fig. 1 POV-ray depictions of (a) **4**, (b) **5**, (c) **8**. Ru: teal, S: yellow, O: red; P: orange; N blue-green, C: black.

distances were also observed to be 1.864(1) Å and 1.848(3) Å in **5** and **6**, respectively.

Replacement of PCy_3 with SIMes ¹⁸ in a similar reaction of the thioacetals with $\text{Ru}(\text{PPh}_3)_3(\text{H})_2$ readily afforded the corresponding alkylidene complexes $\text{E}(\text{CH}_2\text{CH}_2\text{S})_2\text{RuCHPh}(\text{SIMes})$ ($\text{E} = \text{O}$ **7**, S **8**) and $\text{O}(\text{C}_6\text{H}_4\text{S})_2\text{RuCHPh}(\text{SIMes})$ **9**.⁶ Again the spectral data were consistent with these formulations and X-ray structure was also obtained for **8** (Fig. 1(c)). The Ru–C(carbene), Ru–C(alkylidene), Ru–S(thiolate) and Ru–S(thioether) distances were determined to be 1.860(5) Å, 2.084(5) Å, 2.313(1) Å, 2.336(1) Å and 2.380(1) Å similar to those previously reported for **9**.⁶

This synthetic route to Ru-alkylidene is thought to proceed by oxidation addition of the S–C bonds to Ru followed by α -thiolate transfer. In these reactions $\text{Ru}(\text{PPh}_3)_3(\text{H})_2$ reacts as a Ru(0) source, presumable with loss of H_2 . This latter supposition is consistent with the observation of gas evolution upon addition of the dithioacetal to the Ru-synthon. This reaction is conceptually related to the oxidation addition of dihalomethanes to Ru(0),⁹ although the present strategy affords the simultaneous delivery of a tridentate ligand and an alkylidene to Ru, affording access to a family of compounds.

Of the Ru-alkylidenes **4–9** derived herein, compound **7** has been previously shown to be inactive in ring-closing, ring-opening and cross metathesis. However, it is noteworthy that reacting **7** with two equivalents of BCl_3 results in an active cationic metathesis catalyst.⁶ In addition, the products described herein can also act as further synthons. Reaction of **7** with a 2 : 1 mixture of PhCOCl and PCy_3 cleanly liberates the bis-thioester $\text{O}(\text{CH}_2\text{CH}_2\text{SC}(\text{O})\text{Ph})_2$ and generates the Grubbs' generation II catalyst $(\text{Cy}_3\text{P})\text{Cl}_2\text{Ru} = \text{CHPh}(\text{SIMes})$.³ Thus this



Scheme 2 Synthesis of Grubbs' generation II from 7.

synthetic strategy offers a unique and facile, safe and high yielding route to this catalyst. Moreover, this synthetic strategy offers a convenient strategy to prepare a variety of substituted Ru-alkylidenes (Scheme 2).

Conclusions

In conclusion, we have reported a high yielding, facile, safe and variable method for the preparations of Ru-dithiolate alkylidene complexes. These species are known to be precursors to active metathesis catalysts upon activation with BCl_3 but they also serve as synthons to the Grubbs' catalysts. We are continuing to develop the chemistry of other dithioacetals for the synthesis of alkylidene complexes and explore the reactivity of these species in metathesis. The results of these studies will be reported in due course.

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