Dalton Communications

Synthesis and Reactivity of Tungsten Vinylallene Complexes

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Protonation at one of the phenylacetylide substituents of the allylic complexes [W(cp)(CO)$_2${η^3-H$_2$CC[C(C≡CPh)$_2$]CH$_2$R}] (cp = η-C$_5$H$_5$), including the first cationic tungsten–ruthenium allylic vinylidene complex, R = C(Ph)=C=Ru(cp)(PPh$_3$)$_2$ (crystal structure), gave η^4-vinylallene complexes.

The preparation of transition-metal allylic complexes and trimethylenemethane complexes[1] as well as their synthetic applications[2] have attracted a great deal of attention recently. However, few examples of transition-metal complexes containing co-ordinated conjugated vinylallene[3] have been reported and their synthetic relationship to the above complexes has been mostly unnoticed. In this communication we report the synthesis of a number of vinylallene complexes from the reactions of [W(cp)(CO)$_2${η^4-H$_2$CC[C(C≡CPh)$_2$]CH$_2$}]$^+$ **1** (cp = η^5-C$_5$H$_5$) with various nucleophiles followed by protonation. The nucleophilic addition occurs at the non-substituted terminal carbon of the alkyne ligand and subsequent protonation at the acetylide group. Thus from the reaction of **1** with [Ru(cp)(PPh$_3$)$_2$(C≡CPh)] under mild conditions, the first tungsten–ruthenium dinuclear cationic complex [W(cp)(CO)$_2${η^3-H$_2$CC[C(C≡CPh)$_2$]CH$_2$C(Ph)=C=Ru(cp)(PPh$_3$)$_2$}]$^+$ **2a** is isolated. Subsequent protonation yields a dinuclear dicationic complex with a μ-η^4,η^1-vinylallene–vinylidene bridging ligand.
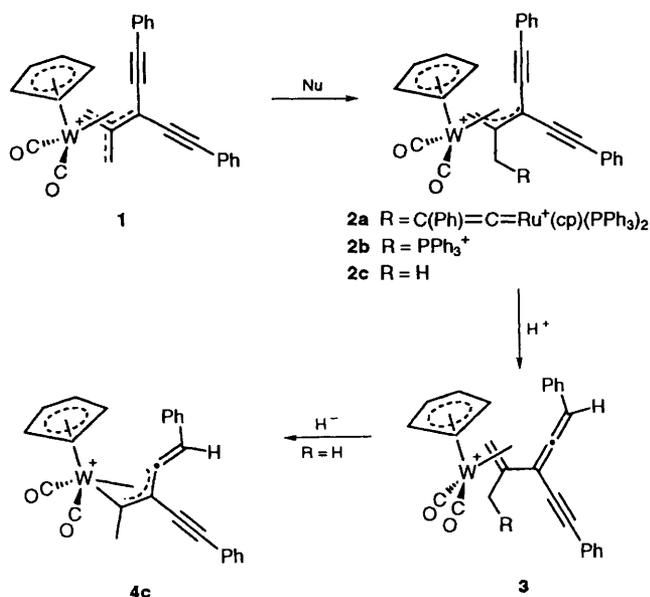
Complex **1** was prepared from the reaction of [W(cp)(CO)$_2${η^3-H$_2$CC[C(OH)(C≡CPh)$_2$]CH$_2$}] with HBF$_4$ in 89% yield and its reactions with [Ru(cp)(PPh$_3$)$_2$(C≡CPh)], PPh$_3$ or H$^-$ cleanly produce the allylic complexes [W(cp)(CO)$_2${η^3-H$_2$CC[C(C≡CPh)$_2$]CH$_2$R}] [R = (Ph$_3$P)$_2$(cp)Ru=C=CPh$^+$ **2a**, PPh$_3^+$ **2b** or H **2c**] at 0 °C in MeCN. All nucleophilic additions occur exclusively at the non-substituted terminus of the trimethylenemethane ligand. In the reaction of **1** with [Ru(cp)(PPh$_3$)$_2$(C≡CPh)] the triple bond of the latter serves as a nucleophilic centre and thus the deep red tungsten–ruthenium dinuclear complex **2a** is produced, see Scheme 1. In the reaction of **1** with PPh$_3$ the phosphine attacks the same position giving **2b** and **2c** is prepared from hydride addition. The spectroscopic data† for **2** are consistent with their formulations. In the IR spectra of **2a** and **2b** the ν_{CO} absorptions (all less than 2000 cm^{-1}) indicate a neutral (cp)W(CO)$_2$ moiety inferring localization of the cationic charge at the Ru atom and PPh$_3$, respectively. In the ^{1}H NMR spectra the *syn* and *anti* protons of **2** appear as two broad resonances in the normal allylic region of δ 3.15–2.70. For **2a** and **2b** the other methylene protons appear as multiplet resonances at lower field (δ 4.61–3.23). In the ^{31}P NMR spectrum of **2a** the resonances of the two PPh$_3$ ligands appear as doublets at δ 41.8 and 43.1 with J_{PP} = 27.0 Hz, in contrast to a singlet resonance for similar ruthenium complexes[4] which show fluxionality of the vinylidene ligand. The inequivalence of the two PPh$_3$ in **2a** is attributed to the steric bulk of the tungsten–allyl moiety hindering rotation of the vinylidene ligand.

The structure of complex **2a** was confirmed by a single-crystal X-ray diffraction analysis‡ and an ORTEP[5] drawing is shown in Fig. 1. The Ru–C(24) [1.86(1) Å], C(24)–C(23) [1.31(2) Å] and Ru–C(24)–C(23) [170(1)°] are typical for

cationic ruthenium vinylidene complexes. The α,α,β-trisubstituted allylic group adopts an *endo* conformation with W–C (centre) 2.28(1) Å being the shortest among the three W–C

2a R = C(Ph)=C=Ru⁺(cp)(PPh₃)₂
2b R = PPh₃⁺
2c R = H

4c   3

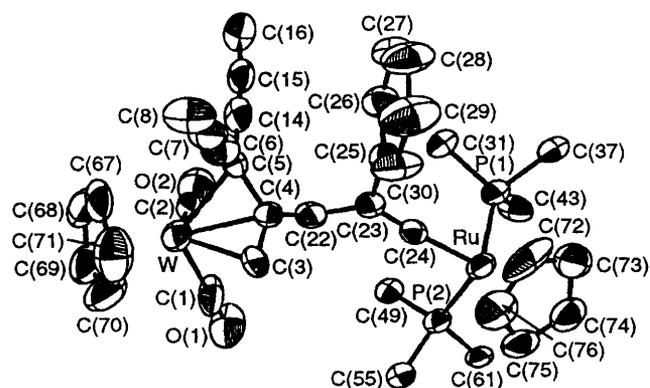Scheme 1   Nu = Ru(cp)(PPh₃)₂(C≡CPh) 2a, PPh₃ 2b or NaBH₄ 2c

Fig. 1   Structure of the cation of complex 2a showing the atom numbering scheme and with 50% probability ellipsoids; all the phenyl groups of the phosphine and of the allylic ligand are omitted for clarity. Atoms C(8), C(16), C(31), C(37), 3(43), C(49), C(55) and C(61) are the *ipso* phenyl carbons. Only the phenyl group of the vinylidene ligand is shown

(allyl) bonds. The newly formed C(22)–C(23) bond of 1.50(2) Å is a normal single bond.

In the protonation reaction of complex 2 the C≡CPh group of the allylic ligand serves as a proton acceptor, thus the η⁴-vinylallene product 3 is produced cleanly. For example, protonation of 2a by HBF₄ gives 3a in quantitative NMR yield, see Scheme 1. Protonation of 2b and 2c also gives 3b and 3c, respectively. In the IR spectrum of 3a the v_{CO} absorptions, all at > 2000 cm⁻¹, indicate the cationic character of the tungsten centre. In the ¹H NMR spectrum of 3a the two broad resonances at δ 2.48 and 1.81 are assigned to the two *gem*-vinylic protons. The relatively upfield shift is due to co-ordination of the vinyl group. The two doublets, at δ 4.23 and 3.40 are assigned to the other methylene group. The resonances of the terminal allenyl proton and the aromatic protons are overlapped. The configuration of the phenyl group at the allene terminal is not clear at this time, however judging by the fact that protonation should occur at the most electron-rich site one could reasonably anticipate a *syn* configuration (with respect to W). Namely direct protonation at the acetylide group should be more favourable than protonation at the metal followed by proton transfer. An η⁴-vinylallene ligand in an iron complex was reported recently.⁶ Two methods are known for the preparation of such complexes: treatment of a vinylketene complex with a stabilized Wittig reagent⁷ and simple complexation of vinylallene to a metal.⁶ Our method provides another approach for such a compound.

The reaction of an excess Na[BH₃(CN)] with complex 3c gave neutral 4c in high yield. Namely, addition of hydride occurs at the terminal CH₂ yielding 4c with two Me groups, *i.e.* the η⁴-vinylallene is converted into an η³-vinylallylic ligand. In the ¹H NMR spectrum the two singlets at δ 2.18 and 1.67 are assigned to the two methyl groups and the singlet at δ 7.95 with relative integration of 1 H is assigned to the vinylic proton; the assignment was confirmed by a deuteriation study. The v_{CO} at 1942 and 1868 cm⁻¹ indicates the neutral character of the metal centre. Vinyl substituents at allylic terminals are known in a few previous examples.⁸ The configuration of the phenyl relative to the allylic group is not known. Similar reactions of 3a and 3b give complex mixtures. Owing to the dicationic charges of 3a and 3b the addition of hydride might occur at two possible sites. No attempt was made to isolate the product.

We have previously reported the synthesis of the analogous 1,1-dimethyltrimethylenemethane complex⁹ [W(cp)(CO)₂{η⁴-H₂CC(CMe₂)CH₂}]⁺ 5, which shows different reactivity from

that of 1. Depending on the nucleophiles used, additions could occur either at the substituted or at the non-substituted site of trimethylenemethane ligand of 5. For example, the addition of H⁻ and N₃⁻ occurs at the substituted site producing [W(cp)(CO)₂{η³-H₂CC(CHMe₂)CH₂}] and [W(cp)(CO)₂-{η³-H₂CC[C(N₃)Me₂]CH₂}] respectively. On the other hand, addition of thio nucleophiles occurs at the non-substituted site of 5, similar to that of 2. Interestingly, in the reaction of 5 with [Ru(cp)(PPh₃)₂(C≡CPh)] the acidic proton of the methyl groups in 5 prohibits formation of the addition product, but the deprotonation reaction produces [W(cp)(CO)₂{η³-H₂CC-[C(Me)=CH₂]CH₂}] and the vinylidene complex [Ru(cp)(PPh₃)₂(=C=CHPh)]⁺.

In summary, in the reaction of the cationic 1,1-di(phenylethynyl)trimethylenemethane complex with nucleophiles, the electron-rich acetylide group controls the site of nucleophilic addition. Furthermore, subsequent protonation at this group also provides an entry to a rare class of vinylallene complex. The synthesis and reactivity of these complexes are currently under investigation.

Acknowledgements

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