Chloro(η^5-dihydropentalenyl)bis(triphenylphosphine)ruthenium(II): synthesis, structural characterization and catalytic activity in the dimerization of phenylacetylene

Rein U. Kirss [a,*], Richard D. Ernst [b], Atta M. Arif [b]

[a] *Department of Chemistry, Northeastern University, 102 Hurtig Hall, Boston MA, 02115, USA*
[b] *Department of Chemistry, University of Utah, 315 S. 1400 E., Salt Lake City, UT 84112, USA*

Abstract

Reactions between $HRuCl(PPh_3)_3$ and 1,3- or 1,5-cyclooctadiene yield the 1,2-dihydropentalenyl complex (η^5-C_8H_9)$Ru(PPh_3)_2Cl$ through a series of steps including olefin insertion and electrocyclization. The reaction is accompanied by the loss of two equivalents of hydrogen. The product crystallizes in the monoclinic space group $P\bar{1}$ (No. 2). (η^5-C_8H_9)$Ru(PPh_3)_2Cl$ catalyzes the dimerization of phenylacetylene to a $\approx$2:1 mixture of Z:E 1,4-diphenyl-1-buten-3-yne. Comparison of the catalytic activity of (η^5-C_8H_9)$Ru(PPh_3)_2Cl$ with (η^5-C_5H_5)$Ru(PPh_3)_2Cl$, (η^5-C_5Me_5)$Ru(PPh_3)H_3$ and {η^5-$HB(pz)_3$}$Ru(PPh_3)_2Cl$ suggests that the more electron-rich η^5 ligands favor formation of the Z isomer.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Electrocyclic reactions; Ruthenium compounds; Dimerization of alkynes

1. Introduction

Flash vacuum pyrolysis (FVP) of (η^5-pentamethylcyclopentadienyl)-(η^5-cyclooctadienyl)ruthenium, ({η^5-C_5Me_5}{η^5-C_8H_{11}}Ru) results in electrocyclic ring closure of the C_8H_{13} ligand, forming (η^5-pentamethylcyclopentadienyl)(η^5-1,2-dihydropentalenyl)ruthenium ({η^5-C_5Me_5}{η^5-C_8H_9}Ru). The reaction is accompanied by the loss of one equivalent of H_2 (Eq. (1)) [1]. The potential synthetic utility of ruthenium-mediated electrocyclic reactions in the construction of [3.n.0] fused ring systems can be better realized if conditions can be identified under which the reaction occurs in solution at lower temperature.

$$(1)$$
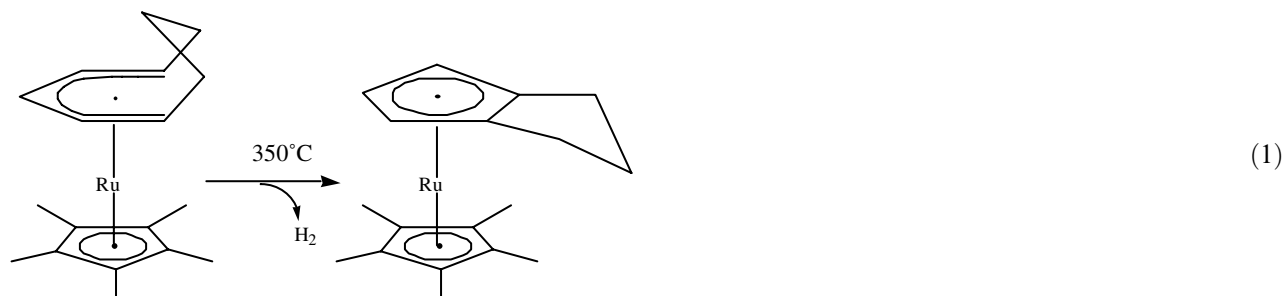
The relatively mild conditions for the electrocyclic reaction of 1,4-pentadiene [2] (Eq. (2)) suggested that $HRuCl(PPh_3)_3$ might be a versatile reagent for the construction of fused [3.n.0] carbocyclic ring systems from cyclic

* Corresponding author. Tel.: +1-617-373-4513; fax: +1-617-373-8795.
E-mail address: rkirss@neu.edu (R.U. Kirss).

dienes. In this paper we report on the reaction between HRuCl(PPh$_3$)$_3$ and cyclooctadienes yielding (η^5-1,2-dihydropentalenyl)Ru(PPh$_3$)$_2$Cl (Eq. (3)). We also report on the activity of (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl in the catalytic dimerization of phenylacetylene to isomeric 1,4-diphenyl-1-buten-3-ynes.

$$(2)$$

$$(3)$$
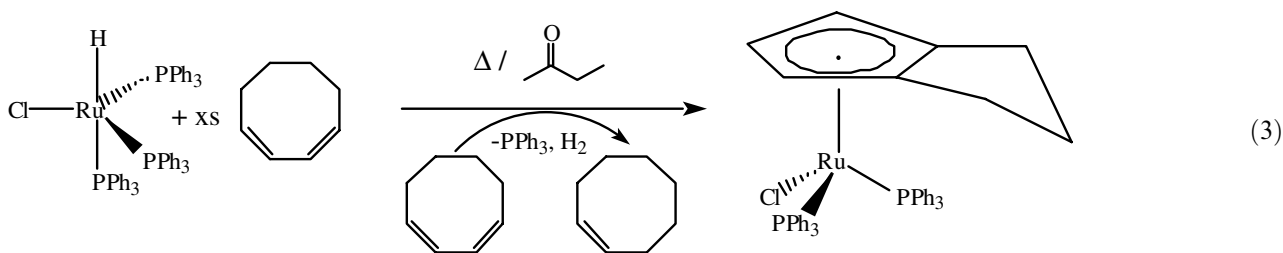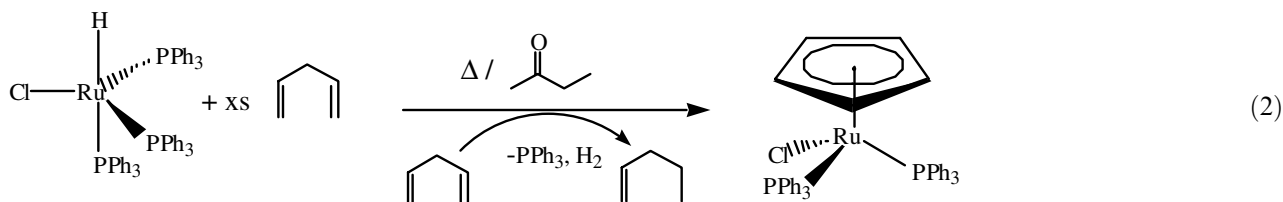
2. Experimental

All compounds described in this work were handled using Schlenk techniques or a M.I. Braun glove-box under purified argon or nitrogen atmospheres [3]. RuCl$_3 \cdot$H$_2$O was purchased from Alfa Inorganics, Inc. 1,3-Cyclooctadiene (Fluka) and 1,5-cyclooctadiene (Aldrich) were used as received. Phenylacetylene was distilled under vacuum prior to use. Solvents were purified by refluxing over Na/benzophenone (toluene, benzene, hexane, pentane), P$_2$O$_5$ (2-butanone, dichloromethane) or MgSO$_4$ (ethanol) and distilled prior to use. HRuCl(PPh$_3$)$_3$ was prepared by literature procedures [4]. Elemental analyses (C, H) were performed by Desert Analytics, Inc.

NMR spectra were recorded at 300 MHz for ^{1}H, 75.4 MHz for ^{13}C{^{1}H} and 121.4 MHz for ^{31}P{^{1}H} on a Varian XL300 spectrometer. Proton chemical shifts are reported relative to residual protons in the solvent (C$_6$D$_5$H at δ 7.15 ppm or CDCl$_3$ at δ 7.24 ppm relative to TMS at 0.00 ppm). Carbon chemical shifts are reported relative to solvent (C$_6$D$_6$ t at δ 128.0 ppm). Phosphorus chemical shifts are reported relative to external 85% H$_3$PO$_4$ at 0.0 ppm.

2.1. Synthesis of (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl

(a) A mixture of 938 mg (1.0 mmol) HRuCl(PPh$_3$)$_3$ and 0.5 mL (4 mmol) 1,5-cyclooctadiene in 40 mL 2-butanone was refluxed under nitrogen for 48 h. Solvent was evaporated from the red-orange solution under vacuum. The crude product was dissolved in 5 mL of toluene and passed through a 1 cm thick pad of Celite. The Celite was washed with 2×2 mL of toluene and the washings combined. Hexane (10 mL) was carefully layered on top of the toluene. An orange brown solid precipitated upon cooling to −20 °C for several days. Single crystals were obtained by re-crystallization from 5 mL CH$_2$Cl$_2$ layered with 5 mL of pentane at −20 °C for several weeks. Red-orange crystals of (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl (257 mg, 33% yield) were isolated. The compound crystallizes with 0.5 equivalents of pentane from integration of the ^{1}H NMR spectrum. The pentane can be removed by heating a finely powdered sample of (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl$_2$ at 100 °C for 8 h under vacuum.

m.p. 135–137 °C Analysis: calculated for C$_{44}$H$_{39}$ClP$_2$Ru: 68.79% C, 5.38% H; found: 68.97% C, 5.13% H.
^{1}H (C$_6$D$_6$) δ 1.98 d (3H), 2.16 pseudo t (2H, $J = 9.6$, 10.5 Hz), 2.48 s (1H), 2.76 br m (1H), 4.07 s (2H), 6.88 m (18H), 7.62 m (12H), 1.25 m (2H, pentane), 0.87 t (2H, pentane) (CDCl$_3$) δ 1.62 br m (4H), 2.09 br m (1H), 2.37 s (1H), 2.49 br m (1H), 3.94 s (2H), 7.12 t (12H), 7.22 d (6H), 7.38 br m (12H), 1.3 m (3 H, pentane), 0.90 t (3H, pentane) ^{13}C (C$_6$D$_6$): δ 139.47, 134.3, 108.92, 77.45, 71.73, 67.80, 29.87, 23.83. ^{31}P{^{1}H} (C$_6$D$_6$): 41.4 s.

(b) A mixture of 1.02 g (1.1 mmol) HRuCl(PPh$_3$)$_3$ and 1.5 mL (12 mmol) 1,5-cyclooctadiene was refluxed in 40 mL 2-butanone for 5 days. Solvent was evaporated under vacuum and the crude solid washed with 50 mL hexane followed by 25 mL ether. The remaining solid was dissolved in 25 mL CH$_2$Cl$_2$ and the solution passed through a 1 cm thick pad of alumina. The volume of the red-orange filtrate was reduced to ≈5–10 mL under vacuum and the remaining solution

carefully layered with an equal volume of pentane. Cooling to −20 °C precipitated 340 mg (40% yield) of (η^5-C_8H_9)Ru(PPh$_3$)$_2$Cl. The product was spectroscopically identical to the sample above.

(c) A solution of 435 mg (0.47 mmol) HRuCl(PPh$_3$)$_3$ in 10 mL (82 mmol) 1,5-cyclooctadiene was heated for 48 h at 110–120 °C. Chromatography on alumina (3 × 8 cm) with 250 mL hexane followed by 300 mL CH$_2$Cl$_2$ eluted a yellow band. Evaporation of the solvent under vacuum yielded 55 mg (15%) of (η^5-C_8H_9)Ru(PPh$_3$)$_2$Cl.

2.2. Crystal structure determination for (η^5-C_8H_9)Ru(PPh$_3$)$_2$Cl · 1/2 pentane

A red prismatic shaped crystal 0.23 × 0.23 × 0.18 mm in size was mounted on a glass fiber with traces of Paratone oil and then transferred to a Nonius KappaCCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). Ten frames of data were collected at 200(0.1) K with an oscillation range of 1°/frame and an exposure time of 20 s/frame [5], Indexing and cell refinement were based on all observed reflections ($\theta_{max} = 33.77°$) which had been indexed, integrated and corrected for Lorentz, polarization and absorption effects using DENZO-SMN and SCALEPAC [6]. Post refinement of the unit cell gave $a = 11.4380(2)$ Å, $b = 12.8395(3)$ Å, $c = 14.1171(3)$ Å, $\alpha = 69.3640(12)°$, $\beta = 87.4640(12)°$, $\gamma = 84.0325(10)°$, and $V = 1929.61(7)$ Å^3. The lack of symmetry in axial photographs and the lack of systematic absences were consistent with the compound having crystallized in the triclinic space group $P\bar{1}$ (No. 2). Crystallographic data are listed in Table 1.

The structure was solved by a combination of direct and heavy atom methods using SIR 97 [7]. All of the non-hydrogen atoms were refined with anisotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{methyl})$), and their coordinates were allowed to ride on their respective carbons. There is a disordered solvent molecule of pentane in the cell sitting on an inversion center. The weighting scheme employed was $w = 1/[\sigma^2(F_{o2}) + (0.0254P)^2 + 1.3619P]$ where $P = (F_{o2} + 2F_{c2})/3$. Scattering factors were taken from the International Tables for Crystallography [8–10].

2.3. Isomerization of 1,5-cyclooctadiene to 1,3-cyclooctadiene catalyzed by HRuCl(PPh$_3$)$_3$

A solution of 34 mg (0.037 mmols, 0.2 mol% Ru) HRuCl(PPh$_3$)$_3$ in 2 mL (16 mmols) 1,5-cyclooctadiene was heated for 20 h at 100 °C. Complete isomerization to 1,3-cyclooctadiene was verified by NMR spectroscopy.

^{13}C(CDCl$_3$): δ 130.78, 125.78, 27.87, 23.00.

Table 1
Crystal data and structure refinement for (η^5-C_8H_9)Ru(PPh$_3$)$_2$Cl

Empirical formula	$C_{46.50}H_{45}ClP_2Ru$
Formula weight	802.29
Temperature	200(0.1) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	$a = 11.4380(2)$ Å $\alpha = 69.3640(12)°$
	$b = 12.8395(3)$ Å $\beta = 87.4640(12)°$
	$c = 14.1171(3)$ Å $\gamma = 84.0325(10)°$
Volume	1929.61(7) Å^3
Z	2
Density (calculated)	1.381 M g/m^3
Absorption coefficient	0.591 mm^{-1}
$F(000)$	830
Crystal size	0.23 × 0.23 × 0.18 mm
θ range for data collection	3.21–33.77°.
Index ranges	$0 \leqslant h \leqslant 17$, $-19 \leqslant k \leqslant 20$, $-21 \leqslant l \leqslant 22$
Reflections collected	14,291
Completeness to $\theta = 33.77°$	92.6%
Absorption correction	Scalepack
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12,173/0/485
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0365$, $wR_2 = 0.0841$
R indices (all data)	$R_1 = 0.0478$, $wR_2(F^2) = 0.0902$
Largest diff. peak and hole	0.763 and −0.700 e Å^{-3}

2.4. Dimerization of phenylacetylene catalyzed by $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$

Following the procedure for the $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)H_3$-catalyzed dimerization of terminal alkynes [11], a 5 mm NMR tube equipped with a Teflon valve (J. Youngs, Inc.) was charged with the ruthenium(II) catalyst, 0.017 mmol $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ or 0.022 mmol $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$, in an argon atmosphere. About 0.5 mL C_6D_6 and 30 equivalents of phenyl acetylene were added. The tubes were sealed and heated to 80 °C in a thermostated sand bath for 24 h. The progress of the reaction was monitored by ^1H NMR spectroscopy. Products were identified by comparison of the observed chemical shifts with literature data [11]. The percent conversion and product ratios were determined from integration of the singlet at 2.74 ppm (PhCC**H**) and the resonances for the vinyl protons of *E*- and *Z*-1,4-diphenyl-1-buten-3-yne (δ 6.31 d, $J = 16.2$ Hz and 5.79 d, $J = 11.7$ Hz, respectively).

3. Results

Reaction of $HRuCl(PPh_3)_3$ with either 1,3- or 1,5-cyclooctadiene for 2–5 days leads to a change from the purple-red color of the starting material to the yellow-orange color of $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$. The product can be routinely isolated in 30–40% yield after crystallization. The reaction takes place in 2-butanone, benzene and neat cyclooctadiene although the highest yields are obtained from reactions in 2-butanone. An excess of cyclooctadiene is essential. We believe that *o*-metallation of intermediates in the reaction may be contributing to the consistently low yield of $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ [12]. Heating $HRuCl(PPh_3)_3$ in neat 1,5-cyclooctadiene is accompanied by complete, catalytic isomerization of the excess $1,5\text{-}C_8H_{12}$ to the conjugated $1,3\text{-}C_8H_{12}$ isomer. No attempts were made to detect the formation of 1,4-cyclooctadiene nor to optimize the conditions for isomerization of 1,5-cyclooctadiene. The complex $(\eta^5\text{-1,2-dihydropentalenyl})$ruthenium bis(triphenylphosphine)chloride was characterized by elemental analysis and by NMR spectroscopy.

The ^1H NMR spectrum of $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ in benzene or chloroform is unusual in that the chemical shift of the unique proton on the η^5 ring is shifted upfield to 2.48 ppm. The other chemically equivalent protons on the η^5-ring are observed at 4.07 ppm, well within the typical range for cyclopentadienyl ruthenium compounds [13]. The ^1H NMR spectrum also contains resonances assigned to 0.5 equivalent of pentane that co-crystallizes with $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$. Some pentane remains even after heating under vacuum.

Three resonances at 67.80, 71.73 and 77.45 ppm in the $^{13}C\{^1H\}$ spectrum are assigned to the carbon atoms of the unsaturated η^5 ring. Two resonances at 29.87 and 23.83 ppm are assigned to the carbon atoms on the saturated portion of the $\eta^5\text{-}C_8H_9$ ring. Resonances assigned to the aryl carbons of the two PPh_3 ligands are observed at 108.92, 134.30 and 139.47 ppm. In the ^1H coupled ^{13}C spectrum, the 71.73 and 77.45 ppm resonances become doublets with $J_{CH} = 175.6$ and 178.5 Hz, respectively. The resonance at 67.80 ppm remains a singlet consistent with its assignment to the bridgehead carbons in the $\eta^5\text{-}C_8H_9$ ring. A singlet is observed in the ^{31}P NMR spectrum at 41.4 ppm, typical of ruthenium(II) triphenylphosphine complexes [13].

The identity of the product was confirmed by single crystal X-ray diffraction. The solid state structure of $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ is shown in Fig. 1. There is a disordered solvent molecule of pentane in the cell sitting on an inversion center. The bond distances and bond angles (Table 2) are similar to those reported for $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ [14], $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl$ [15] and $(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl$ [16]. Comparisons with the latter compound are perhaps the most appropriate from the perspective of the fused hydrocarbon ligand. The average Ru–C bond distance in $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$, 2.221 Å, is about 2% shorter than in $(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl$, 2.272 Å. A key difference, however, is the absence of a ring slippage toward an η^3-coordination of the $\eta^5\text{-}C_8H_9$ ligand in $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$. The slip parameter for $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ is only 0.0421 compared to 0.2053 in $(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl$ [16]. The Ru–Cl and Ru–P distances are nearly identical for $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ and $(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl$, and the P–Ru–P angle in $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ is only about 2° smaller than in $(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl$. Both compounds adopt a conformation in which the Ru–Cl bond bisects the bridgehead C–C bond. Finally, the saturated ring in $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ has an envelope configuration in which C7 is bent down from the plane of the other four atoms with an envelope angle (angle between the C(1,5,6,8) and C(6,7,8) planes) of 26.45°.

The $(\eta^5\text{-}C_8H_9)RuCl(PPh_3)_2$ complex (3 mol%) catalyzes the dimerization of phenylacetylene to a mixture of *Z*- and *E*-1,4-diphenyl-1-buten-3-yne in benzene solution (Table 3). The reaction is slow, with only 44% conversion of phenylacetylene after 24 h at 80 °C. The major products in the dimerization reaction are *E*- and *Z*-1,3-diphenyl-1-buten-3-yne which are readily distinguished by comparison of their ^1H NMR spectra with literature data. The *Z*-isomer has a pair of doublets at 5.79 and 6.41 ppm ($J_{cis} = 11.7$ Hz) while the *E*-isomer has a much larger coupling constant ($J_{trans} = 16.2$ Hz) for its two doublets at 6.30 and 7.04 ppm [11]. The ratio of the *Z*:*E* isomers is found to be 2:1 from integration of the spectra recorded after 24 h of reaction. While these isomers account for 90% of the observed
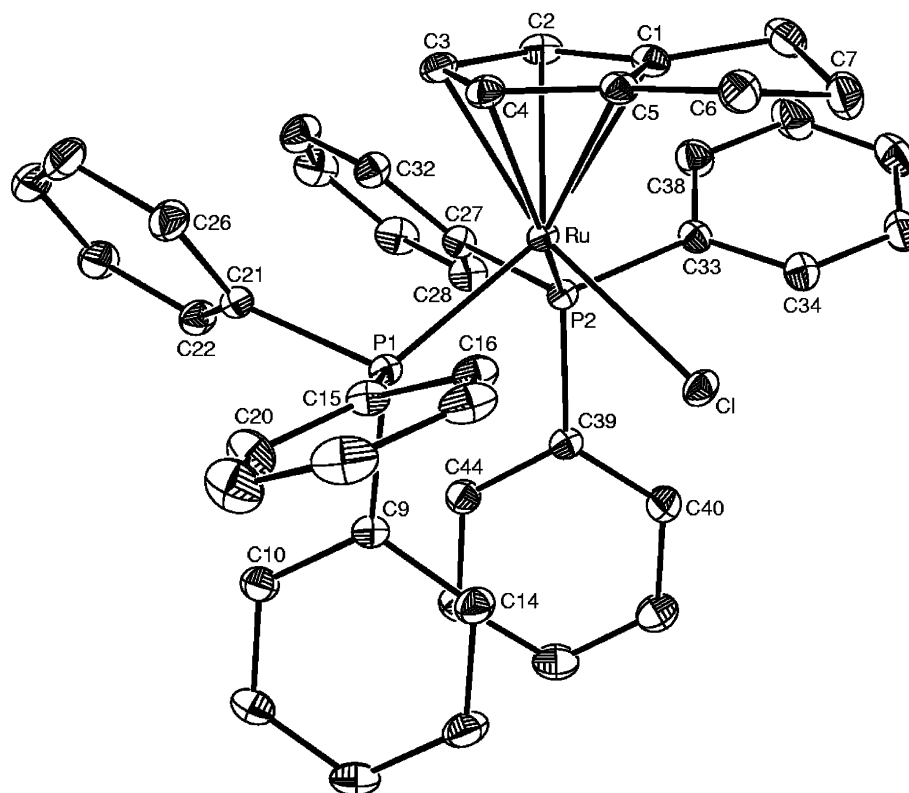
Fig. 1. Solid state structure of $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$.

Table 2
Selected bond distances (Å) and bond angles (°) for $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$

Bond distances (Å)			
Ru–C(3)	2.1719(16)	C(1)–C(2)	1.420(3)
Ru–C(2)	2.1903(17)	C(1)–C(5)	1.428(2)
Ru–C(4)	2.2339(16)	C(1)–C(8)	1.500(3)
Ru–C(1)	2.2505(17)	C(2)–C(3)	1.438(3)
Ru–C(5)	2.2579(16)	C(3)–C(4)	1.448(2)
Ru–P(2)	2.3044(4)	C(4)–C(5)	1.406(3)
Ru–P(1)	2.3220(5)	C(5)–C(6)	1.499(3)
Ru–Cl	2.4462(4)	C(6)–C(7)	1.545(3)
		C(7)–C(8)	1.545(3)
Bond angles (°)			
P(2)–Ru–Cl	90.074(15)	C(5)–C(4)–C(3)	106.99(16)
P(1)–Ru–Cl	90.792(15)	C(4)–C(5)–C(1)	109.76(15)
P(2)–Ru–P(1)	99.963(15)	C(4)–C(5)–C(6)	139.60(17)
C(2)–C(1)–C(5)	107.48(16)	C(1)–C(5)–C(6)	110.29(16)
C(2)–C(1)–C(8)	140.95(18)	C(5)–C(6)–C(7)	102.95(16)
C(5)–C(1)–C(8)	110.77(16)	C(6)–C(7)–C(8)	106.81(17)
C(1)–C(2)–C(3)	108.03(16)	C(1)–C(8)–C(7)	102.20(17)
C(2)–C(3)–C(4)	107.74(16)		

products, other resonances are observed in the region characteristic of vinyl protons. An additional pair of signals is observed at 5.68 (d, $J = 0.9$ Hz) and 5.75 (d, $J = 0.9$ Hz) with another pair of doublets at 5.28 ($J = 1.8$ Hz) and 5.38 ($J = 1.8$ Hz) ppm. These resonances account for 9% and 1% of the products, respectively. The identity of the two minor products has not been firmly established. The chemical shifts and coupling constants of the more prominent of the two minor constituents are similar to the spectroscopic data reported for the vinyl protons of the head-to-tail isomer, 2,4-diphenyl-1-buten-3-yne in CDCl₃ (5.79 d and 6.00 d, $J = 0.9$ Hz) [17]. The 2,4-diphenyl-1-buten-3-yne isomer, however, decomposes upon attempts at purification [16]. The compound responsible for the resonances at 5.28 and 5.38 ppm

Table 3
Product ratios from the catalytic dimerization of phenylacetylene

Catalyst[a]	% Conversion	Z	E
$\{\eta^5\text{-HB(pz)}_3\}\text{Ru(PPh}_3)_2\text{Cl}$	80	6	91
$(\eta^5\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{Cl}$	23	45	43
$(\eta^5\text{-C}_8\text{H}_9)\text{Ru(PPh}_3)_2\text{Cl}$	44	60	30
$(\eta^5\text{-C}_5\text{Me}_5)\text{Ru(PPh}_3)\text{H}_3$	85	67	33

[a] Catalysts (2–5 mol%) in 0.3–0.5 M PhCCH in benzene at 80° for 24 h.

remains unknown although both styrene and 1,4-diphenylbutatriene [18] can be excluded based on comparison with literature data or authentic samples.

Spectra recorded at shorter reaction times (and lower conversions) indicate that the $Z:E$ ratio is nearly time-independent. However, the relative amounts of the suspected head-to-tail dimer decrease as reaction time increases, consistent with the reported thermal instability of 2,4-diphenyl-1-buten-3-yne.

For comparison, $(\eta^5\text{-C}_5\text{H}_5)\text{Ru(PPh}_3)_2\text{Cl}$ was also investigated as a catalyst for the dimerization of phenylacetylene. After 24 h of reaction under identical conditions, only 23% of the phenylacetylene was consumed yielding the same mixture of products but with a different ratio of $Z:E$ isomers (1:1), 6% each of 2,4-diphenyl-1-buten-3-yne and the same unidentified compound responsible for the doublets at 5.28 and 5.38 ppm.

4. Discussion

By analogy to the reaction between $\text{HRu(PPh}_3)_3\text{Cl}$ and 1,4-pentadiene [2] (Eq. (2)) the formation of $(\eta^5\text{-C}_8\text{H}_9)\text{Ru(PPh}_3)_2\text{Cl}$ most likely follows a sequence of steps shown in Scheme 1. The reaction probably starts with the loss of one triphenylphosphine ligand followed by coordination and insertion of cyclooctadiene into the Ru–H bond forming an η^3-cyclooctenyl species. The facile, quantitative isomerization of 1,5-cyclooctadiene to the conjugated 1,3-isomer by only 0.2 mol% $\text{HRu(PPh}_3)_3\text{Cl}$ suggests that the insertion process is both fast and reversible. The olefin insertion product, $(\eta^3\text{-C}_8\text{H}_{13})\text{Ru(PPh}_3)_2\text{Cl}$, then loses hydrogen forming the η^5-cyclooctadienyl ligand in $(\eta^5\text{-C}_8\text{H}_{11})\text{Ru(PPh}_3)_2\text{Cl}$. While it is known that transition metal centers can quite easily bring about activation of C–H bonds in the saturated segments of cyclo-diene or cyclo-dienyl ligands [19], the fate of the hydrogen that is lost is still in question [20]. In the reaction between $\text{HRu(PPh}_3)_3\text{Cl}$ and 1,4-pentadiene (or cycloheptadiene), a transfer of hydrogen to a second equivalent of diene was observed, producing pentene (or cycloheptene) [2,19]. A similar process appears
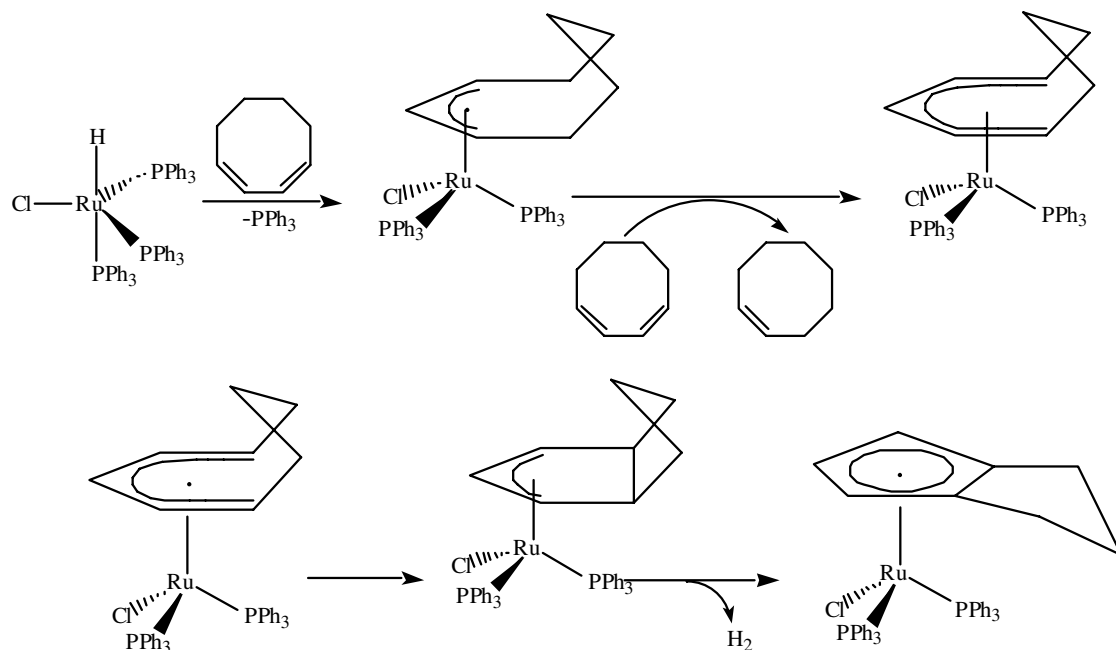

Scheme 1. Proposed mechanism for formation of $(\eta^5\text{-C}_8\text{H}_9)\text{Ru(PP}_3)_2\text{Cl}$ cyclooctadiene and $\text{HRuCl(PPh}_3)_3$.

likely here, as no product was isolated when a stoichiometric amount of cyclooctadiene underwent reaction with HRu(PPh$_3$)$_3$Cl.

In any case, (η^5-C$_8$H$_{11}$)Ru(PPh$_3$)$_2$Cl subsequently underwent a thermally allowed, disrotatory electrocyclization [1] to yield (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl, accompanied by loss of a second equivalent of H$_2$. Others [20] have suggested that this loss of hydrogen does not involve hydrogenation of excess diene but rather direct loss of H$_2$ gas. In this respect, the synthesis of (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl differs from the gas phase chemistry of (η^5-C$_5$Me$_5$)(η^5-C$_8$H$_{11}$)Ru for which the absence of excess diene requires that 2 equivalents of hydrogen are lost as H$_2$.

As noted above, the analogous (η^5-C$_5$H$_7$)Ru(PPh$_3$)$_2$Cl [21] compound cyclizes to (η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$Cl [2] while (η^5-C$_7$H$_9$)Ru(PPh$_3$)$_2$Cl [21] does not, possibly as formation of the [3.2.0] bicyclic product is thermodynamically uphill (Eq. (4)) [18]. It has been reported that at near-ambient temperatures (283 K) reaction between HRuCl(PPh$_3$)$_3$ and 1,5-cyclooctadiene does not result in olefin insertion but stops at a diene complex, (η^4-C$_8$H$_{12}$)Ru(H)(PPh$_3$)$_2$Cl [18]. The much longer reaction times needed to produce (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl (>48 h) than required for the conversion of HRuCl(PPh$_3$)$_3$ and 1,4-pentadiene to (η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$Cl ($\approx$16 h) [21] reveal a dramatically reduced reactivity for cyclooctadienes.

(4)
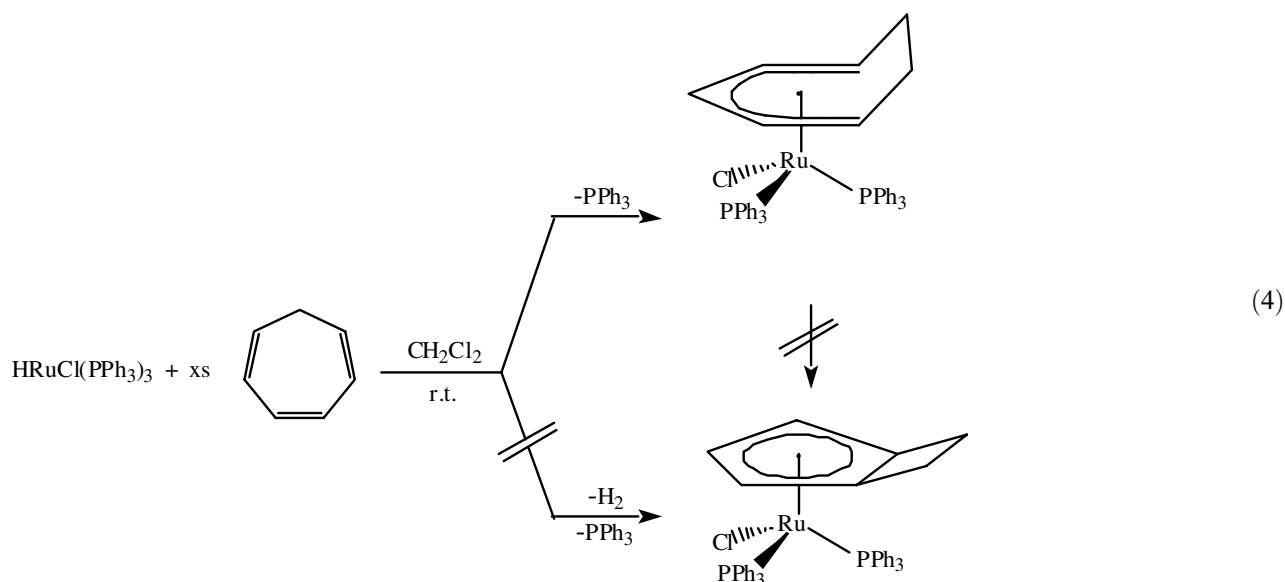
Curiously, spectroscopic evidence from the reaction between HRuCl(PPh$_3$)$_3$ and 1,3,5,7-cyclooctatetraene suggests the formation of (η^5-bicyclo-[5.0.1]octadienyl)Ru(PPh$_3$)$_2$Cl [22] rather than (η^5-C$_8$H$_7$)Ru(PPh$_3$)$_2$Cl, which would contain the η^5-pentalenyl ligand (Eq. (5)) [23]. It may be that the strain induced by ring fusion at sp^2 rather than sp^3 carbon centers (i.e., bottom product of Eq. (5) vs. the top product of (5)) becomes prohibitively unfavorable.

(5)
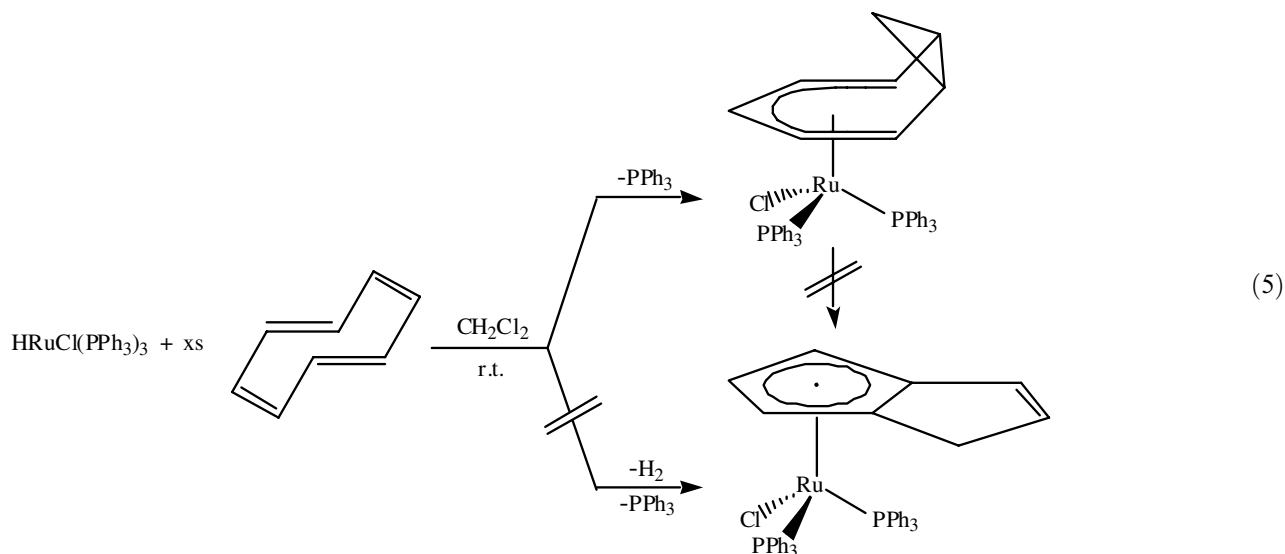
The dimerization of terminal alkynes is catalyzed by a variety of ruthenium(II) compounds including (η^5-C_5Me_5)Ru(PPh$_3$)H$_3$ (a mixed hydrogen/hydride complex) [11], and {HB(pz)$_3$}Ru(PPh$_3$)$_2$Cl [24,25]. The initial steps of the reaction mechanism vary depending on the complex; however, in each case, the key C–C bond forming step involves migration of an acetylide to the α-carbon of the ruthenium-coordinated vinylidene ligand (Scheme 2). On comparison of the structure of the proposed (acetylide)(vinylidene) intermediates derived from (η^5-C_8H_7) Ru(PPh$_3$)$_2$Cl, (η^5-C_5H_5)Ru(PPh$_3$)$_2$Cl, (η^5-C_5Me_5)Ru(PPh$_3$)H$_3$, and {HB(pz)$_3$}Ru(PPh$_3$)$_2$Cl, one finds that the sole distinguishing feature between them is the identity of the η^5 ligand. In each case the coordination sphere of ruthenium contains triphenylphosphine, a phenylacetylide and a phenyl-substituted vinylidene ligand. The "common" intermediate suggests that the product distribution (Z:E ratio) from dimerization of phenylacetylene in the presence of these four Ru(II) compounds may provide clues to the electronic and steric effects of the η^5 ligand on the selectivity of the alkyne dimerization.

The η^5-indenyl complexes (η^5-C_9H_7)Ru(PPh$_3$)$_2$H and (η^5-C_9H_7)Ru(PPh$_3$)$_2$(CCPh) are also active in the catalytic dimerization of phenylacetylene [26]. Unlike the other four compounds cited above, however, ring slip of the indenyl group from η^5 to η^3 coordination plays an important role in the reaction mechanism. This difference in mechanism precludes further meaningful comparisons between (η^5-indenyl)ruthenium(II) complexes and (η^5-C_8H_9)Ru(PPh$_3$)$_2$Cl, (η^5-C_5H_5)Ru(PPh$_3$)$_2$Cl, (η^5-C_5Me_5)Ru(PPh$_3$)H$_3$, or {HB(pz)$_3$}Ru(PPh$_3$)$_2$Cl.

The results of our studies and literature data for the dimerization of phenylacetylene are listed in Table 3. While there are differences in solvent and reaction temperature it is clear that Z- and E-1,4-diphenyl-1-buten-3-yne are the major products in each case. The ratio of the Z to E isomer, however, ranges from $\approx$1:15 (for HB(pz)$_3$) to $\approx$2:1 in favor of the Z isomer (for η^5-C_5Me_5 and η^5-C_8H_9). The Z:E ratio from reactions catalyzed by (η^5-C_5H_5)Ru(PPh$_3$)$_2$Cl lies in between, providing a nearly equal distribution between the Z and E isomers. A systematic study of the three ligands, C_5Me_5, C_5H_5, and HB(pz)$_3$, found that the C_5Me_5 ligand is the most electron-rich of the three η^5 ligands while the
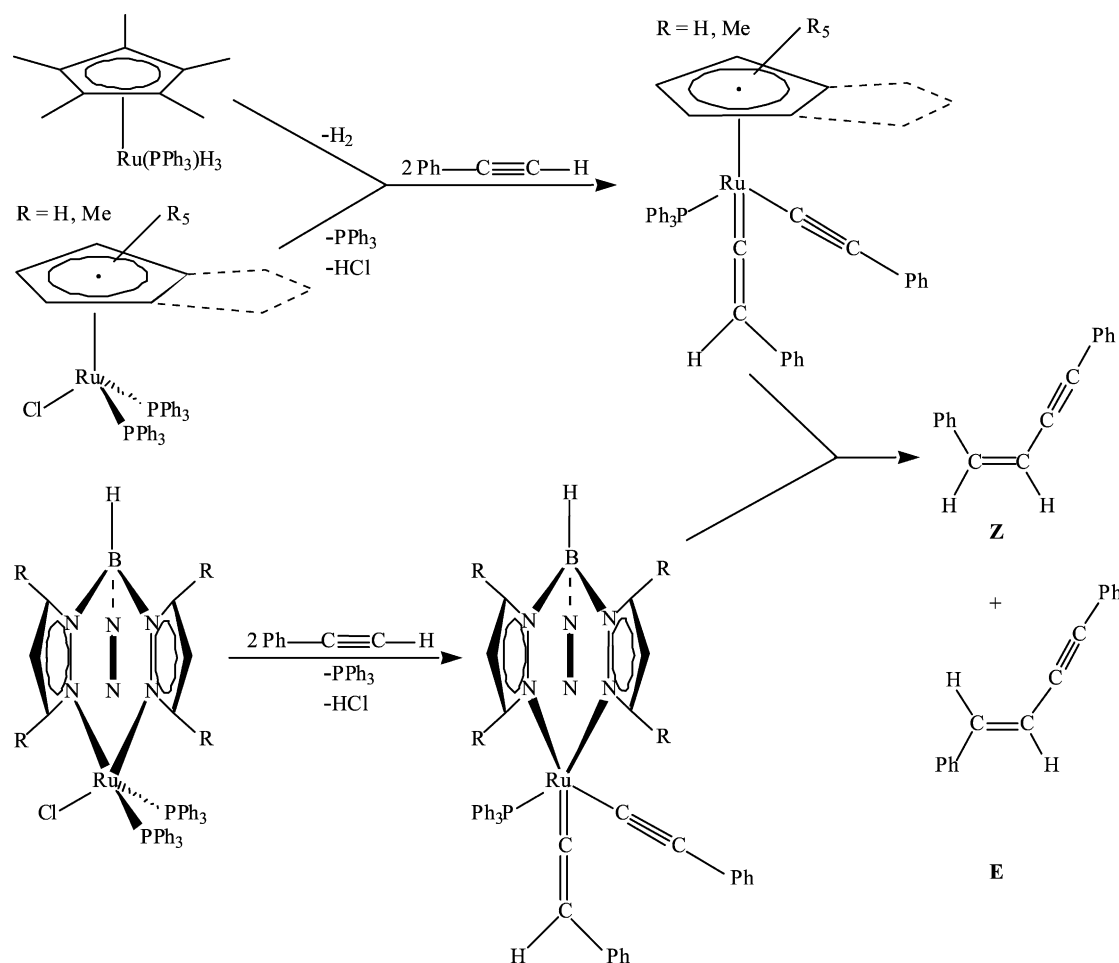
Scheme 2. Access to a common intermediate in the dimerization of phenylacetylene from (η^5-C_8H_9)Ru(PPh$_3$)$_2$Cl, (η^5-C_5H_5)Ru(PPh$_3$)$_2$Cl, (η^5-C_5Me_5)Ru(PPh$_3$)H$_3$, And (η^5-HB{pz}$_3$)Ru(PPh$_3$)$_2$Cl.
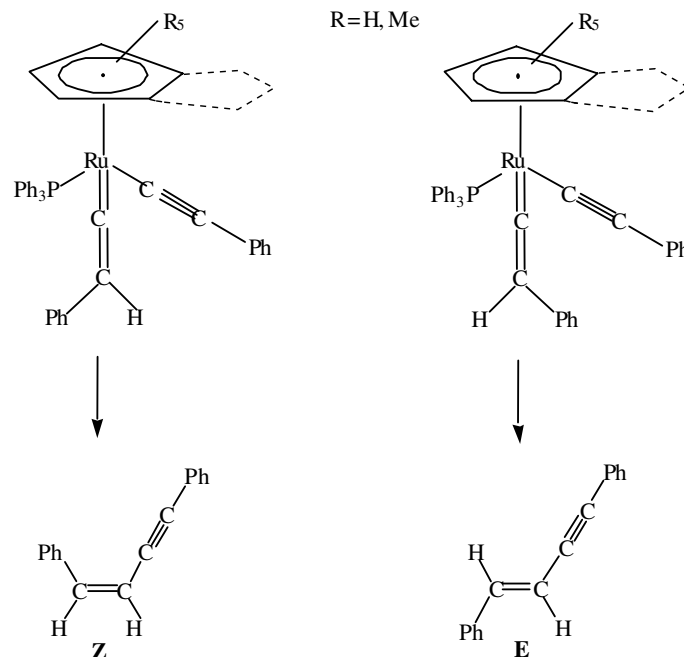
Scheme 3. Proposed geometric isomers contributing to Z- and E-1, 4-diphenyl-1-buten-3-yne in η^5-LRu(PPh$_3$)(C≡CPh){=C=C(H)Ph} (L = C$_5$H$_5$, C$_5$Me$_5$, C$_8$H$_9$, HB{pz}$_3$).

tris(pyrazolyl)borate ligand is actually the least electron rich member of the series [27]. Hence, one sees a possible correlation between the isomer ratio and the electronic properties of the ligands.

While the $Z:E$ ratio remains fairly constant in reactions of phenylacetylene catalyzed by (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl, when (η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$Cl is used as a catalyst, the relative amount of Z-1,4-diphenyl-1,3-butenyne increases with time. A similar observation was reported for the dimerization of phenylacetylene catalyzed by (η^5-C$_9$H$_7$)Ru(PPh$_3$)$_2$Cl and attributed to faster oligomerization of the E-1,4-diphenyl-1,3-butenyne product compared to the Z isomer [25]. A $Z:E$ ratio that favors the E isomer at short reaction times using (η^5-C$_5$H$_5$)Ru(PPh$_3$)$_2$Cl is consistent with the proposed electronic effect of the η^5-ligands. Data at shorter reaction times for (η^5-C$_5$Me$_5$)Ru(PPh$_3$)H$_3$, or {η^5-HB(pz)$_3$}Ru(PPh$_3$)$_2$Cl are unfortunately not available for further comparison of the $Z:E$ ratio as a function of reaction time.

The steric effect of these η^5-coordinated ligands, however, falls in the order HB(pz)$_3$ ≈ C$_5$Me$_5$ > C$_5$H$_5$ [28]. With its fused saturated five-membered ring, the η^5-C$_8$H$_9$ ligand in (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl is expected to be more electron rich than the C$_5$H$_5$ ligand but less than the C$_5$Me$_5$ group. The fused bicyclic ligand in (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl may also exert a significant steric effect along one edge of the η^5-group; however, rotation about the Ru–C$_8$H$_9$ axis makes it unlikely that the dihydropentalenyl ligand would have a greater steric effect than either the C$_5$Me$_5$ or HB(pz)$_3$ ligand.

For a series of (η^5-C$_5$Me$_5$)RuLH$_3$ compounds [11] it has been shown that as the size of L increases (e.g., PCy$_3$ vs PPh$_3$), the Z isomer is increasingly favored over the E isomer despite the greater electron-donating ability of PCy$_3$ vs. PPh$_3$. The selectivity is proposed to arise from the two orientations for the phenyl-substituted vinylidene group shown in Scheme 3. Were the steric effects of the η^5-ligand to play a similar role, one would expect the Z isomer to also be favored in reactions catalyzed by {HB(pz)$_3$}Ru(PPh$_3$)$_2$Cl. The observed trend toward increasing Z isomer in Table 3 follows the order C$_5$Me$_5$ ≈ C$_8$H$_9$ > C$_5$H$_5$ > HB(pz)$_3$, an order which clearly does not reflect the presumed steric effect of the four η^5-ligands. Thus the data in Table 3 suggest that the dimerization of phenylacetylene to the Z isomer is favored as the electron density on the η^5 ring increases.

5. Conclusions

Reaction of HRuCl(PPh$_3$)$_3$ with cyclooctadiene allows the synthesis of a ruthenium(II) complex, (η^5-C$_8$H$_9$)Ru(PPh$_3$)$_2$Cl, containing a fused [3.3.0] ring at moderate temperature through a series of steps including a disrotatory electrocyclic reaction. Thus we have achieved our goal of moderating the conditions needed to effect electrocyclic reactions at a ruthenium center. Relatively few examples of electrocyclic reactions of transition metal

coordinated ligands have been reported [1,28]. While studies to determine the scope of the reaction are in progress, we find that $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ catalyzes the dimerization of phenylacetylene to a mixture of Z- and E-1,4-diphenyl-1-buten-3-yne. Comparison of the Z:E ratio of products using $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$, $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$, $(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl$ and $\{HB(pz)_3\}Ru(PPh_3)_2Cl$ demonstrates the presence of an electronic effect of the η^5-ligand on the selectivity of the reaction.

5.1. Supplementary material

Crystallographic data for the structural analysis of $(\eta^5\text{-}C_8H_9)Ru(PPh_3)_2Cl$ has been deposited with Cambridge Crystallographic Data Centre, CCDC, No. 211774. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ [fax: +44(1223)336-033] or http://www.ccdc.cam.ac.uk.

Acknowledgements

References

[1] R.U. Kirss, A. Quazi, C.H. Lake, M.R. Churchill, Organometallics 12 (1993) 4145.
[2] B.E. Mann, P. Manning, C.M. Spencer, J. Organometal. Chem. 312 (1986) C64.
[3] D.F. Shriver, Manipulation of air Sensitive Compounds, McGraw Hill, New York, 1969.
[4] R.A. Schunn, E.R. Wonchoba, Inorg. Synth. 13 (1972) 131.
[5] COLLECT Data Collection Software Nonius B.V. 1998.
[6] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.
[7] SIR 97(Rlease 1.02) A. Altomare, M.C. Burla, M. Camalli, G. Carcarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliteni, G. Polidori, R. Spagna.
[8] $R(F) = R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR(F^2) = wR_2 = [\sum(wF_{o2} - F_{c2})^2/\sum(F^2)^2]^{1/2}$, and $S =$ goodness-of-fit on $F^2 = [\sum(wF_{o2} - F_{c2})^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.
[9] E.N. Maslen, A.G. Fox, M.A. O'Keefe, in: A.J.C. Wilson, (Ed.), International Tables for Crystallography: Mathematical, Physical and Chemical tables, vol. C, Dordrecht, The Netherlands, 1992, p. 476 (Chapter 6).
[10] D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson, (Ed.), International Tables for Crystallography: Mathematical, Physical and Chemical tables, vol. C, Dordrecht, The Netherlands 1992, p. 206 (Chapter 4).
[11] C.S. Yi, N. Liu, Organometallics 15 (1996) 3968.
[12] B.R. James, L.D. Markham, D.K.W. Wong, J. Chem. Soc. Chem Commun. (1974) 439.
[13] (a) M.I. Bruce, N.J. Windsor, Aust. J. Chem. 30 (1977) 1601;
(b) R.J. Haines, A.L. Du Preez, J. Organometal. Chem. 84 (1975) 357.
[14] M.I. Bruce, F.S. Wong, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1981) 1398.
[15] I.A. Guzei, M.A. Paz-Sandoval, R. Torres-Lubian, P. Juarez-Saavedra, Acta Crystallogr. Sect. C C55 (1999) 1090.
[16] M. Kamigaito, Y. Watanabe, T. Ando, M. Sawamoto, J. Am. Chem. Soc. 124 (2002) 9994.
[17] J. Ohshita, K. Furumori, A. Matsuguchi, M. Ishikawa, J. Org. Chem 55 (1990) 3277.
[18] M.A. Esteruelas, J. Herrero, A.M. Lopez, M. Olivan, Organometallics 20 (2001) 3203.
[19] R. Basta, R.D. Ernst, A.M. Arif, Organometallics 22 (2003) 812.
[20] (a) M. Grassi, B.E. Mann, P. Manning, C.M.J. Spencer, Organometal. Chem. 307 (1986) C55;
(b) G. Alibrandi, B.E. Mann, J. Chem. Soc. Dalton Trans. (1994) 951.
[21] $\eta^5\text{-}C_5H_7$ and $\eta^5\text{-}C_7H_9$ refer to the pentadienyl and cycloheptadienyl ligands, respectively.
[22] G. Alibrandi, B.E. Mann, J. Chem. Soc. Dalton Trans. (1992) 1439.
[23] S. Barlow, D. O'Hare, Chem. Rev. 97 (1997) 637.
[24] $\eta^5\text{-}HB(pz)_3$ refers to the tris(pyrazolyl)borate ligand.
[25] C. Slugovc, K. Mereiter, E. Zobetz, R. Schmid, K. Kirchner, Organometallics 15 (1996) 5275.
[26] M. Bassetti, S. Marini, F. Tortorella, V. Cadierno, J. Diez, M.P. Gamasa, J. Gimeno, J. Organometal. Chem. 593–594 (2000) 292.
[27] D.M. Tellers, S.J. Skoog, R.G. Bergman, T.B. Gunnoe, W.D. Harman, Organometallics 19 (2000) 2428.
[28] (a) N. Kitajima, B.W. Tolman, Prog. Inorg. Chem. 43 (1995) 419;
(b) R.U. Kirss, Organometallics 11 (1992) 497;
(c) H. Lehmkuhl, W. Leuchte, E. Janssen, J. Organomet. Chem. 30 (1971) 407;
(d) K.K. Joshi, R.H.B. Mais, F. Nyman, P.G. Owston, A.M. Wood, J. Chem. Soc. A (1968) 318;
(e) J. Mueller, W. Holzinger, F.H. Kohler, Chem. Ber. 109 (1976) 1222;
(f) R. Basta, R.D. Ernst, Reaction of $FeCl_2$ with the cyclononadienyl anion yields bis(indenyl)diiron, unpublished results.