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Synthesis of ruthenium vinylidene complexes with dppe ligand and their cyclopropenation reaction

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Abstract

A number of cationic ruthenium vinylidene complexes $[Ru]=C=C(Ph)CH_2R^+$ ($[Ru]=(\eta^5\text{-}C_5H_5)(dppe)Ru$, dppe = $Ph_2PCH_2CH_2PPh_2$, **5a**, R = CN; **5b**, R = C_6F_5; **5c**, R = Ph; **5d**, R = *p*-C_6H_4CN; **5e**, R = *p*-$C_6H_4CF_3$; **5f**, R = 1-$C_{10}H_7$; **5g**, R = CO_2CH_3) are prepared from electrophilic addition of organic halides to the acetylide complex [Ru]–C≡CPh at the boiling point of $CHCl_3$. Complex **5g′**, prepared at room temperature, displays similar spectroscopic property as that of **5g** but is easily hydrolyzed to give [Ru]$COCH_2$Ph (**6**). Cyclopropenation of the organic vinylidene moiety of **5a**–**5f** is accomplished in acetone by deprotonation of **5** with *n*-Bu_4NOH yielding the neutral cyclopropenyl complexes $[Ru]\text{–}\overline{C=C(Ph)}\overline{CH}R$ (**7a**, R = CN; **7b**, R = C_6F_5; **7c**, R = Ph; **7d**, R = *p*-C_6H_4CN; **7e**, R = *p*-$C_6H_4CF_3$; **7f**, R = 1-$_{10}H_7$). Protonation of **7b**–**7f** regenerates the corresponding vinylidene complexes. In the presence of allyl iodide, opening of the three-membered ring of **7a**, followed by a subsequent oxidative coupling reaction, gives a dimeric dicationic product $\{[Ru]=C=C(Ph)\text{–}CHCN\}_2^{+2}$ (**9a**). In the processes of preparing the starting material Cp(dppe)RuCl for the acethylide complex, two dppe complexes $Ru(dppe)_2Cl_2$ (**2**) and $[Cp(dppe)RuCl]_2$ (**3**) are isolated. Molecular structures of complexes **2**, **3**, **6**, and **7b** have been confirmed by X-ray diffraction analysis. © 1998 Elsevier Science S.A.

Keywords: Organic halides; Allyl iodide; Oxidative coupling reaction

1. Introduction

During the course of investigations into ruthenium vinylidene chemistry, we previously reported the formation of several interesting neutral cycloropenyl complexes [1]. For example, $Cp(PPh_3)_2Ru=C=C(Ph)CH_2CN^+$ in acetone was found to undergo deprotonation to afford the yellow crystalline cyclopropenyl complex $Cp(PPh_3)_2Ru\text{–}\overline{C=C(Ph)}\overline{CH}CN$. The cationic charge along with the electron-withdrawing CN group appending to the vinylidene ligand make the protons at the γ-carbon acidic enough for facile deprotonation. This reaction generates a racemic mixture of the products with an asymmetric carbon at the three-membered ring. To elaborate the breadth of such a system, we set to study the ruthenium complex with the bidentate dppe ligand. Herein, we report results on this system. In addition, the process of preparing the starting material, two by-products were isolated and the structure determination is also described.

2. Results and discussion

2.1. Preparation of metal dppe complex

Treatment of $Cp(PPh_3)_2RuCl$ with dppe in benzene affords the light yellow product Cp(dppe)RuCl (**1**) in ca. 70% yield [2,3]. Complex **1** is soluble in benzene. In addition to **1**, some by-products are isolated as orange–yellow precipitates from which two ruthenium chloride complexes $Ru(dppe)_2Cl_2$ (**2**) [4] and $[Cp(\mu\text{-dppe})RuCl]_2$ (**3**) were separated by recrystallization from CH_2Cl_2/hexane as yellow and red crystals, respectively Table 1. The yield of **2** is about 20% and the yield of **3** is approximately 5%. In the ^{31}P NMR spectrum of **2** in $CDCl_3$ at room temperature, the singlet resonance at δ 45.75 is assigned to the dppe ligand indicating high symmetry of the complex. Similarly in

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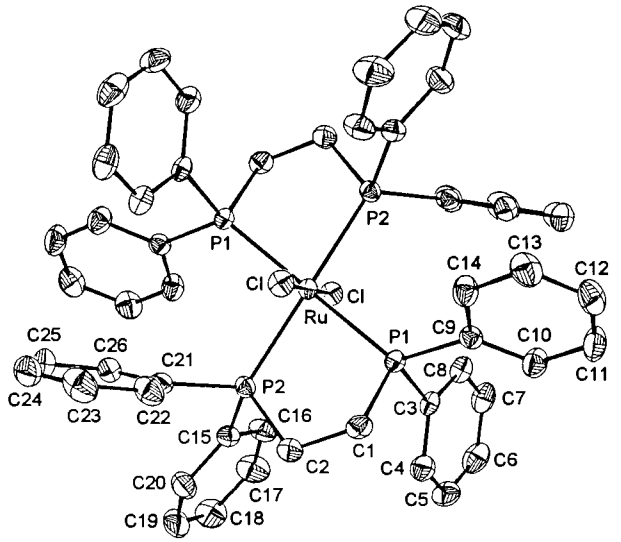

Fig. 1. An ORTEP drawing of $(dppe)_2RuCl_2$ (**2**) with thermal ellipsoids shown at the 50% probability level.

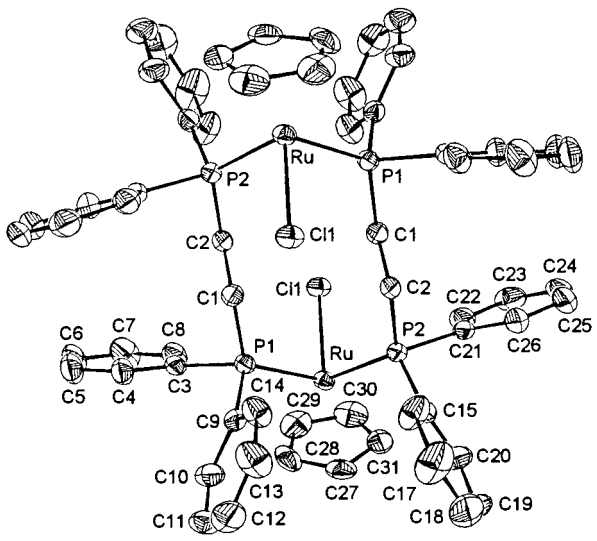

Fig. 2. An ORTEP drawing of $Cp_2(dppe)_2Ru_2Cl_2$ (**3**) with thermal ellipsoids shown at the 50% probability level.

the ^{31}P NMR spectrum of **3**, the singlet resonance at δ 37.05 is observed. Formation of complex **2** has been reported from the reaction of $RuCl_3 \cdot xH_2O$ with dppe however the structure has not been determined. Therefore, we carried out structure determination of **2** and **3** by single-crystal X-ray diffraction analysis and ORTEP drawings of **2** and **3** are shown in Fig. 1 and Fig. 2, respectively. Both complexes contain center of symmetry. In **2**, which contains no Cp ligand, the two bidentate dppe ligands and the two chloro ligands form a pseudo octahedral geometry around the ruthenium metal center and the Ru–P distances (2.356(1), 2.381(1) Å) are slightly longer than the corresponding ones (2.311(2), 2.326(2) Å) in dinuclear complex **3** containing a Cp ligand in each metal center. And the Ru–Cl distance (2.433(1) Å) of **2** Table 2 is slightly shorter than the corresponding one (2.506(2) Å) in **3** Table 3. The two dppe ligands in **3** bridge two metal centers with the P(1)–C(1)–C(2) and P(2)–C(2)–C(1) angles (115.9(5) and 110.2(5)°) approximately the same as that (112.3(3) and 114.2(3)°) of the bidentate one in **2**. The acetylide complex [Ru]-C≡CPh (**4**) is prepared by the reaction of **1** with PhC≡CH in high yield and display identical spectroscopic properties as that in the literature [5].

Table 1
Crystal and intensity collection data for $(dppe)_2RuCl_2$ **2**, $Cp_2(dppe)_2Ru_2Cl_2$, **3**, $Cp(dppe)Ru(COCH_2C_6H_5)$, **6** and $Cp(dppe)Ru|\overline{C{=}C(C_6H_5)}CH(C_6F_5)|$, **7b**

Molecular formula	$C_{60}H_{64}O_2P_4Cl_2Ru$, **2**	$C_{32}H_{30}P_2Cl_4Ru$, **3**	$C_{45}H_{48}O_3P_3F_6Ru$, **6**	$C_{46}H_{35}P_2F_5Ru$, **7b**
Molecular weight	1113.02	719.41	944.84	845.78
Space group	$P\ 2_1/c$	$P\ 2_1/n$	$P\ 2_1/c$	$P\bar{1}$
a (Å)	11.371(3)	13.190(2)	11.777(3)	12.094(7)
b (Å)	13.458(2)	17.166(5)	24.824(4)	12.517(3)
c (Å)	17.232(3)	14.507(5)	15.433(5)	13.050(3)
α (°)	–	–	–	94.19(2)
β (°)	96.02(2)	102.08(2)	105.87(3)	91.33(3)
γ (°)	–	–		94.72(3)
V (Å^3)	2622.5(9)	3211.9(15)	4339.9(19)	1962.8(13)
Z	2	4	4	2
Crystal dimension (mm^3)	0.20 × 0.30 × 0.50	0.32 × 0.40 × 0.50	0.10 × 0.50 × 0.50	0.10 × 0.15 × 0.30
Radiation	Mo Kα λ = 0.7093 Å			
2θ range	2°–50°	2°–50°	2°–50°	2°–45°
Scan type	$\theta/2\theta$			
Total number of reflections	4597	5650	7586	5109
unique reflections $I > 2\sigma(I)$	2839	4145	5196	2498
R	0.039	0.054	0.049	0.053
R_w	0.038	0.064	0.056	0.050

Table 2
Selected interatomic distances (Å) and bond angles (°) of $(dppe)_2RuCl_2$, **2**

Ru–Cl	2.4325(12)	P(1)–C(9)	1.836(5)
Ru–C(1)	2.3563(13)	P(2)–C(2)	1.850(5)
Ru–P(2)	2.3811(13)	P(2)–C(15)	1.845(5)
P(1)–C(1)	1.843(5)	P(2)–C(21)	1.841(5)
P(1)–C(3)	1.823(5)	C(1)–C(2)	1.529(7)
Cl–Ru–P(1)	85.81(4)	P(1)–Ru–P(2)	81.62(5)
Cl–Ru–P(1)a	94.19(4)	P(1)–Ru–P(2)a	98.38(5)
Cl–Ru–P(2)	81.40(4)	P(1)–C(1)–C(2)	112.3(3)
Cl–Ru–P(2)a	98.60(4)	P(2)–C(2)–C(1)	114.2(3)

2.2. Preparation of vinylidene complexes

Treatment of **4** with ICH_2CN at refluxing temperature of $CHCl_3$ affords the cationic vinylidene complex $[Ru]=C=C(Ph)CH_2CN^+I^-$ (**5a**) in 83% yield. In the presence of excess NH_4PF_6, the counter anion is replaced by PF_6^-. Unlike other vinylidene complexes which are normally prepared by treatment of an acetylide complex with primary organic halide at room temperature for **1** d, complex **5a** is prepared by heating the chloroform solution of **4** and primary alkyl halide to reflux for ca. 10 h. The reaction at room temperature also gives the product with the same spectroscopic data but such a product is relatively less stable. Similarly, preparation of other vinylidene complexes $[Ru]=C=C(Ph)CH_2R^+$ (**5b**, R = C_6F_5; **5c**, R = Ph; **5d**, R = *p*-C_6H_4CN; **5e**, R = *p*-$C_6H_4CF_3$; **5f**, R = 1-$C_{10}H_7$; **5g**, R = $COOCH_3$) have been accomplished by reacting **4** with the corresponding halides at refluxing temperature of $CHCl_3$ all with high yields. Interestingly, **5a** is soluble in acetone and insoluble in CH_3CN, $CHCl_3$ and CH_2Cl_2. Complexes **5b**–**5g** are all soluble in polar solvent such as $CHCl_3$, CH_2Cl_2, MeOH and CH_3CN but insoluble in acetone, ether and hexane. All **5a**–**5g** prepared at higher temperature are quite stable even in solution. They display pink to orange color in their solid state. The characteristic spectroscopic data of these vinylidene complexes consist of strongly deshielded C_α resonance as a triplet at δ 340 ± 5 in the ^{13}C NMR spectrum and a singlet ^{31}P NMR resonance normally at around δ 77 ± 1 in $CDCl_3$ at room temperature, which is due to the fluxional behavior of the vinylidene ligand [6,7].

The newly formed carbon–carbon bond of the vinylidene complexes, prepared by carrying out the reaction at room temperature, is easily cleaved in the presence of acid. In addition, the hexafluorophosphate salt NH_4PF_6 used for the preparation is easily converted to HPF_6. Thus complex **5g′** with PF_6^- counter anion prepared at room temperature is unstable when dissolved in CH_2Cl_2/hexane solution. It decomposes to give the acyl complex $[Ru]C(O)CH_2Ph$ (**6**). With Br^- anion, **5g′** is stable for a period of 2 d and then decomposes to some unidentified products. Complexes **5a′** and **5b′** both with PF_6^- anion are prepared at room temperature, they also decompose to give **6** but with the halide as the counter anion they are relatively more stable. It seems that the presence of HPF_6 is required for the formation of **6**.

Table 3
Selected interatomic distances (Å) and bond angles (°) of $Cp_2(dppe)_2Ru_2Cl_2$, **3**

Ru–P(1)	2.3105(20)	Ru–Cl(1)	2.5060(20)
Ru–P(2)	2.3263(20)	C(1)–C(2)a	1.513(10)
P(1)–Ru–P(2)	96.99(7)	P(1)–C(1)–C(2)a	115.9(5)
P(1)–Ru–Cl(1)	93.93(7)	P(2)–C(2)–C(1)a	110.2(5)
P(2)–Ru–Cl(1)	93.95(6)		

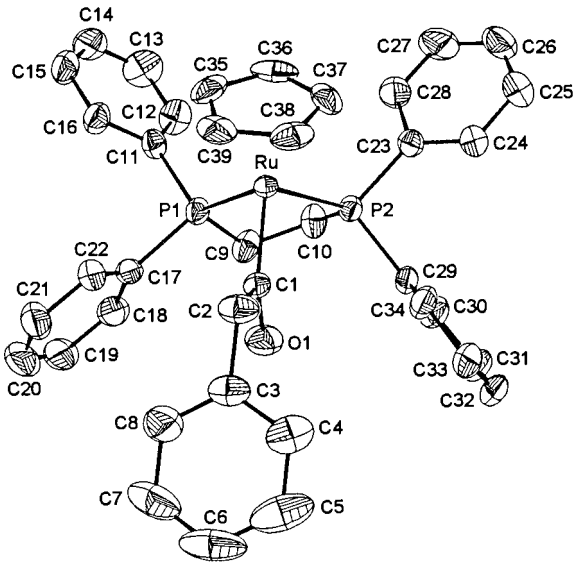

Fig. 3. An ORTEP drawing of $Cp(dppe)Ru(COCH_2C_6H_5)$ (**6**) with thermal ellipsoids shown at the 50% probability level.

In the ^{31}P NMR spectrum of **6**, a singlet resonance at δ 91.10 is observed. The structure of **6** is determined by a single crystal X-ray diffraction analysis. An ORTEP drawing is shown in Fig. 3. The acyl ligand is clearly seen with the acyl plane (Ru, C1, C2, O1) bisecting the P1–Ru–P2 angle Table 4. Such a transformation has been observed in other vinylidene complexes [8]. Pre-

Table 4
Selected interatomic distances (Å) and bond angles (°) of $Cp(dppe)Ru(COCH_2C_6H_5)$, **6**

Ru–P(1)	2.2655(17)	O(1)–C(1)	1.328(7)
Ru–P(2)	2.2713(17)	C(2)–C(3)	1.509(10)
Ru–C(1)	1.992(6)	C(9)–C(10)	1.496(10)
C(1)–C(2)	1.530(10)		
P(1)–Ru–P(2)	84.99(6)	O(1)–C(1)–C(2)	110.6(5)
P(1)–Ru–C(1)	88.45(17)	C(1)–C(2)–C(3)	117.3(5)
P(2)–Ru–C(1)	93.83(17)	P(1)–C(9)–C(10)	111.7(5)
Ru–C(1)–O(1)	127.9(5)	P(2)–C(10)–C(9)	111.8(5)
Ru–C(1)–C(2)	121.5(4)		

sumably, protonation at C_β of the acetylide complex followed by hydroxy-attack at the C_α led to the product. If complex **5** is prepared by thermolysis in $CHCl_3$ solution, no such transformation is observed. For example, treatment of **5g**, prepared at refluxing temperature of $CHCl_3$, with CH_3COOH, H_2O or NH_4PF_6 for 3 days results in recovery of the starting material. The vinylidene complexes **5** and **5′** prepared at room temperature and at 55°C display similar spectroscopic features but their reactivities are quite different.

2.3. Deprotonation / cyclopropenation of vinylidene complexes

Deprotonation of **5a** by *n*-Bu_4NOH in acetone induces a cyclization reaction and yields the neutral cyclopropenyl complex [Ru]–C=C(Ph)CHCN (**7a**) (see Scheme). No cyclopropenation reaction is observed in CH_3CN. The light orange–yellow crystalline product forms directly in the reaction mixture and can be obtained in analytically pure form by filtration. Complex **7a** is stable and is soluble in CH_2Cl_2, $CHCl_3$, and THF but insoluble in ether, *n*-hexane, MeOH and CH_3CN. In the ^1H NMR spectrum of **7a**, the resonance of the methyne proton of the three-membered ring appears at δ 2.13. The ^{31}P NMR spectrum of **7a** displays two doublet resonances at δ 90.14 and 88.47 with $^2J_{P-P}$ = 24.3 Hz assignable to the two non-equivalent phosphorus atoms of the dppe ligand arising from the asymmetric cyclopropenyl ring.

The deprotonation/cyclopropenation process in acetone is a general reaction for a number of vinylidene complexes. Namely, the same reaction occurs for similar complexes **5b**–**5f** giving cyclopropenyl complexes [Ru]–C=C(Ph)CHR, (**7b**, R = C_6F_5; **7c**, R = Ph; **7d**, R = *p*-C_6H_4CN; **7e**, R = *p*-$C_6H_4CF_3$; **7f**, R = 1-$C_{10}H_7$), respectively. Spectroscopic data of complexes **7** are similar. The single crystals of **7b** suitable for X-ray diffraction analysis are obtained when the reaction is carried out at lower concentration. Complexes **7c**–**7f** are not stable in solution. Presence of the pentafluorophenyl group in **7b** exceptionally stabilizes the complex. Thus, complex **7b** is stable in $CHCl_3$, but other cyclopropenyl complexes decompose in $CHCl_3$ within 10 h. Facile deprotonation of **5** by *n*-Bu_4NOH indicates acidic nature of the methylene protons of **5a**–**5f**, which may be associated with the combined influence of the cationic character, the electron withdrawing substituent and the benzylic property of the vinylidene complexes. It also appears that the hybridization of the C_δ atom should be sp^2 for the cyclopropenation reaction to occur. Complex **5g** failed to yield the deprotonation product in the presence of Bu_4NOH. We previously observed formation of cyclopropenyl and furanyl products for the bistriphenylphosphine analogue of **5g**. But with the dppe ligand, the starting material was recovered. Better donor ability of the dppe along with the ester group appending to the vinylidene ligand may make the methylene protons less acidic in **5g** thus, deter the deprotonation process.

Synthesis of metal cyclopropenyl derivatives in which the metal bonds to C(sp^3) of the cyclopropene ring (in this case the three-membered ring can be viewed as an antiaromatic cyclopropenide ions) have been reported in the literature [9–13]. However, to our knowledge, only few example of such derivative in which the metal is bonded to the C(sp^2) of the three-membered ring has been reported [14]. A few structurally different transition metal cyclopropenylidene complexes, mostly prepared from dichlorocyclopropene [15–17] and a number of π-cyclopropene complexes [18–21] are also known. The acidity of the aliphatic protons on a coordinated dppe ligand in a cationic iron vinylidene complex [22] has been employed for inducing the intramolecular cyclization between the dppe and vinylidene ligand.

2.4. Molecular structure of the Ru cyclopropenyl complex *7b*

The molecular structure of **7b** has been determined by X-ray diffraction study. An ORTEP drawing of **7b** is shown in Fig. 4. The cyclopropenyl ring is clearly seen with the pentafluorophenyl group bound to the unique sp^3 carbon. The Ru–C(1) bond length of 2.009(10) Å Table 5 is typical for a Ru–C(sp^2) single bond and the C(1)–C(3) bond length of 1.310(14) Å is a double bond, indicating coordination of the sp^2 carbon of the cyclopropenyl ligand. The bond angles Ru–C(1)–C(3) and C(1)–C(3)–C(4) of 165.6(4)° and 154.0(5)°, respectively, are both far greater than that of an idealized

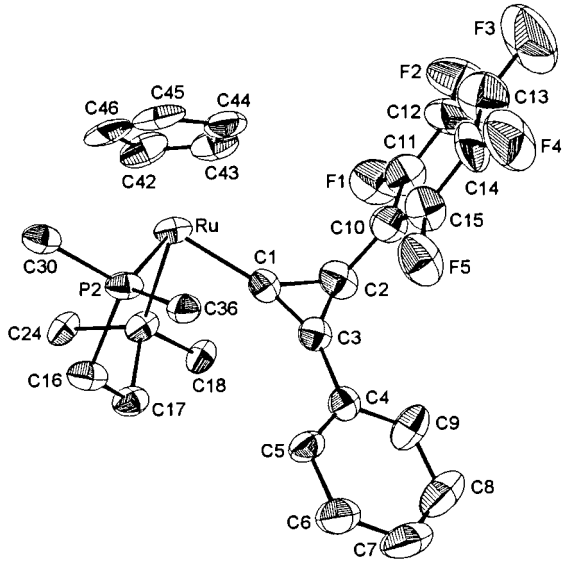

Fig. 4. An ORTEP drawing of Cp(dppe)Ru–C=C(C_6H_5)CH(C_6F_5) (**7b**) (50% thermal ellipsoids) with the phenyl groups on the dppe ligand eliminated for clarity.

Table 5
Selected interatomic distances (Å) and bond angles (°) of Cp(dppe)Ru[C=C(Ph)CH(C_6F_5)], **7b**

Ru–P(1)	2.237(3)	C(1)–C(3)	1.310(14)
Ru–P(2)	2.231(3)	C(2)–C(3)	1.467(15)
Ru–C(1)	2.009(10)	C(2)–C(10)	1.453(16)
C(1)–C(2)	1.584(16)	C(3)–C(4)	1.463(14)
C(16)–C(17)	1.529(15)		
P(1)–Ru–P(2)	84.60(12)	C(1)–C(2)–C(10)	119.7(10)
P(1)–Ru–C(1)	81.0(3)	C(3)–C(2)–C(10)	122.8(9)
P(2)–Ru–C(1)	90.8(3)	C(1)–C(3)–C(2)	69.3(8)
Ru–C(1)–C(2)	133.9(7)	C(1)–C(3)–C(4)	154.0(10)
Ru–C(1)–C(3)	165.6(8)	C(2)–C(3)–C(4)	136.5(10)
C(2)–C(1)–C(3)	60.0(7)	P(2)–C(16)–C(17)	110.5(7)
C(1)–C(2)–C(3)	50.7(6)	P(1)–C(17)–C(16)	107.5(6)

C(sp^2) hybridization. The C(1)–C(2) and C(2)–C(3) bond lengths of 1.58(2) and 1.47(2) Å, respectively, are significantly different, conforming with the favorable cleavage of the C(1)–C(2) bond described below. The phenyl group on the three-membered ring is approximately coplanar with the cyclopropene and lies far away from the Cp.

2.5. Electrophilic additions of ruthenium cyclopropenyl complexes 7

Addition of CF_3COOH at -60°C to **7a** regenerates **5a** in quantitative NMR yield indicating basic character of the methyne carbon of the three-membered ring. But if the reaction is carried out at room temperature, in addition to **5a**, an unidentified product is observed. This ring opening process by protonation is different from the acid induced demethoxylation of the iron cyclopropenyl complex [14]. Treatment of **7b** with $HgCl_2$ also affords the vinylidene product {[Ru]=C=C(Ph)CH(C_6F_5)HgCl}$^+$ (**8b**). In the ^{1}H NMR spectrum of **8b** in $CDCl_3$, the resonance at δ 3.38 is assigned to the methyne proton near the HgCl group. And in the ^{31}P NMR spectrum the two resonances at δ 78.59 and 78.10 with $J_{P-P} = 18.2$ Hz assignable to the dppe are due to the asymmetric center at the C_γ. In the FAB MS spectrum, the parent peak for the cation is observed at $m/z = 1083.1$. The vinylidene complexes **5a** and **8b** are formed by selective cleavage of the single bond of the cyclopropenyl ring near the metal center. This selectivity is similar to that reported for the unsymmetrical organic cyclopropenes where the single bond with a methyl substituent is cleaved [23]. Attempts to carry out cyclopropenation of **8b** by using *n*-Bu_4NOH, *n*-Bu_4NF and DBU result in cleavage of the C–Hg bond yielding **5b**.

2.6. Oxidative coupling reactions of metal cyclopropenyl complex

Treatment of **7a** with 20 fold excess of allyl iodide affords the dimeric dicationic vinylidene complex {[Ru]=C=C(Ph)CHCN}$_2^{+2}$ (**9a**). Other organic iodides such as methyl iodide, ethyl iodide and iodobenzene does not generate the coupling product. No similar product was obtained in the reactions of **7b** or **7c** with allyl iodide. Complex **9a** is insoluble in most of the organic solvents and only sparingly soluble in DMSO wherein it forms an orange colored solution. The mass spectrum of **9a** is consistent with the formulation {[Ru]=C=C(Ph)CHCN}$_2$I$^+$. In the ^{31}P NMR spectrum of **9a**, the chemical shift of the resonances at δ 76.34 and 75.28 is comparable to that observed for **5a**.

Apparently a cationic ruthenium vinylidene radical [24,25] may be formed at the initial stage of the reaction of **7a** with C_3H_5I. Oxidative coupling of such a radical satisfactorily accounts for the formation of the product **9a**. Previous example of oxidative carbon–carbon coupling of the cationic iron vinylidene complex [Cp(dppe)Fe=C=CHMe]$^+$ leading to the formation of a dimer [Cp(dppe)Fe=C=CMe]$_2^{+2}$ has been reported [26], whereas a very similar coupling [27] reaction has been attributed to the presence of 17 electron species confirmed by ESR [28], The coupling of allyl radical resulting in formation of bicyclopropyl molecule [29] and radical annulations of allyl iodomalononitriles [30] have been reported in the literature. Unsubstituted vinylidene complex Cp(PPh_3)$_2$Ru=C=CH_2 also undergoes oxidative coupling in the presence of MeI and generates a similar dimer [31]. There are also few examples of metal acetylide couplings [32–34]. Possible role of azavinylidene [35] in the conversion of nitriles to diimido-bridged dimer in tantalum and niobium complexes [36–38] has been recently addressed. These examples are, nevertheless, different from what is observed in **7a**, namely in our system the oxidative coupling at C_γ results in formation of a C_6 bridge between the two Ru metal centers. Unlike the phosphine analogue [1], the dppe dimer **9a** does not undergo deprotonation to yield the bis(cyclopropenyl) complex.

2.7. Conclusion

The preparation of neutral Ru cyclopropenyl complexes containing dppe ligand has been accomplished by deprotonation of a CH or CH_2 unit at C_γ of the cationic vinylidene complexes in acetone. Preparation of complexes with various substituents such as CN, Ph and 1-naphthyl groups at CH or CH_2 renders this preparation a potentially versatile synthetic method. Protonation of the cyclization products regenerates the vinylidene complexes indicating the nucleophilic nature of the antecedent C_γ carbon of the vinylidene ligand.

Thus, other electrophiles could also be added to this same C_γ site by reaction with cyclopropenyl complex.

3. Experiment

3.1. Materials

All manipulations were performed under nitrogen using vacuum-line, dry box, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded on the Bruker AC-200 and AM-300WB FT–NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_2D_6CO, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Complexes (**1a**) and Cp(dppe)RuC≡CPh [39] were prepared following the method reported in the literature. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

3.2. Preparation of Ru dppe complexes

A Schlenk flask was charged with $Cp(PPh_3)_2RuCl$, **1a** (2.00 g, 2.76 mmol) and dppe (1.21 g, 3.05 mmol) and the atmosphere was replaced with nitrogen, then C_6H_6 (60 ml) was added. The resulting solution was heated to reflux for 8 h to give a yellow solution with some precipitates. After filtration, 20 ml of hexane was added to the filtrate to bring about more precipitation which was also filtered. The solid parts were combined to give two minor products *trans*-$RuCl_2(dppe)_2$ (**2**) and $[RuClCp(\mu\text{-dppe})]_2$ (**3**) which could be separated by recrystallization from 1:1 hexane:CH_2Cl_2. Complex **2** displays yellow and **3** displays red color. The solvent of the clear solution was reduced to about 10 and 80 ml of hexane was added. The yellow precipitates thus formed were filtered and washed with diethyl ether and hexane to give the major product Cp(dppe)RuCl (1.15 g, 1.93 mmol, 70% yield). Spectroscopic data of *trans*-$RuCl_2(dppe)_2$ (**2**): ^{1}H NMR($CDCl_3$): 7.23–6.90 (m, 40H, 8Ph), 2.80–2.65 (m, 8H, CH_2). ^{31}P NMR ($CDCl_3$): 45.75. ^{13}C NMR ($CDCl_3$): 135.6–126.8 (m, Ph), 30.2 (d, CH_2, J_{C-P} = 12.1 Hz). Anal. Calcd. for $C_{52}H_{48}Cl_2P_4Ru$: C, 64.46; H, 4.99; Anal. Found: C, 64.30; H, 4.59. Spectroscopic data of $[RuClCp(\mu\text{-dppe})]_2$ (**3**): ^{1}H NMR ($CDCl_3$):7.50–6.90 (m, Ph), 3.85 (s, Cp), 3.00–2.60 (m, 8H, CH_2). ^{31}P NMR ($CDCl_3$): 37.05. ^{13}C NMR ($CDCl_3$): 130.0–127.0 (m, Ph), 80.4 (s, Cp), 24.2 (d, CH_2 J_{C-P} = 20.6 Hz). MS (*m/e*, FAB, 20 ev, Ru^{102}) 968.1 (M^+), 932.2 (M^+–Cl), 897.2 (M^+–2Cl). Anal. Calcd. for $C_{62}H_{58}Cl_2P_4Ru_2$: C, 62.05; H, 4.87; Anal. Found: C, 61.78; H, 4.96.

3.3. Synthesis of [Cp(dppe)Ru=C=C(Ph)CH_2CN][I], 5a and other vinylidene complexes

To a 20 ml $CHCl_3$ solution of complex Cp(dppe)RuC≡CPh (0.50 g, 0.75 mmol), an aliquot of ICH_2CN (54.4 μl, 0.75 mmol) was added. The solution was heated to reflux for 12 h. Pink precipitates formed while the solution was allowed to cool to room temperature. The solvent was removed under vacuum and 20 ml of ether was added then the mixture was filtered and the solid portion was washed with 20 ml of hexane and 20 ml of diethyl ether and dried under vacuum to give the product [Cp(dppe)Ru=C=C(Ph)CH_2CN][I], **5a** (0.52 g) in 83% yield. Spectroscopic data of **5a**: ^{1}H NMR ($CDCl_3$): 7.60–6.60 (m, 25H, Ph), 5.60 (s, 5H, Cp), 3.50–2.90 (m, 4H, CH_2), 2.52 (s, 2H, CH_2CN). ^{31}P NMR ($CDCl_3$): 76.50. ^{13}C NMR ($CDCl_3$): 364.2 (t, J_{C-P} = 15.1 Hz, C_α), 134.4–126.8 (m, Ph and C_β), 122.1 (*C*N), 92.5 (Cp), 28.1 (d, *C*H_2, J_{C-P} = 10.0 Hz), 18.4 (s, *C*H_2CN). MS (*m/z*, Ru^{102}) 706.1 (M^+, 593.1 (Cp(dppe)RuCO$^+$),565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{41}H_{36}NP_2RuI$: C, 59.14; H, 4.36; N, 1.68; Anal. Found: C, 60.07; H, 4.29, N, 1.50; Complexes **5b** (yield 81%), **5c** (yield 79%), **5d** (yield 71%), **5e** (yield 74%) and **5f** (yield 80%) were prepared using similar procedure. But for **5b**–**5f**, the anion was replaced with PF_6^- by adding NH_4PF_6 to the cold solution after refluxing. Spectroscopic data of [Cp(dppe)Ru=C=C(Ph)$CH_2C_6F_5$][PF_6] (**5b**): ^{1}H NMR ($CDCl_3$): 7.80–6.50 (m, Ph), 5.58 (s, 5H, Cp), 3.60–2.90 (m, 4H, CH_2), 2.80 (s, 2H, $CH_2C_6F_5$). ^{31}P NMR ($CDCl_3$): 76.97. ^{13}C NMR ($CDCl_3$): 343.0 (t, J_{C-P} = 12.1 Hz, C_α), 135.8–126.2 (m, Ph), 112.3 (C_β), 91.9 (Cp), 27.4 (d, *C*H_2, J_{C-P} = 24.3 Hz), 17.1 (*C*$H_2C_6F_5$). MS (*m/z*): 847.1 (M^+), 593.1 (Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{46}H_{36}F_{11}P_3Ru$: C, 55.71; H, 3.66; Anal. Found: C, 55.90; H, 3.86. Spectroscopic data of [Cp(dppe)Ru=C=C(Ph)–$CH_2C_6H_5$][PF_6] (**5c**): ^{1}H NMR ($CDCl_3$): 7.50–6.60 (m, Ph), 5.52 (s, 5H, Cp), 3.50–2.90 (m, 4H, CH_2), 2.85 (s, 2H, $CH_2C_6H_5$). ^{31}P NMR ($CDCl_3$): 77.65. ^{13}C NMR ($CDCl_3$): 349.0 (t, J_{C-P} = 16.4 Hz, C_α), 138.0–126.5 (m, Ph), 125.1 (C_β), 91.7 (Cp), 28.7 (d, *C*H_2, J_{C-P} = 25.0 Hz), 29.6 (*C*$H_2C_6H_5$). MS (*m/z*): 757.1 (M^+-PF_6), 593.1 (Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{46}H_{41}F_6P_3Ru$: C, 61.26; H, 4.58; Anal. Found: C, 60.97; H, 4.67. Spectroscopic data of [Cp(dppe)Ru=C=C(Ph)CH_2(*p*-C_6H_4CN)][PF_6] (**5d**): ^{1}H NMR ($CDCl_3$): 7.80–6.40 (m, Ph), 5.59 (s, 5H, Cp), 3.50–3.10 (m, 4H, CH_2), 2.93 (s, 2H, CH_2(*p*-C_6H_4CN). ^{31}P NMR ($CDCl_3$): 77.40. ^{13}C NMR ($CDCl_3$): 347.2 (t, J_{C-P} = 18.1 Hz, C_α), 132.5–126.8 (m, Ph), 118.7 (C_α), 109.9 (C_β), 88.1 (Cp), 28.2

(d, CH_2, J_{C-P} = 46.8 Hz), 29.4 (CH_2 *p*-C_6H_4CN). MS (*m*/*z*): 782.1 (M^+-PF_6), 593.1 (Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{47}H_{40}F_6NP_3Ru$: C, 60.91; H, 4.35; N, 1.51; Anal. Found: C, 60.65; H, 4.30; N, 1.43. Spectroscopic data of [Cp(dppe)Ru=C=C(Ph)CH_2(*p*-$C_6H_4CF_3$)][PF_6] (**5e**): ^{1}H NMR ($CDCl_3$): 7.50–6.40 (m, Ph), 5.54 (s, 5H, Cp), 3.20–2.80 (m, 4H, CH_2), 2.91 (s, 2H, CH_2(*p*-$C_6H_4CF_3$). ^{31}P NMR ($CDCl_3$): 77.33. ^{13}C NMR ($CDCl_3$): 343.1 (t, J_{C-P} = 12.1 Hz, C_α), 135.8–126.2 (m, Ph), 112.3(C_β), 91.9 (Cp), 27.7 (d, CH_2, J_{C-P} = 14.1 Hz), 17.1 (CH_2(*p*-$C_6H_4CF_3$). MS (*m*/*z*): 825.1 (M^+-PF_6), 593.1 (Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{47}H_{40}F_9P_3Ru$: C, 58.21; H, 4.16; Anal. Found: C, 58.30; H, 4.39. Spectroscopic data of [Cp(dppe)Ru=C=C(Ph)CH_2(1-$C_{10}H_7$)][PF_6] (**5f**): ^{1}H NMR ($CDCl_3$): 7.80–6.50 (m, Ph), 5.53 (s, 5H, Cp), 3.20–2.90 (m, 4H, CH_2), 2.98 (s, 2H, CH_2(1-$C_{10}H_7$)). ^{31}P NMR ($CDCl_3$): 77.40. ^{13}C NMR ($CDCl_3$): 343.6 (t, J_{C-P} = 10.2 Hz, C_α), 136.1–125.4 (m, Ph and C_β), 91.7 (Cp), 30.8 (CH_2(1-$C_{10}H_7$)), 28.2 (d, CH_2, J_{C-P} = 14.1 Hz). MS (*m*/*z*): 807.1 (M^+-PF_6), 593.1 (Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{50}H_{43}F_6P_3Ru$: C, 63.09; H, 4.55; Anal. Found: C, 63.24; H, 4.72.

3.4. Preparation of *5g*

To a 20 ml $CHCl_3$ solution of complex Cp(dppe)RuC≡CPh (0.30 g, 0.45 mmol), an aliquot of $BrCH_2CO_2CH_3$ (142 μl, 1.5 mmol) was added. The solution was heated to reflux for 24 h. Then the solvent was removed under vacuum and 20 ml of ether was added and the slurry was filtered. These solids were washed with 20 ml of hexane and 20 ml of ether and dried under vacuum to give the product Cp(dppe)Ru=C=C(Ph)$CH_2CO_2CH_3^+Br^-$, (**5g**) (0.35 g) in 94% yield. Spectroscopic data of **5g**: ^{1}H NMR ($CDCl_3$): 8.00–6.50 (m, Ph), 5.65 (s, 5H, Cp), 3.50–3.00 (m, 4H, CH_2), 3.49 (s, 3H, CH_3), 2.35 (s, 2H, CH_2). ^{31}P NMR ($CDCl_3$): 76.86. ^{13}C NMR ($CDCl_3$): 349.8 (t, J_{C-P} = 16.1 Hz, C_α), 172.5 (CO_2), 135.6–125.3 (Ph), 123.6 (C_β), 92.9 (Cp), 51.7 (CH_2CO_2), 29.3 (OCH_3), 27.6 (d, CH_2CH_2, J_{C-P} = 30.1 Hz). MS (*m*/*z*): 739.1 (M^+-PF_6), 593.1 (Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{42}H_{39}BrO_2P_2Ru$: C, 61.62; H, 4.80; Anal. Found: C, 61.44; H, 4.56. Complex **5g′** is also prepared by carrying out the reaction at room temperature. The yield (76%) is lower.

3.5. Formation of Cp(dppe)RUCOCH$_2$Ph (6) from *5g′*

Complex **5g′** (0.30 g, 0.36 mmol), prepared at room temperature, was dissolved in 20 ml of $CHCl_3$ and NH_4PF_6 (0.30 g) was added. And the solution was stirred at room temperature for 24 h. Then the solvent was removed under vacuum and the residue was washed with 2 × 20 ml of hexane and 2 × 20 ml of ether to give the product **6** (0.16 g, 64% yield). Spectroscopic data of (**6**): ^{1}H NMR ($CDCl_3$): 7.80–6.00 (m, Ph), 4.84 (s, 5H, Cp), 3.38 (s, 2H, CH_2), 3.00–2.50 (m, 4H, CH_2). ^{31}P NMR ($CDCl_3$): 91.10. ^{13}C NMR ($CDCl_3$): 254.4 (t, J_{C-P} = 13.4 Hz, *C*O), 139.7–127.8 (m, Ph and C_β), 87.5 (Cp), 60.9 ($COCH_2$), 27.5 (t, CH_2CH_2, J_{C-P} = 22.5 Hz). MS (*m*/*z*): 684.1 (M^+), 593.1(Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{39}H_{36}OP_2Ru$: C, 68.51; H, 5.31; Anal. Found: C, 68.38; H, 5.49.

3.6. Preparation of cyclopropenyl complexes

To a 15 ml acetone solution of complex **5a** (0.50 g, 0.60 mmol) an aliquot of (*n*-Bu)$_4$NOH (10 ml) was added. The mixture was stirred at room temperature for 1 h to give a bright yellow solution and then the solvent was removed under vacuum. To the residue, 15 ml of CH_3CN was added and the yellow precipitates was filtered.

The solid residue was further washed with 2 × 20 ml of hexane and 2 × 20 ml of CH_3CN and dried under vacuum to give the product identified as Cp(dppe)Ru–C=(Ph)CHCN, **7a** (0.30 g, 0.42 mmol) in 72% yield. Spectroscopic data of **7a**: ^{1}H NMR (CD_3COCD_3): 7.80–6.30 (m, Ph), 4.95 (s, 5H, Cp), 3.80–3.50 (m, 4H, PCH_2), 2.13 (s, H, CHCN). ^{31}P NMR ($CDCl_3$): 90.14, 88.47 (two doublet with J_{P-P} = 24.3 Hz). ^{13}C NMR ($CDCl_3$): 134.5–126.0 (m, Ph), 124.6 (*C*N), 84.1 (Cp), 32.9, 29.1 (d, 2 P*C*H$_2$), 6.2 (*C*HCN). MS (*m*/*z*): 706.1 (M^+ + 1), 593.1(Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{41}H_{35}NP_2Ru$: C, 69.87; H, 5.01; N, 1.99; Anal. Found: C, 69.64; H, 4.87; N, 1.79. Complexes **7b**, **7c**, **7d**, **7e** and **7f** were similarly prepared. Spectroscopic data of Cp(dppe)Ru–C=(Ph)CHC$_6$F$_5$ (**7b**): ^{1}H NMR ($CDCl_3$): 8.00–6.30 (m, Ph), 4.70 (s, 5H, Cp), 3.00–2.30 (m, 4H, PCH_2), 2.90 (s, 1H, CHC_6F_5). ^{31}P NMR ($CDCl_3$): 91.15, 88.45 (two doublet with J_{P-P}26.7 Hz). ^{13}C NMR ($CDCl_3$): 144.4–117.3 (m, Ph), 83.2 (Cp), 28.8 (dd, CH_2, $^1J_{C-P}$ = 32.3 Hz, $^2J_{C-P}$ = 15.1 Hz),26.7(dd, CH_2, $^1J_{C-P}$ = 34.7 Hz, $^2J_{C-P}$ = 15.8 Hz), 19.1 (*C*HC$_6$F$_5$). MS (*m*/*z*): 847.2 (M^+ + 1), 593.2 (Cp(dppe)RuCO$^+$), 565.2 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{46}H_{35}F_5P_2Ru$: C, 65.32; H, 4.17; Anal. Found: C, 65.47; H, 4.34. Spectroscopic data of Cp(dppe)Ru–C=(Ph)CHC$_6$H$_5$ (**7c**): ^{1}H NMR ($CDCl_3$): 7.50–6.60 (m, Ph), 4.66 (s, 5H, Cp), 3.40–2.90 (m, 4H, CH_2), 2.75 (s, 1H, CHC_6H_5). ^{31}P NMR ($CDCl_3$): 91.58, 90.18(two doublet with J_{P-P}25.5 Hz). ^{13}C NMR ($CDCl_3$): 135.9–122.3 (m, Ph), 83.2 (Cp), 27.3, 26.7 (CH_2CH_2), 30.4 (*C*HC$_6$H$_5$). MS (*m*/*z*): 756.1 (M^+

+ 1), 593.1 (Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{46}H_{40}P_2Ru$: C, 73.10; H, 5.33; Anal. Found: C, 73.22; H, 5.47. Spectroscopic data of Cp(dppe)Ru–C=(Ph)CH(*p*-C_6H_4CN) (**7d**): ^{1}H NMR ($CDCl_3$): 7.80–6.20 (m, Ph), 4.56 (s, 5H, Cp), 3.40–3.20 (m, 4H, CH_2), 2.60 (s, 1H, CH(*p*-C_6H_4CN)). ^{31}P NMR ($CDCl_3$): 90.54, 89.54 (two doublet with J_{P-P} = 24.3 Hz). ^{13}C NMR ($CDCl_3$): 134.3–125.6 (m, Ph and C_α), 120.62 (CN), 83.0 (Cp), 27.4, 27.3 (CH_2CH_2), 32.3 (CH(*p*-C_6H_4CN)). MS (*m*/*z*): 847.2 (M$^+$ + 1), 593.2 (Cp(dppe)RuCO$^+$), 565.2 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{47}H_{39}NP_2Ru$: C, 72.29; H, 5.03; Anal. Found: C, 72.31; H, 4.89. Spectroscopic data of Cp(dppe)Ru–C=(Ph)CH(*p*-$C_6H_4CF_3$) (**7e**): ^{1}H NMR ($CDCl_3$): 8.02–6.22 (m, Ph), 4.64 (s, 5H, Cp), 3.00–2.30 (m, 4H, CH_2), 2.19 (s, 1H, CH(*p*-$C_6H_4CF_3$)). ^{31}P NMR ($CDCl_3$): 91.03, 89.82 (two doublet with J_{P-P}25.5 Hz). ^{13}C NMR ($CDCl_3$): 144.3–123.7 (m, Ph), 83.2 (Cp), 28.7 (dd, CH_2CH_2, $^1J_{C-P}$ = 33.9 Hz, $^2J_{C-P}$ = 16.0 Hz), 26.8 (dd, CH_2CH_2, $^1J_{C-P}$ = 29.0 Hz, $^2J_{C-P}$ = 15.7 Hz), 13.6 (CH(*p*-$C_6H_4CF_3$)). MS (*m*/*z*): 825.2 (M$^+$ + 1), 593.2 (Cp(dppe)RuCO$^+$), 565.2 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{47}H_{39}F_3P_2Ru$: C, 68.52; H, 4.77; Anal. Found: C, 68.35; H, 4.67. Spectroscopic data of Cp(dppe)Ru–C=(Ph)CH(1-$C_{10}H_7$) (**7f**): ^{1}H NMR ($CDCl_3$): 8.10–6.40 (m, Ph), 4.63 (s, 5H, Cp), 3.00–2.30 (m, 4H, CH_2), 1.98 (s, 1H, CH(1-$C_{10}H_7$)). ^{31}P NMR ($CDCl_3$): 91.39, 90.17 (two doublet with J_{P-P} = 25.5 Hz). ^{13}C NMR ($CDCl_3$): 135.2–122.3 (m, Ph), 83.2 (Cp), 24.1 (CH(1-$_{10}H_7$)), 28.1, 27.0 (CH_2CH_2). MS (*m*/*z*): 807.1(M$^+$ + 1), 593.1 (Cp(dppe)RuCO$^+$), 565.1 (Cp(dppe)Ru$^+$). Anal. Calcd. for $C_{50}H_{42}P_2Ru$: C, 74.52; H, 5.25; Anal. Found: C, 74.22; H, 5.03.

*3.7. Synthesis of [[Ru]=C=C(Ph)CH(C_6F_5)HgCl]Cl (**8b**)*

To a mixture of **7b** (0.20 g, 0.24 mmol), and $HgCl_2$ (0.076 g, 0.28 mmol) at room temperature, 15 ml of CH_2Cl_2 was added by syringe. The mixture was stirred under nitrogen for 5 min. The work-up procedure was the same as that in **5b**. The product **8b** was obtained (0.21 g, 86%) and was identified as Cp(dppe)Ru=C=C(Ph)CH(C_6F_5)(HgCl)$^+$Cl$^-$. Spectroscopic data of **8b**: ^{1}H NMR ($CDCl_3$): 7.67–6.60 (m, Ph), 5.59 (s, 5H, Cp), 3.40–2.90 (m, 4H, CH_2), 3.38 (s, 1H, CHHgCl). ^{31}P NMR ($CDCl_3$): 78.59, 78.10 (two doublet with J_{P-P} = 18.2 Hz). ^{13}C NMR ($CDCl_3$): 133.0–127.0 (m, Ph and C_β), 92.1 (Cp), 47.7 (s, H, CHHgCl), 28.8, 27.7 (d, CH_2CH_2, J_{C-P} = 15.9 Hz). MS (*m*/*z*): 1083.1 (M$^+$–Cl), 593.2 (Cp(dppe)RuCO$^+$), 565.2 (Cp(dppe)Ru$^+$).

*3.8. Dimerization of **7a** in the presence of allyl iodide*

Excess freshly distilled allyl iodide (0.65 ml, 7.1 mmol) was added to a solution of **7a** (0.20 g, 0.28 mmol) in 10 ml $CHCl_3$. This mixture was stirred at room temperature for 48 h to give orange red precipitate which was filtered off, washed with 10 ml of acetone and 2 × 10 ml of hexane, then dried in vacuo yielding [[Ru]=C=C(Ph)CH(CN)]$_2I_2$ (**9a**) (0.13 g, 39% yield). Complex **9a** is insoluble in common organic solvents except DMSO. Spectroscopic data of (**9a**): ^{1}H NMR($CDCl_3$): 7.40–6.80 (m, Ph), 5.30 (s, 10H, Cp), 3.20–2.60 (m, 8H, CH_2), 2.48 (s, 2H, CHCN). ^{31}P NMR ($CDCl_3$): 76.34, 75.28 (two doublet with J_{P-P} = 19.5 Hz). ^{13}C NMR ($CDCl_3$): 343.5 (t, J_{C-P} = 15.0 Hz, C_α), 131.5–129.3 (m, Ph), 93.2 (Cp), 26.9, 25.0 (CH_2CH_2), 24.3 ($CHCN$). MS (*m*/*z*): 1537.3 (M$^+$–I_5), 1409.4 (M$^+$ + 1-2I_3), 565.3 (Cp(dppe)Ru$^+$).

*3.9. X-ray analysis of **2**, **3**, **6**, and **7b***

Single crystals of **2** suitable for an X-ray diffraction study were grown as mentioned above. A single crystal of dimensions 0.20 × 0.30 × 0.50 mm^3 was glued to a glass fiber and mounted on an Enraf–Nonius CAD4 diffractometer. Initial lattice parameters were determined from a least-squares fit to 25 accurately centered reflections. Cell constants and other pertinent data are collected in Table 1. Data were collected using the $\theta/2\theta$ scan method. The final scan speed for each reflection was determined from the net intensity gathered during an initial prescan and ranged from 2 to 7° min^{-1}. The scan angle was determined for each reflection according to the equation 0.8 + 0.35 × tan θ.

The raw intensity data were converted to structure factor amplitudes and their esd's by correction for scan speed, background and Lorentz, polarization effects. An empirical correction for absorption based on the azimuthal scan, was applied to the data set. Crystallographic computations were carried out on a Microvax III computer using the NRCC structure determination package [40]. Merging of equivalent and duplicate reflections gave a total of 4597 unique measured data from which 2839 were considered observed, $I > 2.0\,\sigma(I)$. The structure was first solved by using the heavy atom method (Patterson synthesis) which revealed the position of metal, then refined via standard least-squares and difference Fourier techniques. The quantity minimized by the least squares program was $w(|F_o| - |F_c|)^2$. The analytical forms of the scattering factor tables for the neutral atoms were used [41]. All other non-hydrogen atoms were refined by using anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculations in their expected positions on the basis of idealized bonding geometry but were not refined in least squares. Final refinement using full-matrix, least squares converged smoothly to values of $R = 0.039$ and $R_w = 0.038$. Final values of all refined atomic positional parameters (with esd's) and tables of thermal parameters, and structure factors are given in the supporting information.

The procedures for **3**, **6**, and **7b** were similar. The final residues of the refinement were $R = 0.054$, $R_w = 0.064$ for **3**; $R = 0.049$, $R_w = 0.056$ for **6**; and $R = 0.053$, $R_w = 0.050$ for **7b**. Final values of all refined atomic positional parameters (with esd's) and tables of thermal parameters and structure factors are given in the supporting information.

3.10. Supporting information available

Details of the structural determination for complexes **2**, **3**, **6**, and **7b** including tables of crystal data and structure refinement, positional and anisotropic thermal parameters and listings of bond distances and angles (21 pages).

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