Reactivity of Ruthenium Vinylidene Complexes Containing Indenyl/dppe Ligands and Unsaturated Bonds at C8 with Trimethylsilyl Azide

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Abstract: This study presents a new reaction of cationic vinylidene complexes with Me3SiN3 (TMSN3), which yields N-coordinated nitrile complexes 3. Treatment of a ruthenium acetylide precursor containing indenyl and dppe ligands with a series of organic halides produced the corresponding vinylidene complexes 2 in good yield. Further reaction of 2 with TMSN3 at room temperature produced N-coordinated ruthenium nitrile complexes 3. Unlike the reaction of cyclopropenylruthenium complexes with TMSN3, which yielded different products depending on the substituent at Cγ, the vinylidene complexes containing unsaturated bonds at C8 yielded similar N-coordinated nitrile complexes. This transformation did not seemingly occur in the reaction of ruthenium vinylidene complexes containing Cp and PPh3 ligands with TMSN3. Deprotonation of these vinylidene complexes yielded cyclopropenyl or thermodynamic furylruthenium complexes, depending on the substitute at Cγ. Subsequent reactions of the cyclopropenyl or furylruthenium complexes with TMSN3 afforded different products.

Keywords: vinylidene; ruthenium; N-coordinated; cyclopropenyl; furyl; indenyl
1. Introduction

The chemical properties of metal vinylidene complexes are valuable for many organic transformations [1–4]. Vinylidene complexes of various metals also function as strategic intermediates for the catalytic conversion of alkynes [5,6], and active substrates in a series of stoichiometric reactions [7,8]. The formation of a metal vinylidene intermediate has been used to promote various carbon-carbon bond-forming reactions, with the addition of a nucleophilic carbon center to the electrophilic vinylidene α-carbon atom. This subject has been extensively reviewed [9,10]. The optimal entry into the transition metal vinylidene complexes is with the addition of electrophiles to the electron-rich carbon of metal alkynyl complexes [11,12]. Ruthenium vinylidene complexes are well-known active species in organometallic chemistry [1,5,13,14]. The vinylidene complexes of iron with dppe ligands have also been obtained [15–17]. The use of the acidity of the aliphatic protons on a coordinated dppe ligand in a cationic iron vinylidene complex [18] has induced the intramolecular cyclization between the dppe and vinylidene ligand.

We believe the electron-withdrawing group at Cγ of the vinylidene complexes might play a role in the acidity enhancement of its neighboring proton. We have recently reported some preliminary results on vinylidene complexes containing indenyl and dppe ligands [19]. This study reports the synthesis and the reactivity of ruthenium vinylidene complexes containing unsaturated double bonds at Cδ, and the reactivity of these vinylidene complexes with TMSN3. This study also presents a deprotonation reaction of these vinylidene complexes, as well as the subsequent reactivity of the deprotonation products with TMSN3.

2. Results and Discussion

2.1. Preparation of Cationic Ruthenium Vinylidene Complexes 2a–e

Ruthenium acetylide complex 1 was prepared via deprotonation of the corresponding vinylidene precursor following the literature method [20]. The indenylruthenium vinylidene complexes 2a–e containing dppe ligands and various substituents at Cγ were obtained as air-stable pink solids in 96–73% yields. The ruthenium vinylidene complexes 2a–e were synthesized as shown in Scheme 1. Treatment of [Ru]–C≡C–Ph (1, [Ru]=η^5-C_9H_7)(dppe)Ru) with organic halides such as allyl iodide at room temperature produced cationic vinylidene complex 2a in 89% yield. The ^31P{^1H}-NMR spectrum of 2a exhibited a singlet at δ 76.0, indicating the chemical equivalence of the two phosphorus atoms. In the ^13C{^1H} NMR spectrum, the typical low field Ru–Cα resonance appeared as a triplet at δ 352.0, with a C–P coupling constant of 16.9 Hz.

Complex 2a was air-stable at room temperature. Single crystals of 2a suitable for X-ray diffraction analysis were obtained via recrystallization from CH_2Cl_2/ether. The ORTEP drawing of 2a with thermal ellipsoids is shown at the 30% probability level in Figure 1, with selected bond distances and angles listed in Table 1. The C(37)–C(36)–Ru(1) linkage was basically linear. The C(36)–Ru(1) bond length of 1.841(4) Å indicated a typical metal-carbon bond in the vinylidene complexes [21,22]. Ruthenium vinylidene complexes containing indenyl ligand have been reported [23–27]. The X-ray structure of the vinylidene indenyl-ruthenium complex [Ru{≡C≡C(CH_3)(C_6H_5)}(η^5-C_9H_7)(PPh_3)_2]^+
with bond length Ru-C(α) 1.838(5) Å [26]. The bond angle of this complex is 176.2(4) also very close linear.

**Scheme 1.** Reaction of vinylidene complexes with TMSN₃.

Similarly, various vinylidene complexes \([\text{[Ru]}=\text{C} (=\text{C})(\text{Ph})\text{CH}_2\text{R}]^{\dagger}\) 2b–d (2b, \(\text{R}=\text{CO}_2\text{CH}_3\), 2c, \(\text{R}=\text{CO}_2\text{C}_2\text{H}_5\), 2d, \(\text{R}=\text{CH}=\text{CHCO}_2\text{CH}_3\), 2e, \(\text{R}=\text{C} (=\text{CH})\)) were prepared using the same synthesis method as for 2a. All indenylruthenium vinylidene complexes 2a–e displayed a characteristic pink color in the solid state. These complexes were characterized via NMR spectroscopy and X-ray diffraction. In the \(^1\text{H}-\text{NMR}\) spectrum, the singlet or doublet resonances for the CH₂ group at Cβ appeared at 2.2–2.8 ppm.

**Figure 1.** ORTEP plot of complex 2a drawn at the 30% probability level.
Table 1. Selected bond lengths [Å] and angles [deg] for complex 2a.

| Bond Lengths | Bond Angles |
|--------------|-------------|
| C(36)–Ru(1)  | 1.841(4)    | C(36)–C(37) | 1.326(6) |
| C(37)–C(44)  | 1.538(6)    | C(44)–C(45) | 1.515(6) |
| P(1)–Ru(1)   | 2.3380(10)  | P(1)–Ru(1)–P(2) | 83.29(3) |
| P(2)–Ru(1)   | 2.3104(10)  | C(37)–C(36)–Ru(1) | 177.2(4) |
| C(37)–C(36)–Ru(1) | 177.2(4) | C(36)–C(37)–C(44) | 119.1(4) |

2.2. Reactivity of the Vinylidene Complexes with TMSN₃

Cationic vinylidene complexes are known to react with alcohols or water to yield alkoxycarbene or acyl complexes, respectively [24,28–31]. The reaction is believed to proceed by nucleophilic attack at the vinylidene α carbon, followed by a proton shift from the oxonium ion to the β-carbon. A theoretical study of vinylidene complexes indicated localization of electron density on Cβ (HOMO) and the electron deficiency at Cα [32,33]. A study of the reaction of alcohols with ruthenium vinylidene complexes indicated that electron-withdrawing groups on the acetylide unit or on the metal facilitate nucleophilic attack on Cα [34].

The reaction of ruthenium vinylidene complex 2a with TMSN₃ yielded the N-coordinated nitrile complex 3a as a yellow powder in 83% yield. Regardless of the equivalent ligand distribution around ruthenium, the presence of two monodentate phosphine ligands, instead of the chelating diphosphine dppe, marks a difference in the reactivity of their derivatives. Unlike the previously reported reactivity of ruthenium vinylidene complexes, the ruthenium vinylidene complex containing indenyl and dppe ligands therefore demonstrate a distinctly different reactivity from that of the Cp and PPh₃ system.

Complex 3a was stable in solution and air, and soluble in polar solvents, such as CH₂Cl₂, acetone, and THF. Complex 3a was characterized by ¹H-, ³¹P-, ¹³C-NMR, as well as 2D-NMR spectroscopy. In the ³¹P{¹H}-NMR spectrum of 3a, two doublet resonances at δ 83.4 and 81.4 with a P–P coupling constant of 27.2 Hz indicated the presence of an enantiotopic center in the N-coordinated nitrile ligand. In the ¹H-NMR spectrum, a triplet pattern at δ 3.82 with J_H-H = 7.15 Hz was assigned to the proton at this enantiotopic center. The parent peak in the HRMS spectrum of 3a clearly indicated that 3a resulted by adding a nitrogen atom to 2a. Slow diffusion of the diethyl ether into a solution of 3a in dichloromethane permitted a collection of suitable single crystals for X-ray diffraction studies (Table 2). An ORTEP diagram of one of the stereoisomers 3a is shown in Figure 2, showing 30% thermal ellipsoids, and selected structural parameters are listed in Table 3. The nitrile ligand was coordinated to the metal center via the nitrogen atom. The bond lengths of Ru(1)–N(1) of 2.031(4) Å and N(1)–C(27) bond length of 1.130(7), respectively, were typical. The N(1)–C(27)–C(28) bond angle of 176.8° was close to 180°. X-ray analysis unequivocally confirmed the molecular structure (Table 3).

Table 2. Selected bond lengths [Å] and angles [deg] for complex 3a.

| Bond Lengths | Bond Angles |
|--------------|-------------|
| N(1)–Ru(1)   | 2.031(4)    | C(27)–N(1) | 1.130(7) |
| C(27)–C(28)  | 1.494(9)    | C(28)–C(35) | 1.515(10) |
| P(1)–Ru(1)   | 2.2637(13)  | P(2)–Ru(1) | 2.2989(15) |
| C(27)–N(1)–Ru(1) | 174.1(6) | N(1)–C(27)–C(28) | 176.8(8) |
| P(1)–Ru(1)–P(2) | 84.34(5) | N(1)–Ru(1)–P(1) | 88.88(12) |
Figure 2. ORTEP plot of one of the stereoisomers 3a drawn at the 30% probability level.

Table 3. Crystal data and refinement parameters for complexes 2a and 3a.

|          | 2a                  | 3a                  |
|----------|---------------------|---------------------|
| Empirical formula | C₄₆H₄₁IP₂Ru       | C₄₆H₄₂INP₂Ru       |
| Temperature     | 200(2) K           | 200(2) K           |
| Crystal system  | Orthorhombic       | Monoclinic          |
| Space group     | P n a 2₁           | P 2₁/n              |
| a, Å            | 22.1483(8)         | 10.4855(3)          |
| b, Å            | 11.8391(5)         | 19.1064(6)          |
| c, Å            | 14.4101(6)         | 19.8563(6)          |
| α, deg          | 90                 | 90                  |
| β, deg          | 90                 | 92.248(2)           |
| γ, deg          | 90                 | 90                  |
| Volume, Å³      | 3778.6(3)          | 3975.0(2)           |
| Z                | 4                  | 4                   |
| Crystal size, mm³ | 0.27 × 0.14 × 0.11 | 0.28 × 0.24 × 0.08  |
| Refinement method | Full-matrix least-squares on F2 | Full-matrix least-squares on F2 |
| Flack parameters | −0.013(14)         |                      |
| Final R indices [I > 2σ(I)] | R₁ = 0.0240, wR₂ = 0.0548 | R₁ = 0.0465, wR₂ = 0.1133 |
| R indices (all data) | R₁ = 0.0283, wR₂ = 0.0662 | R₁ = 0.0682, wR₂ = 0.1318 |
| Largest diff. peak and hole, Å⁻³ | 0.311 and −0.323 e | 1.323 and −0.897 e |
| CCDC number     | 776702             | 776705              |

Conversion of a vinylidene precursor to an N-coordinated nitrile with hydrazine, an organometallic Beckmann rearrangement, has been reported in an iron system [35] (Scheme 1). In the Cp system, similar products can be obtained via the reaction of cyclopropenyl complex containing a phenyl group
at Cγ, but the N-coordinated ruthenium complex product containing N3− counter anion is unstable. An exchange of the N3− with PF6− stabilized the N-coordinated complex [36,37]. Ruthenium vinylidene complexes containing Cp and PPh3 ligands have been reported. However, no reaction was observed between these vinylidene complexes with TMSN3 [33]. In the indenyl and dppe ligands system, we previously reported that the N-coordinated ruthenium complex product containing N− counter anion is stable. This product can be obtained via the reaction of a cyclopropenyl complex with TMSN3 [19].

The reaction of the vinylidene precursor 2a with TMSN3 may advance through the nucleophilic addition of azide anion at Cα and the electrophilic addition of a (CH3)3Si (TMS) group at Cβ. Subsequent loss of N2 would result in metal migration and hydrolysis of the (CH3)3Si group, to cause N-coordinated nitrile complex 3a, accompanied with the halide anion (Scheme 1). In the Cp and two triphenylphosphine ligands system, no reaction occurs between vinylidene complexes and TMSN3, possibly due to the stereo effect of the vinylidene complexes. In the vinylidene complex 2a, the bond angle P(1)–Ru(1)–P(2) of 83.29(3) is smaller than other vinylidene complexes containing two monodentated ligands [38,39]. The more sterically demanding two triphenylphosphine ligands compared to the bidentated dppe ligand may prevent nucleophilic addition at the Cα position of the vinylidene complexes.

A similar reaction occurs in THF for a number of vinylidene complexes with various unsaturated substituents at Cγ, including the ester group (compounds 2b,c), crotonate group (compound 2d), and alkynyl group (compound 2e). Reaction of vinylidene complexes 2a–e with TMSN3 yielded similar N-coordinated nitrile complexes 3a–e is good yield (Scheme 1).

With the alkyl group at Cγ, vinylidene complex 2e reacting with TMSN3 yielded complex 3e as the major product, and another undetermined minor product with a 5:1 ratio. One of the well-known reactions of organic alkynes with azide can afford trizoles via cycloaddition [40]. The chemistry of the 1,3-dipolar cycloaddition of azides and alkynes is widely used in applications in organic, materials, and medicinal chemistry [41–48]. Ruthenium vinylidene complex 2e containing an alkyl group at Cγ and reacting with TMSN3 yielded an N-coordinated complex as the major product. The electron deficiency at Cα of the ruthenium vinylidene complex 2e may play a significant role in the reaction with TMSN3. That the vinyl group reacting with azide produced 1,2,3-triazoles via 3+2 cycloaddition has also been reported. Unlike the reactivity of cyclopropenyl complexes with TMSN3, different pathways operated depending on the substituent on the cyclopropenyl ring. The N-coordinated nitrile products 3a–e are similar, and were air stable in solid-state and soluble in CH2Cl2, but insoluble in ether and hexane. In this series of the N-coordinated products, complex 3e gave a good yield of 90%.

2.3. Deprotonation Reaction of the Vinylidene Complexes

The synthesis of a number of ruthenium cyclopropenyl complexes by deprotonation of readily accessible ruthenium vinylidene complexes containing a CH2R group bound to Cβ has been reported [49–53]. A cyclopropenylruthenium complex containing pentamethylcyclopentadiethyl (Cp*) and dppe ligands was synthesized as well [50]. In the iron complexes containing Cp and dppe ligands, the vinylidene complex containing an allyl group at Cγ can be synthesized. The deprotonation reaction of this complex, the relatively more acidic proton of the dppe ligand in the cationic iron vinylidene complex could direct the reaction to proceed via a different route. The metallacyclic iron complex was
obtained [54]. The intramolecular cycloaddition of two C=C bond system with an allylic ligand to produce a cyclobutylidene ring has also been reported [55]. This study focuses on the deprotonation reaction of the vinylidene complex containing an allyl group or crotonate group at Cγ.

Deprotonation of the vinylidene complex 2a via n-Bu₄NOH in acetone inducing the intramolecular cyclization reaction yielded a neutral cyclopropenyl complex 4a as a single product (Scheme 2). The reaction produces a yellow crystalline product in analytically pure form. Use of acetone or acetonitrile as a solvent produces a good yield, and use of other bases such as DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) produces 4a with a comparable yield. No metallacyclic product has been observed. The 31P-NMR spectrum of 4a displays two doublet resonances at δ 94.3 and 89.3 of an AX pattern with J_{P-P} = 23.8 Hz, due to the presence of a stereogenic carbon center at the three-membered ring. On the ¹H-NMR spectrum of 4a, the methyne (methine) proton appears at δ 1.88.

The synthesis and chemical reactivity of several neutral rutheniumcyclopropenyl complexes in which the metal bonds to one sp² carbon atom of the three-membered cyclopropenyl ring in the Cp system have been reported [37, 56–58]. These cyclopropenylruthenium complexes can be prepared via deprotonation reaction of their vinylidene precursor. When a crotonate group was at Cγ, the vinylidene complex yielded a cyclopropenyl complex after deprotonation [56].

The reaction of the vinylidene complex 2b containing an ester group at Cγ with n-Bu₄NOH in acetone yields the furyl complex 4b as the thermodynamic product (Scheme 2). The reaction proceeds via deprotonation at Cγ, followed by an intramolecular cyclization first causing the three-membered cyclopropenyl complex 5b as the kinetic product, with a small amount of 4b within 1h. Conversion of 5b to 4b is completed within 4 h. The 31P-NMR spectrum of 4b displays a singlet at δ = 96.7 ppm. However, the 31P-NMR spectrum of the kinetic product 5b displays a two-doublet pattern at δ = 93.8, 88.5 ppm, with J_{P-P} = 26.1 Hz indicating the presence of a stereogenic carbon center at the cyclopropenyl ligand. As shown in Scheme 2, the furyl ruthenium complex 4c was also prepared via deprotonation of the vinylidene complex 2c containing an ethyl acetate at Cγ. Similar reaction has been
reported [52]. Deprotonation reaction of dinuclear vinylideneruthenium complexes containing an ester substituent at Cγ gave the dinuclear bisfuryl complexes [49]. Organic furan adds to [Ir(COD)(PMe3)3]Cl to yield a furyl iridium hydride complex have also been reported [59]. In the Cp and triphenylphosphine ligands system, the furyl complexes reacting with oxygen for two weeks produced the oxygen addition product [56]. In the indenyl and dppe system, complexes 4b and 4c are highly stable, and no oxygen addition reaction was observed.

In the deprotonation reaction of the vinylidene complex containing a methyl crotonate substituent at Cγ, only the cyclopropenyl complex 4d was obtained as the stable product. However, deprotonation of the vinylidene complex 2e containing an alkynyl group at Cγ yielded several unidentifiable decomposition products, and no cyclopropenyl complex was observed (Scheme 3). Deprotonation of vinylidene complexes containing an ester group at Cγ produced furylruthenium complexes as thermodynamic products.

Scheme 3. Deprotonation reaction of vinylidene complex containing alkynyl group at Cγ.

2.4. Reaction of Cyclopropenyl Complexes with TMSN₃

The reaction of the cyclopropenylruthenium complex 4a containing an allyl substituent with an excess of TMSN$_3$ resulted in the formation of a five-membered triazolate ring organic product 6a (Scheme 4) and [Ru]–CN.

Scheme 4. Reaction of cyclopropenyl complex containing an allyl substituent with TMSN₃.

The organic product is 6a [56]. The reaction of 4a with TMSN₃ results in cleavage of the C=C double bond of the cyclopropenyl ring yielding [Ru]–CN and 6a. Scheme 4 shows a possible reaction sequence. The reaction may start with an addition of a TMS group to the double bond of the allyl group. This accompanies the opening of the three-membered ring, resulting in the formation of a
cationic vinylidene intermediate A. Subsequent nucleophilic addition of the azide anion at Cα, accompanied with the hydrolysis of the TMS group yielded B. Further addition of TMS group at Cδ followed by hydrolysis of the TMS group yielded C. The single-bond character of the Cα–Cβ in B may facilitate its cleavage. Loss of N₂ and a [3+2] cycloaddition of the Cβ–Cγ double bond with N₃⁻ produces the triazole 6a and [Ru]–CN.

We altered the substituent at Cγ to the crotonate group. The result is the same as that observed for the reaction of TMSN₃ with the cyclopropenyl complex containing an allyl group (Scheme 5). In the reaction, the TMS group reacts with the unsaturated double bond at Cδ to induce a ring-opening reaction of the three-membered ring. No reaction occurs between the unsaturated double bond at Cδ of the vinylidene complexes and TMSN₃. The reactivity of Cα in the vinylidene complexes causes more activity than the unsaturated bond at Cδ.

Scheme 5. Reaction of cyclopropenyl complex containing an crotonate substituent with TMSN₃.

We reported the reactivity of cyclopropenylruthenium complexes containing indenyl and dppe ligands with TMSN₃. Various substituents at the sp³ carbon of the three-membered ring govern the reactivity of the cyclopropenyl complexes with TMSN₃. The reaction of ruthenium cyclopropenyl complexes containing indenyl and dppe ligands with TMSN₃ may proceed via an electrophilic addition of the TMS group to the three-membered ring, followed by hydrolysis to afford vinylidene intermediates containing an azide counter anion [19]. Further nucleophilic additions of N₃⁻ at Cα, and an electrophilic addition of a second TMS group at Cβ followed by a loss of N₂ leads to the N-coordinated nitrile complexes [56]. This process is similar to the chemistry of other cyclopropenylruthenium complexes. When a CN group was on the cyclopropenyl ring, a [3+2] cycloaddition of the nitrile group with azide afforded the tetrazolate complex [23]. Reactions of the cyclopropenyl complexes containing phenyl and its derivatives at Cγ yielded the stable N-coordinated complexes. In the Cp system, the reaction of cyclopropenyl complexes containing a methyl crotonate substituent or a vinyl substituent on the sp³ carbon of the cyclopropenyl ring with TMSN₃ produced [Ru]–CN and the five-membered triazole ring. The ester group on the cyclopropenyl ring is the kinetic product, while a more stable five-membered furylruthenium product is likely the thermodynamic product. Reaction of the furylruthenium complexes with TMSN₃ yielded [Ru]–N₃ and the corresponding organic products by cleavage of the M–C bond. Unlike the published reactions of ruthenium cyclopropenyl complexes with TMSN₃, which proceed through rupture of the three-membered-ring, the reaction of furylruthenium complexes with TMSN₃ caused cleavage of the M–C bond [56]. However, those reports observed no reaction between ruthenium vinylidene complexes and TMSN₃.
2.5. Reaction of Furyl Complexes with TMSN₃

Upon applying an excess of TMSN₃ to 4b in THF at room temperature, the solution displayed color changes during the course of the reaction. Reaction of the furylruthenium complexes with TMSN₃ yielded [Ru]–N₃ and the corresponding organic products by opening the five-membered ring (Scheme 6). A series of successive color changes were noted during the course of the reaction: the yellow solution of 4b first turned red upon adding TMSN₃ at room temperature, and subsequently turned orange after 1 h, and deep orange after 2 h. Unlike the published reactions of furylruthenium complexes with TMSN₃, which caused cleavage of the M–C bond, the reaction of furylruthenium complexes containing indenyl and dppe ligands with TMSN₃ were similar to the cyclopropenylruthenium complexes [56].

Scheme 6. Reaction of furyl complex with TMSN₃.

The X-ray diffraction analysis of the furylruthenium complex containing Cp and two PPh₃ ligands has been reported [52]. The Ru-Cα bond length in the furylruthenium complex of 2.076(7) Å indicates a single bond. We have reported the X-ray diffraction analysis of the cyclopropenylruthenium complex containing indenyl and dppe ligands [19]. The Ru-Cα bond length in this complex is 2.028(2) Å, slightly shorter than other cyclopropenyl complexes [50,52]. This length might cause the ring-opening reaction when the cyclopropenyl or furylruthenium complexes to react with TMSN₃. The reaction of 4b with TMSN₃ leading to [Ru]–N₃ and the corresponding organic product 6b may proceed via the similar pathway of synthesis complex 3b. Followed by the N₃⁻ attacks at Cα, the organic fragment can be obtained.

3. Experimental

3.1. General

All reagents were purchased from commercial sources and used without further purification. NMR spectra were obtained with a Bruker-AC 500 spectrometer at 500 MHz (¹H), 202 MHz (³¹P), or 125 MHz (¹³C). The chemical shifts are provided in parts per million from SiMe₄ (¹H and ¹³C(¹H)) or 85% H₃PO₄ (³¹P{¹H}), and are reported in units of δ. Mass spectra were recorded using a LCQ Advantage (ESI) instrument. X-ray diffraction studies were conducted at the Regional Center of Analytical Instruments at the National Taiwan Normal University.
All synthetic manipulations were performed in oven-dried glassware under nitrogen using vacuum lines and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. THF was distilled from sodium benzophenone ketyl and CH₂Cl₂ was distilled from CaH₂. Methanol was distilled from Mg/I₂. Complexes (η⁵-C₉H₇)(dppe)Ru–C≡C–Ph (1) [20] was prepared using the methods reported in the literature. The atom labels shown in Figure 3 were used for the ¹H and ¹³C{¹H} spectroscopic data:

![Figure 3. Structure of indenyl ligand.](image)

3.2. Synthesis of [(η⁵-C₉H₇)(dppe)Ru=C=C(Ph)CH₂CH=CH₂][I] (2a)

To a solution of 1 (0.34 g, 0.47 mmol) in CH₂Cl₂ (20 mL) was added allyl iodide (0.22 mL, 2.40 mmol). After stirring overnight at room temperature, the resulting solution was concentrated to about 5 mL. The residue was then slowly added to vigorously stirred diethyl ether (40 mL). The pink precipitate thus formed was filtered off, washed with diethyl ether and hexane and dried under vacuum to give pink product 2a (0.32 g, 0.42 mmol, 89% yield). ¹H-NMR (CDCl₃): δ 7.47–6.57 (m, 29H, 25H of Ph and 4H of H 4–7); 5.88 (d, 2H, H-1, 3, J_{H-H} = 2.7 Hz); 5.79 (t, 1H, H-2, J_{H-H} = 2.7 Hz); 5.24 (m, 1H, CH₂CH₂); 4.83, 4.63 (d, 1H each one, CH=CH₂, J_{H-H} = 10.1, 17.0 Hz); 2.95 (m, 4H, 2CH₂ of dppe); 2.21 (d, 2H, J_{H-H} = 6.0 Hz, CH₂CHCH₂). ³¹P-NMR (CDCl₃): δ 76.0. ¹³C-NMR (CDCl₃): 352.0 (Cα, J_{C-P} = 16.9 Hz); 133.9–127.1 (Ph); 112.3 (Cβ); 97.1 (C-2); 79.8 (C-1, 3); 27.8 (m CH₂ of dppe); 27.6 (CH₂). HRMS (ESI, m/z): 757.2 (M⁺); 615.3 (M⁺–C₂(Ph)CH₂CH=CH₂). Anal. Calcd. for C₄₆H₄₁P₂IRu: C: 62.52, H: 4.68, Found: C: 62.71, H: 4.70.

3.3. Synthesis of [(η⁵-C₉H₇)(dppe)Ru=C=C(Ph)CH₂CO₂CH₃][Br] (2b)

To a solution of 1 (0.37 g, 0.52 mmol) in CH₂Cl₂ (20 mL) was added methylbromoacetate (0.25 mL, 2.6 mmol). After stirring overnight at reflux temperature, the resulting solution was concentrated to about 5 mL. The residue was then slowly added to vigorously stirred diethyl ether (40 mL). The pink precipitate thus formed was filtered off, washed with diethyl ether and hexane and dried under vacuum to give pink product 2b (0.34 g, 0.43 mmol, 83% yield). ¹H-NMR (CDCl₃): δ 7.48–6.86 (m, 27H, 25H of Ph group and 2H of indenyl group); 6.52 (m, 2H, H-4, 7 of indenyl group); 6.08 (m, 2H, H-1, 3 of indenyl group); 6.02 (br, 1H, H-2 of indenyl group); 3.53 (s, 3H, OCH₃); 3.16, 2.83 (m, 2H each one, 2CH₂ of dppe); 2.36 (s, 2H, CH₂). ³¹P-NMR (CDCl₃): δ 74.6. ¹³C-NMR (CDCl₃): 350.9 (Cα, J_{C-P} = 16.9 Hz); 172.2 (C=O); 126.3 (C-5, 6); 123.6 (C-4, 7); 112.8 (Cβ); 97.3 (C-2); 80.0 (C-1, 3); 52.1 (OCH₃); 29.2 (m CH₂ of dppe); 26.8 (CH₂). HRMS (ESI, m/z): 789.3 (M⁺);
3.4. Synthesis of [(η⁵-C₅H₇)(dppe)Ru=CH₂C≡CH][I] (2c)

1 (0.37 g, 0.52 mmol) and ethylidioacetate (0.25 mL, 2.1 mmol) were stirred overnight at reflux in CH₂Cl₂ (20 mL). The purification method described for 2a yielded pink solid product 2c in 79% yield (0.33 g, 0.41 mmol). ¹H-NMR (CDCl₃): δ 7.49–6.83 (m, 27H, 25H of Ph group and 2H of indenyl group); 6.52 (m, 2H, H-4, 7 of indenyl group); 6.10 (m, 2H, H-1, 3 of indenyl group); 6.09 (br, 1H, H-2 of indenyl group); 3.95 (q, 2H, J_H-H = 7.1 Hz, OCH₂); 3.18, 2.80 (m, 2H each one, 2CH₂ of dppe); 2.35 (s, 2H, CH₂); 1.14 (t, 3H, J_H-H = 7.1 Hz, CH₃). ³¹P-NMR (CDCl₃): δ 74.3. ¹³C-NMR (CDCl₃): 345.4 (Cα, J_C-P = 17.2 Hz); 171.8 (C=O); 135.4–127.3 (Ph); 124.2 (C-5, 6); 122.8 (C-4, 7); 110.7 (Cβ); 98.4 (C-2); 78.2 (C-1, 3); 51.7 (OCH₂); 28.8 (m CH₂ of dppe); 25.1 (CH₂); 14.7 (CH₃). HRMS (ESI, m/z): 803.3 (M +); 615.2 (M+-C₂(Ph)CH₂CO₂CH₂CH₃). Anal. Calcd. for C₄₇H₄₃P₂O₂IRu: C: 60.71, H: 4.66, Found: C: 60.81, H: 4.71.

3.5. Synthesis of [(η⁵-C₅H₇)(dppe)Ru=CH₂CH=CHCO₂CH₃][Br] (2d)

1 (0.21 g, 0.29 mmol) and methyl-4-bromocrotonate (0.17 mL, 1.43 mmol) were stirred overnight in CH₂Cl₂ (20 mL). The purification method described for 2a yielded pink solid product 2d in 66% yield (0.16 g, 0.19 mmol). ¹H-NMR (CDCl₃): δ 7.47–6.94 (m, 27H, 25H of Ph group and 2H of indenyl group); 6.53 (m, 2H, H-4, 7); 5.90 (m, 2H, H-1, 3); 6.32 (dt, 1H, J_H-H = 15.6; 5.5 Hz, CH₂C=CH); 5.42 (d, 2H, J_H-H = 15.6 Hz, CO₂CH₃); 3.71 (s, 3H, OCH₃); 3.07 (m, 4H, 2CH₂ of dppe); 2.30 (d, 2H, J_H-H = 5.5 Hz, CH₂). ³¹P-NMR (CDCl₃): δ 75.9. ¹³C-NMR (CDCl₃): 133.8–127.2 (Ph); 125.5 (C-5, 6); 122.9 (C-4, 7); 111.7 (Cβ); 97.3 (C-2); 80.8 (C-1, 3); 83.4 (CH₂C≡C); 70.3 (C≡CH); 26.9 (CH₂). HRMS (ESI, m/z): 815.5 (M +); 615.4 (M+-C₂(Ph)CH₂CH=CHCO₂CH₃). Anal. Calcd. for C₄₈H₄₃P₂BrRu: C: 64.81, H: 4.91.

3.6. Synthesis of [(η⁵-C₅H₇)(dppe)Ru=CHCH₂CH=CH₃][Br] (2e)

Compound 1 (0.37 g, 0.52 mmol) and propargyl bromide (0.23 mL, 2.6 mmol) were stirred at reflux for 48 h in CH₂Cl₂ (20 mL). The purification method described for 2a yielded pink solid product 2e in 96% yield (0.38 g, 0.50 mmol). ¹H-NMR (CDCl₃): δ 7.44–6.95 (m, 27H, 25H of Ph group and 2H of indenyl group); 6.65 (m, 2H, H-4, 7); 5.95 (m, 2H, H-1, 3); 5.74 (t, 1H, H-2); 6.32 (dt, 1H, J_H-H = 15.6; 5.5 Hz, CH₂C≡CH); 5.42 (d, 2H, J_H-H = 15.6 Hz, CO₂CH₃); 3.71 (s, 3H, OCH₃); 2.21 (s, 2H, CH₂); 2.06 (s, 1H, CH). ³¹P-NMR (CDCl₃): δ 75.4. ¹³C-NMR (CDCl₃): 352.2 (Ca, J_C-P = 16.8 Hz); 133.8–127.2 (Ph); 125.5 (C-5, 6); 122.9 (C-4, 7); 111.7 (Cβ); 97.3 (C-2); 80.8 (C-1, 3); 83.4 (CH₂C≡C); 70.3 (C≡CH); 26.9 (CH₂). HRMS (ESI, m/z): 755.5 (M +); 615.4 (M+-C₂(Ph)CH₂CH=CHCH₂CO₂CH₃). Anal. Calcd. for C₄₆H₃₉P₂BrRu: C: 66.43, H: 4.84, Found: C: 66.81, H: 4.91.

3.7. Synthesis of the N-Coordinated Complexes [(η⁵-C₅H₇)(dppe)Ru=NCCH(Ph)CH₂CH=CH₃][I] (3a)

Compound 2a (0.11 g, 0.15 mmol) was dissolved in THF (7 mL). Next, TMSN₃ (0.1 mL, 0.76 mmol) was added and the mixture was stirred overnight at room temperature. The resulting solution was
concentrated to about 5 mL, and the residue was slowly added to vigorously stirred diethyl ether (20 mL). The yellow precipitate thus formed was filtered off, washed with diethyl ether and hexane, and dried under vacuum to give product 3a in 83% yield (0.08 g, 0.11 mmol). ¹H-NMR (CDCl₃): δ 7.51–7.20 (m, 25H of Ph); 7.20, 7.07 (m, 1H each one, H of indenyl group); 6.90 (2H, H of indenyl group); 5.23 (m, 1H, CH₂CH₂CH₂); 5.07, 4.90, 4.86 (br, 1H each one, H of indenyl group); 4.71, 4.67 (d, 1H each one, CH=CH₂, J₇=J₁₁ = 10.3, 17.0 Hz); 3.82 (1H, NCC₃H₃(CH)CH₂, J₇=J₁₁ = 7.0 Hz); 2.48 (m, 4H, 2CH₂ of dppe); 1.95, 1.85 (m, 1H each one, CH(Ph)CH₂). ³¹P-NMR (CDCl₃): δ 83.4, 81.4 (AX, Jₚ₋ₚ = 27.1 Hz). ¹³C-NMR (CDCl₃): 136.8–126.9 (Ph); 124.2 (C=N); 118.9 (CH₂=CH); 131.5 (CH₂=CH); 108.2, 107.7 (C of indenyl group); 92.7 (C of indenyl group); 65.9 (C of indenyl group); 38.3 (OCH₃); 28.6 (CH₂ of dppe). HRMS (ESI, m/z): 772.0 (M⁺); 615.2 (M⁺-NC₂(Ph)HCH₂CH=CH₂). Anal. Calcd. for C₄₆H₄₂P₂INRu: C: 61.47, H: 4.71, Found: C: 61.62, H: 4.74.

3.8. Synthesis of the N-Coordinated Complexes [(η⁵-C₉H₇)(dppe)Ru–NCCH(Ph)CH₂CO₂CH₃][Br] (3b)

Compound 2b (0.10 g, 0.13 mmol) and TMSN₃ (0.1 mL, 0.76 mmol) in 7 mL of THF was stirred overnight at room temperature. The purification method described for 3a yielded yellow solid product 3b in 69% yield (0.07 g, 0.09 mmol). Spectroscopic data for 3b are as follows. ¹H-NMR (CDCl₃): δ 7.49–7.20 (m, 25H of Ph); 7.06, 6.98 (m, 1H each one, H of indenyl group); 6.56 (2H, H of indenyl group); 4.99, 4.96, 4.90 (br, 1H each one, H of indenyl group); 4.00 (br, 1H, NCC₃H₃(CH)CH₂); 3.59 (s, 1H, OCH₃); 2.68, 2.52 (m, 4H, 2CH₂ of dppe); 2.28, 2.21 (m, 1H each one, CH(Ph)CH₂); 1.20 (t, 3H, CH₃). ³¹P-NMR (CDCl₃): δ 83.5, 82.2 (AX, Jₚ₋ₚ = 26.9 Hz). ¹³C-NMR (CDCl₃): 171.2 (CO); 132.8–125.4 (Ph); 123.6 (NCC); 111.1, 109.3 (C of indenyl group); 93.7 (C of indenyl group); 67.2, 66.8 (C of indenyl group); 52.2 (CH₂); 35.1 (CH₃); 27.4 (CH₂ of dppe). HRMS (ESI, m/z): 818.9 (M⁺); 615.4 (M⁺-NC₂(Ph)HCH₂CO₂CH₃). Calcd. for C₄₇H₄₄P₂O₂BrRu: C: 62.52, H: 4.79, Found: C: 62.68, H: 4.82.

3.9. Synthesis of the N-Coordinated Complexes [(η⁵-C₉H₇)(dppe)Ru–NCCH(Ph)CH₂CO₂C₂H₅][I] (3c)

Compound 2c (0.11 g, 0.14 mmol) and TMSN₃ (0.1 mL, 0.76 mmol) in THF (7 mL) were stirred overnight at room temperature. The purification method described for 3a yielded yellow solid product 3c in 64% yield (0.07 g, 0.09 mmol). ¹H-NMR (CDCl₃): δ 7.50–7.19 (m, 25H of Ph); 6.54, 6.53, 6.52 (m, 1H each one, H of indenyl group); 6.10 (1H, H of indenyl group); 5.02, 4.95, 4.91 (br, 1H each one, H of indenyl group); 4.04 (t, 1H, J₇=J₁₁ = 5.1 Hz, NCC₃H₃(CH)CH₂); 3.98 (q, 2H, J₇=J₁₁ = 7.1 Hz, OCH₂); 2.48, 2.20 (m, 4H, 2CH₂ of dppe); 2.18, 2.16 (m, 1H each one, CH(Ph)CH₂); 1.20 (t, 3H, J₇=J₁₁ = 7.1 Hz, CH₃). ³¹P-NMR (CDCl₃): δ 83.5, 82.2 (AX, Jₚ₋ₚ = 26.9 Hz). ¹³C-NMR (CDCl₃): 171.2 (CO); 132.8–125.4 (Ph); 123.6 (NCC); 111.1, 109.3 (C of indenyl group); 93.7 (C of indenyl group); 67.2, 66.8 (C of indenyl group); 52.2 (CH₂); 35.1 (CH₃); 27.4 (CH₂ of dppe). HRMS (ESI, m/z): 818.9 (M⁺); 615.4 (M⁺-NC₂(Ph)HCH₂CO₂C₂H₅). Calcd. for C₄₇H₄₄P₂O₂I: C: 59.75, H: 4.69, Found: C: 59.81, H: 4.73.
3.10. Synthesis of the N-Coordinated Complexes \([(\eta^5-C_9H_7)(dppe)Ru–NCCH(Ph)CH_2CH=CH_2CO_2CH_3]\) [Br] (3d)

Compound 2d (0.12 g, 0.15 mmol) and TMSN\(_3\) (0.1 mL, 0.76 mmol) in THF (7 mL) were stirred overnight at room temperature. The purification method described for 3a yielded yellow solid product 3d in 60% yield (0.08 g, 0.09 mmol). 1H-NMR (CDCl\(_3\)): \(\delta\) 7.49–7.15 (m, 25H of Ph); 7.08, 6.92 (m, 2H, H of indenyl group); 6.39 (m, 1H, CH\(_2\)CH); 5.3 (d, 1H, \(J_{H-H} = 15.6\) Hz, CHC\(_{\text{H}}\)CO); 5.08, 4.96, 4.83 (br, 1H each one, H of indenyl group); 2.19 (m, 2H, CH\(_2\)CH); 2.16 (m, 4H, 2CH\(_2\) of dppe). 31P-NMR (CDCl\(_3\)): \(\delta\) 83.9, 81.2 (AX, \(J_{P-P} = 26.8\) Hz). 13C-NMR (CDCl\(_3\)): 168.8 (C=O); 137.2–125.4 (Ph); 132.7 (CH\(_2\)CH); 123.1 (NCCH(Ph)CH\(_2\)); 122.5 (CHCO); 106.9, 105.3 (C of indenyl group); 91.8 (C of indenyl group); 68.8 (C of indenyl group); 51.3 (OCH\(_3\)); 38.4 (CH\(_3\)CH(Ph)); 37.5 (NCH(Ph)CH\(_2\)); 28.4 (CH\(_2\) of dppe). HRMS (ESI, m/z): 830.1 (M+); 615.5 (M+-NC\(_2\)(Ph)CH\(_2\)CH=CHCO\(_2\)CH\(_3\)). Anal. Calcd. for C\(_{48}\)H\(_{44}\)O\(_2\)P\(_2\)BrNRu: C:63.37, H: 4.87, Found: C: 63.48, H: 4.89.

3.11. Synthesis of the N-Coordinated Complexes \([(\eta^5-C_9H_7)(dppe)Ru–NCCH(Ph)CH_2C≡CH]\) [Br] (3e)

Compound 2e (0.102 g, 0.135 mmol) and TMSN\(_3\) (0.1 mL, 0.76 mmol) in THF (7 mL) were stirred overnight at room temperature. The purification method described for 3a yielded yellow solid product 3e in 66% yield (0.069 g, 0.089 mmol). 1H-NMR (CDCl\(_3\)): \(\delta\) 7.70–7.21 (m, 25H of Ph); 7.10, 7.07 (m, 1H each one, H of indenyl group); 6.64 (2H, H of indenyl group); 5.11, 4.98, 4.91 (br, 1H each one, H of indenyl group); 3.99 (br, 1H, NCC\(_{\text{H}}\)CH(Ph)CH\(_2\)); 2.74, 2.53 (m, 4H, 2CH\(_2\) of dppe); 2.20, (1H, C≡CH); 2.10, 1.99 (m, 1H each one, CH(Ph)CH\(_2\)). 31P-NMR (CDCl\(_3\)): \(\delta\) 83.22, 82.17 (AX, \(J_{P-P} = 26.91\) Hz). 13C-NMR (CDCl\(_3\)): 132.5–128.1 (Ph); 124.9 (C-5, 6); 123.5 (CN); 121.8 (C-4, 7); 112.3 (Cβ); 97.2 (C-2); 84.1 (C-1, 3); 82.3 (CH\(_2\)C=C); 71.9 (C=CH); 27.2 (m CH\(_2\) of dppe); 25.3 (CH\(_3\)). HRMS (ESI, m/z): 771.4 (M++1); 615.7 (M+-NC\(_2\)(Ph)CH\(_2\)CH=CHCO\(_2\)CH\(_3\)). Anal. Calcd. for C\(_{46}\)H\(_{40}\)P\(_2\)BrNRu: C: 65.02, H: 4.74, Found: C: 65.06, H: 4.77.

3.12. Synthesis of Cyclopropenylruthenium Complex \([(\eta^5-C_9H_7)(dppe)Ru–C=C(Ph)CH-CH=CH\(_2\)]\) (4a)

To a solution of 2a (0.27 g, 0.04 mmol) in acetone (10 mL) was added a solution of \(n\)-Bu\(_4\)NOH (2 mL, 2 mmol, 1M in MeOH). After the mixture was stirred at room temperature for 10 hours, the resulting solution was concentrated to about 0.5 mL. Then CH\(_3\)CN (5 mL) was added, the yellow precipitate thus formed was filtered off and washed with CH\(_3\)CN and dried under vacuum to give the product 4a (0.23 g, 0.03 mmol in 75% yield. 1H-NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 7.49–6.64 (m, 29H, 25H of Ph, 4H of indenyl group); 5.70 (br, 2H, H of indenyl group); 5.41 (d, 1H, \(J_{H-H} = 16.6\) Hz, H of CH=CH\(_2\)); 5.24 (m, 1H, CH=CH\(_2\)); 5.15 (br, 1H, H of indenyl group); 4.99 (d, 1H, \(J_{H-H} = 8.5\) Hz, H of CH=CH\(_2\)); 2.52, 2.34, 2.30 (m, 4H, 2CH\(_2\) of dppe); 1.88 (s, 1H, CH=CH\(_2\)). 31P-NMR (CD\(_2\)Cl\(_2\)): \(\delta\) 94.3, 89.3 (AX, \(J_{P-P} = 23.8\) Hz). 13C-NMR (CD\(_2\)Cl\(_2\)): 134.3–124.7 (Ph); 128.1 (CH=CH\(_2\)); 116.5 (Ca, \(J_{C-P} = 10.1\) Hz); 114.3 (CH=CH); 111.2 (C-5, 6); 106.4 (C-4, 7); 95.2 (C-2); 77.6 (C-1, 3); 26.4 (t, \(J_{C-P} = 18.4\) Hz, CH\(_2\) of dppe); 15.8 (CH). HRMS (ESI, m/z): 756.3 (M\(^+\)); 614.7 (M\(^+-\)C\(_2\)(Ph)CH=CH=CH\(_2\)). Calcd. for C\(_{46}\)H\(_{40}\)P\(_2\)Ru: C: 73.10, H: 5.33, Found: C: 73.15, H: 5.37.
A sample of 2b (0.25 g, 0.32 mmol) was dissolved in acetone (10 mL) at room temperature. A methanol solution of n-Bu$_4$NOH (2 mL, 2 mmol, 1M in MeOH) was added. After the mixture stirred for 4 hours, the resulting solution was concentrated to about 0.5 mL. Then CH$_3$CN (5 mL) was added and the yellow precipitate thus formed was filtered off and washed with CH$_3$CN. The product was dried under vacuum and identified as 4b (0.21 g, 0.27 mmol) in 84% yield. $^1$H-NMR (C$_6$D$_6$): $\delta$ 7.21–6.66 (m, 25H of Ph, 4H of indenyl group); 5.43 (br, 1H, H of indenyl group); 5.15 (s, 1H, CH); 4.78 (br, 2H, H-1, 3 of indenyl group); 2.89 (s, 3H, OCH$_3$); 2.73, 2.00 (m, 2H each one, 2CH$_2$ of dppe). $^{31}$P-NMR (C$_6$D$_6$): $\delta$ 96.7. $^{13}$C-NMR (C$_6$D$_6$): 167.5 (CO); 140.3 (Ca, $J_{C-P}$ = 16.3 Hz); 138.5–126.8 (Ph); 127.7 (=CH); 125.6 112.3 (C-5, 6); 106.2 (C-4, 7); 95.1 (C-2); 78.4 (C-1, 3); 53.1 (OCH$_3$); 28.5 (t, $J_{C-P}$ = 19.7 Hz, CH$_2$ of dppe). HRMS (ESI, $m/z$): 788.3 (M$^+$); 615.4 (M$^+$-C$_2$(Ph)CHCO$_2$CH$_3$). Calcd. for C$_{46}$H$_{40}$P$_2$O$_2$Ru: C: 70.13, H: 5.12, Found: C: 70.21, H: 5.15.

By monitoring the reaction using $^{31}$P-NMR spectroscopy, the kinetic cyclopropenylruthenium product 5b was observed at the initial stage of the reaction, which gets converted to 4b in acetone within 2 hours at room temperature.

Spectroscopic data for 5b are as follows: $^1$H-NMR (C$_6$D$_6$): $\delta$ 8.05–6.81 (m, 25H of Ph, 4H of indenyl group); 6.66 (m, 2H, H of indenyl group); 6.49, 5.35, 4.86 (br, 1H, H of indenyl group); 3.65 (s, 3H, OCH$_3$); 2.65, 1.84 (m, 2H each one, 2CH$_2$ of dppe); 1.37 (s, 1H, CH). $^{31}$P-NMR (C$_6$D$_6$): $\delta$ 93.8, 88.5 (AX, $J_{P-P}$ = 26.1 Hz).

3.14. Synthesis of Furylruthenium Complex ($\eta^5$-C$_9$H$_7$)(dppe)Ru–C=C(Ph)CH=C(OCH$_3$)O (4c)

Compound 2c (0.24 g, 0.29 mmol) and n-Bu$_4$NOH (2 mL, 2 mmol, 1 M in MeOH) were stirred for 4 hours in acetone (10 mL) at room temperature. The purification method described for 4a yielded yellow solid product 4c in 83% yield (0.19 g, 0.24 mmol). $^1$H-NMR (C$_6$D$_6$): $\delta$ 7.48–6.66 (m, 29H of Ph, 4H of indenyl group); 5.43(br, 1H, H of indenyl group), 4.76 (s, 1H, CH); 4.78; (br, 2H, H of indenyl group), 2.89 (q, 2H, $J_{H-H}$ = 7.1 Hz, OCH$_2$); 2.73, 2.17 (m, 2H each one, 2CH$_2$ of dppe); 0.86 (t, 3H, $J_{H-H}$ = 7.1 Hz, CH$_3$). $^{31}$P-NMR (C$_6$D$_6$): $\delta$ 96.4. $^{13}$C-NMR (C$_6$D$_6$): 167.5 (CO); 138.4 (Ca, $J_{C-P}$ = 15.1 Hz); 136.2–127.2 (Ph); 128.5 (=CH); 124.2 117.6 (C-5, 6); 108.8 (C-4, 7); 98.7 (C-2); 80.3 (C-1, 3); 38.2 (OCH$_2$); 29.4 (t, $J_{C-P}$ = 18.3 Hz, CH$_2$ of dppe); 15.6 (CH$_3$). HRMS (ESI, $m/z$): 802.2 (M$^+$); 615.3 (M$^+$-C$_2$(Ph)CHCO$_2$C$_2$H$_5$). Calcd. for C$_{47}$H$_{42}$P$_2$O$_2$Ru: C: 70.51, H: 5.31. By monitoring the reaction using $^{31}$P-NMR spectroscopy, kinetic cyclopropenylruthenium product 5c was observed at the initial stage of the reaction which gets converted to 4c in acetone within 2 hours at room temperature. Spectroscopic data for 5c are as follows: $^1$H-NMR (C$_6$D$_6$): $\delta$ 7.84–6.53 (m, 27H of Ph, 2H of indenyl group); 6.52 (m, 2H, H of indenyl group); 6.34, 5.72, 5.11 (br, 1H, H of indenyl group); 3.81(q, 2H, $J_{H-H}$ = 6.8 Hz, OCH$_2$); 2.87, 1.93 (m, 2H each one, 2CH$_2$ of dppe); 1.24 (s, 1H, CH); 1.05 (t, 3H, $J_{H-H}$ = 6.8 Hz, CH$_3$). $^{31}$P-NMR (C$_6$D$_6$): $\delta$ 92.4, 89.1 (AX, $J_{P-P}$ = 24.3 Hz).
3.15. Synthesis of Cyclopropenylruthenium Complex (η^5-C9H7)(dppe)Ru–C=C(Ph)CHCH=CHC(O)OCH3 (4d)

Compound 2d (0.24 g, 0.29 mmol) and n-Bu4NOH (2 mL, 2 mmol, 1 M in MeOH) were stirred for 10 hours in acetone (10 mL) at room temperature. The purification method described for 4a yielded yellow solid product 4d in 79% yield (0.19 g, 0.23 mmol). 1H-NMR (C6D6): δ 7.38–6.85 (m, 28H, 25H of Ph, 2H of indenyl group, 1H of C=CHOC); 6.48 (br, 2H, H of indenyl group); 6.35 (m, 1H, C=CH=CHC(O)); 5.43, 5.35, 5.01 (br, 1H each one, H of indenyl group); 3.58 (s, 1H, OCH3); 2.47, 2.41, 1.85 (m, 4H, 2CH2 of dppe); 1.30 (s, 1H, C=CH=CHC(O)). 31P-NMR (C6D6): δ 92.7, 89.9 (AX, Jp-p = 24.7 Hz). 13C-NMR (CDCl3): 171.3 (=CH); 169.2 (CO); 133.1–128.7 (Ph); 117.4 (=CH); 111.8 (C-5, 6); 107.4 (C-4, 7); 96.3 (C-2); 76.9 (C-1, 3); 55.2 (OCH3); 34.3 (CH2 of dppe). HRMS (ESI, m/z): 814.1 (M+); 615.2 (M+-C2(Ph)CHCHCO2CH3). Calcd. for C48H42P2O2Ru: C: 70.84, H: 5.20, Found: C: 70.96, H: 5.24.

3.16. Reaction of 4a with TMSN3

To a solution of 4a (0.15 g, 0.20 mmol) in THF (5 mL) was added TMSN3 (0.1 mL, 0.76 mmol). The solution was stirred overnight at room temperature. The orange precipitates thus formed were filtered off and washed with hexane and identified as [Ru]-CN (0.08 g, 0.12 mmol) in 60% yield. The organic product was extracted with hexane and collected by extraction with hexane and purified by chromatography, then, the solvent was removed under vacuum to give 6a (0.015 g, 0.087 mmol, 44% yield). Spectroscopic data for 6a are as follows [37]. 1H-NMR (CDCl3): δ 7.35–7.12 (m, 5H, H of Ph group); 2.75 (q, 2H, CH2, JH-H = 7.3 Hz); 1.31 (t, 3H, CH3, JH-H = 7.3 Hz). High resolution MS: 173.1(M+). Calcd. for C10H11N3: C: 69.34, H: 6.40, Found: C: 69.36, H: 6.41. Spectroscopic data for [Ru]–CN are as follows: 1H-NMR (CDCl3): δ 7.40–7.01 (m, 22H, 20H of Ph group and 2H of indenyl group); 6.99 (m, 2H, H-4,7 of indenyl group); 5.18 (br, 1H, H-2 of indenyl group); 4.97 (d, 2H, JH-H = 2.1 Hz, H-1,3 of indenyl group); 2.55, 2.28 (m, 2H each one, CH2 of dppe). 31P-NMR (CDCl3): δ 86.2.

3.17. Reaction of 4b with TMSN3

Compound 4b (0.15 g, 0.19 mmol) and in TMSN3 (0.1 mL, 0.76 mmol) were stirred overnight at room temperature in THF (5 mL). The purification method described for 6a yielded an orange precipitate of [Ru]-N3 (0.10 g, 0.15 mmol) in 79% yield and the organic product 6b (0.02 g, 0.11 mmol) in 58% yield. Spectroscopic data for 6b are as follows: 1H-NMR (CDCl3): δ 7.25–7.11 (m, 5H, H of Ph group); 3.85 (dd, 1H, CH3(Ph), JH-H = 6.2, 7.9 Hz); 3.32 (s, 3H, OCH3); 2.52, 2.31 (AB, 2H, CH2, JH-H = 7.9, 16.3 Hz and JH-H = 6.2, 16.3 Hz). 13C-NMR (CDCl3): δ 171.2 (CO2); 132.1–128.4 (Ph); 120.2 (CN); 52.4 (OCH3); 38.8 (CH2); 31.3 (CH). HRMS: 189.2 (M+). Calcd. for C11H11O2N: C: 69.83, H: 5.86, Found: C: 69.88, H: 5.87.
3.18. Reaction of 4c with TMSN₃

Compound 4c (0.18 g, 0.20 mmol) and in TMSN₃ (0.1 mL, 0.76 mmol) were stirred overnight at room temperature in THF (5 mL). The purification method described for 6a yielded an orange precipitate of [Ru–N₃] (0.08 g, 0.12 mmol) in 60% yield and the organic product 6c (0.02 g, 0.09 mmol) in 45% yield. Spectroscopic data for 6c are as follows: ¹H-NMR (CDCl₃): δ 7.32–7.24 (m, 5H, H of Ph group); 4.12 (dd, 1H, CH(Ph), J₆₋₇ = 7.2, 8.1 Hz); 3.57 (q, 2H, OCH₂, J₆₋₇ = 7.8 Hz); 2.58, 2.46 (AB, 2H, CH₂, J₆₋₇ = 8.1, 16.6 Hz and J₆₋₇ = 7.2, 16.6 Hz); 1.3 (t, 3H, CH₃, J₆₋₇ = 7.8 Hz). ¹³C-NMR (CDCl₃): δ 169.4 (CO₂); 134.3–125.1 (Ph); 118.1 (CN); 51.7 (OCH₂); 39.4 (CH₂); 33.7 (CH); 15.4 (CH₃). HRMS: 203.1 (M⁺). Calcd. for C₁₂H₁₃O₂N: C: 70.92, H: 6.45, Found: C: 70.94, H: 6.46.

3.19. Reaction of 4d with TMSN₃

Compound 4d (0.15 g, 0.18 mmol) and in TMSN₃ (0.1 mL, 0.76 mmol) were stirred overnight at room temperature in THF (5 mL). The purification method described for 6a yielded an orange precipitate of [Ru–CN] (0.07 g, 0.11 mmol) in 61% yield and the organic product 6d (0.017 g, 0.074 mmol) in 41% yield. Spectroscopic data for 6d are as follows [52]: ¹H-NMR (CDCl₃): δ 7.42–7.23 (m, 5H, H of Ph group); 3.51 (s, 3H, OCH₃); 3.11 (t, 2H, CH₂, J₆₋₇ = 7.2 Hz); 2.74 (t, 2H, CH₂, J₆₋₇ = 7.2 Hz). HRMS: 231.1 (M⁺). Calcd. for C₁₂H₁₃O₂N₃: C: 62.33, H: 5.67, Found: C: 62.34, H: 5.68.

3.20. X-ray Analysis of 2a and 3a

Crystal data and refinement parameters for complexes 2a and 3a are listed in Table 3. CCDC-776702, 776705 (see Table 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

4. Conclusions

Ruthenium vinylidene complexes containing indenyl and dppe ligands and unsaturated bonds at C₅ can be synthesized in good yield. Reaction of these vinylidene complexes with TMSN₃ yielded N-coordinated complexes as the stable products. Deprotonation of vinylidene complexes containing allyl or crotonate group at C₅ yielded cyclopropenylruthenium complexes as a single product. When an ester group is at C₅, furyl ruthenium complexes can be obtained as the thermodynamic products. The corresponding kinetic cyclopropenylruthenium products can be observed in the initial stage. Reaction of the cyclopropenylruthenium complexes with TMSN₃ yielded [Ru–CN], and the corresponding organic compounds via transformation of the vinyl group to an ethyl group. Reaction of the furyl ruthenium complexes with TMSN₃ yielded [Ru–N₃], and the corresponding organic compounds via opening the five-membered ring to form the N-coordinated intermediate.

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References

1. Bruce, M.I. Organometallic chemistry of vinylidene and related unsaturated carbenes. *Chem. Rev.* **1991**, *91*, 197–257.
2. Bruce, M.I. Transition Metal Complexes Containing Allenylidene, Cumulenylidene, and Related Ligands. *Chem. Rev.* **1998**, *98*, 2797–2858.
3. Trost, B.M.; McClory, A. Metal Vinylidenes as Catalytic Species in Organic Reactions. *Chem. Asian J.* **2008**, *3*, 164–194.
4. Davies, S.G.; McNally, J.P.; Smallridge, A.J. Chemistry of the Cyclopentadienyl Bisphosphere Ruthenium Auxiliary. *Adv. Organomet. Chem.* **1990**, *30*, 1–76.
5. Cadierno, V.; Gamasa, M.P.; Gimeno, J. Synthesis and reactivity of α,β-unsaturated alkylidene and cumulenylidene Group 8 half-sandwich complexes. *Coord. Chem. Rev.* **2004**, *248*, 1627–1657.
6. Alonso, F.; Beletskaya, I.P.; Yus, M. Transition-Metal-Catalyzed Addition of Heteroatom-Hydrogen Bonds to Alkynes. *Chem. Rev.* **2004**, *104*, 3079–3160.
7. Bruneau, C.; Dixneuf, P.H. Metal Vinylidenes in Catalysis. *Accounts Chem. Res.* **1999**, *32*, 311–323.
8. Trost, B.M.; Toste, F.D.; Pinkerton, A.B. Non-Metathesis Ruthenium-Catalyzed C-C Bond Formation. *Chem. Rev.* **2001**, *101*, 2067–2096.
9. Bruce, M.I.; Swincer, A.G. Vinylidene and Propadienylidene (Allenylidene) Metal Complexes. *Adv. Organomet. Chem.* **1983**, *22*, 59–128.
10. Rigaut, S.; Touchard, D.; Dixneuf, P.H. Ruthenium-allenylidene complexes and their specific behavior. *Coord. Chem. Rev.* **2004**, *248*, 1585–1601.
11. Werner, H.; Weinhand, R.; Knaup, W. Vinylidene transition-metal complexes. 18. (Arene)osmium complexes containing alknyn, vinyl, vinylidene, and thio- and selenoketene units as ligands: A series of organometallic compounds built up from 1-alkynes. *Organometallics* **1991**, *10*, 3967–3977.
12. Rappert, T.O.; Mahr, N.; Wolf, J.; Werner, H. Vinylidene transition-metal complexes. Synthesis, reactivity, and structure of four-coordinate (vinylvinylidene)- and five- and six-coordinate enynyl(hydrido)rhodium complexes with [RhCl(P^3Pr_3)_2] as a molecular unit. *Organometallics* **1992**, *11*, 4156–4164.
13. Puerta, M.C.; Valerga, P. Ruthenium and osmium vinylidene complexes and some related compounds. *Coord. Chem. Rev.* **1999**, *193–195*, 977–1025.
14. Wakatsuki, Y. Mechanistic aspects regarding the formation of metal vinylidenes from alkynes and related reactions. *J. Organomet. Chem.* **2004**, *689*, 4092–4109.
15. Ghazala, S.I.; Paul, F.; Toupet, L.; Roisnel, T.; Hapiot, P.; Lapinte, C. Di-organoiron Mixed Valent Complexes Featuring “(η^2-dppe)( η^1-C_3H_5)Fe” Endgroups: Smooth Class-III to Class-II Transition Induced by Successive Insertion of 1,4-Phenylenes Units in a Butadiyne-Diyl Bridge. *J. Am. Chem. Soc.* **2006**, *128*, 2463–2476.
16. Basallote, M.G.; Besora, M.; Duran, J.; Fernandez-Trujillo, M.J.; Lledos, A.; Manez, M.A.; Maseras, F. The Effect of the “Inert” Counteranions in the Deprotonation of the Dihydrogen Complex trans-[FeH(η²-H₂)(dppe)$_2$]$^+$. Kinetic and Theoretical Studies. *F. J. Am. Chem. Soc.* **2004**, *126*, 2320–2321.

17. Narvor, N.L.; Toupet, L.; Lapinte, C. Elemental Carbon Chain Bridging Two Iron Centers: Syntheses and Spectroscopic Properties of [Cp*(dppe)Fe-C₄-FeCp*(dppe)]$^{n+}$·n[PF₆]$^-$. X-ray Crystal Structure of the Mixed Valence Complex (n = 1). *J. Am. Chem. Soc.* **1995**, *117*, 7129–7138.

18. Adams, R.D.; Davison, A.; Selegue, J.P. Cationic vinylidene complexes. Preparation and structural characterization of (η⁵-cyclopentadienyl)(2-methyl-4,5-bis(diphenylphosphino)-2-penten-3-yl)iron (II). A base-induced interligand reaction in a vinylidene complex. *J. Am. Chem. Soc.* **1979**, *101*, 7232–7238.

19. Sung, H.-L.; Hsu, H.-L. The reactivity of TMSN3 with ruthenium cyclopropenyl complexes containing different ligands and different substituent at Cγ. *J. Organomet. Chem.* **2011**, *696*, 1280–1288.

20. Tanase, T.; Mochizuki, H.; Sato, R.; Yamamoto, Y. Formation of nitriles by a novel metathesis reaction of ruthenium σ-acetylilide complexes, (η⁵-indenyl)Ru(η¹-C≡CR)(phosphine)$_2$, with nitric oxide. *J. Organomet. Chem.* **1994**, *466*, 233–236.

21. Hill, A.F.; Hulkes, A.G.; White, A.J.P.; Williams, D.J. Selenolatovinylidene Complexes: Metal-Mediated Alkynyl Selenoether Rearrangements. *Organometallics* **2000**, *19*, 371–373.

22. Bruce, M.I.; Ellis, B.G.; Low, P.J.; Skelton, B.W.; White, A.H. Syntheses, Structures, and Spectro-electrochemistry of {Cp*(PP)Ru}CCC C{Ru(PP)Cp*} (PP = dppm, dppe) and Their Mono- and Dications. *Organometallics* **2003**, *22*, 3184–3198.

23. Cadierno, V.; Gamasa, M.P.; Gimeno, J.; Perez-Carreno, E.; Garcia-Granda, S. A Novel Route to Functionalized Terminal Alkynes through η¹-Vinylidene to η²-Alkyne Tautomerizations in Indenyl–Ruthenium(II) Monosubstituted Vinylidene Complexes: Synthetic and Theoretical Studies. *Organometallics* **1999**, *18*, 2821–2832.

24. Cadierno, V.; Gamasa, M.P.; Gimeno, J.; Gonzalez-Bernardo, C. Reactivity of Indenyl-Ruthenium(II) Vinylidene Complexes: Selective Synthesis of Alkenyl-Phosphonio Derivatives via Nucleophilic Addition of Triphenylphosphine on Their η²-Alkyne Tautomers. Theoretical Study of the η¹-Vinylidene-η²-Alkyne Tautomerization. *Organometallics* **2001**, *20*, 5177–5188.

25. Gamasa, M.P.; Gimeno, J.; Martin-Vaca, M.B.; Borge, J.; Garcia-Granda, S.; Perez-Carreno, E. Synthesis and Characterization of (Alkyny1)-, (Vinylidene)-, and (Carbene) ruthenium Indenyl Complexes: X-ray Crystal Structure of [Ru(C=CMe₂)(η⁵-C₅H₇)(PF₃)$_2$][CF₃SO$_2$]•1/2CH₂Cl₂ and EHMO Calculation. *Organometallics* **1994**, *13*, 4045–4057.

26. Cadierno, V.; Gamasa, M.P.; Gimeno, J.; Borge, J.; Garcia-Granda, S. Selective Synthesis of Indenylruthenium(II) Vinylvinylidene Complexes via Unstable Allenylidene Intermediates: Unexpected Formation of Alkenyl-Phosphonio Complexes (E)-[Ru{C(H)=C(PPh₃)R}(η⁵-C₅H₇)PPh₃]$_2$[PF₆](R=1-Cyclohexenyl, 1-Cycloheptenyl) through Nucleophilic Addition of Triphenylphosphine on Vinylvinylidene Derivatives. *Organometallics* **1997**, *16*, 3178–3187.

27. Davison, A.; Solar, J.P. The reactivity of cyclopentadienylcarbonyliron acetylides with electrophiles: The isolation of a 1,3-dimetallo-stabilized cyclobutenium ion and a cationic “vinylidene”. *J. Organomet. Chem.* **1978**, *155*, C8–C12.
28. Jolly, P.W.; Pettit, R. 1-(\(\pi\)-Cyclopentadienyliron dicarbonyl)propyne. *J. Organomet. Chem.* 1968, 12, 491–495.

29. Bell, R.A.; Chisholm, M.H.; Couch, D.A.; Rankel, L.A. Reactions of alkyne- and alkenylplatinum(II) compounds. 1. Formation of alkoxy carbene ligands within the coordination sphere of platinum. *Inorg. Chem.* 1977, 16, 677–686.

30. Bell, R.A.; Chisholm, M.H. Reactions of Furylruthenium Complexes with Oxygen and Trimethylsilyl Azide. *Inorg. Chem.* 1977, 16, 687–697.

31. Gamasa, M.P.; Gimeno, J.; Lastra, E.; Lanfranchi, M.; Tiripicchio, A. Reactions of cationic vinylidene complexes [Fe{\(\equiv\)C=C(R1)R2}(\(\eta^5\)-C5H5)(dppm)]+ [dppm=bis(diphenylphosphino)methane] with nucleophiles: Stereoselective synthesis and crystal structure of the alkenyl complex (E)-[Fe{C(H)=C(Me)Ph}(\(\eta^5\)-C5H5)(dppm)]. *J. Organomet. Chem.* 1992, 430, C39–C43.

32. Kostic, N.M.; Fenske, R.F. Molecular orbital study of bonding, conformations, and reactivity of transition-metal complexes containing unsaturated organic ligands. Electrophilic and nucleophilic additions to acetylide, vinylidene, vinyl, and carbene ligands. *Organometallics* 1982, 1, 974–982.

33. Werner, H.; Wolf, J.; Muller, G.; Kruger, C. Ambidentate Behavior of Mononuclear Vinylidenerhodium Complexes—Novel CC Coupling of a Methyl to a Vinylidene Group. *Angew. Chem. Int. Ed. Engl.* 1984, 23, 431–432.

34. Bruce, M.I.; Swincer, A.G. Cyclopentadienyl-ruthenium and -osmium chemistry. X. Reactions of vinylidene complexes with alcohols and water: Syntheses of alkoxy(alkyl)carbene, acyl and alkyl complexes. *Aust. J. Chem.* 1980, 33, 1471–1483.

35. Barrett, A.G.M.; Carpenter, N.E.; Sabat, M.J. Isolation of [\(\text{Cp(CO)(Ph}_3\text{P)FeNCCH}_3\text{]+BF}_4\text{−}\) from a vinylidene precursor; an organometallic Beckmann rearrangement. *Organomet. Chem.* 1988, 352, C8–C12.

36. Chang, K.H.; Lin, Y.C. Reactions of ruthenium cyclopropenyl complexes with trimethylsilyl azide. *Chem. Commun.* 1998, 21, 1441–1442.

37. Chang, K.H.; Lin, Y.C.; Liu, Y.H.; Wang, Y. Reactions of ruthenium cyclopropenyl complexes with trimethylsilyl azide. *J. Chem. Soc. Dalton Trans.* 2001, 21, 3154–3159.

38. Chang, C.W.; Lin, Y.C.; Lee, G.-H.; Huang, S.L.; Wang, Y. Reactions of Ruthenium Acetylide Complexes with Isothiocyanate. *Organometallics* 1998, 17, 2534–2542.

39. Kawata, Y.; Sato, M. Double Deprotonation of a Cationic Ruthenium(II) Terminal Vinylidene Complex and Molecular Structures of the Terminal Vinylidene Complex [(\(\eta^5\)-C5Me5)(PPh3)2Ru(CCH2)]PF6 and the Acetylide Complex (\(\eta^5\)-C5Me5)(PPh3)2Ru(CCSiMe3). *Organometallics* 1997, 16, 1093–1096.

40. Huisgen, R. Descriptive reactions of organic alkynes with azide. In *1,3-Dipolar Cycloadditions Chemistry*; Padwa, A., Ed.; Wiley: New York, NY, USA, 1984; Volume 1, pp. 1–176.

41. Maiorana, S.; Pocar, D.; Croce, P.D. Studies in the enamine field reactions of sulfonyl- and nitro-enamines with azides. *Tetrahedron Lett.* 1966, 7, 6043–6045.

42. Meek, J.S.; Fowler, J. Nucleophilic addition-elimination reactions of 1,2-bis(p-tolylsulfonyl)ethane. *J. Org. Chem.* 1968, 33, 985–991.

43. Gouault, N.; Cupif, J.F.; Sauleau, A.; David, M. \(\gamma\)-Methyl-substituted-\(\gamma\)-butyrolactones: Solid-phase synthesis employing a cyclisation-cleavage strategy. *Tetrahedron Lett.* 2000, 41, 7293–7297.
44. Rostovtsec, V.V.; Green, L.G.; Fokin, V.V.; Sharpless, K.B. A Stepwise Huisgen Cycloaddition Process: Copper(I)-Catalyzed Regioselective “Ligation” of Azides and Terminal Alkynes. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 2596–2599.

45. Raghavendra, M.S.; Lam, Y. Regiospecific solid-phase synthesis of substituted 1,2,3-triazoles. *Tetrahedron Lett.* **2004**, *45*, 6129–6132.

46. Krasinski, A.; Fokin, V.V.; Sharpless, K.B. Direct Synthesis of 1,5-Disubstituted-4-magnesio-1,2,3-triazoles. *Org. Lett.* **2004**, *6*, 1237–1240.

47. Amantini, D.; Fringuelli, F.; Piermatti, O.; Pizzo, F.; Zunino, E.; Vaccaro, L. Synthesis of 4-Aryl-1H-1,2,3-triazoles through TBAF-Catalyzed [3+2] Cycloaddition of 2-Aryl-1-nitroethenes with TMSN3 under Solvent-Free Conditions. *J. Org. Chem.* **2005**, *70*, 6526–6529.

48. Coats, S.J.; Link, J.S.; Gauthier, D.; Hlasta, D.J. Trimethylsilyl-Directed 1,3-Dipolar Cycloaddition Reactions in the Solid-Phase Synthesis of 1,2,3-Triazoles. *Org. Lett.* **2005**, *7*, 1469–1472.

49. Huang, C.C.; Lin, Y.C.; Huang, S.L.; Liu, Y.H.; Wang, Y. Synthesis of Dinuclear and Trinuclear Ruthenium Cyclopropenyl Complexes. *Organometallics* **2003**, *22*, 1512–1518.

50. Chang, C.W.; Lin, Y.C.; Lee, G.H.; Wang, Y. Reactions of Ruthenium Cyclopropenyl Complexes Containing Pentamethylcyclopentadienyl Ligands. *Organometallics* **2000**, *19*, 3211–3219.

51. Lo, Y.H.; Lin, Y.C.; Lee, G.H.; Wang, Y. Synthesis and Reactivity of the Ruthenium Cyclopropenyl Complex with aTp Ligand. *Organometallics* **1999**, *18*, 982–988.

52. Ting, P.C.; Lin, Y.C.; Lee, G.H.; Cheng, M.C.; Wang, Y. Cyclopropenation and Related Reactions of Ruthenium Vinylidene Complexes. *J. Am. Chem. Soc.* **1996**, *118*, 6433–6444.

53. Ting, P.C.; Lin, Y.C.; Cheng, M.C.; Wang, Y. Novel Method for the Preparation of Metal Cyclopropenyl Complexes from Vinylidene Complexes with an Electron-Withdrawing Substituent. *Organometallics* **1994**, *13*, 2150–2152.

54. Yen, Y.S.; Lin, Y.C.; Liu, Y.H.; Wang, Y. Deprotonation of Iron Vinylidene Complexes Containing a dppe Ligand. *Organometallics* **2007**, *26*, 1250–1255.

55. Alvarez, P.; Lastra, E.; Gimeno, J.; Bassetti, M.; Falvello, L.R. Formation of a Cyclobutylidene Ring: Intramolecular [2+2] Cycloaddition of Allyl and Vinylidene CC Bonds under Mild Conditions. *J. Am. Chem. Soc.* **2003**, *125*, 2386–2387.

56. Chang, K.H.; Sung, H.L.; Lin, Y.C. Reactions of Furylruthenium Complexes with Oxygen and Trimethylsilyl Azide. *Eur. J. Inorg. Chem.* **2006**, *3*, 649–655.

57. Lo, Y.H.; Lin, Y.C.; Huang, C.C. Synthesis and reactivity of ruthenium tetrazolate complexes containing a tris(pyrazolyl)borato (Tp) ligand. *J. Organomet. Chem.* **2008**, *693*, 117–127.

58. Chang, K.H.; Lin, Y.C. Reactions of ruthenium cyclopropenyl complexes with trimethylsilyl azide. *Chem. Commun.* **1998**, *14*, 1441–1442.

59. Selnau, H.E.; Merola, J.S. Reactions of iridium complex [Ir(COD)(PMe3)3]Cl with benzene, pyridine, furan, and thiophene: Carbon-hydrogen cleavage vs. ring opening. *Organometallics* **1993**, *12*, 1583–1591.

*Sample Availability*: Samples of complexes 2–5 are available from the authors.

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