A Ru-allenylidene complex with an appended redox-active substituent: spectroscopic characterization of three oxidation states†

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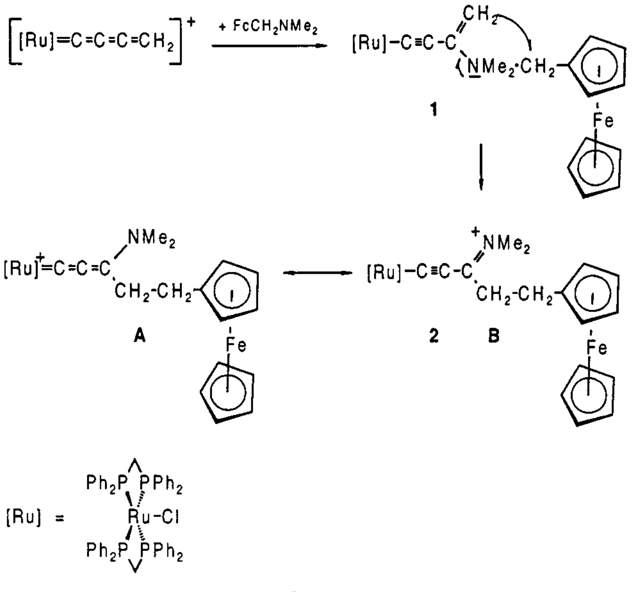
A Ru allenylidene complex with a ferrocenyl substituent in the aliphatic side chain has been prepared and the effects of the consecutive oxidations of the ferrocenyl group and the Ru have been probed by IR and UV/VIS spectroelectrochemistry.

The reactivity of metal-vinylidene and −allenylidene complexes is now well established and may be employed in a variety of useful transformations.[1,2] In contrast, it is only recently that a similar chemistry of the butatrienylidene ligand has begun to emerge. The reactions of the C_4H_2 ligand present in cationic $[Ru]{=}C{=}C{=}C{=}CH_2^+$ intermediates include the addition of aprotic nucleophiles to the electrophilic C_γ[3,4] and the addition of protic nucleophiles to the terminal double bond generating methyl substituted allenylidene complexes. Some interesting cycloaddition/cycloreversion chemistry[5] as well as an unusual Aza-Cope rearrangement following the addition of allyl substituted tertiary amines were also reported.[4]

We have initiated a program aimed at synthesizing novel heteroatom substituted Ru-allenylidene complexes $[Ru]{=}C{=}C{=}C(ER_n)R'^+$ from butatrienylidene precursors *trans*-$[ClRu(L_2)_2{=}C{=}C{=}C{=}CH_2]^+$ (L_2 = chelating diphosphine) and investigating their spectroscopic and electrochemical properties as a function of the heteroatom and the oxidation state of Ru. In this context we are striving for model compounds which allow us to reversibly alter the electronic properties of the unsaturated ligand by attaching redox active substituents to the allenylidene side chain. Here we report our findings on *trans*-$[ClRu(dppm)_2{=}C{=}C{=}C(NMe_2)C_2H_4Fc]^+$ SbF_6^-, **2** [dppm = bis(diphenylphosphino)methane; Fc = ferrocenyl, $(C_5H_4)Fe(C_5H_5)$], which constitutes the first example of such compounds. **2** was prepared in good yield by trapping the *in situ* generated $[ClRu(dppm)_2{=}C{=}C{=}C{=}CH_2]^+$ with ferrocenylmethyldimethylamine, $FcCH_2NMe_2$. Due to the inherent reactivity of the organometallic amine toward dichloromethane,[6] chlorobenzene had to be employed as solvent. As to the formation of **2**, we assume that the initially generated addition product **1** evolves to the title compound by migration of the resonance stabilized ferrocenylcarbenium ion[7] from the quaternary nitrogen to the neighbouring nucleophilic C_δ (Scheme 1). Thus, the overall reaction closely resembles that observed for Ph_2NH with $FcCH_2^+$ instead of a proton. In the crude reaction mixture, **1** was identified as a minor product along with a third, as yet unidentified component.‡ Although numerous attempts to obtain X-ray quality crystals failed the spectroscopic data leave no doubt as to the identity of **2**.‡ The most characteristic features are the intense allenylidene IR stretch at 1992 cm^{-1} (KBr pellet), the low field quintet in the ^{13}C NMR spectrum at δ 201.8 with a $^2J_{P\text{-}C}$ coupling of 13.6 Hz and the two triplets for the ethylene spacer as well as the signals of a monosubstituted ferrocenyl unit in the ^1H NMR spectrum. The methyl groups attached to the nitrogen give rise to two separate resonance signals in the ^1H and ^{13}C NMR spectra, indicating a double bond character of the C=N bond. Even at 368 K these signals remain separate without any indication of exchange broadening. The energy barrier for rotation must therefore well exceed 73 kJ mol^{-1}. These data are in agreement with the iminiumalkynyl resonance form **B** being the predominant contributor to the electronic structure of **2** as was noted before for other aminoallenylidene complexes.[4,8]

Cyclic and square wave voltammetry of **2** in CH_3CN§ reveal three electrochemical processes within the solvent window, one reduction and two oxidations. At room temperature the reduction is essentially irreversible. At lower temperatures, just above the melting point of the solvent, the chemical decomposition is slowed to a degree that allows us to determine the $E_{1/2}$ of this couple as −2.13 V *vs.* the ferrocene/ferrocenium standard. The first oxidation is a chemically and electrochemically reversible Nernstian process with an $E_{1/2}$ of + 0.02 V, *i.e.* close to that of ferrocene itself. We attribute this feature to the oxidation of the appended ferrocenyl substituent, which is further supported by spectroelectrochemistry (*vide infra*). The second oxidation occurs on the Ru fragment. Under appropriate experimental conditions, the Ru(II/III) couple constitutes a chemically reversible one electron step at $E_{1/2}$ = + 0.62 V which suffers, however, from somewhat slow electron transfer kinetics. Quasireversible behavior has been observed for the Ru(II/III) couples in similar systems.[9] Most significantly, the $E_{1/2}$ of this couple is shifted anodically by 50 mV with respect to otherwise identical complexes but containing a butenyl[4] or $CHEtC{=}C{=}CH_2$ side chain[10] instead of the ferrocenylethyl group. We attribute this shift to the increasing electron withdrawing ability of the allenylidene side chain as the appended ferrocenyl substituent is oxidized.

This effect is also evident from following the stepwise *in situ* oxidation of **2** by UV/VIS and IR spectroscopy. The first oxidation is accompanied by the growth of an absorption band at 642 nm, a region which is characteristic of the ferrocenium chromophore (see insert of Fig. 1). At the same time the intense metal-to-ligand charge transfer absorption band of the [Ru]=C



Scheme 1

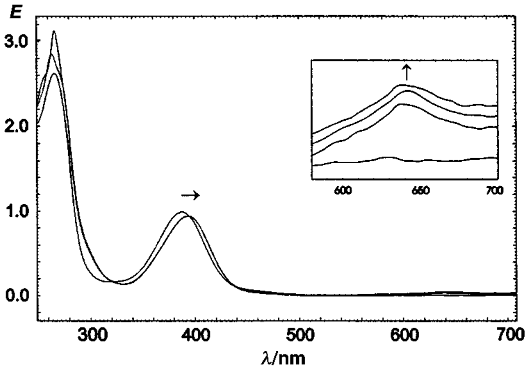


Fig. 1 Spectroscopic changes during the first electrochemical oxidation (Fc/Fc$^+$) of **2** in the UV/VIS region

$=C=C(NR_2)R'^+$ chromophore experiences a bathochromic shift from 386 nm to 394 nm (Fig. 1). A similar, albeit smaller effect just above the resolution power of our spectrometer is seen during IR monitoring of the first oxidation. Here, the intense allenylidene absorption band moves from 1999 cm^{-1} to 1997 cm^{-1}. Essentially no metal–metal coupling is observed over the partially saturated carbon spacer in the formally mixed valent heterobimetallic monooxidation product as shown by the absence of any absorption in the near IR region.

A larger effect is obtained when **2** is further oxidized. Both the UV/VIS and IR absorption bands exhibit a shift in the opposite direction to that found for the first oxidation process. In the fully oxidized trication the visible band is now positioned at 348 nm (Fig. 2). Another weak, broad band centered at 580 nm does also appear, which we attribute to a d–d transition within the Ru(III) fragment (insert of Fig. 2). The ferrocenium band remains essentially unchanged. In IR spectroelectrochemical experiments the intense absorption of the dication is replaced by a much weaker band at 2022 cm^{-1} as the oxidation of Ru(II) proceeds. We wish to emphasize that under our *in situ* conditions all oxidized species are reasonably stable. In fact, rereducing **2**$^{2+}$ reproduced the starting material in near quantitative (UV/VIS) and about 80% yields (IR). The lesser reversibility in the IR experiment is due to the longer electrolysis time required to convert the higher concentrated samples. We can therefore exclude that the loss of intensity in the IR experiment is caused by extensive decomposition rather than being an intrinsic characteristic of our system. Both the decrease in absorptivity of the IR band as well as its blue shift upon oxidation have also been observed in Ru(II)-cyanide complexes[11] thus emphasizing that, in this special situation, there may indeed be an analogy between the CN$^-$ and an electron poor acetylide ligand.[12] The shifts of the visible and the infrared bands do also point to an increase in bond order of the C_α–C_β entity as the ruthenium is oxidized.

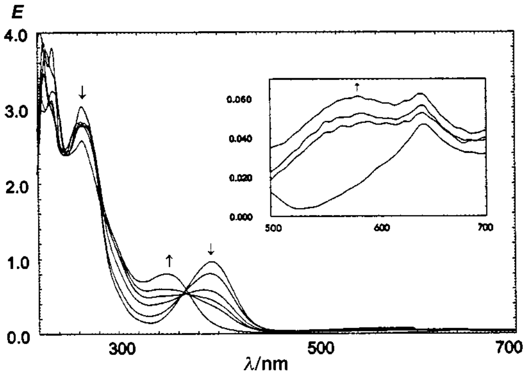


Fig. 2 Spectroscopic changes during the second electrochemical oxidation [Ru(II/III)] of **2** in the UV/VIS region

In summary, we have generated a novel functionalized aminoallenylidene complex by trapping a still elusive $[Ru]=C=C=C=CH_2^+$ intermediate with a suitable tertiary amine. The appended ferrocenyl substituent allows us to reversibly alter the electronic properties of the allenylidene ligand. Ferrocenyl oxidation influences both the Ru(II/III) oxidation potential and the spectroscopic properties of the allenylidene chromophore despite the rather remoteness of the ferrocenyl group and the saturated nature of the connecting bridge. Much larger effects are to be expected if the redox-active tag is attached directly to the delocalized allenylidene system. Work along these lines is in progress.

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Notes and references

† Dedicated to Professor Dr Peter Jutzi on the occasion of his 60th birthday in mid-October.

‡ Selected spectroscopic data: compound **1**: IR (PhCl) 2032; ^{31}P NMR ($CDCl_3$) δ −6.3 (s). Compound **2**: ^{1}H NMR (250 MHz, 298 K, $CDCl_3$), δ 5.12 [2H, d of virtual quint, CH_2 (dppm), $^1J_{H\text{-}H}$ = 10.25, $^2J_{P\text{-}H}$ = $^3J_{P\text{-}H}$ = 4.52 Hz], 4.73 [2H, d of virtual quint, CH_2 (dppm), $^1J_{H\text{-}H}$ = 10.25, $^2J_{P\text{-}H}$ = $^3J_{P\text{-}H}$ = 4.05 Hz], 4.06 (5H, s, Cp), 4.00 (2H, t, C_5H_4, $^3J_{H\text{-}H}$ = 1.75 Hz), 3.69 (2H, t, C_5H_4, $^3J_{H\text{-}H}$ = 1.75 Hz), 2.78 (3H, s, NMe), 2.15 (3H, s, NMe), 1.77 [2H, t (br), CH_2, $^3J_{H\text{-}H}$ = 6.9 Hz], 1.63 [2H, t (br), CH_2, $^3J_{H\text{-}H}$ = 6.9 Hz]. ^{13}C NMR (62.9 MHz, 298 K, $CDCl_3$, assignments aided by a DEPT-135 experiment) δ 201.8 (quint, C_α, $J_{P\text{-}C}$ = 13.6 Hz), 156,7 (br, C_γ), 119.4 (br, C_β), 85.5 (C_{ipso}, C_5H_4), 68.5 (Cp), 67.94 (C_5H_4), 67.87 (C_5H_4), 49.4 [quint, CH_2 (dppm), $J_{P\text{-}C}$ = 10.5 Hz], 43.9 (NMe), 41.7 (NMe), 38.8 (CH_2), 27.6 (CH_2). ^{31}P NMR (101.26 MHz, 298 K, $CDCl_3$) δ −8.2 (s). UV/VIS λ_{max} ($10^{-3}\varepsilon_{max}$): solvent: CH_3OH: 388 (19), 265 (47), 214 (79); CH_3CN: 386 (23), 265 (57); CH_2Cl_2: 397 (20), 267 (49), 234 (60); 1,4-dioxane: 377 (19), 266 (53), 234 (54).

§ Electrochemistry was conducted in a vacuum tight one compartment cell in CH_3CN with 0.2 M NBu_4PF_6 as the supporting electrolyte. Potentials were referenced to internal decamethylferrocene. Conversion to the $Cp_2Fe^{0/+}$ scale was done by comparing the $E_{1/2}$ values of both standards in a separate experiment. Spectro-electrochemistry was performed in a modified thin layer IR cell at room temperature. For more details see ref. 6.

1 M. I. Bruce and A. Swincer, *Chem. Rev.*, 1991, **91,** 197.
2 H. Werner, *Chem. Commun.*, 1997, 903; A. Fürstner, M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998, 1315.
3 M. I. Bruce, P. Hinterding, P. J. Low, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 1009; M. I. Bruce, P. Hinterding, P. J. Low, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1998, 467.
4 R. F. Winter and F. M. Hornung, *Organometallics*, 1997, **16,** 4248.
5 M. I. Bruce, P. Hinterding, M. Ke, P. J. Low, B. W. Skelton and A. H. White, *Chem. Commun.*, 1997, 715.
6 R. F. Winter and G. Wolmershäuser, *J. Organomet. Chem.*, in press.
7 A. A. Korizde, N. M. Astakhova and P. V. Petrowskii, *J. Organomet. Chem.*, 1983, **254,** 345; A. Houlton, J. R. Miller, R. M. G. Roberts and J. Silver, *J. Chem. Soc., Dalton Trans.*, 1986, 2345.
8 M. Duetsch, F. Stein, R. Lackmann, E. Pohl, R. Herbst-Irmer and A. de Meijere, *Chem. Ber.*, 1992, **125,** 2051; F. Stein, M. Duetsch, E. Pohl, R. Herbst-Irmer and A. de Meijere, *Organometallics*, 1993, **12,** 2556.
9 M. C. B. Colbert, J. Lewis, N. J. Long, P. R. Raithby, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 99.
10 R. F. Winter, manuscript in preparation.
11 C. A. Bignozzi, R. Argazzi, J. R. Schoonover, K. C. Gordon, R. B. Dyer and F. Scandola, *Inorg. Chem.*, 1992, **31**, 5260.
12 A comprehensive discussion of this topic is given in: J. Manna, K. D. John and M. D. Hopkins, *Adv. Organomet. Chem.*, 1995, **38**, 79.

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