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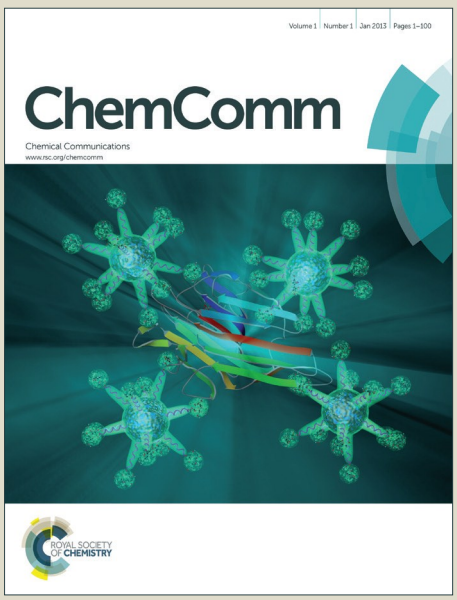

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COMMUNICATION

Rapid Markovnikov Addition of HCl to a Pendant Alkyne: Evidence for a Quinoidal Cumulene

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Samantha G. Eaves,[a,b] Sam J. Hart,[c] Adrian C Whitwood,[c] Dmitry S. Yufit,[a] Paul J. Low*[b] and Jason M. Lynam*[c]

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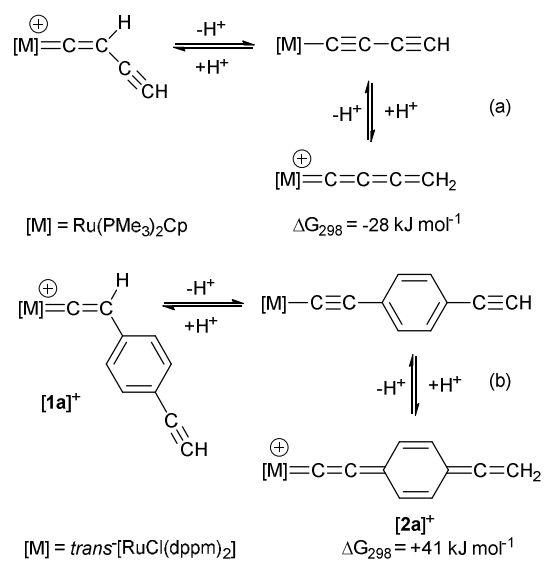
Reaction of *cis*-[RuCl$_2$(dppm)$_2$]BF$_4$ with TlBF$_4$ and 1,4-diethynyl-benzenes results in the formation of the vinylidene cations *trans*-[Ru(=C=CH-C$_6$H$_2$-2,5-R$_2$-4-C≡CH)Cl(dppm)$_2$]$^+$ (R = H, Me). Subsequent reaction with [N^{n}Bu$_4$]Cl results in nucleophilic attack at the coordinated organic ligand but not at the expected metal-bound carbon atom. Instead, *trans*-[Ru(C≡C-C$_6$H$_2$-2,5-R$_2$-4-CCl=CH$_2$)Cl(dppm)$_2$] was generated which, when coupled with DFT calculations, provides evidence for an intermediate quinoidal cumulene complex.

Transition metal cumulene complexes, [M]=C=(C)$_n$=CR$_2$, hold considerable synthetic and structural interest inherently associated with their extended, unsaturated carbon-rich ligand, and from applications as intermediates in the synthetic transformations of alkynes and polyynes.[1] Most typically, rearrangement of an alkyne (or polyyne) within the coordination sphere of a suitable metal fragment leads to the formation of the carbene-like ligand. Charge alternation along the backbone of the cumulene ligand results in facile electrophilic and nucleophilic attack at the even- and odd-numbered carbon atoms of the chain, respectively.[2] Although shorter cumulenes, such as vinylidenes (n = 0), allenylidenes (n = 1) and butatrienylidenes (n = 2), are readily available, examples of complexes containing longer members of this series are rare.[3] Furthermore, for reasons of synthetic convenience, it appears that extended cumulene ligands with odd numbers of carbon atoms are more readily accessible than those with an even number.3[a,b] For example, whilst a heptahexaenylidene (n = 5)[4] has been isolated (albeit stabilised with two dimethylamino-substituents), the existence of a hexapentaenylidene (n = 4)[5] complex has only been inferred from isolation of addition products.

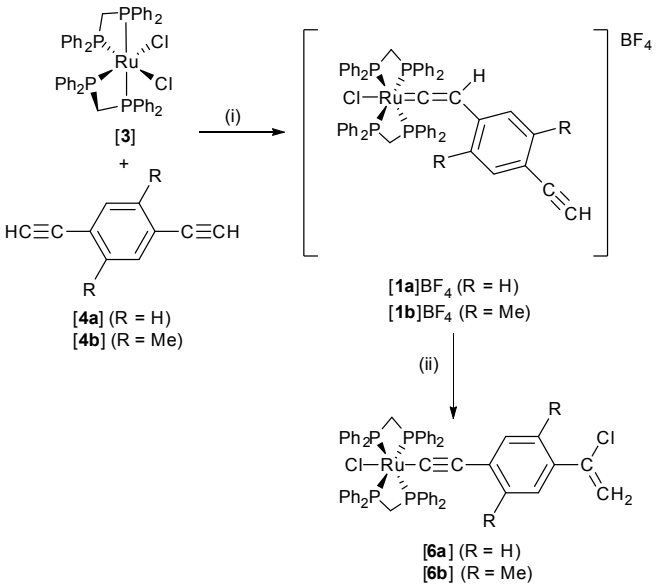
In a recent study, Re has probed the butadiyne to butatrienylidene isomerisation mediated by a half-sandwich ruthenium complex.[6] In this case, an intermediate ethynyl-substituted vinylidene complex was proposed which then underwent a deprotonation / reprotonation process to give the butatrienylidene complex via an intermediate buta-1,3-diynyl species (Scheme 1a). We speculated that this might be a general process to prepare complexes with longer cumulated carbon-chain ligands, but aided through the introduction of quinoidal fragments to increase the stability of the cumulated fragment (Scheme 1b). Whilst (4-ethynylphenyl) vinylidenes are known, the ground state structures lie firmly to the phenylvinylidene isomer.[7] However, our calculations on the isomeric vinylidene and quinoidal cumulene complexes *trans*-[Ru(=C=CH-C$_6$H$_4$-C≡CH)Cl(dppm)$_2$]$^+$ ([**1a**]$^+$) and *trans*-[Ru(=C=C=C$_6$H$_4$=C=CH$_2$)Cl(dppm)$_2$]$^+$ ([**2a**]$^+$) revealed the quinoidal form to lie only some 41 kJ mol^{-1} higher in energy, and therefore a potential target for investigation (Scheme 1b).



Scheme 1

Reaction of a CH$_2$Cl$_2$ solution of *cis*-[RuCl$_2$(dppm)$_2$], [**3**], with TlBF$_4$ and either 1,4-diethynyl benzene ([**4a**]) or 1,4-diethynyl-2,5-dimethylbenzene, ([**4b**]) gave the anticipated vinylidene complexes *trans*-[Ru(=C=CH-C$_6$H$_2$-2,5-R$_2$-4-C≡CH)Cl(dppm)$_2$]$^+$ (R = H, [**1a**]$^+$; R =

Me, [**1b**]$^+$) (Scheme 2). The ^{1}H NMR spectra of [**1a**]$^+$ support the formation of the vinylidene isomers with resonances at δ 3.04 (s, 1H) and 3.07 (quin, J_{PH} = 3 Hz, 1H) for the alkyne and vinylidene protons respectively; similar data were obtained for [**1b**]$^+$. Low field resonances at δ 356.2 ([**1a**]$^+$) and 354.7 ([**1b**]$^+$ in the ^{13}C{^{1}H} NMR confirmed the presence of the vinylidene ligand. The vinylidene isomers [**1**]$^+$ appeared to be stable in solution, and analysis of the NMR spectra did not reveal any evidence for a formal 1,7-hydrogen migration to give detectable concentrations of the proposed quinoidal cumulene form [**2**]$^+$. We elected to probe the possibility of trapping the putative quinoidal cumulene [**2**]$^+$ by addition of chloride as a weakly-basic nucleophile, chosen to avoid formation of *trans*-[Ru(C≡CC$_6$H$_2$-2,5-R$_2$-4-C≡CH)Cl(dppm)$_2$], [**5**], and competitive ligand substitution reactions at the metal centre.



Scheme 2 (i) + TlBF$_4$, - TlCl, CH$_2$Cl$_2$; (ii) +[N^{n}Bu$_4$]Cl, - [N^{n}Bu$_4$]BF$_4$.

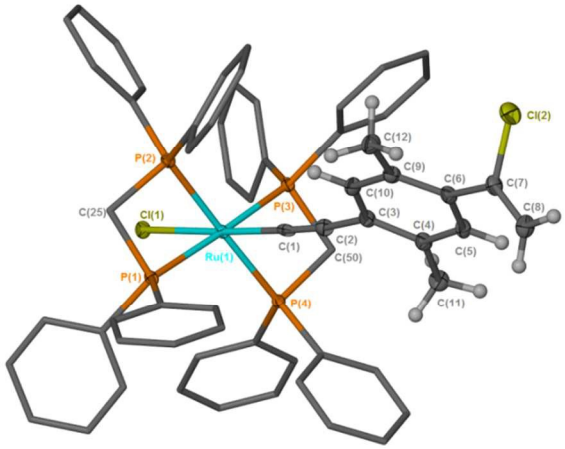


Figure 1 Solid state structure of [**6b**], solvent of crystallisation and selected hydrogen atoms removed for clarity. Anisotropic displacement parameters (where shown) are at the 50 % probability level. Selected bond lengths / Å Ru(1)-C(1) 2.025(2), C(1)-C(2) 1.179(3), C(7)-C(8) 1.321(3), C(7)-Cl(2) 1.757(2). Selected bond angles / ° C(1)-Ru(1)-Cl(1) 177.86(5), Ru(1)-C(1)-C(2) 177.36(17), C(1)-C(2)-C(3) 172.7(2), C(6)-C(7)-Cl(2) 116.32(15), C(8)-C(7)-C(6) 125.6(2).

Addition of [N^{n}Bu$_4$]Cl to [**1a**]$^+$ in CH$_2$Cl$_2$ solution resulted in the rapid formation of a single new compound identified as *trans*-[Ru(C≡CC$_6$H$_4$-4-CCl=CH$_2$)Cl(dppm)$_2$], [**6a**] (Scheme 2). An identical reaction was observed in the reaction between [N^{n}Bu$_4$]Cl and [**1b**]$^+$ to give *trans*-[Ru(C≡CC$_6$H$_2$-2,5-Me$_2$-4-CCl=CH$_2$)Cl(dppm)$_2$], [**6b**]. Evidence for the formation of [**6a**] and [**6b**] arises from the ^{1}H NMR spectrum where two doublet resonances for the germinal protons on the alkene were observed at δ 5.33 and δ 5.60 [**6a**] and δ 5.23 and δ 5.52 [**6b**] with a mutual coupling of 1.5 Hz. The presence of the alkene group was confirmed by resonances at δ 110.0 and 140.7 ([**6a**]) and δ 114.2 and 139.4 ([**6b**]) in the ^{13}C{^{1}H} NMR spectra, the latter showing cross peaks in a HMQC experiment to the two alkene protons described above. The observation of ν(C≡C) bands at 2074 ([**6a**]) and 2056 ([**6b**]) cm^{-1} in the IR spectra confirmed the presence of the alkynyl functionality. Furthermore, the structures of [**6a**] (ESI) and [**6b**] (Figure 1) were also elucidated by a single crystal X-ray diffraction study, which confirmed the predictions made on the basis of the NMR and IR spectra.

It is well established that the metal-bound, carbene carbon atoms of vinylidene ligands are highly electrophilic and attack by chloride at this site might be predicted.3[c] However, given the steric crowding at the metal this process is presumably prohibited, as evidenced by the lack of reaction between *trans*-[RuCl(C=CHPh)(dppm)$_2$]$^+$ and [N^{n}Bu$_4$]Cl under similar conditions. Addition of [N^{n}Bu$_4$]Cl to the alkynyl complex *trans*-[Ru(C≡CC$_6$H$_4$-4-C≡CH)Cl(dppm)$_2$], [**5a**], did not result in any reaction until HBF$_4$ was added, ruling out direct nucleophilic attack at the neutral complex.[8]

The completion between two potential pathways for nucleophilic attack by chloride at cationic complexes was considered (Scheme 3). In the first case (pathway A), rearrangement of [**1a**]$^+$ to give cumulene [**2a**]$^+$ could occur (corresponding to the process shown in Scheme 1b) which would then undergo direct nucleophilic attack at C(7) to give [**6a**]. Whereas in the case of Pathway B addition to C(1) of the vinylidene of [**1a**]$^+$ would afford *trans*-[Ru(CCl=CH-C$_6$H$_4$-4-C≡CH)Cl(dppm)$_2$], [**7a**]. The viability of these pathways was evaluated using Density Functional Theory (see ESI for details of the methodology employed).

In the case of pathway A the calculations demonstrated that [**2a**]$^+$ lies only 41 kJ mol^{-1} higher in energy than [**1a**]$^+$ and, given that in the presence of even weak bases (such as acetate or chloride) low energy proton shuttle pathways become available for transition metal vinylidene complexes,[9] rapid interconversion between [**1a**]$^+$ and [**2a**]$^+$ *via* [**5a**] is proposed. However, the difference in energy between the two isomers indicates that the equilibrium lies in favour of [**1a**]$^+$.

In both pathways A and B, linear transit scans were performed to model the approach of chloride to C(1) of [**1a**]$^+$ and C(7) of [**2a**]$^+$. The energy of a series of complexes with varied C-Cl distances were probed and the species with C-Cl bond lengths between 3.3 and 2.2 Å all exhibited a single imaginary frequency corresponding to C-Cl bond formation. Although the kinetic barriers for attack by Cl$^-$ at C(1) in [**1a**]$^+$ and C(7) in [**2a**]$^+$ appear to be broadly similar and relatively low it is clear that the formation of [**6a**] is thermodynamically preferred as this complex lies 129 kJ mol^{-1} lower in energy than [**1a**]$^+$ with free chloride anion, and 105 kJ mol^{-1} lower in energy than [**7a**]. Indeed, the free energy of formation of [**7a**] is only favourable by 14 kJ mol^{-1} when compared to [**1a**]$^+$ and free chloride (shown as a dotted line in Figure 2) and given that the transit scan shows that the greatest barrier to

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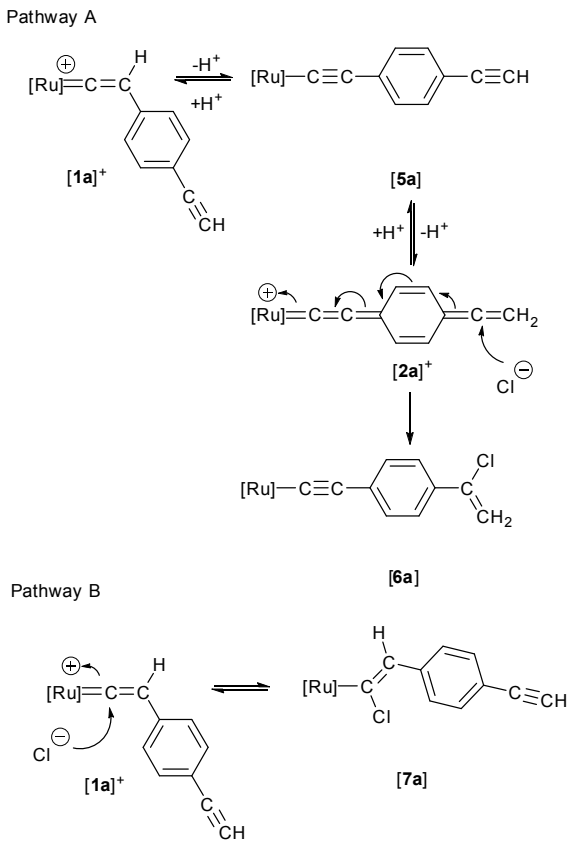

Scheme 3

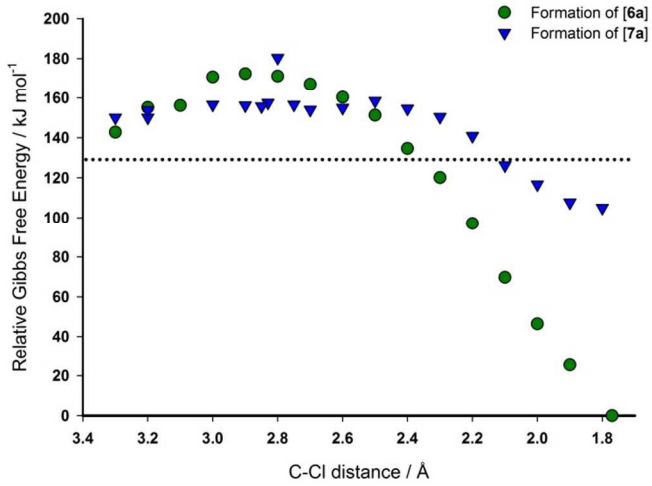

Figure 2 Linear transit scan for nucleophilic attack of Cl^- on complex [**1a**]$^+$ (C_1 position) and [**2a**]$^+$ (C_7 position). Free energies are at 298 K and relative to the optimised structure of [**6a**]. The dotted line shows the relative energy of complex [**1a**]$^+$ and free Cl^-.

the reverse reaction would be 75 kJ mol^{-1}, attack at this position would be expected to be reversible and so the calculations provide a rational for why nucleophilic attack as [**1a**]$^+$ is not observed.

Therefore the DFT calculations not only indicate that [**2a**]$^+$ is accessible in solution, but that there is a significant thermodynamic preference for nucleophilic attack at the coordinated quinoidal cummulene ligand. The nature of the products obtained from these reactions support these suggestions. In considering the scope of the vinylidene / cumulene rearrangement, it is interesting to note that Markovnikov addition of HBr to the pendant alkyne in [Mn(=C=CH-C_6H_4-C≡CH)$(CO)_2$Cp] has also been observed, although at that time no quinoidal cumulene was implicated in the process.[10]

In summary, we have obtained mechanistic evidence for the participation of an extended even-numbered cumulene ligand which promotes facile nucleophilic attack onto a coordinated organic ligand. At present, work in our groups is underway to explore the effects of other aromatic and heterocyclic moieties as conjugated spacers to support extended cumulated ligand structures, and investigate dipolar additions to these extended carbon-rich, unsaturated ligands.

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Notes and references

[a] Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK.
[b] School of Chemistry and Biochemistry, Bayliss Building, The University of Western Australia, 35 Stirling Highway Crawley, Perth Western Australia 6009, e-mail paul.low@uwa.edu.au tel (+61 8) 6488 3045
[c] Department of Chemistry, University of York, Heslington, York, YO10 5DD, e-mail jason.lynam@york.ac.uk tel +44(0)1904322534

Electronic Supplementary Information (ESI) available: Experimental details, DFT calculations, X-Ray data in CIF format. See DOI: 10.1039/c000000x/

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