

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.

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Supplementary Material Available: Absorption spectra of transient NO_3^+ (550–700 nm), B^{++} (400–520 nm), BP^{++} (370–810 nm), TP^{++} (400–550 nm), TP^{++} (810–900 nm), QP^{++} (400–550 nm), and QP^{++} (710–900 nm) in MeCN solvent, absorption spectra of $\text{Li}^+\text{QP}^{--}$ (400–800 nm), $\text{Li}^+\text{QP}^{--}$ (12 000–6000 cm^{-1}), $\text{Li}^+\text{SP}^{--}$ (400–800 nm), K^+SP^{--} (350–900 nm), and $\text{Li}^+\text{SP}^{--}$ (12 000–6000 cm^{-1}) in THF solvent, and a decay trace for NO_3^+ 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

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Detailed mechanistic studies on metal-assisted dimerization reactions of 1-alkynes to butenynes¹ 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) $\eta^2\text{-H}_2$ complex $[(\text{PP}_3)\text{Ru}(\text{H})(\text{H}_2)]\text{BPh}_4$ (1) or the η^1 -dinitrogen derivative $[(\text{PP}_3)\text{Ru}(\text{H})(\text{N}_2)]\text{BPh}_4$ (2) [$\text{PP}_3 = \text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$].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 $\text{HC}\equiv\text{CSiMe}_3$, 1 (or 2) equiv of vinyltrimethylsilane and canary yellow crystals of (*E*)- $[(\text{PP}_3)\text{Ru}(\eta^3\text{-(SiMe}_3)_3\text{C}_3\text{CH(SiMe}_3))] \text{BPh}_4$ (3) are obtained. The molecular structure of the complex cation of 3-acetone is

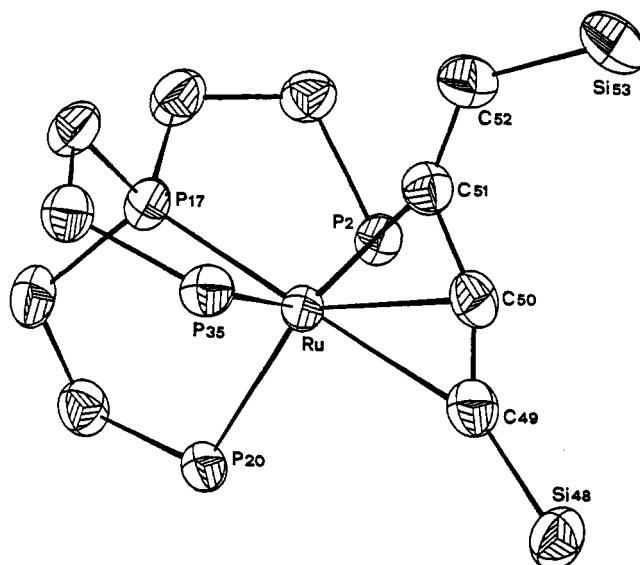


Figure 1. ORTEP drawing of the complex cation in 3. Phenyl rings are omitted for clarity. The relevant geometric features are as follows: Ru-P 2.342 (1) (av), Ru-C(49) 2.485 (3), Ru-C(50) 2.234 (3), Ru-C(51) 2.144 (3), C(49)-C(50) 1.247 (5), C(50)-C(51) 1.392 (5), C(51)-C(52) 1.335 (5) Å; P(2)-Ru-C(51) 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)°.

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) [$\text{C}\equiv\text{CSiMe}_3$] and C(51) [$\text{C}=\text{C(H)SiMe}_3$] [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.

Monitoring the reactions between 2 and variable amounts of $\text{HC}\equiv\text{CSiMe}_3$ by $^3\text{P}\{^1\text{H}\}$ and ^1H NMR shows that the butenynyl 3 forms by addition of 1 equiv of alkyne to the σ -alkynyl $[(\text{PP}_3)\text{Ru}(\sigma\text{-C}\equiv\text{CSiMe}_3)]\text{BPh}_4$ (4) isolable in the solid state as red crystals of the THF solvate. In turn, 4 quantitatively forms by reaction of $\text{HC}\equiv\text{CSiMe}_3$ with (*E*)- $[(\text{PP}_3)\text{Ru}(\text{C(H)=CH(SiMe}_3))] \text{BPh}_4$ (5), which is obtained by trans insertion [$J(\text{HH}) = 18.1$ Hz] of the alkyne across the Ru-H bond (Scheme 1). 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 $\text{HC}\equiv\text{CSiMe}_3$ invariably yields mixtures of 2, 4, and 5. The result of the reaction of 2 with $\text{HC}\equiv\text{CSiMe}_3$ invariably yields mixtures of 2, 4, and 5. The result of the reaction of 2 with $\text{HC}\equiv\text{CCO}_2\text{Et}$ yielding (*G*)- $[(\text{PP}_3)\text{Ru}(\text{C(COOEt)=CH}_2)] \text{BPh}_4$ (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 carboxy substituent.⁶

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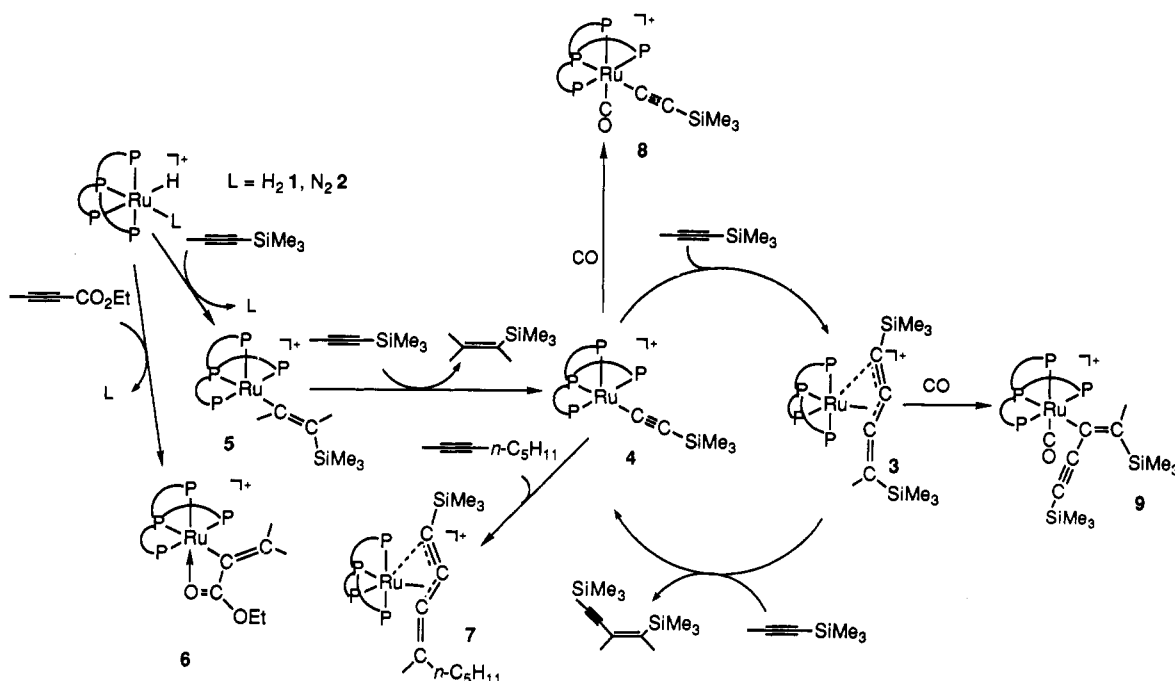
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(3) Crystals suited for an X-ray analysis were obtained by recrystallization from acetone/ethanol: triclinic crystal, space group $P\bar{1}$, $a = 15.495$ (2) Å, $b = 15.596$ (2) Å, $c = 17.006$ (2) Å, $\alpha = 116.14$ (2)°, $\beta = 94.03$ (2)°, $\gamma = 97.38$ (2)°, $Z = 2$, $d_{\text{calc}} = 1.233$ g cm^{-3} , $n_D^{20} = 1.565$, $R = 0.0351$. A clathrated molecule of acetone was located in the cell.

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Scheme I



When **4** is reacted at 20 °C with an excess of HC≡CSiMe₃, 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)-Me₃SiC≡CH=CH(SiMe₃) 95%, (E)-Me₃SiC≡CH=CH(SiMe₃) 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-yne 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 (³¹P{¹H} 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)-[(PP₃)Ru(η^3 -(SiMe₃)₃C₃CH(*n*-C₅H₁₁))]BPh₄ (**7**) by treatment of **4** with 1 equiv of HC≡C-*n*-C₅H₁₁. The geminal position of H and *n*-C₅H₁₁ 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 [(PP₃)Ru(CO)(C≡CSiMe₃)]BPh₄ (**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)-[(PP₃)Ru(CO)(η^1 -(SiMe₃)₃C₃CH(SiMe₃))]BPh₄ (**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 catalytic reactions

at reflux temperature changes neither the conversion nor the selectivity).

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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.

Thiolato- and Selenato-Bridged Dinuclear Iron Carbonyl Radicals

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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 H₂S and H₂Se and (b) draws attention to the

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