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Dehydrogenative Dimerization of Tin Hydrides Catalyzed by Ruthenium – Allenylidene Complexes[**]

Susan M. Maddock and M. G. Finn[*]

The cycloaromatization rearrangement of *ortho* alkyl-substituted aromatic transition metal vinylidene complexes provides a means for a terminal alkyne to act as a synthon for a benzylic radical.[1] In an effort to engender the production of a higher-energy sp^2 radical, we have prepared several metal – allenylidene species with the requisite alkynyl substituents. In the course of screening H-atom donors with which to study the as yet undetermined decomposition pathways of these species, we observed a rapid dehydrogenative dimerization of tributyltin hydride, this dimerization requires the presence of a pendant unsaturated substituent. Here we describe this process and report the results of experiments designed to probe the catalytic mechanism.

The generation of $R_3Sn{-}SnR_3$ dimers from the corresponding monohydrides [Eq. (1)] is known to be catalyzed by a

$$R_3SnH \xrightarrow[\text{MeCN, EtCN, or } CH_2Cl_2]{\text{catalyst}} R_3Sn{-}SnR_3 + H_2 \qquad (1)$$

diverse set of transition metal complexes, including simple Pd^{II} precursors,[2–4] [Cp$_2$YH] (Cp = cyclopentadiene),[5] and [(PPh$_3$)AuCl].[6] By far the most active catalysts are several diphosphane-bridged Fe/Pd heterobimetallic complexes in which the reaction is thought to occur at the Pd center, while the Fe center is proposed to play an important supporting role.[4, 7] Similar dehydrogenative pathways are presumably employed in the synthesis of oligomeric and polymeric diorganostannanes from tin dihydrides,[4] including reactions catalyzed by low-valent metallocene or Group VI hexacarbonyl complexes.[8]

Allenylidene complexes of the $[CpRu(PMe_3)_2]^+$ ion were prepared by the method of Selegue (details in Supporting Information).[9] A total of 13 derivatives were assembled (for the structures of complexes **1** – **13** see Table 1), in all cases, ^{13}C NMR signals were observed at $\delta = 293-299$, $213-228$, and $149-154$, for the C_α, C_β, and C_γ centers, respectively, with no attached protons, and a sharp band was found in the infrared spectrum at 1913 – 1925 cm^{-1}. These data serve to substantiate the allenylidene structure and rule out the cyclic isomer recently identified for analogous complexes of the $[Cl_2(PR_3)_2Ru]$ fragment.[10] An X-ray crystal structure obtained for the *para*-nitro derivative **12** (Supporting Information)[11] is similar to the parent complex **2**.[12]

Complex **1** (see Table 1), prepared for the study of diradical cycloaromatization, induces rapid gas evolution and clean production of $(Bu_3Sn)_2$ when added to a large excess of Bu$_3$SnH in acetonitrile or dichloromethane. With 3 mol% **1** relative to tin hydride, 96% conversion is obtained within 10 mins at room temperature under nitrogen atmosphere. The structural elements necessary for catalysis were probed with complexes **2** – **12** (Table 1).[13] Comparisons of activity were made by determining the extent of conversion of Bu$_3$SnH after exactly 5 mins under a standard set of conditions (1.4 mol% ruthenium catalyst relative to Bu$_3$SnH); such results do not allow separate analysis of the initial rate and lifetime. Of those species bearing substituents in the *ortho* position, allenylidenes **3** and **4** are of comparable activity to **1** (Table 1), demonstrating that the olefinic moiety of **1** (intended as an intramolecular radical trap in the event of cycloaromatization) is not involved in the catalytic process. Vinylidene complexes **14** and **15**, analogous to **4**, and the

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Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.

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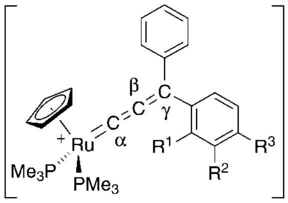
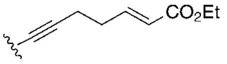
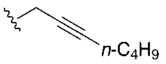
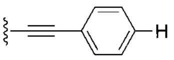
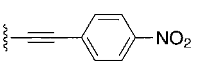
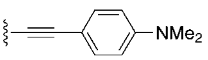
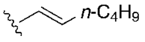
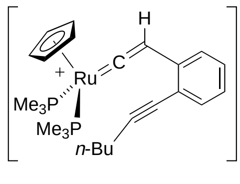
Table 1. Catalytic activity of ruthenium allenylidene complexes.



Compound	R^1	R^2	R^3	Activity (N_2)[a]	Activity (air)[b]
1		H	H	68.3 ± 6	n.d.
2	H	H	H	0	trace
3	$-C\equiv C-CH_3$	H	H	67.8 ± 9	100.0[c], 68.3 ± 8[d]
4	$-C\equiv C-n\text{-}C_4H_9$	H	H	82.5 ± 9	95.9 ± 5
5		H	H	trace	n.d.
6	n-C_6H_{13}	H	H	trace	0
7	I	H	H	0	n.d.
8	H	H		33.8 ± 11	84.6 ± 7
9	H	H		63.5 ± 7	97.4 ± 1
10	H	H		6.8 ± 0.4	10
11	H	$-C\equiv C-n\text{-}C_4H_9$	H	52.7 ± 9	n.d.
12	H	H	NO_2	0	0
13	H	H		13.5 ± 1	46.7 ± 1

[a] Conversion [%] after 5 mins under nitrogen atmosphere (see Experimental Section). [b] Conversion [%] after 5 mins in air (see Experimental Section). [c] Reaction was complete for two independent runs. [d] In the presence of hydroquinone (n.d. = not determined).

Grubbs carbenoid complex **16**, are ineffective, suggesting that the allenylidene unit is required. Complexes **2**, **6**, and **7**, bearing H, *n*-hexyl, and iodo substituents, respectively, all show little or no activity. Furthermore, the introduction of a methylene spacer between the alkyne and aryl groups (complex **5**) also eliminates catalysis. Thus, direct conjugation of the alkyne with the aryl unit is important for catalytic activity.



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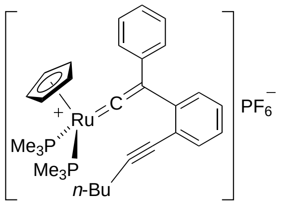

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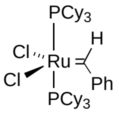


16

Active catalysts are also obtained when the pendant alkyne fragment is moved to the *para* (complexes **8**–**10**) and *meta* (complex **11**) positions, allowing our attention to be directed to the electronic properties of the alkyne as opposed to a coordinative or structural role, and ruling out cycloaromatization as a part of the catalytic cycle. The importance of electronic factors is further highlighted by the observation that activity is enhanced by an electron-withdrawing substituent (**9** versus **8**) and nearly abolished by an electron-donating group (**10** versus **8**). However, the installation of a *para* nitro group in place of a *para* nitro-substituted phenylacetylene unit eliminates catalysis (**12** versus **9**), showing that it is the alkyne fragment that is crucial. An (*E*)-1-hexenyl group at the *para* position (**13**) provides modest catalytic activity, indicating that an olefin is more activating than an alkyl group (**5** and **6**), but not as activating as an alkyne.

The electronic nature of complexes **8**–**10** was probed by cyclic voltammetry in CH_2Cl_2 solution. Reversible reduction waves, presumably arising from the $Ru^{II/I}$ redox couple, were observed at the following potentials (relative to ferrocene/ferrocinium ion (Fc/Fc^+)): **10** −1.030 V, **8** −1.023 V, **9** −0.987 V, representing a trend toward slightly easier reduction with increasing electron-withdrawing power of the *para* substituent. In each case, irreversible one-electron oxidation (ca. +0.8 V versus Fc/Fc^+) and reduction (ca. −1.8 V versus Fc/Fc^+) waves were also observed. No correlation between catalytic activity and ^{13}C NMR spectroscopic chemical shifts, or between catalytic activity and the positions and intensities of UV/Vis bands, or infrared spectral features of the allenylidene complexes are apparent.

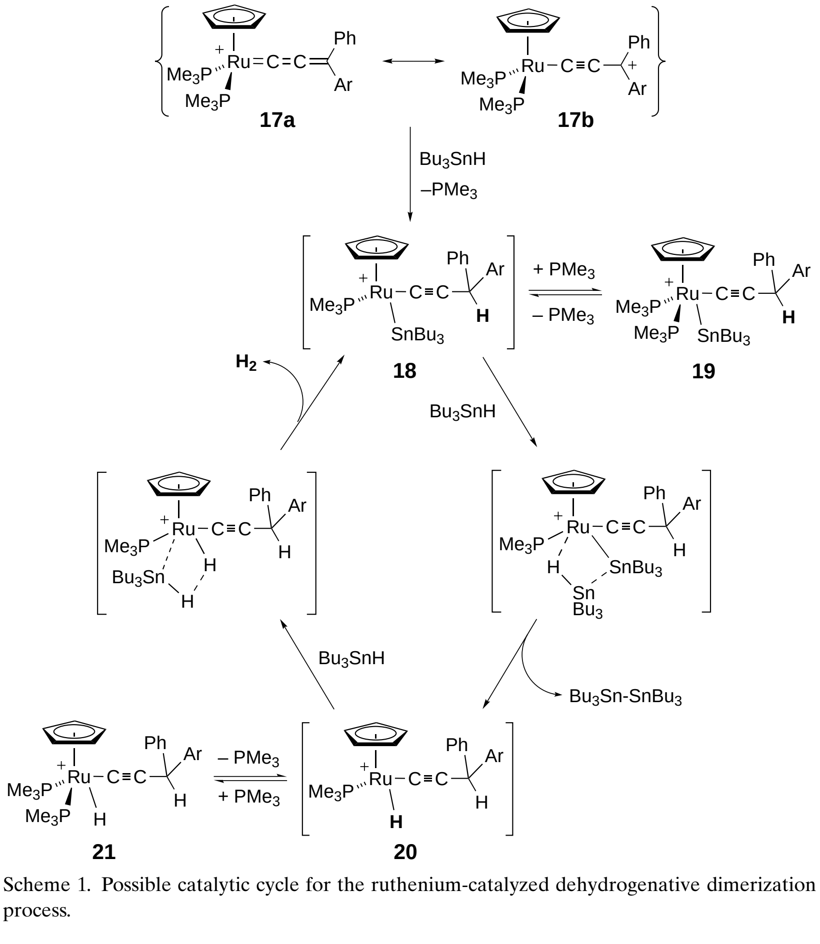
Catalytic reactions involving **3** and **4** were examined further. Under a nitrogen atmosphere, the extent of conversion at 5 min is not affected by the presence of 50 equivalents (with respect to Ru) of hydroquinone, suggesting that the process is not radical in nature.[14] However, it appears that competitive with the catalytic reaction is a decomposition process that is slowed or reversed by the presence of oxygen. For example, reducing the loading of complex **4** to 0.11 mol% gives 98% conversion of Bu_3SnH in 6 h in air (ca. 900 turnovers), but only 79% conversion under a nitrogen atmosphere. In this case, the reactions proceed to the same extent after the first hour (54%), but the reaction in air is longer-lived. For a variety of allenylidene complexes, additional catalytic activity was sometimes observed after a flask that contained a reaction that had slowed or stopped under nitrogen was opened to the air. Thus, dehydrodimerization reactions performed entirely in air using complexes **3**, **4**, **8**, **9**, and **13** show increased activities in the standard assay (Table 1) than those in nitrogen. Note, however, that for complex **3** the beneficial effect of air is eliminated by the presence of hydroquinone.

Even in air, catalyst decomposition masks what is a relatively fast process. Thus, a modest kinetic isotope effect (k_H/k_D) of 1.22 ± 0.1 was measured by competition reactions between Bu_3SnH and Bu_3SnD using complex **3** in air. During these studies, the rapid loss of catalytic function was again noted, with reactions being 50% complete after 30 seconds, 74% complete after 2 mins, 84% complete after 8 mins, and 96% complete after 15 mins. Initial turnover rates are therefore at least $1\,s^{-1}$, substantially greater than are indicated by the activity values shown in Table 1. These allenylidene systems are slower and shorter-lived than the Fe–Pd bimetallic catalysts of Braunstein et al. (maximum turnover frequency of ca. $8000\,s^{-1}$ and turnover number of 1×10^6)[4, 7] but more potent than simple Pd (300–2000 turnovers)[3, 4] or Au[6] catalysts.

Loss of catalytic activity is accompanied by a change in color from brown to yellow. This same color change occurs for the catalytically inactive complex **2** over 5–10 mins in the presence of excess Bu_3SnH, suggesting that the process that deactivates the catalysts may not require an allenylidene unit. Unfortunately, no conclusions could be drawn from NMR spectroscopic investigation of the Ru species remaining after catalysis is complete. No evidence of Ru–H bonds was obtained, and the presence of more than one species was suggested by the presence of multiple resonance signals in ^{31}P NMR spectra.

In analogy with previous mechanistic hypotheses for other catalysts,[4] distannane and dihydrogen may be produced from σ-bond metathesis reactions of $M-SnR_3$ and M–H intermediates, respectively, with R_3Sn-H.[15] The observed kinetic isotope effect, while substantially smaller than that observed for related reactions of Group IV organometallics with silanes ($k_H/k_D = 2.7$–3.6),[16] is close to the value found for a σ-bond metathesis process involving interaction of H centers with $[Cp(PR_3)_2Ru]^+$ and boron ($k_H/k_D = 1.62 \pm 0.13$).[17]

If one accepts the above assumption, then the crucial mechanistic issues are the generation of the required coordinatively unsaturated species containing a Ru–Sn or Ru–H bond, and the roles of the diarylallenylidene fragment and its alkyne or alkene substituents in facilitating that process. The outline of a working hypothesis is shown in Scheme 1. Although not a major contributor (as indicated by X-ray crystal structures and ^{13}C NMR spectroscopic data), resonance form **17b** can be involved in the distribution of charge in allenylidene complexes, and provides a way to connect reactivity at the metal center with substituents on the remote aromatic groups. Oxidative addition of tin hydride across the allenylidene unit would make available 16 electron or 18 electron Ru^{IV} intermediates **18** and/or **19** as the true catalyst(s) of sequential σ-bond metathesis steps to create Sn–Sn and H–H bonds as shown.[18] While the Hammett constants of *para* and *meta* substituents are substantially different for strongly donating groups such as NH_2 ($\sigma_{para} = -0.66$, $\sigma_{meta} = -0.16$), they are quite similar for other π-conjugated units such as CN (0.66, 0.56), Ph (−0.01, 0.06), and even NO_2 (0.78, 0.71). Thus, it is reasonable to expect both *meta* and *para* alkyne substituents to play a similar role if their electron-delocalizing abilities are important, as is indeed observed (complexes **4** and **11**, Table 1). However, the role played by such delocalization (explaining, for example, why **9** is active and **12** is not) and the exact nature of the active catalytic species remain to



Scheme 1. Possible catalytic cycle for the ruthenium-catalyzed dehydrogenative dimerization process.

be established. Although persistent radical species do not appear to be present,[14] paramagnetic ruthenium intermediates may be involved in the ability of dioxygen to slow or reverse catalyst decomposition.

The use of the 16 electron $[(\eta^6\text{-arene})(PR_3)(Cl)\text{-}Ru{=}C{=}C{=}CR_2]^+$ species in ring-closing metathesis[19, 20] represents the only other known example of catalytic reactivity involving metal–allenylidene complexes. The influence of remote aryl substituents on catalytic activity in the present case, along with similar observations for the metathesis process,[19] suggest that metal-centered reactivity in allenylidene systems may be tuned by purely electronic factors.

Experimental Section

Catalytic reactions: Bu_3SnH (0.10 mL, 0.37 mmol) was added rapidly in a single portion to a solution of the ruthenium complex (0.0053 mmol) in CH_2Cl_2 (15 mL), either in the open air or an inert-atmosphere drybox. Immediate gas evolution was observed, along with a gradual color change from dark brown to light yellow. An internal standard ($SnBu_4$, 0.034 mL, 0.104 mmol) was added; after exactly five minutes reaction time, a 2 μL aliquot was removed into 1 mL of solvent, thereby stopping the reaction for analysis by gas chromatography mass spectrometry (GC-MS; DB-5 column). Conversion into $Bu_3SnSnBu_3$ was determined by comparisons of the peak areas of both starting tin hydride and distannane to the internal standard, using independent calibration curves that were periodically updated and found to be highly reproducible. Only peaks for starting material and product were observed; the clean nature of the catalytic reactions was confirmed by NMR spectroscopy of unpurified reaction mixtures. Values reported in Table 1 are the average of 2–5 independent runs. Similar catalytic activities are observed in toluene and acetone solvents. See the Supporting Information for details of the syntheses of ruthenium–allenylidene complexes, determination of the deuterium isotope effect, electrochemistry, and X-ray crystallography.

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[11] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155085. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[12] Steric factors play a large role in the chemistry of these species. For example, complexes derived from benzaldehydes (thus lacking the unsubstituted phenyl group at C_γ in the allenylidene structure) are sensitive to attack of ethanol at C_γ under standard conditions for the reaction of terminal alkyne with the ruthenium precursor. This reaction, essentially the reverse of the dehydration step that converts vinylidene into allenylidene, is blocked for diarylallenylidenes. In addition, when a phenylacetylene group is placed at the *ortho* position, the corresponding allenylidene moiety could not be generated from the derived vinylidene, even upon treatment with strong acid. Attempted installation of an *ortho*-(*E*)-hexenyl group was rewarded with some of the desired allenylidene complex, as an unpurifiable mixture with contaminating by-products.

[13] The addition of 2-hexyne to reactions involving **1**, **3**, or **4** does not substantially inhibit the dehydrogenative dimerization process (kinetic measurements were not performed), nor does 2-hexyne stimulate the parent complex **2** to become an active catalyst. Catalysis using **4** is also unaffected by the presence of a large excess of 1-octene, and added trimethylphosphane irreversibly attacks the allenylidene complex (presumably at $C\gamma$), eliminating catalytic activity. Ph_3SnH undergoes dehydrogenative dimerization slowly with our catalysts, while Et_3SiH is unreactive.

[14] Species with unpaired electrons were not detected when an active reaction mixture was quickly frozen in liquid nitrogen and examined by EPR spectrometry. Thawing of the frozen solution afterwards resulted in a resumption of catalytic activity.

[15] Because of competitive decomposition, initial rates were difficult to obtain with precision and the rate order in ruthenium was not determined. Because of the maintenance of high activity at low Ru concentrations, we assume the reaction to be first order in catalyst.

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