

Selective Linear Coupling Reaction of Acetylene and Acrylonitrile Catalyzed by the Well-Defined Metallacyclopentadiene Complex



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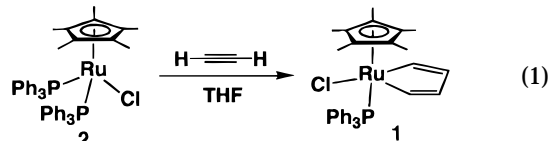
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Summary: The metallacyclopentadiene complex $\text{C}_5\text{Me}_5(\text{PPh}_3)(\text{Cl})\text{RuCH}=\text{CHCH}=\text{CH}$ (**1**) was found to catalyze the linear coupling reaction of acetylene and acrylonitrile to give predominantly 2(E),4(Z),6-heptatrienenitrile (**3**; TON = 15, 85% selectivity). The coupling reaction is proposed to occur via an initial PPh_3 dissociation from **1** and the subsequent insertion of acrylonitrile.

Transition-metal-mediated coupling reactions of alkynes are well-known to form a variety of cyclic compounds.^{1,2} Metallacyclopentadiene complexes have been commonly considered as important intermediate species in these reactions.^{1a,b} In contrast, only a few examples of the linear co-oligomerization reactions of alkynes and alkenes have been reported.³ The selective linear coupling reactions of alkynes and functionalized alkenes would in principle lead to a variety of conjugated olefins. As a part of an ongoing effort to extend the ruthenium-mediated alkyne coupling reactions,⁴ we have begun to explore the co-oligomerization reactions of alkynes and alkenes. Herein we report that the newly synthesized

ruthenacyclopentadiene species $\text{C}_5\text{Me}_5(\text{PPh}_3)(\text{Cl})\text{RuCH}=\text{CHCH}=\text{CH}$ (**1**) selectively catalyzes the 2:1 linear coupling reaction of acetylene and acrylonitrile to form heptatrienenitrile.

We recently reported the synthesis of the chiral ruthenium-vinylidene complex $\text{C}_5\text{Me}_5(\text{PPh}_3)(\text{Cl})\text{Ru}=\text{C}=\text{CHPh}$ from the reaction of $\text{C}_5\text{Me}_5\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**2**) with $\text{PhC}\equiv\text{CH}$.^{4b} An analogous treatment of **2** with excess $\text{HC}\equiv\text{CH}$ (1 atm) at room temperature in THF resulted in the formation of the ruthenacyclopentadiene complex **1**,⁵ which was conveniently isolated in 54% yield by treating with 1.2 equiv of CuCl_2 (eq 1).⁶ The



¹H NMR of **1** in C_6D_6 exhibited an unusually downfield shifted α -proton at δ 10.20 ($J_{\text{PH}} = 6.0$ Hz), which was strongly coupled with both the phosphorus atom and the C_β proton. The carbon resonances at δ 200.9 and 177.5 (d, $J_{\text{PC}} = 27.7$ Hz) were assigned to the α - and β -metallacyclic carbon atoms.⁷ The metallacyclopentadiene structure of **1** was confirmed by X-ray crystallography (Figure 1).⁸ The molecular structure of **1** showed a distorted-trigonal-bipyramidal geometry with Cp^* and PPh_3 groups each occupying apical positions.

(1) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992. (b) Bönnemann, H.; Brijoux, W. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH: New York, 1996; Vol. 2. (c) Melikyan, G. G.; Nicholas, K. M. In *Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: New York, 1995. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (e) Grotjahn, D. B. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1994; Vol. 12. (f) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. (g) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1990; Vol. 5. (h) Vollhart, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(2) For recent examples on the metal-mediated intermolecular alkyne coupling reactions, see: (a) Takeda, A.; Ohno, A.; Kadota, I.; Gevorgyan, V.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4547. (b) Gevorgyan, V.; Takeda, A.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11313. (c) Johnson, E. S.; Balaich, G. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 11086. (d) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Gantzel, P. K.; Fong, B. S.; Adams, M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1997**, *119*, 3631. (e) van Belzen, R.; Hoffmann, H.; Elsevier: C. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1743.

(3) (a) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 5284. (b) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1979**, *101*, 1123. (c) Mitsudo, T.; Zhang, S.-W.; Nagao, M.; Watanabe, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 598. (d) Trost, B. M.; Indolese, A. F.; Müller, T. J. J.; Treptow, B. *J. Am. Chem. Soc.* **1995**, *117*, 615. (e) Bianchini, C.; Caulton, K. G.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Vizza, F. *Organometallics* **1995**, *14*, 933.

(4) (a) Yi, C. S.; Liu, N. *Organometallics* **1996**, *15*, 3968. (b) Yi, C. S.; Liu, N.; Rheingold, A. L.; Liable-Sands, L. M.; Guzei, I. A. *Organometallics* **1997**, *16*, 3729. (c) Yi, C. S.; Liu, N.; Rheingold, A. L.; Liable-Sands, L. M. *Organometallics* **1997**, *16*, 3910.

(5) See the Supporting Information for the characterization data of complexes **1**, **3**, **4**, and **6**.

(6) CuCl_2 has been known to form a stable adduct with PPh_3 . For a recent example, see: Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887 and references therein.

(7) Two metallacyclic carbon resonances were reported at δ 201.3 and 141.3 for the similar ruthenacyclopentadiene complex $\text{Cp}(\text{Br})(\text{L})\text{RuC}(\text{Ph})=\text{CHCH}=\text{C}(\text{Ph})$ (L = $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{O}$) in: Albers, M. O.; deWaal, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680.

(8) Crystal data for **1**· C_6H_6 : $\text{C}_{38}\text{H}_{40}\text{ClIPRu}$, monoclinic, $P2_1/c$, $a = 9.825(4)$ Å, $b = 22.411(7)$ Å, $c = 15.412(5)$ Å, $\beta = 108.440(19)^\circ$, $V = 3219(3)$ Å³, $Z = 4$, $T = 295(2)$ K, $D_{\text{calc}} = 1.370$ g/cm³, $R(F) = 3.63\%$ for 3354 observed independent reflections ($2 \leq 2\theta \leq 22.5^\circ$).

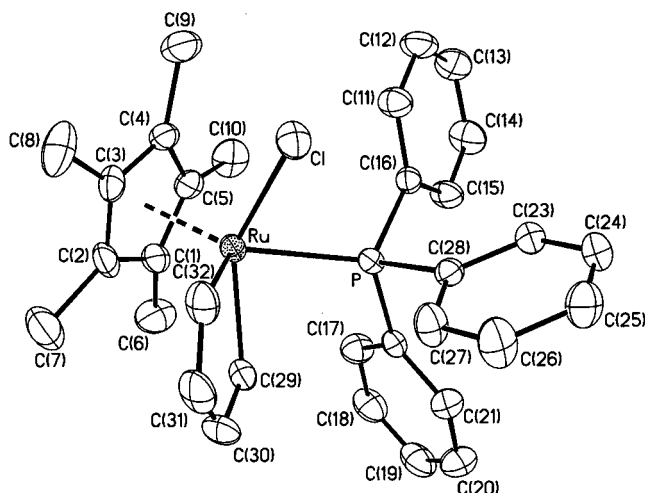
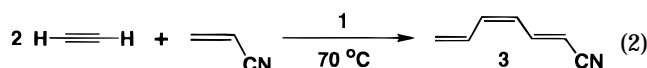


Figure 1. Molecular structure of **1** drawn with 30% thermal ellipsoids. Selected bond lengths (Å) and bond angles (deg): Ru–C(29), 2.092(4); Ru–C(32), 2.059(5); C(29)–C(30), 1.321(6); C(30)–C(31), 1.414(8); Ru–Cl, 2.439(8); Ru–P, 2.381(4); C(32)–Ru–C(29), 74.1(2); C(29)–Ru–Cl, 136.02(12); C(32)–Ru–P, 113.23(12); P–Ru–Cl, 81.24(6).

Both relatively long Ru-to-C_α bond distances (Ru–C(29) = 2.092(4) Å, Ru–C(32) = 2.059(5) Å) and a planar metallacyclopentadiene ring geometry (mean deviation = 0.026(7) Å) suggested a slight contribution from the metallacyclopentatriene resonance structure.⁹ These structural data are also comparable to the those for previously reported mono- and dinuclear ruthenacyclopentadiene species.^{7,10}

Complex **1** was found to catalyze the linear coupling reaction of acetylene and acrylonitrile. In a typical reaction, the treatment of HC≡CH (2.3 mmol) with a catalytic amount of **1** (13 mg, 0.022 mmol) in acrylonitrile (1.0 mL) at 70 °C for 3.5 h produced the predominantly linear product 2(*E*),4(*Z*),6-heptatrienenitrile (**3**) (TON = 15; ~85% selectivity) (eq 2).¹¹ Small amounts

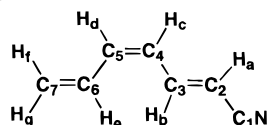


of higher oligomers of both homo- and heterocoupling products were also formed (~15%), but none of the cyclic products such as 2-vinylpyridine or benzene derivatives were detected by GC–MS.¹² The organic product **3** was isolated by column chromatography and its structure

(9) For discussion and examples of the metallacyclopentatriene complexes, see: (a) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 2712. (b) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 7609. (c) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218. (d) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 8235.

(10) (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1990**, *9*, 1106. (b) Braun, T.; Laubender, M.; Gevert, O.; Werner, H. *Chem. Ber.* **1997**, *130*, 559.

(11) TON = turnover number = mol of product (mol of catalyst)^{−1} h^{−1}. The numbering scheme of **3** is

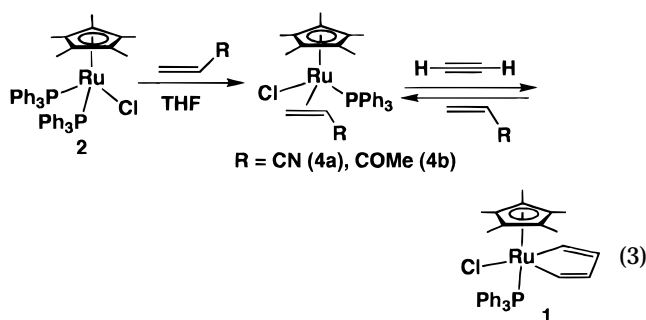


(12) The volatile portion of the solution contained mostly unreacted acetylene and only a trace amount of acetylene homooligomers as analyzed by GC–MS.

was completely determined by spectroscopic methods.⁵ The *cis* stereochemistry of **3** was established from a relatively small coupling constant between two adjacent vinyl protons ($J_{H_c-H_d}$ = 11.3 Hz).

The formation of **3** was found to be dependent on both the concentration of acetylene and the reaction temperature. For example, the reaction at a higher concentration of HC≡CH (4.4 mmol, ~2 atm) resulted in the formation of a complex mixture of products containing **3** (~60%) and higher amounts of oligomeric products (~40%) as detected by GC–MS. A similar reaction at room temperature was found to be quite sluggish (TON < 2), while the reaction in THF (1 mL) resulted in mostly insoluble polyacetylene and other oligomeric products.¹³

The metallacyclopentadiene complex **1** can also be obtained from the reaction of a ruthenium-alkene complex with acetylene (eq 3). The ruthenium-alkene



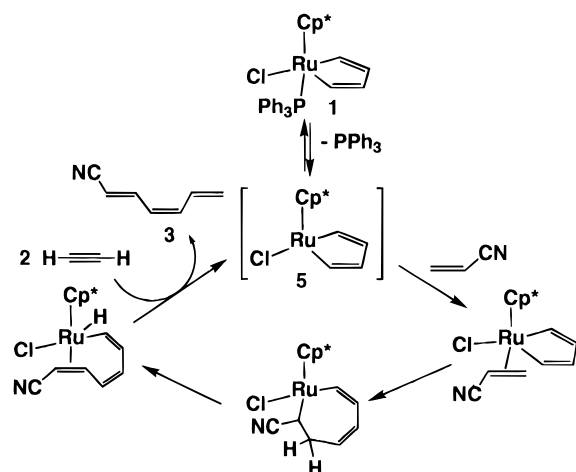
complexes (R = CN (**4a**), COMe (**4b**)) were readily prepared from the reaction of **2** with CH₂=CHR (2.5 equiv) in THF at room temperature (85–97% isolated yields), and their structures were established by spectroscopic methods.⁵ The molecular structure of **4b**, as defined by X-ray crystallography, showed a typical three-legged piano stool geometry.¹⁴ The treatment of complex **4a** with HC≡CH (1 atm) in THF at room temperature cleanly yielded the metallacyclopentadiene complex **1**. Also, complex **1** was readily converted to the alkene complex **4a** by treating with 1.2 equiv of acrylonitrile in C₆D₆ at room temperature. The olefin complexes **4a** and **4b** were shown to be equally active for the linear coupling reaction.

While a detailed mechanism of the reaction still remains to be established, the above results are consistent with the mechanism shown in Scheme 1. Two different mechanisms have been commonly proposed for the coupling step of a metallacyclopentadiene species with an alkyne: an insertion of an alkyne into the metallacyclopentadiene via a cycloheptatriene intermediate or a [4 + 2] cycloaddition between a metallacyclopentadiene and an alkyne.^{1,15} In our case, a facile interconversion between **1** and **4a** suggested that the PPh₃ ligand is readily dissociated from **1**. The fact that

(13) The dark brown insoluble product was isolated after washing with THF and CH₂Cl₂. The IR data (KBr, ν_{C-H} bend = 1009 cm^{−1}) matched well with the previously reported values of *trans*-polyacetylene: (a) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11. (b) Landon, S. J.; Shulman, P. M.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739.

(14) See the Supporting Information for the molecular structure of **4b**. Crystal data for **4b**: C₃₂H₃₆ClOPRu, monoclinic, $P2_1/n$, a = 17.043(5) Å, b = 10.417(3) Å, c = 17.088(6) Å, β = 113.54(2)°, V = 2781.5(15) Å³, Z = 4, T = 248(2) K, D_{calcd} = 1.443 g/cm³, $R(F)$ = 4.77% for 2746 observed independent reflections ($2 \leq \theta \leq 22.5^\circ$).

Scheme 1



addition of PPh_3 (9 mg, 1.5 mol %) to the reaction mixture virtually inhibited the coupling reaction under otherwise similar reaction conditions also supports the reversible dissociation of PPh_3 . When the coupling reaction was run in $\text{CD}_2=\text{CDCN}$ (98% D, Cambridge Isotopes), the ^1H NMR of the isolated product **3** showed selective deuterium incorporation at three vinyl positions: H_a , H_b , and H_f .¹⁶ The selective deuterium

incorporation at the terminal vinyl position (H_f) is consistent with the insertion of an alkene into the metallacyclopentadiene species **5**.¹⁷ The preferential formation of the *cis*-alkene product **3** also suggests that the reaction occurs via the formation of metallacyclopentadiene species **5** from the coupling of two acetylenes. The subsequent steps of the reaction, the β -H elimination and the reductive elimination of the product **3**, are well-established in alkyne coupling reactions.^{1d,e,3}

In a preliminary investigation, we also found that complex **1** effectively catalyzed the linear coupling reaction of $\text{HC}\equiv\text{CH}$ and $\text{CH}_2=\text{CHCO}_2\text{Me}$. In this case, the rate of the coupling reaction was considerably higher than that of the acrylonitrile reaction, and the reaction produced a 2:1 mixture of methyl 2(*E*),4(*Z*),6-heptatrienoate (**6a**) and methyl 2(*Z*),4(*Z*),6-heptatrienoate (**6b**); TON = 24; 89% combined yield based on $\text{HC}\equiv\text{CH}$).⁵ Efforts are currently underway to determine both the scope and selectivity of the coupling reaction by employing substituted alkynes and other functionalized alkenes.

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Supporting Information Available: Tables giving X-ray crystallographic data for **1** and **4b** and text giving characterization data for **1**, **3**, **4**, and **6** (16 pages). Ordering information is given on any current masthead page.

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(15) For recent examples of η^4 -arene species and their implication in alkyne cyclotrimerization reactions, see: (a) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M.-L.; Eisenstein, O.; Jackson, S. A.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010. (b) Bianchini, C.; Caulton, K. G.; Folting, K.; Meli, A.; Peruzzini, M.; Polo, A.; Vizza, F. *J. Am. Chem. Soc.* **1992**, *114*, 7290. (c) Bianchini, C.; Caulton, K. G.; Chardon, C.; Eisenstein, O.; Folting, K.; Johnson, T. J.; Meli, A.; Peruzzini, M.; Rauscher, D. J.; Streib, W. E.; Vizza, F. *J. Am. Chem. Soc.* **1991**, *113*, 5127. (d) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.

(16) An approximately equal amount (> 95%) of deuterium has been incorporated at all three vinyl positions of **3**, as determined by ^1H NMR.

(17) As a reviewer pointed out, an alternate mechanism involving a metallacyclopentene species generated from the coupling of acetylene and an alkene is also consistent with the deuterium-labeling result. While this mechanism seems less likely, since it requires the preferential insertion of acetylene over the elimination of β - CH_2 hydrogen, we cannot rigorously rule out this mechanism at this time.