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Some reactions of the ruthenium allenylidene complex $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp][PF_6]$ with nucleophiles

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Abstract

Reactions between $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp][PF_6]$ and nucleophilic reagents LiMe, NaOMe, KCN and KC_5H_5 have given the neutral substituted alkynyl–ruthenium complexes $Ru\{C{\equiv}CCPh_2(Nu)\}(PPh_3)_2Cp$. The molecular structures of complexes with Nu = OMe, CN and C_5H_5 have been determined. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Allenylidene; Alkynyl; X-ray structures

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1. Introduction

There is presently an increasing interest in the chemistry of transition metal complexes containing unsaturated carbene ligands [1–3]. While the chemistry of vinylidene complexes has been extensively developed, that of the next member, allenylidene, is only now receiving attention [4,5]. The first examples of these complexes of Group 6 and 7 metals were reported as long ago as 1976 [6,7] and the synthesis of $[Ru({=}C{=}C{=}CPh_2)(PMe_3)_2Cp][PF_6]$ by dehydration of an intermediate hydroxyvinylidene complex obtained from $HC{\equiv}CCR_2(OH)$ was first demonstrated by Selegue in 1982 [8].

The reactivity of the allenylidene ligand has been explored by several groups. Addition of electrophiles to C_β in $Mn({=}C{=}C{=}CR_2)(CO)_2Cp$ affords cationic carbyne complexes, $[Mn({\equiv}CCH = CR_2)(CO)_2Cp]^+$ [9]; similar chemistry is found with neutral ruthenium complexes [10]. In contrast, addition of nucleophiles occurs at either C_α or C_γ. These reactions appear to depend on the steric bulk of the other ligands present on the metal centre, since alcohols add to C_α in $[RuCl(PR_3)(\eta^6\text{-arene})]^+$ [11] or $M(CO)_5$ (M = Cr or W) derivatives [12,13] or at C_γ in $[RuL_2Cp]^+$ [14] and *trans*-$[RuCl(dppm)_2]^+$ complexes [15]. In order to examine some features of these reactions in more detail, we began a study of the reactions of $[Ru({=}C{=}C{=}CPh_2)(PPh_3)_2Cp]^+$ and related complexes. However, while this project was under way, closely related chemistry involving the $[Ru(CO)(PPr^i_3)Cp]^+$ [16] and $Ru(L)(L')(\eta^5\text{-}C_9H_7)$ ($L = L' = PPh_3$; $L = CO$, $L' = PPh_3$, PPr^i_3; LL' = dppm, dppe) systems was reported [17–19]. Our results include structural investigations of some of the products and these are described below.

2. Results and discussion

Theoretical studies have indicated that the highly unsaturated three-carbon allenylidene ligand would show an alternation in electronic character of the carbon atoms, C(1) and C(3) being electron-deficient and therefore subject to nucleophilic attack, and C(2) being electron-rich and attracting electrophilic reagents [20], entirely consistent with the chemistry summarised above. The electron-deficient nature of the C(1) and C(3) carbons in the unsaturated carbene ligand may also be derived from consideration of the simple reso-

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nance structures shown below. Addition of nucleophiles to C(3) would be preferred on steric grounds, bulky ligands (such as PPh_3) serving to protect C(1). Similar results have been found for related vinylidene complexes, but in this case, small nucleophiles (H^- [21], MeOH [22]) are able to react with C(1), while protonation at C(2) to give carbyne complexes has been found for several other vinylidene complexes [23].

$$[M^+]{=}C^1{=}C^2{=}C^3R_2 \leftrightarrows [M]{-}{}^+C^1{=}C^2{=}C^3R_2 \leftrightarrows [M]{-}C^1{\equiv}C^2{-}{}^+C^3R_2$$

We have looked at some reactions of the complex $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp]$ $[PF_6]$ (**1**). This compound was obtained in 80% yield by reaction of $RuCl(PPh_3)_2Cp$ with $HC{\equiv}CCPh_2(OH)$ in MeOH in the presence of NH_4PF_6. The deep red crystalline solid was identified by microanalysis and from its spectra, which closely resembled (where appropriate) those found for $[Ru({=}C{=}C{=}CPh_2)(PMe_3)_2Cp][PF_6]$ [8]. In the IR spectrum, there is a strong ν(CCC) absorption at 1934 cm^{-1}, and the characteristic low-field ^{13}C resonance for C(1) is at δ 293.79, showing a 19 Hz coupling to the two ^{31}P nuclei. Atoms C(2) and C(3) give rise to two singlets at δ 209.44 and 159.60, respectively, while the Cp carbons are at δ 93.55. The FAB mass spectrum contains M^+ at m/z 881, which fragments by loss of PPh_3, Cp and C_3Ph_2 groups.

Given the steric protection of C(1) afforded by the Cp and PPh_3 ligands, it was expected that nucleophilic attack would be directed toward C(3). This was confirmed in the reactions between **1** and several carbon-, oxygen- and nitrogen-based nucleophiles which gave functionalised alkynyl–ruthenium complexes containing the nucleophile attached to C(3). Thus, treatment of **1** with the LiMe, NaOMe and KCN gave the neutral acetylide complexes $Ru(C{\equiv}CCPh_2R)(PPh_3)_2Cp$ [R = Me (**2**), OMe (**3**), CN (**4**)]. Similarly, treatment of **1** with cyclopentadiene in the presence of KO^tBu gave $Ru\{C{\equiv}CCPh_2(C_5H_5)\}(PPh_3)_2Cp$ (**5**):

$$[Ru^+]{=}C{=}C{=}CPh_2 \rightarrow [Ru]{-}C{\equiv}C{-}CPh_2(Nu),$$

where $[Ru] = Ru(PPh_3)_2Cp$

and Nu = Me (**2**), OMe (**3**), CN (**4**), C_5H_5 (**5**).

Complexes **2**–**5** were characterised by microanalysis and from their spectra. In the IR spectra, ν(C≡C) bands are found in the range 2065–2095 $\text{cm}-{}^{1}$. The two acetylenic carbons could be distinguished from one another by the coupling to ^{31}P (J_{CP} ca. 20 Hz) shown by C(1). The chemical shifts of both carbons were between δ 95 and 116. The mass spectra of these complexes, obtained using either FAB or ES techniques, were consistent with the proposed structures, containing M^+ ions which fragmented by loss of the nucleophile (except for **5**), alkynyl and PPh_3 groups; it is notable that the alkynyl–C_5H_5 group is retained by major ions in the spectrum of **5** under ES-MS conditions. Other ions typically associated with the $Ru(PPh_3)_2Cp$ group were also present.

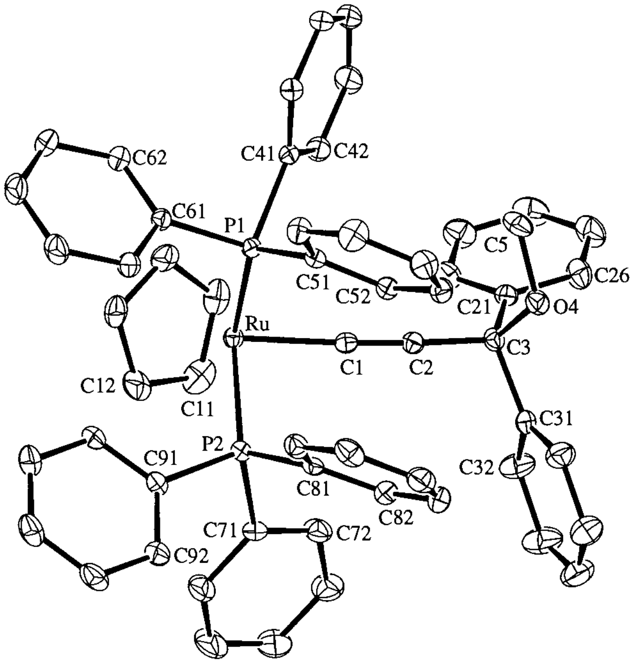


Fig. 1. Molecular structure and crystallographic numbering scheme employed for **3**.

Single crystal X-ray structure determinations was carried out on each of the complexes **3**–**5** (Figs. 1–3, respectively); significant interatomic parameters are collected in Table 1. The structural features of the $Ru(PPh_3)_2Cp$ fragment are unremarkable, with Ru–P

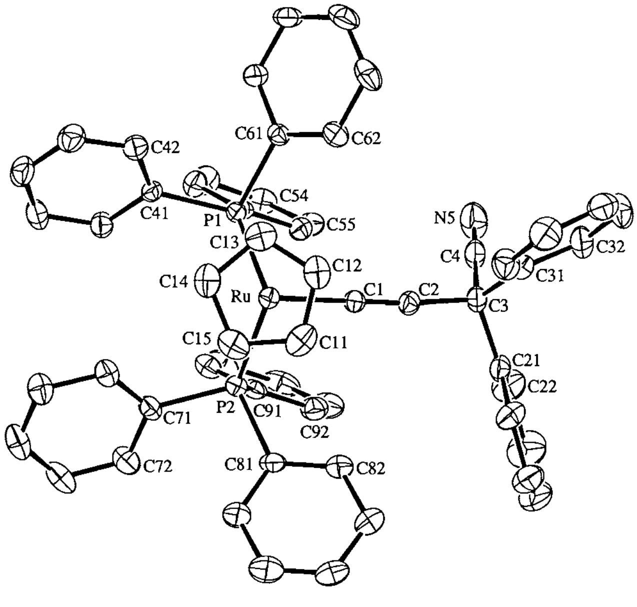


Fig. 2. Molecular structure and crystallographic numbering scheme employed for **4**.

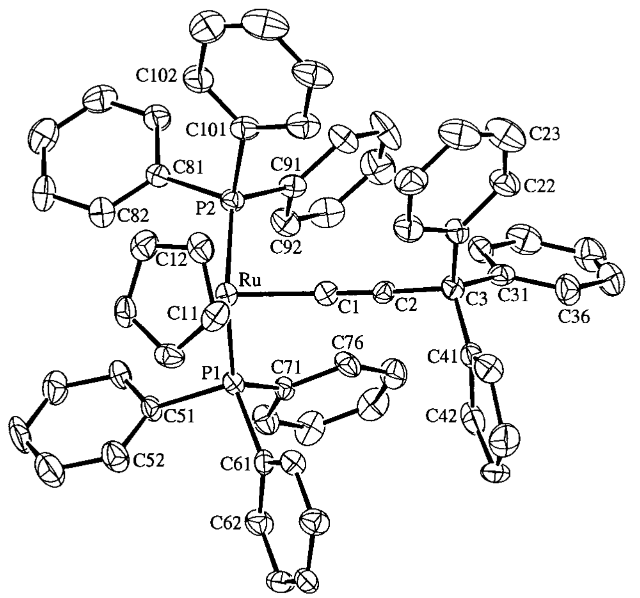


Fig. 3. Molecular structure and crystallographic numbering scheme employed for **5**.

distances between 2.289(2) and 2.308(1) Å, Ru–C(Cp) separations between 2.207(4) and 2.251(4) Å (av. 2.231 Å). For the alkynyl group, Ru–C(1) lies between 2.002(4) and 2.033(8) Å, the C(1)–C(2) triple bond is 1.200(9)–1.204(4) Å and the C(2)–C(3) separations between 1.479(4) and 1.484(9) Å. All these distances are comparable with those previously found in compounds of this type, such as $Ru(C{\equiv}CPh)(L_2)Cp$ [$L_2 = (PPh_3)_2$ [24,25], dppe [25] and a series of more highly substituted arylacetylide complexes recently studied in connection with their non-linear optical properties [26–29]. As expected, angles at Ru are largest for those subtended by the bulky PPh_3 ligands [100.61(5)–104.51(7)°]; the C(1)–Ru–P angles are between 88.7(1) and 90.5(1)°. The phenyl rings of the $C{\equiv}CCPh_2R$ and PPh_3 ligands are disposed in such a way as to minimise any steric interactions. The most significant feature of these structures is the deviation from linearity of the Ru–C(1)–C(2) and C(1)–C(2)–C(3) angles, which lie between 171.2(6) and 177.3(3)°. The largest deviations from linearity are found in **5** (values of 171.1(7) and 174.0(8)°, respectively). This is most likely a result of the increased steric interaction between the C_5H_5 substituent on C(3) and the bulky PPh_3 ligand, such that the C_3 chain is orientated away from the $P(1)Ph_3$ ligand. The substituents show no unusual features, with C(3)–O(4) (in **3**) and C(3)–C(4) (in **4**) distances of 1.448(3) and 1.491(6) Å, respectively. The C(5)–N(5) separation is 1.134(5) Å. For the uncomplexed C_5H_5 ring in **5**, the expected bond length alternation around the ring is found, with C=C double bonds localised between C(41)–C(45) (1.334(9) Å) and C(43)–C(44) (1.42(1) Å). The ring itself is planar to ± 0.007(8) Å, with the mean deviation of atoms C(41)–C(45) from their least-squares plane being 0.005 Å.

These reactions provide an alternative synthesis of ruthenium complexes containing functionalised alkynyl groups which would be difficult to obtain via the more conventional 1-alkyne/vinylidene/alkynyl complex transformations. In principle the reaction can be extended significantly by use of substituents other than Ph (such as CF_3, substituted aryl) on C(3) and as has already been reported by others, replacement of Cp by C_5Me_5 [14] or indenyl [19]. In turn, this should extend the inventory of similar complexes which have been shown to have non-linear optical properties [30].

A labile cationic complex (**6**) was obtained as a lemon yellow solid when **1** was dissolved in neat $NHMe_2$. Subjecting this solid to dynamic vacuum resulted in a slow change in colour to deep red, and **1** was recovered quantitatively. Similarly, solutions of **6** were deep red, and only **1** could be detected spectroscopically. On the basis of the IR spectrum ($\nu(C{\equiv}C)$ 2065, $\nu(PF)$ 843 cm^{-1}), and by comparison with the formation of **2**–**5**, complex **6** is formulated as $[Ru\{C{\equiv}CCPh_2(NHMe_2)\}(PPh_3)_2Cp][PF_6]$:

$$[Ru^+]{=}C{=}C{=}CPh_2 [Ru]{-}C{\equiv}C{-}CR_2(N^+HMe_2)$$

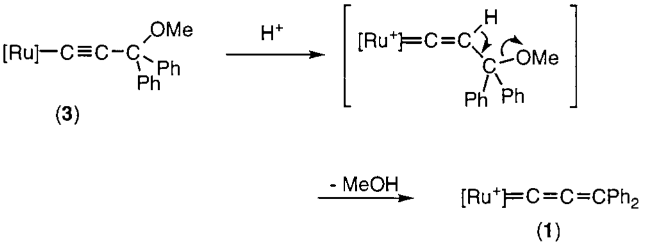
$$[Ru] = Ru(PPh_3)_2Cp$$

Table 1
Selected bond lengths (Å) and angles (°) for complexes **3**–**5**

	3	**4**	**5**
Bond lengths (Å)			
Ru–P(1)	2.294(1)	2.308(1)	2.289(2)
Ru–P(2)	2.276(1)	2.276(1)	2.299(2)
Ru–C(1)	2.013(3)	2.002(4)	2.033(8)
C(1)–C(2)	1.204(4)	1.201(5)	1.200(9)
C(2)–C(3)	1.479(4)	1.482(5)	1.484(9)
C(3)–C(21)	1.542(4)	1.546(5)	1.541(9)
C(3)–C(31)	1.535(5)	1.556(5)	1.55(1)
C(3)–O(4)	1.448(3)		
O(4)–C(5)	1.416(5)		
C(3)–C(4)		1.491(6)	
C(4)–N(5)		1.134(5)	
C(3)–C(41)			1.531(9)
C(41)–C(42)			1.49(1)
C(42)–C(43)			1.51(1)
C(43)–C(44)			1.42(1)
C(44)–C(45)			1.46(1)
C(45)–C(41)			1.334(9)
Bond angles (°)			
P(1)–Ru–P(2)	101.96(3)	100.61(5)	104.51(7)
P(1)–Ru–C(1)	89.09(9)	90.5(1)	90.3(2)
P(2)–Ru–C(1)	88.7(1)	88.8(1)	89.2(2)
Ru–C(1)–C(2)	174.8(3)	173.7(3)	171.2(6)
C(1)–C(2)–C(3)	177.3(3)	175.0(4)	174.0(8)
C(2)–C(3)–C(21)	111.1(3)	109.8(3)	108.8(6)
C(2)–C(3)–C(31)	109.1(3)	111.4(3)	111.5(6)
C(2)–C(3)–O(4)	111.3(3)		
C(2)–C(3)–C(4)		106.8(3)	
C(2)–C(3)–C(41)			108.5(6)
C(3)–C(4)–N(5)		179.0(5)	

As anticipated from earlier studies, addition of the nucleophile to **1** has occurred at C(3), the sterically least encumbered site. Of interest is the addition of cyclopentadienide to give the unusual cyclopentadienyldiphenylmethyl-substituted alkynyl ligand in **5**. In principle, further deprotonation of this group and subsequent reactions with metal substrates could lead to novel heterometallic systems.

Complex **3** reacted rapidly with traces of acid to give **1**. It is highly likely that addition of H^+ occurs at C(2) of **3** and the resulting methoxyvinylidene complex then rapidly eliminates methanol to give **1**, in a reaction which is closely related to the dehydration of the hydroxyvinylidene which affords **1**.



Alternatively, an equilibrium of the type

$$(\mathbf{1}) + MeO^- \rightleftharpoons (\mathbf{3}) + PF6^-$$

may be set up, as proposed for the *trans*-RuCl(dppm)$_2$] system [15].

3. Conclusion

The allenylidene ligand in the complex [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ (**1**) reacts with oxygen-, nitrogen- and carbon-based nucleophiles to give neutral alkynyl derivatives in which the nucleophile has added to the exposed C(3) atom. These reactions allow functionalisation of the C$_3$ ligand and, as shown by others, allow further examples of unusual unstaurated ligands to be made. In the present case, the introduction of the cyclopentadienyl group may allow addition of other metal fragments and the synthesis of novel heterometallic systems.

4. Experimental

4.1. General reaction conditions

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried, distilled and degassed before use. Light petroleum refers to a fraction of b.p. 60–80°C. Elemental analyses were by the Canadian Microanalytical Service, Delta, BC. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF$_{254}$, 0.5 mm thick).

4.2. Instrumental conditions

IR: Perkin Elmer 1700X FT-IR. NMR: Spectra of CDCl$_3$ solutions were recorded on Bruker ACP300 (^{1}H at 300.13 MHz, ^{13}C at 75.47 MHz) or Varian Gemini 200 (^{1}H at 199.98 MHz, ^{13}C at 50.29 MHz) spectrometers. FAB mass spectra: VG ZAB 2HF spectrometer, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV. ES mass spectra: VG Platform II. Solutions in acetonitrile:water (1:1), injected via a 10 µl injection loop. Nitrogen was used as the drying and nebulising gas.

4.3. Reagents

Cyclopentadiene (Fluka) was distilled prior to use. Dimethylamine (Aldrich), KCN (BDH) and KO^{t}Bu (Fluka) were used as received. The compounds RuCl(PPh$_3$)$_2$Cp [31] and HC≡CCPh$_2$(OH) [32] were prepared by literature methods.

4.4. Preparation of [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp][PF$_6$] (1)

A mixture of RuCl(PPh$_3$)$_2$Cp (1.0 g, 1.38 mmol), HC≡CCPh$_2$OH (300 mg, 1.4 mmol) and NH$_4$PF$_6$ (225 mg, 1.38 mmol) was stirred in MeOH (100 ml) overnight. The resulting deep red solution was filtered and the solvent removed. The deep red residue was extracted with the minimum volume of CH$_2$Cl$_2$ and filtered into an excess of rapidly stirred Et$_2$O. The precipitate was collected, washed with a small volume of cold Et$_2$O, and dried. The filtrate was evaporated and worked up as before to give a second crop of [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp][PF$_6$] (**1**) (total yield 1.14 g, 80%). Anal. Found: C 65.34, H 4.30. C$_{56}$H$_{45}$P$_3$F$_6$Ru calc.: C 65.50, H 4.39%. IR (CH$_2$Cl$_2$): ν(C=C=C) 1934s, ν(PF) 840m cm^{-1}. ^{1}H-NMR: δ 7.75–7.05 (40H, m, Ph), 5.12 (5H, s, Cp). ^{13}C-NMR: δ 293.79 [t, $J_{CP} = 19$ Hz, C(1)], 209.44 [s, C(2)], 159.60 [s, C(3)], 143.50–128.32 (m, Ph), 93.55 (s, Cp). ^{31}P-NMR: δ 43.82 (s, PPh$_3$). FAB MS (*m*/*z*): 881 [M]$^+$, 619 [M − PPh$_3$]$^+$, 553 [M − PPh$_{3-}$Cp]$^+$, 429 [Ru(PPh$_3$)(C$_5$H$_5$)]$^+$.

4.5. Reactions of Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp][PF$_6$](1)

4.5.1. With LiMe · LiBr

A solution of [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp][PF$_6$] (150 mg, 0.19 mmol) in THF (15 ml) was treated with MeLi · LiBr (one drop of a 1.5 M solution in Et$_2$O) and was then stirred for 15 min. During this time the solution changed colour from red to green brown. The solvent was removed, the residue extracted with CH$_2$Cl$_2$

Table 2
Crystallographic data for complexes **3**–**5**

Compound	**3**	**4**	**5**
Formula	$C_{57}H_{48}OP_2Ru$	$C_{57}H_{45}NP_2Ru$	$C_{61}H_{50}P_2Ru$
Formula weight	912.0	907.0	946.1
Crystal system	Triclinic	Triclinic	Triclinic
Space group	P	P	P
a (Å)	11.765(7)	11.601(6)	13.896(3)
b (Å)	19.73(1)	19.166(8)	14.820(4)
c (Å)	10.93(1)	11.255(8)	12.172(3)
α (°)	94.01(6)	94.97(5)	91.33(3)
β (°)	117.37(5)	117.43(4)	110.21(1)
γ (°)	86.84(5)	85.94(4)	89.54(2)
V (Å^3)	2246(2)	2211(2)	2352(1)
Z	2	2	2
Crystal size (mm^3)	$0.11\times0.24\times0.24$	$0.11\times0.18\times0.29$	$0.08\times0.11\times0.24$
$D_{\text{calc.}}$ (g cm^{-3})	1.348	1.362	1.336
$F(000)$	944	936	980
No. of data collected	8344	8736	6463
$2\theta_{\max}$ (°)	50.0	55.0	45.0
No. of unique data	7925	8239	6160
No. of reflections with $I\geq3.0\sigma(I)$	6078	5672	3291
R	0.034	0.038	0.045
R_w	0.036	0.038	0.039
Residual $\rho_{\max}$ (e Å^{-3})	0.51	0.45	0.35

and the extracts filtered through a pad of Celite. The yellow solution was diluted with MeOH and concentrated to give a pale yellow powder, which was crystallised (CH_2Cl_2/MeOH) to give $Ru(C{\equiv}CCMePh_2)(PPh_3)_2Cp$ (**2**) (yield: 70 mg, 54%). Anal. Found: C 76.39, H 5.36. $C_{57}H_{49}P_2Ru$ calc.: C 76.33, H 5.47%. IR (nujol): $\nu(C{\equiv}C)$ 2090m cm^{-1}. ^{1}H-NMR: δ 7.63–6.98 (40H, m, Ph), 4.29 (5H, s, Cp), 1.89 (3H, s, Me). ^{13}C-NMR: δ 139.41–125.05 (m, Ph), 95.50 [t, $J_{CP}=23.4$Hz, C(1)], 93.51 [s, C(2)], 85.02 (s, Cp), 47.16 [s, C(3)], 31.73 (s, Me). FAB MS (m/z): 896 M$^+$, 881 [M − Me]$^+$, 691 $[Ru(PPh_3)_2(C_5H_5)]^+$, 633 $[M-PPh_3]^+$, 619 $[M-Me{-}PPh_3]^+$, 429 $[Ru(PPh_3)(C_5H_5)]^+$.

4.5.2. With NaOMe

Addition of NaOMe (1 M in methanol) to $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp][PF_6]$ (150 mg, 0.15 mmol) in MeOH (10 ml) resulted in a rapid colour change from deep red to yellow. After 5 min, the precipitate was filtered and recrystallised (CH_2Cl_2/MeOH) to yield yellow crystals of $Ru\{C{\equiv}CCPh_2(OMe)\}(PPh_3)_2Cp$ (**3**) (yield: 120 mg, 88%). Anal. Found: C 74.98, H 5.22. $C_{57}H_{48}OP_2Ru$ calc.: C 75.08, H 5.27%. IR (nujol): $\nu(C{\equiv}C)$ 2070m cm^{-1}. ^{1}H-NMR: δ 7.62–7.01 (40H, m, Ph), 4.35 (5H, s, Cp), 3.34 (3H, s, OMe). ^{13}C-NMR: δ 147.27–126.87 (m, Ph), 110.51 [s, C(2)], 107.52 [t, $J_{CP}=24$ Hz, C(1)], 85.25 (s, Cp), 82.36 [s, C(3)], 51.51 (s, OMe). ES MS (m/z): 912 M$^+$, 881 [M − OMe]$^+$, 732 $[M+NCMe-C_2C(OMe)Ph_2]^+$.

4.5.3. With KCN

A solution of $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp][PF_6]$ (150 mg, 0.146 mmol) in dry THF (15 ml), was treated with KCN (10 mg, 0.15 mmol) and heated at reflux point for 12 h. The solution changed colour from deep red to yellow. The solvent was removed and the yellow residue was extracted with CH_2Cl_2 (2×5 ml). The filtered extracts were diluted with MeOH (5 ml) and concentrated to ca. 5 ml. The precipitate was washed with MeOH, dried and recrystallised (CH_2Cl_2/MeOH) to give $Ru\{C{\equiv}CC(CN)Ph_2\}(PPh_3)_2Cp$ (**4**) (yield: 108 mg, 81%). Anal. Found: C 71.79, H 4.73. $C_{57}H_{45}NP_2Ru$ calc.: C 75.50, H 4.97%. IR (nujol): $\nu(C{\equiv}C)$ 2083s cm^{-1}. ^{1}H-NMR: δ 7.64–7.04 (40H, m, Ph), 4.34, (5H, s, Cp). ^{13}C-NMR: δ 142.82–127.09 (m, Ph), 121.63 (s, CN), 110.66 [t, $J_{CP}=23.93$ Hz, C(1)], 103.25 [s, C(2)], 85.25 (s, Cp), 50.83 [s, C(3)]. FAB MS (m/z): 907 M$^+$, 691 $[Ru(PPh_3)_2(C_5H_5)]^+$, 644 $[M-PPh_3]^+$, 455 $[Ru(CN)(PPh_3)Cp]^+$, 429 $[Ru(PPh_3)(C_5H_5)]^+$.

4.5.4. With cyclopentadiene in the presence of KOBu^t

To a solution of $[Ru(C{=}C{=}CPh_2)(PPh_3)_2Cp][PF_6]$ (200 mg, 0.19 mmol) in THF (15 ml), cyclopentadiene (250 mg, 3.8 mmol) and KOBu^t (50 mg, 0.45 mmol) were added. The solution immediately turned green–yellow. Solvent was removed and the residue purified by column chromatography on Al_2O_3. Elution with 4:1 light petroleum:acetone gave a bright yellow band, which yielded $Ru\{C{\equiv}CCPh_2(C_5H_5)\}(PPh_3)_2Cp$ (**5**) (130 mg, 70%) after crystallisation (CH_2Cl_2/MeOH). Anal. Found: C 77.17, H 5.75. $C_{61}H_{50}P_2Ru$ calc.: C 77.46, H

Table 3
Fractional atomic coordinates for complexes **3**–**5**

Atom	*x*	*y*	*z*
Complex **3**			
Ru	−0.16441(2)	0.21911(1)	0.49724(3)
P(1)	−0.35939(7)	0.17393(4)	0.35123(8)
P(2)	−0.20862(8)	0.33273(4)	0.47601(8)
O(4)	−0.1616(2)	0.1938(1)	0.0023(2)
C(1)	−0.1237(3)	0.2187(2)	0.3373(3)
C(2)	−0.0923(3)	0.2145(2)	0.2466(3)
C(3)	−0.0526(3)	0.2057(2)	0.1361(3)
C(5)	−0.2279(4)	0.1336(2)	−0.0125(4)
C(11)	0.0337(4)	0.2151(3)	0.6649(5)
C(12)	−0.0468(4)	0.2374(2)	0.7235(4)
C(13)	−0.1299(4)	0.1846(2)	0.7033(4)
C(14)	−0.1007(4)	0.1305(2)	0.6327(4)
C(15)	0.0003(4)	0.1486(2)	0.6082(4)
C(21)	0.0448(3)	0.1460(2)	0.1627(3)
C(22)	0.1013(4)	0.1150(2)	0.2856(4)
C(23)	0.1860(4)	0.0597(2)	0.3064(5)
C(24)	0.2128(4)	0.0359(2)	0.2021(5)
C(25)	0.1585(4)	0.0667(2)	0.0794(5)
C(26)	0.0755(4)	0.1221(2)	0.0587(4)
C(31)	0.0022(3)	0.2726(2)	0.1250(3)
C(32)	0.1271(4)	0.2883(2)	0.2123(5)
C(33)	0.1751(4)	0.3494(3)	0.2073(6)
C(34)	0.0992(6)	0.3956(2)	0.1148(6)
C(35)	−0.0252(6)	0.3808(2)	0.0272(5)
C(36)	−0.0739(4)	0.3192(2)	0.0326(4)
C(41)	−0.3477(3)	0.0862(2)	0.2845(3)
C(42)	−0.2314(4)	0.0590(2)	0.2989(4)
C(43)	−0.2230(5)	−0.0061(2)	0.2452(5)
C(44)	−0.3302(6)	−0.0439(2)	0.1781(5)
C(45)	−0.4465(5)	−0.0179(2)	0.1606(4)
C(46)	−0.4559(4)	0.0471(2)	0.2133(4)
C(51)	−0.4758(3)	0.2081(2)	0.1867(3)
C(52)	−0.4286(3)	0.2287(2)	0.0997(3)
C(53)	−0.5109(3)	0.2484(2)	−0.0318(3)
C(54)	−0.6411(4)	0.2496(2)	−0.0774(4)
C(55)	−0.6891(3)	0.2296(2)	0.0067(4)
C(56)	−0.6078(3)	0.2081(2)	0.1376(4)
C(61)	−0.4541(3)	0.1635(2)	0.4430(3)
C(62)	−0.4462(3)	0.1043(2)	0.5079(4)
C(63)	−0.5059(4)	0.0995(2)	0.5905(4)
C(64)	−0.5743(4)	0.1549(3)	0.6086(4)
C(65)	−0.5840(4)	0.2138(2)	0.5463(4)
C(66)	−0.5241(3)	0.2187(2)	0.4637(4)
C(71)	−0.0560(3)	0.3776(2)	0.5465(4)
C(72)	0.0275(4)	0.3628(2)	0.4897(4)
C(73)	0.1460(4)	0.3928(2)	0.5451(5)
C(74)	0.1844(4)	0.4363(3)	0.6598(5)
C(75)	0.1049(5)	0.4499(3)	0.7194(5)
C(76)	−0.0139(4)	0.4213(2)	0.6632(4)
C(81)	−0.3086(3)	0.3685(2)	0.3072(3)
C(82)	−0.2600(4)	0.3856(2)	0.2195(4)
C(83)	−0.3412(5)	0.4095(2)	0.0912(4)
C(84)	−0.4712(5)	0.4159(2)	0.0477(4)
C(85)	−0.5206(4)	0.3983(2)	0.1326(4)
C(86)	−0.4396(3)	0.3750(2)	0.2614(4)
C(91)	−0.2857(3)	0.3757(2)	0.5753(3)
C(92)	−0.3110(4)	0.4461(2)	0.5703(4)
C(93)	−0.3710(4)	0.4778(2)	0.6436(4)
C(94)	−0.4086(4)	0.4398(2)	0.7181(4)
C(95)	−0.3855(4)	0.3708(2)	0.7234(4)
C(96)	−0.3239(3)	0.3391(2)	0.6511(4)
Complex **4**			
Ru	0.16649(3)	−0.20810(2)	−0.47418(3)
P(1)	0.37064(9)	−0.16753(5)	−0.33204(9)
P(2)	0.20868(10)	−0.32592(5)	−0.46848(10)
N(5)	0.2669(4)	−0.1779(3)	0.1010(4)
C(1)	0.1279(3)	−0.2120(2)	−0.3189(4)
C(2)	0.0941(3)	−0.2106(2)	−0.2326(4)
C(3)	0.0551(4)	−0.2023(2)	−0.1238(4)
C(4)	0.1753(4)	−0.1879(2)	0.0036(4)
C(11)	−0.0370(4)	−0.1953(3)	−0.6320(5)
C(12)	0.0044(4)	−0.1292(3)	−0.5678(4)
C(13)	0.1054(4)	−0.1110(2)	−0.5893(4)
C(14)	0.1298(4)	−0.1660(3)	−0.6696(4)
C(15)	0.0411(5)	−0.2173(2)	−0.6940(4)
C(21)	−0.0035(4)	−0.2708(2)	−0.1163(4)
C(22)	0.0589(5)	−0.3145(3)	−0.0142(5)
C(23)	0.0051(7)	−0.3772(3)	−0.0151(7)
C(24)	−0.1101(7)	−0.3961(3)	−0.1192(7)
C(25)	−0.1741(5)	−0.3526(3)	−0.2202(6)
C(26)	−0.1218(4)	−0.2901(2)	−0.2200(5)
C(31)	−0.0401(4)	−0.1380(2)	−0.1423(4)
C(32)	−0.0604(4)	−0.1091(3)	−0.0374(5)
C(33)	−0.1401(5)	−0.0493(3)	−0.0536(6)
C(34)	−0.2024(5)	−0.0200(3)	−0.1742(7)
C(35)	−0.1875(5)	−0.0501(3)	−0.2807(6)
C(36)	−0.1062(5)	−0.1091(3)	−0.2645(5)
C(41)	0.4635(3)	−0.1611(2)	−0.4250(3)
C(42)	0.4529(4)	−0.1010(2)	−0.4911(4)
C(43)	0.5089(5)	−0.0994(3)	−0.5760(5)
C(44)	0.5779(5)	−0.1565(3)	−0.5941(5)
C(45)	0.5902(4)	−0.2162(3)	−0.5292(4)
C(46)	0.5323(4)	−0.2187(2)	−0.4462(4)
C(51)	0.4879(3)	−0.2057(2)	−0.1747(4)
C(52)	0.6214(4)	−0.2118(2)	−0.1323(4)
C(53)	0.7047(4)	−0.2373(2)	−0.0082(4)
C(54)	0.6570(4)	−0.2551(2)	0.0752(4)
C(55)	0.5259(4)	−0.2464(2)	0.0370(4)
C(56)	0.4421(3)	−0.2223(2)	−0.0871(4)
C(61)	0.3672(4)	−0.0768(2)	−0.2639(4)
C(62)	0.2540(4)	−0.0463(2)	−0.2676(4)
C(63)	0.2530(5)	0.0221(2)	−0.2137(5)
C(64)	0.3647(6)	0.0591(2)	−0.1540(5)
C(65)	0.4789(5)	0.0285(2)	−0.1466(4)
C(66)	0.4801(4)	−0.0391(2)	−0.2009(4)
C(71)	0.2882(4)	−0.3674(2)	−0.5666(4)
C(72)	0.3200(5)	−0.4391(2)	−0.5647(4)
C(73)	0.3763(5)	−0.4698(3)	−0.6430(5)
C(74)	0.4048(5)	−0.4296(3)	−0.7200(5)
C(75)	0.3763(5)	−0.3583(3)	−0.7218(5)
C(76)	0.3174(4)	−0.3281(2)	−0.6449(4)
C(81)	0.0530(4)	−0.3723(2)	−0.5457(4)
C(82)	−0.0367(4)	−0.3566(2)	−0.4970(5)
C(83)	−0.1554(5)	−0.3880(3)	−0.5536(6)
C(84)	−0.1886(5)	−0.4350(3)	−0.6624(6)
C(85)	−0.1025(6)	−0.4500(3)	−0.7132(6)
C(86)	0.0171(5)	−0.4194(3)	−0.6558(5)
C(91)	0.3050(4)	−0.3654(2)	−0.3073(4)
C(92)	0.2524(4)	−0.3799(2)	−0.2237(4)
C(93)	0.3300(6)	−0.4047(2)	−0.0990(5)
C(94)	0.4610(6)	−0.4154(2)	−0.0545(5)
C(95)	0.5157(4)	−0.4012(2)	−0.1341(5)
C(96)	0.4388(4)	−0.3761(2)	−0.2601(4)

Table 3 (continued)

Atom	*x*	*y*	*z*
Complex **5**			
Ru	0.16203(5)	−0.19478(4)	0.16296(6)
P(1)	0.3344(2)	−0.1767(1)	0.2040(2)
P(2)	0.1314(2)	−0.1288(1)	0.3204(2)
C(1)	0.1882(5)	−0.3141(5)	0.2476(6)
C(2)	0.1935(5)	−0.3890(5)	0.2845(6)
C(3)	0.1889(6)	−0.4832(5)	0.3213(6)
C(11)	0.0694(7)	−0.2640(5)	−0.0051(6)
C(12)	0.0032(6)	−0.2198(6)	0.0434(7)
C(13)	0.0230(7)	−0.1258(6)	0.0463(7)
C(14)	0.1003(7)	−0.1132(5)	−0.0004(7)
C(15)	0.1303(6)	−0.1991(6)	−0.0314(6)
C(21)	0.0758(6)	−0.5088(5)	0.2955(7)
C(22)	0.0393(7)	−0.5513(6)	0.3722(7)
C(23)	−0.0619(9)	−0.5726(7)	0.3427(10)
C(24)	−0.1277(8)	−0.5531(8)	0.237(1)
C(25)	−0.0971(7)	−0.5120(6)	0.1565(9)
C(26)	0.0038(7)	−0.4874(6)	0.1862(8)
C(31)	0.2522(6)	−0.4948(5)	0.4523(7)
C(32)	0.2789(6)	−0.4221(5)	0.5288(7)
C(33)	0.3377(7)	−0.4325(7)	0.6454(8)
C(34)	0.3706(8)	−0.5168(8)	0.6884(8)
C(35)	0.3443(7)	−0.5883(7)	0.6141(8)
C(36)	0.2866(7)	−0.5787(5)	0.4985(8)
C(41)	0.2346(6)	−0.5456(5)	0.2501(6)
C(42)	0.3435(7)	−0.5378(6)	0.2584(7)
C(43)	0.3603(8)	−0.6118(8)	0.1799(9)
C(44)	0.2646(9)	−0.6567(6)	0.1294(8)
C(45)	0.1911(6)	−0.6130(5)	0.1753(7)
C(51)	0.3599(6)	−0.0712(5)	0.1439(6)
C(52)	0.3624(7)	−0.0679(6)	0.0303(7)
C(53)	0.3690(8)	0.0142(7)	−0.0207(8)
C(54)	0.3732(8)	0.0927(6)	0.0426(9)
C(55)	0.3705(7)	0.0904(6)	0.1534(8)
C(56)	0.3649(6)	0.0099(5)	0.2052(6)
C(61)	0.3911(6)	−0.2605(5)	0.1277(6)
C(62)	0.4885(7)	−0.2484(5)	0.1247(7)
C(63)	0.5308(7)	−0.3090(6)	0.0667(7)
C(64)	0.4749(8)	−0.3823(5)	0.0100(7)
C(65)	0.3792(7)	−0.3987(5)	0.0136(7)
C(66)	0.3376(6)	−0.3373(5)	0.0727(6)
C(71)	0.4362(6)	−0.1832(5)	0.3480(6)
C(72)	0.5239(7)	−0.1294(5)	0.3858(7)
C(73)	0.6020(6)	−0.1460(6)	0.4896(8)
C(74)	0.5930(7)	−0.2151(6)	0.5584(7)
C(75)	0.5086(7)	−0.2697(6)	0.5238(7)
C(76)	0.4288(6)	−0.2516(5)	0.4190(7)
C(81)	0.1250(6)	−0.0047(5)	0.3275(7)
C(82)	0.1395(6)	0.0462(5)	0.2424(6)
C(83)	0.1324(6)	0.1407(5)	0.2446(7)
C(84)	0.1088(7)	0.1836(6)	0.3324(9)
C(85)	0.0956(7)	0.1338(7)	0.4195(8)
C(86)	0.1035(7)	0.0405(6)	0.4185(7)
C(91)	0.2059(6)	−0.1471(5)	0.4745(6)
C(92)	0.3021(7)	−0.1086(5)	0.5194(7)
C(93)	0.3619(7)	−0.1152(6)	0.6355(9)
C(94)	0.3264(9)	−0.1637(7)	0.7094(8)
C(95)	0.2330(9)	−0.2010(7)	0.6694(8)
C(96)	0.1709(7)	−0.1936(6)	0.5521(8)
C(101)	0.0010(6)	−0.1618(6)	0.3093(6)
C(102)	−0.0796(7)	−0.1020(6)	0.2854(8)
C(103)	−0.1784(8)	−0.1292(9)	0.2720(10)
C(104)	−0.1967(8)	−0.2193(10)	0.2817(10)
C(105)	−0.1183(9)	−0.2821(7)	0.3016(9)
C(106)	−0.0204(7)	−0.2542(6)	0.3161(7)

5.29%. IR (nujol): ν(C≡C) 2095m, ν(C=C) 1652br cm^{-1}. ^{1}H-NMR: δ 7.48–6.98 (40H, m, Ph), 6.41, 6.27 (both 2H, both dd, $^{3}J_{HH} = 5$ Hz, $^{4}J_{HH} = 1$ Hz, CH=CH), 5.87 (1H, s, CH), 4.35 (5H, s, Cp). ^{13}C-NMR: δ 157.41, 154.31, 148.93, 148.14, 136.6 (5 × s, C_5H_5), 148.93–125.2 (m, Ph), 115.47 [s, C(2)], 96.13 [t, $J_{CP} = 24.04$Hz, C(1)], 85.11 (s, Cp), 43.01 [s, C(3)]. ES MS (*m*/*z*): 946 [M + H]$^+$, (with NaOMe) 968 [M + Na]$^+$.

4.5.5. *With $NHMe_2$*

Neat $NHMe_2$ (ca. 2 ml) was condensed into a schlenk flask containing [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp][PF$_6$] (100 mg, 0.097 mmol). The solid rapidly turned yellow and dissolved to give a bright yellow solution. Excess amine was allowed to evaporate to give a lemon yellow solid that resulted was tentatively identified as [Ru{C≡C–CPh$_2$(NHMe$_2$)}(PPh$_3$)$_2$Cp][PF$_6$] (**6**) (yield: 98 mg, 94%). Further attempts to dry the powder in vacuo resulted in a gradual colour change of the solid from yellow to deep red, and [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ was recovered quantitatively. Similarly, when the solid was dissolved in a range of solvents (acetone, $CDCl_3$, CH_2Cl_2, THF, MeOH), a red solution was obtained, from which only [Ru(C=C=CPh$_2$)(PPh$_3$)$_2$Cp]PF$_6$ could be isolated in high yield. Reproducible analyses could not be obtained. Anal. Found: C 62.30, H 5.44, N 3.60. $C_{58}H_{52}NP_3F_6Ru$ calc.: C 64.98, H 4.86, N 1.31%. IR (nujol): ν(C≡C) 2065m, ν(PF) 843s(br) cm^{-1}.

4.6. *Crystallography*

Intensity data for yellow crystals of **3**–**5** were collected at room temperature on a Rigaku AFC6R diffractometer employing Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) and the ω:2θ scan technique. The data sets were corrected for Lorentz and polarisation effects [33] as well as for absorption employing an empirical procedure [34]. Data that satisfied the $I \geq 3.0\sigma(I)$ criterion of observability were used in the subsequent analysis. Crystal data and refinement details are given in Table 2.

The structures were each solved by direct methods (**3** and **5** [35], **4** [36]) and refined by a full-matrix least-squares procedure based on *F* [33]. All non-H atoms were refined with anisotropic displacement parameters and H atoms were included in the models at their calculated positions (C–H 0.97 Å). The refinements were continued until convergence employing σ weights, i.e. $1/\sigma^2(F)$. Fractional atomic coordinates are listed in Table 3, selected interatomic parameters are collected in Table 1 and the crystallographic numbering schemes employed are shown in Figs. 1–3 which were drawn with ORTEP [37].

5. Supplementary material available

A copy of the CIF and the observed and calculated structure factors for each structure are available from E.R.T. Tiekink (etiekink@chemistry. adelaide.edu.au).

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