Journal of Organometallic Chemistry 696 (2011) 1280–1288

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

The reactivity of $TMSN_3$ with ruthenium cyclopropenyl complexes containing different ligands and different substituent at Cγ

Hui-Ling Sung [a,*], Hsiu-Ling Hsu [b]

[a] Department of Mathematics and Science (Pre-college), National Taiwan Normal University, Linkou, Taiwan, ROC
[b] Department of Chemical and Materials Engineering, Lunghwa University of Science and Technology, Taoyuan, Taiwan, ROC

ARTICLE INFO

Article history:
Received 30 September 2010
Received in revised form
8 December 2010
Accepted 10 December 2010

Keywords:
Ruthenium
Vinylidene
Cyclopropenyl
N-Coordinated
Tetrazolate

ABSTRACT

Ruthenium vinylidene complexes **2a**–**2c** containing indenyl and bidentate dppe ligands can be obtained in efficient yields. Treatment of the cationic ruthenium vinylidene complexes with *n*-Bu_4NOH in acetone yields the neutral cyclopropenyl products (η^5-C_9H_7)(dppe)Ru–C=C(Ph)CHR (**3**) (**3a**, R = Ph; **3b**, R = CN; **3c**, R = *p*-C_6H_4–CN) via the deprotonation reaction. Reaction of complexes **3a** and **3c** with Me_3SiN_3 ($TMSN_3$) the N-coordinated complexes **4a** and **4c** can be obtained as stable products. Complex **3b** containing CN group at Cγ in the cyclopropenyl ring reacts with $TMSN_3$ yielded the tetrazolate complex **5b**. Similar cyclopropenyl products containing indenyl and two triphenylphosphine ligands **3′** can also be synthesized. Reaction of complex **3b′** with $TMSN_3$ also yielded the tetrazolate complex as the major product. And the minor products are [Ru]–N_3 and organic compound **6b**. Reaction of **3a′** and **3c′** with $TMSN_3$ yielded [Ru]–N_3. The corresponding organic products can also be obtained via the N_3^- attacking the metal center in the N-coordinated complexes **4a′** and **4c′**.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The organometallic chemistry of transition-metal vinylidene complexes has attracted a great deal of attention in recent years [1,2]. These complexes also play an important role as strategic intermediates [3–5]. The importance of vinylidene intermediates in catalytic conversions such as asymmetric hydrogenation [6–9], cyclization of conjugated enediynes [10,11] and olefin metathesis [12–14] and polymerization [15,16] has been suggested [17,18].

Extensive reviews on this subject exist. The optimal entry into the transition-metal vinylidene complexes is the addition of electrophiles to the electron-rich carbon of metal alkynyl complexes [19,20]. A theoretical study of vinylidene complexes indicated localization of electron density on Cβ and the electron deficiency at Cα [21]. The formation of metal vinylidene complexes has been used to promote new carbon–carbon bond formation by the addition of carbon center to the electrophilic carbon atom.

The vinylidene complexes of iron with dppe ligand have been obtained [22–24]. The acidity of the aliphatic protons on a coordinated dppe ligand in a cationic iron vinylidene complex [25] has been employed for inducing the intramolecular cyclization between the dppe and vinylidene ligand.

Cyclopropene is known to dimerize and polymerize at room temperature [26,27]. Substituted cyclopropenes are generally more stable. They dimerize at higher temperatures [28,29]. Organic cyclopropene is highly strained and plays a crucial role in organic synthesis [30,31]. However, the cyclopropenyl ligand can be stabilized by coordination with a transition metal through back-bonding from the metal d-orbital to Cα. Synthesis of metal cyclopropenyl derivatives in which the metal bonds to C(sp^3) of the cyclopropenyl ring has been reported in literature [32]. However, based on the research of the study, only few of such a derivative in which the metal is bonded to the C(sp^2) of the three-membered ring have been reported [33]. A few structurally different transition metal cyclopropenylidene complexes have been reported. Reaction of the metal anionic silyl complex with organic 3,3-dichlorocyclopropenes in THF at room temperature results in the anticipated carbene complexes. The carbene complexes of this type are stabilized due to electron withdrawal from the cyclopropene complex [34]. In another case, metal cyclopropenyl complex that has the metal bonding to C(sp^3) of the cyclopropenyl ring undergoes a cyclopropenyl migration reaction to CO, yielding the 2-cyclopropene-1-carbonyl complex [35].

Ruthenium cyclopropenyl complexes by deprotonation reaction of ruthenium vinylidene complexes have been reported in literature [36–38]. In the ruthenium system, vinylidene and cyclopropenyl complexes display distinctive reactivity [39,40]. To explore potential applications of such a new type of complex, this study conducted

* Corresponding author. Tel.: +886 2 77148390; fax: +886 2 26022617.
E-mail address: hlsung@ntnu.edu.tw (H.-L. Sung).

0022-328X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.12.017

reactions of cyclopropenyl complexes with various organic substrates.

Trimethylsilyl azide and sodium azide were used widely in organic or organometallic reactions [41–43]. Coupling reaction of azide, such as $TMSN_3$, with simple alkyne and allyl carbonates catalyzed by Pd^0/Cu^I has been reported [44–47]. The azide reagent is also commonly used in the synthesis of metal complexes with N-heterocyclic ligand. The N-coordinated tetrazole derivatives have been obtained by the reaction of sodium azide with the coordinated CN of the N-coordinated iron nitrile complex [48]. The reaction of $TMSN_3$ with a number of ruthenium cyclopropenyl complexes containing different substituents at the cyclopropenyl ring yielded various products. Herein we report the synthesis of ruthenium cyclopropenyl complexes containing indenyl and dppe, or PPh_3 ligands. Then we report the reactions of the cyclopropenyl complexes with $TMSN_3$.

2. Results and discussion

2.1. Preparation of cationic ruthenium vinylidene complexes

Indenylruthenium acetylide complex **1** [Ru(η^5-C_9H_7)(dppe)(η^1-C≡CPh)] was prepared by the reaction of [RuCl(η^5-C_9H_7)(dppe)] with phenylacetylene in the presence of alcoholic CH_3ONa [49]. Treatment of [Ru]–C≡C–Ph (**1**, [Ru]=(η^5-C_9H_7)(dppe)Ru) with organic halides such as benzyl bromide at room temperature furnished cationic vinylidene complex **2a** in 79% yield (Scheme 1). The ^{31}P NMR spectra of **2a** exhibited a singlet at δ 76.1, indicating the chemical equivalence of the two phosphorus atoms. On the $^{13}C\{^1H\}$ NMR spectrum, the Ru–Cα resonance appeared at δ 352.2 as a triplet with a C–P coupling constant of 17.0 Hz.

Complex **2a** was air-stable at room temperature. The molecular structure was confirmed unequivocally by X-ray analysis. The ORTEP drawing of **2a** with thermal ellipsoids is shown at the 30% probability level in Fig. 1. The Ru(1)–C(36) bond length of 1.829 (4) Å was in the range of a regular ruthenium–carbon double bond in other crystallographically characterized ruthenium vinylidene complexes [52,53]. The C(36)–C(37) bond length of 1.328(6) Å was a typical double bond. The bond angles C(37)–C(36)–Ru(1) and C (36)–C(37)–C(45) were 176.5(4)° and 119.3(4)°, respectively.

Similarly, various vinylidene complexes [[Ru]=C=C(Ph)CH_2R]$^+$ **2b** and **2c** (**2b**, R = CN, **2c**, R = *p*-C_6H_4–CN) were prepared using the synthesis method for **2a**. The indenylruthenium vinylidene complexes **2a**, **2b** and **2c** containing dppe ligand and various substituents at Cγ were obtained as air-stable pink solids with 71–86% yields. All indenylruthenium vinylidene complexes can be obtained at room temperature and gave analytically pure complexes. These complexes displayed a characteristic pink color in the solid state. These complexes were characterized by NMR spectroscopy. The characteristic deshielded Cα resonances in the ^{13}C NMR in the region of $\delta = 348 \pm 5$. On the ^1H NMR spectrum, the singlet resonances for the CH_2 group at Cβ appeared at 2.4–2.9 ppm. The ^{31}P NMR resonance appears as a singlet at $\delta = 75.5 \pm 1$ in $CDCl_3$ at room temperature due to the fluxional behavior of the vinylidene ligand [50,51].

The structure of **2b** was also confirmed by an X-ray diffraction study. Fig. 2 shows the results of a single-crystal X-ray diffraction study of **2b**. The Ru(1)–C(36) bond length of 1.820(4) Å was in the range of a regular ruthenium–carbon double bond in other crystallographically characterized ruthenium vinylidene complexes. The C(36)–C(37) bond length of 1.330(5) Å was a typical double bond. The bond angles C(37)–C(36)–Ru(1) and C(36)–C(37)–C(44) were 176.5(3)° and 117.8(3)°, respectively.

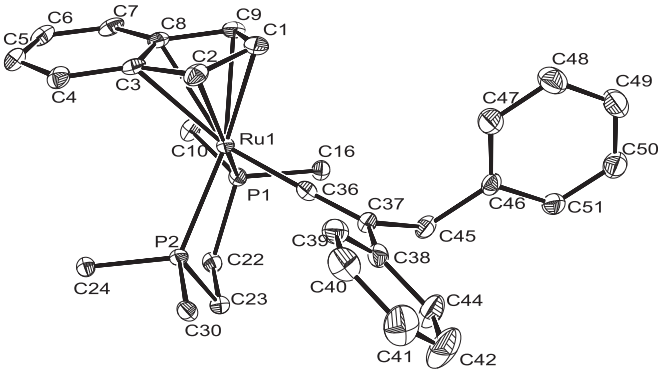
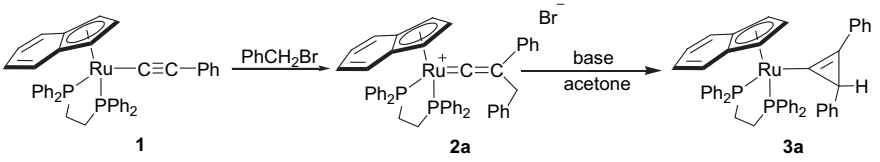


Fig. 1. Molecular structure of complex **2a** (hydrogen atoms and phenyl groups on dppe except the ipso carbon are removed for clarity). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: Ru(1)–P(1), 2.3359(13); Ru(1)–P (2), 2.3067(11); Ru(1)–C(36), 1.829(4); C(36)–C(37), 1.328(6); C(37)–C(45), 1.514(7); P (1)–Ru(1)–P(2), 82.86(4); Ru(1)–C(36)–C(37), 176.5(4); C(36)–C(37)–C(45), 119.3(4); C(37)–C(45)–C(46), 114.8(4).

2.2. Synthesis of the cyclopropenylruthenium complex *3a*

Deprotonation of the vinylidene complex **2a** by *n*-Bu_4NOH in acetone induces the intramolecular cyclization reaction and yielded a neutral cyclopropenyl complex **3a** (Scheme 1). The reaction produces a yellow crystalline product in analytically pure form. Use of acetone or acetonitrile as a solvent gives a good yield, and use of other bases such as DBU (1,8-diazabicyclo[5,4,0] undec-7-ene) give **3a** in comparable yield. The ^{31}P NMR spectrum of **3a** displays two doublet resonances at δ 92.6 and 90.2 of an AX pattern with $J_{P-P} = 23.3$ Hz due to the presence of a stereogenic carbon center at the three-membered ring. On the ^1H NMR spectrum of **3a**, the methyne (methine) proton appears at δ 1.37, and on the $^{13}C\{^1H\}$ NMR spectrum, the triplet at δ 124.1 with $J_{C-P} = 9.5$ Hz is assigned to Cα.

The synthesis and chemical reactivity of several neutral ruthenium cyclopropenyl triphenylphosphine complexes in which the metal bonds to one sp^2 carbon atom of the three-membered cyclopropenyl ring have been reported [54]. Ruthenium cyclopropenyl complex containing pentamethylcyclopentadiethyl (Cp^*) and dppp ligands was also be synthesized [40]. These cyclopropenylruthenium complexes could be prepared from deprotonation reaction of their vinylidene precursor. In the iron vinylidene complexes containing Cp and dppe ligands, 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 [55].



Scheme 1.

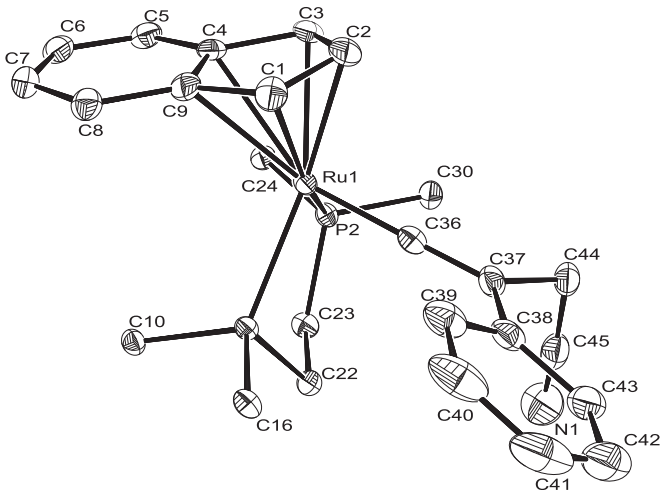


Fig. 2. Molecular structure of complex **2b** (hydrogen atoms and phenyl groups on dppe except the ipso carbon are removed for clarity). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: Ru(1)–P(1), 2.3113(9); Ru(1)–P(2), 2.3360(9); Ru(1)–C(36), 1.820(4); C(36)–C(37), 1.330(5); C(37)–C(44), 1.536(5); C(44)–C(45), 1.453(7); C(45)–N(1), 1.134(6); P(1)–Ru(1)–P(2), 82.04(3); Ru(1)–C(36)–C(37), 176.5(3); C(36)–C(37)–C(44), 117.8(3); C(37)–C(44)–C(45), 111.0(3).

2.3. Reaction of *3a* with $TMSN_3$

Treatment of cyclopropenylruthenium complex **3a** containing phenyl substituent at Cγ with $TMSN_3$ affords the N-coordinated complex **4a** with a 65% yield. The reaction conducted at room temperature for 4 h, longer reaction time even in 8 h complex **4a** is still stable. A series of successive color changes were noted during the course of the reaction: the light yellow solution of **3a** first turned orange upon addition of $TMSN_3$ at room temperature, and then, subsequently seen to turn yellow after 4 h elapsed. Complex **4a** is isolated as the final product, and is stable in air while in the solid state. Complex **4a** is soluble in CH_2Cl_2, MeOH, and THF, but insoluble in diethyl ether and hexane. The ^{31}P NMR spectrum of **4a** displays two doublet resonances at δ 83.3 and 81.4 with $J_{P-P} = 27.3$ Hz indicating the presence of a stereogenic center in the N-coordinated nitrile ligand.

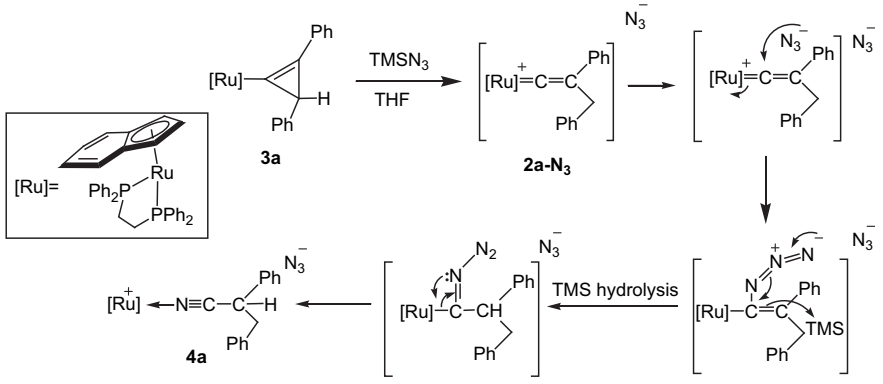
The addition of $TMSN_3$ to cyclopropenyl complex **3a** leading to **4a** may proceed via the following pathway (Scheme 2). An electrophilic addition of a TMS group to the sp^3 carbon at the three-membered ring with concomitant opening of the ring followed by hydrolysis of the added TMS group affords vinylidene intermediate **2a**–**N_3** containing an azide anion. This is followed by nucleophilic addition of an azide anion at Cα of the vinylidene ligand [56,57]. Subsequent electrophilic addition of a second TMS group at Cβ followed by loss of N_2 is accompanied by metal migration and hydrolysis of the TMS group to give the N-coordinated nitrile complex **4a**. Trace of water in the reaction solvent THF is believed to act as the source of the protons that are incorporated into the product through hydrolysis of the TMS group derived from the addition of $TMSN_3$ to the three-membered ring [38,58]. Intermediate complex **2a**–**N_3** is unstable in solution at room temperature and undergoes a further reaction with azide to give **4a** with azide counter anion as stable product. Conversion of a vinylidene precursor to N-coordinated nitrile by hydrazine, an organometallic Beckmann rearrangement, has been reported in an iron system [59]. It has been reported that the similar product N-coordinated ruthenium complex containing N_3^- counter anion is unstable. Exchange of the N_3^- with PF_6^- made the N-coordinated complex more stable [37,38].

2.4. Reaction of *3b* with $TMSN_3$

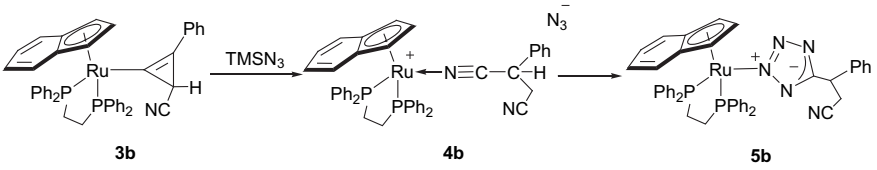
To compare with stereo effect of the cyclopropenyl complexes in the reaction with $TMSN_3$, we change the substituent at the sp^3 carbon of the cyclopropenyl ring. The vinylidene complex **2b** containing CN group at Cγ can be obtained with a good yield. The acetone solution of **2b** added base at room temperature yielded deprotonation product cyclopropenyl complex **3b**.

Treatment of cyclopropenylruthenium complex **3b** containing CN substituent at Cγ with $TMSN_3$ at room temperature for 4 h afford the yellow tetrazolate complex **5b** in 81% yield (Scheme 3). The ^{31}P NMR spectrum of **5b** shows two doublet resonances at δ 93.3 and 85.6 with $J_{P-P} = 27.7$ Hz due to the presence of an asymmetric carbon center in the five-membered ring. On the ^1H NMR spectrum of **5b**, a triplet resonance at δ 3.76 ($J_{H-H} = 7.16$ Hz) is assigned to the methyne proton and two resonances displaying doublets of an AB pattern at δ 2.10 ($J_{H-H} = 16.7$, 5.3 Hz) and 1.95 ($J_{H-H} = 16.7$, 9.0 Hz) are assigned to the diastereotopic methylene group. The parent peak in the ESI mass spectrum of **5b** clearly indicates that **5b** results from N_3 group to the intermediate complex **4b**. By monitoring the reaction using ^{31}P NMR spectroscopy, the mixture of complexes **4b** and **5b** can be observed at the initial stage of the reaction which is converted to complex **5b** in THF within 4 h at room temperature. Complex **5b** is stable at room temperature, soluble in THF, acetone but insoluble in ether and hexane.

Complex **3b** is stable in air and soluble in CH_2Cl_2 and THF but insoluble in CH_3CN and ether. Single crystals of **3b** were obtained by slow evaporation of the acetone/diethyl ether solution of **3b** at room temperature. The solid-state structure of **3b** is determined by an X-ray diffraction analysis. An ORTEP drawing of **3b** is shown in Fig. 3. The Ru(1)–C(36) bond length of 2.028(2) Å is typical for



Scheme 2.



Scheme 3.

a Ru–C single bond and the C(36)–C(39) bond length of 1.301(3) Å is a double bond, indicating coordination of the sp^2 carbon of the cyclopropenyl ligand. The bond angles Ru(1)–C(36)–C(39) and C(36)–C(39)–C(40) of 161.46(19)°and 157.5(2)°, respectively, are both far larger than that of an idealized sp^2 hybridization. The C(36)–C(37) and C(37)–C(39) bond lengths of 1.584(3) and 1.495(3) Å, respectively, are significantly different, consistent with the favorable cleavage of the C(36)–C(37) bond. Other relevant crystal data for complexes **2a**, **2b**, and **3b** are also given in Table 1.

In the reaction of **3b** with $TMSN_3$, the reaction may proceed similarly in the first stage to give an analog of **4b**. Formation of **5b** is then rationalized by a [3 + 2] cycloaddition of the C≡N bond with another azide anion followed by metal migration (linkage isomerization) [60,61]. In some cases, the [3 + 2] cyclization reaction was occurred in an imine compound with an azide group. It has been reported tetrazole compound resulting from an attack of an azide to an imine compound with an appropriate leaving group following cyclization [62]. Unlike the reactivity of **3a** with $TMSN_3$ yield the stable N-coordinated product, the C≡N bond coordinated with the metal center by N atom in the **4b** followed reaction with N_3^- to obtain the tetrazolate product **5b**. The terminal CN group of complex **3b** is smaller than complex **3a** to enhance the N_3^- group addition.

Organic tetrazoles are increasingly important heterocyclic compounds in medicinal chemistry. An enormous number of tetrazole-containing biologically active compounds are known in literature [63–65]. Organic tetrazoles are generally prepared starting from nitriles and NaN_3 or $TMSN_3$ and stoichiometric of catalyst in the solvent [66–68]. Literature has reported that nitrile groups react with azide creating a tetrazolate ring via [3 + 2] cycloaddition reaction [69].

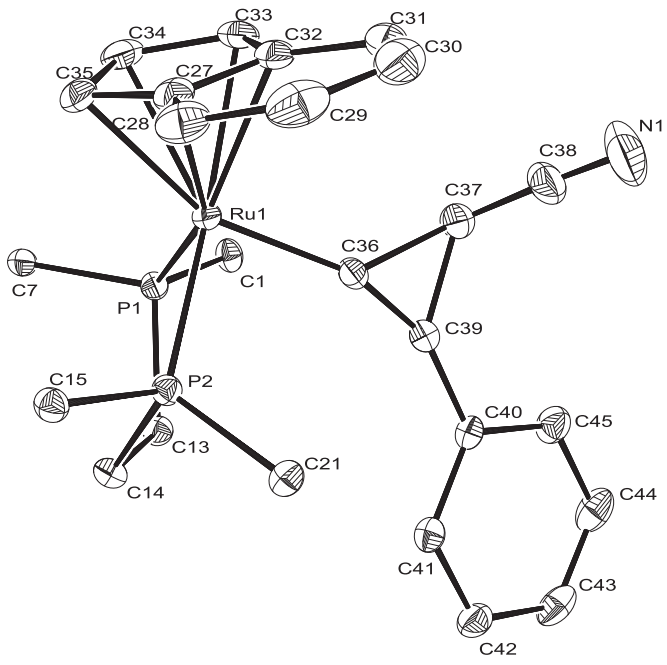


Fig. 3. Molecular structure of complex **3b** (hydrogen atoms and phenyl groups on dppe except the ipso carbon are removed for clarity). Thermal ellipsoids are shown at the 30% level. Selected bond lengths [Å] and angles [deg]: Ru(1)–P(1), 2.2237(6); Ru(1)–P(2), 2.2584(6); Ru(1)–C(36), 2.028(2); C(36)–C(37), 1.584(3); C(36)–C(39), 1.301(3); C(37)–C(39), 1.495(3); P(1)–Ru(1)–P(2), 85.52(2); Ru(1)–C(36)–C(37), 135.89(17); Ru(1)–C(36)–C(39), 161.46(19); C(36)–C(39)–C(40), 157.5(2); C(37)–C(36)–C(39), 61.46(17); C(36)–C(37)–C(39), 49.89(15); C(36)–C(39)–C(37), 68.65(18).

2.5. Reaction of *3c* with $TMSN_3$

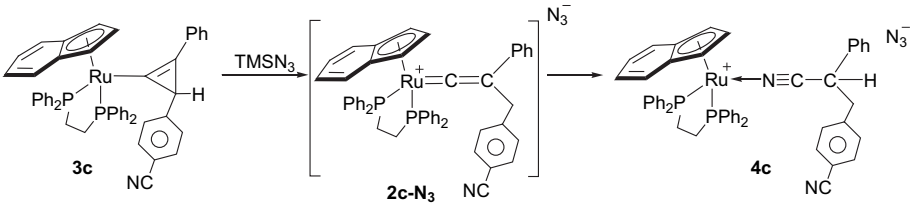
In the vinylidene complex, changing the CN group at Cγ to the *p*-C_6H_4–CN containing the CN group at the *para* position in the phenyl ring, complex **2c** can be obtained. Deprotonation reaction of complex **2c** yielded the cyclopropenyl complex **3c** in 86% yield. Reaction of complex **3c** with $TMSN_3$ yielded N-coordinated complex **4c** as the stable product in air in the solid state. Complex **4c** can be obtained by a similar pathway of complex **4a** (Scheme 4). No tetrazolate complex was obtained even in the long reaction time. On the ^{31}P NMR spectrum of **4c**, two doublet resonances at δ 83.9 and 81.2 with J_{P-P} = 27.1 Hz indicated the presence of a diastereotopic center in the ruthenium N-coordinated complex. On the ^1H NMR spectrum, a triplet pattern at δ 4.37 with J_{H-H} = 7.40 Hz was assigned to the proton at the diastereotopic center.

The cyclopropenyl complexes containing indenyl and dppe ligands can be obtained in good yield. N-coordinated complexes **4a** and **4c** containing phenyl group and its derivatives at Cγ and the counter ion N_3^- are very stable in air while in the solid state. Complexes **4a** and **4c** would not undergo further nucleophilic addition or cyclization is interpreted in terms of relatively larger steric hindrance of a phenyl group relative to a CN group.

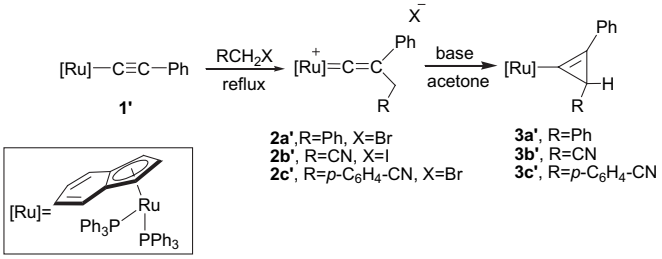
Table 1
Crystal data and refinement parameters for complexes **2a**, **2b**, and **3b**.

	2a·CH_2Cl_2[a]	**2b**	**3b**
Empirical formula	$C_{51}H_{45}BrCl_2P_2Ru$	$C_{45}H_{38}INP_2Ru$	$C_{45}H_{37}NP_2Ru$
Temperature	200(2) K	200(2) K	200(2) K
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P\,2_1/c$	$C\,2/c$	$P-1$
a, Å	17.3657(5)	37.7342(5)	12.1695(5)
b, Å	11.4420(4)	10.75430(10)	12.1789(6)
c, Å	22.2480(6)	18.5556(3)	12.8051(6)
α, deg	90	90	89.182(2)
β, deg	91.5510(10)	93.7030(10)	76.368(2)
γ, deg	90	90	79.858(2)
Volume, $Å^3$	4419.0(2)	7514.23(17)	1814.84(14)
Z	4	8	2
Crystal size, mm^3	0.46 × 0.35 × 0.06	0.3 × 0.21 × 0.08	0.75 × 0.70 × 0.51
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final *R* indices [$I > 2$sigma (I)]	$R1 = 0.0471$, $wR2 = 0.1214$	$R1 = 0.0353$, $wR2 = 0.0960$	$R1 = 0.0252$, $wR2 = 0.0690$
R indices (all data)	$R1 = 0.0676$, $wR2 = 0.1310$	$R1 = 0.0467$, $wR2 = 0.1104$	$R1 = 0.0682$, $wR2 = 0.0769$
Largest diff. peak and hole, $Å^{-3}$	1.901 and −0.602	1.171 and −0.999	0.834 and −0.400
CCDC number	776703	776704	794306

[a] Crystals grown from an CH_2Cl_2–ether mixture are found to incorporate an CH_2Cl_2 molecule.



Scheme 4.



Scheme 5.

2.6. Reaction of cyclopropenylruthenium complexes containing indenyl and two PPh_3 ligands with $TMSN_3$

Cyclopropenylruthenium complexes containing Cp and triphenylphosphine (PPh_3) ligands reacting with $TMSN_3$ conducted similar reactivity with these cyclopropenyl complexes containing indenyl and bidentate ligand [37,38]. Various substituents at the three-membered ring cause different compounds.

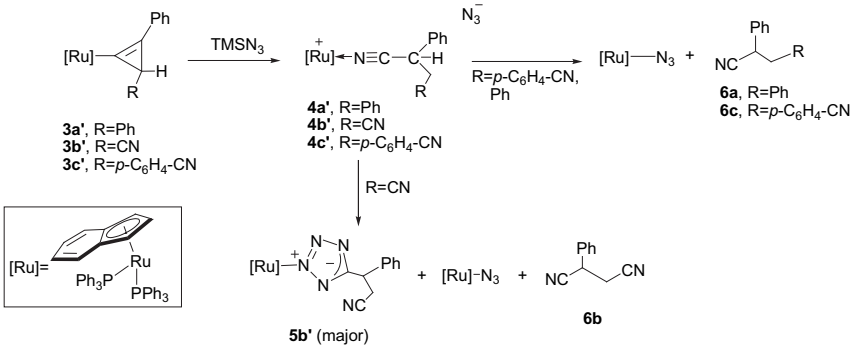
To check the reactivity for the cyclopropenyl complexes containing two PPh_3 and indenyl ligands, complexes **2a′**, **2b′** and **2c′** are prepared from the reaction of organic halides and the ruthenium acetylide complex [Ru]—C≡C—Ph (**1′**), ([Ru]=(η^5-C_9H_7)(PPh_3)$_2$Ru). Treatment of complex **1′** with benzyl bromide at refluxing temperature of CH_2Cl_2 for 18 h afforded cationic vinylidene complex **2a′** in 85% yield. Similarly, preparation of other vinylidene complexes **2b′** and **2c′** have been synthesized by reacting **1′** with the corresponding organic halides at refluxing temperature of CH_2Cl_2 with good yields. Complexes **2a′**–**2c′** are all soluble in polar solvent but insoluble in ether and hexane. The characteristic spectroscopic data of these vinylidene complexes consist of strongly deshielded Cα resonance as a triplet at δ 345 ± 2 in the ^{13}C NMR spectrum and a singlet ^{31}P NMR resonance normally at around δ 38 ± 1 in $CDCl_3$ at room temperature, which is due to the fluxional behavior of the vinylidene ligand [70].

Ruthenium vinylidene complex **2a′** containing two PPh_3 ligands undergo a deprotonation reaction to yield cyclization product **3a′**. The reaction required greater span of time than dppe system. Deprotonation reaction of complex **2a′** by *n*-Bu_4NOH is followed by the expected cyclization, yielding the cyclopropenyl complex **3a′** (Scheme 5). The reaction time needed is 4 h. Complex **3a′** is stable in air and soluble in CH_2Cl_2, THF, and benzene, slightly soluble in acetone and diethyl ether, but insoluble in CH_3CN. The ^{31}P NMR spectrum of **3a′** displays two doublet resonances at δ 52.8 and 43.1 with J_{P-P} = 27.6 Hz in C_6D_6 arising from the presence of a stereogenic center in the three-membered ring. In the ^{1}H NMR spectrum of **3a′**, the resonance of the methine proton appears at δ 2.62, and in the ^{13}C NMR spectrum, the triplet at 126.8 with J_{C-P} = 21.2 Hz is assigned to Cα. Deprotonation reaction of complexes **2a′** and **2c′** containing Ph and derivatives needed 10 h to yield cyclopropenyl complexes **3a′** and **3c′**. Complexes **2a′** and **2c′** needed longer reaction time than complex **2b′** which indicates the acidic nature of the methylene protons, which may be ascribed to the combined effect of the cationic character and electron-withdrawing substituents of the vinylidene complexes. In comparison with the dppe system, the steric effect of the two PPh_3 ligands may hinder the electrophilic addition, therefore requiring longer reaction times. The cyclopropenylruthenium complexes containing the triphenylphosphine system therefore exhibits distinctive reactivity from that of the bidentate ligand, such as dppe, dppp, or dppb.

2.7. Reaction of cyclopropenyl complexes 3a′–3c′ with $TMSN_3$

Treatment of the cyclopropenyl complex **3a′** with excess of $TMSN_3$ in THF at room temperature afforded [Ru]—N_3 and the organic product **6a** (Scheme 6). The reaction conducted at room temperature for 18 h and may proceed via N-coordinated complex **4a′**. The N-coordinated complex **4a′** is unstable and undergoes a further reaction with azide to give [Ru]—N_3 and **6a**. Similar reaction occurred in the **3c′** with $TMSN_3$ to yield [Ru]—N_3 and the corresponding organic product **6c**.

In contrast with the results in dppe ligand system, complexes containing relatively large sterically two PPh_3 ligands make **4a′** and **4c′** unstable. Further N_3^- attack Cα to give final [Ru]—N_3 and the



Scheme 6.

corresponding organic products. In this system, the stereo effect may play an important role in the reactivity of the cyclopropenyl complexes with $TMSN_3$. The bond angle P(1)–Ru(1)–P(2) of 85.52 (2) in complex **3b** is similar to the cyclopropenyl complex containing Cp and dppe ligand [54]. But smaller than that in the system containing Cp and dppp ligand [40] and is also smaller than those cyclopropenyl complexes containing Cp and two triphenylphosphine ligands [39]. In the iron cyclopropenyl complex containing dppe ligand, the bond angle P(1)–Fe(1)–P(2) of 84.81(4) is also similar to complex **3b** [55].

When CN substituent at the sp^3 C is in the ruthenium cyclopropenyl ring, complex **3b′** react with $TMSN_3$ yielding the N-coordinated complex **4b′** initially. Further **4b′** react with N_3^- by the [3 + 2] cycloaddition yielded the tetrazolate complex **5b′** as the stable solids in room temperature. The minor product [Ru]–N_3 and the corresponding organic product **6b** can be observed. A similar result occurred in the reaction of **3b** and **3b′** each containing dppe and two PPh_3 system with $TMSN_3$. The electron-withdrawing and the stereo effects of the CN group in the N-coordinated complex **4b** may enhance the [3 + 2] cycloaddition with the CN group coordinated with the metal and N_3^- to give the tetrazolate complex. Complex **4b′** is obtained by the similar pathway. The minor product [Ru]–N_3 and the corresponding organic product **6b** is considered the reaction of **4b′** and the N_3^- group.

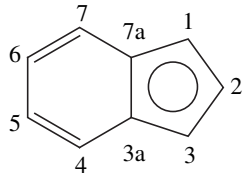
3. Concluding remarks

Ruthenium cyclopropenyl complexes containing indenyl and dppe or two triphenylphosphine ligands can be synthesized. These complexes are stable in the solid state in room temperature. Various substituents at the sp^3 carbon of the three-membered ring govern the reactivity of the cyclopropenyl complexes with $TMSN_3$. Reaction of the cyclopropenyl complexes **3a** and **3c** containing the phenyl and its derivatives at Cγ yield the stable N-coordinated complexes. Reaction of complex **3b** containing a CN group at Cγ with $TMSN_3$ yields the tetrazolate ruthenium complex **5b** via the [3 + 2] cycloaddition of N_3^- with the N-coordinated product. Reaction of the cyclopropenyl complexes containing two PPh_3 ligands **3a′** and **3c′** with $TMSN_3$ yields the [Ru]–N_3 and the corresponding organic product as the final product. The N-coordinated complexes are considered to be intermediate in the reaction. Further, by the reaction of N_3^- attack at Cα yields the final products. When the cyclopropenyl complex **3b′** containing CN group at Cγ reacts with $TMSN_3$, the tetrazolate complex **5b′** can be obtained as the major product.

4. Experimental section

All reagents were purchased from commercial sources and used without further purification. NMR spectra were obtained with Bruker-AC 500 spectrometer at 500 MHz (^1H), 202 MHz (^{31}P), or 125 MHz (^{13}C). The chemical shifts are given in parts per million from $SiMe_4$ (^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 ($^{31}P\{^1H\}$) and are reported in unit δ. The Mass spectra were recorded using LCQ advantage (ESI). X-ray diffraction studies were both carried out at the Regional Center of Analytical Instrument at the National Taiwan Normal University.

All synthetic manipulations were performed in oven-dried glassware under nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. THF was distilled from sodium benzophenone ketyl and CH_2Cl_2 was distilled from CaH_2. Methanol was distilled from Mg/I_2. Complexes (η^5-C_9H_7)(dppe)Ru–C≡C–Ph (**1**) [49] and (η^5-C_9H_7)(PPh_3)$_2$Ru–C≡C–Ph (**1′**) [71] were prepared by following the methods reported in literature. The following atom labels have been used for the ^1H and $^{13}C\{^1H\}$ spectroscopic data:



4.1. Synthesis of [(η^5-C_9H_7)(dppe)Ru=C=C(Ph)CH_2Ph][Br] (**2a**)

To a solution of **1** (0.21 g, 0.29 mmol) in 20 ml of CH_2Cl_2 was added benzyl bromide (0.17 ml, 1.45 mmol). After stirring overnight at room temperature, the resulting solution was concentrated to about 5 ml. The residue was then slowly added to 40 ml of vigorously stirred diethyl ether. The pink precipitate thus formed was filtered off, washed with diethyl ether and hexane and dried under vacuum to give pink product **2a** in 79% yield (0.19 g, 0.23 mmol). Spectroscopic data for **2a** follows. ^1H NMR ($CDCl_3$): δ 7.42–5.83 (m, 37H, H of Ph and indenyl group); 3.01 (m, 4H, $2CH_2$ of dppe); 2.80 (s, 2H, CH_2). ^{31}P NMR ($CDCl_3$): δ 76.1. ^{13}C NMR ($CDCl_3$): 352.2 (Cα, J_{C-P} = 17.0 Hz); 138.3–128.1 (Ph); 126.9 (C-5, 6); 123.7 (C-4, 7); 112.3 (Cβ); 97.3 (C-2); 79.9 (C-1, 3); 28.9 (CH_2); 27.9 (t, J_{C-P} = 23.8 Hz, CH_2 of dppe). HRMS (ESI, *m/z*): 807.4 (M^+); 615.4 (M^+ – C_2(Ph)CH_2Ph). Anal. Calcd. for $C_{50}H_{43}P_2BrRu$: C: 67.72, H: 4.89, found: C: 68.01, H: 4.92.

4.2. Synthesis of [(η^5-C_9H_7)(dppe)Ru=C=C(Ph)CH_2CN][I] (**2b**)

1 (0.30 g, 0.42 mmol) and iodoacetonitrile (0.15 ml, 2.07 mmol) were stirred overnight in 20 ml of CH_2Cl_2. The purification method described for **2a** yielded pink solid product **2b** (0.27 g, 0.36 mmol) in 86% yield. Spectroscopic data for **2b** follows. ^1H NMR ($CDCl_3$): δ 7.50–6.94 (m, 27H, 25H of Ph, 2H of indenyl group); 6.67, 6.07 (m, 2H each one, H of indenyl group); 5.96 (br, 1H of indenyl group); 3.17, 2.84 (m, 4H, $2CH_2$ of dppe); 2.40 (s, 2H, CH_2). ^{31}P NMR ($CDCl_3$): δ 74.5. ^{13}C NMR ($CDCl_3$): 347.8 (Cα, J_{C-P} = 16.4 Hz); 132.5–128.9 (Ph); 126.9 (C-5, 6); 123.6 (C-4, 7); 112.6 (Cβ); 97.4 (C-2); 80.9 (C-1, 3); 27.9 (t, J_{C-P} = 22.7 Hz, CH_2 of dppe); 13.3 (CH_2). HRMS (ESI, *m/z*): 756.6 (M^+); 615.3 (M^+ – C_2(Ph)CH_2CN). Anal. Calcd. for $C_{45}H_{38}NP_2IRu$: C: 61.23, H: 4.34, found: C: 61.45, H: 4.39.

4.3. Synthesis of [(η^5-C_9H_7)(dppe)Ru=C=C(Ph)CH_2(*p*-C_6H_4-CN)][Br] (**2c**)

1 (0.37 g, 0.52 mmol) and α-bromo-*p*-tolunitrile (0.42 g, 2.14 mmol) were stirred overnight in 20 ml of CH_2Cl_2. The purification method described for **2a** yielded pink solid product **2c** in 71% yield (0.31 g, 0.37 mmol). ^1H NMR ($CDCl_3$): δ 7.42–6.88 (m, 31H, 29H of Ph, 2H of indenyl group); 6.52, 5.90 (m, 2H each one, H of indenyl group); 5.82 (br, 1H of indenyl group); 3.12 (m, 4H, $2CH_2$ of dppe); 2.90 (s, 2H, CH_2). ^{31}P NMR ($CDCl_3$): δ 76.1. ^{13}C NMR ($CDCl_3$): 343.4 (Cα, J_{C-P} = 16.1 Hz); 131.8–127.5 (Ph); 126.3 (C-5, 6); 122.8 (C-4, 7); 114.9 (Cβ); 98.1 (C-2); 81.4 (C-1, 3); 28.5 (t, J_{C-P} = 22.4 Hz, CH_2 of dppe); 12.8 (CH_2). HRMS (ESI, *m/z*): 832.3 (M^+); 615.2 (M^+ – C_2(Ph)$CH_2C_6H_4$CN). Anal. Calcd. for $C_{51}H_{42}NP_2BrRu$: C: 67.18, H: 4.64, found: C: 67.33, H: 4.67.

4.4. Synthesis of [(η^5-C_9H_7)(PPh_3)$_2$Ru=C=C(Ph)CH_2Ph][Br] (**2a′**)

To a solution of **1′** (0.23 g, 0.27 mmol) in 20 ml of CH_2Cl_2 was added benzyl bromide (0.22 ml, 1.84 mmol). After refluxing for 18 h, the resulting solution was cooled to room temperature and

concentrated to about 5 ml. The residue was then slowly added to 40 ml of vigorously stirred diethyl ether. The pink precipitate thus formed was filtered off, washed with diethyl ether and hexane and dried under vacuum to give pink product **2a**′ in 85% yield (0.21 g, 0.23 mmol). Spectroscopic data for **2a**′ follows. ^{1}H NMR ($CDCl_3$): δ 7.46–6.28 (m, 40H, Ph); 6.28 (br, 1H, H-2); 5.65 (br, 2H of H-4, 7); 5.33 (d, 2H, H-1, 3, J_{H-H} = 2.3 Hz); 3.49 (s, 2H, CH_2). ^{31}P NMR ($CDCl_3$): δ 39.0. ^{13}C NMR ($CDCl_3$): 344.4 (Cα); 137.5–126.6 (Ph); 123.3 (C-4, 7); 100.0 (C-2); 81.1 (C-1, 3); 31.9 (*C*H_2). HRMS (ESI, *m*/*z*): 933.2 (M^+); 671.1 ($M^+ - PPh_3$); 479.0 ($M^+ - PPh_3$, C_2(Ph)CH_2Ph). Anal. Calcd. for $C_{60}H_{49}P_2BrRu$: C: 71.14, H: 4.88, found: C: 71.98, H: 5.11.

4.5. Synthesis of [(η^5-C_9H_7)(PPh_3)$_2$Ru=C=C(Ph)CH_2CN][I] (**2b**′)

1′ (0.28 g, 0.33 mmol) and iodoacetonitrile (0.15 ml, 2.07 mmol) were refluxed for 18 h in 20 ml of CH_2Cl_2. The purification method described for **2a**′ yielded pink solid product **2b**′ (0.26 g, 0.29 mmol) in 88% yield. Spectroscopic data for **2b**′ follows. ^{1}H NMR ($CDCl_3$): δ 7.50–6.63 (m, 35H of Ph group); 6.62, 5.44, 4.74 (m, 2H each one, H of indenyl group); 5.63 (br, 1H of indenyl group); 3.52 (s, 2H, CH_2). ^{31}P NMR ($CDCl_3$): δ 37.3. ^{13}C NMR ($CDCl_3$): 346.3 (Cα, J_{C-P} = 16.3 Hz); 133.1–127.7 (Ph); 127.2 (C-5, 6); 123.3 (C-4, 7); 112.3 (Cβ); 97.4 (C-2); 81.2 (C-1, 3); 14.1 (*C*H_2). HRMS (ESI, *m*/*z*): 882.1 (M^+); 620.4 ($M^+ - PPh_3$). Anal. Calcd. for $C_{55}H_{44}NP_2IRu$: C: 65.48, H: 4.40, found: C: 65.59, H: 4.48.

4.6. Synthesis of [(η^5-C_9H_7)(PPh_3)$_2$Ru=C=C(Ph)CH_2(p-C_6H_4–CN)][Br] (**2c**′)

1′ (0.34 g, 0.40 mmol) and α-bromo-*p*-tolunitrile (0.42 g, 2.14 mmol) were refluxed for 18 h in 20 ml of CH_2Cl_2. The purification method described for **2a**′ yielded pink solid product **2c**′ in 78% yield (0.30 g, 0.31 mmol). Spectroscopic data for **2c**′ follows. ^{1}H NMR ($CDCl_3$): δ 7.48–6.57 (m, 39H, Ph); 6.93 (br, 1H, H-2); 5.60 (br, 2H of H-4, 7); 5.41 (br, 2H, H-1, 3); 3.61 (s, 2H, CH_2). ^{31}P NMR ($CDCl_3$): δ 38.8. ^{13}C NMR ($CDCl_3$): 343.7 (t, Cα, J_{C-P} = 16.9 Hz); 143.3 (CN); 134.3–128.0 (Ph); 123.5 (C-4, 7); 101.3 (C-2); 81.6 (C-1, 3); 32.0 (*C*H_2). HRMS (ESI, *m*/*z*): 958.2 (M^+); 696.1 ($M^+ - PPh_3$). Anal. Calcd. for $C_{61}H_{48}NP_2BrRu$: C: 70.59, H: 4.66, found: C: 70.83, H: 4.68.

4.7. Synthesis of cyclopropenylruthenium complex (η^5-C_9H_7)(dppe)Ru–C=C(Ph)CHPh (**3a**)

2a (0.25 g, 0.31 mmol) in 2 ml of acetone was treated with *n*-Bu_4NOH (1 M in MeOH) (2 ml, 2.0 mmol). After stirring at room temperature for 2 h, the resulting solution was concentrated to about 0.5 ml. Then 5 ml CH_3CN was added the yellow precipitate thus formed was filter off and washed with CH_3CN and dried under vacuum to give the product **3a** (0.18 g, 0.22 mmol) in 71% yield. Spectroscopic data for **3a** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.42–5.08 (m, 37H, H of Ph and indenyl group); 2.59, 2.17, 1.85, 1.55 (m, 4H, $2CH_2$ of dppe); 1.37 (s, 1H, CH). ^{31}P NMR ($CDCl_3$): δ 92.6, 90.2 (AX, J_{P-P} = 23.3 Hz). ^{13}C NMR ($CDCl_3$): 135.5–126.4 (Ph); 124.1 (Cα, J_{C-P} = 9.5 Hz); 110.3 (C-5, 6); 108.8 (C-4, 7); 94.7 (C-2); 78.2 (C-1, 3); 27.8 (t, J_{C-P} = 21.5 Hz, CH_2 of dppe); 12.3 (*C*H). HRMS (ESI, *m*/*z*): 807.6 ($M^+ + 1$); 615.7 ($M^+ + 1 - C_2$(Ph)CHPh). Anal. Calcd. for $C_{50}H_{42}P_2Ru$: C: 74.52, H: 5.25, found: C: 74.75, H: 5.27.

4.8. Synthesis of cyclopropenylruthenium complex (η^5-C_9H_7)(dppe)Ru–C=C(Ph)CHCN (**3b**)

2b (0.24 g, 0.32 mmol) in 2 ml of acetone was treated with *n*-Bu_4NOH (1 M in MeOH) (2 ml, 2.0 mmol). After stirring at room temperature for 2 h, the resulting solution was concentrated to about 0.5 ml. Then 5 ml CH_3CN was added the yellow precipitate thus formed was filter off and washed with CH_3CN and dried under vacuum to give the product **3b** (0.29 g, 0.25 mmol) in 78% yield. Spectroscopic data for **3b** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.61–6.85 (m, 25H of Ph group); 6.67, 6.51 (m, 2H each one, H of indenyl group); 5.96, 5.33, 4.81 (m, 1H each one, H of indenyl group); 2.56, 2.05, 1.86 (m, 4H, of dppe); 0.65 (s, 1H, CH). ^{31}P NMR ($CDCl_3$): δ 94.3, 88.6 (AX, J_{P-P} = 24.8 Hz). ^{13}C NMR ($CDCl_3$): 142.2–123.6 (Ph); 127.9 (Cα, J_{C-P} = 10.1 Hz); 113.1 (CN); 109.7 (C-5, 6); 109.6 (C-4, 7); 93.1 (C-2); 71.4 (C-1, 3); 28.2 (t, J_{C-P} = 22.3 Hz, CH_2 of dppe); 5.4 (*C*H). HRMS (ESI, *m*/*z*): 756.1 ($M^+ + 1$); 615.7 ($M^+ + 1 - C_2$(Ph)CHCN). Anal. Calcd. for $C_{45}H_{37}NP_2Ru$: C: 71.61, H: 4.94, found: C: 71.89, H: 5.03.

4.9. Synthesis of cyclopropenylruthenium complex (η^5-C_9H_7)(dppe)Ru–C=C(Ph)CH(p-C_6H_4–CN) (**3c**)

2c (0.28 g, 0.35 mmol) in 2 ml of acetone was treated with *n*-Bu_4NOH (1 M in MeOH) (2 ml, 2.0 mmol). After stirring at room temperature for 2 h, the resulting solution was concentrated to about 0.5 ml. Then 5 ml CH_3CN was added the yellow precipitate thus formed was filter off and washed with CH_3CN and dried under vacuum to give the product **3c** (0.26 g, 0.31 mmol) in 86% yield. Spectroscopic data for **3c** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.47–6.83 (m, 25H of Ph group); 6.81, 6.38, 6.43, 5.22, 5.21, 4.95 (m, 7H of indenyl group); 2.51, 2.46, 1.79 (m, 4H, of dppe); 1.42 (s, 1H, CH). ^{31}P NMR ($CDCl_3$): δ 92.6, 89.6 (AX, J_{P-P} = 24.2 Hz). ^{13}C NMR ($CDCl_3$): 138.4–121.7 (Ph); 128.2 (Cα, J_{C-P} = 11.4 Hz); 112.0 (CN); 111.3 (C-5, 6); 110.7 (C-4, 7); 96.2 (C-2); 73.7 (C-1, 3); 27.4 (t, J_{C-P} = 20.6 Hz, CH_2 of dppe); 13.1 (*C*H). HRMS (ESI, *m*/*z*): 832.6 ($M^+ + 1$); 615.8 ($M^+ + 1 - C_2$(Ph)CHC_6H_4CN). Anal. Calcd. for $C_{51}H_{41}NP_2Ru$: C: 73.72, H: 4.97, found: C: 73.87, H: 4.99.

4.10. Synthesis of cyclopropenylruthenium complex (η^5-C_9H_7)(PPh_3)$_2$Ru–C=C(Ph)CHPh (**3a**′)

To a solution of **2a**′ (0.27 g, 0.29 mmol) in 10 ml of acetone was added a solution of *n*-Bu_4NOH (2 ml, 2 mmol, 1 M in MeOH). After the mixture was stirred at room temperature for 10 h, the resulting solution was concentrated to about 0.5 ml. Then 5 ml CH_3CN was added the yellow precipitate thus formed was filter off and washed with CH_3CN and dried under vacuum to give the product **3a**′ (0.23 g, 0.25 mmol) in 86% yield. Spectroscopic data for **3a**′ are as follows: ^{1}H NMR (C_6D_6): δ 7.45–6.95 (m, 40H of Ph group); 6.88, 6.60, 5.82, 5.58, 5.42, 4.88 (m, 7H of indenyl group); 2.62 (s, 1H, CH). ^{31}P NMR (C_6D_6): δ 52.8, 43.1 (AX, J_{P-P} = 27.6 Hz). ^{13}C NMR (C_6D_6): 133.1–123.5 (Ph); 126.8 (Cα, J_{C-P} = 21.2 Hz); 110.3 (C-5, 6); 109.3 (C-4, 7); 98.4 (C-2); 80.1(C-1, 3); 11.9 (*C*H). HRMS (ESI, *m*/*z*): 933.1 ($M^+ + 1$); 671.1 ($M^+ + 1 - PPh_3$); 429.0 ($M^+ + 1 - PPh_3$, C_2(Ph)CHPh). Anal. Calcd. for $C_{60}H_{48}P_2Ru$: C: 77.32, H: 5.19, found: C: 77.54, H: 5.22.

4.11. Synthesis of cyclopropenylruthenium complex (η^5-C_9H_7)(PPh_3)$_2$Ru–C=C(Ph)CHCN (**3b**′)

A sample of **2b**′ (0.24 g, 0.27 mmol) was dissolved in 10 ml of acetone at room temperature. A methanol solvent of *n*-Bu_4NOH (2 ml, 2 mmol, 1 M in MeOH) was added. After the mixture stirred for 4 h, the resulting solution was concentrated to about 0.5 ml. Then 5 ml CH_3CN was added the yellow precipitate thus formed was filter off and washed with CH_3CN. The product was dried under vacuum and identified as **3b**′ (0.21 g, 0.24 mmol) in 89% yield. Spectroscopic data for **3b**′ are as follows: ^{1}H NMR ($CDCl_3$): δ 7.16–6.88 (m, 35H of Ph group); 6.84, 6.05, 5.92, 5.31, 5.00 (m, 7H of indenyl group); 1.61 (s, 1H, CH). ^{31}P NMR ($CDCl_3$): δ 53.9, 49.9 (AX, J_{P-P} = 28.1 Hz). ^{13}C NMR ($CDCl_3$): 134.6–125.1 (Ph); 126.5 (Cα,

J_{C-P} = 22.5 Hz); 113.8 (CN); 112.4 (C-5, 6); 111.5 (C-4, 7); 94.5 (C-2); 78.1 (C-1, 3); 6.5 (*C*H). HRMS (ESI, *m*/*z*): 882.4 (M^+ + 1); 620.3 (M^+ + 1 − PPh_3); 429.1 (M^+ + 1 − PPh_3, C_2(Ph)CHCN).Anal. Calcd. for $C_{55}H_{43}NP_2Ru$: C: 74.99, H: 4.92, found: C: 75.18, H: 4.93.

4.12. Synthesis of cyclopropenylruthenium complex (η^5-C_9H_7)(PPh_3)$_2$Ru−C=C(Ph)CH(p-C_6H_4−CN) (**3c′**)

A sample of **2c′** (0.26 g, 0.27 mmol) was dissolved in 10 ml of acetone at room temperature. A methanol solvent of *n*-Bu_4NOH (2 ml, 2 mmol, 1 M in MeOH) was added. After the mixture stirred for 10 h, the resulting solution was concentrated to about 0.5 ml. Then 5 ml CH_3CN was added the yellow precipitate thus formed was filter off and washed with CH_3CN. The product was dried under vacuum and identified as **3c′** (0.23 g, 0.24 mmol) in 89% yield. Spectroscopic data for **3c′** are as follows: ^{1}H NMR (C_6D_6): δ 7.43–6.92 (m, 39H of Ph group); 6.92, 6.62, 5.79, 5.62, 5.40, 4.92 (m, 7H of indenyl group); 2.60 (s, 1H, CH). ^{31}P NMR (C_6D_6): δ 53.1, 45.1 (AX, J_{P-P} = 27.8 Hz). ^{13}C NMR (C_6D_6): 138.1–126.7 (Ph); 128.1 (Cα, J_{C-P} = 18.7 Hz); 111.9 (CN); 110.5 (C-5, 6); 110.1 (C-4, 7); 93.2 (C-2); 80.7 (C-1, 3); 8.4 (*C*H). HRMS (ESI, *m*/*z*): 958.1 (M^+ + 1); 696.0 (M^+ + 1 − PPh_3); 429.0 (M^+ + 1 − PPh_3, C_2(Ph)CHC_6H_4CN). Anal. Calcd. for $C_{61}H_{47}NP_2Ru$: C: 76.55, H: 4.95, found: C: 76.74, H: 4.97.

4.13. Reaction of **3a** with $TMSN_3$

To a solution of **3a** (0.14 g, 0.17 mmol) in THF (5 ml) was added $TMSN_3$ (0.1 ml, 0.76 mmol). The solution was stirred at room temperature for 4 h. Then the solvent was reduced to about 2 ml, and slowly added to 20 ml of stirring hexane. The yellow precipitates thus formed were filtered off and wash with hexane and identified as **4a** (0.09 g, 0.11 mmol) in 65% yield. Spectroscopic data for **4a** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.48–7.11 (m, 30H, H of Ph group); 6.55, 6.41 (m, 2H each one, H of indenyl group); 4.99, 4.87, 4.78 (br, 1H each one, H of indenyl group); 3.84 (t, 1H, NCC*H*(Ph)CH_2, J_{H-H} = 7.14 Hz); 2.56 (m, 4H, 2CH_2 of dppe); 2.45 (m, 2H, CH(Ph)C*H*$_2$). ^{31}P NMR ($CDCl_3$): δ 83.3, 81.4 (AX, J_{P-P} = 27.3 Hz). ^{13}C NMR ($CDCl_3$): 137.2–126.8 (Ph); 123.7 (*C*N); 107.7, 106.9 (C of indenyl group); 91.8 (C of indenyl group); 65.3 (C of indenyl group); 41.2 (N*C*H(Ph)); 39.8 (NCH(Ph)CH_2); 27.6 (t, J_{C-P} = 22.5 Hz, CH_2 of dppe). HRMS (ESI, *m*/*z*): 821.8 (M^+); 615.7 (M^+ − NC_2(Ph)HCH_2Ph). Anal. Calcd. for $C_{50}H_{44}P_2N_4Ru$: C: 69.51, H: 5.13, found: C: 69.74, H: 5.14.

4.14. Reaction of **3b** with $TMSN_3$

To a solution of **3b** (0.16 g, 0.21 mmol) in THF (5 ml) was added $TMSN_3$ (0.1 ml, 0.76 mmol). The solution was stirred at room temperature for 4 h. Then the solvent was reduced to about 2 ml, and slowly added to 20 ml of stirring hexane. The yellow precipitates thus formed were filtered off and wash with hexane and identified as **5b** (0.13 g, 0.17 mmol) in 81% yield. Spectroscopic data for **5b** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.41–6.89 (m, 25H, H of Ph group); 6.82, 6.49 (m, 2H each one, H of indenyl group); 4.80, 4.78, 4.62 (br, 1H each one, H of indenyl group); 3.76 (t, 1H, NCC*H*(Ph)CH_2, J_{H-H} = 7.16 Hz); 3.05, 2.57 (m, 2H each, 2CH_2 of dppe); 2.10, 1.95 (AB, 2H, CH(Ph)C*H*$_2$, J_{H-H} = 5.3, 16.7 Hz and, J_{H-H} = 9.0, 16.7 Hz). ^{31}P NMR ($CDCl_3$): δ 93.3, 85.6 (AX, J_{P-P} = 27.7 Hz). ^{13}C NMR ($CDCl_3$): 158.7 (N*C*N); 138.5–127.1 (Ph); 112.9 (CN); 106.3, 106.1 (C of indenyl group); 92.4 (C of indenyl group); 68.1 (C of indenyl group); 39.8 (N*C*H(Ph)); 27.6 (t, J_{C-P} = 22.3 Hz, CH_2 of dppe); 23.1 (NCH(Ph)CH_2). HRMS (ESI, *m*/*z*): 813.8 (M^+); 615.1 (M^+ − N_4C_2(Ph)HCH_2CN). Anal. Calcd. for $C_{45}H_{39}P_2N_5Ru$: C: 66.49, H: 4.84, found: C: 66.65, H: 4.87.

4.15. Reaction of **3c** with $TMSN_3$

To a solution of **3c** (0.16 g, 0.19 mmol) in THF (5 ml) was added $TMSN_3$ (0.1 ml, 0.76 mmol). The solution was stirred at room temperature for 4 h, then the solvent was reduced to about 2 ml, and slowly added to 20 ml of stirring hexane. The yellow precipitates thus formed were filtered off and wash with hexane and identified as **4c** (0.12 g, 0.14 mmol) in 74% yield. Spectroscopic data for **4c** are as follows. ^{1}H NMR ($CDCl_3$): δ 7.58–7.11 (m, 30H of Ph group); 6.69, 6.43 (m, 2H each one, H of indenyl group); 5.00, 4.96, 4.83 (br, 1H each one, H of indenyl group); 4.37 (t, 1H, NCC*H*(Ph)CH_2, J_{H-H} = 7.40 Hz); 2.68, 2.52 (m, 4H, 2CH_2 of dppe); 2.45 (m, 2H, CH(Ph)C*H*$_2$). ^{31}P NMR ($CDCl_3$): δ 83.9, 81.2 (AX, J_{P-P} = 27.1 Hz). ^{13}C NMR ($CDCl_3$): 136.8–124.2 (Ph); 118.5 (*C*N); 109.3, 104.8 (C of indenyl group); 92.7 (C of indenyl group); 64.8 (C of indenyl group); 43.1 (NCH(Ph)); 41.2 (NCH(Ph)CH_2); 25.3 (t, J_{C-P} = 21.2 Hz, CH_2 of dppe). HRMS (ESI, *m*/*z*): 851.4 (M^+); 615.1 (M^+ − NC_2(Ph)$HCH_2C_6H_4$CN). Anal. Calcd. for $C_{51}H_{43}P_2N_5Ru$: C: 68.91, H: 4.88, found: C: 69.09, H: 4.90.

4.16. Reaction of **3a′** with $TMSN_3$

To a flask with **3a′** (0.14 g, 0.15 mmol) in THF (15 ml), $TMSN_3$ (0.1 ml, 0.76 mmol) was added. The mixture was stirred for 18 h then the resulting orange solution was dried under vacuum. The mixture was added to a stirred hexane. Orange precipitates thus formed were filtered off and washed with diethyl ether. The organometallic product was identified as [Ru]−N_3 (0.074 g, 0.09 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** (0.016 g, 0.087 mmol) in 58% yield [38].

4.17. Reaction of **3b′** with $TMSN_3$

To a solution of **3b′** (0.15 g, 0.17 mmol) in THF (5 ml) was added $TMSN_3$ (0.1 ml, 0.76 mmol). The solution was stirred at room temperature for 18 h. Then the solvent was reduced to about 2 ml, and slowly added to 20 ml of stirring hexane. The yellow precipitates thus formed were filtered off and wash with hexane and identified as **5b′** and [Ru]−N_3 (the mixture is 0.12 g) in 10:1 ratio. 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 **6b** (0.012 g, 0.077 mmol) in 45% yield.

Spectroscopic data for **5b′** are as follows: ^{1}H NMR ($CDCl_3$): δ 7.41–7.01 (m, 35H, H of Ph group); 6.97, 6.72 (m, 2H each one, H of indenyl group); 5.23, 5.01, 4.87 (br, 1H each one, H of indenyl group); 3.24 (t, 1H, NCC*H*(Ph)CH_2, J_{H-H} = 6.82 Hz); 2.62, 2.48 (AB, 2H, CH(Ph)C*H*$_2$, J_{H-H} = 5.6, 15.8 Hz and, J_{H-H} = 8.5, 15.8 Hz); 2.33, 2.17 (m, 2H each, 2CH_2 of dppe). ^{31}P NMR ($CDCl_3$): δ 47.6, 47.4 (AX, J_{P-P} = 37.3 Hz). ^{13}C NMR ($CDCl_3$): 161.4 (N*C*N); 137.2–126.3 (Ph); 114.5 (CN); 107.2, 106.8 (C of indenyl group); 93.8 (C of indenyl group); 71.3 (C of indenyl group); 41.6 (N*C*H(Ph)); 28.3 (NCH(Ph)*C*H_2). HRMS (ESI, *m*/*z*): 939.4 (M^+); 741.2 (M^+ − N_4C_2(Ph)HCH_2CN). Anal. Calcd. for $C_{55}H_{45}P_2N_5Ru$: C: 70.35, H: 4.83, found: C: 70.51, H: 4.85. Spectroscopic data for **6b** are as follows: ^{1}H NMR ($CDCl_3$): δ 7.35–7.12 (m, 5H of Ph group); 3.14 (dd, 1H, NCC*H*(Ph), J_{H-H} = 6.5, 7.2 Hz); 2.71, 2.48 (AX, 2H, C*H*$_2$CN, J_{H-H} = 7.3, 12.9 Hz and J_{H-H} = 6.7, 12.9 Hz). ^{13}C NMR ($CDCl_3$): δ 142.5–126.8 (Ph); 114.3 (CN); 38.2 (CH_2); 33.1 (CH). MS (EI): 156 (M^+). Anal. Calcd. for $C_{10}H_8N_2$: C: 76.90, H: 5.16, found: C: 77.12, H: 5.17.

4.18. Reaction of **3c′** with $TMSN_3$

To a flask with **3c′** (0.14 g, 0.15 mmol) in THF (15 ml), $TMSN_3$ (0.1 ml, 0.76 mmol) was added. The mixture was stirred for 18 h then

the resulting orange solution was dried under vacuum. The mixture was added to a stirred hexane. Orange precipitates thus formed were filtered off and washed with diethyl ether. The organometallic product was identified as [Ru]–N_3 (0.072 g, 0.092 mmol) in 61% 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 **6c** (0.018 g, 0.078 mmol) in 52% yield.

Spectroscopic data for **6c** are as follows: ^{1}H NMR (C_6D_6): δ 7.41–6.69 (m, 10H, Ph); 3.28 (dd, 1H, NCC*H*(Ph), $J_{H-H} = 6.7$, 7.8 Hz); 2.63, 2.54 (AX, 2H, C*H*$_2$C$_6$H$_4$CN, $J_{H-H} = 7.8$, 13.6 Hz and $J_{H-H} = 6.7$, 13.6 Hz). ^{13}C NMR (C_6D_6): δ 141.4–127.5 (Ph); 119.2 (CN); 40.1(CH_2); 36.9 (CH). MS (EI): 232 (M^+). Anal. Calcd. for $C_{16}H_{12}N_2$: C: 82.73, H: 5.20, found: C: 82.75, H: 5.22.

Acknowledgments

We are grateful for support of this work from the National Science Council of the Republic of China (NSC Grant No. 97-2113-M-003-007-MY2) and National Taiwan Normal University (98031022) for financial support.

Appendix. Supplementary material

CCDC-776703, 776704, 794306 (see Table 1) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] M.I. Bruce, Chem. Rev. 91 (1991) 197–257.
[2] C. Bruneau, P.H. Dixneuf, Acc. Chem. Res. 32 (1999) 311–323.
[3] V. Cadierno, S. Conejero, J. Diez, M.P. Gamasa, J. Gimeno, S. Garcia-Granda, Chem. Commun. 7 (2003) 840–841.
[4] V. Cadierno, S. Conejero, M.P. Gamasa, J. Gimeno, Organometallics 21 (2002) 3837–3840.
[5] V. Cadierno, M.P. Gamasa, J. Gimeno, C. Gonzalez-Bernardo, E. Perez-Carreno, S. Garcia-Granda, Organometallics 20 (2001) 5177–5188.
[6] J.-H. Xie, L.-X. Wang, Y. Fu, S.-F. Zhu, B.-M. Fan, H.-F. Duan, Q.-L. Zhou, J. Am. Chem. Soc. 125 (2003) 4404–4405.
[7] M. Kitamura, M. Tsukamoto, Y. Bessho, M. Yoshimura, U. Kobs, M. Widhalm, R. Noyori, J. Am. Chem. Soc. 124 (2002) 6649–6667.
[8] M. Yamakawa, H. Ito, R. Noyori, J. Am. Chem. Soc. 122 (2000) 1466–1478.
[9] B.M. Trost, F.D. Toste, A.B. Pinkerton, Chem. Rev. 101 (2001) 2067–2096.
[10] Y. Wang, M.G. Finn, J. Am. Chem. Soc. 117 (1995) 8045–8046.
[11] K. Ohe, M. Kojima, K. Yonehara, S. Uemura, Angew. Chem. Int. Ed. Engl. 35 (1996) 1823–1825.
[12] S. Fomine, S.M. Vargas, M.A. Tlenkopatchev, Organometallics 22 (2003) 93–99.
[13] A.E. Sutton, B.A. Seigal, D.F. Finnegan, M.L. Snapper, J. Am. Chem. Soc. 124 (2002) 13390–13391.
[14] M.S. Sanford, M. Ulman, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 749–750.
[15] L. Delaude, A. Demonceau, A.F. Noels, Macromolecules 36 (2003) 1446–1456.
[16] M. Kamigaito, Y. Watanabe, T. Ando, M. Sawamoto, J. Am. Chem. Soc. 124 (2002) 9994–9995.
[17] F. Alonso, I.P. Beletskaya, M. Yus, Chem. Rev. 104 (2004) 3079–3160.
[18] V. Cadierno, M.P. Gamasa, J. Gimeno, Coord. Chem. Rev. 248 (2004) 1627–1657.
[19] H. Werner, R. Weinhand, W. Knaup, Organometallics 10 (1991) 3967–3977.
[20] T.O. Rappert, N. Mahr, J. Wolf, H. Werner, Organometallics 11 (1992) 4156–4164.
[21] N.M. Kostic, R.F. Fenske, Organometallics 1 (1982) 974–982.
[22] S.I. Ghazala, F. Paul, L. Toupet, T. Roisnel, P. Hapiot, C. Lapinte, J. Am. Chem. Soc. 128 (2006) 2463–2476.
[23] M.G. Basallote, M. Besora, J. Duran, M.J. Fernandez-Trujillo, A. Lledos, M.A. Manez, F. Maseras, J. Am. Chem. Soc. 126 (2004) 2320–2321.
[24] N.L. Narvor, L. Toupet, C. Lapinte, J. Am. Chem. Soc. 117 (1995) 7129–7138.
[25] R.D. Adams, A. Davison, J.P. Selegue, J. Am. Chem. Soc. 101 (1979) 7232–7238.
[26] M.J. Schlatter, J. Am. Chem. Soc. 63 (1941) 1733–1737.
[27] K.B. Wiberg, W.J. Bartley, J. Am. Chem. Soc. 82 (1960) 6375–6380.
[28] R. Breslow, P. Dowd, J. Am. Chem. Soc. 85 (1963) 2729–2735.
[29] F.J. Weigert, R.L. Bard, J.R. Shapley, J. Am. Chem. Soc. 92 (1972) 6630–6635.
[30] I.R. Likhotvorik, D.W. Brown, J. Am. Chem. Soc. 116 (1994) 6175–6178.
[31] Y. Chiang, A.S. Grant, A.J. Kresge, S.W. Paine, J. Am. Chem. Soc. 118 (1996) 4366–4372.
[32] D.M. DeSimone, P.J. Desrosiers, R.P. Hughes, J. Am. Chem. Soc. 104 (1982) 4842–4846.
[33] R. Gompper, E. Bartmann, Angew. Chem. Int. Ed. Engl. 24 (1985) 209.
[34] U. Kirchgassner, H. Piana, U. Schubert, J. Am. Chem. Soc. 113 (1991) 2228–2232.
[35] R.P. Hughes, W. Kineui, J.W. Reisch, A. Mueller, Organometallics 4 (1985) 1761–1766.
[36] P.-C. Ting, Y.-C. Lin, G.-H. Lee, M.-C. Cheng, Y. Wang, J. Am. Chem. Soc. 118 (1996) 6433–6444.
[37] K.-H. Chang, Y.-C. Lin, Chem. Commun. 21 (1998) 1441–1442.
[38] K.-H. Chang, Y.-C. Lin, Y.-H. Liu, W. Yu, J. Chem. Soc. Dalton Trans. (2001) 3154–3159.
[39] P.-C. Ting, Y.-C. Lin, M.-C. Cheng, Y. Wang, Organometallics 13 (1994) 2150–2152.
[40] C.-W. Chang, Y.-C. Lin, G.-H. Lee, Y. Wang, Organometallics 19 (2000) 3211–3219.
[41] Z.P. Demko, K.B. Sharpless, J. Org. Chem. 66 (2001) 7945–7950.
[42] P. Magnus, J. Lacour, J. Am. Chem. Soc. 114 (1992) 3993–3994.
[43] Y. Kita, H. Tohma, M. Inagaki, K. Hatanaka, T. Yakura, Tetrahedron Lett. 32 (1991) 4321–4324.
[44] S. Kamijo, T. Jin, Z. Huo, Y. Yamamoto, J. Am. Chem. Soc. 125 (2003) 7786–7787.
[45] S. Kamijo, Y. Yamamoto, Angew. Chem. Int. Ed. 41 (2002) 3230–3233.
[46] S. Kamijo, T. Jin, Y. Yamamoto, J. Am. Chem. Soc. 123 (2001) 9453–9454.
[47] S. Kamijo, T. Jin, Y. Yamamoto, J. Org. Chem. 67 (2002) 7413–7417.
[48] A. Palazzi, S. Stagni, S. Bordoni, M. Monari, S. Selva, Organometallics 21 (2002) 3774–3781.
[49] T. Tanase, H. Mochizuki, R. Sato, Y. Yamamoto, J. Organomet. Chem. 466 (1994) 233–236.
[50] V. Cadierno, M.P. Gamasa, J. Gimeno, J. Borge, S. Garcia-Granda, Organometallics 16 (1997) 3178–3187.
[51] M. Bassetti, P. Alvarez, J. Gimeno, E. Lastra, Organometallics 23 (2004) 5127–5134.
[52] A.F. Hill, A.G. Hulkes, A.J.P. White, D.J. Williams, Organometallics 19 (2000) 371–373.
[53] M.I. Bruce, B.G. Ellis, P.J. Low, B.W. Skelton, A.H. White, Organometallics 22 (2003) 3184–3198.
[54] C.-W. Chang, P.-C. Ting, Y.-C. Lin, G.-H. Lee, Y. Wang, J. Organomet. Chem. 553 (1998) 417–425.
[55] Y.-S. Yen, Y.-C. Lin, Y.-H. Liu, Y. Wang, Organometallics 26 (2007) 1250–1255.
[56] A. Davison, J.P. Selegue, J. Am. Chem. Soc. 102 (1980) 2455–2456.
[57] A.G.M. Barrett, N.E. Carpenter, Organometallics 6 (1987) 2249–2250.
[58] Y.-H. Lo, Y.-C. Lin, C.-C. Huang, J. Organomet. Chem. 693 (2008) 117–127.
[59] A.G.M. Barrett, N.E. Carpenter, M. Sabat, J. Organomet. Chem. 352 (1988) C8–C12.
[60] W.R. Ellis Jr., W.L. Purcell, Inorg. Chem. 21 (1982) 834–837.
[61] W.G. Jackson, S. Cortez, Inorg. Chem. 33 (1994) 1921–1927.
[62] R.N. Bulter, Adv. Heterocycl. Chem. 21 (1977) 323–435.
[63] R.R. Wexler, W.J. Greenlee, J.D. Irvin, M.R. Goldberg, K. Predergast, R.D. Smith, P.B.M.W.M. Timmermans, J. Med. Chem. 39 (1996) 625–656.
[64] A.P. Kozikowski, J. Zhang, F. Nan, P.A. Petukhov, E. Grajkowaska, J.T. Wroblewski, T. Yamamoto, T. Bzdega, B. Wroblewska, J.H. Neale, J. Med. Chem. 47 (2004) 1729–1738.
[65] S. De Lombaert, L. Blanchard, L.B. Stamford, J. Tan, E.M. Wallace, Y. Satoh, J. Fitt, D. Hoyer, D. Simonsbergen, J. Moliterni, N. Marcopoulos, P. Savage, M. Chou, A.J. Trapani, A.Y. Jeng, J. Med. Chem. 43 (2000) 488–504.
[66] Z.P. Demko, K.B. Sharpless, Org. Lett. 4 (2002) 2525–2527.
[67] F. Himo, Z.P. Demko, L. Noodleman, K.B. Sharpless, J. Am. Chem. Soc. 124 (2002) 12210–12216.
[68] F. Himo, Z.P. Demko, L. Noodleman, K.B. Sharpless, J. Am. Chem. Soc. 125 (2003) 9983–9987.
[69] W.G. Finnegan, R.A. Henry, R.J. Lofquist, J. Am. Chem. Soc. 80 (1958) 3908–3911.
[70] M. Bassetti, V. Cadierno, J. Gimeno, C. Pasquini, Organometallics 27 (2008) 5009–5016.
[71] L.A. Oro, M.A. Ciriano, M. Campo, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 289 (1985) 117–131.