Novel Behaviour of Dialkylamino-substituted Propargylic Alcohols in Reactions with Arene Ruthenium(II) Complexes

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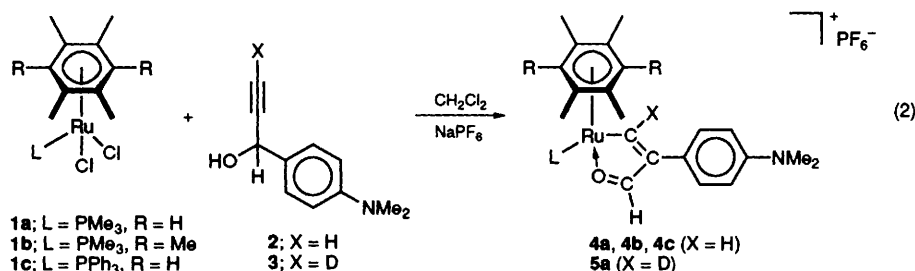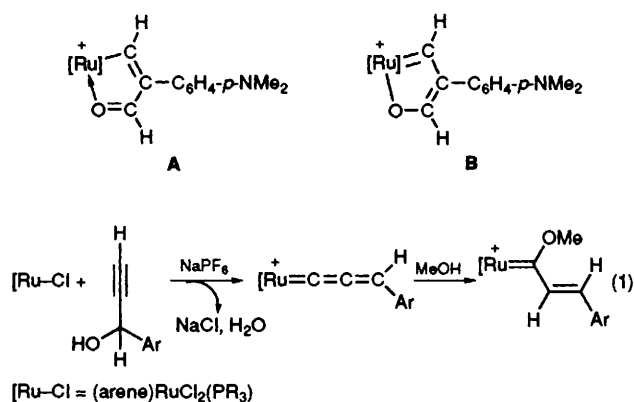
Reaction of arene ruthenium(II) derivatives $(C_6Me_4R_2)RuCl_2(L)$ (R = H, Me; L = PMe_3, PPh_3) with the prop-2-ynylic alcohol derivative $HC\equiv C-C(H)(OH)(C_6H_4-p-NMe_2)$ in dichloromethane results in the formation of new oxametallacyclic ruthenium(II) complexes $\{(C_6Me_4R_2)Ru[CH=C(C_6H_4-p-NMe_2)CHO](L)\}PF_6$ via an unprecedented 1,2-migration of the dimethylaminophenyl substituent; the structure of one compound (R = H; L = PPh_3) is determined by an X-ray crystal structure analysis.
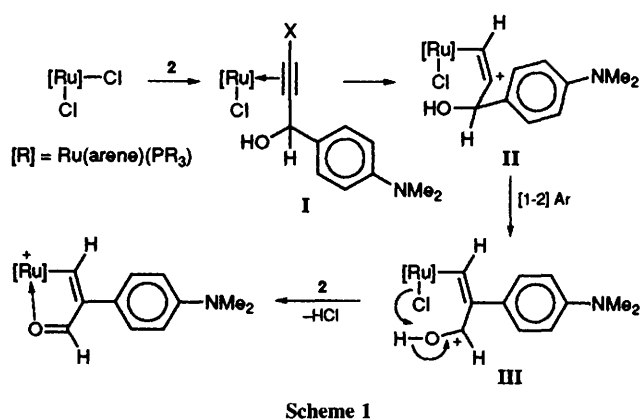
Prop-2-yn-1-ols have recently been shown to be convenient precursors for a variety of unsaturated carbene, allenylidene, alkenyl and polyenyl-carbene compounds, by activation with arene ruthenium(II) complexes.[1,2] The key step of activation was shown to be the dehydration of the propargylic alcohol and formation of an allenylidene intermediate [eqn. (1)]. In attempting to manipulate the electronic properties of these polyunsaturated carbenes by incorporating electron-releasing substituents onto the hydrocarbon chain, we have discovered a new activation type which leads to ruthenium(II) oxametalla-cycles based on vinylaldehydes via an unprecedented 1,2-migration of a dialkylaminophenyl substituent of the prop-2-ynylic alcohol derivative $HC\equiv C-C(H)(OH)(C_6H_4-p-NMe_2)$ 2. This rearrangement, which is supported by a deuterium-labelling experiment, has a direct analogy in phenonium ion migrations in organic chemistry[3] and can be rationalised in terms of polarisation and charge stabilisation in a slipped η^1-alkyne complex leading to the preferred aryl over hydrogen migration. These results have relevance to the recent postulate that slipped η^1-alkyne complexes may be intermediates along one reaction pathway for the rearrangement of η^2-alkyne complexes to vinylidenes.[4] Here, we report the generation of the arene ruthenium(II) oxametallacycles 4, 5, from the prop-2-ynylic alcohol derivative 2 and the X-ray structure of the vinylaldehyde complex 4c.

Treatment of a dichloromethane solution of $(C_6Me_4H_2)$-$RuCl_2(PMe_3)$ 1a with 1-(dimethylaminophenyl)prop-2-yn-1-ol 2 (3 equiv.) in the presence of $NaPF_6$ at room temp. resulted in the formation of the new oxametallacycle complex 4a, isolated in 33% yield as red crystals after purification by column chromatography on alumina, [eqn. (2)]. The arene ruthenium complexes containing a more electron-releasing arene (C_6Me_6) 1b or a bulkier phosphine (PPh_3) 1c activate 2 and lead to the vinylaldehyde chelates 4b and 4c in 39 and 20% yield, respectively.† A labelling experiment with $DC\equiv C-C(H)(OH)(C_6H_4-p-NMe_2)$ 3 was carried out under similar conditions and compound 5a, with the deuterium atom uniquely on C(1), was produced in 24% yield. This demonstrates that migration of the terminal hydrogen did not occur during the reaction. ^1H NMR spectra of 4a, 4b and 4c exhibited two low field signals at δ 11–12.5 and δ 8–9, characteristic of the vinyl and aldehyde protons, respectively. On the other hand, only one low field doublet was observed for 5a at δ 9.06. In the $^{13}C\{^1H\}$ NMR spectra, the C(1) carbon appeared as a doublet at δ 240 ($^2J_{CP}$ 20 Hz) and as a sextuplet at δ 238 ($^2J_{CP}$ 18 Hz, $^1J_{CD}$ 21.5 Hz) for 5a.

Details of the molecular structure of 4c were revealed by a single crystal X-ray structure analysis (Fig. 1).† The principal structural feature of interest is the five membered $Ru-O-C_3$ metallocyclic ring formed by the rearrangement of the prop-2-yn-1-ol. The ring is planar and the C(1)–C(2) [1.377(6) Å] and O(1)–C(3) [1.260(5) Å] bond lengths suggest that the ligand is a vinylaldehyde coordinated to ruthenium via a $Ru-C_{sp^2}$ σ-bond [Ru(1)–C(1) 1.988(4) Å] and the oxygen atom O(1) of an aldehyde group [Ru(1)–O(1) 2.092(3) Å]. The former value is, however, ca. 0.1 Å shorter than the expected value for a $Ru-C_{sp^2}$ bond [Ru–C = 0.2061(10) Å in $RuH(CHC(Me)CO_2C_4H_9)(PPh_3)_3$][5] and approaches the bond lengths observed for related ruthenium(II) carbene complexes [Ru–C = 1.98(1) Å in $\{Ru(\eta^6-C_6Me_6)[=C(OMe)-CH=CPh_2](Cl)(PMe_3)\}PF_6$].[1] There is thus a substantial contribution to the ground state of 4c from the carbene structure B. This observation is supported by the spectroscopic data, with $\delta^{13}C$ for C(1) resonating in the region of a carbene carbon and the ^1H resonance of the attached proton exhibiting a downfield shift.

Although oxametallacycles of ruthenium(II) have been previously prepared, for example by reaction of acetylene

A

B

[Ru–Cl = (arene)RuCl₂(PR₃)]

1a; L = PMe₃, R = H
1b; L = PMe₃, R = Me
1c; L = PPh₃, R = H

2; X = H
3; X = D

4a, 4b, 4c (X = H)
5a (X = D)

[R] = Ru(arene)(PR₃)

Scheme 1

(2)] coupled with the non-migration of acetylenic hydrogen strongly suggests that vinylidene (allenylidene) intermediates are not involved in the formation of **4** and **5**. A mechanism consistent with these observations (Scheme 1) involves the rearrangement of an η^2-alkyne intermediate **I** to its slipped, polarised η^1-isomer **II** bearing a positive charge at C(2). Slipped alkyne species have been postulated by Hoffmann[4] as putative intermediates in the rearrangement of terminal alkynes to vinylidenes. In the present case however, 1, 2-aryl migration rather than hydrogen transfer is favoured by the electron-releasing dialkylamino substituent in the *para* position of the phenyl ring as is observed for such rearrangements in organic chemistry.[8] The last step, loss of hydrogen chloride from **III**, is facilitated by the presence of an excess of the basic dimethylaminophenyl propargylic alcohol **2**.

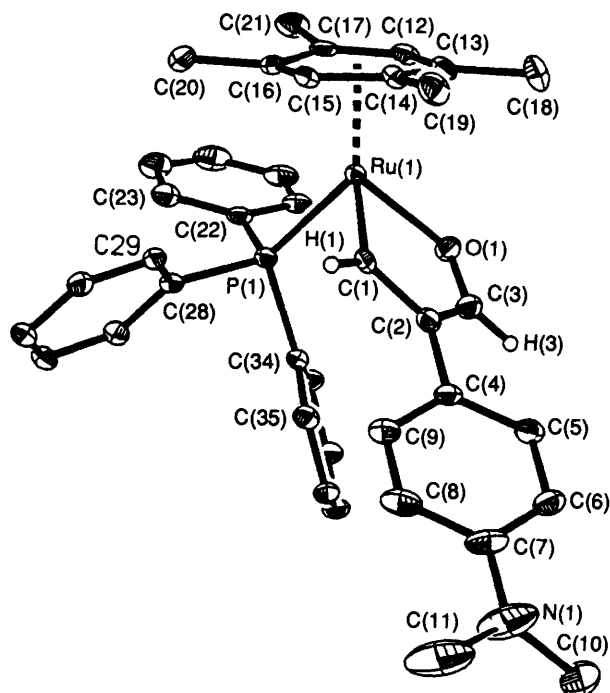*Received, 6th September 1993; Com. 3/05336I*

Fig. 1 Molecular structure of [(C₆Me₄H₂)Ru{CH=C(C₆H₄-*p*-NMe₂)CHO}(PPh₃)]PF₆ **4c** showing the atomic numbering. Selected bond lengths (Å) and angles (°) are as follows: Ru(1)-P(1) 2.333 (1), Ru(1)-C(1) 1.9888 (4), Ru(1)-O(1) 2.092 (3), C(1)-C(2) 1.377 (6), O(1)-C(3) 1.260 (5), C(2)-C(3) 1.415 (6), C(7)-N(1) 1.389 (8); O(1)-Ru(1)-C(1) 76.9 (1), P(1)-Ru(1)-O(1) 89.1 (1).

dicarboxylates with Ru–H bonds,[6] or by addition of water to a penta-2,3,4-trienylidene ruthenium arene complex,[7] vinyl-aldehyde chelates are not accessible *via* insertion routes.

The distinctively different behaviour of dialkylaminophenyl substituted propargylic alcohols in these reactions [eqns. (1),

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