

Dimerization of terminal alkynes catalyzed by chloro(η^5 -pentadienyl) bis(triphenylphosphine)ruthenium(II) and kinetics of phosphine substitution

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Abstract

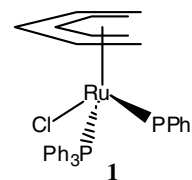
Exchange of PMe_2Ph for PPh_3 in (η^5 -pentadienyl)ruthenium{bis(triphenylphosphine)}chloride, ($\eta^5\text{-C}_5\text{H}_7$)Ru(PPh_3)₂Cl (**1**) under first order conditions proceeds rapidly in THF at room temperature. A pseudo-first order rate constant of $17 \pm 2 \times 10^{-4} \text{ s}^{-1}$ is obtained for the reaction at 21 °C. The rate constant is essentially independent of the phosphine concentration. The activation parameters, $\Delta H^\ddagger = 16.1 \pm 0.4 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -16 \pm 1 \text{ cal K}^{-1} \text{ mol}^{-1}$ differ from those reported for phosphine exchange in CpRu(PPh_3)₂Cl (**2**) and (η^5 -indenyl)Ru(PPh_3)₂Cl (**3**). The reaction of **1** with PMe_2Ph is about 70 times faster than the reaction of **2** at 30 °C and some 40 times faster than the reaction of **3** at 20 °C. ($\eta^5\text{-C}_5\text{H}_7$)Ru(PPh_3)₂Cl(**1**) is more active than the ruthenium(II) complexes **2**, **3**, and TpRu(PPh_3)₂Cl (**4**) in the catalytic dimerization of terminal alkynes with nearly quantitative conversion of PhCCH and FcCCH at ambient temperature in 24 h. The enhanced substitution rate is accompanied by >50% conversion of phenylacetylene to oligomeric products. Reaction of **1** with NaPF_6 in acetonitrile yields the cationic ruthenium(II) complex $[(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2(\text{CH}_3\text{CN})][\text{PF}_6]$ (**7**). The latter complex is much less active in reactions with phenylacetylene than **1** but avoids the formation of oligomeric products.
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Keywords: Pentadienyl ruthenium compounds; Phosphine exchange; Kinetics; Catalytic dimerization of alkynes

1. Introduction

Several decades of research on pentadienyl transition metal compounds have revealed significant differences in the steric and electronic properties of the η^5 -pentadienyl (C_5H_7) and η^5 -cyclopentadienyl (C_5H_5 or Cp) ligands in transition metal compounds [1]. The two ligands are iso-electronic, however, the pentadienyl ligand (cone angle 180°) [2] is sterically more demanding than a Cp ligand (cone angle 145°) [3]. The pentadienyl ligand is also both a better acceptor and a better donor than the Cp ligand [1]. Calculations predict that η^5 to η^3 conversions in the C_5H_7 ligand should be easier than in a C_5H_5 ligand [1].

The potential for ring slippage from η^5 to η^3 in pentadienyl metal complexes raises the possibility of novel reactivity in pentadienyl metal complexes. Such differences between the C_5H_7 and Cp ligands are expected to influence the respective catalytic properties of compounds, such as ($\eta^5\text{-C}_5\text{H}_7$)Ru(PPh_3)₂Cl (**1**) and CpRu(PPh_3)₂Cl (**2**).



The ruthenium(II) complexes CpRu(PPh_3)₂Cl (**2**), (η^5 -indenyl)Ru(PPh_3)₂Cl (**3**), and TpRu(PPh_3)₂Cl (**4**) [4] are all active as catalysts in a number of carbon–carbon bond

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forming reactions [5]. One well-explored reaction is the catalytic dimerization of terminal alkynes in the presence of **2**, **4** and other ruthenium(II) complexes [6]. Three dimeric products, *Z*- and *E*-1,4-substituted-1-buten-3-yne (“head-to-head” dimers, Fig. 1) as well as a “head-to-tail” dimer, 2,4-substituted-1-buten-3-yne, are typically observed in ruthenium catalyzed reactions of terminal alkynes. In some cases, a 1,4-substituted butatriene (a cumulene, $R(H)C=C=C(H)R$), is formed. Changing the ligands around the ruthenium center affects the product distribution and reaction rate. For example, $TpRu(PPh_3)_2Cl$ catalyzed dimerization of phenylacetylene yields a 9:89 ratio of *Z* to *E*-1,4-diphenyl-1-buten-3-yne [6a] while the $CpRu(PPh_3)_2Cl$ catalyzed reaction yields a 11:10 ratio of *Z* to *E* products [6b]. The *Z*:*E* ratio increases to 67:33 when $(\eta^5\text{-dihydropentalenyl})Ru(PPh_3)_2Cl$ is substituted for $CpRu(PPh_3)_2Cl$ [6b]. The conversion rate of phenylacetylene is in the order $TpRu(PPh_3)_2Cl > (\eta^5\text{-dihydropentalenyl})Ru(PPh_3)_2Cl > CpRu(PPh_3)_2Cl$ under similar conditions [6].

Dissociation of one phosphine ligand from the 18-electron ruthenium(II) complexes **1–4** is necessary to open a coordination site for substrates in the catalytic process and is often invoked as the first step in catalytic reactions involving **2–4** [6a]. The rates of phosphine exchange in $CpRu(PPh_3)_2Cl$ and $(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl$ have been reported [7]. The “indenyl effect” [8] has been invoked to explain the faster rate of phosphine substitution in $(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl$. Qualitatively, the substitution of triphenylphosphine in $(\eta^5\text{-C}_5\text{H}_7)Ru(PPh_3)_2Cl$ (**1**) by phosphines is rapid [9], however, the kinetics of phosphine substitution have not been reported. In this paper we report on the kinetics of phosphine substitution in **1** and on the catalytic activity of **1** in the dimerization of terminal alkynes. This reaction is selected as a model given the significant literature available for comparison of our results with those using other of ruthenium(II) catalysts. We have found both a faster rate of phosphine substitution in **1** relative to both **2** and **3** as well as an enhancement in the rate of dimerization of terminal alkynes catalyzed by **1** relative to **2–4**. The formation of *Z*- and *E*-1,4-substituted-1-buten-

3-yne, however, is often accompanied by significant oligomerization in the presence of **1**.

2. Experimental

All compounds described in this work were handled using Schlenk techniques or a M.I. Braun glove-box under purified argon or nitrogen atmospheres [10]. $RuCl_3 \cdot xH_2O$ was purchased from Alfa Inorganics, Inc. Tertiary phosphines, $PMePh_2$, PMe_2Ph , PEt_3 , and PCy_3 , were obtained from Strem Chemical, Inc. and used as received. Alkynes ($PhCCH$, $TMSCCH$, $tBuCCH$, C_4H_9CCH) were distilled prior to use. Solvents were purified by refluxing over Na/benzophenone (toluene, tetrahydrofuran, benzene, hexane, pentane) or P_2O_5 (dichloromethane) and distilled prior to use. Benzene- d^6 (Cambridge Isotope Laboratories) was purified by refluxing over Na/benzophenone and distilled prior to use. Ruthenium(II) compounds $(\eta^5\text{-C}_5\text{H}_7)Ru(PPh_3)_2Cl$ (**1**), $CpRu(PPh_3)_2Cl$ (**2**), $(\eta^5\text{-C}_9\text{H}_7)Ru(PPh_3)_2Cl$ (**3**), $(\eta^5\text{-C}_5\text{H}_7)Ru(PPh_3)(PMe_2Ph)Cl$ (**5**), and ethynylferrocene were prepared by literature procedures [9,11,12]. Elemental analyses (C, H) were performed by Desert Analytics, Inc. Tucson, AZ.

NMR spectra were recorded at 300 MHz for 1H , 75.4 MHz for $^{13}C\{^1H\}$, and 121.4 MHz for $^{31}P\{^1H\}$ on a Varian XL300 spectrometer. Proton chemical shifts are reported relative to residual protons in the solvent (C_6D_5H at δ 7.15 ppm, $CDHCl_2$ at 5.24 ppm, $CD_3CO\text{-}CD_2H$ at δ 2.05 ppm, or CD_2HCN at δ 1.97 ppm relative to TMS at 0.00 ppm). Carbon chemical shifts are reported relative to solvent (C_6D_6 at δ 128.0 ppm or CD_3CN at 1.7 ppm). Phosphorus chemical shifts are reported relative to external 85% H_3PO_4 at 0.0 ppm.

Electrochemical measurements were made under nitrogen on a BAS 100 B/W electrochemical workstation using a 1×10^{-3} M solution of **1** in dry CH_2Cl_2 , 0.1 M nBu_4NPF_6 as supporting electrolyte at a scan rate of 100 mV/s. The working electrode was a 3 mm Pt disk with a Pt wire as auxiliary electrode. A silver wire was used as a reference electrode with all potentials referenced to SCE. The oxidation potential of **1** is measured as 0.46 V relative to SCE.

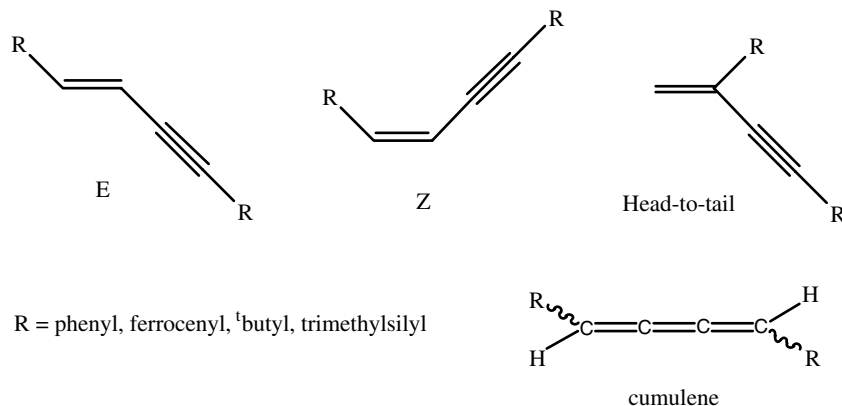


Fig. 1. Structures for isomeric dimers of terminal alkynes.

2.1. Kinetic measurements for reaction of **1** with PMe_2Ph , PMePh_2 , and PEt_3

A 40 mM stock solution of **1** was prepared by dissolving 144 mg (0.20 mol) of **1** in 4.5 mL THF and 0.5 mL C_6D_6 . The C_6D_6 served as a lock signal for the spectrometer. Samples for the kinetic experiments were prepared by adding 40 μL PMe_2Ph (0.28 mmol) to 500 μL aliquots of the stock solution of **1** (40 mM in **1** and 400 mM in PMe_2Ph) in screw capped 5 mm NMR tubes (Norell, Inc) in the glove-box immediately prior the start of the experiment. The start time was recorded. Samples were inserted into the NMR probe as soon as possible after mixing, usually within 2 min. The rate of substitution of PPh_3 by PMe_2Ph in **1** was measured by monitoring the increase in the doublet for $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)(\text{PMe}_2\text{Ph})\text{Cl}$ (**5**) at 11.8 ppm ($J_{\text{PP}} = 27$ Hz) over time relative to the broad singlet for $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ at 28.8 ppm. Kinetic measurements below room temperature used constant temperature baths (ice at 0 °C and salt/ice mixtures, –15 °C) to cool the probe. Samples for lower temperature measurements were pre-cooled (0 °C or –15 °C) before insertion into the NMR probe to ensure rapid equilibration in the probe. The actual temperature in the probe was determined from the frequency difference between the CH_3OH and CH_3OH protons. Three independent measurements of the substitution rate were made at each temperature to determine the rate constant for the reaction. Activation parameters were determined using the Eyring equation (three independent measurements of k_{obs} at each of four temperatures). Errors were calculated using statistical methods described in standard analytic chemistry textbooks [13]. An additional series of experiments were performed using PMe_2Ph concentrations of 310 and 210 mM. Three independent measurements of the substitution rate were made at each phosphine concentration to determine the effect of phosphine concentration on the reaction rate.

The same procedure was used to determine the rate constants for reactions of **1** (40 mM) with PMePh_2 and PEt_3 (400 mM). The product ratios were determined by integration of doublet resonances at 19.6 ppm ($J_{\text{PP}} = 31$ Hz, $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)(\text{PMePh}_2)\text{Cl}$) and 26.6 ($J_{\text{PP}} = 27$ Hz, $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)(\text{PEt}_3)\text{Cl}$) to the broad singlet for $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ at 28.8 ppm. No reaction was observed at ambient temperature or upon refluxing solutions of $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (40 mM) with PCy_3 (400 mM) for 60 h.

2.2. ^1H NMR studies of the dimerization of terminal alkynes catalyzed by $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**1**), $(\eta^5\text{-Indenyl})\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**3**), and $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)(\text{PMe}_2\text{Ph})\text{Cl}$ (**5**)

Solutions of **1**, **3**, or **5** (3–7 mol%), alkyne (0.3–0.7 M PhCCH , FcCCH , TMSCCH , $^t\text{BuCCH}$, or $\text{C}_4\text{H}_9\text{CCH}$) and PPh_3 (0–270 mM) in C_6D_6 were prepared under an argon atmosphere. The reactions were followed by ^1H and ^{31}P NMR spectroscopy. Products were identified by comparison of the chemical shifts of the observed products

with the reported spectral parameters listed below. The % conversion was determined by integration of resonances for RCCH and the dimeric products in the ^1H NMR spectra. The amounts of oligomeric and polymeric products were estimated by comparison of the integrated area of the vinyl protons assigned to dimeric products to the integrated area of the protons assigned to the R groups. The relevant ^1H resonances for the products in C_6D_6 are:

$Z\text{-PhCH=CHCCPh}$ [9]: δ 5.75 d ($J_{\text{HH}} = 11.7$ Hz), 6.38 ($J_{\text{HH}} = 11.7$ Hz).

$E\text{-PhCH=CHCCPh}$ [9]: δ 6.27 d ($J_{\text{HH}} = 16.2$ Hz), 7.01 d ($J = 16.2$ Hz).

$\text{CH}_2=\text{C}(\text{Ph})(\text{CCPh})$ [9]: δ 5.66 ($J_{\text{HH}} = 1$ Hz), δ 5.72 ($J_{\text{HH}} = 1$ Hz).

The aryl protons of all three products overlap in the region 6.5–7.5 ppm.

$Z\text{-FcCH=CHCCFc}$ [14]: δ 4.16 s (5H), 4.27 s (5H), 4.25 t (2H), 4.31 t (2H), 4.50 t (2H), 4.85 t (2H), 5.63 d ($J = 11.4$ Hz, 1H, FcCH=CHCCFc), 6.24 d ($J = 11.4$ Hz, 1H, FcCH=CHCCFc), $E\text{-FcCH=CHCCFc}$: δ 4.15 s (5H), 4.25 s (5H), 4.20 t (2H), 4.36 t (2H), 4.42 t (2H), 4.62 t (2H), 6.02 d ($J = 16.0$ Hz, 1H), 6.82 d ($J = 16.0$ Hz, 1H).

$E/Z\text{-Me}_3\text{SiCH=CHCCSiMe}_3$: δ 6.25 d ($J = 15$ Hz), 6.01 d ($J = 15$ Hz). The ratio of the two geometric (E and Z) isomers cannot be determined by ^1H NMR as the vinyl protons of the products overlap [9].

$\text{CH}_2=\text{C}(\text{SiMe}_3)\text{CCSiMe}_3$ [9]: δ 6.14 d ($J = 3.3$ Hz), 5.55 d ($J = 3.3$ Hz).

Resonances assigned to the TMS (Me_3Si) groups are observed as singlets between 0.1 and 0.15 ppm.

$Z\text{-Me}_3\text{CCH=CHCCMe}_3$ [9]: δ 5.45 d ($J = 11.7$ Hz, $\text{Me}_3\text{CCH=CHCCMe}_3$), 5.55 d ($J = 11.7$ Hz, $\text{Me}_3\text{CCH=CHCCMe}_3$).

$E\text{-Me}_3\text{CCH=CHCCMe}_3$: δ 5.59 d ($J = 16$ Hz, $\text{Me}_3\text{CCH=CHCCMe}_3$), 6.14 d ($J = 16$ Hz, $\text{Me}_3\text{CCH=CHCCMe}_3$).

$\text{CH}_2=\text{C}(\text{CMe}_3)\text{CCMe}_3$ [9]: δ 5.11 d ($J = 2.1$ Hz, 1H, CH), 5.33 d ($J = 2.1$ Hz, 1H, CH).

$(\text{Me}_3\text{C})\text{HC=C=CH}(\text{CMe}_3)$ [9]: δ 5.51 s.

Resonances assigned to the $^t\text{Bu}(\text{Me}_3\text{C})$ groups are observed as singlets between 1.0 and 1.3 ppm.

Two broad signals at 29 and 37 ppm in the ^{31}P NMR spectrum assigned to $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ [6] are replaced by resonances at –4.6 ppm assigned to PPh_3 and a singlet at 25.5 ppm at the end of the experiment.

2.3. Separation and characterization of the products from reactions of phenylacetylene and ethynylferrocene

2.3.1. Reaction of phenylacetylene in benzene at 80 °C

A yellow solution of 167 mg (0.23 mmol, 4.5 mol%) **1** and 550 μL (5 mmol) phenylacetylene in 25 mL C_6H_6 was

refluxed under nitrogen for 2 h. The solution darkens to a brown color in less than a minute. After cooling to ambient temperature, solvent was evaporated under vacuum. The crude product was extracted with 25 mL refluxing ether, cooled, and filtered to remove a brown insoluble ruthenium-containing product (41 mg). The yellow-orange filtrate was evaporated to dryness. Chromatography on silica did not result in good separation of the products, yielding 451 mg (88% yield based on phenylacetylene) of a mixture of dimers, oligomers, and polymers. Chromatography of the latter mixture on alumina using a 10:1 mixture of hexane:CH₂Cl₂ gave a better separation, yielding 110 mg (24% based on phenylacetylene) of *Z/E*-1,4-diphenyl-1-butene-3-yne (8:1 ratio) and 61 mg (12%) of phenylacetylene oligomers. A brown product adsorbed on the column could not be eluted with CH₂Cl₂ or methanol. These products are presumed to be polymeric products derived from phenylacetylene and should account for the remaining products (estimated to be ≈280 mg, 52% based on products collected after chromatography on silica above).

2.3.2. Reaction of phenylacetylene in benzene at ambient temperature

A yellow solution of 175 mg (0.24 mmol, 5 mol%) **1** and 550 μL (5 mmol) phenylacetylene in 25 mL C₆H₆ was stirred under nitrogen for 24 h at ambient temperature. The solution slowly darkens to a brown color over 30 min. Solvent was evaporated under vacuum and the residue extracted with 25 mL of hot diethylether. Chromatography of the extract on alumina yielded 230 mg of *E/Z*-1,4-diphenyl-1-butene-3-yne (45% based on phenylacetylene) and 79 mg of phenylacetylene oligomers (15%) for an overall yield of 60% based on phenylacetylene used in the reaction. The ratio of *Z*- to *E*-1,4-diphenyl-1-butene-3-yne was determined to be 8:1 by ¹H NMR spectroscopy. As before, a brown product adsorbed on the column and could not be eluted with CH₂Cl₂ or methanol. These products are presumed to be polymeric products derived from phenylacetylene and should account for the remaining products.

2.3.3. Reaction of ethynylferrocene in benzene at 80 °C

A solution of 336 mg (1.6 mmol) ethynylferrocene and 93 mg (0.13 mmol, 7.5 mol%) **1** in 25 mL benzene was stirred overnight at ambient temperature. The orange color of ethynylferrocene changes to a dark red. After 24 h at room temperature (or 3 h at reflux) the solvent was evaporated from the reaction mixture under vacuum, yielding a red oil. The crude products were chromatographed on silica using a 2:1 mixture of petroleum ether to benzene. Two red-orange fractions were collected. The first yielded 171 mg (51% yield based on ethynylferrocene) of an 8.5:1 mixture of *Z*-1,3-diferrocenyl-1-buten-3-yne to *E*-1,3-diferrocenyl-1-buten-3-yne identified by comparison of the ¹H NMR spectrum with literature data [14]. The second fraction yielded 88 mg (26% yield based on ethynylferrocene) of a red oil. The ¹H NMR spectrum of this oil consists of a complex multiplet between 4 and 5 ppm.

Changing the eluent to benzene and finally to methanol yielded 69 mg (20% yield based on ethynylferrocene) of a brown solid with a ¹H NMR spectrum similar to the previous product.

2.4. Synthesis of (η⁵-pentadienyl)rutheniumbis(triphenylphosphine)(acetonitrile) hexafluorophosphate (**7**)

A slurry of 250 mg (0.34 mmol) **1** and 180 mg (1.1 mmol) NaPF₆ in 20 mL acetonitrile was stirred for 24 h under nitrogen. The yellow starting material, **1**, slowly dissolves forming a light yellow solution and leaving a white precipitate. The mixture was filtered through a thin pad of Celite and the white solid washed with 5 mL of acetonitrile. The volume of the combined filtrate and washings was reduced to 2 mL under vacuum. Upon cooling a yellow solid precipitates. The solid was collected by filtration and washed twice with 8 mL of diethyl ether and once with 8 mL hexane. Yellow [(η⁵-C₅H₇)Ru(PPh₃)₂(CH₃CN)][PF₆]**7** (237 mg, 79% yield) was isolated after drying in vacuum. The compound darkens upon heating above 150 °C without melting.

Anal. Calc. for C₄₃H₄₀F₆NP₃Ru: C, 58.77; H, 4.59. Found: C, 59.06; H, 4.79%.

¹H (CD₃COCD₃): -0.60 m (1H), -0.44 d (*J* = 10.5 Hz, 1H), 1.59 s (3H, CH₃CN), 2.69 (*J* = 9 Hz, 1H), 2.97 d (*J* = 9 Hz, 1H), 5.06 m (1H), 5.38 m (1H), 5.57 m (1H), 7.15–7.6 m (30H, C₆H₅).

¹H (CD₃CN): -0.63 m (1H), -0.50 d (*J* = 9.6 Hz, 1H), 2.18 s (3H, CH₃CN), 2.60 (*J* = 9.6 Hz, 1H), 2.88 d (*J* = 9.6 Hz, 1H), 4.88 m (1H), 5.22 m (1H), 5.43 m (1H), 7.15–7.6 m (30H, C₆H₅).

¹H (CD₂Cl₂): -0.30 m (1H), -0.15 d (*J* = 12 Hz, 1H), 1.58 s (CH₃CN, 3 H), 2.87 d (*J* = 12 Hz, 1H), 3.17 d (*J* = 12 Hz, 1H), 5.23 m (1H), 5.58 m (1H), 5.70 br s (1H), 7.4, 7.5–7.9 m (C₆H₅).

¹³C (CD₃CN): 44.70, 55.91, 92.22, 97.95 d (*J*_{CP} = 11 Hz), 106.42, 129.38 d (*J*_{CP} = 10 Hz), 130.11 d (*J*_{CP} = 10 Hz), 131.26, 131.86, 134.48 d (*J*_{CP} = 10 Hz), 135.39 d (*J*_{CP} = 10 Hz), 136.0 d (*J*_{CP} = 37 Hz).

³¹P (CD₃CN): 32.9 d (*J*_{PP} = 24 Hz), 48.4 d (*J*_{PP} = 24 Hz), 62.4 heptet (*J*_{PF} = 1006 Hz).

2.5. Dimerization of phenylacetylene catalyzed by [(η⁵-C₅H₇)Ru(PPh₃)₂(CH₃CN)][PF₆]

A pale yellow solution of 120 μL (1.1 mmol, 44 mM) phenylacetylene and 48 mg (0.055 mmol, 5 mol%) **7** in 25 mL THF was stirred at ambient temperature for 6 h with no observable color changes. The mixture was refluxed for 16 h yielding a darker, yellow-brown solution. Solvent was evaporated under vacuum and the oily residue chromatographed on alumina as described above for the dimerization of phenylacetylene in the presence of **1**. 53 mg (47%) of a 4:1 mixture of *Z*:*E* 1,4-diphenyl-1-buten-3-yne was isolated. There were no dark residues left on the column as in the case of the (η⁵-C₅H₇)Ru(PPh₃)₂Cl catalyzed reaction.

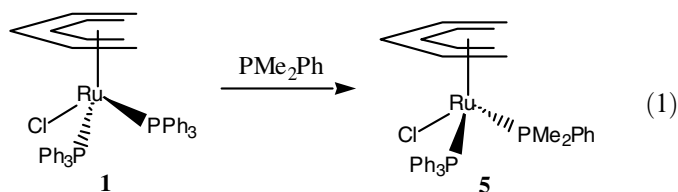
2.6. NMR experiments

Solutions of **7** (5 mol%) and phenylacetylene (0.7–1.2 M) in CD₃CN or CD₂Cl₂ were prepared under an argon atmosphere. The reactions were followed by ¹H spectroscopy. Product ratios and % conversion were determined by integration of resonances assigned to phenylacetylene, *Z*-1,4-diphenyl-1-buten-3-yne and *E*-1,4-diphenyl-1-buten-3-yne. Conversion of phenylacetylene was determined by comparing the integrated area for the terminal proton in phenylacetylene with the integrated area for the vinyl protons of the products. No reaction is observed in either solvent after 24 h at ambient temperature. In CD₃CN, 24% conversion to a 2.5:1 ratio of *Z*:*E* 1,4-diphenyl-1-buten-3-yne is observed after 5 h at 80 °C, increasing to 48% after 26 h of reaction with no change in the product ratio. In CD₂Cl₂, 33% conversion to a 3.5:1 ratio of *Z*:*E* 1,4-diphenyl-1-buten-3-yne is observed after 5 h at reflux increasing to 43% conversion after 26 h of reaction. The product ratio remains constant. Integration of the aryl and vinyl resonances yields a 5:1 ratio suggesting that no oligomerization has taken place.

3. Results

3.1. Kinetics of phosphine substitution

Under pseudo-first order conditions (≈ 10 equiv. PMe₂Ph) the conversion of **1** to (η^5 -C₅H₇)Ru(PPh₃)(PMe₂Ph)Cl (**5**) in benzene (Eq. (1)) is essentially complete upon mixing at ambient temperature and leads to mixtures of **5** and (η^5 -C₅H₇)Ru(PMe₂Ph)₂Cl (**6**) upon standing. The reaction between **5** and PMe₂Ph in C₆D₆ forming **6** is slower than the conversion of **1** to **5** but still has a half-life of less than 2 min at ambient temperature making it unsuitable for our study. Similar mixtures are reported in reactions of (η^5 -C₉H₇)Ru(PPh₃)₂Cl (**3**) with PMe₂Ph in benzene [7]. Rapid reactions were also observed between **1** and PEt₃ or PMePh₂ in benzene as determined by both ¹H and ³¹P NMR spectroscopy



Good kinetic data can be collected for the reaction of **1** with PMe₂Ph, PMePh₂, and PEt₃ at 20 °C and below in THF/C₆D₆ mixtures (90/10 v/v). The reaction is quite rapid at ambient temperature, reaching completion after ≈ 30 min, however, reproducible data could be collected using concentrated solutions to reduce data acquisition times. The monosubstituted product, (η^5 -C₅H₇)Ru(PPh₃)(PMe₂Ph)Cl (**5**), is the only product present at the end of each kinetic run. There is no evidence for the formation of (η^5 -C₅H₇)Ru(PMe₂Ph)₂Cl (**6**) during the kinetic mea-

surements (≈ 30 –40 min per experiment). Formation of **6** is seen in samples allowed to stand at ambient temperatures for several hours. Below room temperature (5 and 0 °C), the reaction is much slower and provides linear plots of the ln[**1**] as a function of time over several half-lives. The first order rate constants for reactions of **1** with PMe₂Ph, PMePh₂, and PEt₃ are listed in Table 1. There is little dependence of the rate constant on the nature of the phosphine although the bulky tertiary phosphine PCy₃ failed to react even after refluxing for 60 h. The rate of substitution of PPh₃ in **1** is at least 70 times faster than in **2** and almost 40 times faster than in **3** at 20 °C. Activation parameters for the reaction of **1** with PMe₂Ph are also listed in Table 1. The reaction rate at 20 °C is essentially independent of the phosphine concentration for three different concentrations (400, 310, and 210 mM) of PMe₂Ph.

3.2. Catalytic activity of (η^5 -C₅H₇)Ru(PPh₃)₂Cl in the dimerization of phenylacetylene

A significant increase in catalytic activity is observed when (η^5 -C₅H₇)Ru(PPh₃)₂Cl (**1**) is used as the catalyst (5 mol%) in the dimerization of phenylacetylene (0.5 M in benzene) relative to **2** and **4** under identical conditions. When followed by ¹H NMR spectroscopy, conversion of phenylacetylene was complete after 90 min at 80 °C compared to 24 h or more for the other ruthenium complexes (Table 2). In fact, reaction at ambient temperature leads to complete conversion after 24 h. The products identified in the reaction mixture by ¹H NMR and confirmed by gc/ms are: *Z*-1,4-diphenyl-1-buten-3-yne and *E*-1,4-diphenyl-1-buten-3-yne along with trace amounts of 2,4-diphenyl-1-buten-3-yne (the “head-to-tail” dimer). The *Z*-isomer is characterized by well-resolved doublets at δ 5.75 ($J_{\text{HH}} = 11.7$ Hz) and δ 6.38 ($J_{\text{HH}} = 11.7$ Hz) while the *E*-isomer has a distinct resonance at δ 6.27 ($J =$

Table 1
Observed rate constants for the reaction of (η^5 -C₅H₇)Ru(PPh₃)₂Cl (**1**), CpRu(PPh₃)₂Cl (**2**), and (η^5 -C₉H₇)Ru(PPh₃)₂Cl (**3**) with tertiary phosphines

Reaction	<i>T</i> (°C)	k_{obs} (s ⁻¹ × 10 ⁴)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal K ⁻¹ mol ⁻¹)
1 + PMe ₂ Ph ^a	0	2.0 ± 0.3		
	5	2.7 ± 0.1		
	21	16.3 ± 1.9		
		17.0 ± 1.8 ^b		
		18.0 ± 1.8 ^c		
	25	24.8 ± 1.3	16.1 ± 0.4	-16 ± 1
1 + PMePh ₂ ^a	22 ± 0.2	14.8 ± 0.4		
1 + PEt ₃ ^a	22 ± 0.2	15.8 ± 0.2		
2 + PMe ₂ Ph ^d	30.0	0.25 ± 0.02		
2 + PMePh ₂ ^d	20.6	0.050 ± 0.005	29 ± 1	17 ± 2
3 + PMe ₂ Ph ^d	20.0	0.42 ± 0.02	26 ± 1	11 ± 2

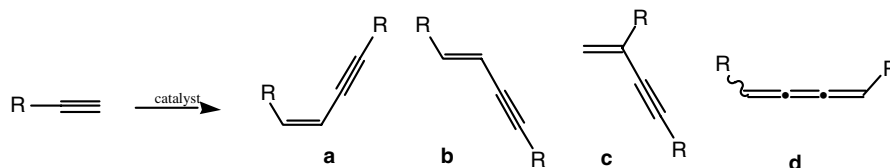
^a 40 mM in **1**, 400 mM in phosphine in THF/C₆D₆ (90/10 v/v).

^b [PMe₂Ph] = 310 mM.

^c [PMe₂Ph] = 210 mM.

^d Ref. [7].

Table 2
Product distribution from ruthenium catalyzed dimerization of terminal alkynes



Substrate	Catalyst ^a	<i>T</i> (°C)	<i>t</i> (h)	% Conversion	% a ^g	% b ^g	% c	% d
PhCCH	1 ^b	5	18					
		20	24	94	40 (40)	5 (5)	5	
		80	1.5	100	22 (21)	3 (3)	3	
	2 ^c	80	24	24	11	10	3	
		3	80	15	80	64	16	
		4 ^d	110	20	98	9	89	
		5	80	1.5	100	25	21	4
7	80 ^e	26	43	33	10			
	80 ^f	16	47	(38)	(9)			
FcCCH	1	20	24	74	57	17		
TMSCCH	1	80	6	64	23		64	
	2 ^c	80	20	70	49 ^h		21	
	4 ^d	110	20	94	77		17	
^t BuCCH	1	80	19	85	30		39	6
	2 ^c	80	24	0				
	4 ^d	110	20	11	10		1	

^a Reactions in C₆D₆ unless other indicated.

^b Remaining products appear to be oligomers and polymers.

^c see Ref. [6a].

^d In toluene, see Ref. [9].

^e CD₃CN.

^f In THF.

^g Ratios from integration of ¹H NMR spectra of reaction mixtures. Values in parentheses represent isolated yields.

^h The resonances for *E*- and *Z*-isomers overlap. A combined yield is reported.

16.2 Hz) [9]. The phenyl resonances and the remaining vinyl resonances overlap with those assigned to other products in solution. Two doublets at δ 5.66 ($J_{\text{HH}} = 1$ Hz) and δ 5.72 ($J_{\text{HH}} = 1$ Hz) are assigned to the head-to-tail dimer, 2,4-diphenyl-1-buten-3-yne [9]. A consistent ratio of 8:1:1 for the *Z*:*E*:head-to-tail dimer is observed after 24 h of reaction at ambient temperature and 80 °C when conversion of phenylacetylene is complete at all temperatures.

Integrated peak areas of the aryl resonances relative to the resonances assigned to the vinyl protons of *E*- and *Z*-1,4-diphenyl-1-buten-3-yne are consistent with the partial oligomerization or polymerization of phenylacetylene. The latter products account for about 50% of the reaction products at ambient temperature in C₆D₆ after 24 h and increase to about 75% in reactions at 80 °C after 90 min. Analysis of the reaction mixtures by gc/ms reveals the presence of isomeric phenylacetylene dimers ($m/e = 204$) and additional products with $m/e = 306$, corresponding to trimers of phenylacetylene as the volatile products. In a separate experiment using toluene as the solvent, essentially no reaction takes place after two weeks in a –18 °C freezer but 80% conversion is observed when the sample is stored in a refrigerator at 5 °C for 24 h. Integration of the aryl and

vinyl resonances reveals that oligomerization occurs even at 5 °C.

When the reaction is carried out on a preparative scale followed by chromatography of the products on alumina, isolated yields of *E*- and *Z*-1,4-diphenyl-1-buten-3-yne decrease from 50% for ambient temperature reactions to 25% for reactions at 80 °C. These yields are comparable to those observed in the NMR experiments. The NMR spectra of the other products (orange to red oils) are characterized by a very broad resonance between 6.8 and 7.8 ppm, and appear to be consistent with formation of oligomeric (PhC=CH)_{*n*}. Accurate yields of these products could not be determined as significant amounts of products absorb strongly on alumina preventing their isolation and characterization. These products may be higher oligomers or polymers of phenylacetylene. For comparison, we note that in the absence of ruthenium-containing catalysts, thermal polymerization accounts for 13% of the products after 13 h at 110 °C in toluene [15].

The catalytic activity of (η^5 -indenyl)Ru(PPh₃)₂Cl (**3**) in the dimerization of phenylacetylene was investigated under the same conditions used in reactions where **1** was the catalyst. The dimerization of phenylacetylene in the presence

of **3** is 80% complete after 20 h at 80 °C. The products were identified as a 4:1 ratio of *Z*:*E*-1,4-diphenyl-1-buten-3-yne. There appears to be minimal oligomerization of the alkyne in this case. When 5 mol% ($\eta^5\text{-C}_5\text{H}_7$)Ru(PPh₃)(P-Me₂Ph)Cl (**5**) is used as a catalyst nearly 100% conversion is observed after 90 min of reaction at 80 °C with formation of nearly equal amounts of *Z*- and *E*-1,4-diphenyl-1,3-buten-1-yne along with smaller amounts of the “head-to-tail” dimer. Integration of the aryl resonances suggests about 50% of the phenylacetylene is converted to oligomeric and polymeric products in the latter reaction.

When additional phenylacetylene is introduced to the NMR tube containing **1** after conversion of alkyne is complete, catalytic dimerization continues but at a diminished rate. Whereas conversion of phenylacetylene (0.5 M, 20 equiv.) is complete after 2 h at 80 °C, significant amounts of unreacted alkyne remain 4 h after adding another 20 equiv. of phenylacetylene and heating at 80 °C. These observations suggest a change in the catalytically active species. The fate of **1** in the reactions with PhCCH was examined by ³¹P NMR. The two broad signals at 29 and 37 ppm assigned to **1** [6] disappear after 30 min of reaction at 80 °C with the appearance of a singlet at -4.6 ppm assigned to PPh₃. No additional resonances are detected in the ³¹P NMR spectrum until the conversion of phenylacetylene is complete (90 min at 80 °C). At this point, a singlet at 25.5 ppm begins to grow in intensity. The same changes are observed at ambient temperature but the disappearance of the resonances for the starting material is slower. A brown powder isolated from the catalytic reactions has a single resonance in the ³¹P spectrum at 25.5 ppm. Resonances characteristic of C_z for ruthenium vinylidene species (e.g. TpRuCl(PPh₃)=C=C(Ph)H [10]) between 345 and 355 ppm have not been detected in the ¹³C NMR spectrum of the ruthenium-containing product. Despite repeated attempts, this material has resisted our efforts at growing crystals suitable for X-ray diffraction. A pure sample for elemental analysis has similarly not been obtained.

The reaction rate and product ratio change in the presence of **1** and excess PPh₃. At constant temperature (22 °C), catalyst concentration (25 mM, 5 mol%), and reaction time (24 h) the conversion of phenylacetylene (500 mM) decreases from 94% (in the absence of 1 equiv. of additional PPh₃) to 19% in the presence of 10 equiv. of PPh₃. A concurrent increase in the amount of oligomeric and polymeric species is observed as the concentration of PPh₃ increases. Adding 1 equiv. of PCy₃ to 0.5 M PhCCH containing 5 mol% **1**, however, has no effect on either the rate of the reaction or the product ratio.

The pentadienyl ruthenium complex **1** is also active as a catalyst for the dimerization of ethynylferrocene, trimethylsilylacetylene, and ^tbutylacetylene (Table 2). The dimerization of ethynylferrocene proceeds smoothly at ambient temperature with 74% conversion after 24 h at ambient temperature. Complete conversion is achieved by heating for 2 h at 80 °C. NMR spectra of the reaction mixtures are consistent with the formation of mostly *Z*-1,4-di(ferr-

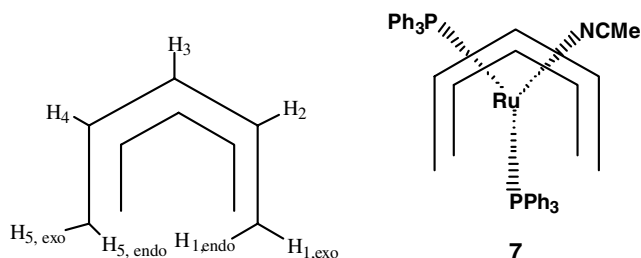
ocenyl)-1-buten-3-yne with lesser amounts of the *E*-isomer. *Z*-1,4-Di(ferrocenyl)-1-buten-3-yne can be isolated in ≈50% yield from reaction of ethynylferrocene with 5 mol% **1**. The remaining products remain poorly characterized but appear to be oligomers or polymers of ethynylferrocene based on ¹H NMR spectra.

In contrast to phenylacetylene and ethynylferrocene, neither trimethylsilylacetylene nor ^tbutylacetylene react at ambient temperature in the presence of **1**. The dimerization of trimethylsilylacetylene in the presence of 3 mol% of **1** proceeds with 64% conversion (by ¹H NMR) at 80 °C after 6 h and yields a 1.8 to 1 mixture of 1,3-bis(trimethylsilyl)-3-buten-1-yne to *E/Z*-1,4-bis(trimethylsilyl)-1-buten-3-yne. In the latter case, the resonances for the vinyl protons of the *E* and *Z* isomers overlap, preventing the determination of an *Z*:*E* ratio. Dimerization of ^tbutylacetylene in the presence of 4.5 mol% of **1** is slower, requiring 19 h of reaction at 80 °C to achieve 85% conversion. By ¹H NMR, the products consist of a mixture of 2,4-di(^tbutyl)-1-buten-3-yne, *Z*-1,4-di(^tbutyl)-1-buten-3-yne and a cumulene, 1,4-di(^tbutyl)butatriene, in a 2.4:1.8:1 ratio. In neither case is there evidence for oligomerization of the alkyne. 1-Hexyne fails to react under these conditions.

A less dramatic rate enhancement for alkyne dimerization is observed at elevated temperatures in reactions catalyzed by **1** relative to reactions catalyzed by **2–4**. Reaction of ^tbutylacetylene in the presence of **5** is 85% complete after 19 h at 80 °C compared to 10% conversion after 68 h at 110 °C [9] in the presence of **4**. No reaction is observed when **2** is used as the catalyst. It is difficult to detect a clear increase in reaction rate with trimethylsilylacetylene for **1** relative to **2** and **4**. Trimethylsilylacetylene (5 mol% **1**) reacts rapidly at 80 °C with 64% conversion after 6 h compared to 70% conversion after 20 h (80 °C) in the presence of 5 mol% of **2** and 94% conversion after 20 h (110 °C) in the presence of 2 mol% **4**.

3.3. Synthesis and catalytic activity of [($\eta^5\text{-C}_5\text{H}_7$)-Ru(PPh₃)₂(CH₃CN)] [PF₆]

The reaction between **1** and NaPF₆ in acetonitrile leads to solvolysis of the Ru-Cl bond forming [($\eta^5\text{-C}_5\text{H}_7$)Ru(PPh₃)₂(CH₃CN)] [PF₆] (**7**) in excellent yield. Satisfactory elemental analysis has been obtained for this new compound. The cationic ruthenium(II) complex **7** is soluble in acetonitrile, THF, CH₂Cl₂, and acetone (although solubility in the latter solvent is lower than in the others). The ¹H NMR spectrum of **7** is characterized by seven well-resolved sets of resonances for the C₅H₇ ligand indicating a static structure for **7**, rather than the fluxional structure reported for **1** at ambient temperature [6]. The spectroscopic data for **7** are consistent with a solution structure in which one PPh₃ ligand lies under the open edge of the pentadienyl ligand. Such an arrangement renders the CH₂ groups at the termini of the pentadienyl ligand inequivalent and accounts for the seven resonances for the C₅H₇ ligand.



The ^{13}C NMR spectrum of **7** is similar to that reported for **1** [6]. Solutions of **7** in acetonitrile- d^3 are stable toward further substitution of PPh_3 by solvent. The spectra of **7** are similar to low temperature spectra of **1** and **5**, where a solution structure is unsymmetrical. In **1**, one PPh_3 ligand rather than the Cl ligand lies under the open edge of the pentadienyl ligand [6b]. It is unclear which ligand occupies this position under the open edge in **5**, but both **1** and **5** are fluxional under the conditions of the kinetic experiments [6b].

The insolubility of **7** in non-polar solvents such as benzene prevents a direct comparison of the activity of **7** as a catalyst in the dimerization of alkynes. Phenylacetylene does not react at ambient temperature in CD_3CN and CD_2Cl_2 in the presence of ≈ 5 mol% **7**. At 80°C in CD_3CN , 26 h are required to effect a 48% conversion of phenylacetylene to a 2.5:1 ratio of *Z*- to *E*-1,4-diphenyl-1-buten-3-yne. A similar rate (43% conversion), but a slightly different ratio of *Z*- to *E*-1,4-diphenyl-1-buten-3-yne (3.3:1, respectively), is observed in CD_2Cl_2 at reflux after 26 h. In refluxing THF, **7** is also active as a catalyst for the dimerization of phenylacetylene yielding a 47% isolated yield of a 4:1 mixture of *Z*- to *E*-1,4-diphenyl-1-buten-3-yne. The absence of dark residues that adhere to an alumina column suggests that oligomerization of phenylacetylene is suppressed.

4. Discussion

4.1. Kinetics of phosphine substitution

The substitution of PPh_3 by smaller tertiary phosphines in $(\eta^5\text{-pentadienyl})\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**1**) is faster than in the iso-electronic $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ (**2**), or $(\eta^5\text{-indenyl})\text{Ru}(\text{PPh}_3)_2\text{Cl}$ (**3**). The enthalpy of activation ($\Delta H^\ddagger = 16.1 \pm 0.4$ kcal mol^{-1}) for the reaction of **1** with PMe_2Ph is much less than for the reaction of **2** with PMePh_2 ($\Delta H^\ddagger = 29$ kcal mol^{-1}) or **3** with PMe_2Ph ($\Delta H^\ddagger = 26$ kcal mol^{-1}). The entropy of activation for the reaction of **1** with PMe_2Ph ($\Delta S^\ddagger = -16 \pm 1$ cal $\text{K}^{-1} \text{mol}^{-1}$) differs from the reaction of **2** and **3** with the same tertiary phosphine ($\Delta S^\ddagger = 17$ and 11 cal $\text{K}^{-1} \text{mol}^{-1}$, respectively). The activation parameters for substitution reactions of **2** and **3** are consistent with a dissociative mechanism. The observed negative entropy of activation in the reaction of **1** suggests the possibility of an associative process, but does not allow us to draw definitive conclusions in a polar solvent like THF [16].

Phosphine substitution in both **2** and **3** is proposed to occur by a dissociative pathway based on the activation parameters [7]. It was suggested that the substitution reactions of **3** are faster as the indenyl ligand is a better donor than the Cp ligand, stabilizing the 16 electron intermediate that results from dissociation of PPh_3 . Electrochemical measurements of the oxidation potentials of **2** (0.56 V) and **3** (0.45 V) support this interpretation. The pentadienyl ligand in **1** (cone angle 180°) [2] is significantly larger than that of the Cp ligand in **2** (136°) [3] and the oxidation potential of **1** (0.45 V) is similar to **3**. The increased rate of phosphine substitution in **1** compared to **2** can be explained on both electronic and steric grounds. The better donor ligand in **1** stabilizes the 16-electron intermediate while the larger size of the C_5H_7 ligand promotes dissociation of PPh_3 . It seems reasonable to assume that the cone angle of the indenyl ligand lies somewhere in between the values for Cp and C_5H_7 . The rate enhancement for phosphine substitution in **1** relative to **3** may reflect steric effects as **3** and **1** have nearly identical oxidation potentials. The possibility of an η^5 to η^3 conversion of the pentadienyl ligand can not be ruled out. There is precedent in the literature for the latter process in pentadienyl metal complexes. For example, refluxing $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3$ with PMe_2Ph in cyclohexane produces $(\eta^5\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_2(\text{PMe}_2\text{Ph})$, apparently by an associative mechanism [17]. An intermediate, $(\eta^3\text{-C}_5\text{H}_7)\text{Mn}(\text{CO})_3(\text{PMe}_2\text{Ph})$, can be isolated at room temperature although the kinetics of the reaction have not been reported. Reaction of $(\eta^5\text{-pentadienyl})\text{-Re}(\text{CO})_3$ with PEt_3 or PMe_3 in refluxing diethylether yields η^1 complexes, $(\eta^1\text{-C}_5\text{H}_7)\text{Re}(\text{CO})_3(\text{PR}_3)_2$ ($\text{R}=\text{Et}, \text{Me}$) [18]. Furthermore, in reactions of **1** with excess PMe_2Ph it is possible to isolate $(\eta^3\text{-C}_5\text{H}_7)\text{Ru}(\text{PMe}_2\text{Ph})_3\text{Cl}$ (**9**) [6]. Nevertheless, we believe that the zero-order dependence of the reaction rate on PMe_2Ph concentration argues for a dissociative pathway for the reaction between **1** and PMe_2Ph . The larger C_5H_7 ligand also prevents successful substitution by large, electron-rich phosphines like tri(cyclohexyl)phosphine. The complete conversion of **1** to **5** at room temperature is observed under pseudo-first order conditions. The observation of $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PMe}_2\text{Ph})_2\text{Cl}$ (**6**) only after complete conversion of **1** to **5** suggests that the rate of substitution in **5** is slower than in **1**.

4.2. Catalytic activity

Having demonstrated the increased rate of phosphine substitution in **1** relative to **2** and **3**, we can begin to compare the catalytic activity of these three complexes in the dimerization of terminal alkynes. The two most interesting results of the investigations of the catalytic activity of **1** are:

- (1) the significant increase in rate of dimerization of phenylacetylene when **1** is used as a catalyst compared to structurally related ruthenium(II) complexes **2–4** and
- (2) the extensive oligomerization of PhCCH in the presence of **1** compared to **2–4**.

Neither **2**, **3**, nor **4** are reported to be active as catalysts at ambient temperature while **1** converts phenylacetylene to a mixture of dimers, oligomers, and polymers after 24 h at ambient temperature. In the presence of 5 mol% of **5**, the conversion of phenylacetylene is complete in 90 min at 80 °C. In contrast, the conversions of PhCCH after 20–24 h at 80 °C in the presence of 5 mol% **2** and 5 mol% **3** are 23% and 80%, respectively. Complete conversion of phenylacetylene to dimers in the presence of $\text{TpRu}(\text{PPh}_3)_2\text{Cl}$ (**4**) is reported at 110 °C [9]. The lability of the PPh_3 ligand in **1** may be responsible for the rate enhancement in the catalytic reactions of phenylacetylene. The rate of PPh_3 substitution for a series of isoelectronic ruthenium(II) complexes has now been shown to be in the order: $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl} > (\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl} > \text{CpRu}(\text{PPh}_3)_2\text{Cl}$. The rate of phosphine substitution in $\text{TpRu}(\text{PPh}_3)_2\text{Cl}$ has not been reported. The accepted mechanism for the coupling of terminal alkynes (Fig. 2) starts with the dissociation of a phosphine ligand. Faster dissociation of PPh_3 could account for a faster dimerization reaction.

One expects $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2(\text{CH}_3\text{CN})^+$ (**7**) to show a different activity in the oligomerization of alkynes given the presence of three potentially labile ligands (two PPh_3 and the coordinated acetonitrile). No reaction is observed at ambient temperature in acetonitrile or THF solutions

of phenylacetylene containing 5 mol% **7**. Heating the mixtures to 80 °C for 26 h led to between 48% and 47% conversion to phenylacetylene dimers. The effect of substitution of CH_3CN for Cl in the coordination sphere of **1** on catalytic activity is not surprising as similar effects are evident in reactions of other ruthenium compounds. For example, significant conversion of phenylacetylene to 1,4-diphenylbut-1-en-3-yne is observed in the presence of **3** (80%) while 68% conversion is found with $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{CCPh}$ and only 52% conversion is reported when $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{H}$ is used as the catalyst. The relative amounts of dimeric and oligomeric products is also highly dependant on the ligands in these complexes.

Significant amounts (>50%) of oligomeric and polymeric products are only observed in reactions of phenylacetylene catalyzed by **1**. Diphenylbutenyne is the major products from reactions of phenylacetylene in the presence of **2–4** and **7**. Nevertheless, the formation of phenylacetylene oligomers in the presence of Ru(II) complexes has precedent in the literature. Even greater amounts of oligomeric and polymeric products are observed in the reactions of PhCCH catalyzed by $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{CCPh}$ (70%) and $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{COD})\text{Cl}$ (80%). Lesser amounts are seen in the presence of $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{H}$ [15]. The polymerization of terminal alkynes is

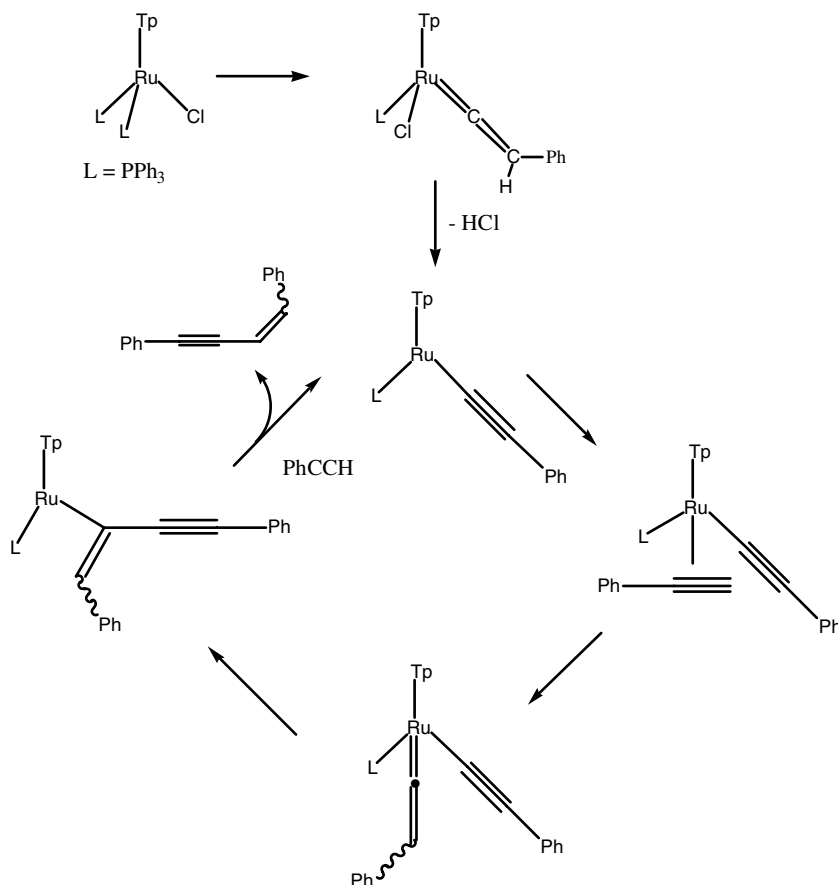


Fig. 2. Proposed mechanism for the dimerization of terminal alkynes in the presence of **4** [9].

also observed in the presence of $\text{TpRu}(\text{COD})\text{Cl}$ [19]. The COD ligand in both $(\eta^5\text{-indenyl})\text{Ru}(\text{COD})\text{Cl}$ and $\text{TpRu}(\text{COD})\text{Cl}$ is very labile and may be responsible for opening two coordination sites at ruthenium upon dissociation and polymerization. These data suggest that the lability of the phosphine ligands in **1** may be responsible for the formation of oligomeric products. The kinetic data for the conversion of **1** to **5** suggest that reaction of **5** with PMe_2Ph (forming **6**) is slower than the conversion of **1** to **5**. Using **5** as the catalyst in the dimerization of phenylacetylene, the observation of a slower reaction rate and less oligomerization correlate with lower rates of phosphine substitution in **5** compared to **1**.

Further insight into the mechanism of the $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ catalyzed dimerization of phenylacetylene is limited. The observation of “free” PPh_3 in reactions catalyzed by $(\eta^5\text{-C}_5\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{Cl}$ is consistent with the first step in the proposed mechanism in Fig. 2 (the formation of a vinylidene complex). The formation of a vinylidene compound, $\text{TpRuCl}(\text{PPh}_3)\{\text{C}=\text{C}(\text{H})\}$ (^{31}P : δ 34 ppm) is reported to be immediate upon addition of excess phenylacetylene to a benzene- d^6 solution of $\text{TpRuCl}(\text{PPh}_3)_2$. The former can be isolated from the reaction mixture [9]. Vinylidene complexes such as $\text{CpRu}(\text{PPh}_3)\{\text{C}=\text{C}(\text{H})\}^+$ and $(\eta^5\text{-indenyl})\text{Ru}(\text{PPh}_3)\{\text{C}=\text{C}(\text{H})\}^+$ are well characterized with non-coordinating anions such as BF_4^- [20]. Evidence for the formation of vinylidene derivatives of **1** remains elusive. The only ruthenium-containing product from reactions between phenylacetylene and **1** lacks ^1H resonances for the pentadienyl group and ^{13}C resonances characteristic of ruthenium vinylidene complexes (≈ 350 ppm) [20]. The sole ^{31}P resonance at 25 ppm in C_6D_6 is nearly identical to the unidentified and catalytically inactive material isolated from reactions between phenylacetylene and $(\eta^5\text{-indenyl})\text{Ru}(\text{PPh}_3)_2\text{H}$ or $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{CCPh}$ (^{31}P resonance at 25 ppm in toluene- d^8) [15].

Loss of HCl generates a 16-electron alkynyl complex as the catalytically active species shown in Fig. 2. While such intermediates are not observed in catalytic dimerization of PhCCH by **2–4**, some 70% of the available phenylacetylene was converted to oligomers at 110°C in the presence of $(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{PPh}_3)_2\text{CCPh}$ [15]. It is possible that similar compounds are formed in reactions of **1** with phenylacetylene leading to oligomerization. Further study on the mechanistic aspects of **1** catalyzed alkyne dimerization is clearly needed.

5. Conclusion

The pentadienyl (C_5H_7) ligand has a significant effect on the catalytic activity of ruthenium(II) complexes. The donor properties of the pentadienyl ligand may account for the increased rate of substitution of PPh_3 ligands in **1** compared to **2** while the steric bulk of the pentadienyl

ligand contributes to the increased rate of substitution of PPh_3 ligands in **1** compared to **3**. The greater lability of the PPh_3 ligands in **1** is reflected in the increased catalytic activity of **1** in the dimerization of terminal alkynes. While an increased rate is often welcome in catalytic process, the reduction in selectivity (dimer vs. polymer) makes **1** less attractive than **3**, **4** and a number of other transition metal catalysts in the dimerization of alkynes. Further work is in progress on exploring the scope of reactions catalyzed by **1** where rapid ligand dissociation and a strong donor/acceptor pentadienyl ligand may lead to improved yields or different selectivity relative to **3**, **4**, or other ruthenium(II) compounds.

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