3910 *Organometallics* **1997,** *16,* 3910−3913

Ruthenium−Acetylide-Mediated Catalytic Dimerization of RC≡CH (R = Ph, CO_2Me) and the Formation of the New Ruthenium η^3-Butadienyl Complex $C_5Me_5Ru(PPh_3)[\eta^3\text{-}PhCHCHC{=}C(Ph)C{\equiv}CCPh]$

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Received May 1, 1997[⊗]

The *in-situ*-generated ruthenium−acetylide species $C_5Me_5Ru(PPh_3)C{\equiv}CPh$ (**1**) was found to catalyze the dimerization of RC≡CH to give predominantly the head-to-head dimers *trans*-RCH═CHC≡CR (R = Ph (**3**), TON = 607 h^{-1}; R = CO_2Me (**4**), TON = 975 h^{-1}). A new ruthenium η^3-butadienyl complex $C_5Me_5Ru(PPh_3)(\eta^3\text{-}PhCHCHC{=}C(Ph)C{\equiv}CPh)$ (**5**) was isolated at the end of the catalytic dimerization of PhC≡CH (81% based on Ru). The structure of the 1.5 benzene-solvated complex $\mathbf{5}\cdot 1.5C_6H_6$ was established by X-ray crystallography. Complex **5** was independently prepared from the stoichiometric reaction of $C_5Me_5Ru(PPh_3)$-(Cl)═C═CHPh (**2**) with the dimer **3** in the presence of NEt_3. The formation of an intermediate η^2-alkyne complex $C_5Me_5Ru(PPh_3)(\eta^2\text{-}PhCH{=}CHC{\equiv}CPh)(C{\equiv}CPh)$ (**6**) was observed during the reaction.

Introduction

The transition-metal-mediated dimerization of terminal alkynes is of considerable current interest because it can lead to a wide variety of organic enyne and oligoacetylene products that are useful synthetic precursors for organic conducting polymers and other carbon-rich allotropes.[1−4] For example, the copper−acetylide catalysts have been employed in an industrial-scale dimerization of HC≡CH to produce CH_2═CH-C≡CH, a key precursor for neoprene rubber.[1a] Recently, transition-metal-based catalysts have been shown to selectively produce both the 1,3-disubstituted enynes[2] and the 1,4-disubstituted enynes[3] from the dimerization of terminal alkynes. The stereoselective formation of *cis*-1,4-disubstituted butatrienes has also been achieved from the dimerization of alkyl-substituted alkynes.[4] We recently reported the ruthenium-catalyzed dimerization of terminal alkynes to produce both 1,3- and 1,4-disubstituted enynes and butatrienes and proposed a mechanism involving a coordinatively unsaturated ruthenium−acetylide species.[5] We also developed an effective route to the coordinatively unsaturated acetylide species $C_5Me_5Ru(PPh_3)C{\equiv}CPh$ (**1**) from the reaction of the vinylidene complex $C_5Me_5Ru(PPh_3)(Cl){=}C{=}CHPh$ (**2**) with a base and found that the ruthenium acetylide **1** was reactive toward a variety of small molecules such as CO, H_2, and CO_2.[6] Herein, we report the ruthenium−acetylide-mediated catalytic dimerization of terminal alkynes and the formation of a new (η^3-butadienyl)-ruthenium complex.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

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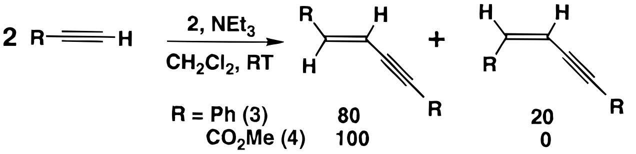
S0276-7333(97)00366-X CCC: $14.00

Results and Discussion

In an attempt to establish the intermediacy of the ruthenium−acetylide complex **1** during the dimerization of terminal alkynes,[5] the reaction of *in-situ*-generated **1** with PhC≡CH was investigated. In a typical reaction, a catalytic amount of **2** (10 mg, 0.016 mmol) and Et$_3$N (22 μL, 0.16 mmol) in CH$_2$Cl$_2$ was treated with excess PhC≡CH (57 μL, 0.52 mmol) at room temperature for 24 h. The ^{1}H NMR spectrum of the reaction mixture showed a predominant formation of the trans dimer *trans*-PhCH=CHC≡CPh (**3a**) over the cis isomer *cis*-PhCH=CHC≡CPh (**3b**) (**3a**:**3b** = 4:1). The organic products were isolated from simple column chromatography on silica gel (3:1 Et$_2$O/hexanes), and the structure of the products was completely established by spectroscopic methods (TON = 607 h^{-1}, 75% yield). The present dimeric product ratio was complementary to the previously reported dimerization of PhC≡CH by the ruthenium−hydride complex C$_5$Me$_5$Ru(PPh$_3$)H$_3$, which produced a 35:65 mixture of **3a** and **3b**.[5]



The ruthenium−acetylide complex **1** also displayed an unusual selectivity toward the dimerization of other functionalized alkynes. For instance, the acetylide **1**-catalyzed dimerization reaction of HC≡CCO$_2$Me produced *exclusively* the linear dimer *trans*-MeO$_2$C-CH=CHC≡CCO$_2$Me (**4**) in an 80% isolated yield. The rate of the formation of **4** at room temperature was slightly faster than that of the formation of **3** (TON = 975 h^{-1}), and no other dimeric or higher oligomeric products was detected by ^{1}H NMR. Normally, a metal-mediated homocoupling reaction of HC≡CCO$_2$Me has been well-known to preferentially give the cyclotrimerization products,[7] and to the best of our knowledge, this is the first example of metal-catalyzed linear dimerization of HC≡CCO$_2$Me.

A small amount of a new ruthenium species was isolated at the end of the catalytic dimerization reaction of PhC≡CH (81% based on Ru). The ^{1}H NMR spectrum of the new species exhibited two allyl protons at δ 3.68 (dd, J_{HH} = 8.8 Hz, J_{PH} = 3.7 Hz) and 3.00 (dd, J_{HH} = 8.8 Hz, J_{PH} = 14.0 Hz) which were coupled both to each other and with the phosphorus atom. The structure of the complex was determined as the η^3-butadienyl complex **5** from the single-crystal X-ray crystallography (Figure 1). The molecular structure of **5** can be described best as a distorted η^3-butadienyl complex, where the ruthenium center is bonded to three butadienyl carbons with an overall *exo,syn*-π-allyl geometry. Significantly longer distances for two of the allyl carbons from the ruthenium center (Ru−C(14) = 2.282(3) Å, Ru−C(13) = 2.124(3) Å) compared to that of the enynyl carbon (Ru−C(12) = 2.026(3) Å) indicated that the complex has a major resonance contribution from the vinyl−alkene structure (Table 1). Also, relatively uniform bond distances between three alllyl carbons (C(12)−C(13) = 1.426(5) Å, C(13)−C(14) = 1.431(5) Å) are indicated of a substantial delocalization of π-electrons. The apparent distortion of the butadienyl ligand may be due in part to the steric interaction between the Ph group and the PPh$_3$ ligand, as indicated by the solid-state structure and a notably small *trans* allylic proton coupling constant (J = 8.8 Hz). Similar ruthenium η^3-butadienyl complexes have been previously prepared from the [2 + 2]-cycloaddition reaction of ruthenium−acetylide complexes with electron-deficient alkenes.[8] Complex **5** was shown to be inactive toward the dimerization of PhC≡CH.

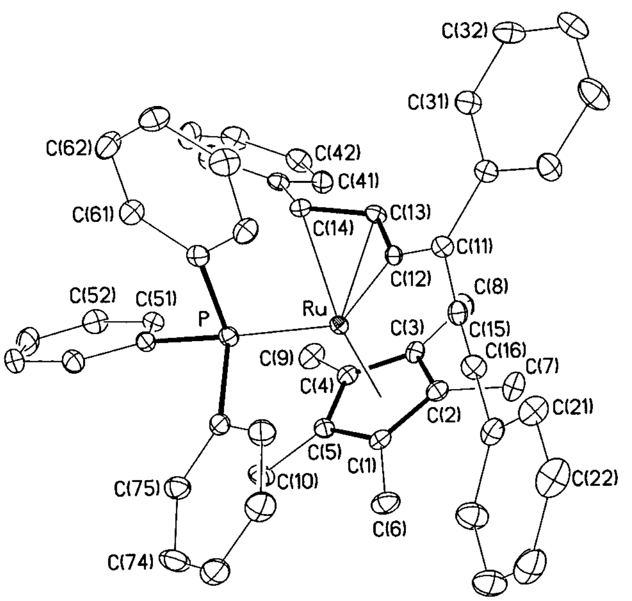


Figure 1. Molecular structure of **5**·1.5C$_6$H$_6$ drawn with 35% thermal ellipsoids.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg)

	Bond Distances		
Ru−C(12)	2.026(3)	Ru−C(13)	2.124(3)
Ru−C(14)	2.282(3)	Ru−Cp*(cent)	1.889(3)
Ru−P	2.322(1)	C(11)−C(12)	1.361(5)
C(12)−C(13)	1.426(5)	C(13)−C(14)	1.431(5)
C(11)−C(15)	1.443(5)	C(15)−C(16)	1.199(5)
	Bond Angles		
C(11)−C(12)−C(13)	136.5(3)	C(12)−C(13)−C(14)	117.9(3)
C(12)−Ru−P	95.64(10)	C(14)−Ru−P	83.43(10)
C(11)−C(12)−Ru	147.0(3)	C(12)−Ru−C(13)	40.11(13)
C(12)−Ru−C(14)	68.95(13)	C(12)−C(11)−C(15)	120.0(3)

To gain some insight on the formation of **5**, the stoichiometric reaction of the vinylidene complex **2** (10 mg, 0.016 mmol) with PhC≡CH (3 μL, 0.032 mmol) and Et$_3$N (4 μL, 0.032 mmol) in CD$_2$Cl$_2$ was followed by ^{1}H NMR spectroscopy at room temperature (Figure 2). Initially, rapid formation of the dimers **3a** and **3b** was observed. After ~20 min, new ruthenium species began to appear, as indicated by the new Cp* resonance at δ 1.44 and the vinyl protons at δ 6.73 and 6.50 (d, J = 15.9 Hz) as well as the resonances due to **5**. The spectroscopic data of the new ruthenium species was consistent with the η^2-alkyne complex **6**.[9] The ruthenium product **5** was gradually formed over 12 h at the

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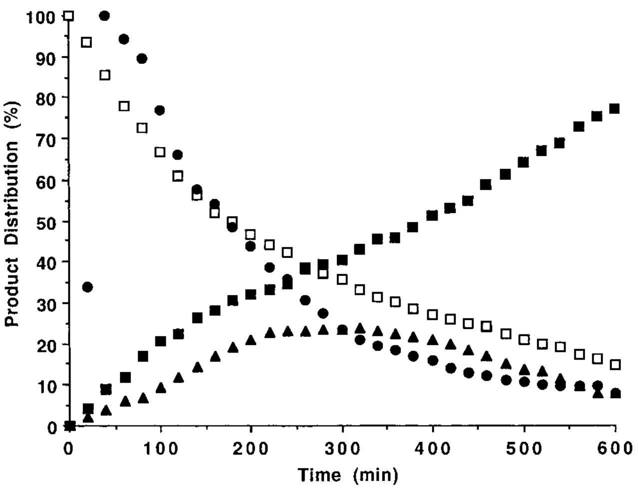
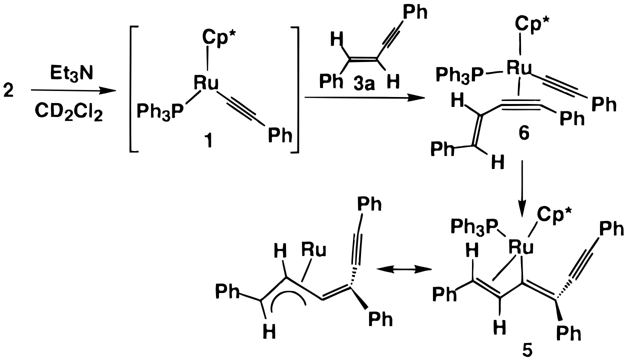


Figure 2. Stoichiometric reaction profile of **2** (10 mg, 0.016 mmol) with PhC≡CH (3 μL, 0.032 mmol, 2 equiv) and Et_3N (4 μL, 0.032 mmol, 2 equiv) in CD_2Cl_2, as monitored by ^1H NMR at 20 °C. For clarity, only complexes **2** (□), 5 (■), **6** (▲), and the dimer **3a** (●) are shown.

Scheme 1



expense of both complexes **6** and **3a**. Interestingly, no notable change in concentration of the cis dimer **3b** was observed during the entire reaction period.

The fact that **5** was generated even after most of PhC≡CH was converted to dimer **3** and that **5** was formed at the expense of both **6** and dimer **3** suggested that **5** was obtained from the coupling reaction of **1** with **3** (Scheme 1). In support of this hypothesis, reaction of **2** with <1 equiv of PhC≡CH produced a relatively long-lived complex **6**, as in this case, it could not be converted to **5** in the absence of **3**. Also, complex **5** was formed independently from a stoichiometric reaction of **2** (500 mg, 0.79 mmol) with PhC≡CH (0.86 mL, 7.9 mmol) and Et_3N (1.1 mL, 7.9 mmol) in 81% isolated yield. The *syn* geometry between the −C≡CPh group and the PPh_3 ligand of **5** was also consistent with the intramolecular migration of the acetylide to the coordinated enyne **3** *via* the alkyne intermediate **6**.

The formation of 1,4-disubstituted enynes **3** can be rationalized readily from a migratory insertion of the coordinated RC≡CH (R = Ph, CO_2Me) to the ruthenium−acetylide and the subsequent reductive coupling with another alkyne substrate.[1b,3] While the formation of the 1,4-enynes has been previously explained by invoking an acetylene-to-vinylidene rearrangement and the subsequent acetylide migration,[3,5] the direct insertion pathway seems to be preferred for alkynes with electron-withdrawing groups at relatively low temperature, where the acetylene-to-vinylidene tautomerization is relatively slow.[1c,2] The formation of η^3-butadienyl complex **5** can be rationalized similarly by invoking the intramolecular migratory insertion of the enyne **3** *via* the alkyne-coordinated **6** in which the acetylide ligand is selectively added to the phenyl-substituted acetylenic carbon. Since the acetylide migration has been commonly known to occur at the most electrophilic alkyne substrate,[1c,d] a relatively more electron-withdrawing vinyl group of **3** should facilitate the acetylide migration to a relatively more electrophilic phenyl-substituted alkyne carbon.

In summary, the ruthenium−acetylide **1** was shown to be an effective catalyst for the dimerization of RC≡CH (R = Ph, CO_2Me). A new ruthenium η^3-butadienyl species **5** was formed from the reaction of **1** with the dimeric product **3** *via* an intermediate **6**. Further studies on the ruthenium−acetylide-mediated coupling reactions of alkenes and alkynes are currently in progress.

Experimental Section

General Information. All reactions were carried out in an inert-atmosphere glovebox or by using standard high-vacuum and Schlenk-line techniques unless otherwise mentioned. Tetrahydrofuran, benzene, and Et_2O were distilled from purple solutions of sodium and benzophenone immediately prior to use. The NMR solvents, C_6D_6 and CD_2Cl_2, were dried from activated molecular sieves (4 Å). The ruthenium complexes, $C_5Me_5Ru(PPh_3)_2Cl$[10] and $C_5Me_5Ru(PPh_3)$(Cl)=C=CHPh (**2**),[6,11] were prepared according to literature procedures. Organic alkynes RC≡CH (R = Ph, CO_2Me) were received from a commercial source (Aldrich Chemical Co.) and used without further purification. The ^1H and ^{13}C NMR spectra were recorded on a GE GN-Omega 300 MHz FT-NMR spectrometer. Mass spectra were recorded on a Hewlett-Packard HP 5970 GC/MS spectrometer. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

Formation of $C_5Me_5Ru(PPh_3)(\eta^3$-PhCHCHC=C-PhC≡CPh) (5). The ruthenium complex $C_5Me_5Ru(PPh_3)$(Cl)=C=CHPh (**2**) (500 mg, 0.79 mmol), Et_3N (1.10 mL, 10 equiv), and PhC≡CH (0.86 mL, 10 equiv) were charged with 30 mL of CH_2Cl_2 in a 100 mL round-bottom flask. The reaction mixture was stirred at room temperature for 24 h. After the solvent was evaporated under high vacuum, the residue was dissolved in C_6H_6 and the solution filtered through a frit. The filtrate was evaporated under vacuum, and the remaining solid was washed with small amounts of Et_2O (3 × 5 mL) and hexanes (3 × 5 mL) to afford **5** as a yellow solid in 81% yield (513 mg).

^1H NMR (CD_2Cl_2, 300 MHz): δ 7.8−7.0 (m, Ph), 3.68 (dd, J_{HH} = 8.8 Hz, J_{PH} = 3.7 Hz, PhCHC*H*), 3.00 (dd, J_{PH} = 14.0 Hz, J_{HH} = 8.8 Hz, PhC*H*CH), 1.36 (s, C_5Me_5). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz): δ 192.6 (d, J_{PC} = 17.1 Hz, Ru−*C*=C), 144.8, 143.3, 133.2, 130.0, 129.3, 129.0, 128.8, 127.8, 127.0, 126.0 (Ph carbons), 125.3 (=*C*(Ph)C≡C), 114.8 (d, J_{PC} = 6.4 Hz, CHPh), 96.4 (CHPh=), 96.3 (*C*≡CPh), 93.4 (*C*$_5$Me$_5$), 88.0 (C≡*C*Ph),

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(9) Selected spectral data for **6**: ^1H NMR (CD_2Cl_2, 300 MHz) δ 6.73 (d, *J* = 15.9 Hz, C*H*=CHPh), 6.50 (d, *J* = 15.9 Hz, CH=C*H*Ph), 1.44 (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.6 MHz) δ 53.7 (s, PPh_3).

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10.8 (C_5Me_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.6 MHz): δ 60.9 (s, PPh_3). Anal. Calcd for $C_{52}H_{47}PRu$: C, 77.68; H, 5.89. Found C, 77.65; H, 6.05.

General Procedure of the Ruthenium-Catalyzed Dimerization of RC≡CH (R = Ph, CO_2Me). In a 25 mL Schlenk tube equipped with a Teflon stopcock, the ruthenium catalyst **1** (3−5 mol %) was generated from the treatment of $C_5Me_5Ru(PPh_3)(Cl){=}C{=}CHPh$ (10 mg, 0.016 mmol) with Et_3N (22 μL, 10 equiv) in 10 mL of CH_2Cl_2. Excess alkyne (0.60 mmol) was added to the solution, and the reaction mixture was stirred at room temperature. Small samples were periodically drawn out from the solution and analyzed by the GC-MS. After 10 h, the solution was evaporated under high vacuum. The residue was extracted with Et_2O, and the Et_2O solution was chromatographed on silica gel (hexane/Et_2O) in air. The rotary evaporation led to the dimeric products as a pale-yellow oil. The spectroscopic data for both **3a** and **3b** have been previously reported.[5]

For *trans*-PhCH=CHC≡CPh (**3a**): ^1H NMR (C_6D_6, 300 MHz) δ 8.10−6.80 (m, Ph), 7.04 (d, J = 16.2 Hz, =CHPh), 6.30 (d, J = 16.2 Hz, =CHC≡C); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 142.3 (=CHPh), 137.3, 132.2, 129.7, 129.4, 129.2, 127.3, 124.4 (Ph carbons), 109.0 (=*C*HC≡C), 92.3 (=CH*C*≡C), 89.8 (=CHC≡*C*Ph); GC-MS *m*/*z* 204 (M^+).

For *cis*-PhCH=CHC≡CPh (**3b**): ^1H NMR (C_6D_6, 300 MHz) δ 8.10−6.80 (m, Ph), 6.40 (d, J = 11.8 Hz, =CHPh), 5.79 (d, J = 11.8 Hz, =CHC≡C); $^{13}H\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 139.1 (=CHPh), 137.1, 131.7, 129.2, 128.7, 128.5, 128.4, 124.0 (Ph carbons), 107.7 (=*C*HC≡C), 96.7 (=CH*C*≡CPh), 88.9 (=CHC≡*C*Ph); GC-MS *m*/*z* 204 (M^+).

For *trans*-$MeO_2CCH{=}CHC{\equiv}CCO_2Me$ (**4**): ^1H NMR (C_6D_6, 300 MHz) δ 6.45 (d, J = 16.2 Hz, $=CHCO_2Me$), 6.03 (d, J = 16.2 Hz, =CHC≡C), 3.23, 3.21 (s, CO_2Me); $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 164.6 ($=CHCO_2Me$), 153.4 ($C{\equiv}CCO_2Me$), 135.1 ($=CHCO_2Me$), 121.3 ($=CHC{\equiv}CCO_2Me$), 87.3 ($C{\equiv}CCO_2Me$), 81.9 ($C{\equiv}CCO_2Me$), 52.6, 51.5 (CO_2Me); GC-MS *m*/*z* 168 (M^+).

X-ray Crystallographic Determination of 5. Bright yellow single crystals of **5** were obtained from the layering of hexanes to a benzene solution at room temperature. A yellow crystal (0.30 × 0.30 × 0.20 mm) was mounted on a Siemens P4/CCD diffractometer equipped with a graphite monochromator. Empirical methods were used to correct for absorption. No symmetry greater than triclinic was evident from the diffraction data. The asymmetric unit consists of one Ru complex and 1.5 molecules of benzene. The half molecule is located on a crystallographic inversion center. All non-hydrogen atoms were treated as idealized contributions. All software used were included in the SMART, SAINT, and SHELXTL program libraries (Siemens XRD, Madison, WI). Crystal data for **5**: $C_{52}H_{47}PRu\cdot 1.5C_6H_6$: yellow block, triclinic, a = 10.2582(1) Å, b = 15.8273(2) Å, c = 16.9688(2) Å, α = 101.0450(1)°, β = 107.5713(2)°, γ = 108.5520(1)°, V = 2360.54(4) Å^3, Z = 2, T = 223 K, $R(F)$ = 0.0508, $R(wF^2)$ = 0.1046.

Acknowledgment. Financial support from Marquette University, Committee on Research, is gratefully acknowledged. The authors from The University of Delaware acknowledge the National Science Foundation for their support in purchasing the CCD-based X-ray diffractometer (Grant No. CHE-9628768).

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **5** (9 pages). Ordering information is given on any current masthead page.

OM970366T