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Further evidence for 'extended' cumulene complexes: derivatives from reactions with halide anions and water.

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Abstract

Reactions of $[Ru{C=C(H)-1,4-C_6H_4C=CH}(PPh_3)_2Cp]BF_4([1a]BF_4)$ with hydrohalic acids, HX, results in the formation of $[Ru{C=C-1,4-C_6H_4-C(X)=CH_2}(PPh_3)_2Cp][X$

= Cl (2a-Cl), Br (2a-Br)], arising from facile Markovnikov addition of halide anions to the putative quinoidal cumulene cation $[Ru(=C=C=C_6H_4=C=CH_2)(PPh_3)_2Cp]^+$. Similarly, $[M{C=C(H)-1,4-C_6H_4-C=CH}(LL)Cp]BF_4[M(LL)Cp' = Ru(PPh_3)_2Cp]$ $([1a]BF_4)$; Ru(dppe)Cp* $([1b]BF_4)$; Fe(dppe)Cp $([1c]BF_4)$; Fe(dppe)Cp* $([1d]BF_4)$] react with H^+/H_2O to give the acyl-functionalised phenylacetylide complexes $[M{C=C-1,4-C_6H_4-C(=O)CH_3}(LL)Cp']$ (**3a-d**) after workup. The Markovnikov addition of the nucleophile to the remote alkyne in the cations $[1a - d]^+$ is difficult to rationalise from the vinylidene form of the precursor and is much more satisfactorily explained from initial isomerisation to the guinoidal cumulene complexes $[M(=C=C=C_6H_4=C=CH_2)(LL)Cp']^+$ prior to attack at the more exposed, remote quaternary carbon. Thus, whilst representative acetylide complexes [Ru(C=C-1,4- $C_6H_4-C=CH$)(PPh₃)₂Cp] (4a) and [Ru(C=C-1,4-C_6H_4-C=CH)(dppe)Cp*] (4b) reacted with the relatively small electrophiles $[CN]^+$ and $[C_7H_7]^+$ at the β -carbon to give the expected vinylidene complexes, the bulky trityl ($[CPh_3]^+$) electrophile reacted with $[M(C=C-1,4-C_{6}H_{4}-C=CH)(LL)Cp']$ $[M(LL)Cp' = Ru(PPh_{3})_{2}Cp$ (4a); Ru(dppe)Cp*(4b); Fe(dppe)Cp (4c); Fe(dppe)Cp* (4d)] at the more exposed remote end of the carbon-rich ligand to give the putative quinoidal cumulene complexes $[M{C=C=C_6H_4=C=C(H)CPh_3}(LL)Cp']^+$, which were isolated as the water adducts $[M{C=C-1,4-C_6H_4-C(=O)CH_2CPh_3}(LL)Cp']$ (6a – d). Evincing the scope of the formation of such extended cumulenes from ethynyl-substituted arylvinylene precursors, the rather reactive half-sandwich (5-ethynyl-2-thienyl)vinylidene complexes $[M{C=C(H)-2,5-^{c}C_{4}H_{2}S-C=CH}(LL)Cp']BF_{4}([7a - d]BF_{4} add water$ readily to give $[M{C=C-2,5-^{c}C_{4}H_{2}S-C(=O)CH_{3}}(LL)Cp']$ (8a – d)].

Graphical Abstract



Reactions of 4-ethynyl metal phenyl- or thienyl-acetylide complexes with electrophiles produce reaction products consistent with the formation of quinoidal and thienyl cumulenes.

Keywords

Cumulenes; alkynes; metal acetylide; vinylidene

Introduction

The coordination chemistry of vinylidenes (: $C=CR_2$) and allenylidenes (: $C=C=CR_2$), which are the first members of a family of unsaturated carbene ligands, has been well developed through many years of persistent investigation. In contrast, very few

examples of complexes with butatrienylidene (:C=C=C=CR₂) and longer cumulated ligands have been isolated due the highly reactive nature of the extended unsaturated carbon chain.^[1] The existence of these highly conjugated species is more usually inferred from the nature of reaction products,^[2] with a pattern of alternate electrophilic [C(α), C(γ), C(ϵ), etc] and nucleophilic [C(β), C(δ), C(ζ), etc] character of the carbon atoms along the cumulated chain being identified.^[3]

More recently, a range of intriguing electronic and electrical properties associated with cumulated carbon chains have been identified, such as an increasing electronic transmission with increasing length through even-carbon cumulenes^[4] and fascinating, helical orbital character in odd-carbon C_2 -symmetric cumulenes.^[5] The identification of similarly helical molecular orbitals in a range of bimetallic C₄-bridged radical cations that would require valence bond descriptions between the butadiyndiyl (-C=C-C=C-) and cumulated butatrienylidiene (=C=C=C=C=) forms provides further indications of the emerging areas of interest in the chemistry and electronic structures of cumulated carbon chains.^[6]

In light of these various interests in cumulated carbon chains, the isolation of complexes *trans*-[Ru{C=C-2,5-R₂-C₆H₂-4-C(Cl)=CH₂}Cl(dppm)₂] (C, R = H, Me; Scheme 1) from reactions of the (4-ethynylphenyl)vinylidene complexes *trans*-[Ru{C=C(H)-2,5-R₂C₆H₂-4-C=CH}Cl(dppm)₂]BF₄ (A) with [NBu₄]Cl points to a further new line of investigation.^[7] The formation of these unusual Markovnikov addition products is consistent with the isomerisation of the (4-ethynylphenyl)vinylidene ligand to a transient quinoidal cumulene **B**, a suggestion

which was supported by DFT based calculations and explorations of possible mechanistic pathways (Scheme 1).



Scheme 1. The reaction of vinylidene complexes **A** to give Markovnokov addition products **C** via putative quinoidal cumulenes **B** (R = H, Me).^[7]

The literature provides some additional hints at other examples of such rearrangements and a wider scope of quinoidal and related arylene extended or spaced cumulene complexes. The Markovnikov product [Mn {C=C(H)-1,4-C₆H₄-C(Br)=CH₂}(CO)₂Cp] was obtained more than 30 years ago from reaction of [Mn {C=C(H)-1,4-C₆H₄-C=CH}(CO)₂Cp] with HBr,^[8] although no discussion of a potential mechanism of formation could be entered into at the time of the original report. Some 20 years later, a cumulated thiophene derivative was specifically proposed to account for a diamagnetic by-product formed upon oxidation of [Fe(C=C-2,5-^cC₄H₂S-C=CH)(dppe)Cp*] on the basis of mass and Mössbauer spectra,^[9] although the identity of this species remains to be fully confirmed.

2,5-^cC₄H₂S-C=CH}(LL)Cp']BF₄ evince the formation of quinoidal cumulenes on a variety of ruthenium and iron half-sandwich platforms ([M(LL)Cp' = Ru(PPh₃)₂Cp, Ru(dppe)Cp*, Fe(dppe)Cp, Fe(dppe)Cp*]). Selected examples of halide addition and substitution reactions of *trans*-[RuCl{C=C(H)-1,4-C₆H₄-C=CH}(dppe)₂]⁺ have also been obtained. Furthermore, reactions of electrophilic trityl cations with similarly composed (4-ethynylphenyl)acetylide complexes [M(C=C-1,4-C₆H₄-C=CH)(LL)Cp'] further support the formation of reactive quinoidal cumulenes [M{C=C=C₆H₄=C=C(H)CPh₃}(LL)Cp']⁺, which are isolated as the Markovnikov water adducts [M{C=C-1,4-C₆H₄-C(=O)CH₂CPh₃}(LL)Cp'].

Results and Discussion

The facile reaction of *trans*-[Ru{C=C(H)-2,5-R₂-C₆H₂-4-C=CH}Cl(dppm)₂]BF₄ (R = H, Me) with [NBu₄]Cl to give *trans*-[Ru{C=C-2,5-R₂-C₆H₂-4-

C(Cl)=CH₂}Cl(dppm)₂]BF₄ (Scheme 1)^[7] prompted consideration of initial, exploratory NMR-scale reactions of the analogous dppe-complex *trans*-[Ru{C=C(H)-1,4-C₆H₄-C=CH}Cl(dppe)₂]BF₄ with a range of tetrabutylammonium halide salts [NBu₄]X (X⁻ = Cl⁻, Br⁻, Γ ; Scheme 2). The formation of further examples of products formally derived from Markovnikov addition of HX to the terminal alkyne moiety was clearly evinced by the characteristic resonances from the methylene protons at 5.42 and 5.72 (X = Cl, *J*_{HH} = 1.8 Hz), 5.67 and 6.07 (X = Br, *J*_{HH} = 2.1 Hz), and 6.00 and 6.44 (X = I, *J*_{HH} = 1.8 Hz) ppm, with further support garnered from mass spectrometry. However, the product solutions derived from addition of bromide and iodide were complicated by the observation of competing chloride addition products, suggesting halide scrambling of the metal-ligated chloride ligand through exchange with the added halide, giving rise to a mixture of the various metal-halide derivatives

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of the various vinyl halide products *trans*-[Ru{C=C-1,4-C₆H₄-C(X)=CH₂}X'(dppe)₂] (X, X' = Br/Cl, I/Cl) (Scheme 2). Clearly, the degenerate exchange of the coordinated and free chloride nucleophile used in our initial study would not be evinced in the isolated product.



Scheme 2 Markovnikov addition of $X^-(X^- = Cl^-, Br^-, I^-)$ to the transient cumulene species *trans*-[RuCl(C=C=C_6H_4R_2=C=CH_2)(dppe)_2]^+ (**D**) and Ru–X scrambling

To simplify the reaction profile by eliminating this side reaction, attention was subsequently turned to the half-sandwich derivative

[Ru{C=C(H)C₆H₄C=CH}(PPh₃)₂Cp]BF₄([**1a**]BF₄),^[10] prepared here from [RuCl(PPh₃)₂Cp] and an excess of 1,4-diethynylbenzene in the presence of NH₄BF₄ (Scheme 3). The vinylidene cation, [**1a**]⁺, was crystallographically characterised as the PF₆ salt (Figure S1). Reaction of [**1a**]BF₄ with [NEt₄]Cl proceeded slowly (48 hours) and gave a mixture of the chlorovinyl complex

[Ru{C=CC₆H₄C(Cl)=CH₂}(PPh₃)₂Cp] (**2a-Cl**), together with the parent acetylide [Ru(C=CC₆H₄C=CH}(PPh₃)₂Cp]. Separation of the two acetylide products proved difficult, and so the reaction was simply performed whilst introducing a slow flow of dry HCl for the duration of the reaction, resulting in the quantitative formation of **2a-Cl**. The bromide analogue **2a-Br** was prepared in a similar manner from [NBu₄]Br /

HBr, albeit in lower isolated yield (40%), as might be expected given the decreased nucleophilicity of bromide vs chloride in aprotic solvents (Scheme 3).



Scheme 3. The preparation of [2a-X] (X = Cl, Br) from $[1a]^+$ via a proposed quinoidal cumulene intermediate.

The structures of **2a-Cl** and **2a-Br** were determined by single crystal X-ray diffraction (Figure 1, Table 1). Structural parameters of the terminal $C(X)=CH_2$ moieties are consistent with those of similar vinyl-halide analogues, such as *trans*-[Ru{C=C-2,5-R₂-C₆H₂-4-C(Cl)=CH₂}Cl(dppm)₂] (R = H, Me)^[7] and [Mn{C=C(H)-1,4-C₆H₄-C(Br)=CH₂}(CO)₂Cp].^[8] The pattern of alternating long / short / long bond lengths along the Ru-C1-C2-C3 chain is typical of ruthenium alkynyl complexes,^[11] but rather less pronounced in the case of **2a-Cl**, which may be indicative of a small contribution from a more cumulated resonance structure stabilised by the electronegative Cl atom.

Table 1.	Selected crystallographically	determined bond lengtl	ns (Å) ar	nd angles ('	') for

	2a-Cl	2a-Br
Ru1-P1	2.2916(5)	2.2898(15)
Ru1-P2	2.2881(5)	2.2852(15)
Ru1-C1	2.005(2)	2.030(7)
C1-C2	1.216(3)	1.173(9)
C2-C3	1.433(3)	1.446(9)
C6-C9	1.480(3)	1.480(10)
C9-C10	1.336(3)	1.328(9)
С9-Х	1.751(2)	1.847(7)
P1-Ru1-P2	99.430(17)	99.26(5)
Ru1-C1-C2	176.81(16)	175.0(5)
C1-C2-C3	171.5(2)	169.5(6)
C6-C9-C10	126.86(19)	127.6(6)
C10-C9-X1	117.25(17)	114.8(6)

2a-Cl and 2a-Br.



Figure 1. ORTEP (50% probability) representations of the molecules: (a) [Ru{C=C-1,4-C₆H₄-C(Cl)=CH₂}(PPh₃)₂Cp] (**2a-Cl**); (b) [Ru{C=C-1,4-C₆H₄-C(Br)=CH₂}(PPh₃)₂Cp] (**2a-Br**) showing the atom labeling schemes. For clarity, only the H-atoms on C(10) are shown.

The isolation of **2a-Cl** and **2a-Br**, together with the spectroscopic observation of vinylhalide products formed from the formal Markovnikov addition of HX to the pendent ethynyl moiety in *trans*-[Ru{C=C(H)-1,4-C₆H₄-C=CH}Cl(dppe)₂], gave

confidence that the rearrangement of the ethynyl-substituted phenylvinylidene complexes to a quinoidal cumulene ligand reported earlier^[7] could be extended to a broader range of metal-ligand fragments and nucleophiles. To advance these studies, further members of the family of half-sandwich ethynyl vinylidene complexes $[M{C=C(H)-1,4-C_6H_4-C=CH}(LL)Cp]BF_4 [M(LL)Cp' = Ru(dppe)Cp* ([1b]BF_4);$ $Fe(dppe)Cp ([1c]BF_4); Fe(dppe)Cp* ([1d]BF_4)]$ were prepared from the respective half-sandwich chloride complexes [MCl(LL)Cp'] and isolated as the $[BF_4]^-$ salts in ca. 60% yield in each case. The vinylidene salt $[1b]BF_4$ was crystallographically characterised by way of further example (Figure S2).





Treatment of each of $[1a - d]BF_4$ with a moist solution of HBF₄•Et₂O in CH₂Cl₂ resulted in the formation of the acetophenone derivatives [M{C=C-1,4-C₆H₄C(=O)Me}(LL)Cp'] (**3a** – **d**) over the course of ca. 48 hours, which were isolated following chromatographic purification and crystallisation (Scheme 4). The complexes were readily identified from the characteristic IR v(C=C) and v(C=O) bands between ca. 2040 - 2060 and 1664 - 1669 cm⁻¹, respectively. The acyl moiety was further evinced by a low field ¹³C{¹H} NMR resonance in the range 190 - 200 ppm each case and a singlet in the ¹H NMR spectrum near 2.5 ppm. The structures of **3b** – **3d** were also determined by single-crystal X-day diffraction analysis (Figure 2, Figure S3, Figure S4), and metric data are summarised in Table 2, although the relatively low precision of the structure determination of **3c** precludes extensive comparison with the other structures.



Figure 2. ORTEP (50% probability) of a molecule of [Ru{C=C-1,4-C₆H₄-C(=O)Me}(dppe)Cp*] (**3b**) showing the atom labeling scheme. H-atoms have been omitted for clarity. **3b**, **3c** and **3d**

	3b (M = Ru)	3c (M = Fe)	3d (M = Fe)
M1-P1	2.2501(7)	2.177(2)	2.1667(16)
M1-P2	2.2648(7)	2.163(2)	2.1758(15)
M1-C1	2.005(3)	1.884(8)	1.903(5)
C1-C2	1.233(4)	1.229(11)	1.210(7)
C2-C3	1.425(4)	1.424(10)	1.438(7)
C6-C9	1.486(4)	1.474(10)	1.484(7)
C9-C10	1.504(5)	1.490(11)	1.498(8)
C9-O1	1.223(4)	1.228(8)	1.227(6)
P1-M1-P2	82.55(3)	86.71(9)	85.28(6)
M1-C1-C2	174.7(2)	175.4(7)	175.1(4)
C1-C2-C3	171.9(3)	170.4(8)	171.0(5)
C6-C9-C10	119.2(3)	119.2(6)	118.7(5)
C10-C9-O1	120.7(3)	120.1(7)	120.5(5)

Table 2. Selected crystallographically determined bond lengths (Å) and angles (°) for

The M-C1 bond lengths of 2.005(3), 1.884(8) and 1.903(5) Å for **3b**, **3c** and **3d** are consistent with reported bond lengths for analogous Group 8 'piano-stool' acetylide complexes [e.g. Ru(PPh₃)₂Cp;^[12] Ru(dppe)Cp*^[11] Fe(dppe)Cp;^[13] Fe(dppe)Cp*^[11, 14]] with the shorter M-C and M-P bond lengths exhibited by the iron complexes **3c** and **3d** a result of the smaller atomic radius of iron. As with other metal acetylide complexes, the M-C1-C2 fragment is essentially linear [174.7(2)° (**3b**); 175.4(7)°

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(3c); 175.1(4)° (3d)] and the C1-C2 bond lengths fall in a narrow range [C1-C2: 1.233(4) Å (3b); 1.229(11) Å (3c); 1.210(7) Å (3d)] due to the limited role played by metal-acetylide back-bonding in the electronic structures of such complexes.^[15] In each case, the acyl fragment is characterised by typical C=O double bond [C9-O1: 1.223(4) Å (3b); 1.228(8) Å (3c); 1.227(6) Å (3d)] and C(9)-C(10) single bond [C9-C10: 1.504(5) Å (3b); 1.490(11) Å (3c); 1.498(8) Å (3d)] lengths, similar to those found in acetophenone.^[16]

At present, the exact mechanistic role of acid in these reactions is unclear. Re and colleagues have examined mechanisms of proton migration from ethynylvinylidene to butatrientylidene supported by a $\{Ru(PMe_3)_2Cp\}^+$ fragment, and proposed that the isomerization proceeds via a deprotonation / re-protonation mechanism.^[17] In our case, it seems that the additional acid is important in promoting protonation at the terminal carbon to give the quinoidal cumulene, albeit as a transient intermediate that we have not yet succeeded in detecting spectroscopically in solution (Scheme 5). The formation of the putative metal-stabilised cumulene is apparently key to the facile addition of water. Reaction of PhC=CH with HBF₄.OEt₂ under similar conditions did not result in the formation of any PhC(O)Me, presumably reflecting that the carbocation formed which would be formed under these conditions is far less stable than the readily accessible ruthenium-containing quinoidal cumulene.



Scheme 5. Protonation equilibria that would allow exchange of ethynyl-substituted phenylvinylidene and quinoidal cumulene ligands on a half-sandwich metal complex coordination sphere.

To gain some further insight and evidence for this concept of a deprotonation / remote re-protonation conceptually illustrated in Scheme 5, we turned attention to the model reactions of the metal acetylide complexes $[M(C=C-1,4-C_6H_4-C=CH)(LL)Cp']$ (4a – d) with electrophiles. The prototypical ethynyl-substituted phenyl acetylide complex $[Ru(C=C-1,4-C_6H_4-C=CH)(PPh_3)_2Cp]$ (4a)^[10] was allowed to react with electrophiles of increasing steric demand, specifically 1-cyano-4-dimethylaminopyridinium tetrafluoroborate ($[CAP]BF_4$) as a convenient source of cyanogen, $[CN]^+$,^[18] tropylium tetrafluoroborate ($[C_7H_7]BF_4$) ^[19] and trityl tetrafluoroborate ($[CPh_3]BF_4$).^[20] Whilst both $[CAP]BF_4$ and $[C_7H_7]BF_4$ afforded the anticipated vinylidene complexes $[Ru {C=C(CN)-1,4-C_6H_4-C=CH}(PPh_3)_2Cp]BF_4$ ([5a-CN]BF_4) and $[Ru {C=C(C_7H_7)-1,4-C_6H_4-C=CH}(PPh_3)_2Cp]BF_4$ ([5a-C7H_7]BF_4), the reaction of 4a with the very bulky trityl electrophile gave $Ru {C=C-1,4-C_6H_4 C(=O)CH_2CPh_3$ {(PPh_3)_2Cp (6a) after workup (Scheme 6).



Scheme 6. The reactions of 4a - d with electrophiles $(E^+ = [CN]^+, [C_7H_7]^+, [CPh_3]^+)$.

The vinylidene complexes [**5a-CN**]BF₄ and [**5a-C**₇**H**₇]BF₄ were characterised by the usual suite of spectroscopic methods, details of which are given in the Experimental section. The complex **6a** was characterised by the metal acetylide v(C=C) band at

2058 cm⁻¹ whilst the carbonyl fragment, presumably derived from water addition to the putative cumulene (Scheme 6) exhibited a v(C=O) band at 1673 cm⁻¹ and a distinctive low field resonance in the ¹³C{¹H} NMR spectrum (δ_C 196.0 ppm). The methylene moiety was evinced by ¹H and ¹³C{¹H} NMR resonances at δ_H 2.54 ppm and δ_C 28.5 ppm, respectively, whilst the addition of the CPh₃ fragment was clear from the observation of the [M+H]⁺ ion in the ESI(+)-MS (1077.3193 amu; calculated 1076.2850 amu).

Similar reactions of [CAP]BF₄ and [C₇H₇]BF₄ with [Ru(C=C-1,4-C₆H₄-C=CH)(dppe)Cp*] (4b) gave the analogous vinylidene complexes [Ru{C=C(CN)-1,4- $C_{6}H_{4}-C=CH_{1}(dppe)Cp^{*}BF_{4}(15b-CN_{1}BF_{4})$ and $[Ru_{1}C=C(C_{7}H_{7})-1_{4}-C_{6}H_{6}-C_{6}H_{4}-C_{6}H$ C=CH (dppe) Cp*] BF₄ ([**5b-**C₇H₇] BF₄), the additional steric bulk at the {Ru(dppe)Cp*} fragment apparently not being sufficient to prevent addition of the electrophile to $C(\beta)$. Again, the very bulky trityl cation was found to add at the terminal carbon, presumably giving a cumulated intermediate, which reacted with adventitious water resulting in formation and isolation of [Ru{C=C-1.4-C₆H₄- $C(=O)CH_2CPh_3$ (dppe)Cp*] (6b). Although 6a and 6b proved resistant to crystallisation in a manner conducive to single-crystal X-ray analysis, the iron compounds [Fe{C=C-1,4-C₆H₄-C(=O)CH₂CPh₃}(dppe)Cp'] [Cp' = Cp (6c), Cp* (6d)], formed from entirely analogous reactions of $[Fe(C=C-1,4-C_6H_4-$ C=CH)(dppe)Cp'] $[Cp' = Cp (4c), Cp* (4d)]^{[21]}$ with $[CPh_3]BF_4$ (Scheme 6), both proved somewhat more amenable to crystallisation. Although the crystal samples were of poor quality, resulting in a high degree of thermal and static disorder in the resulting structures, the crystallographic work allowed the unambiguous

determination of the product structures (Figure 3, Table 3). The C1-C2 bond lengths of 1.14(2) Å (**6c**) / 1.227(7) Å (**6d**) Å are consistent with the formal triple bond character of these fragments, the C10-C11 bond lengths of 1.58(2) Å (**6c**) / 1.514(8) Å (**6d**) Å correspond to sp^3-sp^3 C-C single bonds, whilst the C9-O1 bond lengths of 1.27(2) Å (**6c**) / 1.266(7) Å (**6d**) are consistent with that of a carbonyl group. Together, these data support the formation of new C-C bonds to the trityl fragment and the new C-O bonds of the carbonyl groups. (a)





Figure 3. ORTEP plots of molecules of (a) [Fe{C=C-1,4-C₆H₄-

 $C(=O)CH_2CPh_3\}(dppe)Cp]$ (6c) (20% probability; only one of three molecules in the asymmetric unit shown) and (b) [Fe{C=C-1,4-C₆H₄-C(=O)CH₂CPh₃}(dppe)Cp*] (6d) (20% probability) and showing the atom labeling schemes. H-atoms and solvent of crystallisation omitted for clarity.

Table 3. Selected bind lengths (Å) and angles (°) from the crystallographically

	6c	6d
Fe1-P1	2.165(6)	2.1941(15)
Fe1-P2	2.164(7)	2.1824(15)
Fe1-C1	1.88(2)	1.888(6)
C1-C2	1.14(2)	1.227(7)
C2-C3	1.54(3)	1.414(7)
C6-C9	1.47(2)	1.461(10)
C9-C10	1.48(2)	1.42(9)
C9-O1	1.27(2)	1.266(7)
C10-C11	1.58(2)	1.514(8)
P1-Fe1-P2	86.1(2)	85.93(6)
Fe1-C1-C2	171(2)	176.9(4)
C1-C2-C3	157(3)	172.9(5)
C6-C9-C10	122.8(18)	123.2(8)
C10-C9-O1	118.5(19)	114.5(8)
C9-C10-C11	118.6(16)	122.4(9)

determined structures of 6c and 6d.

The weight of evidence for quinoidal cumulene complexes derived from halfsandwich iron and ruthenium complexes of 1,4-diethynyl benzene prompted further consideration of the potential generality of such rearrangements from other diethynylaryl ligand precursors. Given the lower aromaticity of thiophene relative to

benzene, attention was briefly turned towards the search for complexes evincing the formation of a putative thiophenylene-spaced cumulene ligand.

Although the terminal dialkyne 2,5-diethynyl thiophene is relatively unstable as a neat compound, in situ deprotection of a dilute solution of 2,5-(trimethylsilylethynyl)thiophene provides a convenient entry route to metal complexes derived from this species.^[22] The reaction of excess 2,5diethynylthiophene with $[MCl(LL)Cp'] [M(LL)Cp' = Ru(PPh_3)_2Cp, Ru(dppe)Cp^*,$ Fe(dppe)Cp, Fe(dppe)Cp*] in methanol solution containing NH₄BF₄ at ambient temperature allowed isolation of the vinylidene complexes $[M{C=C(H)-2,5-^{c}C_{4}H_{2}S-$ C=CH(LL)Cp'BF₄ ([7a – d]BF₄) as impure powders in low to moderate yield by precipitation into Et₂O (Scheme 7). The presence of the vinylidene in the crude reaction product was evinced by observation of an ion corresponding to the cation $[M{C=C(H)-2.5-^{c}C_{4}H_{2}S-C=CH}(LL)Cp']^{+}$ in the ESI(+)-MS, vinylidene v(M=C=C) bands in the IR spectra ($[7a]^+$, 1624; $[7b]^+$ 1621; $[7c]^+$, 1625; $[7d]^+$, 1609 cm⁻¹) and characteristic resonances in the ¹H NMR spectra arising from the vinylidene ($\delta_{\rm H}$: $[7a]^+$, 5.44; $[7b]^+$, 4.64; $[7c]^+$, 5.17; $[7d]^+$, 5.35 ppm) and ethynyl (δ_{H} : $[7a]^+$, 3.45; $[7b]^+$, 3.27; $[7c]^+$, 3.29; $[7d]^+$, 3.43 ppm) protons. Whilst samples of $[7b - d]BF_4$ were estimated to be 90 – 95% pure from analysis of the ${}^{31}P{}^{1}H$ NMR spectra. [7a]BF₄ proved to be rather reactive, with evidence of the carbonyl cation $[Ru(CO)(PPh_3)_2Cp]^+$ (v(CO) 1980 cm⁻¹) amongst other unidentified products within the sample. Efforts to purify these samples were rather fraught, and so efforts were made to establish the ligand framework and garner evidence for a similar cumulene rearrangement process through derivative reactions of the crude samples of [7a **d**]BF₄.



Scheme 7. The formation thiophenylethynyl vinylidene complexes $[7a - d]^+$ and reactions with water to give 8a - d.

The samples containing $[7a - d]BF_4$ were allowed to react with moist HBF₄.Et₂O in CH₂Cl₂ causing an immediate change in colour of the solution to an intense purple in each case, which further evolved to green over the course of ca. 1hr. The difficulties

encountered in obtaining pure samples of the thiophene-derived compounds $[7a - d]^+$ and the relatively rapid hydration reactions to give **8a** – **d** are consistent with the proposal that the decreased aromaticity of thiophene permits facile rearrangement of the ethynyl vinylidene to the extended cumulenes. Chromatographic workup on basic alumina afforded the acyl acetylide complexes **8a** – **d**, consistent with the facile formation and reaction of the thienylcumulene intermediates (Scheme 7). These compounds were characterised through the usual spectroscopic and spectrometric methods, which included both v(C=C) and v(CO) bands in the IR spectra, low field resonances in the ¹³C{¹H} NMR spectra associated with the carbonyl carbons, and observation of the molecular ion, $[M]^+$, or $[M+H]^+$ in the ESI(+)-MS. The structures of **8b** and **8c** were determined by single crystal X-ray diffraction analysis, confirming the identity of the products (Figure 4, Table 4).



Figure 4. ORTEP representations (30% probability) of molecules of (a) [Ru{C=C-

 $1,4-^{c}C_{4}H_{2}S-C(=O)CH_{3}$ (dppe)Cp*] (8b) and (b) [Fe{C=C-1,4-^{c}C_{4}H_{2}S-C(=O)CH_{3})

C(=O)CH₃}(dppe)Cp] (8c) showing the atom labelling scheme. H-atoms have been omitted for clarity.

determined structures of 80 and 8c.			
	8b (M = Ru)	$\mathbf{8c} \; (\mathrm{M} = \mathrm{Fe})$	
M1-P1	2.2685(13)	2.1618(8)	
M1-P2	2.2793(12)	2.1765(8)	
M1-C1	1.973(5)	1.890(3)	
C1-C2	1.233(6)	1.217(4)	
C2-C3	1.407(7)	1.413(4)	
C6-C7	1.464(7)	1.465(4)	
C7-C8	1.496(7)	1.501(5)	
C7-O1	1.216(6)	1.225(4)	
P1-M1-P2	83.04(5)	86.72(3)	
M1-C1-C2	171.2(4)	176.2(3)	
C1-C2-C3	173.4(5)	171.7(3)	
C6-C7-C8	117.6(5)	117.6(3)	
C8-C7-O1	121.8(5)	121.2(3)	

Table 4. Selected bond lengths (Å) and angles (°) from the crystallographically

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In addition to establishing the connectivity, the structural parameters of the terminal methyl ketone group are consistent with those reported for the analogous acetophenone derivatives 2b - d, as well as closely related organic compounds, such as 2-bromo-5-acetylthiophene.^[23]

Chemistry - A European Journal

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From a mechanistic perspective the addition of water to the putative quinoidal cumulene provides further insight into the ruthenium-mediated hydration of alkvnes.^[24] In the case of simple alkvnes, there are two principle outcomes from such a reaction, either Markovnikov addition to give a methyl ketone (thought to proceed through attack of water to an η^2 -alkyne intermediate) or anti-Markovnikov addition *via* a vinylidene complex which affords an aldehyde.^[25] The regiochemical outcome of the reaction is, therefore, dictated by the balance between the alkyne and vinylidene tautomers of the coordinated alkyne, which is in turn controlled by the choice of ligands within the coordination sphere of the metal.^[26] For extended cumulenes, the situation has an additional degree of complexity as the carbon atoms of the ligand shown alternating electrophilic-nucleophilic behavior and in complexes $[M]=(C)_n=CR_2$, nucleophilic addition to all the odd-numbered carbon atoms is possible.^[27] For example, in allenylidene ligands (n = 2) nucleophilic attack may occur at C_a or C_y , but only addition to the latter is productive. Therefore, the site(s) of hydration (or more generally nucleophilic addition) depends on the relative electrophilic character of the individual carbon atoms within the cumulene ligand and the steric influence of the metal.

The selectivity of the nucleophilic addition reactions reported in this work is driven by two factors. Firstly, our previous calculations on the addition of chloride to the quinoindal cumulene ligand indicated that addition to the metal-bound carbon atom was kinetically accessible but the resulting product was far less thermodynamically stable than that arising from attack at the remote site, presumably due to the increased steric hinderance on changing from a linear to bent ligand at the metal.^[7] Secondly, the presence of the spacer groups inhibits addition to the central unit of the extended

carbon chain as regaining the aromaticity of the phenyl- or thienyl-substituents following addition of halide anion or water is a key driving force for the reaction. This work demonstrates that the formal hydration of alkynes may take place at centers which are remote from the metal and, through appropriate choice of the metal and ligand, may occur in a highly regioselective manner.

Conclusions

The reactions of $[M{C=C(H)-1,4-C_6H_4-C=CH}(LL)Cp]BF_4 [M(LL)Cp' = Ru(PPh_3)_2Cp ([1a]BF_4); Ru(dppe)Cp* ([1b]BF_4); Fe(dppe)Cp ([1c]BF_4); Fe(dppe)Cp* ([1d]BF_4)] with halides and water afford the Markovnikov addition products [Ru{C=C-1,4-C_6H_4-C(X)=CH_2}(PPh_3)_2Cp] [X = Cl (2a-Cl), Br (2a-Br)] and [M{C=C-1,4-C_6H_4-C(=O)Me}(LL)Cp'] (3a - d). These products are consistent with reactions of the nucleophilic reagents with the putative quinoidal cumulene complexes [M{C=C=C_6H_4C=CH_2}(LL)Cp']^+. Water addition to [M{C=C(H)-2,5-}^{c}C_4H_2S-C=CH}(LL)Cp']BF_4 ([7a - d]BF_4) proved even more facile, consistent with the lower aromatic stabilisation energy of the thiophene ring. Further evidence for the extended cumulene was found in reactions of [M(C=C-1,4-C_6H_4-C=CH)(LL)Cp'] (4a - d) with [CPh_3]^+, which afford [M{C=C-1,4-C_6H_4-C(=O)CH_2CPh_3}(LL)Cp'] (6a - d), presumably via water addition to the cumulated complexes$

 $[M{C=C=C_6H_4C=C(H)CPh_3}(LL)Cp']^+$. These observations hint at a wealth of extended cumulene chemistry to be explored from re-arrangements of ethynyl vinylidene complexes, and new routes for the activation of unsaturated organic molecules within metal coordination spheres. Work to further explore these areas is currently underway in our laboratories.

Experimental

Full descriptions of synthetic procedures and characterization data are given in the Supporting Information accompanying this article. Crystallographic data for the structures reported in this paper can also be found in the Supporting Information of this paper and have been deposited at the Cambridge Crystallographic Data Centre. Copies of the [1a]PF₆, [1b]BF₄, 2a-Cl, 2a-Br, 3b, 3c, 3d, 6c, 6d, 8b, 8c crystallographic data with CCDC numbers 1965102-1965112 can be obtained free of charge via https://www.ccde.cam.ac.uk/structures/, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.KCB21EZ, UK (fax +441223336033; email deposit@ccdc.cam.ac.uk).

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