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# Reactions of ruthenium acetylide complexes with benzylidenemalonitrile †

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Reactions of [RuCp(L)(L′)(C≡CPh)] (Cp = $\eta^5$-$C_5H_5$; L = $PPh_3$, L′ = $P(OMe)_3$ **1a**; LL′ = dppe = $Ph_2PCH_2CH_2PPh_2$ **1b**; L = $PPh_3$, L′ = CN′Bu **1c**) with H(Ph)C=C(CN)$_2$ gave the cyclobutenyl complexes [RuCp(L)(L′){C=C(Ph)CH(Ph)C(CN)$_2$}] **2a**, **2b** and **2c** which readily transform to the butadienyl complexes [RuCp(L)(L′){C[=C(CN)$_2$]C(Ph)CH(Ph)}] **3a**, **3b** and **3c**, respectively. Thermolysis of **3a** in benzene afforded the allylic complex [RuCp{P(OMe)$_3$}[$\eta^3$-C[=C(CN)$_2$]C(Ph)CH(Ph)}] **4** in high yield. Reaction of **4** with ′BuNC gave [RuCp{P(OMe)$_3$}(CN′Bu)[$\eta^1$-C[=C(CN)$_2$]C(Ph)CH(Ph)}] **5**. Treatment of **1a** with Cl(Ph)C=C(CN)$_2$ afforded the neutral vinylidene phosphonate complex [RuCp(PPh$_3$){P(O)(OMe)$_2$}{=C=C(Ph)C(Ph)C(CN)$_2$}] **6**. Reactions of **1b** and **1c,** both lacking phosphite ligands, with Cl(Ph)C=C(CN)$_2$ gave the cationic vinylidene complexes [RuCp(L)(L′){=C=C(Ph)C(Ph)C(CN)$_2$}]$^+$ **7b** and **7c**, respectively. Treatment of **1a** with $ICH_2CN$ afforded [RuCp(PPh$_3$){P(OMe)$_3$}{=C=C(Ph)CH$_2$CN}]I **8a**. In the presence of acid complex **8a** decomposes to give the acyl complex [RuCp(PPh$_3$){P(OMe)$_3$}(COCH$_2$Ph)] **10**. The structures of **3a**, **4**, **6** and the latter complex have been determined by single-crystal X-ray diffraction analysis.

## Introduction

Chemical reactivities of metal acetylide complexes have been the focus of several recent works due to their wide applications in many areas of organometallic[1] and material chemistry.[2] The co-ordinated acetylide ligand on a transition metal is reactive toward electrophiles, undergoing either alkylation or protonation at the β-carbon to give a stable vinylidene complex. The cycloaddition of alkynes with isocyanates has been reported in nickel(0) complexes.[3] This reaction possibly proceeds through a metallacycle formed by the σ-co-ordinated acetylide and isocyanate. One common reaction observed for the acetylide ligand is the [2 + 2] cycloaddition of the triple bond with unsaturated organic substrates.[4] A few cycloadditions of organic substrates such as $CS_2$,[5] $(NC)_2C=C(CF_3)_2$, $(NC)_2C=C(CN)_2$[6] and $Ph_2C=C=O$[7] to the acetylide ligand in various metal complexes have also been reported. Addition of activated alkenes containing an electron-withdrawing group to ruthenium acetylide complexes again resulted in a formal [2 + 2] cycloaddition. This was followed by a facile ring opening of the resultant ruthenium cyclobutenyl complex generating the ruthenium butadienyl species. In some cases, subsequent displacement of a phosphine ligand led to the $\eta^3$-allylic product. For example, reactions between [RuCp(L)(L′)(C≡CR)] (R = Me or Ph; L = $PPh_3$; L′ = CO, $PPh_3$ or $P(OPh)_3$; LL′ = dppe) and tetracyanoethylene gave cyclobutenyl [RuCp(L)(L′){C=CRC(CN)$_2$C(CN)$_2$}], butadienyl [RuCp(L)(L′){C[=C(CN)$_2$]CRC=C(CN)$_2$}] and allylic [RuCp(PPh$_3$){$\eta^3$-C(CN)$_2$CRC=C(CN)$_2$}] complexes.[6]

The stereochemical studies by Criegee and co-workers[8] on the thermal ring opening of *cis*- and *trans*-1,2,3,4–tetramethylcyclobutenes were the first to show unambiguously the contrarotatory nature of the cyclobutene–butadiene electrocyclic interconversion. In 1965 Woodward and Hoffmann[9] proposed a theory to rationalize such electrocyclic reactions. Since then, Brauman and Golden[10] have estimated that the thermally allowed contrarotatory process for cyclobutenes is more favored (by 15.0 kcal mol$^{-1}$) than the disrotatory process. This experimental estimate is in accord with values obtained by Breulet and Schaefer[11] from *ab initio* calculations.

Bruce and his co-workers studied the transformations of cycloadducts of transition metal acetylides and activated olefins, such as $C(CF_3)_2=C(CN)_2$],[12] *trans*-CH(CO$_2$Me)=C(CN)(CO$_2$Me)[13] and 4-(O$_2$N)C$_6$H$_4$CH=C(CN)R (R = CN or CO$_2$Et),[14] using a substrate that permitted the stereochemistry to be determined readily.

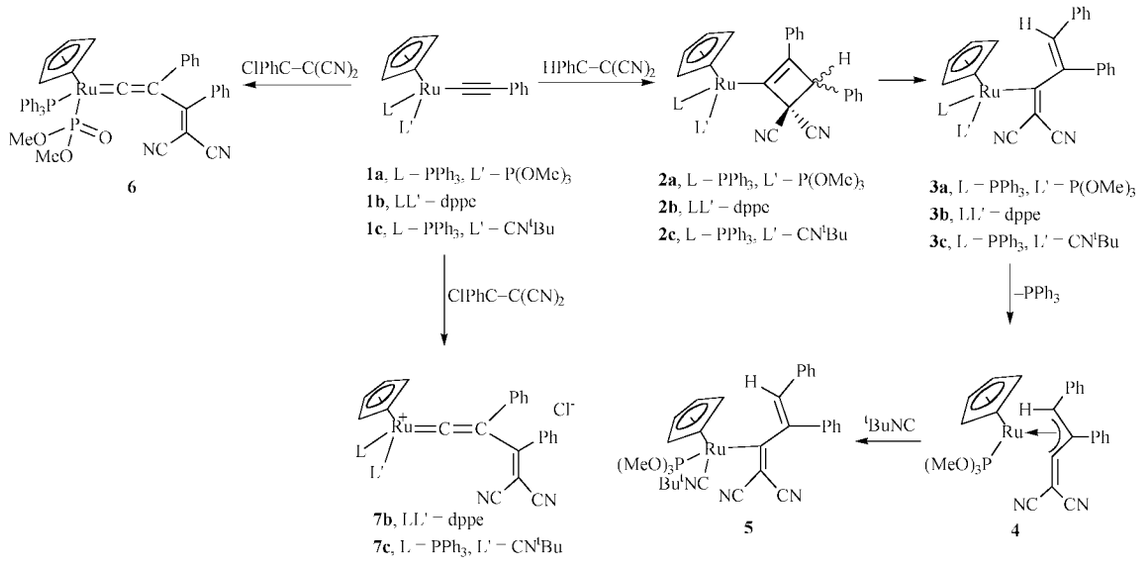
In a search for new chemical properties of the acetylide complexes, we carried out reactions of isocyanate and isothiocyanate with two such ruthenium complexes and recently reported[15] sequential additions of the organic substrate to the acetylide producing a novel heterocyclic ligand not observed before. The [2 + 2] cycloaddition is the first step and is followed by further additions of isothiocyanate to give a trimerization product. In this paper we report the reactions of H(Ph)C=C(CN)$_2$ and Cl(Ph)C=C(CN)$_2$ with ruthenium acetylides. These olefins were chosen because the presence of different electrophilic groups might enable further information to be obtained in the course of these reactions.

## Results and discussion

### Synthesis of cyclobutenyl and butadienyl complexes

Treatment of [RuCp(PPh$_3$){P(OMe)$_3$}(C≡CPh)] **1a** with H(Ph)C=C(CN)$_2$ in $CH_2Cl_2$ at room temperature for 1 h resulted in formation of a mixture of two complexes: [RuCp(PPh$_3$){P(OMe)$_3$}{C=C(Ph)CH(Ph)C(CN)$_2$}] **2a** and [RuCp(PPh$_3$){P(OMe)$_3$}{C[=C(CN)$_2$]C(Ph)CH(Ph)}] **3a** in a ratio of 1 : 1 (Scheme 1). Prolonging the reaction time did not alter the ratio. However, if we carried out this reaction at 0 °C for 3 h the ratio was about 2 : 1, which again changed to 1 : 1 at room temperature. Complexes **2a** and **3a** cannot be separated by column chromatography. Recrystallization of their mixture gave only

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4223/




**Scheme 1**

single crystals of **3a**, which converted into the mixture in solution.

There was no obvious color change in the formation of complexes **2a** and **3a** from **1a**, so the reaction was monitored by $^{31}$P and $^{1}$H NMR spectra. For **1a** the $^{31}$P NMR spectrum displays two doublet resonances at $\delta$ 56.2 and 151.7 with $J_{P-P}$ = 68.8 Hz assignable to $PPh_3$ and $P(OMe)_3$, respectively. Upon addition of 3 equivalents of $H(Ph)C{=}C(CN)_2$ to the $CDCl_3$ solution of **1a**, complexes **2a** and **3a** formed. The $^{31}$P NMR spectrum of the mixture displays four doublet resonances of which the two at $\delta$ 58.8 and 148.9 with $J_{P-P}$ = 70.2 Hz are assigned to the $PPh_3$ and $P(OMe)_3$ of **2a**, respectively, and those at $\delta$ 58.3 and 148.2 with $J_{P-P}$ = 70.4 Hz to the corresponding ones of **3a**. In the $^{1}$H NMR spectrum two singlet resonances at $\delta$ 5.10 and 5.01 and a doublet resonance at $\delta$ 3.27 with $J_{H-P}$ = 10.9 Hz are assigned to CH, Cp and OMe of **2a**, respectively. The corresponding resonances for **3a** appear at $\delta$ 4.66 and 4.74 and 3.27 (doublet with $J_{H-P}$ = 10.9 Hz).

The reactions of complexes **1b** and **1c** with $H(Ph)C{=}C(CN)_2$ yielded kinetic and thermodynamic products. That of **1b** in $CH_2Cl_2$ in 1 h at room temperature afforded **2b** which transformed completely to **3b** in 24 h. For **2b** the $^{31}$P NMR spectrum displays two broad resonances at $\delta$ 98.1 and 96.9 assignable to the dppe ligand and the $^{1}$H NMR spectrum shows two singlet resonances at $\delta$ 5.24 and 4.67 assignable to C*H*Ph and Cp, respectively. For **3b** the $^{31}$P NMR spectrum displays two broad resonances at $\delta$ 94.0 and 92.3 and the $^{1}$H NMR spectrum displays the broad resonance at $\delta$ 5.95 assignable to C*H*Ph and the resonance at $\delta$ 4.43 to Cp. Treatment of **1c** with $H(Ph)C{=}C(CN)_2$ in $CH_2Cl_2$ at room temperature for 10 min afforded **2c** in 87% yield (Scheme 1). If **2c** was not isolated immediately the ring-opening reaction proceeded and **3c** formed. Attempts to recrystallize **2b** and **2c** from $CH_2Cl_2$–hexane (1:2) at −20 °C resulted in isolation of **3b** and **3c**, respectively. Complexes **2a** and **3a** containing $PPh_3$ and $P(OMe)_3$ as their ancillary ligands are in equilibrium. However, no such phenomenon was observed for complexes **2b**/**3b** and **2c**/**3c** possibly because there is no $P(OMe)_3$ ligand in them.

The molecular structure of complex **3a** has been determined by a single-crystal X-ray diffraction analysis, an ORTEP[16] drawing being shown in Fig. 1. Selected bond distances and angles are listed in Table 1. The co-ordination about the ruthenium is a distorted piano-stool geometry with the $\eta^5$-$C_5H_5$ group being symmetrically attached to the metal. All Ru–C (Cp) bond distances range within 2.231(2)–2.249(2) Å with an average of 2.238 Å. The Ru–C1 bond distance of 2.055(8) Å is relatively shorter. The butadienyl ligand is non-planar and there

**Table 1** Selected bond distances (Å) and angles (°) of [RuCp($PPh_3$)-{$P(OMe)_3$}{C[=C(CN)$_2$]C(Ph)=CH(Ph)}] **3a**

| | | | |
|---|---|---|---|
| Ru–P1 | 2.2364(23) | Ru–P2 | 2.3305(23) |
| Ru–C1 | 2.055(8) | C1–C16 | 1.384(11) |
| C1–C2 | 1.506(11) | C2–C3 | 1.319(11) |
| C2–C10 | 1.512(11) | C3–C4 | 1.455(11) |
| C16–C17 | 1.428(11) | C16–C18 | 1.451(11) |
| C17–N1 | 1.143(11) | C18–N2 | 1.131(11) |
| P1–Ru–P2 | 92.33(8) | P1–Ru–C1 | 92.92(22) |
| P2–Ru–C1 | 94.57(21) | Ru–C1–C16 | 126.1(6) |
| Ru–C1–C2 | 122.2(5) | C1–C2–C10 | 111.8(6) |
| C1–C2–C3 | 124.2(7) | C3–C2–C10 | 123.9(7) |

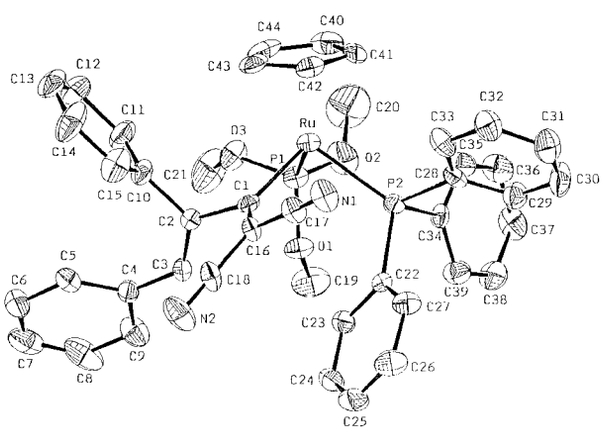


**Fig. 1** An ORTEP drawing of complex **3a** with thermal ellipsoids, (in all Figures) shown at the 30% probability level.

is no obvious delocalization between C–C single and C=C double bonds (C1–C16 1.384; C1–C2 1.506; C2–C3 1.319 Å).

### Synthesis and structure of [RuCp{P(OMe)$_3$}{$\eta^3$-C[=C(CN)$_2$]-C(Ph)CH(Ph)}] 4

Thermolysis of complex **3a** in benzene at refluxing temperature for 2 d afforded the allylic complex [RuCp{P(OMe)$_3$}{$\eta^3$-C[=C(CN)$_2$]C(Ph)CH(Ph)}] **4** by removal of a $PPh_3$ ligand with high yield (Scheme 1). The $^{1}$H NMR spectrum of **4** displays a singlet resonance at $\delta$ 4.94 and two doublet resonances at $\delta$ 3.63 ($J_{H-P}$ = 11.8) and 3.43 ($J_{H-P}$ = 12.3 Hz) attributed to Cp, OMe and C*H*(Ph), respectively. The $^{31}$P NMR spectrum displays a singlet resonance at $\delta$ 159.35 attributed to the $P(OMe)_3$ ligand.

**Table 2** Selected bond distances (Å) and angles (°) of [RuCp{P(OMe)$_3$}{$\eta^3$-C(CN)$_2$C(Ph)C=CH(Ph)}] **4**

| | | | |
|---|---|---|---|
| Ru–P | 2.245(3) | Ru–C1 | 2.250(9) |
| Ru–C2 | 2.142(10) | Ru–C3 | 1.934(10) |
| C1–C2 | 1.422(14) | C2–C3 | 1.418(13) |
| C3–C4 | 1.382(13) | C4–C5 | 1.439(14) |
| C4–C6 | 1.399(14) | C5–N1 | 1.124(13) |
| C6–N2 | 1.135(14) | | |
| P–Ru–C1 | 80.7(3) | P–Ru–C2 | 104.3(3) |
| P–Ru–C3 | 89.3(3) | C1–C2–C3 | 111.1(9) |
| C1–C2–C13 | 128.8(8) | C3–C2–C13 | 120.0(9) |
| Ru–C3–C4 | 144.8(7) | C3–C4–C5 | 120.6(9) |
| C3–C4–C6 | 122.7(9) | Ru–C1–C2 | 67.0(5) |
| Ru–C1–C7 | 118.5(6) | | |

**Table 3** Selected bond distances (Å) and angles (°) of [RuCp(PPh$_3$){P(O)(OMe)$_2$}{C=C(Ph)C(Ph)C(CN)$_2$}]·(OH)(Ph)C=C(CN)$_2$ **6**

| | | | |
|---|---|---|---|
| Ru–P1 | 2.3437(14) | Ru–P2 | 2.2965(16) |
| Ru–C1 | 1.790(5) | C1–C2 | 1.362(6) |
| C2–C3 | 1.434(7) | C2–C5 | 1.501(7) |
| C3–C4 | 1.373(7) | C4–C17 | 1.447(8) |
| C4–C18 | 1.492(7) | O1–H | 1.00(5) |
| O4–H | 1.45(5) | C17–N1 | 1.143(8) |
| C18–N2 | 1.136(7) | P2–O1 | 1.475(3) |
| P2–O2 | 1.593(4) | P2–O3 | 1.585(3) |
| P1–Ru–P2 | 92.01(5) | P1–Ru–C1 | 95.85(14) |
| Ru–C1–C2 | 173.9(4) | C1–C2–C3 | 120.4(4) |
| C2–C3–C4 | 123.5(4) | C3–C4–C17 | 124.7(5) |
| C3–C4–C18 | 122.6(5) | P2–O1–H | 171(3) |

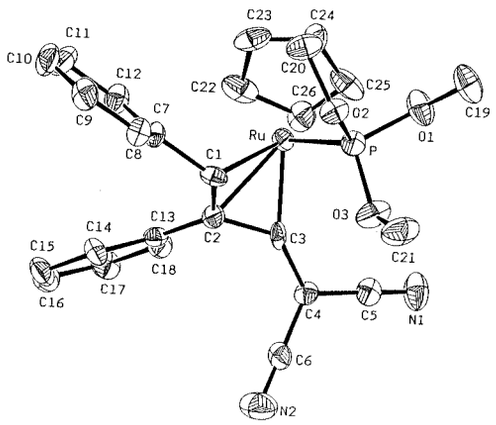



**Fig. 2** An ORTEP drawing of complex **4**.

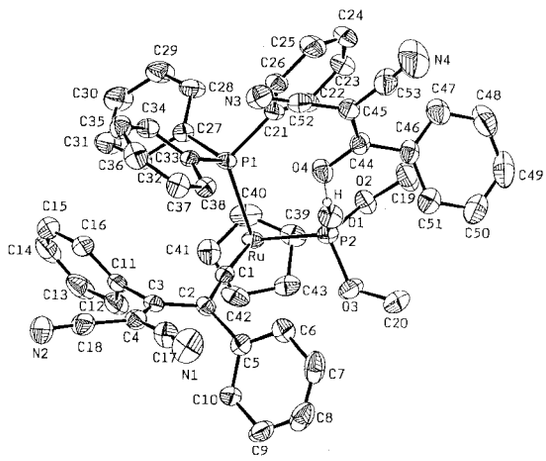



**Fig. 3** An ORTEP drawing of complex **6**.

No similar reaction was observed for **3b** or **3c**. The weak bonding of the PPh$_3$ ligand in **3a** could possibly be owing to the presence of the P(OMe)$_3$ ligand. The Ru–P bonds in **3b** and **3c** should be relatively stronger.

The structure of complex **4** has been determined by a single-crystal X-ray diffraction analysis. An ORTEP drawing is shown in Fig. 2. Selected bond distances and angles are listed in Table 2. The co-ordination sphere consists of a $\eta^5$-C$_5$H$_5$ group (Ru–C(Cp) 2.183–2.253 Å, average 2.214 Å), a P(OMe)$_3$ ligand (Ru–P 2.245(3) Å) and a $\eta^3$-allylic ligand (Ru–C1 2.250(9), Ru–C2 2.142(10), Ru–C3 1.934(10) Å). The $\eta^3$-allylic ligand is formed by co-ordination of the C1–C2 bond of the butadienyl ligand and there is delocalization between C–C single and C=C double bonds (C2–C3 1.418(13); C1–C2 1.422(14); C3–C4 1.382(13) Å).

Reaction of complex **4** with $^t$BuNC in $CH_2Cl_2$ at refluxing temperature for 2 d afforded the butadienyl complex [RuCp{P(OMe)$_3$}(CN$^t$Bu){C[=C(CN)$_2$]C(Ph)CH(Ph)}] **5**. The $^{31}$P NMR spectrum displays a singlet resonance at $\delta$ 159.2 assignable to the P(OMe)$_3$ ligand. The $^1$H NMR spectrum displays three singlet resonances at $\delta$ 5.97, 4.63 and 1.34 assignable to C*H*Ph, Cp and C(CH$_3$)$_3$, respectively, and a doublet resonance at $\delta$ 3.57 with $J_{H-P}$ = 11.6 Hz assignable to P(OMe)$_3$. The $\eta^3$-allylic ligand in **4** became $\eta^1$ bonding and the co-ordination site was replaced by a donor *tert*-butyl cyanide ligand. Complex **5** is thermally more stable than **3b** and **3c**. Thermolysis of complex **5** in benzene at refluxing temperature for two days did not remove the phosphite or the isocyanide ligand.

### Reaction of ruthenium acetylides with Cl(Ph)C=C(CN)$_2$

Metal acetylide complexes are known to react readily with activated olefins containing electron-withdrawing groups affording [2 + 2] cycloaddition products. We therefore treated vinyl chloride with the acetylide complex **1a** to see if the reaction would proceed in a similar manner. The reaction of **1a** with an excess of Cl(Ph)C=C(CN)$_2$ in $CH_2Cl_2$ at room temperature for 24 h gave an orange-red solution from which the neutral vinylidene complex [RuCp(PPh$_3$){P(O)(OMe)$_2$}{=C=C(Ph)C(Ph)C(CN)$_2$}] **6** was obtained in 88% yield. The $^1$H NMR spectrum displays inequivalent OMe resonances at $\delta$ 3.20 and 2.96 both with $J_{H-P}$ = 11.6 Hz. Two doublet $^{31}$P resonances appear at $\delta$ 105.6 and 43.7 with $J_{P-P}$ = 47.8 Hz, the former shifted significantly from $\delta$ 158.3 of P(OMe)$_3$ in **1a** indicating that an Arbuzov-like dealkylation[16] of the P(OMe)$_3$ ligand could have occurred in the reaction. The $^{13}$C NMR spectrum displays a doublet of doublet resonance at $\delta$ 339.8 attributed to C$_\alpha$, indicating the presence of a vinylidene ligand. The product is thus assumed to have a neutral vinylidene structure and a phosphonate ligand.

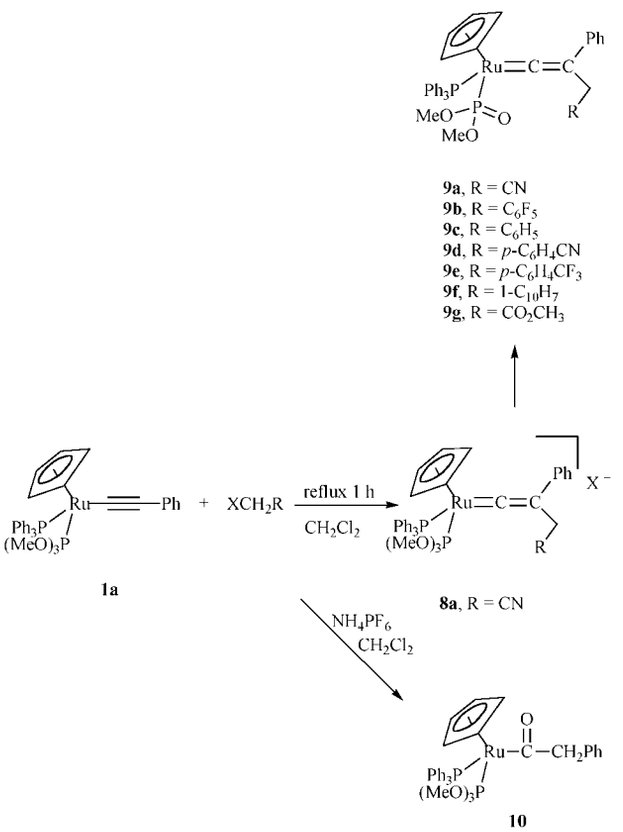
Evaporation of the solvent of the crude product caused formation of orange crystals. Complex **6** cocrystallized with (OH)(Ph)C=C(CN)$_2$, a product resulting from substitution of the chlorine atom of excess of Cl(Ph)C=C(CN)$_2$. The structure of **6** was fully characterized by a single-crystal X-ray diffraction analysis. An ORTEP drawing is shown in Fig. 3. Selected bond distances and angles are listed in Table 3. The short Ru–C1 bond of 1.790(5) Å is typical of a ruthenium vinylidene system and so is the C1–C2 bond of 1.362(6) Å.[18] The ruthenium–vinylidene linkage is nearly linear; the bond angle Ru–C1–C2 is 173.9(4)°. The relatively short bond length P2–O1 (1.475(3) Å) with no methyl group bound to O1 indicates the presence of a phosphonate ligand. The bonds P2–O2 and P2–O3 (1.593(4) and 1.585(3) Å) are relatively longer. There is an intermolecular hydrogen bond between the phosphonate ligand of **6** and (OH)(Ph)C=C(CN)$_2$ with O1–H and O4–H 1.00(5) and 1.45(5) Å, respectively.

Lacking phosphite ligands, both complexes **1b** and **1c**, upon reacting with Cl(Ph)C=C(CN)$_2$, afforded in high yield the cationic vinylidene complexes [RuCp(L)(L′){=C=C(Ph)C(Ph)C(CN)$_2$}]Cl **7b**, (LL′ = dppe) and **7c**, (L = PPh$_3$, L′ = CN$^t$Bu), respectively. For **7b** the $^{31}$P NMR spectrum displays a singlet

resonance at $\delta$ 77.4 assignable to the dppe ligand. In the $^{13}C$ NMR spectrum the triplet resonance at $\delta$ 351.8 with $J_{C-P}$ = 14.8 Hz is assigned to $C_\alpha$. The $^1H$ NMR spectrum of **7c** displays resonances at $\delta$ 5.66 and 1.17 attributed to Cp and $C(CH_3)_3$, respectively, and the $^{31}P$ NMR spectrum displays a singlet resonance at $\delta$ 44.1 assignable to the $PPh_3$ ligand. The $^{13}C$ NMR spectrum displays a doublet resonance at $\delta$ 345.2 with $J_{C-P}$ = 12.0 Hz assignable to $C_\alpha$ of the vinylidene ligand and a doublet resonance at $\delta$ 198.6 with $J_{C-P}$ = 16.3 Hz assignable to the *C*N$^t$Bu. It is not surprising that the chloride atom of $Cl(Ph)C{=}C(CN)_2$ behaved as a good leaving group and ended up as a counter anion after the formation of the cationic vinylidene complexes; $NH_4PF_6$ was added to exchange the counter anion after the reaction was completed.

### Other phosphonate vinylidene complexes

Treatment of complex **1a** with $ICH_2CN$ in $CH_2Cl_2$ for 10 min afforded the vinylidene complex $[RuCp(PPh_3)\{P(OMe)_3\}{=}C{=}C(Ph)CH_2CN\}]I$ **8a** in 64.8% yield (Scheme 2). In the $^1H$ NMR spectrum the two dd resonances at $\delta$ 3.27 and 3.17 are assigned to the two non-equivalent methylene protons. Lengthening the reaction time caused Arbuzov-like dealkylation to occur, leading to formation of the phosphonate complex $[RuCp(PPh_3)\{P(O)(OMe)_2\}\{{=}C{=}C(Ph)CH_2CN\}]$ **9a**. Transformation of the phosphite ligand to a phosphonate ligand was revealed by a significant shift of the $^{31}P$ NMR resonance from $\delta$ 135.3 to 95.4. Formation of $CH_3I$ was seen in the $^1H$ NMR spectrum. The observation of the sequential transformation seems to indicate that formation of the phosphonate ligand required halide ion. The most characteristic spectroscopic data of the two vinylidene complexes consist of a strongly deshielded $C_\alpha$ resonance as a doublet of doublet at $\delta$ 348.6 ± 2.5 in the $^{13}C$ NMR spectrum.[19] Since **8a** is a cationic complex containing a $P(OMe)_3$ ligand, it is not surprising to see an Arbuzov-like dealkylation in the presence of $I^-$ counter anion to give the phosphonate complex **9a**.




**Scheme 2**

**Table 4** Selected bond distances (Å) and angles (°) of $[RuCp(PPh_3)\{P(OMe)_3\}(COCH_2Ph)]$ **10**

| | | | |
|---|---|---|---|
| Ru–P1 | 2.2153(15) | Ru–P2 | 2.3097(15) |
| Ru–C1 | 2.010(5) | C1–C2 | 1.518(7) |
| C1–O1 | 1.326(7) | C2–C3 | 1.510(8) |
| P1–Ru–P2 | 93.53(5) | P1–Ru–C1 | 93.53(15) |
| P2–Ru–C1 | 93.06(15) | Ru–C1–C2 | 120.6(4) |
| Ru–C1–O1 | 128.3(4) | O1–C1–C2 | 111.0(4) |
| C1–C2–C3 | 119.0(5) | | |

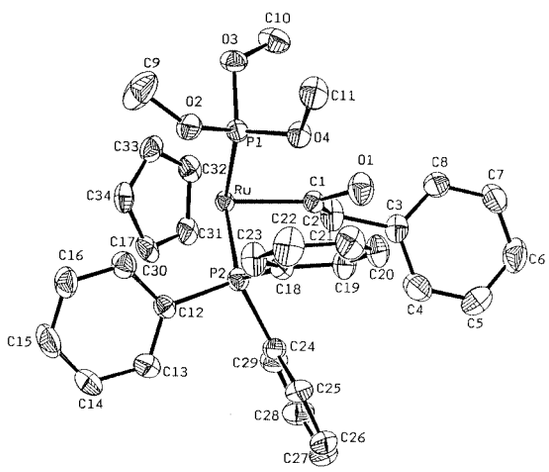



**Fig. 4** An ORTEP drawing of complex **10**.

In the presence of acid the newly formed carbon–carbon bond of complex **8a** is easily cleaved. Since $NH_4PF_6$ was used in the preparation, it was converted into $HPF_6$. Thus complex **8a** with $PF_6^-$ counter anion prepared at room temperature is unstable particularly in $CH_2Cl_2$ solution. It decomposes to give the acyl complex $[RuCp(PPh_3)\{P(OMe)_3\}(COCH_2Ph)]$ **10**. With $I^-$ anion, **8a** is stable for one day and then the Arbuzov-like dealkylation occurs to give neutral vinylidene complex **9a**. The presence of $HPF_6$ is required for the formation of acyl complex **10**. In fact, in 1980, Bruce and Swincer[20] reported a similar reaction and proposed a possible mechanism.

The molecular structure of complex **10** has been determined by an X-ray diffraction study. An ORTEP drawing is shown in Fig. 4. Selected bond distances and bond angles are listed in Table 4. The bond distance of Ru–C1 (2.010(5) Å) is typical for a Ru–C single bond and that of C1–O1 (1.326(7) Å) is typical for a C–O double bond. The bond angles of Ru–C1–O1 (128.3(4)°) and O1–C1–C2 (111.0(4)°) are slightly deviated from that of a typical C ($sp^2$) hybidization which may be due to the steric effect between the phenyl group of the acyl ligand and the bulky $PPh_3$ ligand.

Our attempts to prepare similar vinylidene complexes with a trimethyl phosphite ligand all led to the corresponding neutral phosphonate complexes $[RuCp(PPh_3)\{P(=O)(OMe)_2\}\{{=}C{=}C(Ph)CH_2R\}]$, R = $C_6F_5$ **9b**; R = $C_6H_5$ **9c**; *p*-$NCC_6H_4$ **9d**; R = *p*-$F_3CC_6H_4$ **9e**; 1-$C_{10}H_7$ **9f** or $CO_2CH_3$ **9g** in high yield (Scheme 2). The most characteristic spectroscopic data of these vinylidene complexes again consist of a strongly deshielded resonance as a triplet at $\delta$ 348 ± 3 in the $^{13}C$ NMR spectrum and two doublet $^{31}P$ NMR resonances at around $\delta$ 96 ± 2 and 49 ± 2 attributed to $P(O)(OMe)_2$ and $PPh_3$, respectively. Complexes **9a–9g** are all deep red oils, possibly because of the presence of phosphonate ligand and are stable in solution and in air for more than one month. Attempted deprotonation failed to give a cyclopropenyl complex, possibly due to lack of a positive charge.

## Conclusion

The [2 + 2] cycloaddition of the unsymmetrical olefin HPhC=

$C(CN)_2$ to [RuCp(L)(L′)(C≡CPh)] gave cyclobutenyl complexes **2a–2c** and butadienyl complexes **3a–3c**. Further pyrolysis of **2a** and **3a** gave the $\eta^3$-allylic complex **4** by loss of a $PPh_3$ ligand. The reaction of **1a** with $ClPhC{=}C(CN)_2$ proceeded through an Arbuzov-like dealkylation and resulted in formation of the neutral vinylidene complex $[RuCp(PPh_3)\{P(O)(OMe)_2\}\{{=}C{=}C(Ph)C(Ph)C(CN)_2\}]$ **6**. The reaction of **1b** and **1c** with $Cl(Ph)C{=}C(CN)_2$ afforded cationic vinylidene complexes $[RuCp(L)(L')\{{=}C{=}C(Ph)C(Ph)C(CN)_2\}Cl$ **7**. In $Cl(Ph)C{=}C(CN)_2$, the two strong electron-withdrawing CN groups make the chlorine atom a good leaving group. The Arbuzov-like dealkylation reaction is not uncommon for such a ruthenium entity with a vinylidene ligand. The reaction of **1a** with organic halide $XCH_2R$ afforded neutral phosphonate vinylidene complexes $[RuCp(PPh_3)\{P(O)(OMe)_2\}\{{=}C{=}C(Ph)\text{-}CH_2R\}]$.

## Experimental

### General procedures

All manipulations were performed under nitrogen using vacuum-line, dry-box, and standard Schlenk techniques. Dichloromethane was distilled from $CaH_2$ and diethyl ether and THF from sodium diphenylketyl. All other solvents and reagents were of reagent grade used without further purification. The NMR spectra were recorded on Bruker AC-200 and AM-300WB FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of $\delta$ with residual protons in the solvents as an initial standard ($CDCl_3$, $\delta$ 7.24: acetone-$d_6$, $\delta$ 2.04). The FAB mass spectra were recorded on a JEOL SX-102A spectrometer. The complexes [RuCp(L)(L′)(C≡CPh)] **1a** [L = $PPh_3$, L′ = $P(OMe)_3$], **1b** (LL′ = dppe) and **1c** (L = $PPh_3$, L = CN′Bu) were prepared following the methods reported.[21] Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

### Syntheses

**[RuCp(PPh$_3$){P(OMe)$_3$}{C=C(Ph)CH(Ph)C(CN)$_2$}] 2a and [RuCp(PPh$_3$){P(OMe)$_3$}{C[=C(CN)$_2$]C(Ph)CH(Ph)}] 3a.** To a solution of complex **1a** (500 mg, 0.766 mmol) in $CH_2Cl_2$ (20 mL) was added $H(Ph)C{=}C(CN)_2$ (354.3 mg, 2.29 mmol) and the solution stirred for 1 h at room temperature. The $^1H$ and $^{31}P$ NMR spectra of the product indicated formation of two major products **2a** and **3a** in a ratio of 1 : 1. Reduced the solvent to *ca.* 3 mL under vacuum followed by addition of hexane gave yellow precipitates. After filtration, the solid was further washed with 2 × 20 mL of hexane and 10 mL of diethyl ether and dried under vacuum to give a mixture of **2a** and **3a** (544.5 mg, 0.674 mmol) in a total yield of 75%. Crystallization of the mixture from $CH_2Cl_2$–hexane (1 : 3) gave yellow crystals. At room temperature **3a** in $CDCl_3$ solution was converted into a mixture of **2a** and **3a** (1 : 1) in 30 min. Spectroscopic data for **2a**: $^1H$ NMR ($CDCl_3$): $\delta$ 7.90–6.35 (m, 25 H, Ph), 5.10 (s, 1 H, CH), 5.01 (s, Cp) and 3.27 (d, 9 H, $J_{H-P}$ = 10.93 Hz, $OCH_3$); $^{31}P$ NMR ($CDCl_3$) $\delta$ 148.9 and 58.8 (2d, $J_{P-P}$ = 70.2 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 164.6 (q, $C_\alpha$, $J_{C-P}$ = 12.6, 7.2), 163.0 (*C*Ph), 137.4–123.0 (Ph), 113.7, 112.5 (2CN), 82.9 ($C(CN)_2$), 82.6 (Cp) and 52.2 (d, $J_{C-P}$ = 9.0 Hz, $OCH_3$); MS (*m*/*z*, $^{102}$Ru) 809.1 ($M^+$ + 1), 654.1 ($M^+$ − PhHC=C(CN)$_2$) and 429.0 ($M^+$ − PhHC=C(CN)$_2$-CCPh). Spectroscopic data for **3a**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.76–6.44 (m, 25 H, Ph), 4.66 (s, 1 H, CH), 4.74 (s, Cp) and 3.37 (d, 9 H, $J_{H-P}$ = 11.13 Hz, $OCH_3$); $^{31}P$ NMR ($CDCl_3$) $\delta$ 148.2 and 58.3 (2d, $J_{P-P}$ = 70.35 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 165.8 (q, $C_\alpha$, $J_{C-P}$ = 15.7, 8.9), 162.9 (*C*Ph), 139.6–118.2 (Ph), 117.1, 116.6 (2CN), 84.2 (C(CN)$_2$), 82.7 (Cp), 60.5 (*C*HPh) and 52.1 (d, $J_{C-P}$ = 9.0 Hz, $OCH_3$); MS (*m*/*z*, $^{102}$Ru) 809.1 ($M^+$ + 1), 654.1 ($M^+$ − PhHC=C(CN)$_2$) and 429.0 ($M^+$ − PhHC=C(CN)$_2$-CCPh). Calc. for $C_{44}H_{40}N_2O_3P_2Ru$: C, 65.42; H, 4.99; N, 3.47. Found: C: 65.73; H, 4.85; N, 3.59%.

**[RuCp(PPh$_3$)(CN′Bu){C=C(Ph)CH(Ph)C(CN)$_2$}] 2c.** To a solution of complex **1c** (500 mg, 0.817 mmol) in $CH_2Cl_2$ (20 mL) was added $H(Ph)C{=}C(CN)_2$ (377.5 mg, 2.45 mmol) and the solution was stirred for 10 min at room temperature. Removal of the solvent under vacuum followed by addition of hexane gave a yellow precipitate. After filtration, the solid was further washed with 2 × 20 mL of hexane and 10 mL of diethyl ether and dried under vacuum to give the product **2c** (544.5 mg, yield 87%). Spectroscopic data for **2c**: $^1H$ NMR ($C_6D_6$) $\delta$ 7.89–6.90 (m, 25 H, Ph), 4.98 (s, Cp), 4.85 (s, 1 H, CH) and 1.21 (s, 9 H, $C(CH_3)_3$); $^{31}P$ NMR ($CDCl_3$) $\delta$ 59.2; $^{13}C$ NMR ($CDCl_3$) $\delta$ 243.3 (d, CN′Bu, $J_{C-P}$ = 10.1), 167.2 (d, $C_\alpha$, $J_{C-P}$ = 9.9Hz), 158.7 (*C*Ph), 137.8–125.0 (Ph), 117.6, 115.5 (2CN), 84.0 (Cp), 82.4 ($C(CN)_2$), 58.1 (*C*HPh), 56.6 ($C(CH_3)_3$) and 30.4 (C(*C*H$_3$)$_3$); MS (*m*/*z*, $^{102}$Ru) 767.2 ($M^+$ + 1), 613.0 ($M^+$ − PhHC=C(CN)$_2$) and 512.0 ($M^+$ − PhHC=C(CN)$_2$-CCPh).

**[RuCp(PPh$_3$)(CN′Bu){C[=C(CN)$_2$]C(Ph)CH(Ph)}] 3c.** A $CH_2Cl_2$ solution of complex **2c** (200 mg, 0.261 mmol) was stirred at room temperature for 2 h. Removal of the solvent under vacuum followed by addition of hexane gave a yellow precipitate which was dried under vacuum, giving the product **3c** (186.0 mg, 93%). $^1H$ NMR ($CDCl_3$): $\delta$ 7.89–6.72 (m, 25 H, Ph), 5.33 (s, H), 4.40 (s, Cp) and 1.05 (s, 9 H, $C(CH_3)_3$). $^{31}P$ NMR ($CDCl_3$): $\delta$ 56.0. $^{13}C$ NMR ($CDCl_3$): $\delta$ 233.8 (d, $J_{C-P}$ = 10.1, *C*N′Bu), 158.3 (d, $C_\alpha$, $J_{C-P}$ = 9.9 Hz), 155.1 (*C*Ph), 137.4–115.5 (Ph), 113.6, 112.5 (2CN), 88.9 ($C(CN)_2$), 84.2 (Cp), 57.0 ($C(CH_3)_3$), 56.7 (*C*HPh) and 30.5 (C(*C*H$_3$)$_3$); MS (*m*/*z*, $^{102}$Ru): 767.2 ($M^+$ + 1), 505.0 ($M^+$ + 1 − $PPh_3$) and 422.0 ($M^+$ + 1 − $PPh_3$-$^t$BuNC). Calc. for $C_{40}H_{46}N_3PRu$: C, 72.04; H, 5.26; N, 5.48. Found: C, 72.66; H, 5.07; N, 5.33%.

**[RuCp(dppe){C=C(Ph)CH(Ph)C(CN)$_2$}] 2b.** This complex (523.3 mg, 0.638 mmol, yield 85%) was prepared from **1b** (500 mg, 0.751 mmol) using the same procedure as that for **2c** and a reaction time of 1 h at room temperature. $^1H$ NMR ($C_6D_6$): $\delta$ 8.17–6.63 (m, 30 H, Ph), 5.24 (s, 1 H, CH), 4.67 (s, Cp) and 2.68–2.40 (m, $CH_2CH_2$). $^{31}P$ NMR ($CDCl_3$): $\delta$ 98.1 and 96.9 (2br). $^{13}C$ NMR ($CDCl_3$): $\delta$ 164.9 (t, $C_\alpha$, $J_{C-P}$ = 17.0), 157.1 (*C*Ph), 136.8–122.8 (Ph), 119.1, 117.4 (2CN), 84.9 (Cp), 82.3 ($C(CN)_2$), 30.1 and 29.5 (2d, $J_{C-P}$ = 18.0 Hz); MS (*m*/*z*, $^{102}$Ru) 821.1 ($M^+$ + 1), 666.0 ($M^+$ − PhHC=C(CN)$_2$) and 565.0 ($M^+$ − PhHC=C(CN)$_2$-CCPh). Complex [RuCp(dppe){C[=C(CN)$_2$]-C(Ph)CH(Ph)}] **3b** (180.0 mg, yield 90%) was prepared from **2b** (200 mg, 0.244 mmol) using the same procedure as that for **3c** and the reaction time was 8 h at room temperature. $^1H$ NMR ($C_6D_6$): $\delta$ 7.91–6.97 (m, 30H, Ph), 5.95 (br, 1H, CH), 4.43 (s, Cp) and 2.70–2.05 (m, $CH_2CH_2$). $^{31}P$ NMR ($CDCl_3$): $\delta$ 94.0 and 92.3 (2br). $^{13}C$ NMR ($CDCl_3$): $\delta$ 164.9 (t, $C_\alpha$, $J_{C-P}$ = 17.0), 157.1 (*C*Ph), 136.8–122.8 (Ph), 119.1, 117.4 (2CN), 84.9 (Cp), 82.3 (*C*(CN)2), 30.1 and 29.5 (2d, $J_{C-P}$ = 18.0 Hz); MS (*m*/*z*, $^{102}$Ru) 821.1 ($M^+$ + 1) and 565.0 ($M^+$ − PhHC=C(CN)$_2$-CCPh). Calc. for $C_{49}H_{40}N_2P_2Ru$: C, 71.78; H, 4.92; N, 3.42. Found: C, 72.05; H, 4.75; N, 3.32%.

**[RuCp{P(OMe)$_3$}{η$^3$-C[=C(CN)$_2$]C(Ph)CH(Ph)}] 4.** To a solution of complex **1a** (500 mg, 0.766 mmol) in benzene $H(Ph)C{=}C(CN)_2$ (345.3 mg, 2.29 mmol) was added and the solution refluxed for 48 h. Removal of benzene solution under vacuum followed by addition of 50 mL of hexane gave a yellow precipitate. After filtration, the solid was further washed with 20 × 2 mL of hexane, 10 mL of diethyl ether and dried under vacuum, giving the product **4** (368 mg) in 88% yield. $^1H$ NMR ($CDCl_3$): $\delta$ 7.45–6.72 (m, 10 H, Ph), 4.94 (s, Cp), 3.63 (d, 9 H, $J_{H-P}$ = 11.75, $OCH_3$) and 3.43 (d, 1 H, CH(Ph), $J_{H-P}$ = 12.30 Hz). $^{31}P$ NMR ($CDCl_3$): $\delta$ 159.35 ($P(OMe)_3$). $^{13}C$ NMR ($CDCl_3$):

$\delta$ 223.5 (d, $J_{C-P}$ = 14.6, $C_\alpha$), 141.6, 137.0, 131.0–126.0 (Ph), 118.2, 113.0 (2CN), 86.1 (Cp), 78.6 (d, $J_{C-P}$ = 8.68, $C(CN)_2$), 71.3 ($C$(Ph)=CH(Ph)) and 52.6 (d, $J_{C-P}$ = 7.67 Hz, $OCH_3$); MS (*m*/*z*, $^{102}$Ru): 546.1 ($M^+$) and 291.0 ($M^+$ − PhHC=C(CN)$_2$-CCPh). Calc. for $C_{26}H_{25}N_2O_3PRu$: C, 57.24; H, 4.62; N, 5.14. Found: C, 57.65; H, 4.48; N, 5.03%.

**[RuCp{P(OMe)$_3$}(CN$^t$Bu){C[C(CN)$_2$]C(Ph)CH(Ph)}] 5.** To a solution of complex **4** (100 mg, 0.183 mmol) in $CH_2Cl_2$, $^t$BuCN (62.1 μL, 0.550 mmol) was added and the solution refluxed for 48 h. Removal of the solvent under vacuum followed by addition of 30 mL of hexane gave a yellow precipitate. After filtration, the solid was further washed with 10 × 2 mL of hexane, 10 mL of diethyl ether and dried under vacuum, giving the product **5** (82.7 mg, yield 72%). $^1$H NMR ($CDCl_3$): $\delta$ 7.65–6.96 (m, 25 H, Ph), 5.97 (s, 1 H, CH), 4.63 (s, Cp), 3.57 (d, 9 H, $J_{H-P}$ = 11.55 Hz, $OCH_3$) and 1.34 (s, $C(CH_3)_3$). $^{31}$P NMR ($CDCl_3$): $\delta$ 159.2. $^{13}$C NMR ($CDCl_3$): $\delta$ 236.0 (d, CN$^t$Bu, $J_{C-P}$ = 17.9), 154.5, 138.7–117.8 (Ph, $C_\beta$ and $C_\gamma$), 119.6, 115.3 (2CN), 85.2 (Cp), 57.0 (s, $C(CH_3)_3$), 51.8 (d, $J_{C-P}$ = 3.8 Hz, $OCH_3$) and 29.6 (s, $C(CH_3)_3$); MS (*m*/*z*, $^{102}$Ru): 629.1 ($M^+$), 505.1 ($M^+$ − P(OMe)$_3$) and 422.0 ($M^+$ − P(OMe)$_3$-$^t$BuNC). Calc. for $C_{31}H_{34}N_3O_3PRu$: C, 59.22; H, 5.45; N, 6.68. Found: C, 59.76; H, 5.32; N, 6.47%.

**[RuCp(PPh$_3$){P(O)(OMe)$_2$}{=C=C(Ph)C(Ph)C(CN)$_2$}] 6.** To a solution of complex **1a** (150 mg, 0.230 mmol) in $CH_2Cl_2$, Cl(Ph)C=C(CN)$_2$ (24.9 mg, 0.689 mmol) was added and the solution stirred at room temperature for 24 h, the solution changing from yellow to red. At this stage, crystals of **6** containing (OH)PhC=C(CN)$_2$ formed if the solvent slowly evaporated in the air. The solvent was reduced to *ca*. 5 mL then the mixture was added to a 50 mL solution of diethyl ether yielding orange-red precipitates of **6**. In order to remove (OH)PhC=C(CN)$_2$ (which could be formed by the reaction of water in the solution and excess of Cl(Ph)C=C(CN)$_2$), the precipitate was further washed with 10 mL of diethyl ether and subsequently with 10 × 2 mL of hexane, then dried under vacuum giving **6** (160.0 mg, yield 87.9%). $^1$H NMR ($CDCl_3$): $\delta$ 7.80–7.14 (m, 25 H, Ph), 5.33 (s, Cp), 3.20 (d, 3 H, $J_{H-P}$ = 11.61, $OCH_3$) 2.96 (d, 3 H, $J_{H-P}$ = 11.63 Hz, $OCH_3$). $^{31}$P NMR ($CDCl_3$): $\delta$ 105.6 and 43.7 (2d, $J_{P-P}$ = 47.8 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 339.8 (q, $^1J_{C-P}$ = 14.1, $^2J_{C-P}$ = 4.7, $C_\alpha$), 167.6 ($C_\beta$), 134.4–127.8 (Ph), 114.8, 114.0 (2CN), 94.2 (Cp), 85.6 ($C_\gamma$), 78.2 ($C(CN)_2$) and 52.3 (t, $J_{C-P}$ = 11.2 Hz, P(O)($OCH_3$)$_2$); MS (*m*/*z*, $^{102}$Ru): 793.0 ($M^+$ + 1), 539.0 ($M^+$ − CH=C(CN)$_2$) and 428.9 ($M^+$ − CH=C(CN)$_2$-P(O)(OMe)$_2$). Calc. for $C_{43}H_{36}N_2O_3P_2Ru$: C, 65.22; H, 4.58; N, 3.54. Found: C, 65.56; H, 4.77; N, 3.34%.

Complexes [RuCp(dppe){=C=C(Ph)C(Ph)C(CN)$_2$}][$PF_6$] **7b** (83% yield) and [RuCp(PPh$_3$)($^t$BuNC){=C=C(Ph)C(Ph)-C(CN)$_2$}][$PF_6$] **7c** (76% yield) were prepared using the same procedure as that for **6** and $NH_4PF_6$ was added to exchange the counter anion after the reaction was complete. Spectroscopic data for **7c**: $^1$H NMR ($CDCl_3$) $\delta$ 7.78–6.92 (m, 25 H, Ph), 5.66 (s, Cp) and 1.17 (s, 9 H, $C(CH_3)_3$); $^{31}$P NMR ($CDCl_3$) $\delta$ 44.07; $^{13}$C NMR ($CDCl_3$) $\delta$ 345.2 (d, $J_{C-P}$ = 12.0, $C_\alpha$), 198.6 (d, $J_{C-P}$ = 16.3, $C$N$^t$Bu), 164.7 ($C_\alpha$), 137.1–126.0 (Ph), 113.7, 112.4 (2CN), 94.9 (Cp), 85.5 (d, $J_{C-P}$ = 13.74 Hz, $C_\gamma$), 78.3 ($C(CN)_2$), 60.5 ($C(CH_3)_3$) and 29.8 (s, $C(CH_3)_3$); MS (*m*/*z*, $^{102}$Ru): 766.1 ($M^+$ − $PF_6$), 540.0 ($M^+$ − $PF_6$ − CH=C(CN)$_2$ + CO) and 512.0 ($M^+$ − $PF_6$-CH=C(CN)$_2$). Calc. for $C_{49}H_{39}F_6N_2P_3Ru$: C, 61.06; H, 4.08; N, 2.91. Found: C, 61.37; H, 3.96; N, 2.78%. Spectroscopic data for **7b**: $^1$H NMR ($CDCl_3$) $\delta$ 7.81–6.49 (m, 30H, Ph), 5.46 (s, Cp) and 3.70–3.15 (m, 4H, $CH_2CH_2$); $^{31}$P NMR ($CDCl_3$) $\delta$ 77.4; $^{13}$C NMR ($CDCl_3$) $\delta$ 351.8 (t, $J_{C-P}$ = 14.8, $C_\alpha$), 166.0 ($C_\beta$), 135.8–126.2 (Ph), 114.1, 113.2 (2CN), 93.9 (Cp), 85.6 ($C_\gamma$), 80.3 ($C(CN)_2$) and 28.9 (t, $J_{C-P}$ = 22.9 Hz, P$CH_2CH_2$P); MS (*m*/*z*, $^{102}$Ru) 819.1 ($M^+$ − $PF_6$), 593.0 ($M^+$ − $PF_6$-CH=C(CN)$_2$+CO), 565.0 ($M^+$ − $PF_6$-CH=C(CN)$_2$). Calc. for $C_{46}H_{39}F_6N_3P_2Ru$: C, 60.66; H, 4.32; N, 4.61. Found: C, 61.04; H, 4.40; N, 4.08%.

**[RuCp(PPh$_3$){P(OMe)$_3$}{=C=C(Ph)CH$_2$CN}]I 8a.** A Schlenk flask was charged with $ICH_2CN$ (0.20 mL, 1.53 mmol), complex **1a** (0.20 g, 0.31 mmol) and 10 mL of $CH_2Cl_2$. The mixture was stirred at room temperature for 10 min. The solvent was reduced to about 3 mL under vacuum and 20 mL of ether were added resulting in an orange precipitation. The mixture was filtered and the solid portion was washed with 20 mL of n-pentane and 20 mL of diethyl ether and dried under vacuum to give **8a** (0.163 g, 64.8% yield). $^1$H NMR ($CDCl_3$): $\delta$ 7.49–7.06 (m, 20 H, Ph), 5.54 (s, Cp), 3.37 (d, 9 H, $J_{H-P}$ = 11.1, P($OMe_3$), 3.27 and 3.17 (dd, $CH_2CN$, $J_{H-H}$ = 17.8 Hz). $^{31}$P NMR ($CDCl_3$): $\delta$ 135.4 and 44.8 (2d, $J_{P-P}$ = 49.30 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 351.7 (q, $C_\alpha$, $^2J_{C-P}$ = 13.9, 20.0), 133.1–126.4 (m, Ph), 118.2 (CN), 116.4 ($C_\beta$), 93.0 (Cp), 54.2 (d, $J_{C-P}$ = 9.6 Hz, P($OMe_3$) and 12.3 ($CH_2$CN); MS (*m*/*z*, $^{102}$Ru): 694.1 ($M^+$ − I), 553.1 ($M^+$ − I-$CH_2$CN-CCPh) and 429.1 ($M^+$ − I-$CH_2$CN-CCPh-P($OMe_3$). Calc. for $C_{36}H_{36}INO_3P_2Ru$: C, 52.69; H, 4.42; N, 1.71. Found: C, 52.89; H, 4.36; N, 1.65%.

**[RuCp(PPh$_3$){P(O)(OMe)$_2$}{=C=C(Ph)CH$_2$CN}] 9a.** A Schlenk flask was charged with $ICH_2CN$ (0.20 mL, 1.53 mmol), complex **1a** (200 mg, 0.31 mmol) and 10 mL of $CH_2Cl_2$. The mixture was heated to reflux for 1 h. The solvent was removed under vacuum and the residue washed with hexane and dried under vacuum to give the red oily product **9a** (186.9 mg, 90% yield). $^1$H NMR ($CDCl_3$): $\delta$ 7.50–6.86 (m, 20H, Ph), 5.32 (s, Cp), 3.45, 3.37 (2d, $J_{H-H}$ = 12.4, $CH_2CN$), 3.31 and 2.95 (2d, 6 H, $J_{H-P}$ = 11.5 Hz, $OCH_3$). $^{31}$P NMR ($CDCl_3$): $\delta$ 95.4 and 48.1 (2d, $J_{P-P}$ = 47.0 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 346.2 (t, $C_\alpha$, $J_{C-P}$ = 16.0), 133.5–119.7 (m, Ph), 117.8 (CN), 116.7 ($C_\beta$), 92.3 (Cp), 50.3 (d, $J_{C-P}$ = 8.4, P($OMe_3$), 49.8 (d, $J_{C-P}$ = 9.4 Hz, P($OMe_3$) and 12.3 ($CH_2$); MS (*m*/*z*, $^{102}$Ru): 680.1 ($M^+$ + 1), 539.1 ($M^+$ − $CH_2$CN-CCPh) and 429.1 ($M^+$ − $CH_2$CN-CCPh − P(O)($OMe_2$). Calc. for $C_{35}H_{33}NO_3P_2Ru$: C, 61.94; H, 4.90; N, 2.06. Found: C, 62.09; H, 4.72; N, 1.68%. The complexes [RuCp(PPh$_3$){P(=O)(OMe)$_2$}{=C=C(Ph)$CH_2$R}] (R = $C_6F_5$ **9b**; Ph **9c**; *p*-$NCC_6H_4CN$ **9d**; *p*-$F_3CC_6H_4$ **9e**; 1-$C_{10}H_7$ **9f** or $CO_2CH_3$ **9g**) were prepared from the reaction of **1a** (0.20 g, 0.31 mmol) with $BrCH_2C_6F_5$, $BrCH_2Ph$, $BrCH_2(C_6H_4CN$-*p*), $BrCH_2(C_6H_4CF_3$-*p*), $BrCH_2$(1-$C_{10}H_7$) or $BrCH_2CO_2CH_3$ using a similar procedure to that for **9a**. Spectroscopic data for **9b**: $^1$H NMR ($CDCl_3$) $\delta$ 7.86–6.82 (m, 20 H, Ph), 5.28 (s, Cp), 3.89, 3.65 (2d, $J_{H-H}$ = 15.6, $CH_2$), 3.16 and 2.99 (2d, 6 H, $J_{H-P}$ = 11.5 Hz, $OCH_3$); $^{31}$P NMR ($CDCl_3$) $\delta$ 97.9 and 50.4 (2d, $J_{P-P}$ = 45.5 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 346.4 (t, $C_\alpha$, $^2J_{C-P}$ = 17.4), 146.3–125.8 (m, Ph), 123.0 ($C_\beta$), 92.1 (Cp), 50.2, 49.7 (2d, $J_{C-P}$ = 7.3 Hz, $OCH_3$) and 17.2 ($CH_2$); MS (*m*/*z*, $^{102}$Ru) 821.1 ($M^+$ + 1), 539.1 ($M^+$-$CH_2C_6F_5$-CCPh) and 429.1 ($M^+$ − $CH_2C_6F_5$-CCPh-P(O)-($OMe_2$). Calc. for $C_{35}H_{33}F_5O_3P_2Ru$: C, 58.61; H, 4.06. Found: C, 58.97; H, 3.92%. Spectroscopic data for **9c**: $^1$H NMR ($CDCl_3$) $\delta$ 7.76–6.89 (m, 20 H, Ph), 5.29 (s, Cp), 3.84, 3.68 (2d, $J_{H-H}$ = 16.2, $CH_2$), 3.30 and 3.06 (2d, 6 H, $J_{H-P}$ = 11.6 Hz, $OCH_3$); $^{31}$P NMR ($CDCl_3$) $\delta$ 97.5 and 51.2 (2d, $J_{P-P}$ = 48.7 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 347.1 (t, $C_\alpha$, $J_{C-P}$ = 16.2, 15.7), 133.5–119.7 (m, Ph), 117.8 (CN), 116.7 ($C_\beta$), 92.3 (Cp), 50.3, 49.8 (2d, $J_{C-P}$ = 8.93 Hz, $OCH_3$) and 12.3 ($CH_2$); MS (*m*/*z*, $^{102}$Ru) 732.1 ($M^+$ + 1), 539.1 ($M^+$ − $CH_2$Ph-CCPh) and 429.1 ($M^+$ − $CH_2$-Ph-CCPh-P(O)($OMe_2$). Calc. for $C_{40}H_{38}O_3P_2Ru$: C, 65.83; H, 5.25. Found: C, 66.01; H, 5.16%. Spectroscopic data for **9d**: $^1$H NMR ($CDCl_3$) $\delta$ 7.77–6.82 (m, Ph), 5.24 (s, Cp), 3.91, 3.68 (2d, $J_{H-H}$ = 16.4, $CH_2$), 3.15 and 2.98 (2d, 6 H, $J_{H-P}$ = 11.2 Hz, $OCH_3$). $^{31}$P NMR ($CDCl_3$) $\delta$ 95.9, 50.8 (2d, $J_{P-P}$ = 47.5 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 349.4 (t, $C_\alpha$, $^2J_{C-P}$ = 16.0), 147.5–118.3 (m, Ph), 117.8 (CN), 116.7 ($C_\beta$), 92.1 (Cp), 50.3, 49.9 (2d, $J_{C-P}$ = 9.0 Hz, $OCH_3$) and 29.8 ($CH_2$); MS (*m*/*z*, $^{102}$Ru) 757.1 ($M^+$ + 1), 539.1 ($M^+$ − $CH_2C_6H_4CN$-CCPh) and 429.1 ($M^+$ − $CH_2C_6H_4CN$-CCPh-P(O)($OMe_2$). Calc. for $C_{41}H_{37}NO_3P_2Ru$: C, 65.24; H,

**Table 5** Crystal data and structure refinement for $[RuCp(PPh_3)\{P(OMe)_3\}\{C[=C(CN)_2]C(Ph)=CH(Ph)\}]$ **3a**, $[RuCp\{P(OMe)_3\}\{\eta^3\text{-}C(CN)_2\text{-}C(Ph)C=CH(Ph)\}]$ **4**, $[RuCp(PPh_3)\{P(O)(OMe)_2\}\{=C=C(Ph)C(Ph)C(CN)_2\}]$ **6** and $[RuCp(PPh_3)\{P(OMe)_3\}(COCH_2Ph)]$ **10**

| | **3a** | **4** | **6** | **10** |
|---|---|---|---|---|
| Formula | $C_{44}H_{40}N_2O_3P_2Ru$ | $C_{26}H_{25}N_2O_3PRu$ | $C_{53}H_{42}N_4O_4P_2Ru$ | $C_{34}H_{36}O_4P_2Ru$ |
| *M* | 807.82 | 546.54 | 961.95 | 935.01 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| *T*/K | 298 | 298 | 298 | 298 |
| *a*/Å | 11.3426(14) | 12.1184(18) | 10.4298(14) | 18.016(3) |
| *b*/Å | 31.489(5) | 14.917(8) | 13.883(3) | 10.071(3) |
| *c*/Å | 11.0026(15) | 13.498(3) | 18.082(4) | 22.979(4) |
| *α*/° | | | 107.468(22) | |
| *β*/° | 104.206(12) | 92.155(14) | 91.791(20) | 105.838(14) |
| *γ*/° | | | 108.375(15) | |
| *V*/Å$^3$ | 3809.6(10) | 2438.2(14) | 2347.2(8) | 4011.1(15) |
| *Z* | 4 | 4 | 2 | 4 |
| *μ*/cm$^{-1}$ | 5.262 | 7.877 | 4.392 | 7.646 |
| Measured reflections | 4954 | 4271 | 8273 | 7034 |
| Observed reflections | 2517 | 2169 | 4526 | 4591 |
| *R*, *R*′ | 0.043, 0.040 | 0.058, 0.052 | 0.044, 0.035 | 0.045, 0.047 |



4.94; N, 1.86. Found: C, 65.53; H, 4.78; N, 1.77%. Spectroscopic data for **9e**: $^1$H NMR ($CDCl_3$) $\delta$ 7.76–6.89 (m, Ph), 5.27 (s, Cp), 3.91, 3.68 (2d, $J_{H-H}$ = 16.3, $CH_2$), 3.25 and 3.01 (2d, 6 H, $J_{H-P}$ = 11.6 Hz, $OCH_3$); $^{31}$P NMR ($CDCl_3$) $\delta$ 96.6, 50.9 (2d, $J_{P-P}$ = 42.8 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 350.2 (t, $C_\alpha$, $^2J_{C-P}$ = 17.1), 145.7–124.9 (m, Ph, $C_\beta$), 92.1 (Cp), 50.4 (d, $J_{C-P}$ = 8.75, $OCH_3$), 49.9 (d, $J_{C-P}$ = 9.21 Hz, $OCH_3$) and 29.4 ($CH_2$); MS (*m*/*z*, $^{102}$Ru) 800.1 ($M^+$ + 1), 539.1 ($M^+ - CH_2C_6H_4CF_3$-CCPh) and 429.1 ($M^+ - CH_2C_6H_4CF_3$-CCPh-P(O)$(OMe)_2$). Calc. for $C_{35}H_{33}F_5O_3P_2Ru$: C, 61.73; H, 4.68. Found: C, 61.98; H, 4.55%. Spectroscopic data for **9f**: $^1$H NMR ($CDCl_3$) $\delta$ 7.75–6.84 (m, Ph), 5.24 (s, Cp), 3.89, 3.71 (2d, $J_{H-H}$ = 16.4, $CH_2$), 3.23 and 2.99 (2d, 6 H, $J_{H-P}$ = 11.5 Hz, $OCH_3$); $^{31}$P NMR ($CDCl_3$) $\delta$ 97.0 and 50.0 (2d, $J_{P-P}$ = 48.4 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 351.0 (t, $C_\alpha$, $^2J_{C-P}$ = 16.4), 138.8–124.3 (m, Ph), 117.1 ($C_\beta$), 92.0 (Cp), 50.2, 49.8 (2d, $J_{C-P}$ = 9.2 Hz, $OCH_3$) and 29.8 ($CH_2$); MS (FAB, $^{102}$Ru) *m*/*z* 782.1 ($M^+$ + 1), 539.1 ($M^+ - CH_2C_{10}H_7$-CCPh) and 429.1 ($M^+ - CH_2C_{10}H_7$-CCPh-P(O)$(OMe)_2$). Calc. for $C_{44}H_{40}O_3P_2Ru$: C, 67.77; H, 5.17. Found: C, 67.95; H, 5.06%. Spectroscopic data for **9g**: $^1$H NMR ($CDCl_3$) $\delta$ 7.84–6.88 (m, 20 H, Ph), 5.22 (s, Cp), 3.89, 3.75 (2d, $J_{H-H}$ = 16.5, $CH_2CO_2CH_3$), 3.17 and 2.90 (2d, 6 H, $J_{H-P}$ = 11.6 Hz, $OCH_3$); $^{31}$P NMR ($CDCl_3$) $\delta$ 96.9 and 50.2 (2d, $J_{P-P}$ = 49.1 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 350.8 (t, $C_\alpha$, $^2J_{C-P}$ = 15.6), 173.1 ($CO_2CH_3$), 135.5–124.8 (m, Ph), 121.0 ($C_\beta$), 92.1 (Cp), 50.0, 49.6 (2d, $J_{C-P}$ = 8.7 Hz, $OCH_3$), 51.5 ($CH_2CO_2CH_3$) and 28.7 ($CO_2CH_3$); MS (*m*/*z*, $^{102}$Ru) 712.1 ($M^+$ + 1), 539.1 ($M^+ - CH_2CO_2CH_3$-CCPh) and 429.1 ($M^+ - CH_2CO_2CH_3$-CCPh-P(O)$(OMe)_2$). Calc. for $C_{36}H_{36}O_5P_2Ru$: C, 60.75; H, 5.10. Found: C, 61.03; H, 5.02%.

**[RuCp(PPh$_3$){P(OMe)$_3$}{COCH$_2$Ph)] 10.** A Schlenk flask was charged with $ICH_2CN$ (0.20 mL, 1.53 mmol), complex **1a** (200 mg, 0.31 mmol), $NH_4PF_6$ (74.8 mg, 0.459 mmol), and 20 mL of $CH_2Cl_2$. The solution was stirred at room temperature for 24 h. Then the solvent was removed under vacuum and the residue washed with 20 × 2 mL of hexane and 20 × 2 mL of ether to give the pale yellow product **10** (168.3 mg, 82% yield). $^1$H NMR ($CD_3COCD_3$): $\delta$ 7.65–6.80 (m, 20 H, Ph), 5.27 (s, Cp), 4.77, 4.68 (dd, $J_{H-H}$ = 17.65, $CH_2$) and 3.53 (d, 9 H, $J_{H-P}$ = 10.87 Hz, $P(OMe)_3$). $^{31}$P NMR ($CD_3COCD_3$): $\delta$ 154.2 and 55.8 (2d, $J_{P-P}$ = 61.1 Hz); MS (*m*/*z*, $^{102}$Ru) 672.1 ($M^+$), 553.1 ($M^+ - COCH_2Ph$) and 429.1 ($M^+ - COCH_2Ph$-P(OMe)$_3$).

### X-Ray analysis of complex 3a

Single crystals of complex **3a** were grown as mentioned above. A single crystal was mounted on an Enraf-Nonius CAD4 diffractometer. Cell constant and other pertinent data are collected in Table 5. The NRCC structure determination package[21] was used for crystallographic computations. Merging of equivalent and duplicate reflections gave a total of 4954 unique data, from which 2517 were considered observed ($I > 2\sigma(I)$). The structure was solved by the heavy atom method then refined *via* standard least-squares and Fourier-difference techniques. The analytical forms of the scattering factor tables for the neutral atoms were used.[23] Final refinement converged smoothly to values of $R = 0.043$ and $R' = 0.040$. The procedures for the structure determination of **4**, **6**, and **10** were similar.

CCDC reference number 186/1698.

See http://www.rsc.org/suppdata/dt/1999/4223/ for crystallographic files in .cif format.

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