# ORGANOMETALLICS

# *Communications*

## Hydrovinylation and [2+2] Cycloaddition Reactions of Alkynes and Alkenes Catalyzed by a Well-Defined Cationic Ruthenium−Alkylidene Complex

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*Summary: The cationic ruthenium−alkylidene complex $[(PCy_3)_2(CO)(Cl)Ru=CHCH=C(CH_3)_2]^+BF_4^-$ (1) was found to catalyze both hydrovinylation and [2+2] cycloaddition reactions of alkynes and alkenes. The reaction of $R'C≡CR''$ (R' = H, Ph, n-Pr; R'' = Ph, n-Pr, p-Tol, $SiEt_3$, $CH_2CH_2OH$) with ethylene in the presence of 1 (3 mol %) produced the hydrovinylation products 2 and 3. The analogous reaction of dimethyl acetylenedicarboxylate (R' = R'' = $CO_2Me$) with ethylene and norbornene resulted in the formation of the [2+2] cycloaddition products 4. Based on the experimental evidence, a plausible mechanism of the hydrovinylation reaction has been proposed via a sequential insertion of alkyne and ethylene to the hydride complex 7.*

Metal-catalyzed cross-coupling reactions of alkynes and alkenes are a versatile method for forming conjugated organic compounds.[1] For example, metallacyclopentadiene complexes have been well-known to mediate [2+2+2] cycloaddition reactions of alkynes and alkenes to form cylohexadiene compounds.[1b,c] Recently, different catalytic methods of 1:1 alkyne-to-alkene coupling reactions have been reported including (1) the formation of 1,3-dienes from the linear coupling reaction of alkynes

and alkenes,[2] (2) the cross-metathesis reaction of enynes by Grubb's ruthenium−alkylidene catalyst $(PCy_3)_2Cl_2$-Ru=CHPh,[3] and (3) the formation of cyclobutenes from the [2+2] cycloaddition reaction.[4] We previously reported the formation of heptatriene compounds from a 2:1 linear coupling reaction of acetylene and alkenes using a ruthenacyclopentadiene complex as a catalyst.[5] Herein we wish to report that the well-defined ruthenium−alkylidene complex $[(PCy_3)_2(CO)(Cl)Ru=CHCH=C(CH_3)_2]^+BF_4^-$ (1)[6] catalyzes two different types of 1:1 alkyne-to-alkene cross-coupling reactions, namely, the hydrovinylation and [2+2] cycloaddition reactions.

We explored catalytic activity of the complex 1 toward the coupling reaction of alkynes and alkenes in anticipation that it could lead to enyne metathesis products.

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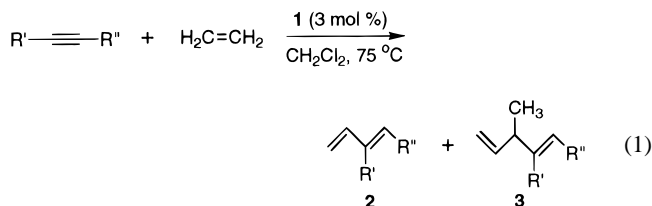
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(6) The synthesis and reactions of the P(i-Pr)$_3$ analogue of 1 have been extensively described in: Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Oñate, E.; Peinado, E.; Ruiz, N. *Organometallics* **1997**, *16*, 5748, and references therein.

$$R'{-}{\equiv}{-}R'' \ + \ H_2C{=}CH_2 \xrightarrow[\text{CH}_2\text{Cl}_2,\ 75\ ^\circ\text{C}]{\textbf{1}\ (3\ \text{mol}\ \%)}$$



(1)

Instead, the treatment of PhC≡CPh (27 mg, 0.15 mmol) with $CH_2{=}CH_2$ (2.3 atm, 3.2 mmol) in the presence of **1** (4 mg, 3 mol %) in $CH_2Cl_2$ at 75 °C after 5 h cleanly yielded the hydrovinylation product **2a** in 90% isolated yield (eq 1). In the crude product mixture, a trace amount of the 2:1 product **3a** (<2%) was also detected by GC−MS. The product **2a** was readily isolated by column chromatography, and its structure was completely established by spectroscopic methods.[7] The phosphine ligand was shown to inhibit the coupling reaction; for example, addition of 10 mol % of PCy₃ to the reaction mixture produced virtually no products after 12 h under otherwise similar reaction conditions.

The scope of the hydrovinylation reaction was explored by employing both terminal and internal alkynes using **1** as a catalyst (Table 1). In general, the 1:1 coupling product **2** was formed predominantly for internal alkynes, while a mixture of both 1:1 and 2:1 coupling products **2** and **3** was isolated for terminal alkynes. The ratio of products was found to be dependent on the reaction time; for example, a 74:26 mixture of **2c**:**3c** initially formed after 2 h converted mostly to the 2:1 coupling product **3c** after a prolonged reaction time (14 h). For internal alkynes, the formation of 2:1 products was found to be sluggish, yielding <10% of **3** after 14 h. The 2:1 product **3** was most likely formed from the secondary hydrovinylation reaction of **2**, where the vinyl group was selectively added to the internal vinyl carbon of **2**. This type of regioselectivity pattern has been commonly observed in metal-catalyzed hydrovinylation of dienes.[8]

In an attempt to extend the scope of reaction, we next examined the coupling reaction of functionalized alkynes. We found that the reaction of dimethyl acetylenedicarboxylate (DMAD) with ethylene in the presence of **1** (5 mol %) produced mostly the [2+2] product **4a** at 60 °C under otherwise similar reaction conditions (Scheme 1). Interestingly, a mixture of both **4a** and **2f** was formed at a higher temperature (**4a**:**2f** = 3:1 at 75 °C). The similar reaction of DMAD with norbornene also yielded the [2+2] product **4b**.[7] The heating of **4a** in $CH_2Cl_2$ at 85 °C for 24 h in the presence or absence of **1** did not give the 1,3-butadiene product **2f**. Examples of metal-catalyzed [2+2] cycloaddition reaction of alkynes and alkenes are quite rare,[4] and to the best of our knowledge, this is the first example in which a single metal catalyst has been shown to promote both hydrovinylation and [2+2] cycloaddition reactions of alkynes and alkenes.

A number of different mechanisms have been proposed for the cross-coupling reactions of alkynes and

**Table 1. Hydrovinylation of Alkynes Catalyzed by 1**[a]

| entry | R′ | R″ | product ratio[b] | reaction time (h) | yield (%)[c] |
|---|---|---|---|---|---|
| 1 | Ph | Ph | **2a**:**3a** = 98:2 | 5 | 91 |
| 2 | *n*-Pr | *n*-Pr | **2b**:**3b** = >98:2 | 7 | 90 |
| 3 | H | *p*-Tol | **2c**:**3c** = 74:26 | 2 | 95 |
| 4 | H | SiEt₃ | **2d**:**3d** = 94:6 | 2 | 82 |
| 5 | H | CH₂CH₂OH | **2e**:**3e** = 92:8 | 2 | 57 |

[a] Reaction conditions: 0.15 mmol of alkyne; 3.2 mmol of ethylene; 3 mol % of **1**; 3 mL of $CH_2Cl_2$; 75 °C. [b] Determined by the GC-MS. [c] Combined isolated yield of **2** and **3**.

**Scheme 1**
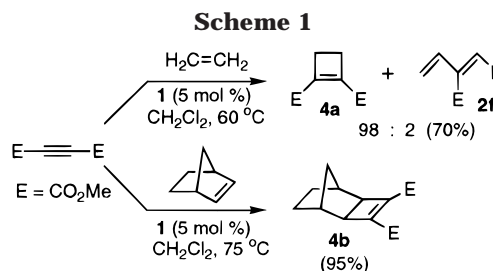


alkenes.[1,9,10] For example, metallacyclopentene species have been commonly proposed in metal-catalyzed coupling reactions of enynes,[9] while similar transformations have been shown to occur via a metal−carbene intermediate in some reactions.[10] In a related ruthenium-catalyzed hydrosilylation of terminal alkynes, a mechanism involving an insertion of alkyne to a metal−hydride species has also been proposed.[11] In our case, the formation of hydrovinylation products **2** and **3** can be explained by invoking a sequential insertion of alkyne and ethylene to metal−hydride and −vinyl species. To test this hypothesis, we prepared both the ruthenium−hydride complex (PCy₃)₂(CO)(Cl)RuH (**5**) and the vinyl complex (PCy₃)₂(CO)(Cl)RuCH=CHPh (**6a**), following the literature procedure.[12] The exposure of ethylene (1 atm) to a C₆D₆ solution containing **6a** cleanly converted to a ca. 1:1 mixture of both **3f** and the ruthenium−hydride complex **5** as identified by NMR (eq 2). Furthermore, both the hydride and the vinyl complexes **5** and **6a** were found to catalyze the hydrovinylation reaction of alkynes, although their catalytic activity was considerably lower than **1** under similar reaction conditions.[13]

(7) See the Supporting Information for the characterization data of these compounds.

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(10) (a) Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020. (b) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. (c) Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9104.
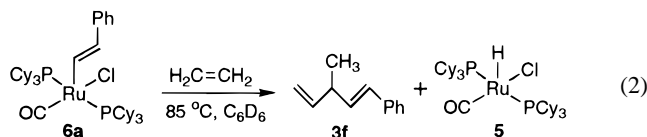
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(13) For example, the hydrovinylation reaction of PhC≡CPh in the presence of **5** or **6a** yielded 43% of the hydrovinylation product **2a** along with *ca.* 50% of the unreacted alkyne after 2 h under similar reaction conditions.

$$(2)$$

In an attempt to distinguish the insertion vs the enyne metathesis mechanism,[3] the labeled compound $H_2^{13}C={}^{13}CHC(Ph)=CHPh$ (**2a**-$^{13}C$) (>95% $^{13}C$) was prepared from an analogous reaction of $PhC\equiv CPh$ with $H_2^{13}C={}^{13}CH_2$ (Cambridge Isotopes, 99% $^{13}C$). The treatment of the labeled **2a**-$^{13}C$ with excess $CD_2=CD_2$ (1 atm) in the presence of **1** led to the extensive deuterium incorporation on all vinyl positions of **2a**-$^{13}C$ with no detectable scrambling of $^{13}C$ atoms. This result is consistent with the insertion mechanism of alkyne and ethylene via a metal−hydride species and further suggests that the alkene insertion/$\beta$-hydride elimination step is reversible and fast compared to the formation of the 2:1 product.

While a detailed mechanism of the coupling reaction still remains to be established, the above results suggest a mechanistic path for the hydrovinylation reaction as shown in Scheme 2. We propose that the deprotonation of the $\delta$-methyl group of **1** followed by the elimination of $Cy_3PH^+BF_4^-$ and the triene $CH_2=CHCH=CHC(CH_3)=CH_2$ would form the hydride species **7**. In support of this hypothesis, the formation of $Cy_3PH^+BF_4^-$ in the crude product mixture was identified by $^{31}P$ NMR ($\delta$ 31.3), which matched well with an independently generated phosphonium salt. The $\delta$-methyl group of **1** was also shown to be acidic;[14] the treatment of **1** with $Et_3N$ in THF cleanly produced the vinyl complex $(PCy_3)_2(CO)(Cl)RuCH=CHC(CH_3)=CH_2$ (**6b**).[7] Furthermore, all three complexes **1**, **5**, and **6** were shown to be active toward the hydrovinylation reaction, and this suggests that the reaction proceeds via a common intermediate species such as **7**. The reason for superior catalytic activity of **1** in both hydrovinylation and [2+2] cycloaddition reactions compared to **5** and **6** may be due to the conversion of $PCy_3$ into $Cy_3PH^+$ in the reactions catalyzed by **1**.[15] As shown in Scheme 2, the sequential insertions of alkyne and alkene followed by the $\beta$-H

**Scheme 2**
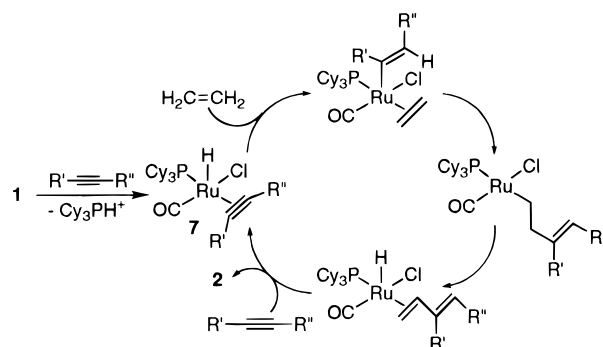


elimination have been imposed to explain the product formation.[16] We believe that the [2+2] product **4** was formed from an independent pathway, probably via the formation of a metallacyclopentene species and the subsequent reductive elimination of cyclobutene. While metallacyclopentene species have been commonly proposed in alkyne-to-alkene coupling reactions,[9] the factors governing the formation of [2+2] products have not been clearly established at this time. Further research is currently under way to establish both the detailed mechanism and the factors leading to different reaction pathways for these coupling reactions.

**Supporting Information Available:** Experimental procedure and characterization data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

(14) Protons $\alpha$ to the carbene carbon in electrophilic metal−carbene complexes are known to be mildly acidic. For representative examples, see: (a) Casey, C. P. In *Transition Metal Organometallics in Organic Synthesis*; Alper, H., Ed.; Academic Press: New York, 1976; Vol. 1. (b) Casey, C. P.; Vosejpka, P. C.; Askham, F. R. *J. Am. Chem. Soc.* **1990**, *112*, 3713. (c) Montgomery, J.; Wieber, G. M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 6255.
(15) We believe that the formation of $Cy_3PH^+$ effectively sequesters the phosphine ligand from coordinating to the metal center, making the catalyst **1** more reactive compared to **5** or **6**. In contrast, the reactions catalyzed by **5** and **6** would be inhibited by an initially dissociated $PCy_3$ ligand.

(16) We have also considered a mechanism involving metallacyclopentene species generated from an oxidative coupling of an alkyne and ethylene.[2] In an attempt to test this possibility, reactions of alkynes with substituted alkenes have been examined under similar reaction conditions. For example, the reaction of $HC\equiv CSiEt_3$ with cyclopentene in the presence of 5 mol % of the catalyst **1** cleanly gave the product **8** (85% yield) (eq 3).[7]



$$(3)$$
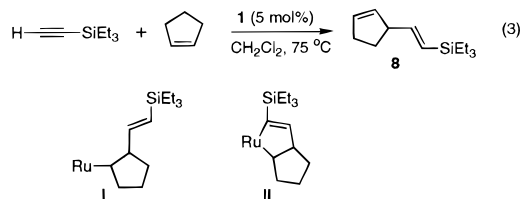


The formation of **8** is consistent with the insertion mechanism involving the $\beta$-H elimination of a less substituted $CH_2$ group from the secondary alkyl intermediate **I**, but the possibility of involving metallacyclopentene intermediate **II** still cannot be rigorously ruled out at the present time.