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Reactions of ruthenium cyclopropenyl complexes with trimethylsilyl azide

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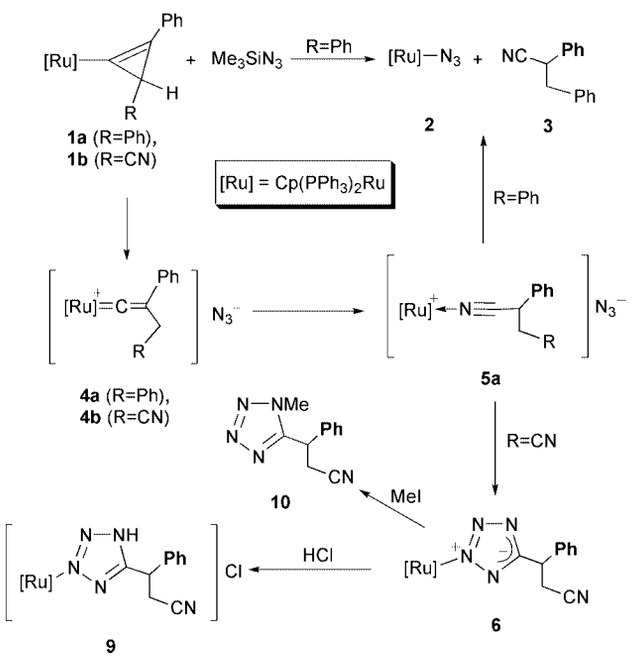
Treatment of the phenyl substituted cyclopropenyl complex [Ru]–C=C(Ph)CHPh (**1a**, [Ru] = (η^5-C_5H_5)(PPh_3)$_2$Ru) with Me_3SiN_3 in THF in the presence of NH_4PF_6 at room temperature afforded the nitrile complex {[Ru]NCCH(Ph)CH_2Ph}PF_6 **5a**. Similar reaction of the cyano substituted cyclopropenyl complex [Ru]–C=C(Ph)CHCN **1b** with Me_3SiN_3 gave the tetrazolate complex [Ru]–N_4CCH(Ph)CH_2CN **6**. Proposals are made concerning the mechanism for the synthesis of these compounds. The reaction of [Ru]–C=C(Ph)CHCH=CH_2 **1c** with Me_3SiN_3 takes a different route and gives the nitrile complex [Ru]–CN **7** and the five-membered-ring organic compound PhC=$CN_3HCH_2CH_3$ **11**. The structures of complexes **5a** and **6** have been determined by single crystal X-ray diffraction analysis.

Introduction

Cyclopropene is a highly strained cycloalkene and its estimated strain energy is >50 kcal mol^{-1}.[1] This molecule has played a crucial role in the development of important concepts such as aromaticity and chemical reactivities.[2] Many recent studies have focused on the use of various cyclopropenes in organic synthesis.[3] However, little is known about synthetic applications of metal–cyclopropenyl systems. To date, deprotonation of a number of vinylidene ruthenium complexes [Ru]=C=C(Ph)-CH_2R^+ ([Ru] = (η^5-C_5H_5)(PPh_3)$_2$Ru; R = Ph, CN or CH=CH_2) is known to produce cyclopropenyl derivatives.[4] Further reaction with an electrophile readily opens the three-membered cyclopropenyl ring of these Ru complexes to restore the vinylidene moiety. In the ruthenium system, cyclopropenyl and vinylidene complexes display distinctive reactivities. In order to explore potential applications of such a new type of complex, we carried out reactions of cyclopropenyl complexes with various organic substrates. Reactions of Me_3SiN_3 with several ruthenium cyclopropenyl complexes containing various substituents at the cyclopropenyl ring modestly yield nitrogen containing heterocyclic products. Following a preliminary account[5] of this work, we now disclose the results of detailed synthetic and structural investigations on the reactions of Me_3SiN_3 with a Ru–cyclopropenyl complex.



Scheme 1

Results and discussion

Reaction of 1a with Me_3SiN_3

Treatment of the cyclopropenyl complex [Ru]–C=C(Ph)CHPh **1a** with a five-fold excess of Me_3SiN_3 in THF at room temperature afforded [Ru]–N_3 **2**[6] and $PhCH_2CHPhCN$ **3**[7] in about equal amount as two major end products in high yield (Scheme 1). A series of successive color changes were noted during the course of the reaction: the light yellow solution of **1a** first turned deep red upon addition of Me_3SiN_3 at room temperature, and was subsequently seen to turn light orange after 3 h and orange after 7 h. Complexes **2** and **3** were isolated as the final product, whereas the red intermediates were quenched at −10 °C in a separate experiment, giving the vinylidene complex {[Ru]=C=C(Ph)CH_2Ph}N_3 **4a** as the major product, along with small amounts of the N-coordinated nitrile complex {[Ru]NCCH(Ph)CH_2Ph}N_3. The reaction carried out at room temperature for 2 h then at 0 °C for 1 h in the presence of NH_4PF_6 gave a light orange solution from which **5a** with counter anion PF_6^- could be isolated in high yield. Finally longer times gave **2** and **3**. Complex **4a** is unstable in solution at room temperature and undergoes a further reaction with azide to give **5a** with azide counter anion, which is also unstable in solution and gives **2** and **3**. Both **4a** and **5a**, can be isolated in stable form by replacing the counter anion N_3^- by PF_6^-.

The ^{1}H NMR spectrum of **4a** displays a singlet resonance at δ 3.50 assignable to the CH_2 group and the ^{31}P NMR spectrum of **4a** displays a singlet resonance at δ 42.5. The ^{31}P NMR spectrum of **5a** displays two doublet resonances at δ 42.2 and 41.5 with J_{P-P} = 35.2 Hz indicating the presence of a stereogenic center in the N-coordinated nitrile ligand. In the ^{1}H NMR spectrum, the same pattern, *i.e.* a two-doublet-resonance at δ 3.16, (J_{H-H} = 13.9, 8.9 Hz) and 2.86 (J_{H-H} = 13.9, 7.8 Hz) assigned to the diastereotopic CH_2 group is consistent with the ^{31}P NMR data. The parent peak in the FAB mass spectrum of **5a** clearly

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Table 1 Selected bond distances (Å) and angles (°) for **5a**

Ru–P1	2.3721(13)	Ru–P2	2.3552(14)
Ru–N	2.038(4)	N–C1	1.129(7)
C1–C2	1.495(9)	C2–C3	1.386(11)
C2–C15	1.540(11)	C3–C9	1.511(11)
C4–C8	1.378(10)		
N–Ru–P1	89.01(12)	N–Ru–P2	91.11(12)
P2–Ru–P1	99.72(5)	C1–N–Ru	175.3(5)
N–C1–C2	176.6(8)	C3–C2–C1	116.5(8)
C3–C2–C15	118.6(7)	C1–C2–C15	111.3(6)
C2–C3–C9	121.2(7)		

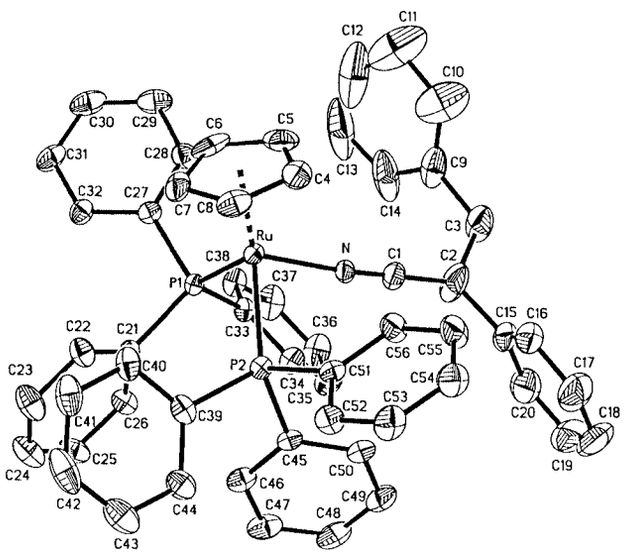


Fig. 1 An ORTEP drawing of **5a** with thermal ellipsoids shown at the 30% probability level.

indicates that **5a** results from addition of a nitrogen atom to **4a**. The structure of **5a** has been determined by a single crystal X-ray diffraction analysis. An ORTEP[8] drawing is shown in Fig. 1. Selected bond distances and angles are listed in Table 1. The nitrile ligand is coordinated to the Ru center *via* the nitrogen atom. The Ru–N–C1 and N–C1–C2 bond angles of 175.3(5) and 176.6(8)°, respectively, are both close to 180°. The Ru–N and N–C1 distances of 2.038(4) and 1.129(7) Å, respectively, are typical.

Reaction of 1b with Me_3SiN_3

Treatment of [Ru]–C=C(Ph)CHCN **1b** with Me_3SiN_3 at room temperature for 3 h leads to the addition of four nitrogen atoms to **1b** and readily affords the yellow tetrazolate complex [Ru]–N_4CCH(Ph)CH_2CN **6** in high yield (Scheme 1). The yield of minor product [Ru]–CN **7** was *ca.* 5% (observed by ^{1}H NMR spectroscopy before recrystallization). Traces of water in THF are believed to act as the source of protons that are incorporated into the product through hydrolysis of the Me_3Si substituent derived from addition of Me_3SiN_3 to the three-membered ring. From the reaction mixture Me_3SiOH was distilled off with THF and was identified by mass spectrometry. In both reactions of **1a** and **1b** with Me_3SiN_3, addition of D_2O to THF led to incorporation of two deuterium atoms at two vicinal carbon atoms of both **3** and **6**. Complex **6** is stable at room temperature, thus in the course of the reaction only a deep red color attributed to a vinylidene intermediate was observed before the solution turned to light yellow. The vinylidene intermediate {[Ru]=C=C(Ph)CH_2CN}N_3 **4b** could also be isolated from the reaction carried out at 0 °C after a shorter reaction time. However, no reaction was observed between {[Ru]=C=C(Ph)CH_2CN}PF_6 and Me_3SiN_3. This might be due to the covalent character of the Si–N bond in Me_3SiN_3 and

Table 2 Selected bond distances (Å) and angles (°) for **6**

Ru–P1	2.348(3)	Ru–P2	2.346(3)
Ru–N1	2.121(7)	N1–N2	1.263(11)
N1–N4	1.383(10)	N2–N3	1.356(11)
N3–C1	1.328(12)	N4–C1	1.339(12)
N5–C10	1.103(13)	C1–C2	1.512(13)
C2–C3	1.541(14)	C2–C9	1.523(14)
C9–C10	1.479(14)		
P1–Ru–P2	102.65(9)	P1–Ru–N1	95.15(21)
P2–Ru–N1	90.09(20)	Ru–N1–N2	122.5(6)
Ru–N1–N4	124.3(5)	N2–N1–N4	112.9(7)
N1–N2–N3	107.9(7)	N2–N3–C1	105.5(8)
N1–N4–C1	101.0(7)	N3–C1–N4	112.6(8)
N3–C1–C2	124.8(8)	N4–C1–C2	122.6(8)
C1–C2–C3	110.9(8)	C1–C2–C9	109.2(7)
C3–C2–C9	114.8(8)	C2–C9–C10	114.6(9)
N5–C10–C9	177.1(12)		

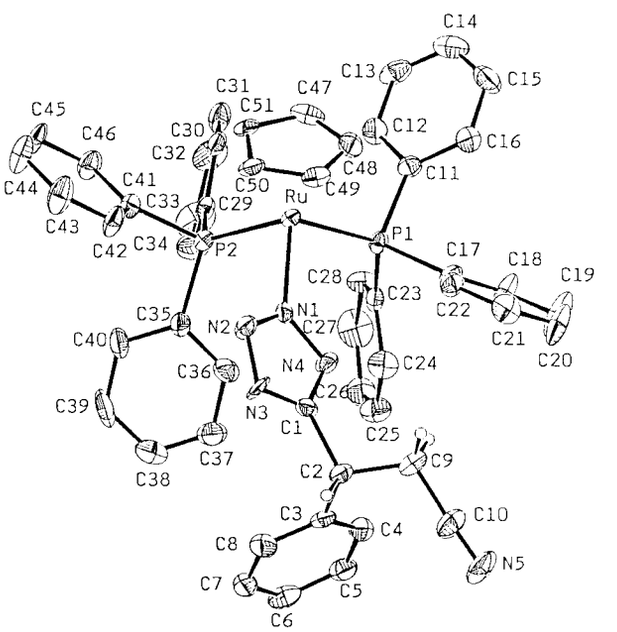


Fig. 2 An ORTEP drawing of **6** with thermal ellipsoids shown at the 30% probability level.

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 **1b** with Me_3SiCl in the presence of NaN_3 gave a mixture of **6**, **7** and **2** in a 3 : 1 : 1 ratio. For **4b** with a PF_6^- counter anion, attempts to exchange the counter anion to a N_3^- 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 and the presence of a Me_3Si group as a relatively good electrophile is also required for opening of the ring.

In the ^{1}H NMR spectrum of **6**, a dd resonance at δ 4.45 (J_{H-H} = 7.4, 7.7 Hz) is assigned to the methyne proton and two resonances displaying doublets of an AB pattern at δ 2.66 (J_{H-H} = 16.6, 7.4 Hz) and 2.44 (J_{H-H} = 16.6, 7.7 Hz) are assigned to the diastereotopic methylene group. In the ^{31}P NMR spectrum of **6**, two doublet resonances at δ 43.8 and 41.6 with J_{P-P} = 38.9 Hz are assigned to the two PPh_3 ligands due to the presence of a stereogenic carbon center in the substituent of the tetrazolate ring. The structure of **6** has been determined by a single crystal X-ray diffraction analysis. An ORTEP[8] drawing is shown in Fig. 2. Selected bond distances and angles are listed in Table 2. The planar five-membered tetrazolate ring is coordinated to the Ru center *via* the N1 atom. The N1–N2 distance of 1.263(11) Å is significantly shorter than the other two N–N distances (1.356(11) and 1.383(10) Å) indicating localization of a double

bond character at N1–N2 with localization of a positive charge at N1. The C1–N3 and C1–N4 distances of 1.328(12) and 1.339(12) Å, respectively, are about the same indicating delocalization of negative charge at the N3–C1–N4 unit.

Possible mechanism for the formation of 5a and 6

The reaction of **1a** with Me_3SiN_3 leading to **5a** may proceed *via* the following pathway. An electrophilic addition of a Me_3Si group at the three-membered ring with concomitant opening of the ring followed by hydrolysis of the added Me_3Si group affords **4a** containing an azide counter anion.[4] This is followed by nucleophilic addition of an azide anion at C_α of the vinylidene ligand.[9] Subsequent electrophilic addition of a second Me_3Si group at the 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 **5a** (Scheme 1). In the reaction of **1b** with Me_3SiN_3, the reaction may proceed similarly in the first stage to give an analogue of **5a**. Formation of **6** is then rationalized by a [3 + 2] cycloaddition of the C≡N bond with another azide anion followed by metal migration (linkage isomerization).[10] A possible pathway *via* direct cyclization of the imine intermediate with azide anion to result in formation of **6** could also occur.[10] In a previous study, organic tetrazole compounds were synthesized *via* routine [3 + 2] cycloaddition reaction of a nitrile group with azide.[11] In some systems, cyclization was observed in the case of an imine compound with an azide group.[11] Additionally, tetrazole compounds resulted from attack of an azide to an imine compound with an appropriate leaving group following cyclization have also been reported.[12] The fact that **5a** 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.

Metal-coordinated azide ligands undergo 1,3-dipolar cycloaddition reactions with carbon–carbon and carbon–heteroatom multiple bonds. The metals involved are most often palladium(II),[13] platinum(II)[14] or cobalt(III)[15] although a whole range of other transition metals[16–19] has been used. Formation of tetrazolate ring in **6** should not proceed *via* this pathway since the reaction of organic nitrile with [Ru]–N_3 does not yield **6**. We also found that the reaction of the acetylide complex [Ru]–C≡C–Ph with an excess of Me_3SiN_3 afforded **2** and an organic product identified as $PhCH_2CN$ by elemental analysis and high resolution mass spectrometry. In the presence of NH_4PF_6 the reaction gave {[Ru]$NCCH_2Ph$}PF_6 **8** in high yield. Thus transformation of an acetylide ligand to a nitrile ligand by Me_3SiN_3 possibly proceeds *via* the same electrophilic addition of an Me_3Si group yielding vinylidene followed by a nucleophilic addition of an azide anion at C_α. Conversion of a vinylidene precursor to an N-coordinated nitrile by hydrazine, an organometallic Beckmann rearrangement, has been reported in an iron system.[20]

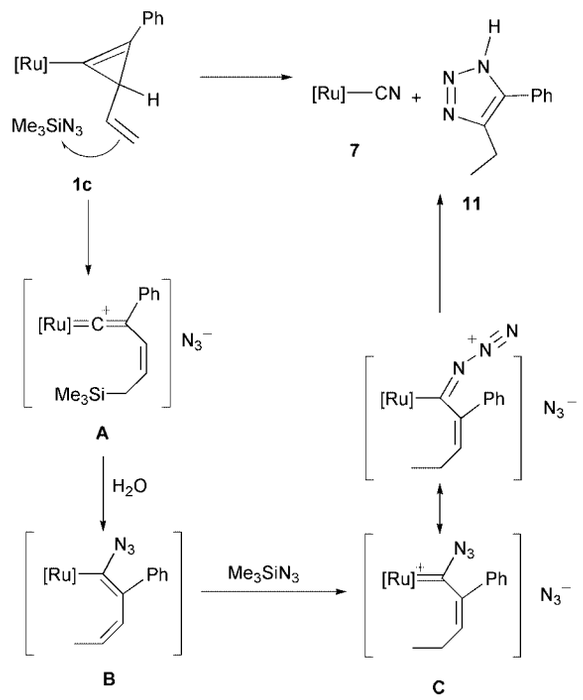
Reactions of 6 with electrophiles

Protonation of **6** with HCl takes place at the tetrazolate ring and gives {[Ru]–$N_4HCCH(Ph)CH_2CN$}Cl **9** as the only product (Scheme 1). The ^{1}H NMR spectrum of **9** displays the characteristic pattern for a $CHCH_2$ group. In the ^{31}P NMR spectrum the two doublet resonances at δ 42.2 and 42.4 is a result of the presence of a diastereotopic center in the coordinated organic ligand indicating that the tetrazolate ligand should be bound to the metal. The protonation might have occurred at one of two nitrogen atoms near the carbon because of localization of the negative charge at these two nitrogen atoms in **6**.

An alkylation reaction of **6** with the alkyl halide CH_3I at 50 °C in $CHCl_3$ caused cleavage of the M–N bond and gave [Ru]–I and $CH_3N_4CCH(Ph)CH_2CN$ **10** (Scheme 1). Two products were separated by chromatography and the organic product **10**, eluted by MeOH, was identified by NOE data and its high-resolution mass spectrum. For the same reason described before, we expect that alkylation should take place also at the nitrogen atom next to the ring carbon. The NOE effect (2.64%) between the CH and Me groups is consistent with the proposed structure of **10**.

Reaction of 1c with Me_3SiN_3

Treatment of [Ru]–$\overline{C{=}C(Ph)}CHCH{=}CH_2$ **1c** with an excess of Me_3SiN_3 afforded [Ru]–CN **7** and $PhCN_3HCCH_2CH_3$ **11** (Scheme 2). Compound **11** is identified by elemental analysis



Scheme 2

and spectroscopic methods including high-resolution mass spectrometry. Formation of **7** and **11** from **1c** is a result of cleavage of the C=C bond of the cyclopropenyl ring, along with an addition of a triazo group and transformation of the vinyl to an ethyl group. Addition of a Me_3Si group to the terminal carbon atom of the vinyl group accompanied with opening of the three-membered ring results in formation of the cationic vinylidene intermediate, **A** (Scheme 2). We previously reported that the reaction of TCNQ with **1c** gives similar electrophilic addition at the terminal carbon of the vinyl group. Subsequent nucleophilic addition of N_3^- at C_α followed by hydrolysis gave **B**. Further addition of Me_3SiN_3 at C_δ followed by hydrolysis led to formation of **C**. Two resonance forms of **C** are depicted in Scheme 1. The single bond character at C_α–C_β in both forms facilitates its cleavage. This cleavage is accompanied with a [3 + 2] cycloaddition of the C=C bond with an azide anion to give the triazole compounds **11** and **7**. The fact that **7** is isolated in this reaction as the only organometallic product suggests that it is not possible to produce the terminal N-coordinated nitrile intermediate. Formation of **7** as a minor product in the reaction of **1b** with Me_3SiN_3 could proceed through the same pathway.

Concluding remarks

In conclusion, various substituents at the sp^3 carbon of the three-membered ring govern the reactivity of the ruthenium cyclopropenyl complexes toward Me_3SiN_3. Reaction of the ruthenium complex **1a** containing a phenyl substituent on the cyclopropenyl ring with Me_3SiN_3 afforded the N-coordinated nitrile complex **5a**. The reaction of Me_3SiN_3 with **1b** containing a CN group on the cyclopropenyl ring gave the tetrazolate complex **6** which proceeded through the same type of

intermediate as that in the reaction of **1a** followed by a further addition of Me_3SiN_3. The reaction of **1c** containing a vinyl substituent on the cyclopropenyl ring with Me_3SiN_3 gave the organic product **11**, which contains a five-membered triazole ring. Characterization of these products has led to a better understanding of the mechanism of these reactions. The reaction can be explained in terms of combined effects of the nucleophilic sp^3 carbon of the cyclopropenyl ring and the electrophilic nature of the Me_3Si group.

Experimental

General procedures

All manipulations were performed under nitrogen using vacuum-line, dry box, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded on Bruker DMX-500, AM-300 and AC-200 FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvent as standard ($CDCl_3$, δ 7.24; C_6D_6, δ 7.15; $(CD_3)_2CO$, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Complexes [Ru]–C=C(Ph)CHR ([Ru] = (η^5-C_5H_5)(PPh_3)$_2$Ru, R = Ph, **1a**; R = CN, **1b**; R = CH=CH_2, **1c**)[4] were prepared following the method reported in the literature. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

Reaction of 1a with Me_3SiN_3

To a solution of complex **1a** (0.21 g, 0.23 mmol) in THF (20 ml) was added Me_3SiN_3 (0.18 mL, 1.34 mmol) and the mixture was stirred at room temperature for 7 h. Then the resulting orange solution was dried *in vacuo*. The residue was extracted with hexane and the residual solid was further washed with water to give [Ru]N_3 **2** (0.14 g, 73% yield). The hexane extract was concentrated and was then eluted with diethyl ether on a silica gel packed column and the solvent of the band containing the organic compound was removed on a rotary evaporator to give NCCH(Ph)CH_2Ph **3** (0.046 g, 64% yield). Spectroscopic data for **2**: ^{1}H NMR ($CDCl_3$): δ 7.68–7.09 (m, 30H, Ph); 4.19 (s, 5H, Cp). ^{31}P NMR ($CDCl_3$): δ 41.6. ^{13}C NMR ($CDCl_3$): δ 138.4–127.5 (Ph); 81.3 (Cp). MS (FAB): *m*/*z* 733 (M^+), 705 ($M^+ - N_2$); 691 ($M^+ - N_3$). Anal. Calc. for $C_{41}H_{35}N_3P_2Ru$: C, 67.20; H, 4.81; N, 5.73. Found: C, 67.12; H, 4.77; N, 5.70%. Spectroscopic data for **3**: ^{1}H NMR ($CDCl_3$): δ 7.43–7.09 (m, 10H, Ph); 3.98 (dd, 1H, CH, J_{H-H} = 8.4, 6.7 Hz); 3.17, 3.11 (dd, 2H, CH_2, J_{H-H} = 8.4, 6.7, 13.7 Hz). High resolution MS: calc. for $C_{15}H_{13}N$: *m*/*z* 207.1048, found: 207.1050.

Preparation of {[Ru]NCCH(Ph)CH_2Ph}PF_6 5a

To a solution of complex **1a** (0.45 g, 0.51 mmol) in THF (20 mL), Me_3SiN_3 (0.4 mL, 3.02 mmol) was added. The reaction mixture turned orange in 2 h and starting material disappeared as indicated by the ^{31}P NMR spectrum. Then NH_4PF_6 (0.1 g, 0.6 mmol) was added and the solution stirred at 0 °C for 1 h. The mixture was filtered through Celite, and the filtrate concentrated to *ca.* 5 mL at reduced pressure. Addition of hexane afforded a yellow–orange powder, which was filtered and dried *in vacuo* to give **5a** (0.43 g, 80%). Spectroscopic data for **5a**: ^{1}H NMR ($CDCl_3$): δ 7.68–6.84 (m, 35H, Ph); 4.40 (dd, 1H, CH, J_{H-H} = 8.9, 7.8 Hz); 4.37 (s, 5H, Cp); 3.16, 2.86 (dd, 2H, CH_2, J_{H-H} = 8.9, 7.8 Hz, J_{H-H} = 13.9 Hz). ^{31}P NMR ($CDCl_3$): δ 42.2, 41.5 (AB, J_{P-P} = 35.2 Hz). ^{13}C NMR ($CDCl_3$): δ 135.8–127.1 (Ph), 118.6 (CN); 83.7 (Cp); 40.8 (CH); 39.7 (CH_2). MS (FAB): *m*/*z* 897.9 ($M^+ - PF_6$), 691 ($M^+ - PF_6$, NCCHPhCH_2Ph), 429.1 ($M^+ - PF_6$, PPh_3, NCCH(Ph)CH_2Ph). IR (KBr): 2254 cm^{-1}. Anal. Calc. for $C_{56}H_{48}F_6NP_3Ru$: C, 64.49; H, 4.64; N, 1.34. Found: C, 64.52; H, 4.93; N, 1.54%.

Synthesis of [Ru]N_4CCH(Ph)CH_2CN 6

To a solution of complex **1b** (0.51 g, 0.60 mmol) in THF (20 mL), Me_3SiN_3 (0.50 ml, 3.77 mmol) was added. After 3 h the mixture was concentrated to *ca.* 5 mL, and slowly added to 60 mL of a stirring hexane. The yellow precipitate thus formed was filtered off, and washed with hexane. The product was recrystallized from acetone–hexane (1 : 4) and identified as **6** (0.45 g, 85%). Spectroscopic data for **6**: ^{1}H NMR (C_6D_6): δ 7.59–6.81 (m, 35H, Ph); 4.45 (dd, 1H, CH, J_{H-H} = 7.4, 7.7 Hz); 4.29 (s, 5H, Cp); 2.66, 2.44 (dd, 2H, CH_2, J_{H-H} = 16.6, 7.4, 7.7 Hz). ^{31}P NMR ($CDCl_3$): δ 43.8, 41.6 (dd, J_{P-P} = 38.9 Hz). ^{13}C NMR ($CDCl_3$): δ 164.1 (NCN); 140.2 (C_{ipso} of Ph); 138.3–127.1 (Ph); 118.6 (CN); 83.1 (Cp); 39.9 (CH); 23.5 (CH_2). MS (FAB): *m*/*z* 889.2 (M^+, Ru = 102), 691 ($M^+ - N_4CCH(Ph)CH_2CN$), 429.1 ($M^+ - PPh_3$; $N_4CCH(Ph)CH_2CN$). Anal. Calc. for $C_{51}H_{43}N_5P_2Ru$: C, 68.91; H, 4.88; N, 7.88. Found: C, 68.84; H, 4.84; N, 7.87%.

Synthesis of [Ru]N_4CCD(Ph)CDHCN (6-D)

To a solution of complex **1b** (0.10 g, 0.12 mmol) and D_2O (12.96 μL, 0.72 mmol) in THF (10 mL) was added Me_3SiN_3 (0.10 mL, 0.75 mmol). After stirring for 4 h, the mixture was concentrated to *ca.* 3 mL, and slowly added to 30 mL of stirring hexane. The yellow precipitate thus formed was filtered off, and washed with hexane. The major product was identified as **6**-D (0.08 g, 80%). Spectroscopic data for **6**-D: ^{1}H NMR ($CDCl_3$): δ 7.78–7.02 (m, Ph, 35H), 4.30 (s, 5H, Cp); 2.58, 2.51 (two s, 1H, CH, diastereomers). ^{31}P NMR: δ 43.7, 41.4 (J_{P-P} = 37.9 Hz). MS (FAB): *m*/*z* 891.2 (M^+), 691 ($M^+ - N_4CCD(Ph) - CDHCN$), 429.1 ($M^+ - PPh_3$, $N_4CCD(Ph)CDHCN$).

Protonation of 6 with HCl

The reaction was carried out in a NMR tube. To a solution of complex **6** (20 mg, 0.022 mmol) in $CDCl_3$ prepared under N_2, 5 μL of HCl (1 M in H_2O) was added. The reaction completed immediately and the color changed from yellow to green. The solvent and HCl were removed *in vacuo* over 5 h at 60 °C. The green product was washed with hexane, dried *in vacuo* and identified as {[Ru]–N_4HCCH(Ph)CH_2CN}Cl **9** (19 mg, 90% yield). Spectroscopic data for **9**: ^{1}H NMR ($CDCl_3$): δ 7.76–6.85 (m, 5H, Ph); 4.76 (t, 1H, CH, J_{H-H} = 7.5 Hz); 4.34 (s, 5H, Cp); 2.83 (d, 2H, CH_2, J_{H-H} = 7.5 Hz). ^{31}P NMR ($CDCl_3$): δ 42.2, 42.4 (AB, J_{P-P} = 36.2 Hz). MS (FAB): *m*/*z* 890.1 ($M^+ - Cl$); 691.0 ($M^+ - Cl$, N_4HCCH(Ph)CH_2CN).

Reaction of complex 6 with CH_3I

To a solution of complex **6** (22 mg, 0.024 mmol) in $CDCl_3$ prepared under N_2 in a NMR tube, 10 μL of CH_3I 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 CH_3I were removed *in vacuo*. 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, [Ru]–I and MeOH eluted the organic product identified as $CH_3N_4CCH(Ph)CH_2CN$ **10**. Spectroscopic data for **10**: ^{1}H NMR ($CDCl_3$): δ 7.76–6.85 (m, 5H, Ph); 4.42 (dd, J_{H-H} = 8.7, 6.4 Hz, 1H, CH); 3.72 (s, 3H, CH_3); 3.44, 3.24 (dd, J_{H-H} = 16.6, 8.7, 6.4 Hz, 2H, CH_2). High resolution MS: calc. for $C_{11}H_{11}N_5$: *m*/*z* 213.1014, found: 213.1009.

Reaction of [Ru]–C≡CPh with Me_3SiN_3

To a solution of complex [Ru]–C≡CPh (0.11 g, 0.14 mmol) in THF (20 ml) was added Me_3SiN_3 (0.10 mL, 0.75 mmol). After

Table 3 Summary of crystallographic data for **5a** and **6**

	5a	**6**·$(CH_3)_2CO$ [a]
Formula	$C_{56}H_{48}F_6NP_3Ru$	$C_{51}H_{43}N_5P_2Ru\cdot(CH_3)_2CO$
M	1042.93	947.02
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	11.0640(1)	13.251(4)
b/Å	25.2988(4)	17.142(5)
c/Å	18.4569(1)	19.855(7)
β/°	95.915(1)	93.18(3)
V/Å	5138.7(1)	4503.2(25)
Z	4	4
T/K	296	298
μ/mm^{-1}	0.457	0.442
Unique reflections collected	9045 (R_{int} = 0.0737)	5879
Observed data [$I > 2\sigma(I)$]	8610	3393
Data/parameters	8610/604	3393/549
Final $R1$, $wR2$ indices [$I > 2\sigma(I)$]	0.0643, 0.1728	0.056, 0.056 (R_f; R_w) [b]

[a] Crystals grown from an acetone–hexane mixture are found to incorporate an acetone molecule. [b] $R_f = \Sigma(F_o - F_c)/\Sigma(F_o)$; $R_w = [\Sigma(w(F_o - F_c)^2)/\Sigma(wF_o^2)]^{1/2}$.

24 h, the resulting red solution was dried *in vacuo*. The residue, which was a mixture of [Ru]–N_3 **2** and an organic product, was extracted with hexane and eluted through a silica gel packed column with diethyl ether to obtain pure $PhCH_2CN$ (14.28 mg, 86%) identified by comparing the spectroscopic data with that of an authentic sample. Complex **2** was identified from the NMR spectrum of the mixture.

Synthesis of {[Ru]NCCH$_2$Ph}PF$_6$

The complex [Ru]–C≡CPh (0.34 g, 0.42 mmol) was dissolved in THF (15 mL), and Me_3SiN_3 (0.24 mL, 1.81 mmol) added. After stirring for 8 h, ^{31}P NMR spectroscopy indicated completion of the reaction after which NH_4PF_6 (0.10 g, 0.6 mmol) was added. The solution was stirred at 0 °C for 3 h, the mixture filtered through Celite, and the filtrate concentrated to *ca.* 5 mL. Addition of hexane to the filtrate afforded a pale yellow powder which was isolated after filtration and washing with hexane and identified as {[Ru]N≡CCH$_2$Ph}PF$_6$ **8** (0.34 g, 85%). Spectroscopic data for **8**: ^{1}H NMR ($CDCl_3$): δ 7.73–6.78 (m, 35H, Ph); 4.46 (s, 5H, Cp); 3.97 (s, 2H, CH_2). ^{13}P NMR ($CDCl_3$): δ 42.18. IR (acetone): 2268 cm^{-1}. MS(FAB): m/z 808.1 ($M^+ - PF_6$), 691.0 ($M^+ - PF_6$, $NCCH_2Ph$).

Reaction of 1c with Me$_3$SiN$_3$

To a solution of complex **1c** (0.40 g, 0.48 mmol) in THF (20 mL) was added Me_3SiN_3 (0.40 mL, 3.02 mmol). The solution was stirred for 3 h, then the solution concentrated to *ca.* 5 mL, and slowly added to 60 mL of stirring hexane. The yellow precipitate thus formed was filtered off, and washed with hexane. The product was recrystallized from CH_2Cl_2–hexane (1 : 5) and identified as [Ru]–CN **7** (0.31 g, 90%). Spectroscopic data for **7**: ^{1}H NMR ($CDCl_3$): δ 7.69–6.95 (m, 30H, Ph); 4.35 (s, 5H, Cp). ^{31}P NMR ($CDCl_3$): δ 50.3. ^{13}C NMR ($CDCl_3$): δ 138.2–127.3 (Ph); 85 (Cp). MS (FAB): m/z 717.2 (M^+), 691.1 ($M^+ - CN$), 429.1 ($M^+ - CN$, PPh_3). The organic product was collected by extraction with hexane. The pure organic fragment was obtained by elution with diethyl ether on a silica gel packed column and the solvent removed on a rotary evaporator. The organic product was identified as $PhC{=}C(C_2H_5)N_2NH$ **11** (81%). Spectroscopic data of **11**: ^{1}H NMR ($CDCl_3$): δ 7.31–7.19 (m, 5H, Ph); 2.89 (q, 2H, CH_2, J_{H-H} = 7.6 Hz); 1.32 (t, 3H, CH_3, J_{H-H} = 7.6 Hz). High resolution MS: calc. for $C_{10}H_{11}N_3$: 173.0953, found: 173.0952.

X-Ray analysis of 6 and 5a

A single crystal of **6** of dimensions 0.10 × 0.25 × 0.45 mm was mounted on an Enraf-Nonius CAD4 diffractometer. Initial lattice parameters were determined from 25 reflections with $10.0 < 2\theta < 25°$. Data were collected using the $\theta/2\theta$ scan method. The raw intensity data were converted to structure factor amplitudes and their e.s.d.s by correction for scan speed, background and Lorentz, polarization effects. An empirical correction for absorption was applied to the data set. Computations were carried out using the NRCC structure determination package.[21] Merging of equivalent and duplicate reflections gave a total of 5879 unique measured data from which 3393 were considered observed ($I > 2.0\sigma(I)$). The structure was first solved by using the heavy atom method (Patterson synthesis) then refined *via* least-squares and difference Fourier techniques. The analytical forms of the scattering factor tables for the neutral atoms were used.[22] Hydrogen atoms were included in the structure factor calculation in their expected positions on the basis of idealized bonding geometry but were not refined in the least squares refinement. Final refinement using full-matrix, least-squares converged smoothly to values of R_f = 0.056 and R_w = 0.056. A single crystal of **5a** (0.10 × 0.15 × 0.20) was glued to a glass fiber and mounted on a Bruker SMART CCD automated diffractometer. Details of the crystal data, data collections and structure refinements are summarized in Table 3. The structure was solved by direct method and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms giving $R1$ = 0.0643 and $wR2$ = 0.1728. Other relevant crystal data for both crystals are also given in Table 3.

CCDC reference numbers 169474 and 169475.

See http://www.rsc.org/suppdata/dt/b1/b104635g/ for crystallographic data in CIF or other electronic format.

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