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Synthesis and reactivity of ruthenium tetrazolate complexes containing a tris(pyrazolyl)borato (Tp) ligand

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Abstract

Facile ligand substitutions are observed when the neutral ruthenium cyclopropenyl complex (PPh_3)[Ru]–C=C(Ph)CHCN (**1**, [Ru] = Tp(PPh_3)Ru) is treated with MeCN and pyrazole yielding the nitrile substituted ruthenium cyclopropenyl complex (MeCN)[Ru]–C=C(Ph)CHCN (**4a**) and the ruthenium metallacyclic pyrazole complex (C_3H_3NN)[Ru]–C=C(Ph)CH_2CN (**7a**), respectively. The reactions of Me_3SiN_3 with **1**, **4a** and **7a** are investigated. Treatment of **1** with Me_3SiN_3 affords in high yield the cationic N-coordinated nitrile complex {(PPh_3)[Ru]NCCH(Ph)CH_2CN}N_3 (**3**). Interestingly, the reaction of **4a** with Me_3SiN_3 in CH_2Cl_2 in the presence of NH_4PF_6 results in an insertion of four nitrogen atoms into the Ru–C_α bond to form a diastereomeric mixture of the bright yellow zwitterionic tetrazolate complex (MeCN)[Ru]–N_4CCH(Ph)CH_2CN (**6a**) in a 3:2 ratio. The reaction of **7a** with Me_3SiN_3 gives the zwitterionic tetrazolate complex (C_3H_3NNH)[Ru]–N_4CCH(Ph)CH_2CN (**9a**). The two cationic tetrazolate complexes {(C_3H_3NNH)[Ru]–N_4(R)CCH(Ph)CH_2CN}$^+$ (**12a**, R = CH_3, **12b**, R = $C_6H_5CH_2$) are prepared by electrophilic addition of organic halides to **9a**. All of the complexes are identified by spectroscopic methods as well as elemental analysis. Pathways for the synthesis of these compounds are proposed.

Keywords: Tris(pyrazolyl)borato; Ruthenium; Vinylidene; Azide; Cyclopropenyl; Tetrazolate

1. Introduction

Tris(pyrazoly)borate anion (Tp, $HB(pz)_3$) has been introduced by Trofimenko as a ligand in the preparation of various transition metal complexes [1]. The development of Tp chemistry within group VIII has picked up the pace since then. The Tp ligand is often compared with the Cp (Cp = η^5-C_5H_5) ligand due to their charge and number of electrons donated in the formation of complex. Notwithstanding, differences in size and electronic properties are obvious. Thus the cone angle of Tp close to 180° is well above the 100° calculated for Cp. The steric bulk of the Tp ligand appears to disfavor higher coordination numbers or bulky structure of the metal center [2]. The chemistry of organometallic ruthenium complexes have been the focus of many recent investigations, such as asymmetric hydrogenation [3], olefin metathesis [4], and polymerization [5]. Metal-mediated processes in many instances make possible certain reactions, which are not feasible without the involvement of metal ions. It is therefore important to better understand how an organic moiety attached on the metal undergoes chemical transformation. We previously reported the synthesis of cyclopropenyl complexes of ruthenium through a deprotonation reaction of cationic vinylidene complexes [6]. The same approach could also be used for the synthesis of metal-coordinated azirinyl complexes from cationic metal isocyanide complexes [7]. Highly strained organic cyclopropene and azirine compounds are synthetically useful [8]. Participation of d orbital of Ru metal may stabilize this highly strained organic moiety consisting of a three-membered ring thus making

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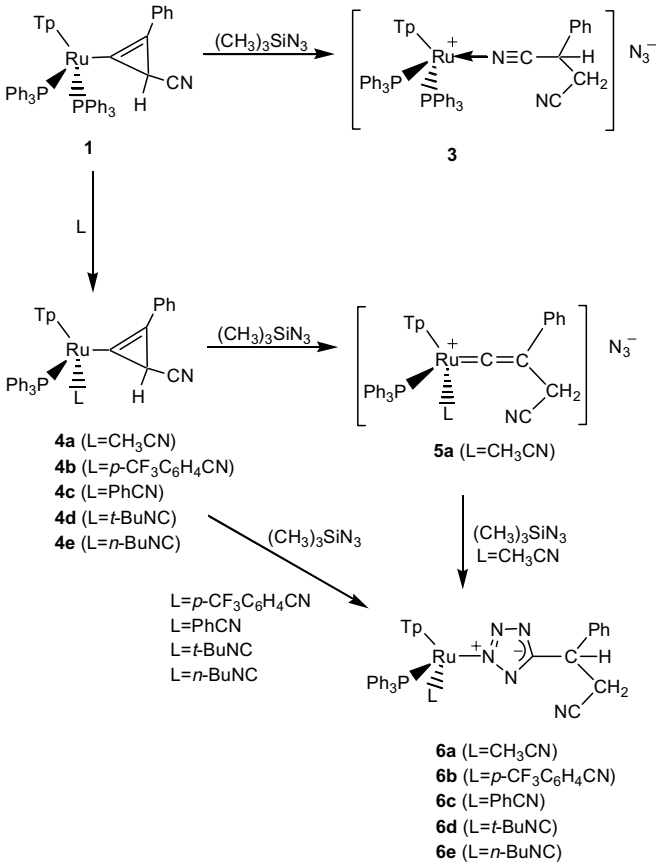
these complexes readily accessible for further exploitation for the preparation of organic molecules. For example, reactions of ruthenium azirinyl complexes with aldehyde or acetone gave oxazolinyl complexes [7]. The previously reported regiochemistry of the carbon–carbon bond formation in the photoreaction of organic azirine with carbonyl group is reversed [9]. Much of character of the chemistry of the $[Cp(PPh_3)_2Ru]^+$ fragment can be traced to strongly π-basic nature of the ruthenium center. Replacing Cp with Tp increases the basicity of the metal center further, and it has been argued that it also leads to more ideally octahedral hybridization [2].

Trimethylsilyl azide and sodium azide were used widely in organic or organometallic reactions [10]. Organic azides react with alkenes or alkynes giving triazoline or triazole compounds through a [3+2] cycloaddition [11]. However, for an efficient [3+2] cycloaddition to give triazoles, the presence of an electron-withdrawing group is needed either at the alkyne or at the azide part. Coupling reaction between azide, such as Me_3SiN_3, with simple alkyne and allyl carbonates catalyzed by Pd^0/Cu^I was reported by Yamamoto and his co-workers [12] as an efficient method for the synthesis of triazoles. The azide reagent is also commonly used in the synthesis of metal complexes with N-heterocyclic ligand. A number of N-coordinated Fe tetrazole derivatives were obtained by the reaction of sodium azide with the coordinated CN of the N-coordinated iron nitrile complex. The mechanism probably involves nucleophilic attack of the azide anion to the carbon atom of the coordinated nitrile followed by cyclization [13].

During the course of investigations into ruthenium cyclopropenyl chemistry, we previously established the formation of interesting neutral ruthenium tetrazolate complex [14]. For example, the cyclopropenyl complex $Cp(PPh_3)_2Ru–C{=}C(Ph)CHCN$ was found to react with an excess amount of Me_3SiN_3 to afford the zwitterionic tetrazolate complex $Cp(PPh_3)_2Ru–N_4CCH(Ph)CH_2CN$. We thought similar complex containing a Tp ligand would be a logical extension. Herein, we report preparation of several zwitterionic Tp ruthenium tetrazolate complexes. Electrophilic addition to the zwitterionic Tp ruthenium tetrazolate complex also affords new cationic complex. This study again shows that the Tp ligand, while similar to the Cp ligand in many ways, creates a new and unique chemistry for exploration.



Scheme 1.

2. Results and discussion

2.1. Reaction of 1 with Me_3SiN_3

The reaction of the Tp ruthenium cyclopropenyl complex $(PPh_3)[Ru]–C{=}C(Ph)CH–CN$ (**1**, $[Ru] = Tp(PPh_3)$-Ru) with a fivefold excess of Me_3SiN_3 in CH_2Cl_2 at room temperature lead to the formation of the cationic N-coordinated nitrile complex $\{(PPh_3)[Ru]NCCH(Ph)CH_2$-$CN\}N_3$ (**3**) as a light yellow powder in 63% yield (Scheme 1). Complex **3** is soluble in polar solvent such as $CHCl_3$, THF, CH_3OH and CH_3CN but insoluble in ether and hexane. In a separate experiment, a green colored intermediate was acquired at 0 °C as the major product, along with a small amount of complex **3**. The reaction carried out at 0 °C for 5 h in the presence of NH_4PF_6 gave a green solution from which an intermediate with counter anion PF_6^- could be isolated in high yield. In the absence of NH_4PF_6 the intermediate is proposed as the cationic vinylidene complex $\{(PPh_3)[Ru]{=}C{=}C(Ph)CH_2CN\}N_3$ (**2**). Complex **2** is unstable in solution at room temperature and undergoes a further reaction with Me_3SiN_3 to give **3**, which is stable in solution. Complex **2** can be isolated in a stable form by replacing the counter anion N_3^- by PF_6^-. Trace of water in CH_2Cl_2 is believed to act as the source of protons that are incorporated into the product through hydrolysis of the Me_3Si group derived from addition of Me_3SiN_3 to the three-membered ring. From the reaction mixture Me_3SiOH was also distilled off with CH_2Cl_2 and was identified by mass spectrometry. The characteristic spectroscopic data of **2** consist of a strongly deshielded C_α resonance as a triplet at δ 375.3 with $J_{P-C} = 16.5$ Hz in the ^{13}C NMR spectrum and a singlet ^{31}P NMR resonance at δ 36.5 in $CDCl_3$ at 0 °C, which is due to fluxional behavior of the vinylidene ligand [6]. For comparison, the spectroscopic data of the Cp analogue are similar; the triplet C_α resonance appears at δ 345.6 with $J_{P-C} = 17.9$ Hz in the ^{13}C NMR spectrum and a singlet ^{31}P NMR resonance

is observed at δ 42.4 [6a]. Formation of **2** occurs by selective cleavage of the cyclopropenyl C–C single bond near the metal center. This selectivity is similar to that reported for the unsymmetrical cyclopropenes where the single C–C bond with a metal-substituent is cleaved [6a]. The ^{31}P NMR spectrum of **3** displays two doublet resonances at δ 39.1 and 38.7 with $J_{P-P} = 29.4$ Hz assigned to the two PPh_3 ligands owing to the presence of a diastereotopic center in the N-coordinated nitrile ligand. In the ^1H NMR spectrum, the same pattern, *i.e.* a two multiplet resonance at δ 3.41 and 3.05 assigned to the diastereotopic CH_2 group is consistent with the ^{31}P NMR data. The C≡N stretching of N-coordinated nitrile ligand of **3** in IR spectrum appears at 2253 cm^{-1}. In the FAB mass spectrum of **3**, the parent peak for the cationic complex is observed at $m/z = 995.1$ indicating addition of one nitrogen atom and two hydrogen atoms to **1**. On the basis of these data, it is clear that the nitrile ligand is coordinated to the $[Tp(PPh_3)_2Ru]^+$ moiety via the nitrogen atom. Conversion of a vinylidene precursor to N-coordinated nitrile by hydrazine, an organometallic Beckmann rearrangement, has been reported in an iron system [15].

2.2. Reaction of cyclopropenyl complexes with Me_3SiN_3

We previously reported [6] the analogous Cp complex of **1**, which is stable with respect to the ligand substitution reaction making the coordination site of **1** unavailable for an incoming substrate. In contrast, the Tp complex **1** is susceptible to ligand substitution reaction under relatively mild conditions. This may be attributed to the increased steric bulk of the Tp ligand relative to the Cp. For example, when 2 equiv. of PhCN, *p*-$CF_3C_6H_4CN$, *n*-BuNC or *t*-BuNC were added at room temperature to a CH_2Cl_2 solution of **1** a smooth reaction ensued over 1 h affording good yields of various bright yellow cyclopropenyl complexes (L)[Ru]–C═C(Ph)CHCN (**4a**, L = MeCN; **4b**, L = *p*-$CF_3C_6H_4CN$; **4c**, L = PhCN;**4d**, L = *t*-BuNC; **4e**, L = *n*-BuNC), respectively. Treatment of complex **4a** with a fivefold excess of Me_3SiN_3 in CH_2Cl_2 in the presence of NH_4PF_6 at room temperature for 24 h results in a ring-opening reaction followed by the insertion of four nitrogen atoms into the Ru–C_α bond to form the yellow zwitterionic tetrazolate complex (MeCN)[Ru]–N_4CCH(Ph)CH_2CN (**6a**) (Scheme 1). A series of successive color changes were noted during the course of the reaction. The light yellow solution of **4a** first turned deep green upon addition of Me_3SiN_3at room temperature, and subsequently turned light yellow after 10 h and then yellow after 24 h. In both reactions of **1** and **4a** with Me_3SiN_3, addition of D_2O to CH_2Cl_2 led to incorporation of two deuterium atoms at two vicinal carbon atoms of both **3** and **6a**. The green vinylidene intermediate {(MeCN)[Ru]═C═C(Ph)CH_2-CN}N_3 (**5a**) could also be isolated from the reaction carried out at 0 °C for a shorter reaction time. However, no reaction was observed between {(MeCN)[Ru]═C═C(Ph)-CH_2CN}PF_6 and Me_3SiN_3. Significantly, the reaction of {(MeCN)[Ru]═C═C(Ph)CH_2CN}PF_6 with NaN_3 can give a mixture of **5a** and other unidentified products. Only in the presence of both Me_3SiN_3 and NaN_3 the reaction of the vinylidene can afford **6a** indicating the requirement of both the electrophile and nucleophile for the reaction to take place. This might be due to the covalent character of the Si–N bond in Me_3SiN_3 and weak nucleophilicity of the vinylidene ligand of the cationic complex to cleave the Si–N bond. The presence of a Me_3Si group in the reaction system assists the ring-opening process. Thus the reaction of **4a** with Me_3SiCl in the presence of NaN_3 gave a mixture of **5a** and other unidentified products. For **5a** with a PF_6 counter anion, attempts to exchange the counter anion to a N_3 anion led to decomposition of the vinylidene complex. To initiate a clean addition reaction at C_α it is therefore essential to have the three-membered cyclopropenyl ring. The presence of a Me_3Si group as an electrophile is also required for the opening of the three-membered ring. For complex **6a** diastereomers in a 3:2 ratio are observed. The major and minor isomers display singlet ^{31}P NMR resonance at δ 53.1 and 53.2, respectively. In the ^1H NMR spectrum of **6a**, the dd resonance at δ 4.54 and 4.49 are assigned to the methyne proton and two resonances displaying doublets of an AB pattern at δ 3.19, 2.94 and δ 3.02, 2.76 are assigned to the diastereotopic methylene group of major and minor isomers, respectively. By comparing the spectroscopic data of **6a** with that of the Cp analogue, it is clear that the organic ligands are the same [14].

Similarly, preparation of other zwitterionic tetrazolate complexes (L)[Ru]–N_4CH(Ph)CH_2CN (**6b**, L = *p*-$CF_3C_6H_4CN$; **6c**, L = PhCN; **6d**, L = *t*-BuNC; **6e**, L = *n*-BuNC) have all been accomplished with high yields by reacting a fivefold excess of Me_3SiN_3 with the corresponding Tp ruthenium cyclopropenyl complexes **4b–e**, which were readily prepared from the reaction of **1** with corresponding reagents [6]. Significantly, when these reactions were repeated using only 1 equiv. of Me_3SiN_3 much lower yields of the product (ca. 15%) were obtained. Complexes **6b–e** all contain diastereomers in a 3:2 ratio. With the exception of **6d**, other tetrazolate complexes mentioned above are prepared in CH_2Cl_2 at room temperature. For the synthesis of **6d**, heating is required and a mixture of $CH_2Cl_2/CHCl_3$ (3:1 v/v) was used as a solvent in order to achieve a slightly higher reaction temperature. Complexes **6a–e** all display yellow color in their solid state. Interestingly, major isomers of **6a**, **6b** and **6c**, are more stable than their corresponding minor isomer. Complexes **6d** and **6e** are stable in ether, and THF, and in $CHCl_3$, **6a**, **6b**, **6c** and **6d** are less stable than **6e**. Furthermore, **6d** decomposes in $CHCl_3$ producing (*t*-BuNC)[Ru]–Cl and other unidentifiable organic products. Decomposition of **6a**, **6b** and **6c** produces complicated mixture. The stability of substituted tetrazolate complexes are found to decrease in the following order: *n*-BuNC > *t*-BuNC > *p*-$CF_3C_6H_4CN$ > PhCN > CH_3CN. This could mean that a better π accepter ligand makes

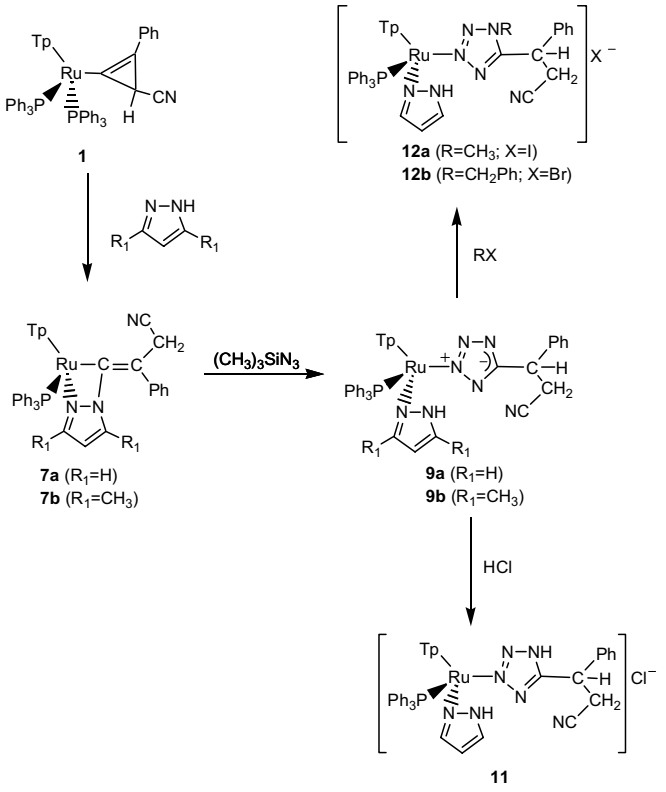
the tetrazolate complex more stable which may be attributed to the strong trans influence of the Tp ligand.

2.3. Possible mechanism for the formation of 3 and 6a

The reaction of **1** with Me_3SiN_3 leading to **3** may proceed *via* the following pathway. An electrophilic addition of the Me_3Si group to the three-membered ring with concomitant ring-opening followed by hydrolysis of the added Me_3Si group affords **2** containing an azide counter anion. This is followed by nucleophilic addition of the azide anion at C_α of the resulting vinylidene ligand. Subsequent electrophilic addition of a second Me_3Si group at C_β followed by loss of N_2 is accompanied by a metal migration and hydrolysis of the Me_3Si group to give the N-coordinated nitrile complex **3** (Scheme 1). In the reaction of **4a** with Me_3SiN_3, the reaction may proceed similarly in the first stage to give an analogue of **3**. Formation of **6a**is then rationalized by a [3+2] cycloaddition of the C≡N bond with another azide anion followed by metal migration (linkage isomerization). A possible pathway *via* direct cyclization of the imine intermediate with azide anion to result in formation of **6a** could also occur. In a previous study, organic tetrazole compound was synthesized *via* a [3+2] cycloaddition reaction of a nitrile group with azide [16]. In some systems, cyclization was observed in the case of an imine compound with an azide group [16]. Additionally, tetrazole compounds resulted from attack of an azide to an imine compound with an appropriate leaving group followed by cyclization have also been reported [17]. The fact that compound **3** would not undergo further nucleophilic addition or cyclization is interpreted in terms of relatively larger steric hindrance of a PPh_3 relative to the MeCN ligand. Interestingly, we have previously reported [6c] that the reaction of the analogous Cp complex of **1** with Me_3SiN_3 did not yield the N-coordinated nitrile complex but rather the tetrazolate complex. This could mean that the steric bulk of the Tp ligand makes the N-coordinated nitrile complex less reactive for further nucleophilic addition or cyclization. Metal-coordinated azide ligands undergo 1,3-dipolar cycloaddition reactions with carbon–carbon and carbon–heteroatom multiple bonds. The metals involved in such reactions are Pd(II) [18], Pt(II) [19] or Co(III) [20]. although a whole range of other transition metals has been used. Formation of tetrazolate ring in **6a** should not proceed *via* this pathway since the reaction of organic nitrile with (CH_3CN)[Ru]–N_3 does not yield **6a**.

2.4. Reaction of metallacyclic complex with Me_3SiN_3

The reaction of **1** with pyrazole in CH_2Cl_2 at room temperature did not yield the expected neutral substituted cyclopropenyl complex, but instead gave the metallacyclic complex (C_3H_3NN)[Ru]–C═C(Ph)CH_2CN (**7a**) see Scheme 2. At room temperature addition of excess Me_3SiN_3 to a CH_2Cl_2 solution of **7a** leads to the formation of the tetrazolate complex (C_3H_3NNH)[Ru]–N_4CCH(Ph)-



Scheme 2.

CH_2CN (**9a**), obtained as a bright yellow powder in high yield (Scheme 2). Complex **9a** contains two diastereomers in a 3:2 ratio and is soluble in CH_2Cl_2, THF, and ether. In the ^1H NMR spectrum of the mixture containing both major and minor isomers, two multiplet resonances displaying doublets of an AB pattern at δ 3.03, 2.85 and δ 3.12, 2.93 are assigned to two methylene groups, respectively. The major and minor isomers display singlet ^{31}P NMR resonances at δ 54.6 and 54.1, respectively. The intermediate {(C_3H_3NNH)[Ru]═C═C(Ph)CH_2CN}N_3 (**8a**–$\mathbf{N_3}$) was observed in the initial stage of the reaction when the reaction is monitored by spectroscopic method. Reaction of (Me_2C_3HNN)[Ru]–C═C(Ph)CH_2CN (**7b**) with Me_3SiN_3 gives similar product (Me_2C_3HNNH)[Ru]–N_4CCH(Ph)CH_2CN (**9b**) in lower yield which may be attributed to the slightly higher steric effect.

The reaction of **7a** with Me_3SiCl in CH_2Cl_2 did not yield the expected carbene complex, instead, the cationic vinylidene complex **8a**–**Cl** was obtained. No nucleophilic reaction was observed between {(C_3H_3NNH)[Ru]═C═C(Ph)CH_2CN}$^+$ and Cl^- possibly owing to weak nucleophilicity of the chloride. In addition, the corresponding reaction between Me_3SiCl and **7b** proceeded in a similar fashion to afford the cationic vinylidene complex {(Me_2C_3HNNH)[Ru]═C═C(Ph)CH_2CN}Cl (**8b**–**Cl**) in lower yield. Similarly, treatment of **7a** with $HgCl_2$ affords the addition product {(C_3H_3NNH)[Ru]═C═C(Ph)CH(HgCl)CN}Cl (**10a**) and treatment of **7b** with $HgCl_2$ also gives {$(Me_2C_3$-HNNH)[Ru]═C═C(Ph)CH(HgCl)CN}Cl (**10b**). These

reactions were carried out at −20 °C in CH_2Cl_2 since complex **10a** and **10b** are thermally unstable. However, upon dissolution at room temperature, complexes **10a** and **10b** immediately convert back to **7a** and **7b**, respectively. Formation of these vinylidene complexes occurs by selective cleavage of the single N–C_α bond of the four-membered ring, which may have high ring strain.

2.5. Reactions of *9a* with electrophiles

The reaction of **9a** with HCl results in a protonation at the tetrazolate ring and gives **11** as the only product (Scheme 2). In the presence of excess NH_4PF_6 the counter anion is replaced by PF_6^-. The ^1H NMR spectrum of **11** displays the characteristic pattern for the $CHCH_2$ group. Two singlet ^{31}P NMR resonances at δ 53.7 and 53.5 are assigned to the major and minor isomer, respectively. The protonation might have occurred at one of two nitrogen atoms next to the unique carbon of the tetrazolate ring because of localization of the negative charge at these two nitrogen atoms in **9a** [14]. Similarly, preparation of the cationic tetrazolate complex $\{(C_3H_3NNH)[Ru]\text{-}N_4(R)CCH(Ph)CH_2CN\}^+$ (**12a**, R = CH_3, **12b**, R = $C_6H_5CH_2$) have all been accomplished by reacting **9a** with the corresponding halides resulting in electrophilic addition with high yields. Complexes **11**, **12a** and **12b** are all soluble in polar solvent such as $CHCl_3$, CH_2Cl_2, MeOH and MeCN but insoluble in ether and hexane. These complexes all display green color in their solid state. The newly formed nitrogen–carbon bond of tetrazolate complexes **12a** and **12b**, prepared by carrying out the reaction at room temperature, is easily cleaved in the presence of acid. The hexafluorophosphate salt NH_4PF_6 used for the preparation is easily converted to HPF_6. Complexes **11**, **12a** and **12b** in solution are all stable for a period of 3 days and then decomposed to some unidentifiable products.

2.6. Conclusions

Reaction of the ruthenium complex **1** with Me_3SiN_3afforded the N-coordinated nitrile complex **3**. Upon addition of Me_3SiN_3 to the neutral ruthenium cyclopropenyl complex **4a** in the presence of NH_4PF_6 four nitrogens insert into the Ru–C_α to form the yellow zwitterionic tetrazolate complexes **6a**. The reaction may proceed through the same type of intermediate as that in the formation of **3** from **1** followed by a further addition of Me_3SiN_3. Treatment of the ruthenium metallacyclic complex **7a** with Me_3SiN_3 also gives the tetrazolate complex **9a** but the reaction of **7a** with Me_3SiCl affords the cationic vinylidene complex **8a**. Several new cationic tetrazolate complexes are prepared by electrophilic addition of organic halides to complex **9a**. Characterization of these products has led to a better understanding on the chemical reactivity of the cyclopropenyl complexes. The reaction can be explained in terms of combined effects of the nucleophilicity of the sp^3 carbon of the cyclopropenyl ring and the electrophilic nature of the Me_3Si group.

3. Experimental

3.1. Materials

All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagents grade and were used without further purification. NMR spectra were recorded on Bruker AC-200 and AM-300WB FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in unit δ with residual protons in the solvent as an internal standard ($CDCl_3$, δ 7.24; CD_3CN, δ 1.93; C_2D_6CO, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Elemental analyses were carried out at the Regional Center of Analytical Instrument at National Taiwan University. The complexes **1**, **4a**–**e**, **5a** and **7a**,**b** were prepared according to literature methods [6c].

3.2. Synthesis of $\{(PPh_3)[Ru]{=}C{=}C(Ph)CH_2CN\}N_3$ (*2*)

To a solution of complex **1** (0.66 g, 0.67 mmol) in 20 mL CH_2Cl_2 at 0 °C was added Me_3SiN_3 (0.4 mL, 3.02 mmol). After 5 h, the solution was slowly added to 90 mL of a diethyl ether solution. The green precipitate thus formed was filtered off and washed with diethyl ether and hexane to give a green product identified as **2** (0.44 g, 64% yield). Spectroscopic data for **2**: ^1H NMR ($CDCl_3$): δ 7.89 (br, 1H, Tp), 7.62 (br, 2H, Tp), 7.42–6.94 (m, PPh_3, C_2Ph, Ph), 6.78 (br, 1H, Tp), 6.66 (br, 1H, Tp), 5.73 (br, 2H, Tp), 5.60 (br, 1H, Tp), 5.47 (br, 1H, Tp). 3.08 (s, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 375.3 (t, J_{P-C} = 16.5 Hz, C_α), 146.2–106.8 (m, Ph, Tp, PPh_3, C_β), 117.4 (CN), 11.4 (CH_2). ^{31}P NMR ($CDCl_3$): δ 36.5. MS (FAB) *m*/*z*: 980.5 (M^+-N_3), 718.4 (M^+-N_3, PPh_3), 577.2 (M^+-N_3, PPh_3, C_2PhCH_2CN). Anal. Calc. for $C_{55}H_{47}BN_{10}P_2Ru$ (1022.3): C, 64.65; H, 4.64; N, 13.71. Found: C, 64.47; H, 4.69; N, 13.67%.

3.3. Synthesis of $\{(PPh_3)[Ru]NCCH(Ph)CH_2CN\}N_3$ (*3*)

To the solution of complex **1** (0.66 g, 0.67 mmol) in 20 mL CH_2Cl_2 at room temperature was added Me_3SiN_3 (0.4 mL, 3.02 mmol). After 5 h, the solution was slowly added to a 70 mL of diethyl ether solution. The light yellow precipitate thus formed was filtered off and washed with diethyl ether and hexane to give the product identified as **3** (0.44 g, 63% yield). Spectroscopic data of **3**: IR (KBr, cm^{-1}): ν(B–H) 2465(br), ν(C≡N) 2253(m), 2243(w) cm^{-1}. ^1H NMR ($CDCl_3$, δ): δ 7.58 (d, J_{H-H} = 2.1 Hz, 1H, Tp), 7.40 (d, J_{H-H} = 2.0 Hz, 2H, Tp), 7.24–6.91 (m, Ph, Tp), 5.54 (t, J_{H-H} = 2.3 Hz, 2H, Tp), 5.31 (t, J_{H-H} = 2.1 Hz,

1H, Tp), 5.20 (d, $J_{H-H} = 1.8$ Hz, 1H, Tp), 4.11 (dd, 1H, $^3J_{H-H} = 6.7$ Hz, $^3J_{H-H} = 7.0$ Hz, CH), 3.41 (dd, $^3J_{H-H} = 6.7$ Hz, $^3J_{H-H} = 7.0$ Hz $^2J_{H-H} = 16.9$ Hz, 1H, CH), 3.05 (dd, $^3J_{H-H} = 6.7$ Hz, $^3J_{H-H} = 7.0$ Hz, $^2J_{H-H} = 16.7$ Hz, 1H, CH). ^{13}C NMR ($CDCl_3$): δ 146.2–106.8 (m, Ph, Tp, PPh_3), 117.4 (CN), 116.5 (CH_2CN), 41.2 (CH), 39.1 (CH_2). ^{31}P NMR ($CD_3C(O)CD_3$, ppm): δ 39.1, 38.7 (AB, $J_{P-P} = 29.4$ Hz). MS (FAB) *m/z*: 995.1 (M^+-N_3), 733.4 (M^+-N_3,PPh_3), 577.1 (M^+-N_3,PPh_3, NCCH(Ph)CH_2CN). Anal. Calc. for $C_{55}H_{48}BN_{11}P_2Ru$ (1037.3): C, 63.71; H, 4.67; N, 14.86. Found: C, 63.47; H, 4.55; N, 14.74%.

3.4. Synthesis of (*CH*$_3$*CN*)[*Ru*]–*N*$_4$*CH*(*Ph*)*CH*$_2$*CN* (**6a**)

To a solution of complex **4a** (0.52 g, 0.69 mmol) in 30 mL CH_2Cl_2 was added Me_3SiN_3 (0.4 mL, 3.02 mmol). After 24 h, the solvent was removed under vacuum, then the solid residue was extracted with diethyl ether, and the extract was filtered. The resulting solution was removed under vacuum and washed with 5 mL hexane. The product was dried under vacuum. The bright yellow product was identified as **6a** (0.30 g, 54% yield). Spectroscopic data of **6a**: IR (KBr, cm^{-1}): ν(B–H) 2478(br), ν(C≡N) 2254(m), 2241(w), ν(N=N) 1436(w) cm^{-1}. ^{1}H NMR ($CD_3C(O)CD_3$): major isomer: δ 7.65 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.57 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.49 (d, $J_{H-H} = 1.9$ Hz, 1H, Tp), 7.42–7.17 (m, Ph), 6.98 (1H, Tp), 6.78 (1H, Tp), 6.76 (1H, Tp), 6.33 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 5.98 (t, J_{H-H}=2.2 Hz, 1H, Tp), 5.85 (t, J_{H-H}=2.2 Hz, 1H, Tp), 4.54 (dd, 1H, $^3J_{H-H} = 7.6$ Hz, $^3J_{H-H} = 7.7$ Hz, CH), 3.19, 2.94 (dd, AB, $^3J_{H-H} = 7.6$ Hz, $^3J_{H-H} = 7.7$ Hz, $^2J_{H-H} = 16.9$ Hz, 2H, CH_2), 2.22 (s, 3H, CH_3CN); minor isomer: δ 7.65 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.57 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.49 (d, $J_{H-H} = 1.9$ Hz, 1H, Tp), 7.48–7.17 (m, Ph), 6.98 (1H, Tp), 6.78 (1H, Tp), 6.76 (1H, Tp), 6.33 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 5.98 (t, $J_{H-H} = 2.2$ Hz, 1H, Tp), 5.85 (t, $J_{H-H} = 2.2$ Hz, 1H, Tp), 4.49 (dd, 1H, $^3J_{H-H} = 7.5$ Hz, $^3J_{H-H} = 7.3$ Hz, CH), 3.02, 2.76 (dd, AB, $^3J_{H-H} = 7.5$ Hz, $^3J_{H-H} = 7.3$ Hz, $^2J_{H-H} = 16.9$ Hz, 2H, CH_2), 2.27 (s, 3H, CH_3CN). ^{13}C NMR ($CDCl_3$): major isomer: 146.9–105.6 (m, Ph, PPh_3, Tp), 123.7 (CH_3CN), 114.4 (CN), 38.4 (CH), 22.7 (CH_2), 3.6 (CH_3CN); minor isomer: 146.9–105.6 (m, Ph, PPh_3, Tp), 124.1 (CH_3CN), 115.3 (CN), 37.8 (CH), 21.9 (CH_2), 3.4 (CH_3CN). ^{31}P NMR ($CD_3C(O)CD_3$, ppm): δ 53.1, 53.2 (3:2). MS (FAB) *m/z*: 816.4 (M^+), 701.2 ($M^+-N_4CCH(Ph)CH_2CN$), 577.1 ($M^+-N_4CCH(Ph)CH_2$-CN, CH_3CN). Anal. Calc. for $C_{39}H_{36}BN_{12}PRu$ (816.2): C, 57.43; H, 4.45; N, 20.61. Found: C, 57.27; H, 4.54; N, 20.48%.

3.5. Synthesis of (*p*-*CF*$_3$*C*$_6$*H*$_4$*CN*)[*Ru*]–*N*$_4$*CH*(*Ph*)-*CH*$_2$*CN* (**6b**)

To a solution of **4b** (0.76 g, 0.86 mmol) in 20 mL of CH_2Cl_2 was added excess $TMSN_3$ (0.6 mL, 4.5 mmol). After stirring for 20 h, the solvent was removed under vacuum, then the solid residue was extracted with diethyl ether, and the extract was filtered. The resulting solution was removed under vacuum and washed with 5 mL hexane. The product was dried under vacuum. The bright yellow product was identified as **6b** (0.57 g, 69% yield). Spectroscopic data of **6b**: IR (KBr, cm^{-1}): ν(B–H) 2497(br), ν(C≡N) 2251(m), 2236(w), ν(N=N) 1438(w) cm^{-1}. ^{1}H NMR ($CD_3C(O)CD_3$): major isomer: δ 7.81 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.80 (d, $J_{H-H} = 2.2$ Hz, 1H, Tp), 7.69 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 7.40–7.07 (m, Ph), 6.86 (br, 1H, Tp), 6.78 (br, 1H, Tp), 6.76 (br, 1H, Tp), 6.02 (t, $J_{H-H} = 1.8$ Hz, 1H, Tp), 5.98 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 5.85 (t, $J_{H-H} = 2.2$ Hz, 1H, Tp), 4.38 (dd, 1H, $^3J_{H-H} = 7.6$ Hz, $^3J_{H-H} = 7.7$ Hz, CH), 3.12, 2.97 (dd, AB, $^3J_{H-H} = 7.6$ Hz, $^3J_{H-H} = 7.7$ Hz, $^2J_{H-H} = 16.7$ Hz, 2H, CH_2); minor isomer: δ 7.81 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.80 (d, $J_{H-H} = 2.2$ Hz, 1H, Tp), 7.69 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 7.40–7.07 (m, Ph), 6.86 (br, 1H, Tp), 6.78 (br, 1H, Tp), 6.76 (br, 1H, Tp), 6.02 (t, $J_{H-H} = 1.8$ Hz, 1H, Tp), 5.98 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 5.85 (t, $J_{H-H} = 2.2$ Hz, 1H, Tp), 4.32 (dd, 1H, $^3J_{H-H} = 7.7$ Hz, $^3J_{H-H} = 7.4$ Hz, CH), 3.21, 2.87 (dd, AB, $^3J_{H-H} = 7.7$ Hz, $^3J_{H-H} = 7.4$ Hz, $^2J_{H-H} = 16.9$ Hz, 2H, CH_2). ^{13}C NMR ($CD_3C(O)CD_3$) major isomer: δ 148.2–126.6 (m, Ph, Tp), 118.1 (CN), 111.2 (NCPh), 110.6 (q, $J_{F-C} = 282.0$ Hz, CF_3), 40.3 (CH), 24.3 (CH_2); minor isomer: δ 147.7–125.1 (m, Ph, Tp), 118.5 (CN), 110.9 (NCPh), 109.8 (q, $J_{F-C} = 279.0$ Hz, CF_3), 39.9 (CH), 24.9 (CH_2). ^{31}P NMR ($CD_3C(O)CD_3$): δ 55.3, 54.7 (3: 2). MS (FAB) *m/z*: 946.4 (M^+), 824.3 ($M^+-N_4CCH(Ph)CH_2CN$), 577.1 (M^+-N_4-$CCH(Ph)CH_2CN$, $CF_3C_6H_4CN$). Anal. Calc. for $C_{45}H_{37}BF_3N_{12}PRu$ (946.2): C, 57.5; H, 3.94; N, 17.77. Found: C, 57.07; H, 4.04; N, 17.68%.

3.6. Synthesis of (*PhCN*)[*Ru*]–*N*$_4$*CH*(*Ph*)*CH*$_2$*CN* (**6c**)

To a solution of **4c** (1.17 g, 1.42 mmol) in 20 mL of CH_2Cl_2 was added excess $TMSN_3$ (0.95 mL, 7.2 mmol). After stirring for 16 h, the solvent was removed under vacuum, then the solid residue was extracted with diethyl ether, and the extract was filtered. The resulting solution was removed under vacuum and washed with 5 mL hexane. The product was dried under vacuum. The bright yellow product was identified as **6c** (0.79 g, 63% yield). Spectroscopic data of **6c**: IR (KBr, cm^{-1}): ν(B–H) 2481(br), ν(C≡N) 2257(m), 2238(w), ν(N=N) 1432(w) cm^{-1}. ^{1}H NMR ($CD_3C(O)CD_3$) major isomer: δ 7.91 (d, $J_{H-H} = 2.2$ Hz, 2H, Tp), 7.69–7.03 (m, Ph), 6.97 (br, 1H, Tp), 6.78 (br, 1H, Tp), 6.06 (br, 1H, Tp), 6.02 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 5.90 (t, $J_{H-H} = 2.0$ Hz, 1H, Tp), 4.56 (dd, 1H, $^3J_{H-H} = 7.9$ Hz, $^3J_{H-H} = 7.4$ Hz, CH), 3.24, 2.89 (dd, AB, $^3J_{H-H} = 7.9$ Hz, $^3J_{H-H} = 7.4$ Hz, $^2J_{H-H} = 16.7$ Hz, 2H, CH_2); minor isomer: δ 7.91 (d, $J_{H-H} = 2.2$ Hz, 2H, Tp), 7.69–7.03 (m, Ph), 6.97 (br, 1H, Tp), 6.78 (br, 1H, Tp), 6.06 (br, 1H, Tp), 6.02 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 5.90 (t, $J_{H-H} = 2.0$ Hz, 1H, Tp), 4.41 (dd, 1H, $^3J_{H-H} = 7.7$ Hz, $^3J_{H-H} = 7.3$ Hz, CH), 3.19, 2.74

(dd, AB, $^3J_{H-H} = 7.7$ Hz, $^3J_{H-H} = 7.3$ Hz, $^2J_{H-H} = 16.7$ Hz, 2H, CH_2,). ^{13}C NMR ($CD_3C(O)CD_3$) major isomer: δ 149.3–121.3 (m, Ph, Tp), 118.1 (CN), 115.3 (NCPh), 39.1 (CH), 23.9 (CH_2); minor isomer: δ 149.8–122.4 (m, Ph, Tp), 118.9 (CN), 116.3 (NCPh), 39.7 (CH), 23.0 (CH_2). ^{31}P NMR ($CDCCl_3$, ppm): δ 55.7, 55.6 (3:2). MS (FAB) *m/z*: 878.3 (M^+), 680.2 ($M^+-N_4CCH(Ph)$-CH_2CN), 577.1 ($M^+-N_4CCH(Ph)CH_2CN$, PhCN). Anal. Calc. for $C_{44}H_{38}BN_{12}PRu$ (877.7): C, 60.21; H, 4.36; N, 19.15. Found: C, 59.97; H, 4.36; N, 18.98%.

3.7. Synthesis of (t-BuNC)[Ru]–$N_4CH(Ph)CH_2CN$ (6d)

A mixture of complex **4d** (0.58 g, 0.73 mmol) and Me_3SiN_3 (0.24 mL, 1.52 mmol) in 20 mL of CH_2Cl_2/CH_3Cl (3:1) was heated to reflux for 20 h. The solvent was removed under vacuum, then the solid residue was extracted with diethyl ether, and the extract was filtered. The resulting solution was removed under vacuum and washed with 5 mL hexane. The product was dried under vacuum. The yellow product was identified as **6d** (0.40 g, 64% yield). Spectroscopic data of **6d**: IR (KBr, cm^{-1}): ν(B–H) 2468(br), ν(C≡N) 2232(w), ν(N≡C) 2135(s), ν(N=N) 1436(w) cm^{-1}. ^1H NMR ($CD_3C(O)CD_3$): major isomer: δ 7.81 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.82 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 7.71 (d, $J_{H-H} = 1.9$ Hz, 1H, Tp), 7.67–7.11 (m, Ph), 6.65 (m, 1H, Tp), 6.11 (br, 1H, Tp), 6.04 (br, 1H, Tp), 5.92 (t, $J_{H-H} = 1.9$ Hz, 1H, Tp), 5.89 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 5.81 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 4.34 (dd, 1H, $^3J_{H-H} = 7.2$ Hz, $^3J_{H-H} = 7.2$ Hz, CH), 3.11, 2.92 (dd, AB, $^3J_{H-H} = 7.2$ Hz, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 16.9$ Hz, 2H, CH_2,), 1.42 (s, 9H, Me); minor isomer: δ 7.81 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.82 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 7.71 (d, $J_{H-H} = 1.9$ Hz, 1H, Tp), 7.67–7.11 (m, Ph), 6.65 (m, 1H, Tp), 6.11 (br, 1H, Tp), 6.04 (br, 1H, Tp), 5.92 (t, $J_{H-H} = 1.9$ Hz, 1H, Tp), 5.89 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 5.81 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 4.34 (dd, 1H, $^3J_{H-H} = 7.2$ Hz, $^3J_{H-H} = 7.2$ Hz, CH), 3.21, 2.98 (dd, AB, $^3J_{H-H} = 7.2$ Hz, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 16.1$ Hz, 2H, CH_2,), 1.32 (s, 9H, Me). ^{13}C NMR ($CD_3C(O)CD_3$) major isomer: δ 163.4 (d, $J_{P-C} = 21.4$ Hz, *C*NC(Me)$_3$), 141.9–129.3 (m, Ph, Tp), 119.4 (CN), 58.7 (CN*C*Me$_3$), 32.1 (CNC*Me*$_3$), 39.8 (CH), 24.2 (CH_2); minor isomer: δ 167.8 (d, $J_{P-C} = 22.1$ Hz, *C*NC(Me)$_3$), 145.1–125.6 (m, Ph, Tp), 118.1 (CN), 57.8 (CN*C*Me$_3$), 31.9 (CNC*Me*$_3$), 39.9 (CH), 25.6 (CH_2). ^{31}P NMR ($CDCCl_3$, ppm): δ54.1, 54.7 (3:2). MS (FAB) *m/z*: 858.4 (M^+), 660.2 ($M^+-N_4CCH(Ph)CH_2CN$), 577.1 (M^+-N_4-$CCH(Ph)CH_2CN$, *t*-BuNC). Anal. Calc. for $C_{42}H_{42}$-$BN_{12}PRu$ (858.3): C, 58.81; H, 4.94; N, 19.60. Found: C, 58.91; H, 5.14; N, 19.37%.

3.8. Synthesis of (n-BuNC)[Ru]–$N_4CH(Ph)CH_2CN$ (6e)

Solution of complex **4e** (0.20 g, 0.25 mmol) in 20 mL CH_2Cl_2 was added Me_3SiN_3 (0.16 mL, 0.76 mmol). After stirring for 16 h, the solvent was removed under vacuum, then the solid residue was extracted with diethyl ether, and the extract was filtered. The resulting solution was removed under vacuum and washed with 5 mL hexane. The product was dried under vacuum. The bright yellow product was identified as **6e** (0.19 g, 89% yield). Spectroscopic data of **6e**: IR (KBr, cm^{-1}): ν(B–H) 2475(br), ν(C≡N) 2233(w), ν(N≡C) 2141(s), ν(N=N) 1436(w) cm^{-1}. ^1H NMR ($CD_3C(O)CD_3$) major isomer: δ 7.57 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 7.79 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.71 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 7.40–6.91 (m, Ph), 6.86 (m, 1H, Tp), 6.74 (br, 1H, Tp), 6.71 (br, 1H, Tp), 5.92 (t, $J_{H-H} = 1.9$ Hz, 1H, Tp), 5.88 (t, $J_{H-H} = 2.0$ Hz, 1H, Tp), 5.76 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 4.43 (dd, 1H, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, CH), 3.69 (t, $J_{H-H} = 6.6$ Hz, 2H, $CNCH_2CH_2$), 3.21, 2.76 (dd, AB, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 16.7$ Hz, 2H, CH_2,), 1.53 (m, 2H, $CNCH_2CH_2$), 1.23 (m, 2H, CH_2CH_3), 0.93 (s, 1H, $C_2PhCHCN$), 0.75 (t, $J_{H-H} = 7.5$ Hz, 3H, CH_3); minor isomer: δ 7.57 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 7.79 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.71 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 7.40–6.91 (m, Ph), 6.86 (m, 1H, Tp), 6.74 (br, 1H, Tp), 6.71 (br, 1H, Tp), 5.92 (t, $J_{H-H} = 1.9$ Hz, 1H, Tp), 5.88 (t, $J_{H-H} = 2.0$ Hz, 1H, Tp), 5.76 (t, $J_{H-H} = 2.1$ Hz, 1H, Tp), 4.47 (dd, 1H, $^3J_{H-H} = 7.1$ Hz, $^3J_{H-H} = 7.3$ Hz, CH), 3.54 (t, $J_{H-H} = 6.7$ Hz, 2H, $CNCH_2CH_2$), 3.01, 2.89 (dd, AB, $^3J_{H-H} = 7.1$ Hz, $^3J_{H-H} = 7.3$ Hz, $^2J_{H-H} = 16.1$ Hz, 2H, CH_2,), 1.63 (m, 2H, $CNCH_2CH_2$), 1.10 (m, 2H, CH_2CH_3), 0.91 (s, 1H, $C_2PhCHCN$), 0.71 (t, $J_{H-H} = 7.4$ Hz, 3H, CH_3). ^{13}C NMR ($CD_3C(O)CD_3$) major isomer: δ 162.4 (d, $J_{P-C} = 22.9$ Hz, *C*NCH$_2$CH$_2$), 143.6–126.9 (m, Ph, Tp), 125.9 (d, $J_{P-C} = 11.6$ Hz, Cα), 114.9 (CN), 43.6 (CN*C*H$_2$CH$_2$), 33.7 (CNCH$_2$*C*H$_2$), 21.5 (*C*H$_2$CH$_3$), 13.8 (CH$_2$*C*H$_3$), 37.9 (CH), 25.1 (CH_2); minor isomer: δ 165.1 (d, $J_{P-C} = 22.5$ Hz, *C*NCH$_2$CH$_2$), 145.1–128.9 (m, Ph, Tp), 127.8 (d, $J_{P-C} = 11.7$ Hz, Cα), 114.8 (CN), 44.1 (CN*C*H$_2$CH$_2$), 32.5 (CNCH$_2$*C*H$_2$), 20.9 (*C*H$_2$CH$_3$), 13.1 (CH$_2$*C*H$_3$), 39.4 (CH), 25.1 (CH_2). ^{31}P NMR ($CD_3C(O)CD_3$): δ 54.1, 53.9 (3:2). MS (FAB) *m/z*: 858.4 (M^+), 660.2 ($M^+-N_4CCH(Ph)CH_2CN$), 577.1 ($M^+-N_4CCH(Ph)CH_2CN$, *n*-BuNC). Anal. Calc. for $C_{42}H_{42}BN_{12}PRu$ (858.3): C, 58.81; H, 4.94; N, 19.60. Found: C, 58.67; H, 5.04; N, 19.48%.

3.9. Synthesis of {$(C_3H_3NNH)[Ru]$=C=C(Ph)-CH_2CN}Cl (8a–Cl)

Solution of complex **7a** (10 mg, 0.013 mmol) in $CD_3C(O)CD_3$prepared under N_2 in NMR tube, one drop (5 μL) of $(CH_3)_3SiCl$ was added. The reaction accomplished immediately, and the color changed fro bright yellow to green. The solvent was removed under vacuum and washed with hexane. The green product was identified as **8a–Cl**. Spectroscopic data of **8a–Cl**: ^1H NMR ($CD_3C(O)CD_3$): δ 12.58 (s, NH), 8.13 (d, $J_{H-H} = 2.2$ Hz, 1H, Tp), 8.04 (d, $J_{H-H} = 2.4$ Hz, 1H, Tp), 7.70–6.58 (m, Ph, Tp), 6.53 (d, $J_{H-H} = 2.1$ Hz,1H, Tp), 6.44 (d, $J_{H-H} = 2.3$ Hz, Tp), 6.17 (m, 2H, Tp), 5.96 (d, $J_{H-H} = 2.3$ Hz,

1H, Tp), 3.94 (d, $J_{H-H} = 17.9$ Hz, 1H, $C_2PhCHHCN$), 3.84 (d, $J_{H-H} = 17.9$ Hz, 1H, $C_2PhCHHCN$). ^{13}C NMR ($CD_3C(O)CD_3$): δ 375.3 (d, $J_{P-C} = 16.5$ Hz, C_α), 151.6–129.4 (Ph, PPh_3, Tp), 117.4 (CN), 16.7 (CH_2). ^{31}P NMR ($CD_3C(O)CD_3$): δ 35.2. MS (FAB) *m/z*: 786.3 (M^+-Cl), 718.3 (M^+-Cl, NCHCHCHNH), 577.1 (M^+-Cl, NCHCHCHNH, C_2PhCH_2CN). Anal. Calc. for $C_{40}H_{36}BClN_9PRu$ (822.1): C, 58.51; H, 4.42; N, 15.35. Found: C, 58.47; H, 4.64; N, 15.48%.

3.10. Synthesis of {(Me_2C_3HNNH)[Ru]=C=C(Ph)-CH_2CN}Cl (**8b–Cl**)

Solution of complex **7b** (16 mg, 0.015 mmol) in $CD_3C(O)CD_3$prepared under N_2 in NMR tube, one drop (5 μL) of $(CH_3)_3SiCl$ was added. The reaction accomplished immediately, and the color changed fro bright yellow to green. The solvent was removed under vacuum and washed with hexane. The green product was identified as **8b–Cl**. Spectroscopic data of **8b–Cl**: ^1H NMR ($CD_3C(O)CD_3$): δ 12.67 (s, NH), 8.10 (d, $J_{H-H} = 2.2$ Hz, 1H, Tp), 8.04 (t, $J_{H-H} = 2.4$ Hz, 2H, Tp), 7.94 (br, 1H), 7.69–6.82 (m, Ph, Tp), 6.41 (d, $J_{H-H} = 2.1$ Hz,1H, Tp), 6.29 (d, $J_{H-H} = 2.3$ Hz,1H, Tp), 6.21 (m, 2H, Tp), 6.17 (t, $J_{H-H} = 2.3$ Hz, 1H, Tp), 6.09 (t, $J_{H-H} = 2.2$ Hz, 1H, Tp), 5.92 (t, $J_{H-H} = 2.3$ Hz, 1H, Tp), 3.96 (d, $J_{H-H} = 18.0$ Hz, 1H, $C_2PhCHHCN$), 3.81 (d, $J_{H-H} = 18.0$ Hz, 1H, $C_2PhCHHCN$), 2.22 (s, 3H, Me), 1.92 (s, 3H, Me). ^{31}P NMR ($CD_3C(O)CD_3$): δ 35.7. MS (FAB, Ru^{102}) *m/z*: 814.2 (M^+-Cl), 718.3 (M^+-Cl, $NC(CH_3)CHC(CH_3)$-NH), 577.1 (M^+-Cl, $NC(CH_3)CHC(CH_3)NH$, C_2PhCH_2-CN). Anal. Calc. for $C_{42}H_{40}BClN_9PRu$ (849.2): C, 59.41; H, 4.75; N, 14.85. Found: C, 59.27; H, 4.84; N, 14.66%.

3.11. Synthesis of (C_3H_3NNH)[Ru]–$N_4CCH(Ph)CH_2CN$ (**9a**)

Solution of complex **7a** (0.2 g, 0.21 mmol) in 20 mL CH_2Cl_2 was added Me_3SiN_3 (0.2 mL, 1.51 mmol). After stirring for 10 h, the solvent was removed under vacuum, then the solid residue was extracted with diethyl ether, and the extract was filtered. The resulting solution was removed under vacuum and washed with 5 mL hexane. The product was dried under vacuum. The yellow product was identified as **9a** (0.16 g, 89% yield). Spectroscopic data of **9a**: IR (KBr, cm^{-1}): ν(B–H) 2486(br), ν(C≡N) 2235(w), ν(N=N) 1432(w) cm^{-1}. ^1H NMR ($CDCl_3$): major isomer: δ 14.83 (s, 1H, N*H*), 7.77–6.93 (m, Ph, Tp, HPz), 6.12 (d, $J_{H-H} = 2.1$ Hz, 2H, Tp, HPz), 6.07 (d, $J_{H-H} = 2.1$ Hz, 2H, Tp, HPz), 5.90 (s, 1H, Tp, HPz), 5.87 (t, $J_{H-H} = 2.1$ Hz, 2H, Tp, HPz), 5.86 (t, $J_{H-H} = 2.0$ Hz, 2H, Tp, HPz), 4.57 (dd, 1H, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, CH), 3.03, 2.85 (dd, AB, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 16.7$ Hz, 2H, CH_2); minor isomer: 14.77 (s, 1H, N*H*), 7.77–6.93 (m, Ph, Tp, HPz), 6.12 (d, $J_{H-H} = 2.1$ Hz, 2H, Tp, HPz), 6.07 (d, $J_{H-H} = 2.1$ Hz, 2H, Tp, HPz), 5.90 (s, 1H, Tp, HPz), 5.87 (t, $J_{H-H} = 2.1$ Hz, 2H, Tp, HPz), 5.86 (t, $J_{H-H} = 2.0$ Hz, 2H, Tp, HPz), 4.57 (dd, 1H, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, CH), 3.12, 2.94 (dd, AB, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 16.7$ Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$) major isomer: δ 172.1 (NCN), 147.6–127.4 (m, Ph, Tp, HPz), 118.4 (CN), 39.6 (CH), 24.5 (CH_2); minor isomer: δ 170.3 (NCN), 149.1–126.3 (m, Ph, Tp, HPz), 119.7 (CN), 38.2 (CH), 21.4 (CH_2). ^{31}P NMR ($CD_3C(O)CD_3$, ppm): δ 54.6, 54.5 (3:2). MS (FAB) *m/z*: 843.4 (M^+), 645.2 (M^+-N_4CCH-$(Ph)CH_2CN$), 577.1 ($M^+-N_4CCH(Ph)CH_2CN$, HPz). Anal. Calc. for $C_{40}H_{37}BN_{13}PRu$ (843.2): C, 57.01; H, 4.43; N, 21.61. Found: C, 57.07; H, 4.51; N, 21.46%.

3.12. Synthesis of (Me_2C_3HNNH)[Ru]–$N_4CCH(Ph)$-CH_2CN (**9b**)

Solution of complex **7b** (0.65 g, 0.80 mmol) in 20 mL CH_2Cl_2 was added Me_3SiN_3 (0.6 mL, 4.0 mmol). After stirring for 10 h, the solvent was removed under vacuum, then the solid residue was extracted with diethyl ether, and the extract was filtered. The resulting solution was removed under vacuum and washed with 5 mL hexane. The product was dried under vacuum. The yellow product was identified as **9b** (0.51 g, 73% yield). Spectroscopic data of **9b**: IR (KBr, cm^{-1}): ν(B–H) 2477(br), ν(C≡N) 2237(w), ν(N=N) 1433(w) cm^{-1}. ^1H NMR ($CDCl_3$): major isomer: δ 13.54 (s, 1H, N*H*), 7.91–6.87 (m, Ph, Tp), 6.57 (br, 2H, Tp), 6.16 (d, $J_{H-H} = 2.0$ Hz, 3H, Tp, HPz), 6.04 (s, 2H, Tp), 5.85 (t, $J_{H-H} = 2.1$ Hz, 2H, Tp, HPz), 5.72 (t, $J_{H-H} = 1.9$ Hz, 2H, Tp, HPz), 4.43 (dd, 1H, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-H} = 7.4$ Hz, CH), 3.11, 2.93 (dd, AB, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-H} = 7.4$ Hz, $^2J_{H-H} = 16.5$ Hz, 2H, CH_2), 2.18, 2.10 (s, 3H, CH_3); minor isomer: 13.47 (s, 1H, N*H*), 7.91–6.87 (m, Ph, Tp), 6.57 (br, 2H, Tp), 6.16 (d, $J_{H-H} = 2.0$ Hz, 3H, Tp, HPz), 6.04 (s, 2H, Tp), 5.85 (t, $J_{H-H} = 2.1$ Hz, 2H, Tp, HPz), 5.72 (t, $J_{H-H} = 1.9$ Hz, 2H, Tp, HPz), 4.43 (dd, 1H, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-H} = 7.4$ Hz, CH), 3.20, 2.86 (dd, AB, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-H} = 7.4$ Hz, $^2J_{H-H} = 16.5$ Hz, 2H, CH_2), 2.21, 2.08 (s, 3H, CH_3). ^{31}P NMR ($CD_3C(O)CD_3$, ppm): δ 54.1, 53.8 (3:2). MS (FAB) *m/z*: 873.1 (M^+), 645.2 ($M^+-N_4CCH(Ph)CH_2CN$), 577.1 ($M^+-N_4CCH(Ph)CH_2CN$, $Me_2C_3N_2H_2$). Anal. Calc. for $C_{42}H_{41}BN_{13}PRu$ (871.7): C, 57.93; H, 4.75; N, 20.91. Found: C, 57.83; H, 4.84; N, 20.78%.

3.13. Synthesis of {(C_3H_3NNH)[Ru]=C=C(Ph)-$CH(HgCl)CN$}Cl (**10a**)

To a solid mixture of **7a** (0.27 g, 0.29 mmol) and $HgCl_2$ (0.096 g, 0.35 mmol), 30 mL of CH_2Cl_2 was added. The mixture was stirred for 10 min at −20 °C then the solvent was removed under vacuum. The residual solid was extracted with 2 × 20 mL ether and, after filtration, the solvent was removed under vacuum to give **10a** (0.22 g, 73% yield). Spectroscopic data of **10a**: ^1H NMR ($CD_3C(O)CD_3$): δ 8.10 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 8.01 (d, $J_{H-H} = 2.2$ Hz, 1H, Tp), 7.74–6.51 (m, Ph, Tp), 6.52

(d, $J_{H-H} = 2.3$ Hz, 1H, Tp), 6.41 (d, $J_{H-H} = 2.3$ Hz, Tp), 6.13 (m, 2H, Tp), 5.92 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 3.93 (d, $J_{H-H} = 16.9$ Hz, 1H, $C_2PhCHHCN$), 3.73 (d, $J_{H-H} = 16.9$ Hz, 1H, $C_2PhCHHCN$). ^{13}C NMR ($CD_3C(O)CD_3$): δ 379.3 (d, $J_{P-C} = 16.1$ Hz, C_α), 149.6–121.2 (Ph, PPh_3, Tp), 118.2 (CN), 15.6 (CH_2). ^{31}P NMR ($CD_3C(O)CD_3$): δ 36.2. MS (FAB) *m/z*: 1023.3 (M^+-Cl), 718.3 (M^+-Cl, NCHCHCHN(HgCl)), 577.1 (M^+-Cl, NCHCHCHN-(HgCl), C_2PhCH_2CN). Anal. Calc. for $C_{40}H_{35}BCl_2HgN_9PRu$ (1057.1): C, 45.49; H, 3.34; N, 11.94. Found: C, 45.47; H, 3.54; N, 11.48%.

3.14. Synthesis of {(Me_2C_3HNNH)[Ru]=C=C(Ph)-CH(HgCl)CN}Cl (**10b**)

To a solid mixture of **7b** (0.31 g, 0.41 mmol) and $HgCl_2$ (0.11 g, 0.41 mmol), 30 mL of CH_2Cl_2 was added. The mixture was stirred for 10 min at −20 °C then the solvent was removed under vacuum. The residual solid was extracted with 2 × 20 mL ether and, after filtration, the solvent was removed under vacuum to give **10b** (0.21 g, 65% yield). Spectroscopic data of **10b**: ^1H NMR ($CD_3C(O)CD_3$): δ 8.03 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 7.95 (d, $J_{H-H} = 2.0$ Hz, 1H, Tp), 7.69–6.77 (m, Ph, Tp), 6.63 (d, $J_{H-H} = 2.0$ Hz,1H, Tp), 6.52 (d, $J_{H-H} = 1.9$ Hz, Tp), 6.23 (m, 2H, Tp), 5.89 (d, $J_{H-H} = 2.1$ Hz, 1H, Tp), 3.89 (d, $J_{H-H} = 16.7$ Hz, 1H, $C_2PhCHHCN$), 3.71 (d, $J_{H-H} = 16.7$ Hz, 1H, $C_2PhCHHCN$), 2.31 (s, 3H, Me), 2.01 (s, 3H, Me). ^{31}P NMR ($CD_3C(O)CD_3$): δ 36.8. MS (FAB) *m/z*: 1053.1 (M^+-Cl), 718.3 (M^+-Cl, $NMe_2C_3HN(HgCl)$), 577.1 (M^+-Cl, $NMe_2C_3HN(HgCl)$, C_2PhCH_2CN). Anal. Calc. for $C_{42}H_{39}BCl_2HgN_9PRu$ (1085.1): C, 46.53; H, 3.63; N, 11.63. Found: C, 46.27; H, 3.64; N, 11.44%.

3.15. Synthesis of {(C_3H_3NNH)[Ru]–N_4(H)CCH(Ph)-CH_2CN}Cl (**11**)

Solution of tetrazolate complex **9a** (10 mg, 0.012 mmol) in $CDCl_3$ prepared under N_2 in NMR tube, one drop (5 μL) of HCl was added. The reaction accomplished immediately. The solvent was removed under vacuum over 5 h at 60 °C. The green product was washed with hexane, dried under vacuum and identified as {(C_3H_3NNH)[Ru]–N_4(H)CCH(Ph)CH_2CN}Cl. Spectroscopic data of **11**: IR (KBr, cm^{-1}): *ν*(B–H) 2483(br), *ν*(C≡N) 2243(w), *ν*(N=N) 1448(m) cm^{-1}. ^1H NMR ($CDCl_3$, ppm): major isomer: δ 13.51 (s, 1H, NH), 13.12 (s, 1H, NHCCH(Ph)), 7.89–6.86 (m, Ph, Tp, HPz), 6.11 (d, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 6.15 (d, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 5.94 (s, 1H, Tp, HPz), 5.80 (t, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 5.76 (t, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 4.49 (dd, 1H, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-H} = 7.3$ Hz, CH), 3.11, 2.97 (dd, AB, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-H} = 7.3$ Hz, $^2J_{H-H} = 16.8$ Hz, 2H, CH_2); minor isomer: 13.3 (s, 1H, NH), 13.1 (s, 1H, NHCCH(Ph)), 7.89–6.86 (m, Ph, Tp, HPz), 6.15 (d, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 6.11 (d, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 5.94 (s, 1H, Tp, HPz), 5.80 (t, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 5.76 (t, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 4.39 (dd, 1H, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, CH), 3.21, 2.91 (dd, AB, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 16.8$ Hz, 2H, CH_2). ^{31}P NMR ($CD_3C(O)CD_3$, ppm): δ 53.7, 53.5 (3:2). MS (FAB) *m/z*: 844.3 (M^+), MS (FAB) *m/z*: 844.3 (M^+), 776.2 (M^+-HPz), 577.1 (M^+-HPz, $HN_4CCH(Ph)CH_2$-CN). Anal. Calc. for $C_{40}H_{38}BClN_{13}PRu$ (879.2): C, 54.65; H, 4.36; N, 20.71. Found: C, 54.49; H, 4.33; N, 20.54%.

3.16. Synthesis of {(C_3H_3NNH)[Ru]N_4(CH_3)CCH(Ph)-CH_2CN}I (**12a**)

Solution of tetrazolate complex **9a** (10 mg, 0.012 mmol) in $CDCl_3$ prepared under N_2 in NMR tube, one drop (5 μL) of CH_3I was added. The reaction was carried out at 50 °C for 10 h, and the color changed from yellow to green. Then the solvent and excess of CH_3I were removed under vacuum. The green product was extracted with diethyl ether, and passed through a silica column. A 1:1 diethyl ether–hexane solution eluted the organometallic compound, {(C_3H_3NNH)[Ru]N_4(CH_3)CCH(Ph)CH_2CN}I. Spectroscopic data of **12a**: IR (KBr, cm^{-1}): *ν*(B–H) 2481(br), *ν*(C≡N) 2242(w), *ν*(N=N) 1449 (m) cm^{-1}. ^1H NMR ($CDCl_3$, ppm): ^1H NMR ($CDCl_3$, ppm): major isomer: δ 13.56 (s, 1H, NH), 7.79–6.12 (m, Ph, Tp, HPz), 6.15 (d, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 5.86 (s, 1H, Tp, HPz), 5.73 (t, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 5.67 (t, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 4.45 (dd, 1H, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.4$ Hz, CH), 3.67 (s, 3H, CH_3), 3.08, 2.89 (dd, AB, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.4$ Hz, $^2J_{H-H} = 16.8$ Hz, 2H, CH_2); minor isomer: 13.41 (s, 1H, NH), 7.79–6.12 (m, Ph, Tp, HPz), 6.15 (d, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 5.86 (s, 1H, Tp, HPz), 5.73 (t, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 5.67 (t, $J_{H-H} = 2.2$ Hz, 2H, Tp, HPz), 4.31 (dd, 1H, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, CH), 3.76 (s, 3H, CH_3), 3.19, 3.01 (dd, AB, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 16.9$ Hz, 2H, CH_2). ^{31}P NMR ($CD_3C(O)CD_3$, ppm): δ 51.0, 50.9 (3:2). MS (FAB) *m/z*: 858.3 (M^+), 790.3 (M^+-HPz), 577.1 (M^+-MeN_4CCH-(Ph)CH_2CN, HPz). Anal. Calc. for $C_{41}H_{40}BIN_{13}PRu$ (985.1): C, 50.01; H, 4.09; N, 18.49. Found: C, 50.11; H, 4.16; N, 18.37%.

3.17. Synthesis of {(C_3H_3NNH)[Ru]N_4(CH_2Ph)-CCH(Ph)CH_2CN} Br (**12b**)

Solution of tetrazolate complex **9a** (10 mg, 0.012 mmol) in $CDCl_3$prepared under N_2 in NMR tube, one drop (ca. 5 μL) of $PhCH_2Br$ was added. The reaction was carried out at 50 °C for 10 h, and the color changed from yellow to red. Then the solvent and excess of $PhCH_2Br$ were removed under vacuum over 5 h at 80 °C. The organic product was extracted with diethyl ether, and passed through a silica column. A 1:1 diethyl ether–hexane solution eluted the organometallic compound, {(C_3H_3NNH)[Ru]N_4(CH_2Ph)CCH-(Ph)CH_2CN}Br. Spectroscopic data of **12b**: IR (KBr,

cm^{-1}): ν(B–H) 2492(br), ν(C≡N) 2240(w), ν(N=N) 1450(m) cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): major isomer: δ 14.12 (s, 1H, N*H*), 7.68–6.34 (m, Ph, Tp, HPz), 6.11 (d, $J_{H-H} = 2.3$ Hz, 2H, Tp, HPz), 5.89 (s, 1H, Tp, HPz), 5.77 (t, $J_{H-H} = 2.3$ Hz, 2H, Tp, HPz), 5.65 (t, $J_{H-H} = 2.3$ Hz, 2H, Tp, HPz), 4.65 (dd, 1H, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.4$ Hz, CH), 4.23 (s, 2H, CH_2Ph), 3.11, 2.96 (dd, AB, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.4$ Hz, $^2J_{H-H} = 16.9$ Hz, 2H, CH_2); minor isomer: 13.89 (s, 1H, N*H*), 7.68–6.34 (m, Ph, Tp, HPz), 6.11 (d, $J_{H-H} = 2.3$ Hz, 2H, Tp, HPz), 5.89 (s, 1H, Tp, HPz), 5.77 (t, $J_{H-H} = 2.3$ Hz, 2H, Tp, HPz), 5.65 (t, $J_{H-H} = 2.3$ Hz, 2H, Tp, HPz), 4.36 (dd, 1H, $^3J_{H-H} = 7.4$ Hz, $^3J_{H-H} = 7.3$ Hz, CH), 4.54 (s, 2H, CH_2Ph), 3.18, 3.01 (dd, AB, $^3J_{H-H} = 7.3$ Hz, $^3J_{H-H} = 7.2$ Hz, $^2J_{H-H} = 16.9$ Hz, 2H, CH_2). ^{31}P NMR ($CD_3C(O)CD_3$, ppm): δ 50.8, 50.7 (3:2). MS (FAB) *m*/*z*: 934.3 (M^+), 866.2 (M^+−HPz), 577.1 (M^+−HPz, CH_2Ph-$N_4CCH(Ph)CH_2CN$). Anal. Calc. for $C_{47}H_{44}BBrN_{13}PRu$ (1013.2): C, 55.69; H, 4.38; N, 17.96. Found: C, 55.59; H, 4.33; N, 17.84%.

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