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Syntheses of complexes containing substituted 4-ethynylquinolines or 1-azabuta-1,3-dienes by addition of imines to a cationic butatrienylidene-ruthenium complex

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Abstract

Reactions of $[Ru(=C=C=C=CH_2)(PR_3)_2Cp]^+$ (R = Ph or OMe) with arylimines $ArN=CH(C_6H_4R)$ afford either substituted quinolines, $Ru\{C{\equiv}CC_9H_4RN(Ar)\}(PR_3)_2Cp$, by attack of the terminal carbon of the butatrienylidene ligand at the imine carbon, followed by C–C bond formation between the *ortho* carbon of the *N*-aryl group and C_γ of the unsaturated carbene, or 1-azabuta-1,3-dienyl complexes, formed by cycloaddition of the N=CH group to $C_\gamma=C_\delta$ of the carbene, followed by opening of the resulting four-membered ring. Some product dependence on the nature of the substituents in the *N*- and *C*-aryl groups is found. The N atoms in the products are strongly basic, being readily protonated, methylated or aurated. The molecular structures of nine complexes are reported, together with that of a new modification of $RuCl\{P(OMe)_3\}_2Cp$.

Keywords: Ruthenium; Butatrienylidene; 4-Ethynylquinoline; 1-Azabuta-1,3-dienes

1. Introduction

The synthesis and chemistry of transition metal complexes containing unsaturated carbenes, $M\{=C(=C)_n=CR_2\}L_n$, continues to attract attention. Whereas the reactions of the first member of the series (vinylidenes, $n = 0$) have been explored in some detail [1], those of the next higher members of the series, allenylidenes ($n = 1$) and butatrienylidenes ($n = 2$), have not received so much attention [2]. Theoretical and experimental evidence points to the alternating electron deficiency and richness of the carbons of the unsaturated chain, resulting in specific reactivities towards nucleophiles (at odd-numbered carbons) and electrophiles (at even-numbered carbons) [3]. Much of the chemistry of vinylidene complexes has utilised metal–ligand combinations that are both electron rich and also have sterically large ligands, such as PPh_3, which give a measure of steric protection to C_α, allowing a rich chemistry derived from the nucleophilic properties of these complexes. Examples of reaction sequences involving both C_α and C_β are rare. The steric protection does not extend beyond C_β, so that allenylidenes ($n = 1$) and higher members might be expected to enter into cycloaddition reactions with suitable reagents. This has been demonstrated recently with $[Ru(=C=C=CPh_2)(CO)(PPr^i_3)Cp]^+$ to give tetrahydronaphthofuranyl [4] and pyrazolopyrazolyl [5] derivatives, and with cycloaddition of alkynyl complexes to Group 6 diarylallenylidenes to give cyclobutenylidene complexes [6].

Recently, we described the reaction between buta-1,3-diyne and $[Ru(THF)(PPh_3)_2Cp]^+$, which at low temperatures affords an intermediate which, on the basis of its synthesis and chemistry, appears to be the cationic butatrienylidene complex $[Ru(=C=C=C=CH_2)(PPh_3)_2Cp]^+$ or a close relative [7]. Although we have not yet managed to characterise this

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species fully, we have observed and briefly reported its reactions with imines to give products containing quinoline or azabutadiene moieties, the formation of which suggests that a sequence of electrophilic and nucleophilic attack of the complex on the imine has occurred [8]. This paper describes these reactions in more detail, together with the crystal and molecular structures of several of the products.

2. Results and discussion

The formation of the cation $[Ru(=C=C=C=CH_2)(PPh_3)_2Cp]^+$ has been described before [7]. In the present work we have used this complex and the related derivative containing $P(OMe)_3$ ligands, which was prepared similarly. The latter is also very reactive, but was chosen to simplify the NMR assignments of the products. The ^{1}H-NMR spectra of these complexes contain characteristic doublets for the $P(OMe)_3$ groups (separation ca. 12 Hz), while the region above δ 5 contains only aromatic protons for the ligands derived from the imines. The Cp groups in the $Ru(PPh_3)_2Cp$ complexes give rise to singlet resonances between δ 4.20 and 4.76, values tending to higher fields for the azabutadiene derivatives. In the $P(OMe)_3$ complexes, the Cp resonances are found between δ 4.90 and 5.10; the quinolines show H–P coupling of ca. 1 Hz, whereas most of the azabutadienes give only singlet resonances. As described earlier, we have carried out these reactions by generating the butatrienylidene complex in situ, from the reaction of buta-1,3-diyne with $[Ru(THF)(L)_2Cp]^+$ [L = PPh_3 or $P(OMe)_3$], the latter obtained by addition of $AgPF_6$ to a solution of $RuCl(L)_2Cp$ in THF. Experimentally, it is convenient to add a solution of buta-1,3-diyne in THF to a mixture of the cation and the imine in the same solvent kept between -100 and -78°C. After warming to r.t., the now orange–red solution is treated with KOBu^t and worked up to give the neutral products, which form yellow–orange crystals.

The reactions may proceed to give either of two products, namely the substituted 4-ethynylquinoline or a 1-azabuta-1,3-dien-2-yl complex. The identities of these were originally established by the X-ray structural determinations but, as described in detail below, it has also been possible to distinguish between them using NMR spectroscopy.

2.1. Quinoline derivatives

The reaction of $[Ru(=C=C=C=CH_2)(PPh_3)_2Cp]^+$ with benzylideneaniline proceeded to give the orange complex **1** in moderate yield. Consideration of the stoichiometry of the reaction, in which a total of $(2H + H^+)$ is lost from the combination $(C_4H_2^+ +$ PhCH=NPh), suggested that the imine also acts as a hydrogen-acceptor in the reaction. This was confirmed by the identification of benzylaniline as also being formed in the reaction. Consequently, improved (but not high) yields were obtained when two equivalents of imine were employed in this and subsequent reactions (see Scheme 1). Difficulties in isolation of this and related complexes arose from their extremely basic nature, which led to their ready protonation, even by water. This was accompanied by a colour change from orange to claret red and was particularly evident during attempted purification by TLC, for example. In part, this is overcome by addition of KOBu^t to the reaction mixture before work-up. The spectroscopic properties of the complexes are summarised in Table 1.

Assignments of the ^{1}H-NMR spectra are based on H,H-COSY and homonuclear decoupling experiments, and are also listed in Table 1 (Scheme 2). The preferred solvent for these studies was C_6D_6. Resonances of hydrogen atoms that are on carbons adjacent to N are generally somewhat broadened, which helps in the assignments. Similarly, H atoms close to NO_2 groups are found at relatively low field. In the benzoquinoline derivative **10**, the large downfield shift of H_5 (δ 12.25) is probably the result of its close proximity to the C≡C triple bond.

Complex **1** was identified as the 4-substituted quinoline by an X-ray study (see below). Its formulation as a deprotonated 1/1 adduct between the imine and the butatrienylidene cation was indicated by analysis and its mass spectrum, which showed a parent ion at m/z 919. In the IR spectrum, a band at 2048 cm^{-1} was assigned to a ν(C≡C) absorption, not unexpected if addition of a nucleophile to C_γ had occurred. After the structure was established, detailed examination of the ^{1}H-NMR spectrum, using COSY and other decoupling techniques, allowed assignment of most of the resonances as detailed in Table 1.

We have briefly examined the influence of a variety of substituents on the course of this reaction. Similar quinoline complexes were obtained when H or electron-donating substituents were present on the *N*-aryl group, or H or electron-withdrawing groups were in the *C*-aryl group. Thus the reactions of $RC_6H_4N{=}CHC_6H_4R'$ (R = Me, R′ = H; R = H, R′ = NO_2-4; R = OMe-4, R′ = NO_2-4) afforded complexes **2**, **3** and **7**, respectively. Using the $P(OMe)_3$ precursor, we made similar derivatives from imines with R = H, R′ = NO_2-4 (**4**), CO_2Me (**6**) and R = OMe-4, R′ = NO_2-4 (**8**). All complexes were readily identified as the substituted ethynylquinolines by elemental analysis, mass spectrometry and analyses of their ^{1}H-NMR spectra. In addition, X-ray structural studies were carried out on **2**, **3**, **6** and **8** (see below).

The product from 3-ClC_6H_4N=CHPh and the PPh_3 complex was shown to be the corresponding quinoline

9, but the ^{1}H-NMR spectrum showed that it was formed as a 4/1 mixture of isomers. Two Cp singlet resonances at δ 4.67 (major) and 4.58 (minor) were present and detailed analysis allowed the structural assignments shown in Scheme 1.

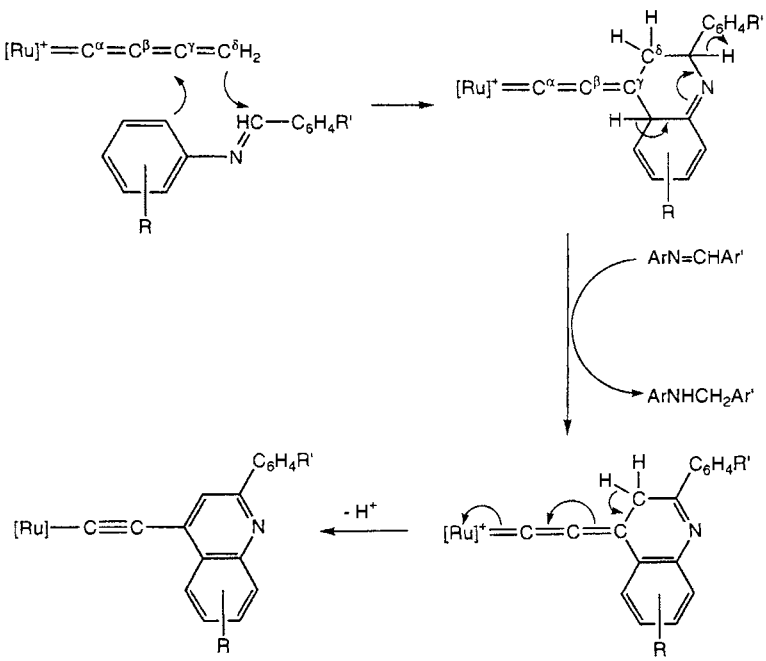
Use of imines containing naphthyl groups was investigated as a possible route to tricyclic systems. Cyclisation to the naphthyl group occurred with (2-$C_{10}H_7$)N=CHPh, when the orange benzo[*h*]quinoline complex **10** was obtained. The mass spectrum contained M^+ at *m*/*z* 969 and detailed examination of the ^{1}H-NMR spectrum enabled assignment of individual resonances to the eight protons of the benzoquinoline ligand as shown. In particular, there is a low-field resonance at δ 12.25 which we suggest arises from H(13), which from the X-ray structural study is found in close proximity to the C≡C triple bond [H(13)···C(13) separation is 2.3 Å].

2.2. 1-Azabuta-1,3-dienyl complexes

In contrast to the product found with the PPh_3 complex, the reaction between [Ru(THF){$P(OMe)_3$}$_2$-Cp]$^+$, buta-1,3-diyne and PhCH=NPh afforded the corresponding azabuta-1,3-dienyl derivative, **11** (Scheme 3). This was readily identified from its ES mass spectrum, which contained $[M + H]^+$ at *m*/*z* 646, and from its ^{1}H-NMR spectrum, in which a resonance assigned to the vinylic proton H_4 at δ 7.71 is characterised by a 15.8 Hz coupling to H_3 *trans* to it (the H_3 resonance is contained within the multiplet at δ 7.02–7.40). The ν(C≡C) absorption is found at 2051 cm^{-1}.

Similarly, complexes **12**, **14**, **16**–**19** and **21** were obtained from reactions between [Ru(=C=C=C=CH_2)-(PPh_3)$_2$Cp]$^+$ and RC_6H_4N=CHC_6H_4R' (R = R′ = Me-4, OMe-4; R = NO_2-3, NO_2-4, R′ = H; R = H, R′ = CO_2Me-4; R = NO_2-4, R′ = CO_2Me-4), respectively. The $P(OMe)_3$ analogues **11**, **13**, **15** and **20** (with R = R′ = H, Me-4, OMe-4; R = NO_2-4, R′ = CO_2Me-4) were also prepared. The distinction from the quinoline structure is readily made, the two *trans* vinylic protons giving characteristic doublets with *J*(HH) ca. 16 Hz.

It is notable that similar complexes were obtained in both series [PPh_3 and $P(OMe)_3$] from the bis-tolyl and bis-anisyl imines, 4-RC_6H_4N=CHC_6H_4R-4 (R = Me, OMe). These complexes (**12**–**15**) were identified from their ^{1}H-NMR spectra and the molecular structure of **15** was confirmed by a single-crystal X-ray study. How-



	R	R'	L
1	H	H	PPh3
2	Me-6	H	PPh3
3	H	NO_2-4	PPh3
4	H	NO_2-4	P(OMe)3
5	H	NO_2-3	PPh3
6	H	CO_2Me-4	P(OMe)3
7	OMe-6	NO_2-4	PPh3
8	OMe-6	NO_2-4	P(OMe)3
9	Cl-5/7	H	PPh3
10	benzo	H	PPh3

Scheme 1.

Table 1
Analytical and spectroscopic data

Compound and analysis	Spectroscopic data [a]
1 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-PhC_9H_5N yellow; m.p. 136–138°C (dec.) Anal. Found: C, 73.99; H, 5.18; N, 1.51. $C_{58}H_{45}NP_2Ru{\cdot}0.2CH_2Cl_2{\cdot}0.5Et_2O$ calc.: C, 74.31; H, 5.22; N, 1.44; M (solvent-free), 919 (both solvate molecules were detected by NMR)	IR: ν(C≡C) 2048s ^{1}H-NMR: 4.60 (s, 5H, Cp), 7.00 (m, 18H, H_m+H_p of PPh_3), 7.29 [t, J(HH) 7.5, 1H, H_{11}], 7.44 [t, J(HH) 7.5, 2H, H_{10}], 7.49 [t, J(HH) 7.5, 1H, H_6 or H_7], 7.62 [t, J(HH) 7.5, 1H, H_7 or H_6], 7.78 (m, 12H, H_o of PPh_3), 8.05 (s, 1H, H_3), 8.59 [d, J(HH) 7.5, 3H, H_9 + H_5 or H_8], 9.03 [d, J(HH) 7.5, 1H, H_8 or H_5] ^{13}C-NMR: 85.7 (s, Cp), 112.8 (s), 116.1 (s), 119.7 (s), 128.0 (s), 124.9 (s), 125.9 (s), 128.7 (t), 129.4 (s), 131.4 (s), 133.4 (t), 136.6 (s), 138.5 (m), 140.7 (s), 148.6 (s), 157.0 (s), 160.4 (s) ES MS: 919, M^+; 657, $[M-PPh_3]^+$
2 4-{Cp(PPh_3)$_2$Ru(C≡C)}-6-Me-2-PhC_9H_4N bright yellow; m.p. 191–195°C Anal. Found: C, 74.50; H, 5.00; N, 1.48. $C_{59}H_{47}NP_2Ru$ calc.: C, 75.97; H, 5.04; N, 1.50; M, 933	IR: ν(C≡C) 2051s ^{1}H-NMR: 2.36 (s, 3H, Me), 4.33 (s, 5H, Cp), 7.1–8.3 (m, 39H, aromatic H) FAB MS: 933, M^+; 671, $[M-PPh_3]^+$; 428, $[Ru(PPh_3)(C_5H_5)]^+$
3 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-(4-$NO_2C_6H_4$)C_9H_5N yellow; m.p. 208–210°C (dec.) Anal. Found: C, 71.85; H, 4.63; N, 2.86. $C_{58}H_{44}N_2O_2P_2Ru$ calc.: C, 72.26; H, 4.60; N, 2.91; M, 964	IR: ν(C≡C) 2046s, ν(NO) 1511s, 1343s, ν(CN) 846m ^{1}H-NMR: 4.38 (s, 5H, Cp), 7.03 [t, J(HH) 7, 12H, H_m of PPh_3], 7.16 [t, J(HH) 7, 6H, H_p of PPh_3], 7.30 (s, 1H, H_3), 7.35 [t, J(HH) 8, 1H, H_6], 7.40 (m, 12H, H_o of PPh_3), 7.59 [t, J(HH) 8, 1H, H_7], 7.99 [d, J(HH) 8, 1H, H_5], 8.16 [d, J(HH) 9, 2H, H_9], 8.28 [d, J(HH) 9, 2H, H_{10}], 8.40 [d, J(HH) 8, 1H, H_8] FAB MS: 965, $[M+H]^+$; 702, $[M-PPh_3]^+$; 625, $[M-PPh_3-Ph]^+$; 429, $[Ru(PPh_3)(C_5H_5)]^+$
4 4-{Cp[P(OMe)$_3$]$_2$Ru(C≡C)}-2-(4-$NO_2C_6H_4$)C_9H_5N orange; m.p. 129–131°C Anal. Found: C, 47.22; H, 4.56; N, 4.07. $C_{28}H_{32}N_2O_8P_2Ru$ calc.: C, 48.90; H, 4.56; N, 4.07; M, 688	IR: ν(C≡C) 2062s, ν(NO) 1525s, 1347s, ν(PO) 1024vs (br) ^{1}H-NMR: 3.68 [t, J(HP) 11.7, 18H, OMe], 5.09 [t, J(HP) 0.9, 5H, Cp], 7.45 [t, J(HH) 8.1, 1H, H_7], 7.61 (s, 1H, H_3), 7.64 [t, J(HH) 8.4, 1H, H_6], 8.03 [d, J(HH) 9.0, 1H, H_5], 8.25, 8.33 [2 × d, J(HH) 9.0, 4H, $H_{9,10}$], 8.58 [d, J(HH) 8.1, 1H, H_8] ES MS: 689, $[M+H]^+$
5 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-(3-$NO_2C_6H_4$)C_9H_5N yellow: m.p. 202–204°C (dec.) Anal. Found: C, 71.09; H, 4.57; N, 2.86. $C_{58}H_{44}N_2O_2P_2Ru.0.2CH_2Cl_2$ calc.: C, 71.26; H, 4.56; N, 2.86; M (solvent-free), 964 (CH_2Cl_2 detected in NMR)	IR: ν(C≡C) 2054s, ν(NO) 1529s, 1350s, ν(CN) 808m ^{1}H-NMR: 4.45 (s, 5H, Cp), 7.03 [t, J(HH) 7, 13H, H_m of PPh_3+H_{11}], 7.10 [t, J(HH) 7, 6H, H_p of PPh_3], 7.54 [td, J(HH) 8, 1.5, 1H, H_6], 7.63 [td, J(HH) 8, 1.5, 1H, H_7], 7.75 (m, 12H, H_o of PPh_3), 7.89 (s, 1H, H_3), 7.96 [dt, J(HH) 8, 1.5, 1H, H_9], 8.52 [d, J(HH) 8, 1H, H_8], 8.81 [dt, J(HH) 8, 1.5, 1H, H_{10}], 9.05 [t, J(HH) 1.5, 1H, H_{13}], 9.15 [dd, J(HH) 8, 1.5, 1H, H_5] ES MS: 965, $[M+H]^+$; 703, $[M+H-PPh_3]^+$
6 4-{Cp[P(OMe)$_3$]$_2$Ru(C≡C)}-2-(4-$MeO_2CC_6H_4$)C_9H_5N yellow; m.p. 155–156°C Anal. Found: C, 51.53; H, 5.04; N, 1.98. $C_{30}H_{35}NO_8P_2Ru$ calc.: C, 51.43; H, 5.04; N, 2.00; M, 701	IR: ν(C≡C) 2064s, ν(CO) 1719s, ν(PO) 1023vs(br) ^{1}H-NMR: 3.69 [t, J(HP) 12.0, 18H, OMe], 3.95 (s, 3H, CO_2Me), 5.10 (s, 5H, Cp), 7.43 [t, J(HH) 7.2, 1H, H_7], 7.62 (s, 1H, H_3), 7.63 [t, J(HH) 7.2, 1H, H_6], 8.05 [d, J(HH) 8.0, 1H, H_5], 8.16 [2 × d, J(HH) 8.4, 4, 4H, $H_{9,10}$], 8.51 [d, J(HH) 8.4, 1H, H_8] ES MS: 702, $[M+H]^+$
7 4-{Cp(PPh_3)$_2$Ru(C≡C)}-6-MeO-2-(4-$NO_2C_6H_4$)C_9H_4N yellow; m.p. 220–222°C (dec.) Anal. Found: C, 70.45; H, 4.56; N, 2.87. $C_{59}H_{46}N_2O_2P_2Ru.0.2CH_2Cl_2$ calc.: C, 70.33; H, 4.63; N, 2.77; M (solvent-free), 994 (CH_2Cl_2 detected in NMR)	IR: ν(C≡C) 2037s, ν(NO) 1513s, 1339s, ν(CN) 853m ^{1}H-NMR: 3.43 (s, 3H, OMe), 4.42 (s, 5H, Cp), 7.08 [t, J(HH) 7, 12H, H_m of PPh_3], 7.21 [t, J(HH) 7, 6H, H_p of PPh_3], 7.29 [dd, J(HH) 9, 3, 1H, H_7], 7.40 (s, 1H, H_3), 7.49 (m, 12H, H_o of PPh_3), 7.82 [d, J(HH) 3, 1H, H_5], 7.96 [d, J(HH) 9, 1H, H_8], 8.22 [d, J(HH) 9, 2H, H_9], 8.35 [d, J(HH) 9, 2H, H_{10}] ES MS: 994, M^+; 731, $[M-H-PPh_3]^+$
8 4-{Cp[P(OMe)$_3$]$_2$Ru(C≡C)}-6-MeO-2-(4-$NO_2C_6H_4$)-C_9H_4N orange; m.p. 115–116°C Anal. Found: C, 48.38; H, 4.73; N, 3.89. $C_{29}H_{34}N_2O_9P_2Ru$ calc.: C, 48.53; H, 4.77; N, 3.90; M, 740	IR: ν(C≡C) 2061s, ν(NO) 1524s, 1347s, ν(PO) 1030vs(br) ^{1}H-NMR: 3.68 [t, J(HP) 12.0, 18H, OMe], 3.96 (s, 3H, OMe), 5.09 (s, 5H, Cp), 7.32 [dd, J(HH) 9.3, 2.7, 1H, H_7], 7.57 (s, 1H, H_3), 7.87 [d, J(HH) 3.0, 1H, H_5], 7.95 [d, J(HH) 9.3, 1H, H_8], 8.23, 8.30 [2d, J(HH) 9.3, 4H, $H_{9,10}$] ES MS: 741, $[M+H]^+$
9 4-{Cp(PPh_3)$_2$Ru(C≡C)}-(5/7)-Cl-2-PhC_9H_4N yellow; m.p. 154–156°C (dec.) Anal. Found: C, 70.91; H, 4.71; N, 1.43. $C_{58}H_{44}ClNP_2Ru.0.4CH_2Cl_2.0.2Et_2O$ calc.: C, 70.94; H, 4.71; N, 1.40; M, 953 (both solvate molecules found in NMR)	IR: ν(C≡C) 2039s ^{1}H-NMR: (**9a**, ~80%) 4.67 (s, 5H, Cp), 7.01* (m, 18H, H_m and H_p of PPh_3), 7.20 [t, J(HH) 8, 1H, H_7], 7.31* [t, J(HH) 7.5, 1H, H_{11}], 7.41 [t, J(HH) 7.5, 2H, H_{10}], 7.53 [d, J(HH) 8, 1H, H_6 or H_8], 7.77* (m, 12H, H_o of PPh_3), 7.88 (s, 1H, H_3), 8.35 [d, J(HH) 8, 1H, H_8 or H_6], 8.45 [d, J(HH) 7.5, 2H, H_9] (**9b**, ~20%) 4.58 (s, 5H, Cp), 7.41 (m, 1H, H_6), 8.00 (s, 1H, H_3), 8.50 [d, J(HH) 7.5, 2H, H_9], 8.58 (s, 1H, H_8), 8.72 [td, J(HH) 8, 2H, H_5] * resonances so indicated are common to both isomers FAB MS: 953, M^+; 691, $[M-PPh_3]^+$; 614, $[M-PPh_3-Ph]^+$; 429, $[M-2PPh_3]^+$ or $[Ru(PPh_3)(C_5H_5)]^+$
10 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-$PhC_{13}H_8N$ yellow; m.p. 133–134°C (dec.) Anal. Found: C, 76.88; H, 5.32; N, 1.46. $C_{62}H_{47}NP_2Ru$ calc.: C, 76.84; H, 4.89; N, 1.45; M, 969	IR: ν(C≡C) 2038s ^{1}H-NMR: 4.76 (s, 5H, Cp), 6.95 (m, 18H, H_m and H_p of PPh_3), 7.35 [t, J(HH) 7.5, 1H, H_{13}], 7.48 [t, J(HH) 7.5, 2H, H_{12}], 7.65 [t, J(HH) 7.5, 1H, H_7], 7.77 (m, 12H, H_o of PPh_3), 7.87 (m, 3H, $H_{6,8}+H_9$ or H_{10}), 8.12 (s, 1H, H_3), 8.52 [d, J(HH) 9, 1H, H_{10} or H_9], 8.60 [d, J(HH) 7.5, 2H, H_{11}], 12.25 d, J(HH) 9, 1H, H_5] FAB MS: 969, M^+; 707, $[M-PPh_3]^+$; 630, $[M-PPh_3-Ph]^+$; 429, $[Ru(PPh_3)(C_5H_5)]^+$; 154, $[Ph_2]^+$

Table 1 (Continued)

Compound and analysis	Spectroscopic data [a]
11 Ru{C≡CC(=NPh)CH=CHPh}{P(OMe)$_3$}$_2$Cp pale yellow, m.p. 152–154°C Anal. Found: C, 52.59; H, 5.40; N, 2.16. $C_{28}H_{35}NO_6P_2Ru$ calc.: C, 52.16; H, 5.47; N, 2.17; M, 645	IR: ν(C≡C) 2051s, ν(PO) 1041vs(br) ^{1}H-NMR: 3.52 [t, J(HP) 12.0, 18H, OMe], 4.89 [t, J(HP) 1.0, 5H, C_5H_5], 7.02–7.40 (m, 9H, $H_{1,2,3,5,7,8}$), 7.51 [d, J(HH) 6.9, 2H, H_6], 7.71 [d, J(HH) 15.8, 1H, H_4] ES MS: 646, $[M+H]^+$
12 Ru{C≡CC[=N(C_6H_4Me-4)]CH=CH(C_6H_4Me-4)}-(PPh_3)$_2$Cp yellow Anal. Found: C, 75.22; H, 5.98; N, 1.72. $C_{60}H_{51}NP_2Ru$ calc.: C, 75.93; H, 5.42; N, 1.48; M, 949	IR: ν(C≡C) 2022s ^{1}H-NMR: 2.26 (s, 3H, Me), 2.35 (s, 3H, Me), 4.21 (s, 5H, Cp), 6.90–7.43 (m, 40H, aromatic H) ES MS: 950, $[M+H]^+$; 688, $[Ru(PPh_3)_2(C_5H_5)-2H]^+$
13 Ru{C≡CC[=N(C_6H_4Me-4)]CH=CH(C_6H_4Me-4)}-{P(OMe)$_3$}$_2$Cp orange; m.p. 119–120°C Anal. Found: C, 53.59; H, 5.83; N, 2.05. $C_{30}H_{39}NO_6P_2Ru$ calc.: C, 53.57; H, 5.84; N, 2.08; M, 673	IR: ν(C≡C) 2049s, ν(PO) 1024vs(br) ^{1}H-NMR: 2.33, 2.35 (2×s, 6H, Me), 3.52 [t, J(HP) 12.0, 18H, OMe], 4.91 (s, 5H, Cp), 7.01 [d(br), J(HH) 15.9, 1H, H_5], 7.07, 7.14 [2×d, J(HH) 7.9, 4H, $H_{2,3}$], 7.16, 7.40 [2d, J(HH) 7.8, 4H, $H_{6,7}$], 7.67 [d, J(HH) 15.8, 1H, H_4] ES MS: 674, $[M+H]^+$
14 Ru{C≡CC[=N(C_6H_4OMe-4)]CH=CH(C_6H_4OMe-4)}-(PPh_3)$_2$Cp orange M, 981	IR: ν(C≡C) 2024s ^{1}H-NMR: 3.74, 3.77 (2×s, 6H, OMe), 4.29 (s, 5H, Cp), 6.58 [d, J(HH) 9.0, 2H, H_7], 6.75 [d, J(HH) 8.8, 2H, H_2], 6.97 [t, J(HP) 7, 12H, H_m of PPh_3], 7.11 [t, J(HP) 7, 6H, H_p of PPh_3], 7.25 (m, 17H, 12 o-H of PPh_3+H_2, H_4 or $_5$, H_6), 7.32 [d, J(HH) 16, 1H, H_4 or $_5$] ES MS: 982, $[M+H]^+$; 720, $[M+H-PPh_3]^+$
15 Ru{C≡CC[=N(C_6H_4OMe-4)]CH=CH(C_6H_4OMe-4)}-{P(OMe)$_3$}$_2$Cp orange; m.p. 90–91°C Anal. Found: C, 51.88; H, 5.90; N, 1.97. $C_{30}H_{39}NO_8P_2Ru$ calc.: C, 51.13; H, 5.58; N, 1.99; M, 705	IR: ν(C≡C) 2046s, ν(PO) 1033vs(br) ^{1}H-NMR: 3.53 [t, J(HP) 12.0, 18H, P-OMe], 3.79, 3.80 (2×s, 6H, OMe), 4.97 (s, 5H, Cp), 6.84, 6.86 [2×d, J(HH) 9.0, 4H, $H_{2,3}$], 7.14 [d, J(HH) 15.8, 1H, H_5], 7.50 (m, 4H, $H_{6,7}$), 7.67 [d, J(HH) 15.8, 1H, H_4] ES MS: 706, $[M+H]^+$
16 Ru{C≡CC[=N($C_6H_4NO_2$-4)]CH=CHPh}(PPh_3)$_2$Cp yellow; m.p. 101–104°C (dec.) Anal. Found: C, 71.38; H, 5.32; N, 2.84. $C_{58}H_{46}N_2O_2P_2Ru.0.2CH_2Cl_2.0.2C_6H_{14}$ calc.: C, 71.33; H, 4.96; N, 2.80; M, 966 (both solvate molecules found in NMR)	IR: ν(C≡C) 2016s, ν(NO) 1502s, 1329s, ν(CN) 846m ^{1}H-NMR: 4.38 (s, 5H, Cp), 6.97 (m, 18H, H_m+H_p of PPh_3), 7.15 (m, 3H, H_1+H_2 or H_3), 7.30 [d, J(HH) 9, 2H, H_6 or H_7], 7.46 (m, 14H, H_o of PPh_3+H_3 or H_2), 7.62 [d, J(HH) 16, 1H, H_4 or H_5], 8.07 [d, J(HH) 16, 1H, H_5 or H_4], 8.09 [d, J(HH) 9, 2H, H_7 or H_6] ES MS: 966, M^+; 703, $[M-H-PPh_3]^+$
17 Ru{C≡CC[=N($C_6H_4NO_2$-3)]CH=CHPh}(PPh_3)$_2$Cp yellow; m.p. 171–172°C Anal. Found: C, 71.89; H, 4.91; N, 2.87. $C_{58}H_{46}N_2O_2P_2Ru$ calc.: C, 72.11; H, 4.80; N, 2.90; M, 966	IR: ν(C≡C) 2048s, ν(NO) 1530s, 1351s, ν(CN) 831m ^{1}H-NMR: 4.56 (s, 5H, Cp), 7.08 [t, J(HH) 7.5, 12H, H_m of PPh_3], 7.21 [t, J(HH) 7.5, 6H, H_p of PPh_3], 7.3–7.6 (m, 12H, H_o of PPh_3+H_1, H_2, H_6, H_8, H_9), 7.62 [t, J(HH) 16, 1H, H_4 or H_5], 8.04 [d, J(HH) 7.5, 2H, H_3], 8.21 [d, J(HH) 7.5, 1H, H_7 or H_9] FAB MS: 966, M^+; 702, $[M-2H-PPh_3]^+$; 427, $[Ru(PPh_3)(C_5H_5)-2H]^+$
18 Ru{C≡CC(=NPh)CH=CH($C_6H_4CO_2$Me -4)}(PPh_3)$_2$Cp orange Anal. Found: C, 72.87; H, 5.30; N, 2.16. $C_{60}H_{49}NO_2P_2Ru$ calc.: C, 73.65; H, 5.04; N, 1.43; M, 980	IR: ν(C≡C) 2033s, ν(CO) 1715s ^{1}H-NMR: 3.88 (s, 3H, OMe), 4.38 (s, 5H, Cp), 6.71 [d, J(HH) 16.6, 1H, H_4 or H_5], 7.02 [t, J(HP) 7, 12H, H_m of PPh_3], 7.19 [t, J(HP) 7, 6H, H_p of PPh_3], 7.33–7.46 (m, 13H, 12 o-H of PPh_3+H_4 or H_5), 7.58 [t, J(HH) 8.6, 1H, H_8], 7.90 [d, J(HH) 8.4, 2H, H_3], 8.00 [d, J(HH) 8.4, 2H, H_7], 8.07 [d, J(HH) 8.0, 2H, H_6], 8.40 [d, J(HH) 8.6, 1H, H_2] ES MS: 980, $[M+H]^+$; 718, $[M+H-PPh_3]^+$
19 Ru{C≡CC[=N($C_6H_4NO_2$-4)]CH=CH($C_6H_4CO_2$Me-4)}-(PPh_3)$_2$Cp red Anal. Found: C, 70.36; H, 5.32; N, 2.70. $C_{60}H_{48}N_2O_4P_2Ru$ calc.: C, 70.37; H, 4.72; N, 2.74; M, 1025	IR: ν(C≡C) 2017s, ν(CO) 1718, ν(NO) 1505, 1331 ^{1}H-NMR: 3.90 (s, 3H, OMe), 4.22 (s, 5H, Cp), 6.55 (m, 2H, H_6), 6.98 [t, J(HP) 7, 12H, H_m of PPh_3], 7.15 (m, 18H, H_o+H_p of PPh_3), 7.28 [d, J(HH) 8.6, 2H, H_2], 7.43 [d, J(HH) 15, 1H, H_4 or H_5], 7.90 [dd, J(HH) 8.6, 5.8, 2H, H_3], 8.04 [d, J(HH) 15, 1H, H_5 or H_4], 8.14 [d, J(HH) 8.6, 2H, H_7] ES MS: 1025, $[M+H]^+$; 763, $[M+H-PPh_3]^+$
20 Ru{C≡CC[=N($C_6H_4NO_2$-4)]CH=CH($C_6H_4CO_2$Me-4)}-{P(OMe)$_3$}$_2$Cp bright orange, m.p. 158–159°C Anal. Found: C, 48.15; H, 4.35; N, 3.79. $C_{30}H_{36}N_2O_{10}P_2Ru$ calc.: C, 48.19; H, 4.85; N, 3.75; M, 748	IR: ν(C≡C) 2048s, ν(CO) 1718s, ν(NO) 1519s, 1340s, ν(PO) 1025vs(br) ^{1}H-NMR: 3.51 [t, J(HP) 12.0, 18H, OMe], 3.92 (s, 3H, CO_2Me), 4.90 (s, 5H, Cp), 7.07 [d, J(HH) 15.8, 1H, H_4], 7.26 [d, J(HH) 9.0, 2H, H_6], 7.56 [d, J(HH) 8.2, 2H, H_3], 7.77 [d, J(HH) 15.8, 1H, H_5], 8.04 [d, J(HH) 8.2, 2H, H_2], 8.17 [d, J(HH) 9.0, 2H, H_7]; ES MS: 749, $[M+H]^+$
21 Ru{C≡CC[=N($C_6H_4CO_2$Et-4)]CH=CHPh}(PPh_3)$_2$Cp yellow; m.p. 191–193°C (dec.) Anal. Found: C, 72.96; H, 5.13; N, 1.43. $C_{61}H_{49}NO_2P_2Ru.0.2CH_2Cl_2$ calc.: C, 72.77; H, 5.13; N, 1.39; M, 993 (solvate molecule observed in NMR)	IR: ν(C≡C) 2027s, ν(CO) 1702s ^{1}H-NMR: 1.11 [t, J(HH) 7, 3H, Me], 4.24 [q, J(HH) 7, 2H, CH_2], 4.37 (s, 5H, Cp), 7.00 (m, 18H, H_m+H_p of PPh_3), 7.14 (m, 3H, H_1+H_2), 7.41 [d, J(HH) 6.5, 2H, H_3], 7.54 (m, 12H, H_o of PPh_3), 7.63 [d, J(HH) 8.5, 2H, H_6 or H_7], 7.64 [d, J(HH) 16, 1H, H_4 or H_5], 7.92 [d, J(HH) 16, 1H, H_5 or H_4], 8.39 [d, J(HH) 8.5, 2H, H_7 or H_6] ES MS: 993, M^+; 731, $[M-PPh_3]^+$

Table 1 (Continued)

Compound and analysis	Spectroscopic data [a]
22 Ru{C≡CC(=NPh)CH=CH($C_{10}H_7$-1)}(PPh_3)$_2$Cp yellow; m.p. 177–179°C (dec.) Anal. Found: C, 76.61; H, 5.15; N, 1.44. $C_{62}H_{49}NP_2Ru$ calc.: C, 76.68; H, 5.09; N, 1.44; M, 971	IR: ν(C≡C) 2011s[^{1}H-NMR: 4.45 (s, 5H, Cp), 6.96 (m, 18H, H_m+H_p of PPh_3), 7.15 (m, 2H, H_2+H_{12}), 7.25 (m, H_1 or H_3, H_5+H_6; resonance coincides with C_6H_6), 7.41 [t, J(HH) 7.5, 2H, H_{11}], 7.60 (m, 12H, H_o of PPh_3), 7.70 [d, J(HH) 7, 2H, H_4 or H_7], 7.72 [d, J(HH) 16, 1H, H_8 or H_9], 7.73 [d, J(HH) 7, 1H, H_7 or H_4], 7.80 [d, J(HH) 7.5, 2H, H_{10}], 8.02 [d, J(HH) 8.5, 1H, H_3 or H_1], 8.72 [d, J(HH) 16, 1H, H_9 or H_8] FAB MS: 972, $[M+H]^+$; 709, $[M-PPh_3]^+$; 633, $[M+H-PPh_3-Ph]^+$; 429, $Ru(PPh_3)(C_5H_5)]^+$; 154, $[Ph_2]^+$
23 [4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-PhC_9H_5NH][BF_4] red; m.p. 177°C (dec.)	IR: ν(C≡C) 2009s, ν(BF) 1092vs(br) ^{1}H-NMR: 4.56 (s, 5H, Cp), 7.1–8.5 (m, 40H, aromatic H) (NH not observed) FAB MS: 922, $[M+2H-BF_4]^+$; 659, $[M+H-BF_4-PPh_3]^+$; 428, $[Ru(PPh_3)(C_5H_5)]^+$
24 [4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-$PhC_{13}H_8NH$][PF_6] black Anal. Found: C, 65.23; H, 4.30; N, 1.2. $C_{62}H_{48}F_6NP_3Ru.0.4CH_2Cl_2$ calc.: C, 65.23; H, 4.28; N, 1.22; M, 933 (solvate observed in NMR)	IR: ν(C≡C) 1988s, ν(PF) 841vs(br) ^{1}H-NMR: 4.65 (s, 5H, Cp), 7.0–8.4 (m, 42H, aromatic H), 11.55 (d, 1H, aromatic H) FAB MS: 969, $[M-H-PF_6]^+$; 708, $[M-PF_6-PPh_3\}^+$; 446, $[M-H-PF_6-2PPh_3]^+$; 154, $[Ph_2]^+$
25 [Ru{C≡CC(=NHPh)CH=CH($C_{10}H_7$-1)}(PPh_3)$_2$Cp][PF_6] red; m.p. 210–212°C (dec.) Anal. Found: C, 67.97; H, 4.77; N, 1.32. $C_{62}H_{50}F_6NP_3Ru$ calc.: C, 67.82; H, 4.58; N, 1.28; M, 972 (for material containing ~15% **22**, as shown by NMR)	IR: ν(C≡C) 1985s, ν(PF) 846vs(br) ^{1}H-NMR: 4.58 (s, 5H, Cp), 6.9-8.4 (m, 42H, aromatic H), 10.86 [s(br), 1H, NH] FAB MS: 972, $[M–PF_6]^+$; 710, $[M-PF_6-PPh_3]^+$; 429, $[Ru(PPh_3)(C_5H_5)]^+$; 154, $[Ph_2]^+$
26-OTf [4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-PhC_9H_5NMe][OTf] dark red; m.p. 134–135°C (dec.) Anal. Found: C, 64.21; H, 4.32; N, 1.24. $C_{60}H_{48}F_3NO_3P_2RuS.0.5CH_2Cl_2$ calc.: C, 64.56; H, 4.39; N, 1.24; M, 934 (CH_2Cl_2 solvate found in NMR)	IR: ν(C≡C) 2003s ^{1}H-NMR: 4.12 (s, 3H, Me), 4.55 (s, 5H, Cp), 6.7–8.5 (m, 40H, aromatic H) FAB MS: 934, $[M-SO_3CF_3]^+$; 672, $[M-SO_3CF_3-PPh_3]^+$; 154, $[Ph_2]^+$
26-PF_6 [4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-PhC_9H_5NMe][PF_6] red	IR: ν(C≡C) 1997s; ν(PF) 841vs(br) ^{1}H-NMR: 4.07 (s, 3H, Me), 4.55 (s, 5H, Cp), 6.7–8.5 (m, 40H, aromatic H) FAB MS: 934, $[M-PF_6]^+$; 672, $[M-PF_6-PPh_3]^+$; 154, $[Ph_2]^+$
27 [Ru{C≡CC[=N(C_6H_4Me-4){Au(PPh_3)}]CH=CH-(C_6H_4Me-4)}(PPh_3)$_2$Cp][PF_6] dark red Anal. Found: C, 59.61; H, 4.05; N, 1.19. $C_{78}H_{67}AuF_6NP_3Ru$ calc.: C, 60.31; H, 4.28; N, 0.90; M, 1408	IR: ν(C≡C) 2050s ^{1}H-NMR: 2.20, 2.22 (2 × s, 6H, Me), 4.38 (s, 5H, Cp), 6.95–7.46 (m, 56H, aromatic H) ES MS: 1408, M^+; 1144, $[M-PPh_3]^+$; 950, $[M-Au(PPh_3)]^+$; 844, $[M-2PPh_3]^+$; 684, $[M-Au-2PPh_3]^+$

[a] IR (cm^{-1}); NMR: δ, J (Hz); MS (m/z). See Scheme 2 for NMR numbering schemes.

ever, with PhN=$CHC_6H_4CO_2$Me-4, the PPh_3 complex **18** was identified as the quinoline, while the $P(OMe)_3$ derivative **11** is the azabutadienyl, as confirmed by an X-ray structure after provisional identification from the ^{1}H-NMR spectrum.

The reaction with PhN=CH(1-$C_{10}H_7$) afforded complex **22**, which was assigned the azabutadienyl structure on the basis of the $[M+H]^+$ ion at m/z 972 in the ES mass spectrum and by analysis of the ^{1}H-NMR spectrum which contains *trans* vinylic H atoms at δ 7.72 and 8.72, showing a typical J(HH) of 16 Hz.

2.3. Reactions with electrophiles

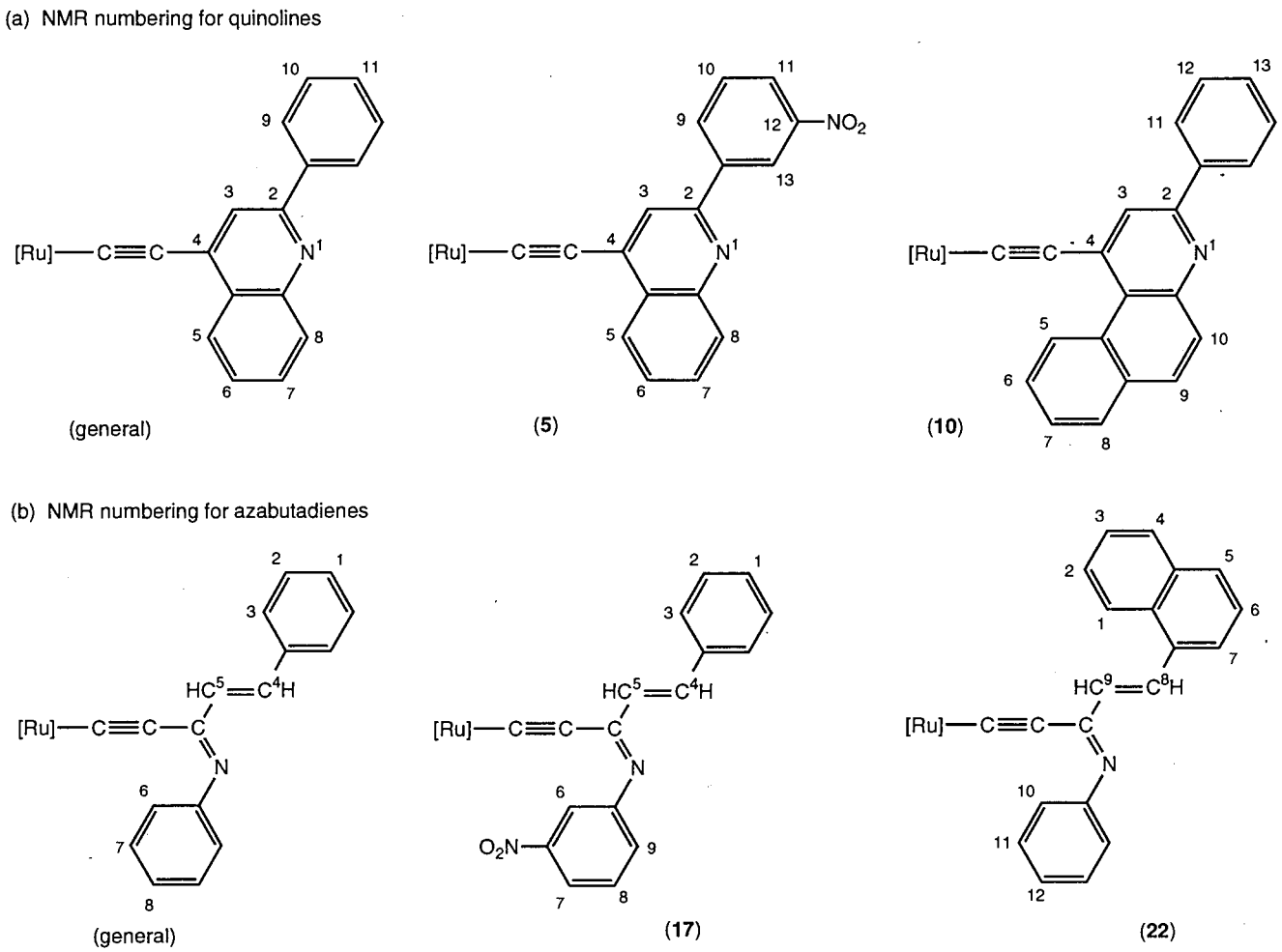
As mentioned above, these complexes are quite basic, even traces of water being sufficient to result in a colour change from yellow or orange to deep red. This colour change can be reversed by addition of a base and is consistent with a reversible protonation of the neutral complex (Scheme 4). In this regard, there is a similarity with the equilibrium that can be established between alkynyl and vinylidene complexes, e.g. the pK_a of Fe(C≡CMe)(PMe_3)$_2$Cp is 7.78 [9]. Given the presence of the alkynyl group in the present complexes, we were interested to determine whether C(2) or the N atom is the more basic centre. Protonation of complexes **1**, **10** or **22** with HBF_4 or HPF_6 afforded cationic complexes **23**–**25**, of which the latter exhibited an NH resonance at δ 10.86. In addition, the site of protonation as the N atom was further suggested by the presence of ν(C≡C) bands in the IR spectra near 1990 cm^{-1}. The lower frequency, compared with the absorption in **1**, suggests some contribution from the allenylidene mesomer depicted. However, the X-ray structural data gives little support for this idea, the distances within the Ru–C(12)–C(11)–C(1) fragment (albeit imprecisely) being consistent with those found in the neutral analogues. In no case is there any evidence for electrophilic addition to C_b of the alkynyl group.

Methylation of **1** was achieved either with methyl triflate or with MeI in the presence of NH_4PF_6, from which reactions the OTf and PF_6 salts, respectively, of the *N*-methylquinolinium cation **26** were obtained. The retention of the ν(C≡C) absorption at 2003 cm^{-1} serves to indicate that the N atom is the site of methylation in this case also.

Finally, auration of azabutadiene **12** was achieved by addition of $AuCl(PPh_3)/TlPF_6$ to the neutral complex. A rapid reaction ensued, with precipitation of TlCl. From the resulting solution, dark red **27** was isolated, the IR spectrum of which contained ν(C≡C) at 2050 cm^{-1}, again suggesting that the N atom is the site of addition of the $[Au(PPh_3)]^+$ fragment.

2.4. Molecular structures of quinoline and azabutadiene complexes

The crystal and molecular structures of complexes **1**–**3**, **6**, **8**, **10**, **15**, **17** and **23** have been determined by single-crystal X-ray methods; those of **2** and **17** were reported in our original communication, but are discussed here for completeness, atoms being renumbered for consistency. Figs. 1–4 contain plots of molecules of the quinolines **1**–**3**, **6** and **8**, benzoquinoline **10**, azabutadiene complexes **15** and **17** and the cation of **23**. The structural parameters for all complexes determined are collected in Table 2. The metal–ligand fragment $Ru(C{\equiv}C{-})(PR_3)_2Cp$ (R = Ph or OMe) is common to all complexes and is similar to those found to a host of similar complexes. Thus, the familiar distorted octahedral geometry of the Ru atom is achieved by the tridentate Cp ligand [Ru–C(Cp) ranges between 2.20(1) and 2.265(3) Å, average for all structures 2.23 Å, with no significant differences between the PPh_3 and $P(OMe)_3$ complexes], the two PR_3 ligands and C(12) of the alkynyl groups. The Ru–PPh_3 distances are between 2.28(1) and 2.319(2) Å (average 2.30 Å), the Ru–$P(OMe)_3$ distances being appreciably shorter at 2.2113–2.2301(9) Å, while the Ru–C(12) separations [ignoring one imprecise value of 1.97(3) Å] are found between 1.978(8) and 2.015(3) Å. The C(12)–C(11) triple bond length lies between 1.197(4) and 1.220(3) Å. Angles at Ru range between 97.25(8)–102.3(4)° (PPh_3)

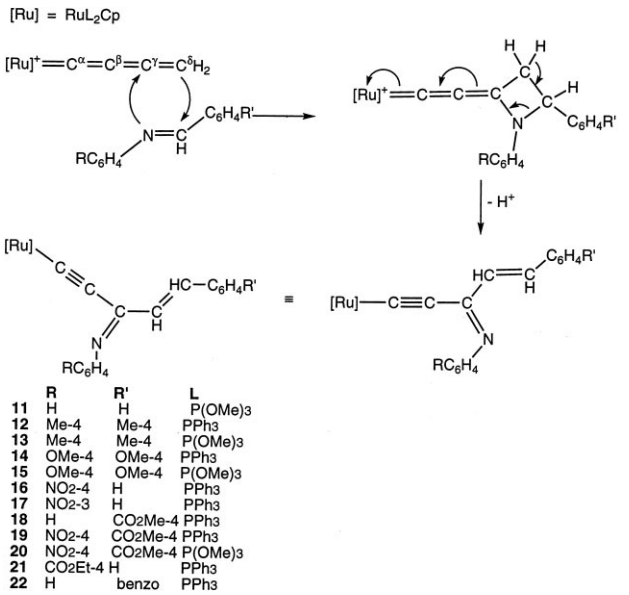


Scheme 2.

Table 2
Selected structural parameters

Complex	**1**	**2**	**3**	**6**	**8**	**10**	**15**	**17**	**23**	**28** $P2_1/c$ form (2 molecules)	**28** $Pna2_1$ form (Ref. [12])
Q or A	Q	Q	Q	Q	Q	Q	A	A	Q	(Cl)	(Cl)
R	H	Me-6	H	H	OMe-6	Benzo	OMe-4	NO_2-3	H	–	–
R′	H	H	NO_2-4	CO_2Me-4	NO_2-4	H	OMe-4	H	H	–	–
R″ in PR''_3	Ph	Ph	Ph	OMe	OMe	Ph	Ph	Ph	Ph	OMe	OMe
Bond distances (Å)											
Ru–P(1)	2.2954(5)	2.2966(7)	2.2971(8)	2.2113(8)	2.2199(7)	2.293(1)	2.215(1)	2.293(2)	2.30(1)	2.225(1) 2.2301(9)	2.234(2)
Ru–P(2)	2.3030(6)	2.3079(2)	2.2945(8)	2.2287(8)	2.2114(8)	2.295(1)	2.2133(7)	2.319(2)	2.28(1)	2.2285(7) 2.2230(8)	2.199(3)
Ru–C(cp)	2.235– 2.252(2)	2.224(3)– 2.259(4)	2.219(4)– 2.253(3)	2.229– 2.261(4)	2.221– 2.253(3)	2.223– 2.251(4)	2.238(5)– 2.265(3)	2.21(1)– 2.240(7)	2.20– 2.24(2)	2.176(3)– 2.241(3)	
(av.)	2.24_2	2.24_1	2.23_7	2.24_7	2.23_8	2.23_8	2.25_0	2.22_6	2.22	2.21_7	2.28_2
Ru–C(12)	1.995(2)	1.997(3)	1.990(2)	2.012(3)	2.015(2)	2.004(4)	2.001(3)	1.978(8)	1.97(3)	2.4307(8), 2.434(1) [a]	2.393(3) [a]
C(12)–C(11)	1.220(3)	1.197(4)	1.219(4)	1.203(4)	1.197(3)	1.202(5)	1.220(4)	1.22(1)	1.21(4)	–	
C(11)–C(1)	1.422(2)	1.431(4)	1.428(4)	1.432(4)	1.436(3)	1.431(5)	1.436(4)	1.43(1)	1.41(4)	–	
C(1)–C(2)	–	–	–	–	–	–	1.469(3)	1.48(1)	–	–	
C(1)–N(4)	–	–	–	–	–	–	1.295(3)	1.280(9)	–	–	
C(2)–C(3)	–	–	–	–	–	–	1.320(4)	1.32(1)	–	–	
Bond angles (°)											
P(1)–Ru–P(2)	101.19(2)	99.00(3)	100.30(3)	94.10(3)	95.79(2)	101.44(4)	93.89(3)	97.25(8)	102.3(4)	94.03(3), 93.96(3)	91.2(1)
P(1)–Ru–C(12)	91.06(6)	90.30(8)	89.72(9)	87.05(8)	91.36(6)	87.5(1)	89.55(9)	89.7(2)	87(1)	92.28(3), 89.85(4) [a]	91.8(1) [a]
P(2)–Ru–C(12)	87.65(6)	88.78(7)	89.50(8)	91.11(8)	89.13(6)	89.1(1)	90.22(7)	96.0(2)	88(1)	93.14(3), 90.92(3) [a]	95.0(1) [a]
Ru–C(12)–C(11)	173.9(2)	175.9(3)	174.0(2)	176.8(2)	173.2(2)	174.3(3)	173.9(2)	171.2(6)	175(3)	–	
C(12)–C(11)–C(1)	171.0(2)	169.4(3)	170.7(3)	176.9(3)	174.6(2)	173.8(4)	178.6(3)	176.9(6)	174(3)	–	
C(11)–C(1)–C(2)	–	–	–	–	–	–	118.5(2)	119.6(6)	–	–	
C(11)–C(1)–N(4)	–	–	–	–	–	–	125.2(2)	124.2(7)	–	–	
C(2)–C(1)–N(4)	–	–	–	–	–	–	116.2(2)	116.0(8)	–	–	

[a] For C(12), read Cl.+Ref. [12]. For **15** and **17**: angles at N(4) are 120.3(2), 119.4(7)°; angles at C(2) are 125.6(2), 124.1(8)°; angles at C(3) are 126.12(3), 127.2(8)°.

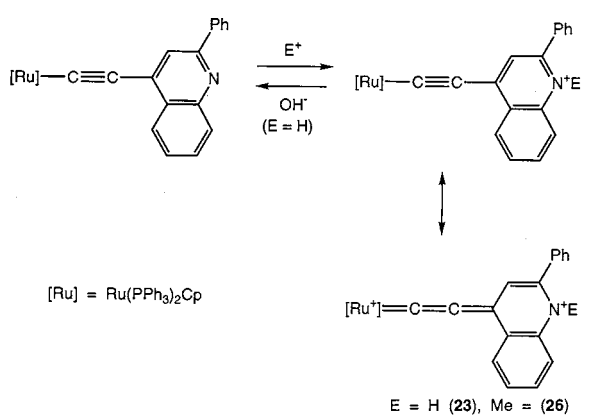


	R	R'	L
11	H	H	P(OMe)3
12	Me-4	Me-4	PPh3
13	Me-4	Me-4	P(OMe)3
14	OMe-4	OMe-4	PPh3
15	OMe-4	OMe-4	P(OMe)3
16	NO2-4	H	PPh3
17	NO2-3	H	PPh3
18	H	CO2Me-4	PPh3
19	NO2-4	CO2Me-4	PPh3
20	NO2-4	CO2Me-4	P(OMe)3
21	CO2Et-4	H	PPh3
22	H	benzo	PPh3

Scheme 3.

and 94.10(3)–95.79(2)° [P(OMe)$_3$] [P–Ru–P], paralleling the diminution in Ru–P distances, and 87.05(8)–96.0(2)° [P–Ru–C(12)]. The Ru–C(12)–C(11) group is close to linear with angles at C(12) and C(11) of between 173.2(2)–176.8(2) and 169.4–178.6(3)°, respectively. Comparison with the structure of Ru(C≡CPh)(PPh$_3$)$_2$Cp [10] shows that the structural parameters of the present complexes do not differ significantly, similar conclusions being drawn from a study of other ethynyl–ruthenium complexes containing extended unsaturated substituents of relevance to their non-linear optical behaviour [11]. Further detailed discussion is unwarranted as a result of the differing precisions of the various structural determinations.

The presence of the quinoline nucleus is quite evident in **1**–**3**, **6**, **8** and **10**, with the location of the nitrogen atom consistent with that expected from the precursor imines. The structural determinations also confirm that the *C*-aryl substituent is in the 2-position in the quinoline, and the formation of the tricyclic benzo[*h*]-quinoline nucleus in **10**. The close proximity of H(13) to the C≡C triple bond, mentioned above, also affects the intra-ring angles, C(11)–C(1)–C(2, 10) being 117.7(3) and 125.0(3)°, respectively. As can be seen from Fig. 2, the benzoquinoline nucleus is non-planar. The peripheral planes have dihedrals of 8.5(1), 7.2(1)° to the central plane, with a dihedral between them of 15.2(1)°, the bulk of the distortion being in the peripheral plane pendant to the acetylide and the central plane (χ^2 433, 422, cf. the outer plane 78.5°). The pendant acetylide atom lies 0.254(6) Å out of the attached ring plane.



Scheme 4.

In contrast, complexes **15** and **17** (Fig. 3) contain the Ru(C≡C–)(PR$_3$)$_2$Cp fragment attached to C(2) of an N=CC=C chain that has a direct relationship to the parent imine. In the two structures, the substitution pattern of the imine is preserved and for **15**, at least, all H atoms have also been resolved. The C=N and C=C bonds are within the expected ranges and angles at the atoms of the chains are 119.4(7)° or greater, consistent with the expected sp^2 hybridisation of these atoms.

The imprecisely determined structure of the protonated complex **23** (Fig. 4) shows a similar metal fragment to those found in the neutral complexes: the presence of the charge does not affect the bond parameters which are consistent with the site of protonation being the N atom of the quinoline, the protonic hydrogen not being directly located in the structural determination; the crystal lattice contains the BF_4 anion.

In the course of these studies, the structure of a new modification of RuCl{P(OMe)$_3$}$_2$Cp, a precursor of the related butatrienylidene cation, was also determined (Fig. 5). In comparison with that of the present monoclinic ($P2_1/c$) form, it shows a significant difference in the average Ru–P distance (2.21_7 Å compared with 2.28_2 Å found for the orthorhombic ($Pna2_1$) form previously reported [12]). The latter study was recorded using Cu–K$_\alpha$ radiation, resulting in very large absorption effects that may account for the anomaly. The Ru–Cl distance is substantially longer in the present form [2.4307(8) vs. 2.393(3) Å]. Significant differences in the angles subtended at Ru by the Cl and P atoms [92.28(3), 93.15(3), 94.02(3) vs. 91.8(1), 95.0(1), 91.2(1)°] are also found.

3. Discussion

The chemistry described above is consistent with the intermediacy of the butatrienylidene complex in these reactions; separate experiments demonstrated that the performed complex, obtained from buta-1,3-diyne and [Ru(THF)(PPh$_3$)$_2$Cp]$^+$, reacts with the imines to afford the same products. The formation of the quinoline or azabutadiene appears to be a function of the sub-

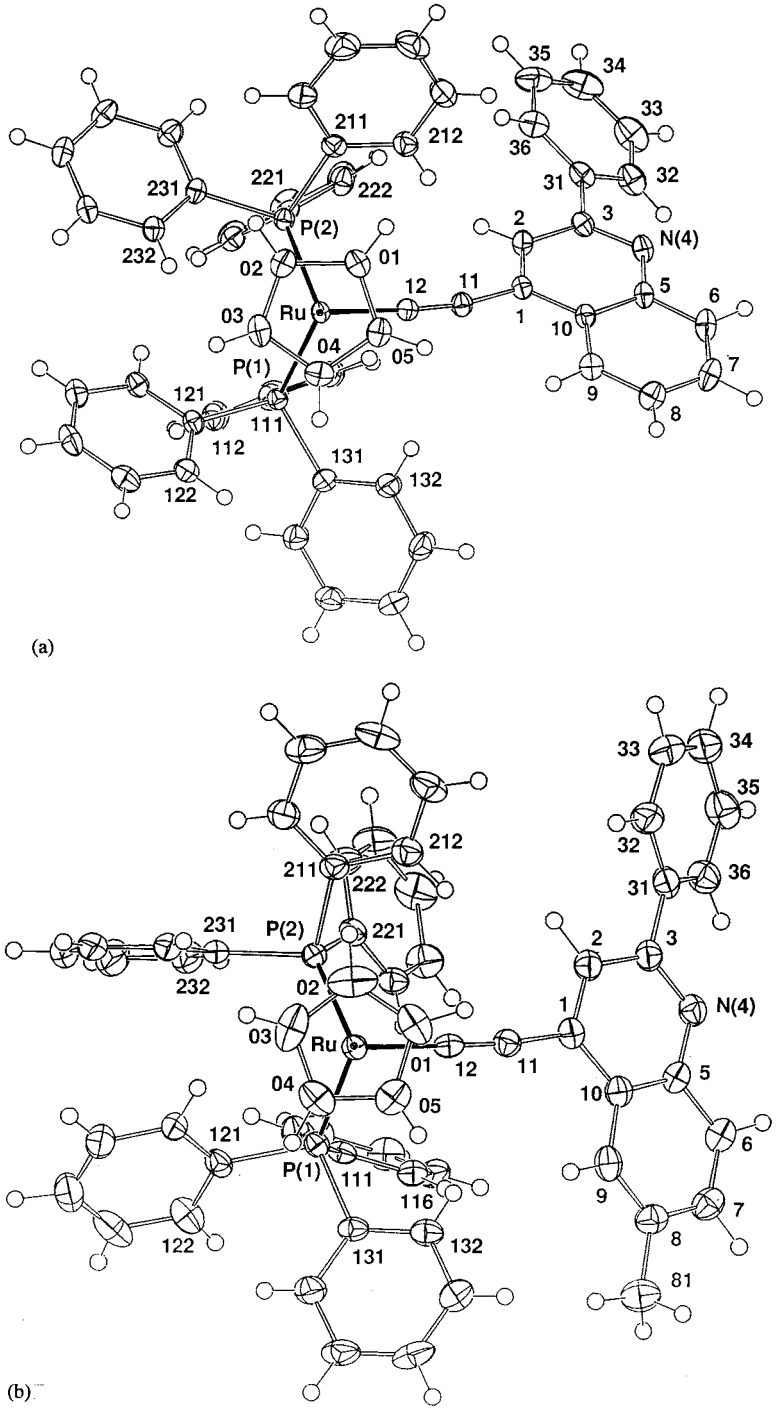
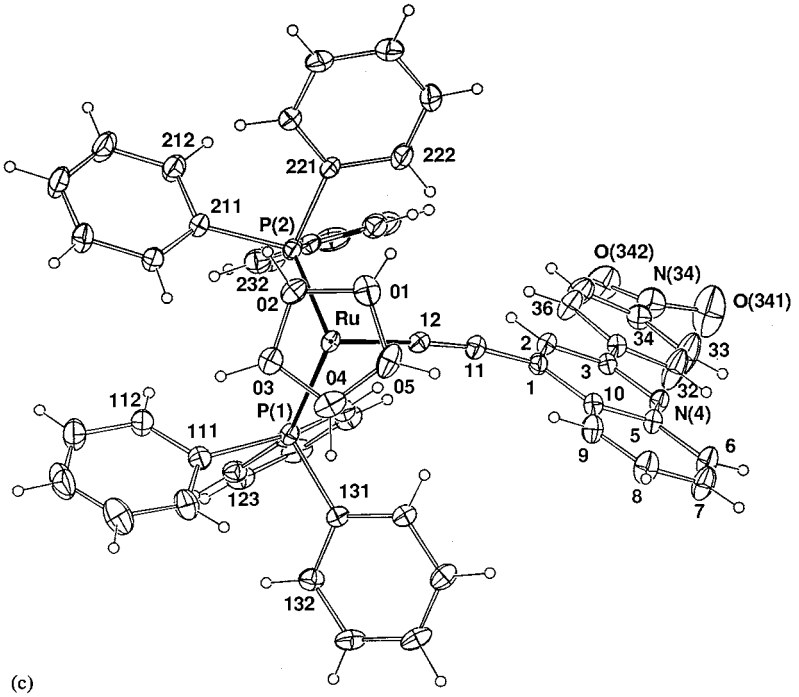


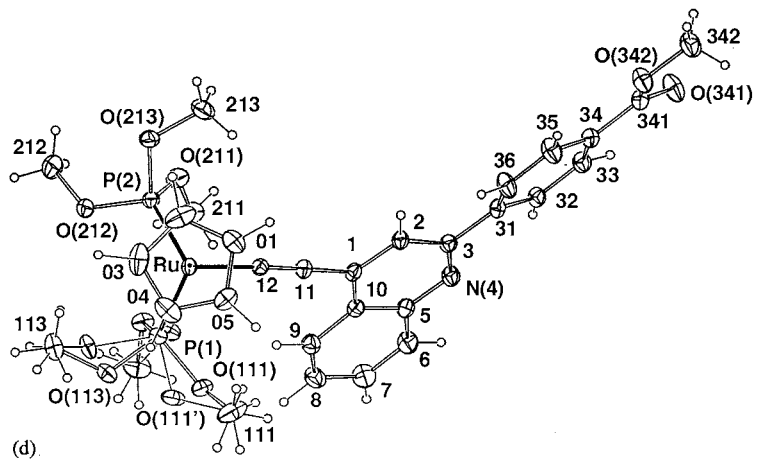
Fig. 1. Plot of a molecule of (a) 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-PhC_9H_5N (**1**); (b) 4-{Cp(PPh_3)$_2$Ru(C≡C)}-6-Me-2-PhC_9H_4N (**2**); (c) 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-(4-$NO_2C_6H_4$)C_9H_5N (**3**); (d) 4-{Cp[P($OMe)_3$]$_2$Ru(C≡C)}-2-(4-$MeO_2CC_6H_4$)C_9H_5N (**6**) and (e) 4-{Cp[P($OMe)_3$]$_2$-Ru(C≡C)}-6-MeO-2-(4-$NO_2C_6H_4$)C_9H_4N (**8**), showing the atom numbering schemes. In this and subsequent Figures, non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å. Settings of the figures correspond to Scheme 2.

stituents present on the imine and the metal-bonded *P*-ligand, rather than whether or not the reaction is carried out with performed butatrienylidene complex.

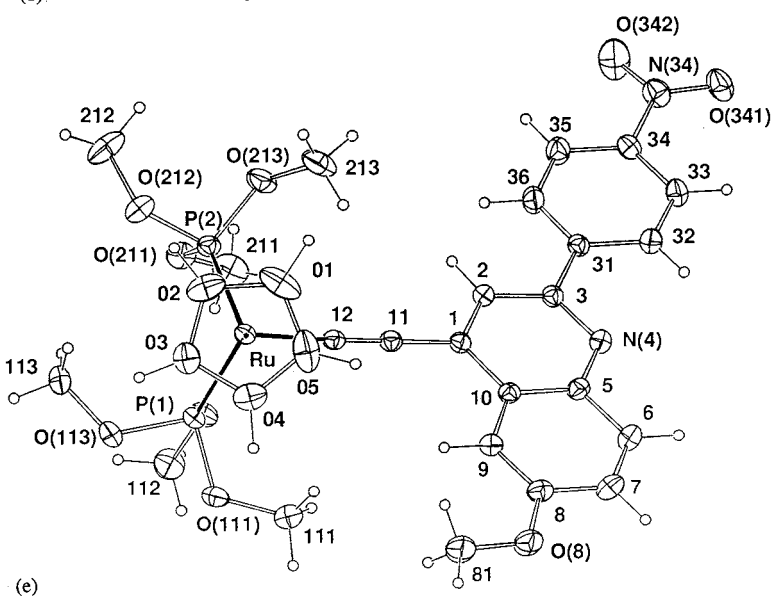
The formation of the products can be understood in terms of reaction of the imine with carbons of differing electronic character, although at this stage we are not able to determine the sequence of bond formation. Thus, C_δ of the butatrienylidene ligand is electron rich and would be expected to attack the imine at the methine carbon. Subsequent reaction of C_γ, which is electron deficient, might occur at the electron-rich *ortho* carbon of the *N*-aryl group or with the imine N atom.



(c)



(d)



(e)

Fig. 1. (*Continued*)

In the former case, formation of a new C–C bond results in formation of the bicyclic *N*-heterocycle, dihydroquinoline, aromatisation of which drives the formal elimination of 2H (Scheme 1). By virtue of the *C*-aryl group, substituents on the *N*-aryl group and the metal–ligand fragment which becomes attached to C(6), a variety of polysubstituted quinolines may be formed by this reaction.

The alternative route is followed when electron-withdrawing substituents are present at the *meta* position of the *N*-aryl group. These reduce the nucleophilic character of the *ortho* carbon, resulting in cycloaddition of the C_γ=C_δ unit of the butatrienylidene to the N=CH system of the imine and generating a four-membered ring (Scheme 2). The observed product is formed by a subsequent ring-opening reaction, which is reminiscent of and no doubt related to the similar reactions found between alkynyl–metal complexes and electron-deficient olefins [12–14]. The reaction can be directed along this pathway if the electron density in the *N*-aryl group is reduced, for example, by the presence of electron-withdrawing groups such as NO_2 or CO_2Me. However, this is not an exclusive condition, since formation of azabutadienes was also found for methyl- and methoxy-substituted systems.

The formation of a quinoline with PhN=CHPh in the PPh_3 system, but the azabutadiene with the $P(OMe)_3$ system, may be related to the degree of electron richness of the metal fragment and thereby to the degree of transfer of electron density along the chain. It is generally accepted that PPh_3 is a much more basic ligand that $P(OMe)_3$, so that in the former case, the metal centre is more electron rich. In turn, the expectation would be that C_β and C_δ of the unsaturated carbon chain would have more nucleophilic character. That this is not the whole story, however, can be seen by comparing these results with those obtained with 4-RC_6H_4N=CHC_6H_4R-4 (R = Me, OMe), which uniformly produce the azabutadienes. Further work is necessary to understand fully the course of these interesting reactions and also to devise suitable methods for removal of the metal-containing fragment.

Related chemistry has been described. The reactions between M(=C=CR_2)L_n (ML_n = $W(CO)_5$, R = Ph [15]; $Mn(CO)_2Cp$, R_2=H_2, HMe, HPh [16]; $Re(CO)_2Cp$, R=H [16]; $[Fe(CO)(L)Cp]^+$, L = PPh_3, $P(OMe)_3$; R = H, Me [17]) and RN=CHPh (R = Me, Ph) resulted in cycloaddition of the imine to the C_α=C_β double bond to give the corresponding [2 + 2] cycloaddition products. The likely pathway is via initial addition of C_α to the N atom, followed by ring closure. η^4-Isoquinolinium derivatives have been obtained from alkynes and cycloruthenated complexes derived from dimethylaminomethylbenzenes [18]. Quinoline-2-thiolates have been constructed by cycloaddition of electron deficient alkynes to isothiocyanates [19].

4. Conclusions

The possible intermediacy of cationic butatrienylidene complexes as the products from buta-1,3-diyne and $[Ru(THF)(PR_3)_2Cp]^+$ is further shown in their subsequent reactions with arylimines which, according to substituent, afford either quinoline or azabutadiene derivatives. The formation of these products can be partially rationalised in terms of cycloaddition of C_γ

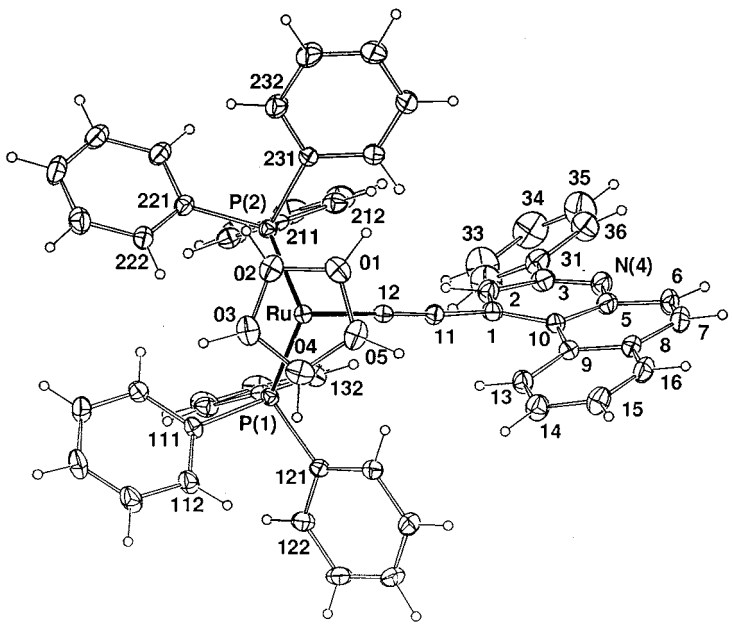


Fig. 2. Plot of a molecule of 4-{$Cp(PPh_3)_2Ru(C{\equiv}C)$}-2-$PhC_{13}H_8N$ (**10**), showing atom numbering scheme.

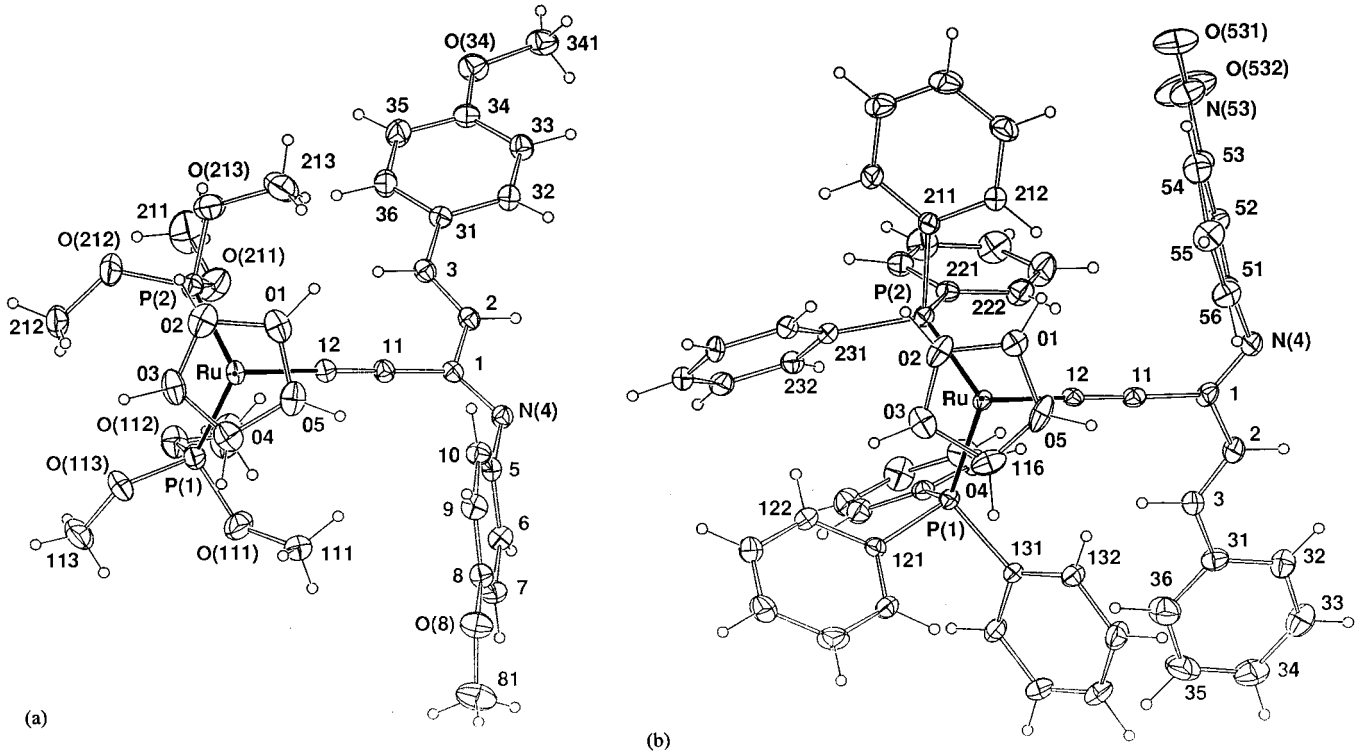


Fig. 3. Plots of a molecule of (a) Ru{C≡CC[=N(C_6H_4OMe-4)]CH=CH(C_6H_4OMe-4)}{P(OMe)$_3$}$_2$Cp (**15**) and (b) Ru{C≡CC[=N($C_6H_4NO_2$-3)]CH=CHPh}(PPh_3)$_2$Cp (**17**), showing atom numbering schemes.

and C_δ of the unsaturated carbene to either the unsaturated N=CH group followed by ring-opening, or by attack at the imine carbon and addition to the *ortho* carbon of the *N*-aryl group. These reactions extend the range of reactions reported for this unsaturated carbene ligand, which also include addition of nucleophiles to C_γ to give alkenylvinylidenes that may rearrange to allenylidenes [7]. More work is required, however, to delineate the precise effects of substituents and nature of the metal centre on the course of these reactions.

5. Experimental

5.1. General reaction conditions

All reactions were carried out under dry, high-purity 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, B.C. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

5.2. Instrumentation

Analytical and spectroscopic data are collected in Table 1. IR: Perkin–Elmer 1700X FT-IR; 683 double beam, NaCl optics; NMR: Gemini 200 (^{1}H-NMR at 199.975 MHz, ^{13}C-NMR at 50.289 MHz; Bruker ACP300 (^{1}H-NMR at 300.13 MHz, ^{13}C-NMR at 75.47 MHz). FAB MS: VG ZAB 2HF, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV. Electrospray (ES) MS: The samples were dissolved in methanol, unless otherwise indicated, and injected into a 10 μl injection loop attached to a VG Platform II instrument or directly infused, using a syringe pump, into a Finnegan LCQ spectrometer. Nitrogen was used as the drying and nebulising gas. Samples were examined over a range of cone voltages (20–90 V) to find the best conditions in the former. Chemical aids to ionisation are indicated where used [20].

5.3. Reagents

$AgPF_6$ (Pennwalt) and KO^{t}Bu (Merck) were used as received. The compounds RuCl(PPh_3)$_2$Cp [21], [Ru(NCMe)(PPh_3)$_2$Cp][PF_6] [22], AuCl(PPh_3) [23], HC≡CC≡CH [24] and the imines ArN=CHAr′ [25] were prepared using the cited literature methods.

5.4. General method of preparation

The complexes RuCl(PPh_3)$_2$Cp (200 mg, 0.28 mmol) or RuCl{P(OMe)$_3$}$_2$Cp (125 mg, 0.28 mmol) in THF

(50 ml) was treated with $AgPF_6$ (70 mg, 0.28 mmol) and stirred at room temperature (r.t.) for 5 min. The resulting orange solution was cooled to −94°C (MeOH slush bath), then filtered (from precipitated AgCl; however, the reaction proceeds in similar yield if the AgCl is not removed) into a second flask containing buta-1,3-diyne (0.3 ml of 1.1 M solution in THF, large excess) and the imine (0.56 mmol) in THF (5 ml) at the same temperature. The cold bath was removed and the mixture allowed to warm to r.t. During this time the colour of the solution changed from orange to deep red. The solution was then treated with KOBu^t (40 mg); after 30 min, the solvent was removed. A CH_2Cl_2 extract of the residue was purified by column chromatography on Al_2O_3, elution with Et_2O giving a deep yellow band, which afforded the pure product after crystallisation (Et_2O–pentane). In some cases, further purification could be achieved by TLC (silica gel; 3:2 hexane–CH_2Cl_2).

In this manner were prepared:

1. 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-PhC_9H_5N (**1**), from pentane–Et_2O (41%). In this case, extraction of the residue (after removal of solvent) with hexane (2 ml) and evaporation gave a pale yellow solid. A THF solution (0.5 ml) of this residue was analysed by GLC (Pye Series 104 Chromatograph, 15% FFAP column, 200°C, FID detector), both NHPh(CH_2Ph) and unreacted PhN=CHPh being confirmed by comparison of retention times with those of standard samples.
2. 4-{Cp(PPh_3)$_2$Ru(C≡C)}-6-Me-2-PhC_9H_4N (**2**), from pentane–Et_2O (26%).
3. 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-(4-$NO_2C_6H_4$)C_9H_5N (**3**), from CH_2Cl_2–hexane (54%). If a solution of **3** in benzene (10 mg/2 ml) was left under sunlight for 30 min, the complex is partly decomposed, to give a black solid.
4. 4-{Cp[P(OMe)$_3$]$_2$Ru(C≡C)}-2-(4-$NO_2C_6H_4$)C_9H_5N (**4**) (31%).
5. 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-(3-$NO_2C_6H_4$)C_9H_5N (**5**), from CH_2Cl_2–hexane (40%). This complex required further purification by chromatography on Al_2O_3.
6. 4-{Cp[P(OMe)$_3$]$_2$Ru(C≡C)}-2-(4-$MeO_2CC_6H_4$)C_9H_5N (**6**), from THF–pentane (22 mg, 6%; in this case, difficulties in separation from residual imine were experienced).
7. 4-{Cp(PPh_3)$_2$Ru(C≡C)}-6-MeO-2-(4-$NO_2C_6H_4$)C_9H_4N (**7**), from CH_2Cl_2–hexane after rechromatography (41%).
8. 4-{Cp[P(OMe)$_3$]$_2$Ru(C≡C)}-6-MeO-2-(4-$NO_2C_6H_4$)C_9H_4N (**8**), from CH_2Cl_2–hexane (28%).
9. 4-{Cp(PPh_3)$_2$Ru(C≡C)}-(5/7)-Cl-2-PhC_9H_4N (**9**), from Et_2O–hexane (39%). The ^{1}H-NMR spectrum (C_6D_6) showed the presence of two isomers (**9a** and **9b**) in ~4:1 ratio which could not be separated by chromatography or by recrystallization. Attempts to grow single crystals were unsuccessful. The sample decomposes slowly in solution, even in the dark.
10. 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-Ph$C_{13}H_8N$ (**10**), from THF–hexane (30%).
11. Ru{C≡CC(=NPh)CH=CHPh}{P(OMe)$_3$}$_2$Cp (**11**), from CH_2Cl_2–hexane (22%).

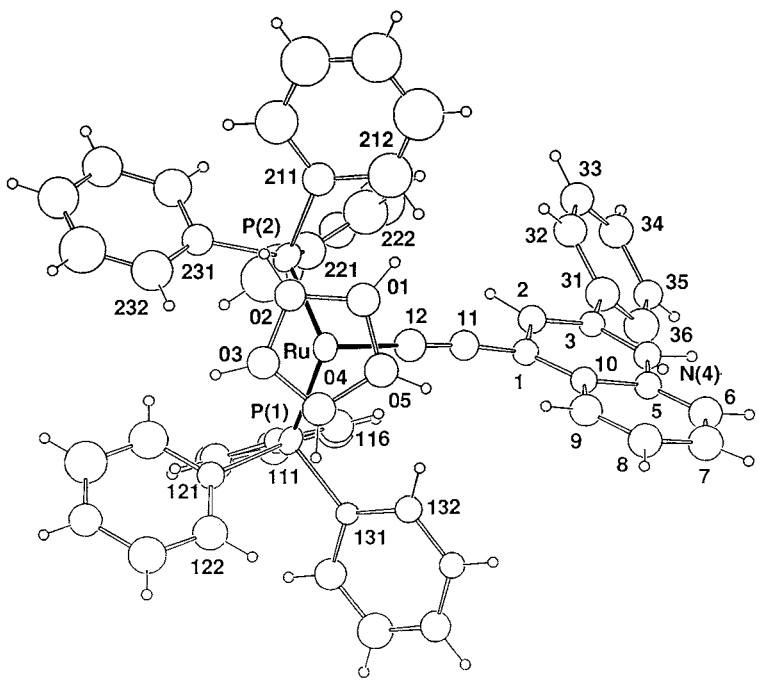


Fig. 4. Plot of the cation of [4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-PhC_9H_5NH][BF_4] (**23**), showing atom numbering scheme.

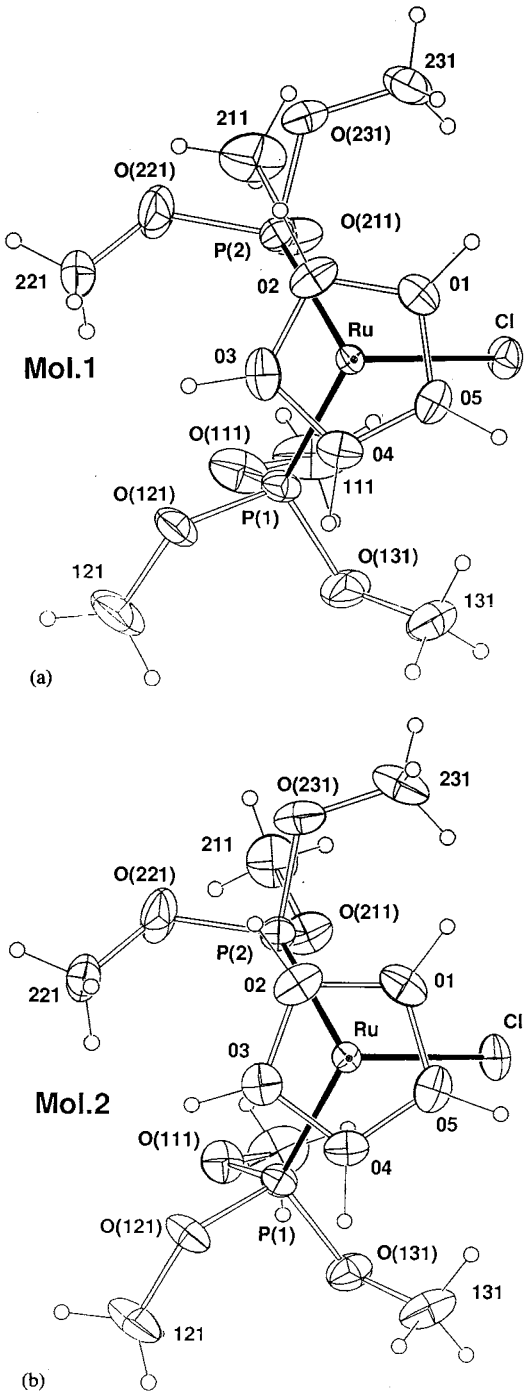


Fig. 5. Plots of the two independent molecules of RuCl{P-(OMe)$_3$}$_2$Cp (**28**), showing atom numbering scheme.

12. Ru{C≡CC[=N(C_6H_4Me-4)]CH=CH(C_6H_4Me-4)}-(PPh_3)$_2$Cp (**12**), from CH_2Cl_2–hexane (29%).
13. Ru{C≡CC[=N(C_6H_4Me-4)]CH=CH(C_6H_4Me-4)}-{P(OMe)$_3$}$_2$Cp (**13**), from light petroleum–CH_2Cl_2 (28%).
14. Ru{C≡CC[= N(C_6H_4OMe-4)]CH=CH(C_6H_4OMe-4)}(PPh_3)$_2$Cp (**14**), from CH_2Cl_2–MeOH (39%).
15. Ru{C≡CC[=N(C_6H_4OMe - 4)]CH=CH(C_6H_4OMe - 4)}{P(OMe)$_3$}$_2$Cp (**15**) from CH_2Cl_2–hexane (25%).
16. Ru{C≡CC[=N($C_6H_4NO_2$ - 4)]CH=CHPh}(PPh_3)$_2$Cp (**16**), from CH_2Cl_2–hexane (34%).
17. Ru{C≡CC[=N($C_6H_4NO_2$ - 3)]CH=CHPh}(PPh_3)$_2$Cp (**17**), from Et_2O–hexane in the dark (29%). This compound is sunlight/UV-light sensitive, changing to an unidentified blue species after photolysis.
18. Ru{C≡CC(=NPh)CH=CH($C_6H_4CO_2$Me - 4)}(PP - h_3)$_2$Cp (**18**), from CH_2Cl_2–hexane (70%).
19. Ru{C≡CC[=N($C_6H_4NO_2$-4)]CH=CH($C_6H_4CO_2$Me-4)}(PPh_3)$_2$Cp (**19**), from CH_2Cl_2–hexane (32%).
20. Ru{C≡CC[=N($C_6H_4NO_2$-4)]CH=CH($C_6H_4CO_2$Me-4)}{P(OMe)$_3$}$_2$Cp (**20**), from CH_2Cl_2–hexane (24%).
21. Ru{C≡CC[=N($C_6H_4CO_2$Et-4)]CH=CHPh}(PPh_3)$_2$-Cp (**21**), from CH_2Cl_2–hexane after rechromatography (37%).
22. Ru{C≡CC(=NPh)CH=CH($C_{10}H_7$-1)}(PPh_3)$_2$C (**22**), precipitated from Et_2O with C_6H_6 (34%).

5.5. Protonation

5.5.1. [4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-PhC_9H_5NH][BF_4] (23)

A solution of HBF_4 (5 mg, 0.057 mmol) in THF (4 ml) was added to a solution of **1** (50 mg, 0.054 mmol) in THF (5 ml). The solution turned red and the solvent was evaporated to give [4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-PhC_9H_5NH][BF_4] (**23**) (50 mg, 84%) as a red solid after washing the solid residue three times with Et_2O.

5.5.2. [4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-$PhC_{13}H_8NH$][PF_6] (24)

Two drops of HPF_6 in Et_2O were added to a solution of 4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-$PhC_{13}H_8N$ (**10**) (50 mg, 0.052 mmol) in benzene (10 ml). The solution became red immediately, and a precipitate formed. After evaporation, dissolution in CH_2Cl_2 and precipitation with hexane, [4-{Cp(PPh_3)$_2$Ru(C≡C)}-2-$PhC_{13}H_8NH$][PF_6] (**24**) (90%) was obtained as a black solid.

5.5.3. [Ru{C≡CC(=NHPh)CH=CH($C_{10}H_7$-1)}-(PPh_3)$_2$Cp][PF_6] (25)

This complex was prepared in 73% yield from Ru{C≡CC(=NPh)CH=CH($C_{10}H_7$-1)}(PPh_3)$_2$Cp (**22**) by the method described above for **24**. Analytical and NMR data are consistent with the presence of some neutral **22** in the product.

Table 3
Crystal data and refinement details for complexes

Compound	**1**	**2**	**3**	**6**	**8**	**10**	**15**	**17**	**23**	**28**
Diffractometer [a]	AXS	AXS	AXS	AXS	AXS	CAD4	AXS	CAD4	CAD4	AXS
Formula	$C_{58}H_{45}NP_2Ru$	$C_{59}H_{47}NP_2Ru$	$C_{58}H_{44}N_2O_2P_2Ru$	$C_{30}H_{35}NO_8P_2Ru$	$C_{29}H_{34}N_2O_9P_2Ru$	$C_{62}H_{47}NP_2Ru\cdot C_4H_8O$	$C_{30}H_{39}NO_8P_2Ru\cdot 0.5CH_2Cl_2$	$C_{58}H_{46}N_2O_2P_2Ru$	$C_{58}H_{46}NP_2Ru^+\cdot BF_4^-\cdot Et_2O$	$C_{11}H_{23}ClO_6P_2Ru$
M_w	919.0	933.1	964.0	700.6	717.6	1041.2	747.1	966.0	1081.0	449.8
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	15.958(1)	11.242(1)	13.023(2)	8.216(1)	19.947(4)	11.934(3)	10.0633(8)	19.787(8)	13.697(11)	22.433(1)
b (Å)	16.980(1)	11.402(1)	13.263(2)	12.516(2)	7.867(2)	14.724(3)	12.1873(9)	11.684(3)	23.764(20)	9.3819(7)
c (Å)	16.553(1)	17.899(2)	14.554(2)	15.741(3)	20.598(4)	31.157(6)	14.9825(10)	10.688(3)	17.038(9)	18.411(1)
α (°)		87.703(2)	80.841(2)	78.169(3)			90.796(1)	98.26(2)		
β (°)	96.681(1)	82.419(2)	81.407(2)	88.641(3)	100.875(3)	106.03(2)	108.182(1)	101.18(3)	100.37(6)	110.568(1)
γ (°)		86.529(2)	69.541(2)	77.320(3)			102.009(1)	101.39(3)		
V (Å^3)	4455	2269	2313	1545	3174	5262	1701	2333	5455	3628
Z	4	2	2	2	4	4	2	2	4	8
$D_{calc.}$ (g cm^{-3})	1.37_0	1.36_6	1.38	1.50_6	1.50_1	1.31_4	1.45_8	1.37_5	1.31_5	1.64_7
Crystal size (mm)	$0.20\times0.15\times0.12$	$0.24\times0.20\times0.07$	$0.30\times0.18\times0.12$	$0.25\times0.17\times0.10$	$0.33\times0.25\times0.11$	$0.75\times0.52\times0.20$	$0.61\times0.51\times0.30$	$0.40\times0.12\times0.24$	$0.08\times0.16\times0.14$	$0.55\times0.18\times0.07$
T [a] (min, max)	0.71, 0.86	0.93, 0.98	0.81, 0.91	0.43, 0.56	0.80, 0.89	0.82, 0.93	0.69, 0.83	0.87, 0.94	0.96, 0.97	0.61, 0.89
μ (cm^{-1})	4.6	4.6	4.5	6.6	6.5	4.0	6.8	4.5	4.0	12.2
N_{total}	52798	27145	26193	17940	36843		18939			42311
N (R_{int})	11440 (0.034)	11314 (0.036)	11268 (0.025)	7507 (0.026)	8004 (0.017)	11792	8285 (0.014)	8225	6436	9070 (0.023)
N_0	9171	8372	7560	5648	6570	8421	7206	4544	1315	7389
R	0.034	0.041	0.037	0.036	0.031	0.044	0.041	0.059	0.088	0.031
R_w	0.040	0.041	0.037	0.040	0.043	0.048	0.058	0.058	0.076	0.040

[a] CAD4: single-counter instrument data ($T\sim295$ K; Gaussian absorption correction). AXS: CCD instrument data ($T\sim300$ K, $2\theta_{max}=58°$; empirical absorption correction (SADABS).

5.6. Methylation

5.6.1. [4-{Cp(PPh$_3$)$_2$Ru(C≡C)}-2-PhC$_9$H$_5$NMe][OTf] (**26**-OTf)

An excess of MeOTf (50 μl, 0.44 mmol) was added to a solution of **1** (20 mg, 0.022 mmol) in CH_2Cl_2 (5 ml). The solution turned red and was stirred for 10 min before the solvent was evaporated. Reprecipitation from CH_2Cl_2–hexane gave [4-{Cp(PPh$_3$)$_2$Ru(C≡C)}-2-PhC$_9$H$_5$NMe][OTf] (**26**-OTf) as a dark red solid (20 mg, 85%).

5.6.2. [4-{Cp(PPh$_3$)$_2$Ru(C≡C)}-2-PhC$_9$H$_5$NMe][PF$_6$] (**26**-PF$_6$)

MeI (0.5 ml, freshly passed through Al_2O_3) was added to a solution of **1** (100 mg, 0.11 mmol) in THF (20 ml) and the mixture was degassed. The solution was then refluxed for 8 h, the colour becoming deep red–purple. NH_4PF_6 (20 mg, 0.12 mmol) was added to the mixture which was then stirred for 30 min before removing solvent. The residue was extracted with CH_2Cl_2, addition of hexane giving [4-{Cp(PPh$_3$)$_2$-Ru(C≡C)}-2-PhC$_9$H$_5$NMe][PF$_6$] (**26**-PF$_6$) as a red solid. Attempts to purify it by reprecipitation were unsuccessful.

5.7. Auration of [Ru{C≡CC[=N(C$_6$H$_4$Me-4)-{Au(PPh$_3$)}]CH=CH(C$_6$H$_4$Me-4)}(PPh$_3$)$_2$Cp][PF$_6$] (**27**)

A mixture of AuCl(PPh$_3$) (54 mg, 0.11 mmol), Ru{C≡CC[=N(C$_6$H$_4$Me-4)]CH=CH(C$_6$H$_4$Me-4)}(PPh$_3$)$_2$-Cp (**12**) (100 mg, 0.11 mmol) and $TlPF_6$ (38 mg, 0.11 mmol) was heated in refluxing THF (20 ml) for 1.5 h. The solution was filtered to remove TlCl and the solvent was removed. Precipitation of the product from CH_2Cl_2 with hexane gave [Ru{C≡CC[=N(C$_6$H$_4$-Me-4){Au(PPh$_3$)}]CH=CH(C$_6$H$_4$Me-4)}(PPh$_3$)$_2$Cp][PF$_6$] (**27**) (155 mg, 91%) as a dark red solid.

5.8. Structure determinations

Diffraction data were measured in two ways, all instruments being fitted with monochromatic Mo–K$_\alpha$ radiation sources ($\lambda = 0.7107_3$ Å). (a) Using a single counter/four-circle instrument at ca. 295 K, N unique data were measured, N_0 with $I > 3\sigma(I)$ being used in the refinement after analytical absorption correction. (b) Using a Bruker AXS CCD/area detector instrument at ca. 300 K, N_{total} reflections were measured, merging, after empirical absorption correction (R_{int} quoted) to N unique data using the proprietary software SMART/SAINT/SADABS/XPREP, N_0 with $F > 4\sigma(F)$ being considered observed and used in the refinement. In all structures an isotropic thermal parameter form was refined for the non-hydrogen atoms, (x, y, z, U_{iso})$_H$ being included, constrained at estimated values. Conventional residuals R, R_w (statistical weights) on $|F|$ are quoted at convergence; neutral atom complex scattering factors were employed, as was the XTAL 3.4 program system [26]. Pertinent results are given in the figures and tables, full crystallographic data being deposited. Individual variations/idiosyncrasies are cited in Section 5.9 below (Table 3).

5.9. Variata

1, **2**. Data were measured at ca. 153 K. (x, y, z, U_{iso})$_H$ were refined for all hydrogen atoms.

3. (x, y, z, U_{iso})$_H$ were refined for all hydrogen atoms.

6. Methoxy groups of ligand 1 were modelled with the oxygen atoms each disordered over pairs of sites, separations 0.95(2), 0.68(1), 1.07(1) Å, site occupancies of the two sets of components constrained as equal after trial refinement, occupancy 0.69(1) and complement.

10. Difference-map residues were modelled as solvent THF, refining to an occupancy of unity, albeit with very high thermal motion.

15. Difference-map residues were modelled as dichloromethane, disposed close to an inversion image, site occupancy set at 0.5 after trial refinement.

17. Data were measured rapidly as the crystal was photosensitive.

23. Available material offered only very small specimens, enabling assignment of broad structural features only via single counter data (the material had deteriorated by the arrival of the CCD facility). Only Ru, P, F were refined with anisotropic thermal parameter forms, difference map residues being modelled as diethyl ether of solvation, site occupancy set at unity after trial refinement, albeit with high thermal motion. The structure determination does not definitively locate the protonating hydrogen atom at N(4), although the remainder of the geometry is consistent with that.

A new phase of RuCl{P(OMe)$_3$}$_2$Cp (**28**). From one fraction obtained during the purification of **6**, crystals of **28** were obtained by vapour diffusion of pentane into a THF solution.

6. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre as CCDC nos. 127434–127443 for compounds **1** (127435), **2** (127436), **3** (127439), **6** (127441), **8** (127442), **10** (127437), **15** (127443), **17** (127438), **23** (127434) and **28** (127440; $P2_1/c$ form). Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, England (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.ac.uk).

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