One-step Synthesis of Alkenyloxy–Alkenylcarbene Complexes and the Unprecedented Formation of an η^5-Allyl-alkene Ruthenium Complex

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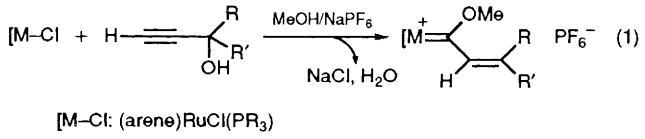
Tetramethylbenzene alkenyloxy–alkenylcarbene ruthenium(II) derivatives $[(C_6Me_4H_2)Ru\{=C[O(CH_2)_mCH=CH_2]CH=CH-(CH=CH)_n\text{-}R\}Cl(PMe_3)]PF_6$ ($m = 1, 2$; $n = 0, 1, 2$) are produced in a one-step reaction from $(C_6Me_4H_2)RuCl_2(PMe_3)$ in the presence of propynylic alcohol derivatives $HC{\equiv}C\text{–}C(H)(OH)[(CH=CH)_n\text{-}R]$ and ethylenic alcohols, whereas a similar reaction with $HC{\equiv}C\text{–}C(OH)Me_2$ affords a novel η^5-allyl–alkene ruthenium complex, which is characterised by X-ray crystal structural analysis.

Fischer-type carbene complexes have attracted interest as useful reagents for organic synthesis and as precursors to new functional organometallic compounds.[1] Among them, alkenyloxy-carbene complexes have found several useful applications in synthesis such as intramolecular cyclopropanation[2] and Diels–Alder reactions.[3] These complexes are generally prepared either by base-catalysed reaction of ethylenic alcohols with methoxy-carbene complexes,[2a] or by alcoholysis of the unstable acyloxy-carbene complexes.[2b,3] We have recently developed a new strategy to prepare methoxy-alkenyl-carbene ruthenium complexes, in one step, by activation of prop-2-yn-1-ol derivatives with (arene)ruthenium(II) complexes in methanol, eqn. (1).[4] To assess the synthetic potential of this method, we have investigated the activation of prop-2-yn-1-ol derivatives in the presence of unsaturated alcohols. We now report the versatile behaviour of this reaction in the presence of allylic alcohol and we show that (*i*) the ruthenium activation of monosubstituted prop-2-yn-1-ol derivatives constitutes a

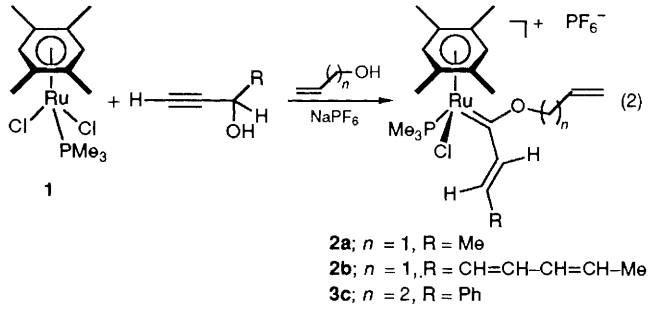


[M–Cl: (arene)RuCl(PR$_3$)

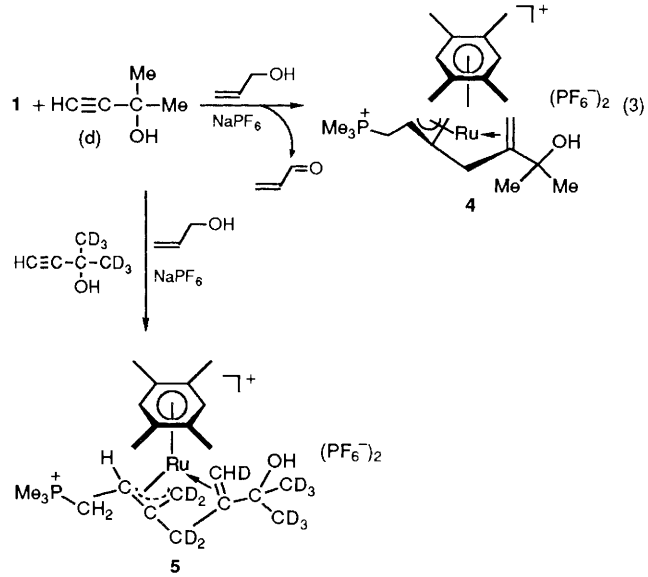
straightforward route to new allyloxyalkenyl carbene ruthenium complexes, *via* addition of allylic alcohol but (*ii*) when the disubstituted substrate HC≡C–C(OH)Me$_2$ is used, the allylic alcohol behaves as a hydrogen-donor reagent in the unprecedented formation of a novel η^5-allyl–alkene ligand.

Arene ruthenium(II) complex **1** and monosubstituted propynylic alcohols derivatives **a** and **b** in 1 : 6 allylic alcohol : dichloromethane solution gave after 18 h of stirring at room temp. the new allyloxy-propenylcarbene and allyloxy-octatrienylcarbene ruthenium complexes **2a** and **2b** in 46 and 70% yield, respectively, eqn. (2). By this procedure but-3-enyloxystyrylcarbene complex **3c** was also prepared in 53% yield from **1**, 1-phenylprop-2-yn-1-ol **c** and but-3-en-1-ol (5 equiv.).† NMR spectra of compounds **2** and **3** showed at δ 297–303 a low field doublet characteristic of the carbene carbon atom, and the ^{1}H NMR data were diagnostic of *E*-isomers for the alkenylcarbene ruthenium moiety. The formation of complexes **2–3** is likely to result from the addition of the ethylenic alcohol to the monosubstituted allenylidene intermediate [Ru=C=C=CHR]$^+$.[4]

The reaction of **1** with 2-methylbut-3-yn-1-ol **d** and allylic alcohol took a different course and led to the unexpected pale-yellow dicationic complex **4** in 47% yield, eqn. (3).† A single-crystal X-ray study was required to establish the



2a; *n* = 1, R = Me
2b; *n* = 1, R = CH=CH–CH=CH–Me
3c; *n* = 2, R = Ph



structure of **4**.‡ As shown in Fig. 1, this molecule consists of a ruthenium atom coordinated by η^6-tetramethylbenzene and a new η^5-allyl-alkene ligand containing a phosphonium group. This ligand can be viewed as resulting from a carbon–carbon coupling between two molecules of alkyne **d**, with concomitant transformations such as dehydration and proton shifts. In addition the crystal structure reveals an unusual metal-to-ligand migration of the trimethylphosphine.

A remarkable feature is related to the key role of allylic alcohol, which was found to act as a hydrogen source: thus, dehydrogenation of allylic alcohol to acroleine was observed during the reaction, and by using H$_2$C=CHC*D*$_2$OH partial deuteriation at the C*H*$_2$–PMe$_3$ position occurred. Labelling experiment with HC≡C(CD$_3$)$_2$OH was carried out and under similar conditions, compound **5** was isolated in 48% yield, eqn. (3).† ^{1}H and ^{13}C NMR spectroscopy confirmed that the

† Satisfactory elemental analyses were obtained for derivatives **2a–4**. Selected spectroscopic data for: **2b**: ^{1}H NMR (300.13 MHz, CD_2Cl_2, 297 K) δ 8.27 (dd, 1 H, CH=, $^3J_{HH}$ 13.8, $^3J_{HH}$ 11.7 Hz), 7.09 (dd, 1 H, CH=, $^3J_{HH}$ 14.6, $^3J_{HH}$ 9.7 Hz), 6.79 (d, 1 H, CH=, $^3J_{HH}$ 13.7 Hz), 6.57 (dd, 1 H, CH=, $^3J_{HH}$ 14.6, $^3J_{HH}$ 11.7 Hz), 6.47–6.31 (m, 2 H, C*H*=C*H*-Me), 6.20–6.06 (m, 1 H, C*H*=CH$_2$), 5.57–5.51 (m, 2 H, CH=C*H*$_2$), 4.99–4.93 (m, 2 H, OCH$_2$), 1.98 (s, 6 H, C$_6$H$_2$*Me*$_4$), 1.88 (d, 3 H, *Me*-CH, $^3J_{HH}$ 5.8 Hz); ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 297 K) δ 294.07 (d, Ru=C, $^2J_{PC}$ 20.3 Hz), 170.61, 151.87, 143.89 (s, CH=), 132.32 (s, *C*H=CH$_2$), 131.43, 130.30, 130.10 (s, CH=), 124.08 (s, CH=*C*H$_2$), 78.73 (s, OCH$_2$), 19.59 (*s*, *Me*-CH=).

3c: ^{1}H NMR (300.13 MHz, CD_2Cl_2, 297 K) δ 8.53 (d, 1 H, CH=C*H*-Ph, $^3J_{HH}$ 14.8 Hz), 7.81–7.77 (m, 2 H, Ph), 7.63–7.48 (m, 3 H, Ph), 7.44 (dd, 1 H, C*H*=CH-Ph, $^3J_{HH}$ 14.9, $^4J_{HH}$ 0.8 Hz), 5.95–5.81 (m, 1 H, C*H*=CH$_2$), 5.33–5.22 (m, 2 H, CH=C*H*$_2$), 4.81–4.66 (m, 2 H, OCH$_2$), 2.80–2.72 (m, 2 H, –CH$_2$–); ^{13}C{^{1}H} NMR (75.47 MHz, CD_2Cl_2, 297 K) δ 300.03 (d, Ru=C, $^2J_{PC}$ 20.0 Hz), 168.67 (s, CH=CH-Ph), 134.91, 134.06 (s, Ph), 133.62 (s, *C*H=CH$_2$), 130.84, 130.08 (s, Ph), 129.78 (s, *C*H=CH-Ph), 119.45 (s, CH=*C*H$_2$), 107.56, 77.96 (s, OCH$_2$), 33.84 (s, –CH$_2$–).

4: ^{31}P{^{1}H} NMR (121.49 MHz, CD_3COCD_3, 297 K) δ 28.86 (s, +PMe$_3$), −143.20 (sept, PF_6^-); ^{1}H NMR (300.13 MHz, CD_3COCD_3, 297 K) δ 4.32 (s, 1 H, –CH$_2$–Ru), 3.95 (s, 1 H, OH), 3.22–3.08 (m, 1 H, C*H*$_2$-PMe$_3$), 3.02 (s, 1 H, CH$_2$=), 2.94–2.82 (m, 1 H, C*H*$_2$-PMe$_3$), 2.73 (s, 2 H, C—CH$_2$C), 2.38 (t, 1 H, CH, $^3J_{HH}$ 3.2 Hz), 2.35 (s, 1 H, –CH$_2$–Ru), 2.09 (d, 1 H, =CH$_2$, $^2J_{HH}$ 1.3 Hz), 2.05 (d, 9 H, +PMe$_3$, $^2J_{PH}$ 14.5 Hz), 1.37, 1.28 (s, 3 H, Me$_2$C(OH)–); ^{13}C{^{1}H} NMR (75.47 MHz, CD_3COCD_3, 2.97 K) δ 85.69, 73.25, 71.85 (s, Cq), 59.13 (s, CH$_2$–Ru), 54.46 (d, CH, $^2J_{PC}$ 5.8 Hz), 48.71 (s, =CH$_2$), 30.83, 28.58 [s, *Me*$_2$C(OH)–], 25.47 (s, C–CH$_2$-C), 23.33 (d, *C*H$_2$-PMe$_3^+$, $^1J_{PC}$ 46.7 Hz), 7.42 (d, +PMe$_3$, $^1J_{PC}$ 53.9 Hz).

5: ^{31}P{^{1}H} NMR (121.49 MHz, CD_3COCD_3, 297 K) δ 28.85 (s, +PMe$_3$), −143.20 (sept, PF_6^-); ^{1}H NMR (300.13 MHz, CD_3COCD_3, 297 K) δ 3.95 (s, 1H, OH), 3.22–3.08 (m, 1 H, C*H*D-PMe$_3$), 3.00 (s, 1 H, C*H*D=), 2.94-2.82 (m, 1 H, C*H*D-PMe$_3$), 2.45, 2.38 (t, 1 H, CH, $^3J_{HH}$ 3.2 Hz), 2.05 (d, 9 H, +PMe$_3$, $^2J_{PH}$ 14.5 Hz); ^{2}H NMR (46.07 MHz, MeCOMe, 2.97 K) δ 4.28 (s, 1 D, –CD$_2$–Ru), 3.02 (s, 1 D, CH*D*=), 2.73 (s, 2 D, C–CD$_2$–C), 2.35 (s, 1 D, –CD$_2$–Ru), 2.09 (d, 1 D, =CH*D*), 1.27, 1.20 (s, 3 D, (C*D*$_3$)$_2$C(OH)-), ^{13}C{^{1}H} NMR (75.47 MHz, CD_3COCD_3, 297 K) δ 85.58, 72.93, 71.20 (s, Cq), 54.28 (d, CH, $^2J_{PC}$ 5.8 Hz), 48.37 (t, =CHD, $^1J_{CD}$ 23.7 Hz).

‡ *Crystal data*: $C_{23}H_{39}O_1F_{12}P_3Ru$, orthorhombic, *Pbca*, *a* = 14.005(4), *b* = 19.708(6), *c* = 22.741(3) Å, *V* = 6202(2) Å^3, *Z* = 8, D_c = 1.614 g cm^{-3}, *F*(000) = 3056, μ_c = 7.346 cm^{-1}. Data collected on a CAD-4 diffractometer with Mo-Kα radiation [9000 measured ($2 \leqslant \theta \leqslant 30°$), 3570 used ($I > 3\sigma(I)$ reflections)]. The structure was solved by heavy-atom methods, the ruthenium atom being identified in the Patterson map and light atoms *via* subsequent Fourier syntheses. After isotopic refinement [*R* = 0.10], an empirical absorption correction was applied, the max and min absorption corrections being 1.392 and 0.860, respectively. A further anisotropic full-matrix least-squares refinement on *F* of the non-hydrogen atoms using unit weights gave *R* = 0.066. A subsequent difference Fourier syntheses allowed the identification of all atoms (all H-atoms as isotopic fixed) included 361 variable parameters and converged to the unweighted and weighted agreement factors of *R* = 0.064 and R_w = 0.061. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

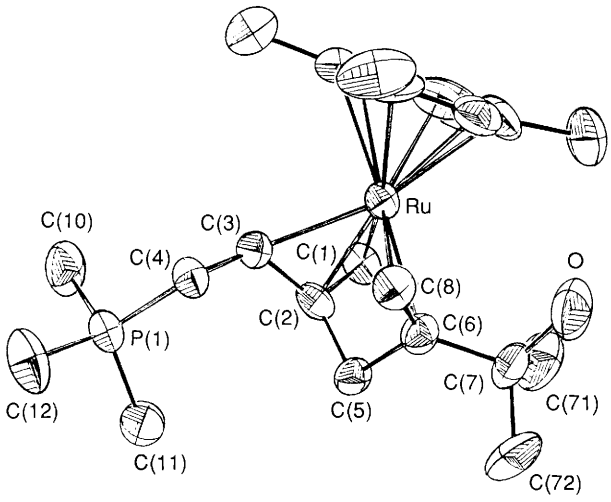


Fig. 1 Molecular structure of the cation of **4** (ORTEP view). Selected bond distances (Å): Ru–C(1) 2.228(9), Ru–C(2) 2.167(8), Ru–C(3) 2.248(8), Ru–C(6) 2.269(9), Ru–C(8) 2.186(8), C(1)–C(2) 1.430(13), C(2)–C(3) 1.425(11), C(6)–C(8) 1.406(13).

allyl-alkene ligand arose from two molecules of 2-methylbut-3-yn-1-ol: deprotonation of two CD_3 groups of one molecule of alkyne **d** is observed along with a deuterium shift to the terminal carbon of a second molecule of alkyne. Finally, compound **4** was prepared in similar yield in the presence of other primary and secondary alcohols such as cinnamyl alcohol (45%), but-3-en-1-ol (48%), and propan-2-ol (48%) but not by using the tertiary alcohol Bu^{t}OH.

A different reactivity of 2-methylbut-3-yn-1-ol **d** has previously been observed by Selegue[5] who reported the synthesis of a diruthenium vinylidene-alkylidene complex from the reaction of $CpRu(PPh_3)_2Cl$ and **d**. The present results show another unprecedented type of activation of this propynylic alcohol derivative to produce a phosphonium ligand isoelectronic with a cyclopentadienyl ligand, and represent a good example of strategy *vs.* serendipity.

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