Further studies with higher oligomers of *p*-phenylene and oligomers of pyrrole and thiophene are being pursued, as are further applications of the CAN/LFP technique for generation of radical cations.

Acknowledgment. Support of this research by the National Science Foundation EPSCoR program and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Ms. Kezi Ezell and Mr. Troy Lewis for invaluable technical assistance.

Supplementary Material Available: Absorption spectra of transient $NO_3^{\bullet}$ (550–700 nm), $B^{\bullet+}$ (400–520 nm), $BP^{\bullet+}$ (370–810 nm), $TP^{\bullet+}$ (400–550 nm), $TP^{\bullet+}$ (810–900 nm), $QP^{\bullet+}$ (400–550 nm), and $QP^{\bullet+}$ (710–900 nm) in MeCN solvent, absorption spectra of $Li^+QP^{\bullet-}$ (400–800 nm), $Li^+QP^{\bullet-}$ (12 000–6000 cm^{-1}), $Li^+SP^{\bullet-}$ (400–800 nm), $K^+SP^{\bullet-}$ (350–900 nm), and $Li^+SP^{\bullet-}$ (12 000–6000 cm^{-1}) in THF solvent, and a decay trace for $NO_3^{\bullet}$ in MeCN solvent (13 pages). Ordering information is given on any current masthead page.

A Ru(II) Enynyl Complex Mediates the Catalytic Dimerization of 1-Alkynes to *Z*-1,4-Disubstituted Enynes

Claudio Bianchini,[*,†] Maurizio Peruzzini,[*,†]
Fabrizio Zanobini,[†] Piero Frediani,[‡] and Alberto Albinati[§]

Istituto per lo Studio della Stereochimica ed
Energetica dei Composti di Coordinazione, CNR
Via J. Nardi 39, 50132, Firenze, Italy
Dipartimento di Chimica Organica
Università di Firenze, Firenze, Italy
Istituto Chimico
Farmaceutico e Tossicologico dell'Università di Milano
Milano, Italy

Received February 27, 1991

Detailed mechanistic studies on metal-assisted dimerization reactions of 1-alkynes to butenynes[1] have not been published, and the factors that govern regio- and stereoselectivity are not yet fully understood.

Herein we report that the selective coupling of terminal alkynes to *Z*-1,4-disubstituted butenynes can be achieved in a catalytic way by using either the Ru(II) η^2-H_2 complex $[(PP_3)Ru(H)(H_2)]BPh_4$[2] (**1**) or the η^1-dinitrogen derivative $[(PP_3)Ru(H)(N_2)]BPh_4$ (**2**) [$PP_3 = P(CH_2CH_2PPh_2)_3$].[2] We describe in detail the reaction sequence leading to 1,4-bis(trimethylsilyl)but-3-en-1-yne, but comparisons with other 1-alkynes are given in the text showing the applicability of our method to the catalytic homo coupling and stoichiometric cross coupling of 1-alkynes.

When a solution of **2** (or **1**) in THF is stirred for 1 h under argon or nitrogen with 3 (or 4) equiv of $HC\equiv CSiMe_3$, 1 (or 2) equiv of vinyltrimethylsilane and canary yellow crystals of (*E*)-$[(PP_3)Ru\{\eta^3\text{-}(SiMe_3)C_3CH(SiMe_3)\}]BPh_4$ (**3**) are obtained. The molecular structure of the complex cation of **3**·acetone is shown in Figure 1.[3] The coordination geometry around ruthenium is distorted octahedral with four coordination positions occupied by the phosphorus atoms of PP_3 and the remaining edge taken by the butenynyl ligand. The bond distances between ruthenium and the atoms C(50) [$C\equiv CSiMe_3$] and C(51) [$C{=}C(H)SiMe_3$] [2.234 (3) and 2.144 (3) Å, respectively] are in line with those found for other η^3 butenynyl complexes.[4] The weakest interaction is present with C(49) [$CSiMe_3$] [2.485 (2) Å] and probably originates from repulsion between the Si(48) $SiMe_3$ group and the many phenyl rings. The C–C bond distances within the η^3-butenynyl ligand are suggestive of some degree of electronic delocalization.

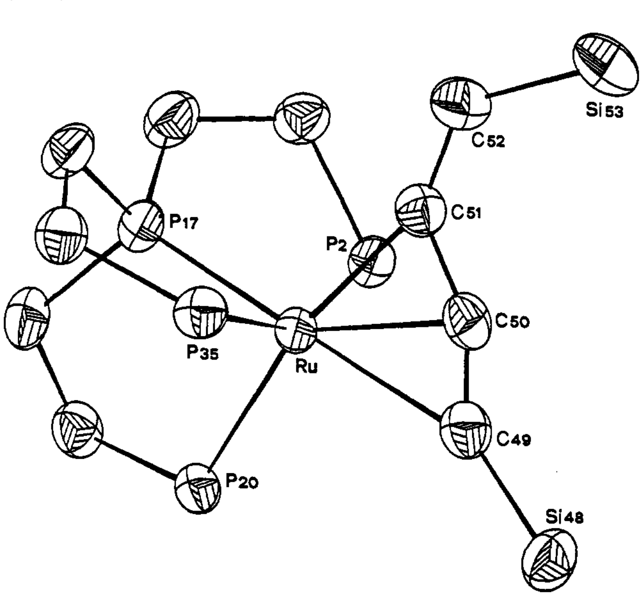


Figure 1. ORTEP drawing of the complex cation in **3**. Phenyl rings are omitted for clarity. The relevant geometric features are as follows: Ru–P 2.342 (1) (av), Ru–C(49) 2.485 (3), Ru–C(50) 2.234 (3), Ru–C(51) 2.144 (3), C(49)–C(50) 1.247 (5), C(50)–C(51) 1.392 (5), C(51)–C(52) 1.335 (5) Å; P(2)–Ru–C(51) 81.57 (9), P(17)–Ru–C(49) 172.1 (1), P(17)–Ru–C(51) 107.9 (1), P(20)–Ru–C(51) 166.30 (9), P(35)–Ru–C(50) 89.17 (9), C(49)–C(50)–C(51) 154.0 (3), C(50)–C(51)–C(52) 133.5 (3), C(50)–C(49)–Si(48) 142.0 (3), C(51)–C(52)–Si(53) 126.0 (3)°.

Monitoring the reactions between **2** and variable amounts of $HC\equiv CSiMe_3$ by $^{31}P\{^1H\}$ and ^1H NMR shows that the butenynyl **3** forms by addition of 1 equiv of alkyne to the σ-alkynyl $[(PP_3)Ru(\sigma\text{-}C\equiv CSiMe_3)]BPh_4$ (**4**) isolable in the solid state as red crystals of the THF solvate. In turn, **4** quantitatively forms by reaction of $HC\equiv CSiMe_3$ with (*E*)-$[(PP_3)Ru\{C(H){=}CH(SiMe_3)\}]BPh_4$ (**5**), which is obtained by trans insertion [*J*(HH) = 18.1 Hz] of the alkyne across the Ru—H bond (Scheme I). Pure samples of the σ-alkenyl complex **5** cannot be obtained since its reaction with the alkyne to give **4** is much faster than that of the alkyne with **2**. As a matter of fact, treatment of **2** with 1 equiv of $HC\equiv CSiMe_3$ invariably yields mixtures of **2**, **4**, and **5**. The result of the reaction of **2** with $HC\equiv CSiMe_3$ invariably yields mixtures of **2**, **4**, and **5**. The result of the reaction of **2** with $HC\equiv CCO_2Et$ yielding (*G*)-$[(PP_3)Ru\{C(COOEt){=}CH_2\}]BPh_4$ (**6**) confirms that the insertion of the alkyne across the Ru—H bond is the first step.[5] The geminal structure of the alkenyl ligand is in keeping with the electron-withdrawing character of the carbethoxy substituent.[6]

[†] Istituto ISSECC CNR.

[‡] Università di Firenze.

[§] Università di Milano.

(1) (a) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, p 371. (b) Trost, B. M.; Chan, C.; Ruhter, G. *J. Am. Chem. Soc.* **1987**, *109*, 3486. (c) Kovalek, I. P.: Yevdakov, K. V.; Strelenko, Y. A.; Vinogradov, M. G.; Nikishin, G. I. *J. Organomet. Chem.* **1990**, *386*, 139. (d) Ishikawa, M.; Ohshita, J.; Ito, Y.; Minato, A. *J. Organomet. Chem.* **1988**, *346*, C58.

(2) Bianchini, C.; Perez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279.

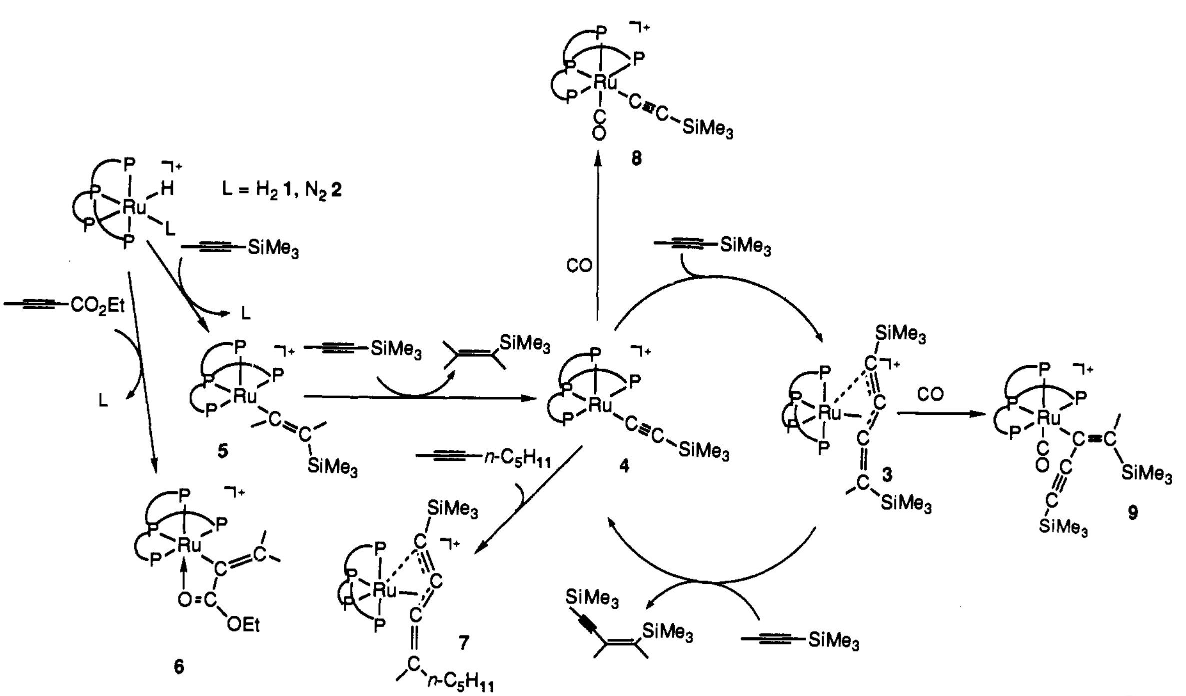
(3) Crystals suited for an X-ray analysis were obtained by recrystallization from acetone/ethanol: triclinic crystal, space group $P\bar{1}$, $a = 15.495$ (2) Å, $b = 15.596$ (2) Å, $c = 17.006$ (2) Å, $\alpha = 116.14$ (2)°, $\beta = 94.03$ (2)°. $\gamma = 97.38$ (2)°, $Z = 2$, $d_{calcd} = 1.233$ g cm^{-3}, $n_{obsd} = 7565$, $R = 0.0351$. A clathrated molecule of acetone was located in the cell.

(4) (a) Jia, G.; Rheingold, A. L.; Meek, D. W. *Organometallics* **1989**, *8*, 1378. (b) Gotzig, J.; Otto, H.; Werner, H. *J. Organomet. Chem.* **1985**, *287*, 247.

(5) Lundquist, E. G.; Folting, K.; Streib, W. E.; Huffmann, J. C.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 855.

0002-7863/91/1513-5453$02.50/0

Scheme I



When **4** is reacted at 20 °C with an excess of HC≡CSiMe$_3$, we observe selective, catalytic production of (Z)-1,4-bis(trimethylsilyl)but-3-en-1-yne [substrate to catalyst ratio 100, 10 mL of THF, 6 h, 30% conversion, (Z)-Me$_3$SiC≡CCH=CH(SiMe$_3$) 95%, (E)-Me$_3$SiC≡CCH=CH(SiMe$_3$) 5%]. At reflux temperature the catalytic activity significantly increases (90% conversion, Z isomer 93%, E isomer 7%). The mixtures remain catalytically active. Similar conversion (90%) and selectivity (92% in the Z isomer) are found for the catalytic dimerization of HC≡CPh to 1,4-diphenylbut-3-en-1-ynes by using **1** or **2** as catalyst precursors. For both 1-alkynes, the η^3-butenynyl complexes are the only species observable in the course of the catalysis (^{31}P{^{1}H} NMR), suggesting that such complexes are reagents in the rate-determining step.

Valuable mechanistic information on the catalytic cycle is provided by the isolation of (E)-[(PP$_3$)Ru{η^3-(SiMe$_3$)C$_3$CH(n-C$_5$H$_{11}$)}]BPh$_4$ (**7**) by treatment of **4** with 1 equiv of HC≡C-n-C$_5$H$_{11}$. The geminal position of H and n-C$_5$H$_{11}$ in the cross-coupling product **7** [^3J(HH) = 6.3 Hz] indicates that the alkyne has undergone a 1,2-hydrogen shift, which constitutes one of the known paths of the 1-alkyne to vinylidene tautomerization at metal centers.[7] Once the alkyne has rearranged to vinylidene, the butenynyl ligand may form via C–C bond formation between the α-carbons of cis vinylidene and alkynyl ligands.[4a] In accord with the proposed mechanism, when the metal coordination sphere of the σ-alkynyl **4** is saturated by CO, the six-coordinate complex [(PP$_3$)Ru(CO)(C≡CSiMe$_3$)]BPh$_4$ (**8**) forms and no further reactions with 1-alkynes occur.

The weak bonding interaction between ruthenium and the alkynyl moiety of the butenynyl ligand is present also in solution as shown by the reaction with CO in THF yielding the η^1-butenynyl (E)-{[(PP$_3$)Ru(CO){η^1-(SiMe$_3$)C$_3$CH(SiMe$_3$)}]BPh$_4$ (**9**). The facile unfastening of the alkynyl functionality in **3** is certainly an essential requisite for the occurrence of a catalytic cycle as it provides a free coordination site for the incoming 1-alkyne molecule (the replacement of **4** with **3** in the catlytic reactions at reflux temperature changes neither the conversion nor the selectivity).

Acknowledgment. C.B. thanks the EEC for Contract SC1.0027C.

Supplementary Material Available: Experimental details for the synthesis and characterization of all of the new complexes described in this paper and for the catalytic reactions and X-ray crystallographic data for **3** including experimental details, selected distances and angles, atomic coordinates, and thermal parameters (17 pages); listing of observed and calculated structure factors for **3** (59 pages). Ordering information is given on any current masthead page.

---

(6) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P. *Organometallics* **1990**, *9*, 1146. (b) Bianchini, C.; Innocenti, P.; Masi, D.; Meli, A.; Sabat, M. *Organometallics* **1986**, *5*, 72.

(7) (a) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59. (b) Antonova, A. B.; Ioganson, A. A. *Russ. Chem. Rev.* **1989**, *58*, 693. (c) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 241.

Thiolato- and Selenato-Bridged Dinuclear Iron Carbonyl Radicals

Petra N. Keizer,[†] Paul J. Krusic,*[,‡] John R. Morton,[†] and Keith F. Preston[†]

Contribution No. 32830, Steacie Institute for
Molecular Sciences, National Research Council of Canada
100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R9
Contribution No. 5791, Central Research and Development
Department, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received January 29, 1991

Substantial advances have been made toward the understanding of reaction mechanisms of homogeneous catalysis through spectroscopic studies of photochemically generated, coordinatively unsaturated metal carbonyls and their reactions.[1] In particular, Fe(CO)$_5$ has an extensive odd-electron chemistry, which we are exploring by EPR spectroscopy. This report (a) exemplifies the variety of novel radical intermediates that can be obtained from organosulfur and -selenium compounds by photolysis of Fe(CO)$_5$ in the presence of H$_2$S and H$_2$Se and (b) draws attention to the

---

[†] National Research Council of Canada.

[‡] E. I. du Pont de Nemours and Company.

(1) For example: (a) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*: Academic Press: New York, 1979. (b) Poliakoff, M. *ACS Symp. Ser.* **1983**, *No. 211*, 35. (c) Weitz, E. *J. Phys. Chem.* **1987**, *91*, 3945.

0002-7863/91/1513-5454$02.50/0 © 1991 American Chemical Society