Transition-Metal Hydrides as Hydrogen Atom Donors: Stronger Metal−Hydrogen Bonds Can Be Advantageous

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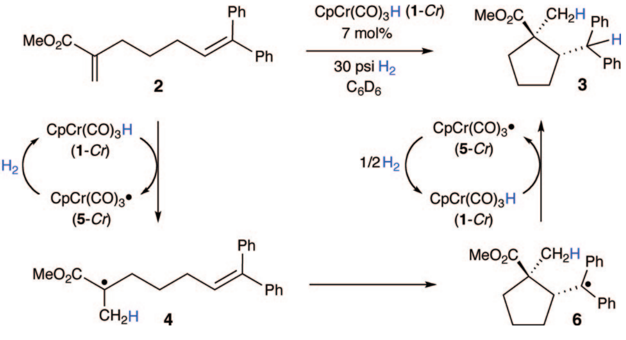
*Summary: The tungsten hydride complex (η^5-C_5H_5)W(CO)$_3$H (**1**-W) functions as a hydrogen atom donor in the [(η^5-C_5Me_5)Ru(NCMe)$_3$]PF$_6$-mediated Bergman cycloaromatization reaction of (Z)-dodeca-4,8-diyn-6-ene. The strong M−H bond in **1**-W does not react with the enediyne substrate but does react with the diradical arising from cyclization, thereby demonstrating the advantages of strong metal−hydrogen bonds in the hydrogen atom transfer reactions of metal hydrides with substrates involving alkenes and alkynes.*

A key consideration in the development and application of many radical reactions concerns the nature of the hydrogen atom donor that is employed for trapping carbon-based radicals.[1] Very recently there have been efforts to replace the traditional stoichiometric organotin reagents with transition-metal hydrides.[2−4] In principal, transition-metal hydrides can be generated in situ from H_2 and a metal complex, thereby permitting the use of hydrogen gas as the ultimate atom-economical hydrogen atom donor. For example, Gansäuer and co-workers recently reported that Wilkinson's catalyst functions in this manner for the titanocene dichloride catalyzed radical reduction of epoxides.[4] In cases where the organic substrate contains an alkene, the metal hydride may play a dual role, both by triggering formation of a carbon radical, via initial hydrogen atom transfer to the alkene, and by subsequent trapping of the rearranged carbon radical, by a second hydrogen atom transfer. Norton and co-workers have demonstrated that, under 30 psi of hydrogen gas, (η^5-C_5H_5)Cr(CO)$_3$H (**1**-*Cr*) catalyzes the radical cyclization of diene **2** over the course of 4−10 days, to give the cyclopentane derivative **3** as the major product (Scheme 1).[2] The mechanism of this reaction involves initial hydrogen atom transfer from **1**-*Cr* to the disubstituted alkene of **2**, to generate the tertiary radical **4** and (η^5-C_5H_5)Cr(CO)$_3^{\bullet}$ (**5**-*Cr*). Intermediate **4** undergoes spontaneous cyclization to **6**, and reaction of **5**-*Cr* with H_2 regenerates **1**-*Cr*, which in turn transfers a hydrogen atom to **6**. In order to increase the rate of reaction, a metal hydride with a weaker metal−hydrogen bond was sought, and V(CO)$_4$(dppe)H was found to undergo more rapid reaction with **2** than did **1**-*Cr*. The vanadium hydride, however, is relatively unreactive toward hydrogen gas, thereby rendering the vanadium system stoichiometric in metal hydride.[3] Thus, weak metal−hydrogen bonds are needed to transfer a hydrogen atom to the alkene, but strong metal−hydrogen bonds facilitate oxidative addition of hydrogen gas. This quandary is rendered moot when the hydrogen atom donor functions only to deliver hydrogen atoms to reactive carbon radicals. In such cases, metal hydrides with strong metal−hydrogen bonds should be advantageous.

Scheme 1. Norton's Chromium Hydride Catalyzed Radical Cyclization



The Bergman cycloaromatization of enediynes[5] is an ideal test case for the use of metal hydrides for selective hydrogen atom transfer to carbon radicals—with no competitive reduction of alkene and alkyne functional groups. We recently demonstrated that [(η^5-C_5Me_5)Ru(NCMe)$_3$]PF$_6$ (**7**) functions as a room-temperature trigger for the Bergman cycloaromatization of enediynes (e.g., **8**) to give ruthenium arene products (**9**) (eq 1).[6] When THF-d_8 is employed as the solvent, the arene ligand in **9** is enriched with deuterium in the 1,4-positions. When chloroform is employed as the solvent, it is necessary to add a hydrogen atom donor, such as 1,4-cyclohexadiene, to the reaction mixture. Here we report the first example in which a transition-metal hydride functions as a hydrogen atom donor in the Bergman cycloaromatization reaction. More generally, this work represents the first instance where transition-metal hydrides are utilized as hydrogen atom donors for alkene-/alkyne-containing substrates, without hydrogen atom transfer to the carbon−carbon multiple bond(s).

The use of metal hydrides as hydrogen atom donors in the ruthenium-triggered Bergman cycloaromatization reaction has a number of potential pitfalls. The metal hydride must not undergo competitive reaction with the alkene, the alkyne, or

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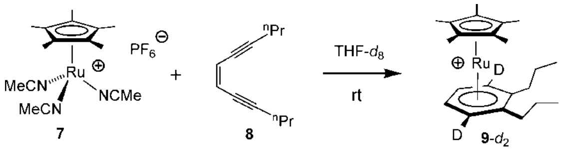
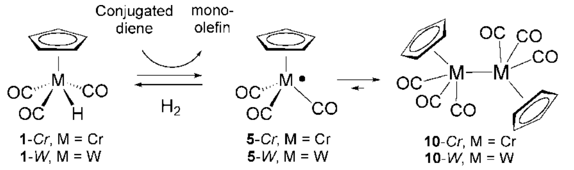


(1)

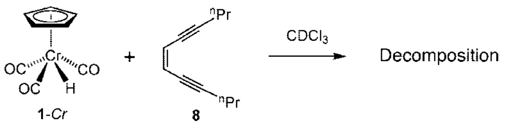
the ruthenium cation. Furthermore, the metallo radical generated upon hydrogen atom transfer must be unreactive toward both the enediyne substrate and the ruthenium reagent. In order to achieve a catalytic system, the rate of metal hydride regeneration must also be rapid relative to the rate of aryne formation. In order to test the feasibility of using metal hydrides as hydrogen atom donors in the ruthenium-triggered Bergman cycloaromatization reaction, we first examined the use of metal hydrides in stoichiometric amounts.

We were attracted to the use of **1**-*Cr* and **1**-*W* as potential stoichiometric hydrogen atom donors on the basis of the work of Norton[2] and of Bullock[7] and by prior reports which indicated that **1**-*M* reduces conjugated dienes to monoolefins and the metallo radical **5**-*M* (M = Cr, Mo, W).[8] The metallo radicals exist in equilibrium with the corresponding metal dimers [(η^5-C_5H_5)M$(CO)_3$]$_2$ (**10**-*M*, eq 2). It was anticipated that the formation of **10**-*M* would decrease the likelihood that **5**-*M* would undergo undesired reactions with enediyne **8** or ruthenium reagent **7**.



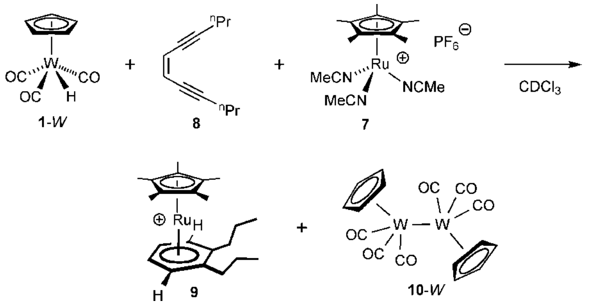
(2)

The weak metal−hydrogen bond in (η^5-C_5H_5)Cr$(CO)_3$H (**1**-*Cr*) is expected to favor hydrogen atom transfer to the enediyne substrate over the desired reaction of **7** with enediyne. Indeed, when **1**-*Cr* was added to a $CDCl_3$ solution containing only **8**, an immediate reaction ensued to give substantial decomposition of the starting materials (eq 3).[9]



(3)

The tungsten−hydrogen bond in **1**-*W* is estimated from the work of Norton[2c] and Tilset[10] to be approximately 10 kcal/mol stronger than the chromium−hydrogen bond in **1**-*Cr*. In addition, the W−W bond in **10**-*W* has been estimated to be approximately 43 kcal/mol stronger than the Cr−Cr bond in **10**-*Cr*.[8b] Thus, the equilibrium between **5**-*W* and **10**-*W* lies much farther to the right than in the case of the chromium analogue. As anticipated, when a room-temperature $CDCl_3$ solution containing **1**-*W* and enediyne **8** was monitored by ^{1}H NMR spectroscopy, there was no evidence for the occurrence of a reaction. Less promising was the observation that addition of **7** to a $CDCl_3$ solution of **1**-*W* led to significant decomposition within 10 min at room temperature. Remarkably, when enediyne **8** (2.5 mg, 0.015 mmol, 0.025 M) and **1**-*W* (103 mg, 0.31 mmol) were dissolved in $CDCl_3$, followed by addition of **7** (8.3 mg, 0.016 mmol) to the solution, the cycloaromatized product **9** was formed in 91% yield after 10 min, as determined by integration of the ^{1}H NMR resonances for **8** and **9** relative to those of the 1,3,5-tritertbutylbenzene internal standard (eq 4).[9b] In addition to arene complex **9**, the formation of the expected tungsten dimer **10**-*W* was observed. When the ratio of **1**-*W* to **8** was decreased from 20:1 to 10:1, the yield of **9** decreased negligibly to 90%; even at a 2.5:1 ratio of **1**-*W* to **8**, the yield of **9** was 83%. For comparison, we examined the reaction of **7** and **8**, in the presence of 2.5 equiv of 1,4-cyclohexadiene as the hydrogen atom donor, and observed a 95% yield of **9** after 10 min.



(4)

The results reported herein demonstrate that it is possible to utilize transition-metal hydrides as hydrogen atom donors for organic radicals, with no significant transfer of the hydrogen atom to carbon−carbon multiple bonds in the substrate. A key requirement for reactions of this type is the employment of metals with relatively strong metal−hydrogen bonds, which should also facilitate the activation of H_2. In the case of **1**-*W*, the tungsten dimer that is formed subsequent to hydrogen atom transfer contains a relatively strong metal−metal bond, thereby requiring high temperatures for reaction with H_2 and conversion back to **1**-*W*. We are now focusing on the use of dihydrogen complexes which lack cis coordination sites in order to circumvent undesired alkene and alkyne hydrogenations. If successful, such a system would represent a new mechanism for the use of hydrogen gas as the ultimate hydrogen atom donor.

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Supporting Information Available: Text giving experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) As pointed out by a reviewer, transition-metal hydrides are notorious for reacting with $CHCl_3$ by a radical chain process and this may be part of what is happening in eq 3. (b) For the reaction shown in eq 4, integration of the ^{1}H NMR resonances for the arene ligand of **9** indicates that there is no detectable deuterium atom enrichment due to hydrogen atoms that might arise from $CDCl_3$ solvent.

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