Cycloaddition of aromatic imines to a ruthenium butatrienylidene complex: synthesis of 4-ethynylquinoline and 1-azabuta-1,3-diene complexes

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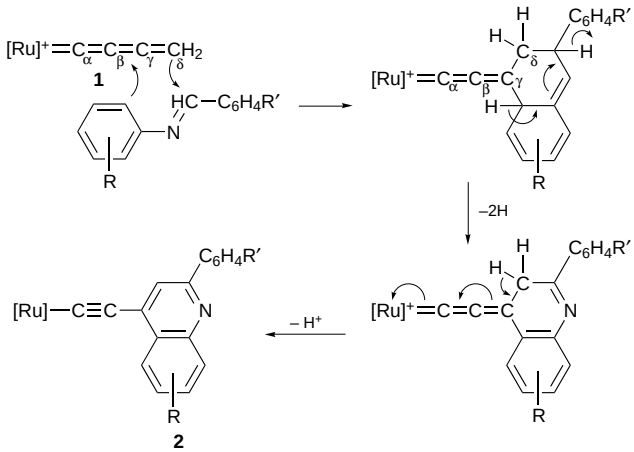
Reactions of aromatic imines with the putative butatrienylidene–ruthenium cation $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ gives complexes containing either 4-ethynylquinoline or 1-azabuta-1,3-diene ligands; the molecular structures of $[Ru(C{\equiv}CC_9H_4MeN)(PPh_3)_2(\eta\text{-}C_5H_5)]$ and $[Ru\{C{\equiv}CC(CH{=}CHPh){=}N(C_6H_4NO_2\text{-}3)\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ are reported.

We have recently described the formation of an intermediate cationic complex from the reaction between buta-1,3-diyne and $[Ru(thf)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ which, from its method of formation and subsequent reactions, is proposed to be the butatrienylidene cation $[Ru(C{=}C{=}C{=}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ **1**.[1] We showed that its reactivity is characterised by nucleophilic attack at C_γ, as predicted by theoretical studies.[2]

The availability of **1**, in which the outer carbons of the four-carbon unsaturated ligand are not sterically protected by the bulky PPh_3 ligands as are atoms C_α and C_β, encouraged us to study its chemistry in more detail. In particular, we were interested in the possibility of cycloaddition to the unsaturated C_4 chain through reactions which might involve successive electro- and nucleo-philic attack on a suitable substrate. We chose to examine first *N*-benzylideneaniline and were pleased to discover that the sought-after reaction occurred readily and in high yield.

Thus, addition of *N*-benzylideneaniline (2 equiv.) to a solution of **1** in thf at −50 °C resulted in an immediate colour change to orange–red. Work up by preparative thin layer chromatography (TLC) afforded the yellow complex **2a** (Scheme 1), which was initially characterised as a 1 : 1 adduct by mass spectrometry.† The reaction can be extended to other imines containing substituted C-bonded aryl groups and/or electron-donating substituents on the N-bonded aryl group. The X-ray determined structure of **2b**, obtained from **1** and $PhCH{=}NC_6H_4Me$-4, is shown in Fig. 1 and important bond parameters are collected in the caption. A conventional $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$ fragment is attached by an Ru–C σ bond to an acetylenic ligand of which the other substituent is a 4-quinolinyl group. Structural characteristics of this ligand are not exceptional and further discussion will be deferred until the full report. Similar tricyclic heterocycles are obtained with naphthylimines.



Scheme 1 R = H, 4-Me, 4-OMe; R′ = H, 3- or 4-NO_2 [Ru] = $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$

A remarkable property of complexes **2** is their extreme sensitivity towards protonation, traces of water being sufficient to form to deep claret coloured cations, $[Ru(C{\equiv}CC_9H_4RNH)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ **3**,† also characterised by an X-ray study for R = H, full details of which will be reported elsewhere.‡ N-Methylation can be achieved using methyl triflate. Complexes **2** and **3** form a readily reversible base–acid system, but in contrast with the well known acetylide–vinylidene systems,[3] there is no evidence for protonation occurring at the acetylide β-carbon.

A likely pathway for this reaction is (*i*) attack of C_δ of cation **1** on the electron-deficient carbon of the imine, (*ii*) electrophilic attack of C_γ on the N-bonded aryl group (Scheme 1). The resulting dihydroquinoline is dehydrogenated to form **2** by a second molecule of imine which is thereby reduced to the corresponding benzylamine, which has been isolated and characterised. Consequently, optimum yields are obtained from reactions between **1** and 2 equiv. of imine.

The presence of electron-withdrawing substituents on the N-bonded aryl group results a different reaction course being followed. Thus, the reaction between **1** and $PhCH{=}N(C_6H_4NO_2\text{-}3)$ gives **4** (Scheme 2)† which was also fully characterised by a single-crystal X-ray study.‡ A molecule of **4** is shown in Fig. 2 and significant bond parameters are included in the caption. Again an $Ru(PPh_3)_2(\eta\text{-}C_5H_5)$-substituted alkynyl fragment is present, now attached to a 1-azabuta-1,3-diene ligand through C(3). No cyclisation involving either aryl group is found in this case, nor does any dehydrogenation take place. Similar complexes have been obtained from

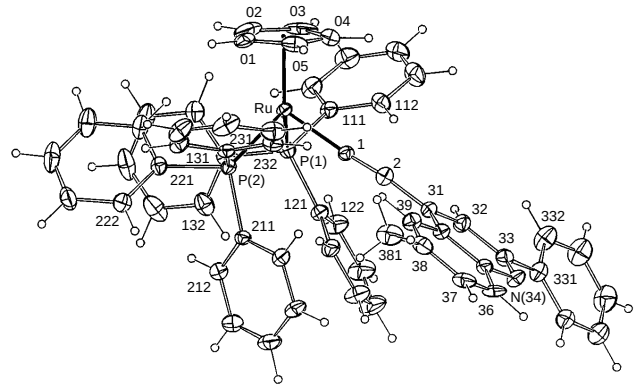
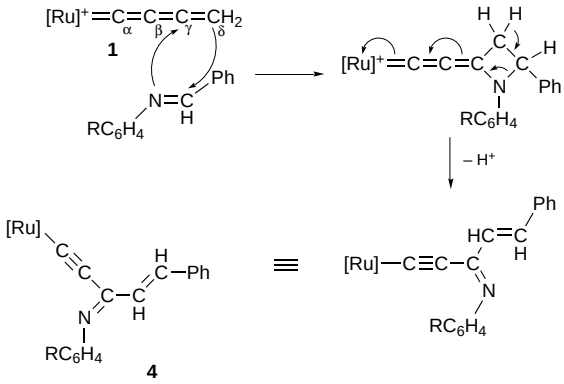


Fig. 1 Plot of a molecule of $[Ru(C{\equiv}CC_9H_4MeN)(PPh_3)_2(\eta\text{-}C_5H_5)]$ **2b** showing the atom numbering scheme; carbon atoms are designated by number only. In both Figures, non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å. Significant bond parameters: Ru–P(1) 2.308(2), Ru–P(2) 2.300(2), Ru–C(1) 1.997(7), C(1)–C(2) 1.19(1), C(2)–C(31) 1.42(1) Å; Ru–C(1)–C(2) 175.6(7), C(1)–C(2)–C(31) 170.2(8)°.

reactions between **1** and PhCH=N(C_6H_4R-4) (R = NO_2, CO_2Et) and PhCH=N(1-$C_{10}H_7$).

In this variant, we propose that a formal [2 + 2] cycloaddition of the C_γ=C_δ double bond in **1** to the N=CH of the imine occurs, possibly by attack of the imine N atom on C_γ rather than the aryl carbon, after initial C_δ–C(imine) bond formation as in (*i*) above. There is little precedent for this reaction, although it resembles the [2 + 2] cycloadditions of tetracyanoethene (tcne) to transition-metal σ acetylide complexes.[4] In the present case, we do not observe any deep coloured intermediates, but nevertheless, it is unlikely that a concerted addition occurs (which would contravene the Woodward–Hoffmann rules). The initial four-membered C_3N ring formed in such a reaction could undergo ring cleavage (also found with the alkyne–tcne cycloadducts) to give the observed products (Scheme 2).



Scheme 2 R = NO_2-3 or -4, CO_2Et-4; [Ru] = Ru(PPh_3)$_2$(η-C_5H_5)

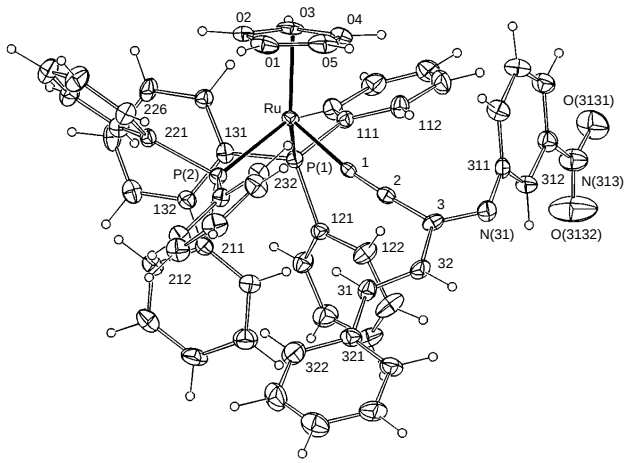


Fig. 2 Plot of a molecule of [Ru{C≡CC(CH=CHPh)=N($C_6H_4NO_2$-3)}(PPh_3)$_2$(η-C_5H_5)] **4** showing the atom numbering scheme. Significant bond parameters: Ru–P(1) 2.319(2), Ru–P(2) 2.293(2), Ru–C(101) 1.978(8), C(1)–C(2) 1.22(1), C(2)–C(3) 1.43(1), C(3)–C(32) 1.48(1), C(3)–N(31) 1.280(9), C(31)–C(32) 1.32(1) Å; Ru–C(1)–C(2) 171.2(6), C(1)–C(2)–C(3) 176.9(6)°.

Preliminary studies show that other 1,3-dynyl complexes undergo similar reactions. Further discussion of these interesting transformations will be given in the full report.

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Footnotes

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† *Selected spectroscopic data*: for **2b**. IR: ν(C≡C) 2051 cm^{-1}. ^{1}H NMR: δ 2.36 (Me), 4.43 (C_5H_5), 7.05–8.24 (aromatics). FABMS: *m/z* 933, M^+; 671, [M − PPh_3]$^+$; 429, [Ru(PPh_3)(C_5H_5)]$^+$. For **4**. IR: 2048s (C≡C), 1530, 1351s (NO), 831 (CN). ^{1}H NMR: δ 4.56 (s, 5 H, C_5H_5), 7.0–8.3 (m, 41 H, atomatic). FABMS: *m/z* 966, M^+; 702, [M − 2 H − PPh_3]$^+$; 429, [Ru(PPh_3)(C_5H_5)]$^+$.

‡ *Crystal data and refinement details*: **2b**; [Ru(C≡CC_9H_4MeN)(PPh_3)$_2$(η-C_5H_5)]≡$C_{59}H_{47}NP_2$Ru, M = 933.1; triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 18.067(9), b = 11.472(3), c = 11.279(8) Å, α = 86.08(4), β = 82.47(5), λ = 87.06(3)°, U = 2310 Å^3, Z = 2. D_c = 1.34 g cm^{-3}; F(000) = 964. μ(Mo-Kα) 4.5 cm^{-1}; specimen: 0.18 × 0.65 × 0.04 mm; A*(min., max.) = 1.02, 1.08.

4: [Ru{C≡CC(CH=CHPh)=N($C_6H_4NO_2$-3)}(PPh_3)$_2$(η-C_5H_5)]≡$C_{58}H_{46}N_2O_2P_2$Ru, M = 966.0; triclinic, space group $P\bar{1}$, a = 19.787(8), b = 11.684(3), c = 10.688(3) Å, α = 98.26(2), β = 101.18(2), γ = 101.39(3)°, U = 2333 Å^3, Z = 2. D_c = 1.37$_5$ g cm^{-3}; F(000) = 966. μ(Mo-Kα) 4.5 cm^{-1}; specimen: 0.40 × 0.12 × 0.24 mm; A*(min., max.) = 1.06, 1.15.

Unique data sets were measured at *ca*. 295 K within the limit $2\theta_{max}$ = 50° using an Enraf-Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ = 0.7107$_3$ Å); for **2b**, 7404 independent reflections were obtained [8225 for **4**], 4645 [4544] with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z, U_{iso})$_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are 0.058, 0.059 (for **2b**) and 0.059, 0.058 (for **4**), statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.0 program system[5] implemented by S. R. Hall; neutral atom complex scattering factors were employed.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the referenece number 182/387.

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