Dalton Transactions

PAPER

Cite this: *Dalton Trans.*, 2015, **44**, 9289

Preparation and reactivity of diazoalkane complexes of ruthenium stabilised by an indenyl ligand†

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Diazoalkane complexes [Ru(η^5-C_9H_7)(N_2CAr1Ar2)(PPh_3)L]BPh_4 (**1–3**) [L = PPh_3, $P(OMe)_3$, $P(OEt)_3$; Ar1 = Ar2 = Ph; Ar1 = Ph, Ar2 = *p*-tolyl; Ar1Ar2 = $C_{12}H_8$ fluorenyl] were prepared by allowing chloro-complexes [RuCl(η^5-C_9H_7)(PPh_3)L] to react with an excess of diazoalkane in ethanol. Complexes **1–3** reacted with ethylene CH_2=CH_2 (1 atm) and maleic anhydride [ma, CH=CHCO(O)CO] to afford η^2-alkene complexes [Ru(η^5-C_9H_7)(η^2-CH_2=CH_2)(PPh_3)L]BPh_4 (**4**, **5**) and [Ru(η^5-C_9H_7){η^2-CH=CHCO(O)CO}(PPh_3)L]BPh_4 (**7**). Further, complexes **1–3** underwent cycloaddition with acrylonitrile CH_2=C(H)CN, giving 1*H*-pyrazoline derivatives [Ru(η^5-C_9H_7){η^1-N=C(CN)CH_2C(Ar1Ar2)NH}(PPh_3)L]BPh_4 (**6**). Treatment of diazoalkane complexes **1–3** with acetylene CH≡CH under mild conditions (1 atm, room temperature) led to dipolar cycloaddition, affording 3*H*-pyrazole complexes [Ru(η^5-C_9H_7)-{η^1-N=NC(Ar1Ar2)CH=CH}(PPh_3)L]BPh_4 (**8**), whereas reaction with terminal alkynes RC≡CH (R = Ph, *p*-tolyl, Bu^t) gave vinylidene derivatives [Ru(η^5-C_9H_7){=C=C(H)R}(PPh_3)L]BPh_4 (**9**). The latter reacted with nucleophiles such as amines and alcohols to give amino- and alkoxy-carbene derivatives [Ru(η^5-C_9H_7){=C($NHPr^n$)(CH_2Ph)}(PPh_3)L]BPh_4 (**11**) and [Ru(η^5-C_9H_7){=C(CH_3)(OEt)}(PPh_3)L]BPh_4 (**10**), respectively. In addition, complexes **9** reacted with phenylhydrazine to afford nitrile derivatives [Ru(η^5-C_9H_7)(N≡CCH_2R)(PPh_3)L]BPh_4 (**12**) and phenylamine, whereas the reaction with water led to hydrolysis of the alkyne and formation of carbonyl complexes [Ru(η^5-C_9H_7)(CO)(PPh_3)L]BPh_4 (**13**). Lastly, treatment of vinylidene complexes **9** with the phosphines PPh_3 and $P(OMe)_3$ afforded alkenylphosphonium derivatives [Ru(η^5-C_9H_7){C(H)=C(R)PPh_3}(PPh_3)L]BPh_4 (**14**) and [Ru(η^5-C_9H_7){C(R)=C(H)P$(OMe)_3$}(PPh_3)L]BPh_4 (**15**), respectively. Compound [Ru(η^5-C_9H_7){C(H)=C(H)PPh_3}(PPh_3)L]BPh_4 (**16**) was also prepared. The complexes were characterised by spectroscopy (IR and NMR) and X-ray crystal structure determinations of [Ru(η^5-C_9H_7){N_2C($C_{12}H_8$)}(PPh_3){$P(OEt)_3$}]BPh_4 (**3c**), [Ru(η^5-C_9H_7){=C=C(H)Ph}(PPh_3){$P(OEt)_3$}]BPh_4 (**9d**) and [Ru(η^5-C_9H_7){C(H)=C(Ph)PPh_3}(PPh_3){$P(OEt)_3$}]-BPh_4 (**14d**).

Received 20th February 2015,
Accepted 10th April 2015

DOI: 10.1039/c5dt00755k

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Introduction

The interaction of diazoalkanes Ar1Ar2CN_2 with transition metal complexes has been extensively studied,[1–3] due to their usefulness in the synthesis of carbene derivatives,[2,3] which are active in the catalytic cyclopropanation of alkene[4] and olefin metathesis.[5] The diazoalkane can also sometimes coordinate to the metal centre, yielding the corresponding [M]–N_2CR1R2 complexes,[6–9] which may be of interest due to the different coordination modes shown by the azo ligand[1] and as a model for understanding N_2 coordination and functionalisation.[10,11] However, little attention has been devoted to the reactivity of coordinate diazoalkane, which, according to its coordination mode, may react along different pathways. Although the η^2-C,N coordination leads to N_2 extrusion and metal carbene formation,[2,3,8f] σ-bound diazoalkanes can undergo cycloaddition with alkenes and alkynes.[13] In addition, σ-diazoalkane derivatives have been suggested to transfer carbenes to imines[2f] and are thus relevant to imine aziridination. Cleavage of the N–N bond[2c] of diazoalkane on a metal centre was also observed, together with the reduction of the coordinated N_2CAr1Ar2 ligand.[8i]

Our ongoing interest in the chemistry of diazoalkane complexes[9,12,13] led us to the synthesis of compounds with the cyclopentadienyl ligand, [Ru(η^5-C_5H_5)(N_2CAr1Ar2)(PPh_3)L]BPh_4, which undergo unprecedented (3 + 2) cycloaddition of coordinated N_2CAr1Ar2 to alkenes and alkynes, affording 3*H*-

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†CCDC 1050294–1050296. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt00755k

pyrazole derivatives.[13] These results prompted us to extend our studies to the half-sandwich indenyl fragment $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)L]^+$,[14] to test whether related diazoalkane complexes could be formed and how their properties change. The results of these studies are reported here.

Results and discussion

Preparation of diazoalkane complexes

Indenyl complexes $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)L]$ [L = PPh_3, $P(OMe)_3$, $P(OEt)_3$] react with an excess of $Ar1Ar2CN_2$ in the presence of $NaBPh_4$ to give diazoalkane derivatives $[Ru(\eta^5\text{-}C_9H_7)(N_2CAr1Ar2)(PPh_3)L]BPh_4$ (**1–3**), which were isolated in good yields and characterised (Scheme 1).

The reaction proceeds with substitution of the Cl^- ligand by $Ar1Ar2CN_2$, affording the final diazo complexes **1–3**. Important for the synthesis is the presence of the $NaBPh_4$ salt which, favouring the substitution of Cl^-, allows the complex to separate out as a red or orange solid. Both bis(triphenylphosphine) $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)_2]^+$ and mixed-ligand $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)L]^+$ fragments (L = phosphite) can stabilise diazoalkane derivatives, which were separated as orange solids stable in air and solutions of polar organic solvents, in which they behave as 1 : 1 electrolytes.[15] Their characterisation is supported by analytical and spectroscopic (IR, NMR) data and by X-ray crystal structure determination of $[Ru(\eta^5\text{-}C_9H_7)\{N_2C(C_{12}H_8)\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**3c**).

The asymmetric unit in **3c** contains the complex cation and a tetraphenylborate anion. Fig. 1 shows the cation complex and in Table 1 a selection of bond distances and angles is set out. The cation contains a ruthenium atom in a classical half-sandwich piano-stool structure, coordinated by a η^5-indenyl ligand yielding two phosphane ligands, one PPh_3 and one $P(OEt)_3$, and a 9-fluorenediazenido ligand bound to the Ru centre *via* the terminal nitrogen atom. In such half-sandwich species, the overall geometry of the complex is well-known to be octahedral and is marked by near 90° values for angles P–Ru–P and N–Ru–P. The angles between the centroid of the five-membered ring on the indenyl (CT) and the legs are close to the theoretical 125.3°.

The coordinative behaviour of the indenyl ligand shows that the metal is centred in a η^5-fashion, with scarce slippage, similar to that found in other Ru(η^5-indenyl) complexes.[14a,16] The indenyl ligand can act in a η^5-fashion, a η^3-fashion,[14c] or even a η^1-coordination mode,[14f] and slippage is a good indicator of its behaviour. Slippage measurements for **3c**, and also for other complexes described below, are the parameters quoted in Table 2. The distance between the perpendicular projection of the Ru atom on the ring best plane and ring centroid (entry 1) is quite short, showing little slippage.[17] Fold angle Ω (entry 2), which is the angle between the plane of carbon atoms 1, 2, 3 and carbon atoms 1, 3, 8, 9, where C(8) and C(9) are hinge carbon atoms, and the root-mean-square deviation of the five-membered ring from the best-fitted plane pentagon (entry 3), are also good indicators of the proposed

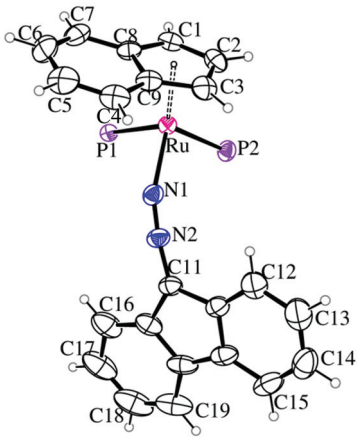
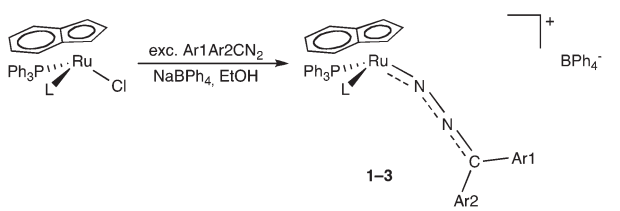


Fig. 1 ORTEP drawn for **3c** at 30% probability level. P1 = PPh_3, P2 = $P(OEt)_3$.

Table 1 Selected bond lengths [Å] and angles [°] for **3c**[a]

Ru–CT1	1.93986(16)	Ru–N(1)	1.990(2)
Ru–P(1)	2.3571(5)	N(2)–C(11)	1.299(3)
Ru–P(2)	2.2063(6)	N(1)–N(2)	1.154(3)
Ru–C(1)	2.216(2)	Ru–C(8)	2.394(2)
Ru–C(2)	2.205(3)	Ru–C(9)	2.383(2)
Ru–C(3)	2.237(3)	Ru–C_{av}	2.287
CT1–Ru–P(1)	122.937(15)	N(1)–Ru–P(1)	92.64(6)
CT1–Ru–P(2)	122.677(19)	N(1)–Ru–P(2)	93.34(7)
CT1–Ru–N(1)	124.21(7)	Ru–N(1)–N(2)	150.5(2)
P(1)–Ru–P(2)	92.33(2)	N(1)–N(2)–C(11)	171.2(3)

[a] CT1 represents the centroid of the five membered ring of the η^5-indenyl ligand. This code is also used in the text.



Scheme 1 L = PPh_3 (**1**), $P(OMe)_3$ (**2**), $P(OEt)_3$ (**3**); Ar1 = Ar2 = Ph (**a**); Ar1 = Ph, Ar2 = *p*-tolyl (**b**); Ar1Ar2 = $C_{12}H_8$ (**c**).

Table 2 Some parameters on the coordination mode of the indenyl ligand

[a]	3c	9d	14d
1. CT-projection distance (Å)	0.206	0.232	0.172
2. Fold angle Ω (°)	7.2(4)	7.2(3)	6.7(14)
3. rms 5-membered ring (Å)	0.0304	0.0292	0.0293
4. ΔM–C	0.17	0.17	0.14

[a] See text for entries definitions.

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coordination mode, because envelope puckering of this ring would be observed otherwise.[14c] Lastly, the average between the two sets of distances (ΔM–C, entry 4) when Ru–C(1), Ru–C(2) and Ru–C(3) averages are compared with Ru–C(8) and Ru–C(9) average bond distances, is again consistent with η^5-behaviour. The average five Ru–C bond length resulted in 2.287 Å, longer than the value found for the related Cp cation complex [Ru(Cp)P^{1}P^2{NNC(Ph)Tol}], 2.234 Å,[13a] since indenyl is probably a weaker donor than cyclopentadienyl.[18]

Coordination of the diazoalkane ligand in **3c** shows a severely "bent" configuration, with a N(2)–N(1)–Ru bond angle of 150.5(2)°. Note that this angle is more acute than that found in Cp diaryldiazoalkane Ru complex [Ru(Cp)P^{1}P^2{NNC(Ph)-Tol}] [156.0(1)°],[13a] or even in the 9-diazofluorene one [RuCl$_2${NNC($C_{12}H_8$)}(PNP)], [158.3(2)°],[8i] and is far from the values found in the other diazoruthenium complexes, as 171.9(5)° found in [RuCl$_3$(*p*-$N_2C_6H_4$Me)(PPh$_3$)$_2$],[19,20] or 175.4(3)° in the cation [Ru(Cp)(PPh$_3$)$_2$(NNC$_6$H$_4$OMe)]$^{2+}$.[21] It should be noted that the N(1)–N(2)–C(11) bond angle is 171.2(3)°, revealing a sp character on the N(2) atom, quite different from the usual sp^2 geometry [about 120°] around this atom found in aryldiazenido compounds,[22] or even 158.9(4)° in the cation [Ru(Cp)(PPh$_3$)$_2$(NNC$_6$H$_4$OMe)]$^{2+}$.[21] However, this behaviour was previously found in the Cp diaryldiazoalkane Ru complex [Ru(Cp)P^{1}P^2[{NNC(Ph)Tol}]$^+$ [173.8(6)°],[13a] or in the 9-diazofluorene one [RuCl$_2${NNC($C_{12}H_8$)}(PNP)], [170.1(3)°].[8i]

The bond distances at the diazenido moiety, Ru–N(1) of 1.990(2), N(1)–N(2) of 1.154(3) and N(2)–C(11) of 1.299(3) Å, are virtually the same values as those found in the above-mentioned 9-diazofluorene ruthenium complex [RuCl$_2${NNC-($C_{12}H_8$)}(PNP)], or in [Ru(Cp)P^{1}P^2{NNC(Ph)Tol}]$^+$, in such a way that a double bond between the nitrogen atoms and also between N(2) and C(11) may be proposed. Due the multiple character of the Ru–N bond, its length is shorter than that found in nitrile complexes, like [Ru(Cp)(NCPh)P^{1}P^2],[23] 2.029(2) Å, or in other ruthenium benzonitrile complexes, average 2.033 Å.[24]

In conclusion, when geometrical features of **3c** are compared with the related Cp diaryldiazenido Ru complex [Ru(Cp)-P^{1}P^2[{NNC(Ph)Tol}]$^+$,[13a] longer Ru–C bond lengths are found, with an Ru–C_{av} 0.05 Å longer and a Ru–CT 0.06 Å longer, but there are no differences in the Ru–N bond distance, which is only less than 0.02 Å longer. However, in **3c**, the angle Ru–N–N is more acute than in the Cp complex, and this should be probably due to a sterical effect rather than other factors, since the N–N–C angle differs only by less than 0.3° [171.2(3)° in **3c** and 173.8(6)° in the Cp complex]. These data indicate a Ru=N=N=C coordinative behaviour for the diazoalkane ligand.[2f]

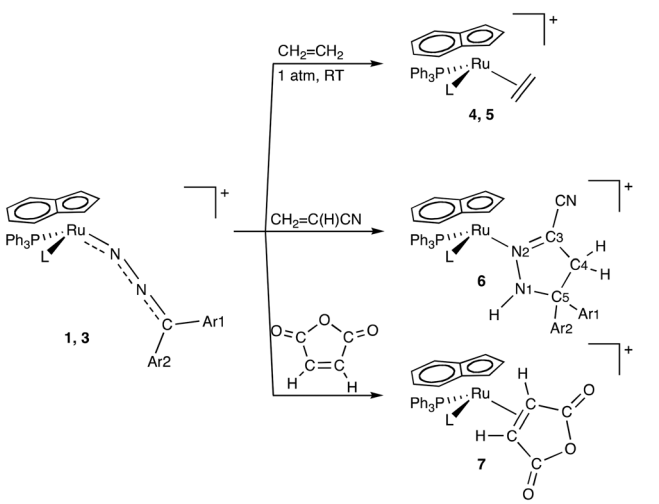
The IR spectra of diazoalkane complexes **1–3** show a medium-intensity band at 1967–1911 cm^{-1}, attributed to $\nu_{C=N=N}$ of the coordinated diazoalkane. A comparison of these values with literature data[1] also suggests the end-on η^1-coordination mode of the Ar1Ar2CN$_2$ group, like that found in the solid state. The ^{1}H NMR spectra confirm the presence of the diazo ligand, showing the signals of substituents Ar1 and Ar2, whereas the ^{31}P NMR spectra are singlets at 46.1–45.1 ppm for **1** and AB systems for **2** and **3**, fitting the proposed formulation for the complexes.

Reactions with alkenes and alkynes

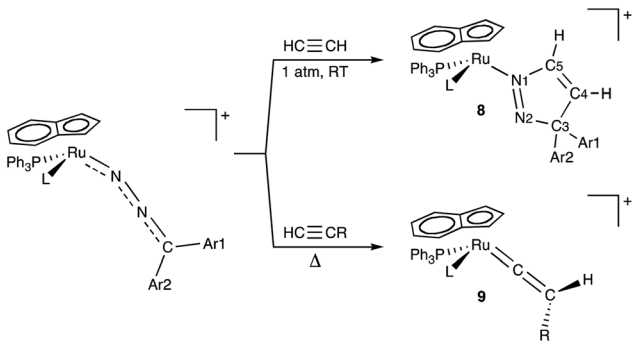
The reactions of diazoalkane complexes **1–3** with alkenes and alkynes was extensively studied, in order to test whether (3 + 2) cycloaddition of the coordinated Ar1Ar2CN$_2$ can occur. The results are summarised in Schemes 2 and 3.

Under mild conditions (1 atm, RT), ethylene reacts with diazoalkane complexes **1–3** to give ethylene complexes [Ru(η^5-C_9H_7)(η^2-CH_2=CH_2)(PPh$_3$)L]BPh$_4$ (**4**, **5**), which were isolated in good yields and characterised. The reaction proceeds with substitution of the diazoalkane ligand and exclusive formation of η^2-CH_2=CH_2 derivatives **4** and **5**.

This result is somewhat surprising, because the related cyclopentadienyl complexes [Ru(η^5-C_5H_5)(N_2CAr1Ar2)(PPh$_3$)-{P(OEt)$_3$}]BPh$_4$ underwent dipolar (3 + 2) cycloaddition of the coordinated diazoalkane to ethylene, affording 3,5-dihydro-3*H*-pyrazole derivatives.[13] Replacement of cyclopentadienyl by indenyl in half-sandwich ruthenium complexes does favour substitution rather than cyclisation of the diazoalkane ligand. In other words, indenyl fragments [Ru(η^5-C_9H_7)(PPh$_3$)L]$^+$ do not activate the coordinated N_2CAr1Ar2 ligand towards a cyclisation reaction with ethylene, affording only the η^2-CH_2=CH_2 substitution products. As suggested by a reviewer, this behaviour may be explained by the weaker donor ability of indenyl as compared with cyclopentadienyl.[18] Preliminary DFT studies[25] on the model systems [Ru(Cp)(N_2CPh$_2$)(PH$_3$)(PF$_3$)]$^+$ and [Ru(Ind)(N_2CPh$_2$)(PH$_3$)(PF$_3$)]$^+$ showed that the frontier MOs of the two complexes are strictly similar and are composed of d-type orbitals of the metal centre and the π-system of the diazoalkane ligand. Replacement of cyclopentadienyl by indenyl causes little variations of the HOMO energy, which is about 0.05 eV higher in [Ru(Ind)(N_2CPh$_2$)(PH$_3$)(PF$_3$)]$^+$. On the



Scheme 2 L = PPh$_3$ (**4**), P(OEt)$_3$ (**5–7**); Ar1 = Ph, Ar2 = *p*-tolyl (**b**); Ar1Ar2 = $C_{12}H_8$ (**c**).

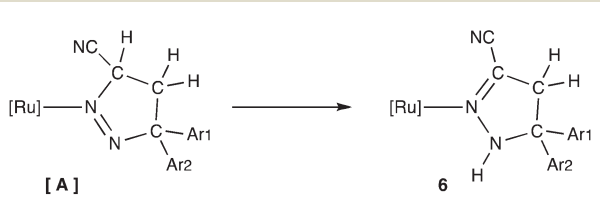


Scheme 3 L = $P(OMe)_3$ (**8**), $P(OEt)_3$ (**9**); Ar1Ar2 = $C_{12}H_8$ (**c**); R = Ph (**d**), *p*-tolyl (**e**), Bu^t (**f**).

other hand, the LUMO of the indenyl complex is more stable than the analogous cyclopentadienyl derivatives by about 0.21 eV and this should make indenyl complexes more reactive towards cyclisation than Cp homologous ones, owing to the smaller HOMO–LUMO gap. Therefore, the lower tendency of complexes **1–3** to undergo cycloaddition may be attributed to steric factors or easy substitution of the $Ar1Ar2CN_2$ ligand rather than to electronic reasons.

However, despite these unfavourable results, we extended the study to activated alkenes such as acrylonitrile and maleic anhydride, and results showed that the former does react with diazoalkane complexes **3** to give 1*H*-pyrazoline derivatives $[Ru(\eta^5\text{-}C_9H_7)\{\eta^1\text{-}N{=}NC(CN)CH_2C(Ar1Ar2)NH\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**6**), which were isolated and characterised (Scheme 2). The reaction probably proceeds with (3 + 2) cycloaddition of $CH_2{=}C(H)CN$ to the coordinate diazoalkane, giving a 3*H*-pyrazole derivative [Ru]–η^1-N=NC(Ar1Ar2)CH_2CH(CN) **[A]**, which tautomerises to the final 1*H*-pyrazoline derivative **6** (Scheme 4).

Tautomerisation of the azacycle involves a 1,3-H shift from C to N and is probably favoured by the CN group, which makes the CH(CN) hydrogen atom slightly acidic. Instead, the reaction of maleic anhydride (ma) with diazoalkane complexes proceeds with substitution of the $Ar1Ar2CN_2$ ligand and formation of the η^2-alkene complex $[Ru(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}CH{=}CHCO(O)CO\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**7**). Thus, only an activated alkene having an electron-withdrawing group and little steric hindrance $[CH_2{=}C(H)CN]$ gives dipolar (3 + 2) cycloaddition with diazoalkane bonded to the indenyl fragment $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)L\}]^+$, affording 1*H*-pyrazoline derivatives.



Scheme 4 [Ru] = $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)\{P(OEt)_3\}]^+$.

Instead, non-activated alkenes such as $CH_2{=}CH_2$ or the ones containing bulkier substituents (ma) only give substitution of the diazoalkane, producing η^2-alkene derivatives.

Under mild conditions (1 atm, RT), acetylene HC≡CH quickly reacted with diazoalkane complex **2c** to give the 3*H*-pyrazole derivative $[Ru(\eta^5\text{-}C_9H_7)\{\eta^1\text{-}N{=}NC(C_{12}H_8)CH{=}CH\}(PPh_3)\{P(OMe)_3\}]BPh_4$ (**8c**), which was isolated and characterised. The reaction proceeds with dipolar (3 + 2) cycloaddition of acetylene to the coordinated diazoalkane giving 3*H*-pyrazole complex **8c**, in which the heterocycle acts as a ligand.

At room temperature, terminal alkynes RC≡CH (R = Ph, *p*-tolyl, Bu^t) do not react with the diazoalkane complex **3c**, and the starting material can be recovered unchanged. Instead, under reflux conditions, the reaction did proceed to give vinylidene complexes $[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(H)R\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**9**), which were isolated and characterised. Substitution of diazoalkane probably gives rise to the η^2-alkyne complex, which undergoes the known tautomerisation[26–28] of the coordinated RC≡CH, yielding the final vinylidene derivative. These results highlight the important influence of the substituent on the alkyne in determining the cyclisation reaction, which only proceeds with acetylene HC≡CH, whereas substitution of the $Ar1Ar2CN_2$ ligand and formation of the vinylidene take place with monosubstituted alkynes RC≡CH.

All our results on the reactivity of diazoalkane complexes **1–3** towards alkene and alkyne indicate that the indenyl fragment $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)L]^+$ can activate coordinated diazoalkane towards dipolar (3 + 2) cycloaddition, but only with activated alkene $CH_2{=}C(H)CN$ and acetylene CH≡CH, affording either 1*H*-pyrazoline or 3*H*-pyrazole complexes. In addition, a comparison with previous results on the cyclopentadienyl fragment[13] $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)L]^+$ highlights the fact that not only cyclopentadienyl but also indenyl half-sandwich fragments can activate coordinated diazoalkane towards (3 + 2) cycloaddition with alkene and alkyne. However, in indenyl complexes **1–3**, the substitution reaction is predominant with respect to cyclisation, with the result that this ligand is less capable of activating ArN1N2 towards the formation of 3*H*-pyrazole species. The facile substitution of the diazoalkane ligand in complexes **1–3** is probably due to a mere indenyl effect, attributable to ring slippage.

The new indenyl complexes **4–9** were all isolated as their BPh_4^- salts and are stable in air and in a solution of polar organic solvents, in which they behave as 1 : 1 electrolytes.[15] Analytical and spectroscopic (IR and NMR) data support the proposed formulations for the complexes, which are further confirmed by X-ray crystal structure determination of $[Ru(\eta^5\text{-}C_9H_7)\{{=}C{=}C(H)Ph\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**9d**).

The asymmetric unit in **9d** also contains the complex cation and a tetraphenylborate anion. Only the cation is shown in Fig. 2; Table 3 gives a selection of bond distances and angles. The cation contains a ruthenium atom in a classical half-sandwich piano-stool structure coordinated by a η^5-indenyl ligand, two phosphane ligands, one PPh_3 and one $P(OEt)_3$, and a 2-phenylvinylidene ligand. The overall geometry of the complex is well-known to be octahedral and is marked by near

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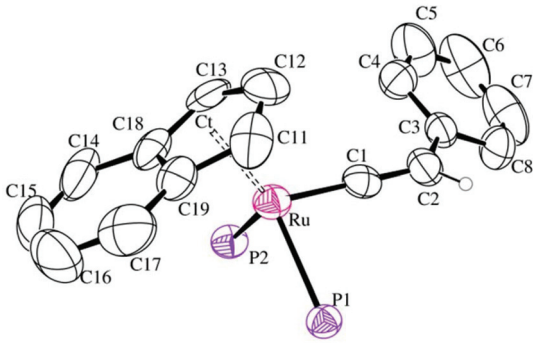


Fig. 2 ORTEP drawn for **9d** [with H at C(2)] at 30% probability level. P1 = PPh_3; P2 = $P(OEt)_3$.

Table 3 Selected bond lengths [Å] and angles [°] for **9d**[a]

Ru–CT1	1.9631(7)	Ru–C(1)	1.828(10)
Ru–P(1)	2.348(2)	Ru–P(2)	2.283(2)
Ru–C(11)	2.266(9)	Ru–C(18)	2.365(9)
Ru–C(12)	2.225(10)	Ru–C(19)	2.447(9)
Ru–C(13)	2.211(8)	C(1)–C(2)	1.281(15)
C(2)–C(3)	1.460(16)		
CT1–Ru–P(1)	128.83(6)	CT1–Ru–C(1)	124.6(3)
CT1–Ru–P(2)	120.76(7)	P(1)–Ru–P(2)	93.54(8)
C(1)–Ru–P(1)	86.1(3)	C(1)–Ru–P(2)	92.7(3)
Ru–C(1)–C(2)	174.8(8)	C(1)–C(2)–C(3)	128.7(10)

[a] CT1 represents the centroid of the five membered ring of the η^5-indenyl ligand.

90° values for angles P–Ru–P and C–Ru–P or the angles between the centroid of the five-membered ring on the indenyl (CT) and the legs, close to the theoretical 125.3°.

As was shown for **3c**, and from the values set out in Table 2, the coordinative behaviour of the indenyl ligand shows that the metal is centered in a η^5-fashion, with little slippage. The ruthenium vinylidene Ru=C=C moiety is almost linear, with a Ru–C(1)–C(2) angle of 174.8(8)°. The vinylidene Ru–C(1) bond length, 1.828(10) Å, corresponds to a ruthenium–carbon double bond and is only slightly longer than that found in related compounds, such as 1.81(1) Å in cation $[Ru(Tp)(=C=CHPh)(PEt_3)_2]^+$,[29] or 1.76(1) Å in $[Ru(Cp^*)(=C=CHPh)(PPhMe_2)_2]^+$,[30] but shorter than that in $[Ru(\eta^5\text{-}C_5H_5)(=C=CHUr)(PPh_3)_2]^+$.[31] The C(1)–C(2)–C(3) angle, 128.7(10)°, is also consistent with a sp^2 hybridisation for the C(2) atom. However, the phenyl ring and vinylidene units are not coplanar, contrasting with the planar Ru=C=CHR moiety found in the above-mentioned complexes.[29–31] Therefore, if the plane of the phenyl ring is considered (r.m.s. deviation of 0.0072 Å), in **9d** the C(2) atom is coplanar [deviated by 0.011(2) Å] but C(1) is deviated by 0.55(3) Å and the ruthenium atom lies at 1.20(4) Å from the plane.

At room temperature, besides the signals of the supporting ligands, the ^{1}H NMR spectra of ethylene complexes $[Ru(\eta^5\text{-}C_9H_7)(\eta^2\text{-}CH_2=CH_2)(PPh_3)L]BPh_4$ (**4**, **5**) show a triplet at 2.19 ppm for **4** and two multiplets at 2.41 and 1.94 ppm for **5**, attributed to the protons of the ethylene ligand. Lowering the sample temperature caused some variation in the spectra, but ethylene peaks were still broadened even at −90 °C, suggesting that rotation of $CH_2=CH_2$ still occurred at this temperature. However, the room temperature pattern of mixed–ligand complex **5** can be simulated by an ABCDXY model (X, Y = ^{31}P) with the parameters reported in the Experimental section, and the good fit between calculated and experimental spectra strongly supports the proposed attribution. In the temperature range +20 to −80 °C, the $^{31}P\{^1H\}$ NMR spectra show either a singlet at 44.64 ppm for **4** or an AB system for **5**, fitting the proposed formulations for the complexes.

The IR spectrum of the η^2-ma complex $[Ru(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}CH=CHCO(O)CO\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**7**) shows two bands of medium intensity at 1824 and 1724 cm^{-1}, attributed to the ν_{CO} of the maleic anhydride. The ^{1}H NMR spectrum confirms the presence of this ligand, showing two multiplets at 3.13 and 2.59 ppm, which can be simulated with an ABXY model (X, Y = ^{31}P) and were attributed to vinylic =CH hydrogen atoms. Further support for the presence of the η^2-ma came from the ^{13}C NMR spectrum which, besides the signals of the ancillary ligand, showed two singlets at 170.8 and 170.2 ppm, attributed to the two CO carbon resonances, and two doublets at 30.11 and 27.31 ppm of the olefinic CH=CH carbon resonances, fitting the proposed formulation for **7**.

The IR spectra of 1*H*-pyrazoline complexes $[Ru(\eta^5\text{-}C_9H_7)\{\eta^1\text{-}N=C(CN)CH_2C(Ar1Ar2)NH\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**6**) show weak bands at 2230–2228 cm^{-1}, attributed to the ν_{CN} of the 1*H*-pyrazoline ligand. Apart from the signals of the ancillary indenyl and phosphine groups, the proton NMR spectrum of **6b**, obtained as a mixture of diastereoisomers (about 1 : 1 ratio), shows two AB systems at 3.07 and 3.02 ppm, attributed to the methylene protons (H4) of the pyrazoline ligand. Coupling with NH is probably so weak that it could not be observed by us. The ^{31}P and ^{13}C NMR spectra also confirm the presence of two diastereoisomers, due to the two stereocentres in the molecule – *i.e.*, the ruthenium atom and the C5 atom of the heterocyclic ligand – showing two AB systems for the ^{31}P nuclei and two sets of signals for the ^{13}C carbon atoms of the ligand, fitting the proposed formulation. The ^{1}H NMR spectrum of **6c**, which contains fluorene $C_{12}H_8$ as a substituent, shows only one AB system for the methylene protons H4, and only one AB system appears in the ^{31}P spectrum.

The ^{1}H NMR spectrum of the 3*H*-pyrazole complex $[Ru(\eta^5\text{-}C_9H_7)\{\eta^1\text{-}N=NC(C_{12}H_8)CH=CH\}(PPh_3)\{P(OMe)_3\}]BPh_4$ (**8c**) shows two doublets at 7.89 and 6.86 ppm, attributed to H4 and H5 of the heterocycle, and the characteristic signals of the substituents at C3. The ^{13}C spectrum confirms the presence of the heterocyclic ligand, showing two singlets at 155.41 and 141.65 ppm which, in an HMQC experiment, were correlated with the doublet at 7.89 and 6.86 ppm observed in the ^{1}H spectrum and attributed to the C4 and C5 carbon resonances of the 3*H*-pyrazole ligand. A singlet at 105.12 ppm was attributed to C3. In the spectra, the signals of the ancillary ligands, BPh_4 anion and $C_{13}H_8$ substituent also appear, whereas the

^{31}P spectrum is an AB system, fitting the proposed formulation for the complex.

The IR spectra of vinylidene complexes [Ru(η^5-C_9H_7)-{=C=C(H)R}(PPh$_3$){P(OEt)$_3$}]BPh$_4$ (**9**) show a medium-intensity band at 1673–1656 cm^{-1}, attributed to the $\nu_{Ru=C=C}$ of the vinylidene ligand. However, the presence of vinylidene was confirmed by the high-frequency signal observed in the ^{13}C spectra (dd at 357.30–351.61 ppm), characteristic of vinylidene Cα carbon resonance.[26–28] A singlet at 122.5–116.88 ppm is also present and, in an HMQC experiment, was correlated with the multiplet at 5.29–4.03 ppm in the ^{1}H spectra and attributed to the Cβ carbon resonance of the =C=C(H)R group. The ^{31}P NMR spectra appear as AB systems, suggesting that a geometry like that observed in the solid state for **9d** also occurs in solution.

Reactivity of vinylidene complexes

The preparation of vinylidene complexes [Ru(η^5-C_9H_7){C=C(H)R}-(PPh$_3$){P(OEt)$_3$}]BPh$_4$ (**9**), stabilised by the mixed-ligand half-sandwich fragment, prompted us to study their reactivity, the results of which are summarised in Scheme 5.

First of all, vinylidene complexes **9** were also prepared by treating chloro-complexes [RuCl(η^5-C_9H_7)(PPh$_3$){P(OEt)$_3$}] with terminal alkynes HC≡CR in the presence of NaBPh$_4$, as shown in Scheme 6.

The NaBPh$_4$ salt favours the substitution of Cl$^-$ by alkyne, which tautomerises on the metal centre,[26–28] yielding vinylidene complex **9**. The reaction with acetylene HC≡CH does not give vinylidene but the carbene complex [Ru(η^5-C_9H_7)-{=C(CH$_3$)(OEt)}(PPh$_3$){P(OEt)$_3$}]BPh$_4$ (**10**), which was isolated and characterised (Scheme 7).

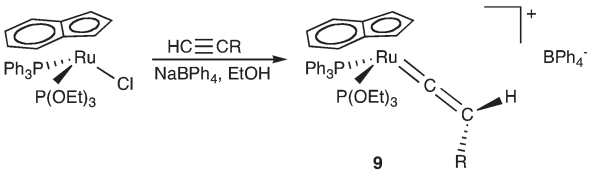
Diagnostic for the presence of ethoxycarbene in complex [Ru(η^5-C_9H_7){=C(CH$_3$)(OEt)}(PPh$_3$){P(OEt)$_3$}]BPh$_4$ (**10**) is the characteristic signal at 304.66 ppm in the ^{13}C NMR spectrum, attributed to the carbene carbon resonance. The signals of methyl and ethoxy substituents are observed at 44.03 and at 72.30 and 14.60 ppm, respectively, whereas the ^{31}P NMR spectrum appears as an AB system, fitting the proposed formulation for complex **10**.

Also in this case, the reaction probably proceeds to give the vinylidene complex [Ru]=C=CH$_2$, which undergoes a nucleophilic attack on the Cα by the oxygen atom of ethanol to afford ethoxycarbene derivative **10** (Scheme 8).

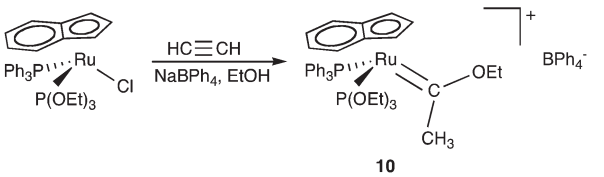
However, in contrast with the simplest [Ru]=C=CH$_2$ species, the monosubstituted vinylidene complexes [Ru]=C=C(H)R (**9**) do not give ethoxycarbene in the reaction with alcohol either at room temperature or at reflux. Instead, a nucleophilic attack on the Cα of substituted vinylidene complexes **9** was observed with amine, affording amino-carbene complexes [Ru(η^5-C_9H_7){=C(NHR)(CH$_2$R)}(PPh$_3$){P(OEt)$_3$}]-BPh$_4$ (**11**), which were isolated and characterised (Scheme 5).

The IR spectrum of aminocarbene complex [Ru(η^5-C_9H_7)-{=C[NH(CH$_2$CH$_2$CH$_3$)](CH$_2$Ph)}(PPh$_3$){P(OEt)$_3$}]BPh$_4$ (**11**) shows a medium-intensity band at 3290 cm^{-1}, attributed to the ν_{NH} of the amino group. The ^{1}H NMR spectrum supports the presence of the carbene ligand, showing the characteristic signals of the substituents NH(CH$_2$CH$_2$CH$_3$) and CH$_2$Ph, whereas the ^{13}C NMR spectrum shows a doublet of doublets at 248.62 ppm, attributed to the carbene carbon resonance, matching the proposed formulation for complex **11**.

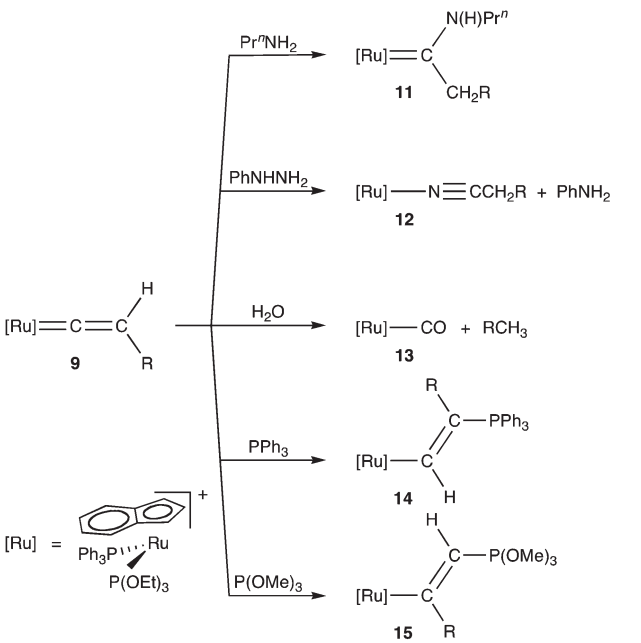
Phenylhydrazine also reacts with vinylidene complexes **9** to yield nitrile derivatives [Ru(η^5-C_9H_7)(N≡CCH$_2$R)(PPh$_3$)L]BPh$_4$



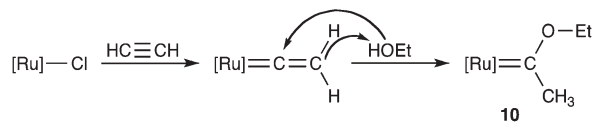
Scheme 6 R = Ph (**d**), *p*-tolyl (**e**), Bu^t (**f**).



Scheme 7 [Ru] = [Ru(η^5-C_9H_7)(PPh$_3$){P(OEt)$_3$}]$^+$.



Scheme 5 R = Ph (**d**), *p*-tolyl (**e**), Bu^t (**f**).



Scheme 8 [Ru] = [Ru(η^5-C_9H_7)(PPh$_3$){P(OEt)$_3$}]$^+$.

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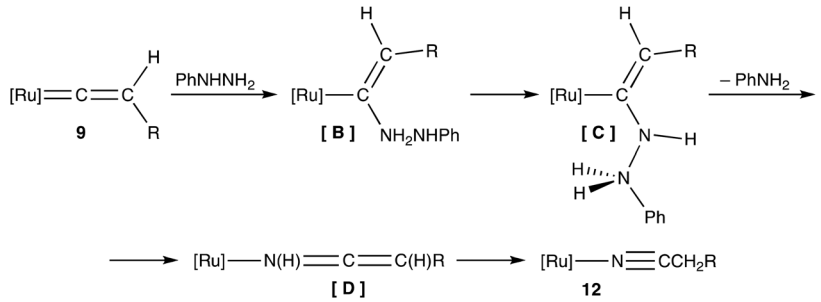


Scheme 9 [Ru] = [Ru(η^5-C_9H_7)(PPh_3){$P(OEt)_3$}]$^+$.

(**12**) and phenylamine $PhNH_2$ (Scheme 5). The reaction involves non-symmetric N–N bond cleavage of hydrazine and probably proceeds, like the related cyclopentadienyl derivatives,[23] through a nucleophilic attack of $PhNHNH_2$ on the Cα carbon atom of the vinylidene, affording η^1-alkenyl-hydrazinio complex **[B]** (Scheme 9).

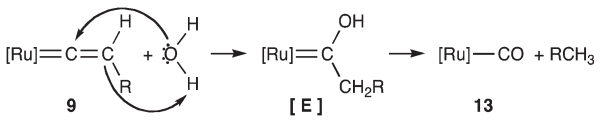
The 1,2-shift of one hydrogen atom may give **[C]**, in which cleavage of the N–N bond affords $PhNH_2$ and etheneimine **[D]**. Tautomerisation of this species yields the final benzylnitrile derivatives **12**.

The reaction with H_2O is interesting, since it yields the carbonyl complex [Ru(η^5-C_9H_7)(CO)(PPh_3){$P(OEt)_3$}]BPh_4 (**13**). Its formation may be the result of the reaction of H_2O with the vinylidene [Ru]═C═C(H)R shown in Scheme 10, giving an unstable carbene intermediate **[E]**.

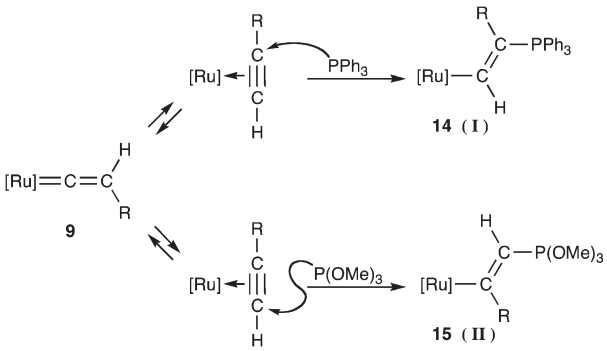
Decomposition of this intermediate **[E]** may involve the H-shift from the hydroxo group to the alkyl carbon atom of the carbene, yielding carbonyl **13** and free hydrocarbon RCH_3. The presence of RCH_3 in the reaction mixture was confirmed by GC analyses, thus fitting the reaction path proposed in Scheme 10. The reaction therefore entails hydrolysis of the terminal alkyne with C≡C bond cleavage and the formation of carbonyl derivative **13** and free hydrocarbon.

Metal-assisted hydrolysis of alkynes with H_2O has previously been reported for some metals[32] and the use of the mixed-ligand fragment [Ru(η^5-C_9H_7)(PPh_3){$P(OEt)_3$}]$^+$ highlights a new example of such a reaction.

At room temperature, vinylidene complexes [Ru(η^5-C_9H_7)-{═C═C(H)R}(PPh_3){$P(OEt)_3$}]BPh_4 (**9**) react with both triphenylphosphine PPh_3 and trimethylphosphite $P(OMe)_3$ to give alkenylphosphonium[33] derivatives [Ru(η^5-C_9H_7){C(H)═C(R)-PPh_3}(PPh_3){$P(OEt)_3$}]BPh_4 (**14**) and [Ru(η^5-C_9H_7){C(R)═C(H)-$P(OMe)_3$}(PPh_3){$P(OEt)_3$}]BPh_4 (**15**), which were isolated in good yields and characterised. As proposed for the comparable



Scheme 10 [Ru] = [Ru(η^5-C_9H_7)(PPh_3){$P(OEt)_3$}]$^+$.

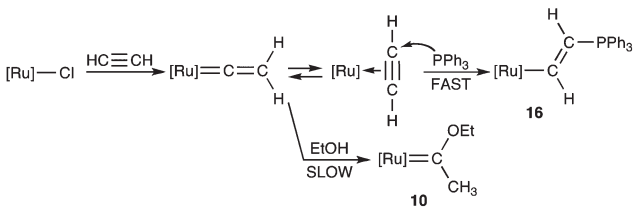


Scheme 11 [Ru] = [Ru(η^5-C_9H_7)(PPh_3){$P(OEt)_3$}]$^+$.

[Ru(η^5-1,2,3-$R_3C_9H_4$){C(H)═C(PPh_3)(Ph)}(CO)(PPh_3)]BF_4,[33b] alkenylphosphonium derivatives are probably formed by a nucleophilic attack of phosphine on the carbon atom of the η^2-alkyne in equilibrium with the vinylidene species (Scheme 11).

However, a different behaviour was shown by the two phosphines, probably due to their different steric hindrance. Their attack proceeds in one case on the substituted RC≡ and, in the other on the terminal HC≡ carbon atom of the η^2-alkyne, affording different alkenylphosphonium derivatives **14** and **15**.

We also treated the chloro-complex [RuCl(η^5-C_9H_7)(PPh_3)-{$P(OEt)$}] first with acetylene HC≡CH (1 atm) and then with PPh_3, to test whether alkenylphosphonium and/or alkoxycarbene complexes could form. As a result, compound [Ru(η^5-C_9H_7){C(H)═C(H)PPh_3}(PPh_3){$P(OEt)_3$}]BPh_4 (**16**) was obtained in high yield, suggesting that the nucleophilic attack of PPh_3 on the HC≡ alkyne carbon atom is faster than that of ethanol, affording exclusively alkenylphosphonium species **16** (Scheme 12).



Scheme 12 [Ru] = [Ru(η^5-C_9H_7)(PPh_3){$P(OEt)_3$}]$^+$.

Alkenylphosphonium complexes are very rare, and only three examples are known with indenyl and cyclopentadienyl as supporting ligands.[33] Our compounds **14–16** are new examples of these types of complexes.

Compounds **10–16** were isolated as yellow or orange solids stable in air and in a solution of polar organic solvents, in which they behave as 1 : 1 electrolytes.[15] Analytical and spectroscopic data support the proposed formulations, which were further confirmed by X-ray crystal structure determination of $[Ru(\eta^5\text{-}C_9H_7)\{C(H){=}C(Ph)(PPh_3)\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**14d**).

The asymmetric unit in **14d** contains the complex cation and a tetraphenylborate anion. Only the cation is shown in Fig. 3; Table 4 gives a selection of bond distances and angles. Once more the cation contains a ruthenium atom in a classical half-sandwich piano-stool structure coordinated by a η^5-indenyl ligand, two phosphane ligands, one PPh_3 and one $P(OEt)_3$, and a alkenyl-phosphonium ligand. As was shown for the above-described cation complexes, the overall geometry of the complex is octahedral and the coordinative behaviour of the indenyl ligand shows that the metal is centered in a η^5-fashion, with little slippage (see data in Table 2). The alkenyl-phosphonium group shows that the phosphine bonds to the Cβ atom of the alkenyl group with an *E* configuration. The Ru–C(1) bond length, 2.056(7) Å, is similar to that reported for other alkenylphosphonio-ruthenium(II) complexes, like those described by Lynam *et al.*, between 2.063(5) and 2.090(2) Å or others included in its publication for comparative purpose.[33c] The C(1)–C(2) bond length, 1.34(1) Å, is typical of a carbon–carbon double bond, and the P–Cβ bond length, C(2)–P(3) 1.805(8) Å, is not very different from that found for other phosphonium compounds, like those studied by Lyman *et al.*[33c]

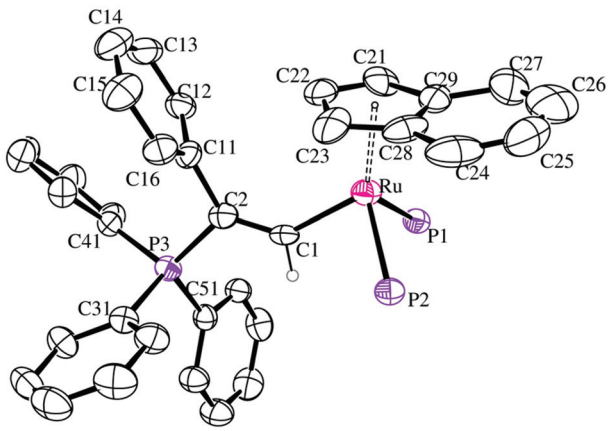


Fig. 3 ORTEP drawn for **14d** at 30% probability level. P1 = PPh_3; P2 = $P(OEt)_3$. Only the hydrogen atom H1 was drawn.

Table 4 Selected bond lengths [Å] and angles [°] for **14d**[a]

Ru–CT1	1.9654(7)	Ru–C(1)	2.056(7)
Ru–P(1)	2.302(2)	Ru–P(2)	2.2266(19)
Ru–C(21)	2.263(8)	Ru–C(28)	2.344(8)
Ru–C(22)	2.249(8)	Ru–C(29)	2.415(8)
Ru–C(23)	2.216(8)	C(1)–C(2)	1.337(10)
C(2)–P(3)	1.805(8)	C(2)–C(11)	1.514(10)
CT1–Ru–P(1)	126.46(6)	CT1–Ru–P(2)	122.32(6)
CT1–Ru–C(1)	128.6(2)	P(1)–Ru–P(2)	93.16(7)
C(1)–Ru–P(1)	86.5(2)	C(1)–Ru–P(2)	88.22(18)
Ru–C(1)–C(2)	133.9(5)	C(1)–C(2)–C(11)	129.6(7)

[a] CT1 represents the centroid of the five membered ring of the η^5-indenyl ligand.

The conformation of the alkenylphosphonium ligand is worth noting, since the C=C bond plane is almost perpendicular to the indenyl plane, as shown by the value [85.0(3)°] of the dihedral angle between the P(3)–C(11)–C(2)–C(1)–H1–Ru plane and the indenyl plane. This arrangement is similar to that found in the cation $[Ru(Cp)(E\text{-}CH{=}C(PPh_3)Ph)(PPh_3)_2]^+$,[33c] or in $[Ru(\eta^5\text{-}C_9H_7)\{CH{=}C(PPh_3)\text{cyclohexenyl}\}(PPh_3)_2]^+$,[33a] but contrasts with that found in the cation $[Ru(\eta^5\text{-}1,2,3\text{-}Me_3C_9H_4)\{CH{=}C(PPh_3)Ph\}(CO)(PPh_3)]^+$,[33b,c] probably due to the presence on it of the three methyl groups.

The ^{1}H NMR spectrum of the alkenylphosphonium complex $[Ru(\eta^5\text{-}C_9H_7)\{C(H){=}C(R)PPh_3\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**14d**) shows a multiplet at 10.20, simulated with an ABCX model (X = ^{1}H) and attributed to the CH proton of the alkenylphosphonium ligand. The ^{31}P NMR spectrum appears as an ABC system, simulated with the parameters reported in the Experimental section and suggesting a geometry in solution like that found in the solid state (Fig. 3).

Besides the signals of the indenyl and phosphine ligands and the BPh_4 anion, the ^{1}H NMR spectrum of the alkenylphosphonium complex $[Ru(\eta^5\text{-}C_9H_7)\{C(p\text{-tolyl}){=}C(R)P(OMe)_3\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (**15e**) shows a different pattern with respect to that of the related **14d**, showing an apparent doublet at 6.74 ppm. This signal was simulated with an ABCX model (X = ^{1}H; A, B, C = ^{31}P), the parameters of which (see the Experimental section) indicated that the hydrogen is strongly coupled (J_{HP} = 85.69 Hz) with only one phosphorus nucleus, suggesting a β-position of the vinyl proton, as in geometry **II** (Scheme 11). The ^{31}P NMR spectrum appears as an ABC system, with parameters fitting the proposed geometry for the complex. Further support came from the ^{13}C NMR spectrum, which shows a multiplet at 167.16, simulated with an ABCY model (Y = ^{13}C; A, B, C = ^{31}P) with the parameters reported in the Experimental section and attributed to the Cα carbon resonance of the alkenylphosphonium ligand, matching the proposed formulation.

Conclusions

We report in this paper that the indenyl ligand in half-sandwich fragments $[Ru(\eta^5\text{-}C_9H_7)(PPh_3)L]^+$ can stabilise diazoalkane complexes [Ru]–N_2CAr1Ar2. Among the properties shown by these complexes, worthy of note is the dipolar (3 + 2) cycloaddition of the coordinate diazoalkane, both with activated

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alkene CH_2═C(H)CN, yielding 1*H*-pyrazoline, and with acetylene HC≡CH, yielding 3*H*-pyrazole derivatives. Substitution of the diazoalkane ligand was also observed both with ethylene, giving η^2-CH_2═CH_2 complexes, and with terminal alkynes RC≡CH, giving vinylidene [Ru(η^5-C_9H_7){═C═C(H)R}-(PPh_3)L]BPh_4 derivatives. Nucleophilic attack on these [Ru]═C═C(H)R species with amines and alcohols yielded carbene, whereas with phenylhydrazine the nitrile complex [Ru(η^5-C_9H_7)(N≡CCH_2R)(PPh_3)L]BPh_4 formed. Reaction with water led to hydrolysis with C≡C bond cleavage, and reaction with phosphine PR_3 yielded alkenylphosphonium derivatives [Ru(η^5-C_9H_7){C(H)═C(R)PPh_3}(PPh_3)L]BPh_4 and [Ru(η^5-C_9H_7)-{C(R)═C(H)P$(OMe)_3$}(PPh_3)L]BPh_4.

Experimental

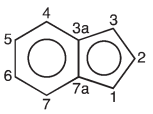
Materials and physical measurements

All synthetic work was carried out in an appropriate atmosphere (Ar, N_2) using standard Schlenk techniques or in an inert atmosphere dry-box. All solvents were dried over appropriate drying agents, degased on a vacuum line, and distilled into vacuum-tight storage flasks. $RuCl_3{\cdot}3H_2O$ was a Pressure Chemical Co. (USA) product; phosphites $P(OMe)_3$ and $P(OEt)_3$ were Aldrich products and used as received; diazoalkanes were prepared following the known method;[34] other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra (^{1}H, ^{13}C, ^{31}P) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between −90 and +25 °C, unless otherwise noted. ^{1}H and ^{13}C spectra are referred to internal tetramethylsilane. $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The iNMR software package[35] was used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze del Farmaco, University of Padova (Italy).

Synthesis of the complexes

Indenyl complexes [RuCl(η^5-C_9H_7)(PPh_3)$_2$] and [RuCl(η^5-C_9H_7)-(PPh_3){P$(OR)_3$}] (R = Me, Et) were prepared following the method previously reported.[36,37]

[Ru(η^5-C_9H_7)(N_2CAr1Ar2)(PPh_3)$_2$]BPh_4 (1) [Ar1 = Ph, Ar2 = *p*-tolyl (b); Ar1Ar2 = $C_{12}H_8$ (c)]. In a 25 mL three-necked round-bottomed flask were placed solid samples of [RuCl-(η^5-C_9H_7)(PPh_3)$_2$] (0.10 g, 0.13 mmol), an excess of the appropriate diazoalkane N_2CAr1Ar2 (0.40 mmol), an excess of $NaBPh_4$ (0.26 mmol, 89 mg), 7 mL of ethanol and 5 mL of dichloromethane. The reaction mixture was stirred at room temperature for 15 h and then the solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL). A reddish-brown solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥70%.



1b: IR (KBr, cm^{-1}) ν_{N_2} 1964 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.32–6.84 (m, 63H, Ph + H4–H7 Ind), 5.08 (br, 1H, H2 Ind), 4.73 (d, 2H, H1 + H3 Ind), 2.44 (s, 3H, CH_3 *p*-tolyl); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A_2 spin syst, 46.1 (s); Anal. Calcd for $C_{83}H_{69}BN_2P_2Ru$ (1268.28): C, 78.60; H, 5.48; N, 2.21; found: C, 78.41; H, 5.57; N, 2.13%; Λ_M = 52.7 Ω^{-1} mol^{-1} cm^2.

1c: IR (KBr, cm^{-1}) ν_{N_2} 1962 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.97–6.87 (m, 62H, Ph + H4–H7 Ind), 5.21 (br, 1H, H2 Ind), 4.92 (br, 2H, H1 + H3 Ind); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A_2 spin syst, 45.1 (s); Anal. Calcd for $C_{82}H_{65}BN_2P_2Ru$ (1252.24): C, 78.65; H, 5.23; N, 2.24; found: C, 78.48; H, 5.09; N, 2.30%; Λ_M = 53.0 Ω^{-1} mol^{-1} cm^2.

[Ru(η^5-C_9H_7)(N_2CAr1Ar2)(PPh_3)L]BPh_4 (2, 3) [L = P$(OMe)_3$ (2), P$(OEt)_3$ (3); Ar1 = Ar2 = Ph (a); Ar1 = Ph, Ar2 = *p*-tolyl (b); Ar1Ar2 = $C_{12}H_8$ (c)]. In a 25 mL three-necked round-bottomed flask were placed solid samples of [RuCl(η^5-C_9H_7)(PPh_3)L] (0.15 mmol), an excess of the appropriate diazoalkane N_2CAr1Ar2 (0.40 mmol), an excess of $NaBPh_4$ (0.3 mmol, 103 mg) and 6 mL of ethanol. The reaction mixture was stirred for 30 h and then the solvent was removed under reduced pressure to about 3 mL. The reddish-brown solid which slowly separated out was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥75%.

2a: IR (KBr, cm^{-1}) ν_{N_2} 1933 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.60–6.36 (m, 49H, Ph + H4–H7 Ind), 5.88 (br, 1H, H2 Ind), 5.63 (br, 2H, H1 + H3 Ind), 3.31 (d, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 144.2, δ_B 46.4, J_{AB} = 62.0 Hz; Anal. Calcd for $C_{67}H_{61}BN_2O_3P_2Ru$ (1116.04): C, 72.10; H, 5.51; N, 2.51; found: C, 71.93; H, 5.44; N, 2.63%; Λ_M = 52.4 Ω^{-1} mol^{-1} cm^2.

2b: IR (KBr, cm^{-1}) ν_{N_2} 1911 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.65–6.36 (m, 48H, Ph + H4–H7 Ind), 5.86 (m, 1H, H3 Ind), 5.62 (t, 1H, H2 Ind), 4.13 (br, 1H, H1 Ind), 3.31 (d, 9H, CH_3 phos), 2.36 (s, 3H, CH_3 *p*-tolyl); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 144.3, δ_B 46.5, J_{AB} = 62.0 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 165–122 (m, Ph + C4–C7 Ind), 94.5 (s, C2 Ind), 70.89 (d, C1 or C3 Ind), 70.53 (s, C1 or C3 Ind), 53.7 (d, CH_3 phos), 21.3 (s, CH_3 *p*-tolyl); Anal. Calcd for $C_{68}H_{63}BN_2O_3P_2Ru$ (1130.07): C, 72.27; H, 5.62; N, 2.48; found: C, 72.05; H, 5.74; N, 2.36%; Λ_M = 52.5 Ω^{-1} mol^{-1} cm^2.

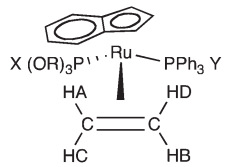
2c: IR (KBr, cm^{-1}) ν_{N_2} 1959 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.86–6.44 (m, 47H, Ph + H4–H7 Ind), 6.00 (t br, 1H, H2 Ind), 5.07 (br, 2H, H1 + H3 Ind), 3.33 (d, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 141.9, δ_B 46.6, J_{AB} = 60.8 Hz; Anal. Calcd for $C_{67}H_{59}BN_2O_3P_2Ru$ (1114.03): C, 72.24; H, 5.34; N, 2.51; found: C, 72.37; H, 5.22; N, 2.40%; Λ_M = 51.8 Ω^{-1} mol^{-1} cm^2.

3b: IR (KBr, cm^{-1}) ν_{N_2} 1931 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.54–6.37 (m, 48H, Ph + H4–H7 Ind), 5.93 (t br, 1H, H2 Ind), 5.65 (m, 2H, H1 + H3 Ind), 3.72 (qnt, 6H, CH_2), 2.36 (s, 3H, CH_3 *p*-tolyl), 1.12 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 139.1, δ_B 45.9, J_{AB} = 60.8 Hz; Anal. Calcd for $C_{71}H_{69}BN_2O_3P_2Ru$ (1172.15): C, 72.75; H, 5.93; N, 2.39; found: C, 72.56; H, 5.81; N, 2.48%; Λ_M = 53.4 Ω^{-1} mol^{-1} cm^2.

3c: IR (KBr, cm^{-1}) ν_{N_2} 1967 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 9.07 (m), 7.87–6.45 (m) (47H, Ph + H4–H7 Ind), 6.05 (t br, 1H, H2 Ind), 5.77 (m, 2H, H1 + H3 Ind), 3.73 (qnt, 6H, CH_2), 1.03 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 136.6, δ_B 45.9, J_{AB} = 58.3 Hz; Anal. Calcd for $C_{70}H_{65}BN_2O_3P_2Ru$ (1156.11): C, 72.72; H, 5.67; N, 2.42; found: C, 72.54; H, 5.79; N, 2.33%; Λ_M = 53.1 Ω^{-1} mol^{-1} cm^2.

$[Ru(\eta^5\text{-}C_9H_7)(\eta^2\text{-}CH_2{=}CH_2)(PPh_3)_2]BPh_4$ (4) and $[Ru(\eta^5\text{-}C_9H_7)(\eta^2\text{-}CH_2{=}CH_2)(PPh_3)\{P(OEt)_3\}]BPh_4$ (5). A solution of the diazoalkane complex **1b** (100 mg, 0.08 mmol) or **3b** (100 mg, 0.085 mmol) in 10 mL of CH_2Cl_2 was stirred under ethylene $H_2C{=}CH_2$ (1 atm) for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). An orange solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥80%.

4: ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.80–6.87 (m, 52H, Ph + H5 + H6 Ind), 5.92 (m, 2H, H4 + H7 Ind), 5.46 (br, 1H, H2 Ind), 4.48 (m, 2H, H1 + H3 Ind), 2.19 (t, 4H, $CH_2{=}CH_2$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: A_2 spin syst, 44.64 (s); Anal. Calcd for $C_{71}H_{61}BP_2Ru$ (1088.07): C, 78.37; H, 5.65; found: C, 78.19; H, 5.76%; Λ_M = 51.7 Ω^{-1} mol^{-1} cm^2.



5: ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.65–6.86 (m, 39H, Ph + H4–H7 Ind), 5.82 (br, 1H, H2 Ind), 5.41 (br), 5.13 (m) (2H, H1 + H3 Ind), 3.87 (m, 6H, CH_2 phos), 1.24 (t, 9H, CH_3), ABCDXY spin syst (ABCD = ^1H, XY = ^{31}P) (4H, $CH_2{=}CH_2$), δ_A, δ_B 2.41, δ_C, δ_D 1.94, J_{AB} = J_{CD} = 12.66, J_{AC} = J_{BD} = −0.6, J_{AD} = J_{BC} = 8.80, J_{AX} = J_{BX} = 4.70, J_{AY} = J_{BY} = 0.7, J_{CX} = J_{DX} = 0.1, J_{CY} = J_{DY} = 0.1 Hz; $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 136.4, δ_B 55.3, J_{AB} = 57.3 Hz; Anal. Calcd for $C_{59}H_{61}BO_3P_2Ru$ (991.94): C, 71.44; H, 6.20; found: C, 71.27; H, 6.11%; Λ_M = 53.3 Ω^{-1} mol^{-1} cm^2.

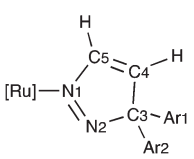
$[Ru(\eta^5\text{-}C_9H_7)\{\eta^1\text{-}N{=}C(CN)CH_2C(Ar1Ar2)NH\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (6) [Ar1 = Ph, Ar2 = *p*-tolyl (b); Ar1Ar2 = $C_{12}H_8$ (c)]. An excess of acrylonitrile (14 μL, 0.25 mmol) was added to a solution of the appropriate diazoalkene $[Ru(\eta^5\text{-}C_9H_7)(N_2CAr1Ar2)(PPh_3)\{P(OEt)_3\}]BPh_4$ (**3**) (0.089 mmol) in 10 mL of dichloromethane and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.18 mmol, 62 mg). A reddish-brown solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥75%.

6b: IR (KBr, cm^{-1}) ν_{CN} 2230 (w); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.62–6.54 (m, 48H, Ph + H4–H7 Ind), 5.43–5.38 (m, 2H, H1 + H3 Ind), 5.21–5.16 (m, 1H, H2 Ind), 3.74 (m, 6H, CH_2 phos), AB spin syst (AB = ^1H) (2H, CH_2 pyraz), δ_A 3.07, δ_B 3.02, J_{AB} = 16.8, δ_A 3.11, δ_B 2.98, J_{AB} = 16.7 Hz, 2.36, 2.34 (s, 3H, CH_3 *p*-tolyl), 1.18 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 139.37, δ_B 51.04, J_{AB} = 64.4; AB, δ_A 139.82, δ_B 51.29, J_{AB} = 64.4 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 164–122 (m, Ph + Ind), 119.26 (s, CN), 111.49, 109.57 (s, C3a + C7a Ind), 93.07, 92.97 (s, C2 Ind), 76.85 (s, C3 pyraz), 67.87, 67.12 (d), 63.30 (br) (C1 + C3 Ind), 62.62, 62.54 (d, CH_2 phos), 46.19 (s, C4 pyraz), 21.18, 21.06 (s, CH_3 *p*-tolyl), 16.24, 16.20 (d, CH_3 phos); Anal. Calcd for $C_{74}H_{72}BN_3O_3P_2Ru$ (1225.21): C, 72.54; H, 5.92; N, 3.43; found: C, 72.37; H, 5.81; N, 3.48%; Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2.

6c: IR (KBr, cm^{-1}) ν_{CN} 2228 (w); ^1H NMR (CD_2Cl_2, 20 °C) δ: 8.96, 8.28–6.87 (m, 47H, Ph + H4–H7 Ind), 5.45 (m, 2H, H1 + H3 Ind), 5.14 (br, 1H, H2 Ind), 3.79 (m, 6H, CH_2 phos), 2.97 (q br, 2H, CH_2 pyraz), 1.16 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 139.50, δ_B 51.10, J_{AB} = 65.6 Hz; Anal. Calcd for $C_{73}H_{68}BN_3O_3P_2Ru$ (1209.17): C, 72.51; H, 5.67; N, 3.48; found: C, 72.64; H, 5.80; N, 3.33%; Λ_M = 52.8 Ω^{-1} mol^{-1} cm^2.

$[Ru(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}CH{=}CHCO(O)CO\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (7). In a 25 mL three-necked round-bottomed flask were placed solid samples of **3b** (100 mg, 0.085 mmol), an excess of maleic anhydride (ma) (50 mg, 0.45 mmol) and 5 mL of dichloromethane. The resulting solution was stirred for 24 h and then the solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.17 mmol, 58 mg). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥65%. IR (KBr, cm^{-1}) ν_{CO} 1824, 1724 (m); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.90–6.70 (m, 39H, Ph + H4–H7 Ind), 5.61 (br, 1H, H2 Ind), 5.24 (br, 2H, H1 + H3 Ind), ABXY spin syst (2H, CH=CH), δ_X 3.13, δ_Y 2.59, J_{AX} = J_{AY} = 7.7, J_{BX} = J_{BY} = 7.2, J_{XY} = 13.2 Hz, 3.86 (m, 6H, CH_2), 1.25 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 125.47, δ_B 44.17, J_{AB} = 52.0 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 170.8, 170.2 (br, CO), 165–122 (m, Ph), 96.61 (s br, C2 Ind), 84.35 (br, C1 + C3 Ind), 66.70 (d, CH_2), 30.11, 27.31 (s br, CH=CH), 16.16 (d, CH_3); Anal. Calcd for $C_{61}H_{59}BO_6P_2Ru$ (1061.95): C, 68.99; H, 5.60; found: C, 68.73; H, 5.49%; Λ_M = 52.3 Ω^{-1} mol^{-1} cm^2.

$[Ru(\eta^5\text{-}C_9H_7)\{\eta^1\text{-}N{=}NC(C_{12}H_8)CH{=}CH\}(PPh_3)\{P(OMe)_3\}]BPh_4$ (8c).



A solution of the diazoalkane complex **2c** (100 mg, 0.09 mmol) in 10 mL of dichloromethane was stirred under acetylene

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HC≡CH (1 atm) for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL) containing an excess of $NaBPh_4$ (0.18 mmol, 62 mg). A red-orange solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥75%. ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 8.19–6.19 (m, 47H, Ph + H4–H7 Ind), 7.89 (d), 6.86 (m, 2H, CH=CH), 5.50 (m, 1H, H2 Ind), 5.44, 3.96 (br, 2H, H1 + H3 Ind), 3.40 (d, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 144.5, δ_B 46.4, J_{AB} = 68.1 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 165–122 (m, Ph), 155.41 (s, C4 pyraz), 141.65 (s, C5 pyraz), 105.12 (s, C3 pyraz), 93.68 (s, C2 Ind), 69.18, 68.15 (s, C1 + C3 Ind), 53.76 (d, CH_3); Anal. Calcd for $C_{69}H_{61}BN_2O_3P_2Ru$ (1140.06): C, 72.69; H, 5.39; N, 2.46; found: C, 72.55; H, 5.46; N, 2.37%; Λ_M = 54.0 Ω^{-1} mol^{-1} cm^2.

[Ru(η^5-C$_9$H$_7$){=C=C(H)R}(PPh$_3$){P(OEt)$_3$}]BPh$_4$ (9) [R = Ph (d), *p*-tolyl (e), Bu^t (f)]. *Method 1*: An excess of the appropriate alkyne HC≡CR (0.45 mmol) was added to a solution of the diazoalkane complex **3** (0.15 mmol) in 10 mL of 1,2-dichloroethane and the reaction mixture was refluxed for 20 min. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.30 mmol, 103 mg). A pink solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥65%. *Method 2*: In a 25 mL three-necked round-bottomed flask were placed 100 mg (0.29 mmol) of [RuCl(η^5-C$_9$H$_7$)(PPh$_3$){P(OEt)$_3$}], an excess of $NaBPh_4$ (0.60 mmol, 205 mg), 5 mL of ethanol and an excess of the appropriate alkyne HC≡CR (0.45 mmol). The reaction mixture was stirred for 24 h and then the pink solid which formed was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥85%.

9d: IR (KBr, cm^{-1}) $\nu_{=C=C}$ 1656 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.51–6.54 (m, 44H, Ph + H4–H7 Ind), 5.77 (m, 1H, H2 Ind), 5.73, 5.63 (m, 2H, H1 + H3 Ind), 5.29 (m, 1H, =CH), 3.75 (qnt, 6H, CH_2), 1.11 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 129.79, δ_B 44.24, J_{AB} = 48.6 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 357.30 (dd, Cα, J_{CP} = 22.6, J_{CP} = 18.9 Hz), 165–122 (m, Ph + Ind), 116.88 (s, Cβ), 98.33 (s, C2 Ind), 81.29, 80.82 (d, C1 + C3 Ind), 64.33 (d, CH_2), 15.92 (d, CH_3); Anal. Calcd for $C_{65}H_{63}BO_3P_2Ru$ (1066.02): C, 73.23; H, 5.96; found: C, 73.06; H, 5.88%; Λ_M = 53.9 Ω^{-1} mol^{-1} cm^2.

9e: IR (KBr, cm^{-1}) $\nu_{=C=C}$ 1648 (s); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.50–6.47 (m, 43H, Ph + H4–H7 Ind), 5.76 (m), 5.61 (br) (2H, H1 + H3 Ind), 5.71 (br, 1H, H2 Ind), 5.27 (m, 1H, =CH), 3.75 (qnt, 6H, CH_2), 2.33 (s, 3H, CH_3 *p*-tolyl), 1.11 (t, 9H, CH_3 phos); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 130.15, δ_B 44.60, J_{AB} = 48.6 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 358.70 (m br, Cα, J_{CP} = 22.6, J_{CP} = 18.9 Hz), 164–122 (m, Ph + Ind), 116.74 (s, Cβ), 98.32 (s, C2 Ind), 81.11, 80.86 (d, C1 + C3 Ind), 64.29 (d, CH_2), 21.21 (s, CH_3 *p*-tolyl), 16.01 (d, CH_3 phos); Anal. Calcd for $C_{66}H_{65}BO_3P_2Ru$ (1080.05): C, 73.40; H, 6.07; found: C, 73.51; H, 5.96%; Λ_M = 51.5 Ω^{-1} mol^{-1} cm^2.

9f: IR (KBr, cm^{-1}) $\nu_{=C=C}$ 1673 (s), 1645 (m); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.50–6.43 (m, 39H, Ph + H4–H7 Ind), 5.61 (br, 2H, H1 + H3 Ind), 5.52 (m, 1H, H2 Ind), 4.03 (m, 1H, =CH), 3.76 (qnt, 6H, CH_2), 1.19 (t, 9H, CH_3 phos), 1.01 (s, 9H, CH_3 Bu^t); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 132.36, δ_B 44.58, J_{AB} = 49.8 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 351.61 (dd br, Cα), 165–122 (m, Ph), 122.5 (s, Cβ), 80.60, 80.16 (d, C1 + C3 Ind), 72.39 (s, C2 Ind), 63.96 (d, CH_2), 32.56 (s, C–Me$_3$), 32.14 (s, CH_3 Bu^t), 16.04 (d, CH_3 phos); Anal. Calcd for $C_{63}H_{67}BO_3P_2Ru$ (1046.03): C, 72.34; H, 6.46; found: C, 72.17; H, 6.35%; Λ_M = 52.4 Ω^{-1} mol^{-1} cm^2.

[Ru(η^5-C$_9$H$_7$){=C(CH$_3$)(OC$_2$H$_5$)}(PPh$_3$){P(OEt)$_3$}BPh$_4$] (10). In a 25 mL three-necked round-bottomed flask were placed 100 mg (0.29 mmol) of [RuCl(η^5-C$_9$H$_7$)(PPh$_3$){P(OEt)$_3$}], an excess of $NaBPh_4$ (0.60 mmol, 205 mg) and 5 mL of ethanol. The reaction mixture was stirred under acetylene HC≡CH (1 atm) for 24 h and then the solid formed was filtered and crystallised from CH_2Cl_2 and EtOH. A further amount of solid was separated by cooling the mother liquor to −25 °C; yield ≥75%. ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 7.15–6.87 (m, 37H, Ph + H5 + H6 Ind), 5.70 (br, 2H, H4 + H7 Ind), 5.68, 5.21 (br, 2H, H1 + H3 Ind), 5.55 (br, 1H, H2 Ind), 3.93, 3.83 (m, 6H, CH_2 phos), 3.88, 3.16 (m, 2H, CH_2 =C(OEt)), 2.38 (s, 3H, =C(CH_3)), 1.20 (t, 9H, CH_3 phos), 1.07 (t, 3H, CH_3 =C(OEt)); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 143.20, δ_B 49.25, J_{AB} = 49.8 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 304.66 (t, =C, J_{CP} = J_{CP} = 12.8 Hz), 165–122 (m, Ph), 99.45 (s br, C2 Ind), 78.51, 74.89 (d, C1 + C3 Ind), 72.30 (s, CH_2 OEt(C=)), 62.80 (d, CH_2 phos), 44.03 (s, CH_3(C=)), 16.07 (d, CH_3 phos), 14.60 (s, CH_3 OEt(C=)); Anal. Calcd for $C_{61}H_{65}BO_4P_2Ru$ (1035.99): C, 70.72; H, 6.32; found: C, 70.58; H, 6.20%; Λ_M = 54.1 Ω^{-1} mol^{-1} cm^2.

[Ru(η^5-C$_9$H$_7$){=C(NHPr^n)(CH$_2$Ph)}(PPh$_3$){P(OEt)$_3$}]BPh$_4$ (11). An excess of *n*-propylamine (16 μL, 0.27 mmol) was added to a solution of the vinylidene complex **9d** (100 mg, 0.09 mmol) in 7 mL of dichloromethane and the reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.18 mmol, 62 mg). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥85%. IR (KBr, cm^{-1}) ν_{NH} 3290 (s); ^{1}H NMR (CD_2Cl_2, 20 °C) δ: 8.61 (br, 1H, NH), 7.50–6.42 (m, 44H, Ph + H4–H7 Ind), 5.46 (br, 1H, H2 Ind), 5.15, 4.97 (br, 2H, H1 + H3 Ind), 4.63, 3.77 (d, 2H, CH_2(C=)), 4.00 (m, 6H, CH_2 phos), 2.86, 2.26 (m, 2H, N–CH_2 propyl), 1.31 (t, 9H, CH_3 phos), 1.09 (m, 2H, C–CH_2 propyl), 0.64 (t, 3H, CH_3 propyl); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 146.23, δ_B 54.05, J_{AB} = 52.25 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 248.62 (t, =C, J_{CP} = J_{CP} = 15.1 Hz), 165–122 (m, Ph), 96.90 (s, C2 Ind), 76.02 (m), 74.69 (d) (C1 + C3 Ind), 63.34 (d, CH_2 phos), 54.40 (s, CH_2(C=)), 51.20 (s, CH_2NH), 21.98 (s, CH_2 propyl), 16.20 (d, CH_3 phos), 11.12 (s, CH_3 propyl); Anal. Calcd for $C_{68}H_{72}BNO_3P_2Ru$ (1125.13): C, 72.59; H, 6.45; N, 1.24; found: C, 72.36; H, 6.33; N, 1.29%; Λ_M = 52.8 Ω^{-1} mol^{-1} cm^2.

[Ru(η^5-C$_9$H$_7$)(N≡CCH$_2$R)(PPh$_3$){P(OEt)$_3$}]BPh$_4$ (12) [R = Ph (d), *p*-tolyl (e)]. These complexes were prepared following the method used for the aminocarbene complex **11**, by reacting vinylidene complexes **9d** and **9e** with an excess of phenylhydrazine instead of *n*-propylamine; yield ≥90%.

12d: IR (KBr, cm^{-1}) ν_{CN} 2264 (w); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.58–6.42 (m, 44H, Ph + H4–H7 Ind), 5.40 (br), 3.76 (s br), (2H, H1 + H3 Ind), 5.18 (m, 1H, H2 Ind), 3.70 (qnt, 6H, CH_2 phos), 3.56 (br, 2H, CH_2CN), 1.12 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 140.29, δ_B 49.92, J_{AB} = 65.62 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 165–110 (m, Ph), 129.5 (br, C≡N), 92.55 (s, C2 Ind), 66.90 (s), 66.83 (t) (C1 + C3 Ind), 62.47 (d, CH_2 phos), 25.76 (s, CH_2(CN)), 16.24 (d, CH_3); Anal. Calcd for $C_{65}H_{64}BNO_3P_2Ru$ (1081.04): C, 72.22; H, 5.97; N, 1.30; found: C, 72.06; H, 6.11; N, 1.23%; Λ_M = 53.5 Ω^{-1} mol^{-1} cm^2.

12e: IR (KBr, cm^{-1}) ν_{CN} 2258 (w); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.60–6.46 (m, 43H, Ph + H4–H7 Ind), 5.38 (m br), 3.77 (s br) (2H, H1 + H3 Ind), 5.18 (m, 1H, H2 Ind), 3.71 (qnt, 6H, CH_2 phos), 3.53 (s br, 2H, CH_2CN), 2.32 (s, 3H, CH_3 *p*-tolyl), 1.12 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 140.33, δ_B 50.03, J_{AB} = 65.62 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: 165–122 (m, Ph), 129.8 (br, C≡N), 92.52 (s, C2 Ind), 66.99 (d), 66.84 (s) (C1 + C3 Ind), 62.46 (d, CH_2 phos), 25.42 (s, CH_2(CN)), 21.16 (s, CH_3 *p*-tolyl), 16.22 (d, CH_3 phos); Anal. Calcd for $C_{66}H_{66}BNO_3P_2Ru$ (1095.06): C, 72.39; H, 6.07; N, 1.28; found: C, 72.18; H, 5.95; N, 1.34%; Λ_M = 51.9 Ω^{-1} mol^{-1} cm^2.

$[Ru(\eta^5\text{-}C_9H_7)(CO)(PPh_3)\{P(OEt)_3\}]BPh_4$ (13). An excess of water (0.2 mL, 11 mmol) was added to a solution of the vinylidene complex **9d** (100 mg, 0.09 mmol) in 5 mL of acetone and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.18 mmol, 62 mg). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥80%. IR (KBr, cm^{-1}) ν_{CO} 2000 (s); ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.52–6.56 (m, 39H, Ph + H4–H7 Ind), 5.56 (m, 2H, H1 + H3 Ind), 4.73 (br, 1H, H2 Ind), 3.82 (m, 6H, CH_2), 1.21 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: AB spin syst, δ_A 138.42, δ_B 47.38, J_{AB} = 48.6 Hz; Anal. Calcd for $C_{58}H_{57}BO_4P_2Ru$ (991.90): C, 70.23; H, 5.79; found: C, 70.15; H, 5.68%; Λ_M = 53.0 Ω^{-1} mol^{-1} cm^2.

$[Ru(\eta^5\text{-}C_9H_7)\{C(H)=C(Ph)PPh_3\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (14d) and $[Ru(\eta^5\text{-}C_9H_7)\{C(p\text{-tolyl})=C(H)P(OMe)_3\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (15e). To a solution of the appropriate vinylidene complex **9d** and **9e** (0.1 mmol) in 5 mL of dichloromethane was added an excess of the appropriate phosphine PPh_3 or $P(OMe)_3$ (0.3 mmol) and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of $NaBPh_4$ (0.2 mmol, 68 mg). A yellow solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥75%.

14d: ^1H NMR (CD_2Cl_2, 20 °C) δ: ABCX spin syst (X = ^1H), δ_X 10.20, J_{AX} = 4.3, J_{BX} = 3.1, J_{CX} = 13.9 Hz (1H, =CH), 7.65–6.87 (m, 59H, Ph + H4–H7 Ind), 5.56, 4.69 (d, 2H, H1 + H3 Ind), 5.03 (br, 1H, H2 Ind), 3.75 (qnt, 6H, CH_2), 1.07 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: ABC spin syst, δ_A 146.54, δ_B 54.69, δ_C 16.44, J_{AB} = 60.7, J_{AC} = 6.86, J_{BC} = 4.16 Hz; Anal. Calcd for $C_{83}H_{78}BO_3P_3Ru$ (1328.31): C, 75.05; H, 5.92; found: C, 74.87; H, 6.13%; Λ_M = 54.7 Ω^{-1} mol^{-1} cm^2.

15e: ^1H NMR (CD_2Cl_2, 20 °C) δ: 7.55–6.87 (m, 43H, Ph + H4–H7 Ind), ABCX spin syst, δ_X 6.74, J_{AX} = J_{BX} = 1.0, J_{CX} = 85.69 Hz (1H, =CH), 5.34 (t br, 1H, H2 Ind), 5.22, 5.07 (br, 2H, H1 + H3 Ind), 3.75 (m, 6H, CH_2), 3.47 (d, 9H, CH_3 OMe), 2.29 (s, 3H, CH_3 *p*-tolyl), 1.11 (t, 9H, CH_3 OEt); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: ABC spin syst, δ_A 145.77, δ_B 56.69, δ_C 41.45, J_{AB} = 66.1, J_{AC} = 4.40, J_{BC} = 2.10 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: ABCY spin syst (Y = ^{13}C), δ_Y 167.16, J_{AY} = 4.6, J_{BY} = 5.4, J_{CY} = 9.6 Hz (=CH), 165–122 (m), 114.30, 106.38 (br) (Ph + Ind), 92.22 (s, C2 Ind), 70.49 (br), 69.05 (t) (C1 + C3 Ind), 62.22 (d, CH_2 OEt), 55.70 (d, CH_3 OMe), 21.32 (s, CH_3 *p*-tolyl), 16.17 (d, CH_3 OEt); Anal. Calcd for $C_{69}H_{74}BO_6P_3Ru$ (1204.12): C, 68.82; H, 6.19; found: C, 68.65; H, 6.31%; Λ_M = 52.6 Ω^{-1} mol^{-1} cm^2.

$[Ru(\eta^5\text{-}C_9H_7)\{C(H)=C(H)PPh_3\}(PPh_3)\{P(OEt)_3\}]BPh_4$ (16). In a 25 mL three-necked round-bottomed flask were placed solid samples of $[RuCl(\eta^5\text{-}C_9H_7)(PPh_3)\{P(OEt)_3\}]$ (100 mg, 0.15 mmol), an excess of $NaBPh_4$ (0.30 mmol, 103 mg), an excess of PPh_3 (0.30 mmol, 79 mg), 5 mL of ethanol and enough dichloromethane to obtain a solution (3–5 mL). The reaction mixture was stirred under acetylene HC≡CH (1 atm) for 24 h and then the solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). A yellow solid separated out, which was filtered and crystallised from CH_2Cl_2 and EtOH; yield ≥80%. ^1H NMR (CD_2Cl_2, 20 °C) δ: ABCXY spin syst, δ_X 9.87, δ_Y 6.15, J_{AX} = 5.2, J_{AY} = 1.3, J_{BX} = 5.2, J_{BY} = 0.1, J_{CX} = 31.5, J_{CY} = 37.3, J_{XY} = 17.8 Hz (2H, =CH), 7.65–6.87 (m, 54H, Ph + H4–H7 Ind), 5.24 (s br, 1H, H2 Ind), 5.21, 4.76 (br, 2H, H1 + H3 Ind), 3.66 (qnt, 6H, CH_2), 1.07 (t, 9H, CH_3); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: ABC spin syst, δ_A 149.1, δ_B 56.4, δ_C 7.34, J_{AB} = 59.4, J_{AC} = 5.0, J_{BC} = 5.3 Hz; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ: ABCY spin syst (Y = ^{13}C), δ_Y 215.23, J_{AY} = 12.5, J_{BY} = 14.0, J_{CY} = 20.46 Hz (Cα), 165–122 (m, Ph + Ind), 102.44 (d, Cβ, J_{CP} = 70.9 Hz), 94.77 (C2 Ind), 77.35 (s), 73.99 (d, C1 + C3 Ind), 61.72 (d, CH_2), 16.23 (d, CH_3); Anal. Calcd for $C_{77}H_{74}BO_3P_3Ru$ (1252.21): C, 73.86; H, 5.96; found: C, 73.70; H, 6.08%; Λ_M = 52.7 Ω^{-1} mol^{-1} cm^2.

Crystal structure determinations

Crystallographic data were collected at room temperature using a Bruker Smart 6000 CCD detector and Cu-Kα radiation (λ = 1.54178 Å) was generated by an Incoatec microfocus source equipped with Incoatec Quazar MX optics. The software APEX2[38] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[38] for integration of intensity of reflections, and SADABS[38] for scaling and empirical absorption correction. The crystallographic treatment was performed with the Oscail program.[39] The structure was solved by direct methods and refined by a full-matrix least-squares based on F^2.[40] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. In the case of **9d**, all bonds in the indenyl ligand were subjected to a 'rigid bond' restraint, by means of a DELU instruction. Details of crystal data and structural refinement are given in Table 5.

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Table 5 Crystal data and structure refinement

Identification code	3c	9d	14d
Empirical formula	$C_{70}H_{65}BN_2O_3P_2Ru$	$C_{65}H_{62}BO_3P_2Ru$	$C_{83}H_{78}BO_3P_3Ru$
Moiety formula	$C_{46}H_{46}N_2O_3P_2Ru$, $C_{24}H_{20}B$	$C_{41}H_{43}O_3P_2Ru$, $C_{24}H_{20}B$	$C_{59}H_{58}O_3P_3Ru$, $C_{24}H_{20}B$
Formula weight	1156.06	1064.97	1328.24
Temperature	296(2) K	296(2) K	296(2) K
Wavelength	1.54178 Å	1.54178 Å	1.54178 Å
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions	a = 15.3586(5) Å	a = 11.8068(8) Å	a = 11.0701(19) Å
	b = 17.5065(5) Å	b = 13.0733(9) Å	b = 17.550(3)Å
	c = 22.5506(7) Å	c = 19.3806(15) Å	c = 20.754(3)Å
	α = 90°	α = 108.948(5)°	α = 72.786(9)°
	β = 104.0830(9)°	β = 89.640(5)°	β = 76.549(9)°
	γ = 90°	γ = 95.878(5)°	γ = 71.730(9)°
Volume	5881.1(3) Å^3	2813.3(3) Å^3	3613.5(10) Å^3
Z	4	2	2
Density (calculated)	1.306 mg m^{-3}	1.257 mg m^{-3}	1.221 mg m^{-3}
Absorption coefficient	3.054 mm^{-1}	3.135 mm^{-1}	2.746 mm^{-1}
F(000)	2408	1110	1388
Crystal size	0.22 × 0.21 × 0.09 mm	0.12 × 0.07 × 0.05 mm	0.31 × 0.25 × 0.06 mm
Theta range for data collection	2.97 to 68.37°	2.41 to 68.26°	2.26 to 67.45°
Index ranges	$-18 \le h \le 18$	$-14 \le h \le 13$	$-12 \le h \le 12$
	$-21 \le k \le 20$	$-15 \le k \le 15$	$-20 \le k \le 20$
	$-26 \le l \le 26$	$-23 \le l \le 22$	$-24 \le l \le 24$
Reflections collected	88 517	28 313	69 131
Independent reflections	10 708 [R(int) = 0.0611]	9573 [R(int) = 0.1303]	11 910 [R(int) = 0.0702]
Reflections observed (>2σ)	9656	5684	8852
Data completeness	0.992	0.929	0.916
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.4672 and 0.2938	0.7529 and 0.3955	0.7530 and 0.4713
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10 708/0/715	9573/13/652	11 910/0/823
Goodness-of-fit on F^2	1.079	1.070	1.183
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0452	R_1 = 0.1268	R_1 = 0.1075
	wR_2 = 0.1273	wR_2 = 0.2831	wR_2 = 0.1926
R Indices (all data)	R_1 = 0.0484	R_1 = 0.1719	R_1 = 0.1461
	wR_2 = 0.1314	wR_2 = 0.3348	wR_2 = 0.2173
Largest diff. peak and hole	0.792 and −1.355 e Å^{-3}	1.985 and −0.676 e Å^{-3}	1.770 and −0.816 e Å^{-3}

CCDC 1050294–1050296 contain the supplementary crystallographic data for this paper.

Acknowledgements

We thank Daniela Baldan, from the Università Ca' Foscari Venezia (Italy), for technical assistance.

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