Synthesis, Structure and Redox Chemistry of the Aminoallenylidene Complex \([\text{Mo}\{\text{C}=\text{C}(\text{Me})\text{N\text{Et}_2}\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\text{BPh}_4\)

Huriyyah A. Alturaifi,\textit{a} Hawa Gerriow,\textit{a} Josef B. G. Gluyas,\textit{b} Sebastian Mjörnstedt,\textit{a} James Raftery,\textit{a} Paul J. Low,\textit{b}\textsuperscript{*} and Mark W. Whiteley\textit{a}\textsuperscript{*}

\textit{a}School of Chemistry, University of Manchester, Manchester M13 9PL, UK
\textit{b} School of Chemistry and Biochemistry, University of Western Australia, 35 Stirling Highway, Crawley 6009, Australia,

Corresponding Authors. Email paul.low@uwa.edu.au, Mark.Whiteley@manchester.ac.uk

Abstract

The reaction of \([\text{MoBr(dppe)}(\eta\text{-C}_7\text{H}_7)]\) (dppe = Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2}) with HC≡CC≡CSiMe\textsubscript{3} and Na[BPh\textsubscript{4}] in 1:1 NHEt\textsubscript{2}/thf as solvent, yields the aminoallenylidene complex \([\text{Mo}\{\text{C}=\text{C}(\text{Me})\text{N\text{Et}_2}\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\text{BPh}_4\), \([1]\text{BPh}_4\). The reaction likely proceeds via nucleophilic addition of NHEt\textsubscript{2} at C\textsubscript{γ} of a butatrienylidene intermediate. Structural and spectroscopic characterisation of \([1]\text{BPh}_4\) indicate a significant contribution of an iminium-alkynyl resonance form to the overall structure of the heteroatom stabilised allenylidene ligand. The X-ray structural study of \([1]\text{BPh}_4\) determines a Mo-C\textsubscript{α} bond length of 2.077(3) Å, intermediate between that of the cumulenic diphenylallenylidene analogue \([\text{Mo}(\text{C}=\text{CPh}_2)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\text{PF}_6\) (1.994(3)Å) and the alkynyl \([\text{Mo}(\text{C}=\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\) (2.138(5)Å). Complex \([1]\text{BPh}_4\) undergoes a reversible one-electron oxidation with \(E_{1/2} = -0.19\) V with respect to the FeCp\textsubscript{2}/FeCp\textsubscript{2}\textsuperscript{+} couple and the stable 17-electron radical dication \([1]^{2+}\) is readily observed by spectroelectrochemical methods. IR spectroelectrochemistry in \text{CH}_2\text{Cl}_2 demonstrates that the \(\nu(\text{CCC})\) stretch, characteristic of the allenylidene ligand, shifts to higher wavenumber (from 1959 to 2032 cm\textsuperscript{-1}) as a result of oxidation of \([1]^+\) to \([1]^{2+}\), consistent with a strongly metal-centred redox process and an enhancement in the alkynyl character of the allenylidene ligand following one-electron oxidation.

Keywords
Molybdenum, Allenylidene, Alkynyl, Redox chemistry, Spectroelectrochemistry
Introduction


In addition to potential applications in synthesis [1e,12] and catalysis [1e,13], an important feature of metal allenylidene systems is the detail of the bonding interaction between the metal centre and the allenylidene ligand [14]. Heteroatom stabilised, cationic metal allenylidene complexes \([\{M\}=\text{C}=\text{C}=(\text{R})\text{ER}{'_n}]^+\) have been described as a hybrid of four resonance forms (Figure 1, (I) to (IV)) with cumulenic structures represented by (I) and (II) and alkynyl resonance forms by (III) and (IV). As discussed previously in several reports, a series of factors influence the relative contributions of cumulenic type resonance forms vs. alkynyl type resonance structures where the positive charge resides either at the terminal carbon Cγ (III) or on the ER′n group (IV). In general, the importance of the alkynyl resonance forms is enhanced by increased donor capacity of the heteroatom ER′n group and this can be confirmed by observation of changes in the IR active, asymmetric \(\nu\) (CCC) stretch of the allenylidene ligand and crystallographically determined M-Cα, Cα-Cβ and Cβ-Cγ distances [8a].

![Figure 1](image)

Figure 1 Resonance structures of a cationic heteroatom (E) substituted allenylidene complex.
A further well documented procedure to examine the details of a metal-ligand bonding interaction is to monitor the structural and spectroscopic changes that occur as a result of a redox process which leads to an isolable or spectroscopically observable redox pair [15]. In this context, Winter and co-workers have investigated the spectroelectrochemistry of a series of heteroatom substituted allenylidene complexes of the type \([\text{Ru}\{C=C=C(R)ER'_2\}\text{Cl}(\text{dppm})_2]^+\) and monitored the changes in the IR active \(\nu(\text{CCC})\) stretch and the UV-Vis spectrum following one-electron oxidation to the 17-electron dication and one-electron reduction to a 19-electron neutral system [8a,9]. One limitation to these investigations is the high redox potential associated with the Ru(II)/Ru(III) couple for one-electron oxidation and the associated relatively poor thermodynamic stability of the resulting 17-electron species.

In a series of investigations, we have demonstrated that cycloheptatrienyl molybdenum complexes of the type \([\text{MoX(dppe)}(\eta\text{-C}_7\text{H}_7)]^{n+}\) exhibit an extensive oxidative redox chemistry of thermodynamically stable 17-electron radical systems [16]. These findings are attributable to a high energy, metal based \(d_{z^2}\) HOMO in the fragment \(\{\text{Mo(dppe)}(\eta\text{-C}_7\text{H}_7)\}\) and resultant symmetry attenuated interaction with ligand X. A few examples of stable 17-electron dications of the type \([\text{MoX(dppe)}(\eta\text{-C}_7\text{H}_7)]^{2+}\) are known [16a], including the heteroatom substituted cyclic oxacarbene \([\text{Mo}\{\text{C(CH}_2_3O}\}\text{(dppe)}(\eta\text{-C}_7\text{H}_7)]^{2+}\) and this suggested that a related heteroatom substituted allenylidene could also exhibit the requisite stability. The diphenylallenylidene complex \([\text{Mo}(C=C=C\text{Ph}_2)(\text{dppe})(\eta\text{-C}_7\text{H}_7)])[\text{PF}_6]\) has been prepared previously [17] via the classical method of Selegue but in the current work, the focus was upon the development of the synthesis of a heteroatom substituted derivative \([\text{Mo}\{C=C=C(R)NR'_2\}\text{(dppe)}(\eta\text{-C}_7\text{H}_7)]^+\) for which the redox potential for one-electron oxidation may be expected to be significantly more thermodynamically favourable due to the enhanced contribution of alkynyl resonance forms (III) and (IV) to the structure.

**Results and discussion**

1. **Synthetic Studies.**

The synthetic protocol selected for generation of \([\text{Mo}\{C=C=C(R)NR'_2\}\text{(dppe)}(\eta\text{-C}_7\text{H}_7)]^+\)
follows the principle of nucleophilic addition at Cγ of an intermediate cationic butatrienyldiene. For example, treatment of cis-[RuCl2(dppm)2] with buta-1,3-diyne (HC≡CC≡CH) and NaSbF6 followed by addition of a secondary amine NHR2 results in the formation of the aminoallenylidene complexes trans-[Ru{C≡C=CH2}Cl(dppm)2]SbF6 via the butatrienyldiene trans-[Ru(C≡C=CH2)Cl(dppm)2]⁺ [9c]. Alternatively the buta-1,3-diyne synthon HC≡CC≡CSiMe3 which is considerably easier to handle has been employed [10] in the synthesis of the alkoxy-allenylidene [{Fe}{C≡C=CH2}OME}dppe]Cp*PF6 and this synthetic method provided a conceptual basis for the current work.

The reaction of [MoBr(dppe)(η-C7H7)] with HC≡CC≡CSiMe3 and Na[BPh4] dissolved in a 1:1 solvent mixture of NHEt2/thf resulted in a colour change from brown-green to a deep purple colour and after stirring for 21 h. the aminoallenylidene complex [Mo{C≡C=CH2}Cl(dppe)(η-C7H7)]BPh4, [1]BPh4 was isolated in good yield as a deep green solid. The synthesis likely proceeds as shown in Scheme 1 via the initial formation of the butatrienyldiene intermediate [Mo{C≡C=CH2}Cl(dppe)(η-C7H7)]BPh4 (R = H or SiMe3). Subsequent addition of the solvent-based nucleophile NHEt2 at Cγ followed by proton migration to the neighbouring Cδ terminal carbon gives the final product [1]⁺. There was no evidence for the presence of the SiMe3 protecting group in the final product and therefore at some juncture in the reaction sequence, SiMe3 is replaced by H as is widely reported for reactions of SiMe3 protected alkynes with organometallics in methanol or dichloromethane [18]. The use of Na[BPh4] was essential to the success of the synthesis and attempts to isolate complex [1]⁺ as a [PF6]⁻ salt by replacement of Na[BPh4] with K[PF6] were unproductive.

Complex [1]BPh4 was fully characterised by microanalysis, mass spectrometry, IR and ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectroscopy (see Experimental Section) and by an X-ray structural determination. As discussed below, the structural and spectroscopic features of [1]BPh4 are fully consistent with the properties of a heteroatom stabilised allenylidene ligand and a substantial contribution of the alkynyl resonance forms (III) and (IV) (Fig. 1) to the overall structure.
Scheme 1

2. Structural and Spectroscopic Investigations

To establish the identity of complex [1]+ as a heteroatom substituted aminoallenylidene complex, X-ray quality crystals of [1]BPh₄ were obtained by vapour diffusion of diethylether into an acetonitrile solution of the complex. The molecular structure of [1]BPh₄, annotated with the atomic numbering scheme is shown in Figure 2 and important bond lengths and angles are summarised in Table 1 together with key comparative data for the structurally related systems, [Mo(C≡CPh)(dppe)(η-CH₂-CH₃)]PF₆, [2]PF₆, [17], [Mo(C≡CPh)(dppe)(η-C₇H₇)], 3, [19] and Z-trans-[Ru{C≡C=CH₂(Me)N(Me)CH₂Ph}Cl(dppm)₂]SbF₆, [4]SbF₆.[9c]
**Figure 2** Molecular structure of [1]BPh₄ with thermal ellipsoids plotted at 50% probability. H atoms and BPh₄ counter-ion omitted for clarity.

**Table 1**: Key structural data for [1]BPh₄ and structurally related allenylidene and alkynyl complexes.

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<tbody>
<tr>
<td>Bond lengths (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-Cα</td>
<td>2.077(3)</td>
<td>1.994(3)</td>
<td>2.138(5)</td>
<td>1.947(6)</td>
</tr>
<tr>
<td>Cα-Cβ</td>
<td>1.224(4)</td>
<td>1.258(5)</td>
<td>1.205(6)</td>
<td>1.217(9)</td>
</tr>
<tr>
<td>Cβ-Cγ</td>
<td>1.391(4)</td>
<td>1.354(5)</td>
<td>-</td>
<td>1.398(9)</td>
</tr>
<tr>
<td>Cγ-R</td>
<td>1.507(4)(R = Me)</td>
<td>1.479(5), 1.490(5)(R = Ph)</td>
<td>-</td>
<td>1.526(12)(R = Me)</td>
</tr>
<tr>
<td>Cγ-N</td>
<td>1.318(4)</td>
<td>-</td>
<td>-</td>
<td>1.290(10)</td>
</tr>
<tr>
<td>M-P</td>
<td>2.4531(6), 2.499(2)</td>
<td>2.5132(9), 2.5102(9)</td>
<td>2.467(1), 2.477(1)</td>
<td>2.3446(19), 2.349(2), 2.3593(19), 2.3474(19)</td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-Cα-Cβ</td>
<td>176.4(2)</td>
<td>176.1(3)</td>
<td>178.5(4)</td>
<td>175.6(6)</td>
</tr>
<tr>
<td>Cα-Cβ-Cγ</td>
<td>175.9(3)</td>
<td>174.4(4)</td>
<td>-</td>
<td>170.8(8)</td>
</tr>
<tr>
<td>Cβ-Cγ-R</td>
<td>118.9(3)</td>
<td>121.1(3), 119.1(3)</td>
<td>-</td>
<td>117.4(7)</td>
</tr>
<tr>
<td>Cγ-Cγ-N</td>
<td>120.9(3)</td>
<td>-</td>
<td>-</td>
<td>123.6(8)</td>
</tr>
</tbody>
</table>

The structural data for [1]BPh₄ are consistent with a substantial contribution of alkynyl resonance forms (III) and (IV) to the overall structure. For example, by comparison with the diphenyl-allenylidene analogue [2]^+ (which is well described in terms of a cumulenic structure), complex [1]^+ exhibits elongated Mo-Cα and Cβ-Cγ distances and a shorter Cα-Cβ separation, consistent with enhanced multiple bond character of the latter. The Mo-Cα distance in [1]^+, (Mo(1)-C(34) = 2.077(3) Å) is still significantly shorter than found for analogous alkynyl complexes (typically 2.11–2.14 Å) [16b] but is correspondingly much longer than the Mo-Cα distance in [2]^+ and the vinylidene complex [Mo(C≡CHPh)(dppe)(η-C₇H₇)]BF₄ (1.93(1) Å) [20].

In addition to the Mo-Cα distance, the Mo-P bond lengths provide an indirect indicator of the character of the Mo-Cα bond by acting as a monitor of electron density at the Mo centre. For the cumulenic complex [Mo(C≡C=CPh₂)(dppe)(η-C₇H₇)]PF₆, [2]PF₆, the average Mo-P distance is 2.51 Å, (cf. [Mo(C≡CHPh)(dppe)(η-C₇H₇)]BF₄, Mo-P(average) = 2.53 Å). This quite long distance reflects a reduction in Mo to P back bonding effects as electron density at the Mo centre is depleted by the electron accepting cumulenic diphenylallenylidene ligand. By contrast, the average Mo-P distance in heteroatom stabilised [1]BPh₄ (2.48 Å) is rather shorter (cf. [Mo(C≡CPh)(dppe)(η-C₇H₇)], Mo-P(average) = 2.47 Å [19]), consistent with enhanced Mo-P back bonding and a corresponding reduction in the electron acceptor capacity of the heteroatom stabilised aminoallenylidene ligand.

The global geometry of the aminoallenylidene ligand of [1]BPh₄, may be compared with that of Z-trans-[Ru{C≡C=C(Me)NMeCH₂Ph}Cl(dpmm)]SbF₆, [4]SbF₆. The majority of bond lengths and angles are comparable within the limits of the accuracy of the structure determinations. A key feature of the aminoallenylidene ligand is the shortening of the Cγ-N bond; the Cγ-N bond lengths of [1]^+ and [4]^+ (1.318(4), 1.290(10) Å respectively) are much closer in length to a typical C≡N double bond (ca. 1.30 Å) than a C≡N single bond (ca. 1.47Å) and also similar to the Cα-N bond length determined for heteroatom stabilised aminocarbene complexes [M{C(Me)NH₂}(dppe)Cp']^+ (M = Fe, Ru; Cp' = Cp, Cp*) [21]. These data indicate a substantial contribution of the iminium-alkynyl resonance form (IV) (Fig 1) to the structure of [1]^+. 

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A summary of key spectroscopic data for [1]+ together with comparative data for the cycloheptatrienyl complexes [2]+ and 3 and the direct diethylaminoallenylidene ligand analogue of [1]+ supported by {RuCl(dppe)}2, trans-[Ru{C=C=C(Me)NEt2}Cl(dppe)}2]SbF6, [5]SbF6 is presented in Table 2. A detailed analysis of the spectroscopic properties of heteroatom substituted allenylidene complexes is available in the literature [8a] and therefore only a brief discussion of the salient spectroscopic features of [1]+ will be presented here.

Table 2 Key spectroscopic data for [1]BPh4 and related complexes. a

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<tbody>
<tr>
<td>IR b ν(CCC)/(C≡C)</td>
<td>1959</td>
<td>1876</td>
<td>2045</td>
<td>1993c</td>
</tr>
<tr>
<td>ν(C=N)</td>
<td>1542</td>
<td>-</td>
<td>-</td>
<td>1557c</td>
</tr>
<tr>
<td>31P{1H} NMR a C α: 228.9, t {25}</td>
<td>C α: 285.4, t {33}</td>
<td>C α: 144.3, q {14}</td>
<td></td>
<td></td>
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<tr>
<td>C β: 130.6</td>
<td>C β: 178.7, t, {10}</td>
<td>C β: 119.1, q, {2}</td>
<td></td>
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</tr>
<tr>
<td>C γ: 146.2</td>
<td>C γ: 136.3, t, {6}</td>
<td>C γ: 154.2, q, {1}f</td>
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a [2]PF6 = [Mo(C≡CPh2)(dppe)(η-C7H7)]PF6, 3 = [Mo(C≡CPh)(dppe)(η-C7H7)], [5]SbF6 = trans-[Ru{C=C=C(Me)NEt2}Cl(dppe)}2]SbF6. b In CH2Cl2 unless stated otherwise. c In 1,2-C2H4Cl2. d In CD2Cl2 unless stated otherwise, values in parentheses {} indicate J(C-P) in Hz, t = triplet, q = quintet, br = broad. e In CDCl3. f In CD3CN.

The IR spectrum of complex [1]+ in CH2Cl2 solution exhibits two key absorptions, one at 1959 cm⁻¹ attributable to the asymmetric ν(CCC) stretching mode and a second band at 1542 cm⁻¹ arising from the Cγ=N stretch. Consistent with the enhanced alkynyl character of the aminoallenylidene ligand of [1]+, the position of the ν(CCC) band is to high wavenumber of the cumulenic diphenyldiynylidene analogue [2]+, although it is still much lower in wavenumber than the ν(C≡C) stretch of a typical alkynyl complex [Mo(C≡CR)(dppe)(η-C7H7)] (ν(C≡C) in the range 2040-2060 cm⁻¹).[16b] The 31P{1H} NMR chemical shift of the dppe ligand phosphorus atoms also appears to be sensitive to the alkynyl character of [1]+ with the chemical
shift of 60.3 ppm, quite close to typical values determined for alkynyl complexes (generally in the range 64-66 ppm) [16b], and distinct from cumulenylidene complexes such as [2]+ and the vinylidenes [Mo{C=C(H)R}2(dppe)(C7H7)]+ which exhibit 31P{1H} NMR shifts in the range 51-54 ppm. [17] The ν(C=N) stretching frequency at 1542 cm⁻¹ is in the correct region for the C=N multiple bond of aminoallenylidene complexes and, in common with related complexes based on the {RuCl(dppe)2} moiety [9c], restricted rotation about the aminoallenylidene C=N bond results in inequivalence of the amino ethyl substituents in both 1H and 13C{1H} NMR spectra. The chemical shift order of the constituent carbons of the allenylidene chain of [1]+ also follows the order expected for a heteroatom substituted system with Cβ shifted to high field of Cγ [8a], consistent with increased alkynyl character at the beta carbon; the assignment of the resonance for Cβ in [I]+ was assisted by a HMBC (Heteronuclear multiple bond correlation) experiment, exploiting the proximity of the methyl substituent on Cγ.

3. Electrochemistry

The principal motivation in the synthesis of complex [1]+ was to investigate the structural and spectroscopic changes resulting from one-electron oxidation of [1]+ to the 17-electron dication [1]2+. A series of electrochemical and spectroelectrochemical investigations on heteroatom substituted allenylidene complexes supported by the {RuCl(dppe)2} unit have been reported previously [8a,9]. However in the current work the use of the {Mo(dppe)(η-C7H7)} system was expected to promote low thermodynamic potentials for oxidation and a strongly metal centred redox orbital, essentially decoupled from allenylidene ligand contributions.

The electrochemical response of the allenylidene complexes [1]+ and [2]+ was examined by cyclic voltammetry; the results are presented in Table 3 together with data for related complexes for comparison. Under the conditions given in Table 3, each of complexes [1]+ and [2]+ undergoes a diffusion controlled, chemically and electrochemically reversible, one-electron oxidation with the separation between cathodic and anodic peak potentials comparable to that determined for the internal ferrocene standard.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$ (V)</th>
<th>$P_L$</th>
<th>ref.</th>
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<tbody>
<tr>
<td>[1]$^+$</td>
<td>$-0.19$</td>
<td>$-0.86$</td>
<td>this work</td>
</tr>
<tr>
<td>[2]$^+$</td>
<td>$+0.41$</td>
<td>$-0.27$</td>
<td>this work</td>
</tr>
<tr>
<td>3</td>
<td>$-0.72$</td>
<td>$-1.26$</td>
<td>16b</td>
</tr>
<tr>
<td>[Mo{C=C(Me)Bu'$}$(dppe)(η-C$_7$H$_7$)]$^+$</td>
<td>$+0.49$</td>
<td>$-0.11$</td>
<td>16a</td>
</tr>
<tr>
<td>[5]$^+$</td>
<td>$+0.41$</td>
<td>$-0.84$</td>
<td>9c</td>
</tr>
</tbody>
</table>

*All potentials are reported vs. FeCp$_2$/FeCp$_2^+$ = 0.00 V. Data for complexes [1]$^+$ and [2]$^+$ from 0.2 M $n$Bu$_4$NPF$_6$/CH$_2$Cl$_2$ solutions at ambient temperature at a glassy carbon working electrode. [2]$^+$ = [Mo(C=C=CPh$_2$)(dppe)(η-C$_7$H$_7$)]$^+$, 3 = [Mo(C≡CPh)(dppe)(η-C$_7$H$_7$)], [5]$^+$ = trans-[Ru{C=C(C(Me)NEt$_2$)}Cl(dppm)$_2$]SbF$_6$. |

There is a substantial difference between measured $E_{1/2}$ values for the one-electron oxidation of [1]$^+$ and [2]$^+$ with $E_{1/2}$ shifted to negative potential by 0.60 V by exchange of the cumulenic ligand of [2]$^+$ for the heteroatom substituted ligand of [1]$^+$. For [2]$^+$, the $E_{1/2}$ value of $+0.41$ V vs. FeCp$_2$/FeCp$_2^+$ is not significantly different to that of the vinylidene [Mo{C=C(Me)Bu'}(dppe)(η-C$_7$H$_7$)]$^+$, and this serves to emphasise the strong acceptor cumulenic character of the diphenylallenylidene ligand. By comparison the $E_{1/2}$ value of $-0.19$ V vs. FeCp$_2$/FeCp$_2^+$ for [1]$^+$ is intermediate between that of [2]$^+$ and an authentic metal alkynyl such as 3, consistent with enhanced electron density at the metal centre by comparison with [2]$^+$. Table 3 also presents the ligand $P_L$ parameters, determined as described by Pombeiro [22]. The $P_L$ value of $-0.86$ V estimated for the diethylaminoallenylidene ligand of [1]$^+$ agrees very well with the equivalent value at a {RuCl(dppm)$_2$} centre and indicates that the diethylaminoallenylidene ligand acts as a strong net donor group to the metal centre.

4. Spectroelectrochemical Investigations

The $E_{1/2}$ value for one-electron oxidation of [1]$^+$ is 0.60 V negative of that of the corresponding {RuCl(dppm)$_2$}-based diethylaminoallenylidene complex [5]$^+$ and this relatively low potential
for the generation of 17-electron species \([\text{I}]^{2+}\) indicated that the latter should be readily observable by spectroscopic methods. The oxidised species \([\text{I}]^{2+}\) was generated in an OTTLE cell [23] from a solution in CH\(_2\)Cl\(_2\) / 0.1 M \(n\text{Bu}_4\text{NPF}_6\), and the UV-Vis-NIR and IR spectra recorded \textit{in situ}. The initial spectra corresponding to \([\text{I}]^{+}\) were completely regenerated upon re-reduction of the sample during the spectroelectrochemical experiments indicating that the species observed was indeed \([\text{I}]^{2+}\). The electronic spectrum of \([\text{I}]^{+}\) is characterised by MLCT absorption envelopes with apparent absorption maxima at 17440 and 22470 cm\(^{-1}\). Upon oxidation to \([\text{I}]^{2+}\) these absorption bands collapse, and give rise to a series of overlapping and unresolved absorption features from the UV region into the visible; the complex is NIR silent in both oxidation states. The key observation in the IR spectrum of \([\text{I}]^{2+}\) is the replacement of bands for \([\text{I}]^{+}\) at 1959 (\(\nu\text{(CCC)}, \text{s}\)) and 1542 (\(\nu\text{(C=N)}, \text{m}\)) cm\(^{-1}\) with new bands at 2032 (\(\nu\text{(CCC)}, \text{w}\)) and 1598 (\(\nu\text{(C=N)}, \text{m}\)) cm\(^{-1}\) (Figure 3).

**Figure 3** IR spectra of \([\text{I}]^{n+}\) (\(n = 1, 2\)) recorded spectroelectrochemically in dichloromethane / 0.1 M \(n\text{Bu}_4\text{NPF}_6\).

On oxidation of \([\text{I}]^{+}\) to \([\text{I}]^{2+}\), the aminoallenylidene \(\nu\text{(CCC)}\) band shifts to high wavenumber by approximately 70 cm\(^{-1}\) and is also significantly decreased in intensity. The decrease in intensity in \(\nu\text{(CCC)}\) following one-electron oxidation has been observed previously for \textit{trans-}\[\text{Ru}\{\text{C=C=C(Me)NEt}_2\}\text{Cl(dppm)z}\]^{n+} (\(n = 1, 2\)), \([5]^{n+}\) and related complexes and may be
attributed to a reduction in molecular dipole on progressing from the mono- to the di- cation as a positive charge resides both at the metal centre and on the aminoallenylidene ligand in the oxidised dicaticionic system [9b]. However the shift in \( \nu(\text{CCC}) \) to higher wavenumber following one-electron oxidation of \([1]^+\) to \([1]^{2+}\) is in direct contrast to the observed decrease in the equivalent parameter reported to result from one-electron oxidation of \([5]^+\) to \([5]^{2+}\). The result for the \([5]^+ / [5]^{2+}\) couple is in common with several other heteroatom substituted allenylidene complexes supported by the \{RuCl(dppe)\}_2\ system and, with one exception [9a], a shift in \( \nu(\text{CCC}) \) to low wavenumber by 40-60 cm\(^{-1}\) is observed following one-electron oxidation.

A comparison of redox induced changes in \( \nu(\text{CCC}) / \nu(\text{C=\=C}) \) and \( \nu(\text{C=\=C}) \) for the couple \([1]^+ / [1]^{2+}\) with equivalent data for a series of closely related aminoallenylidene and phenylalkynyl 18- / 17-electron redox pairs is presented in Table 4.

**Table 4** Redox induced changes in \( \nu(\text{CCC}) / \nu(\text{C=\=C}) \) and \( \nu(\text{C=\=N}) \) for selected aminoallenylidene and phenylalkynyl complexes.a

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \nu(\text{CCC}) / \nu(\text{C==C}) ) (cm(^{-1}))</th>
<th>( \Delta \nu(\text{CCC}) / \nu(\text{C==C}) ) (cm(^{-1}))</th>
<th>( \nu(\text{C==N}) ) (cm(^{-1}))</th>
<th>( \Delta \nu(\text{C==N}) ) (cm(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([1]^+ / [1]^{2+})</td>
<td>1959 / 2032</td>
<td>+73</td>
<td>1542 / 1598</td>
<td>+56</td>
<td>t/w</td>
</tr>
</tbody>
</table>

\(^{a}\) 3/[3]\(^+\) = [Mo(C=\=CPh)(dppe)(\eta-C\(_7\)H\(_7\))]\(^{n^+}\), \([5]^+ / [5]^{2+}\) = trans-[Ru{C=\=C(C(Me)NEt\(_2\))Cl(dppe)}\(_2\)]\(^{n^+}\), 6/[6]\(^+\) = trans-[Ru(C=\=CPh)Cl(dppe)\(_2\)]\(^{n^+}\). IR data recorded spectroelectrochemically in CH\(_2\)Cl\(_2\) / 0.1 M \( n\text{Bu}_4\text{NPF}_6\) (or for \([5]^+ / [5]^{2+}\) 1,2-C\(_2\)H\(_4\)Cl\(_2\) / \( n\text{Bu}_4\text{NPF}_6\)). t/w = this work.

The apparently anaomalous behaviour of the redox-induced changes in \( \nu(\text{CCC}) \) of the aminoallenylidene ligand may be rationalised by a consideration of the extended bonding character of the ligand and the specific electronic features of the metal supporting groups Mo(dppe)(\eta-C\(_7\)H\(_7\)) and RuCl(P-P)\(_2\) (P-P = bidentate phosphine ligand). Figure 4 presents some key resonance forms of an aminoallenylidene ligand (A) to (D), which illustrate the evolution of
ligand bonding properties from the $\pi$-acceptor character of cumulenic form (A) in the 18-electron monocation, through iminium-alkynyl structures (B) and (C) to the formally $\pi$-donor character of resonance form (D) in the 17-electron dication. In terms of the IR active $\nu$(CCC) stretching frequency, contributions from both resonance forms (A) and (D) might be expected to result in a lowering in wavenumber. Superimposed upon this ligand bonding description are the electronic properties of the supporting metal group \{M\}. When \{M\} = Mo(dppe)(\eta-\text{C}_7\text{H}_7), the metal centre has a high energy, metal based HOMO whereas, by contrast where \{M\} = RuCl(dpdm)$_2$, the HOMO is much lower in energy (see $E_{1/2}$ values in Table 3) and possesses enhanced ligand character. As a consequence, as explained below, it is suggested that the transition in the bonding character of the aminoallenylidene ligand resulting from one-electron oxidation is rather different for the two metal support types and this leads to the contrasting behaviour observed in the shift in $\nu$(CCC).

Figure 4 Key resonance forms of a metal aminoallenylidene complex in 18- and 17-electron configurations.

Where \{M\} = Mo(dppe)(\eta-\text{C}_7\text{H}_7), the monocation [1]$^+$ may be expected to have an important contribution from the cumulenic, $\pi$-acceptor resonance form (A) arising from back donation from the high energy HOMO of the electron rich metal centre, [8a]; evidence for this is provided by the unusually low value for the $\nu$(CCC) stretching frequency in [1]$^+$ (a similar observation may also be made for the diphenylallenylidene derivative [2]PF$_6$, see Table 2). This metal to ligand back bonding interaction is effectively eliminated following one-electron oxidation of [1]$^+$ to [1]$^{2+}$. The strongly metal-centred character of the redox process [1]$^+$ / [1]$^{2+}$ results in a predominance of the iminium alkynyl resonance form (C) contributing to the
structure of \([1]^{2+}\); indirect evidence for the extremely limited contribution from the cumulenic structure (D) may be inferred from the very small change in \(\nu(C=C)\) following one-electron oxidation of the phenylalkynyl derivative 3 to 17-electron [3]\(^+\) (see Table 4). Overall therefore conversion of [1]\(^+\) to [1]\(^{2+}\) results in a decrease in the contribution of cumulenic resonance forms to the overall structure and the enhanced iminium alkynyl character resulting from one-electron oxidation leads to a shift in \(\nu(CCC)\) to higher wavenumber. Where \(\{M\} = RuCl(dppe)\) the opposite arguments apply. In this case, by comparison with \(\{M\} = Mo(dppe)(\eta-C_7H_7)\), there is a reduced contribution of resonance form (A) to 18-electron [5]\(^+\) but correspondingly an enhanced contribution of resonance form (D) in the 17-electron dication [5]\(^{2+}\). Alkynyl complexes supported by Ru(dppe)Cp’ and RuCl(P-P)\(_2\) (P-P = chelate phosphine) units are known to have a significant contribution to the redox orbital from the alkynyl ligand [24,25] and one-electron oxidation results in a large decrease (ca. 100-150 cm\(^{-1}\), see Table 4) in the alkynyl \(\nu(C=C)\) stretching frequency [24,26]. The net effect of one-electron oxidation of [5]\(^+\) to [5]\(^{2+}\) is therefore to increase the cumulenic character of the aminoallenylidene ligand and accordingly a shift in \(\nu(CCC)\) to lower wavenumber is observed.

**Conclusions**

The aminoallenylidene complex [Mo\{C=C=C(Me)NEt\(_2\}\}(dppe)(\eta-C_7H_7)]BPh\(_4\), [1]BPh\(_4\), has been obtained in a convenient, one-pot synthesis from the reaction of [MoBr(dppe)(\eta-C_7H_7)] with HC≡CC≡CSiMe\(_3\) in a mixed thf/NHEt\(_2\) solvent system. Spectroscopic and X-ray structural investigations indicate that the metal-ligand bonding in [1]BPh\(_4\) includes a significant contribution from an iminium-alkynyl resonance structure. The electrochemistry of [1]BPh\(_4\) displays the operation of a reversible one-electron oxidation process to give the thermodynamically stable 17-electron radical dication [1]\(^{2+}\). Spectroelectrochemical investigations on the redox pair [1]\(^+\) / [1]\(^{2+}\) reveal an increase in the IR active \(\nu(CCC)\) stretching frequency of ca. 70 cm\(^{-1}\) following one-electron oxidation in contrast to the redox-induced behaviour of the aminoallenylidene ligand in [Ru\{C=C=C(Me)NEt\(_2\}\}Cl(dppe)\(_n\)]\(^{2+}\) (n = 1, 2), where a shift in \(\nu(CCC)\) to lower wavenumber is observed. These observations serve to highlight the highly flexible bonding character of the aminoallenylidene ligand which might be considered as a special case of an alkynyl ligand with additional \(\pi\)-acceptor capability. The use of the Mo(dppe)(\eta-C_7H_7) support unit in the current work brings the
advantage that the redox process is strongly metal based and therefore interpretation of the IR spectroscopic data can essentially be simplified to a consideration of the expected decrease in π-back donation and increase in iminium alkynyl character following one-electron oxidation.

**Experimental**

**General Procedures.**

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The complex [MoBr(dppe)(η-C7H7)] was prepared by a published procedure [27]. NMR spectra were recorded on a Bruker Avance III HD (500 MHz 1H, 125 MHz 13C{1H}, 202 MHz 31P{1H}) spectrometer. Solution Infrared spectra were obtained on a Shimadzu IR Affinity-1S FTIR spectrometer and MALDI mass spectra were recorded using a Shimadzu Axima Confidence spectrometer. Microanalyses were conducted by the staff of the Microanalytical Service of the School of Chemistry, University of Manchester. Cyclic voltammograms were recorded from 0.2 M nBu4NPF6/CH2Cl2 solutions ca. 1 x 10⁻⁴ M in analyte using a three-electrode cell equipped with a glassy carbon working electrode, Pt wire counter electrode and Ag/AgCl reference electrode. All redox potentials are reported with reference to an internal standard of the ferrocene / ferrocenium couple (FeCp2/FeCp2⁺ = 0.00 V). Spectroelectrochemistry was conducted in an OTTLE cell [23] using solutions in dichloromethane containing 0.1 M nBu4NPF6 as the supporting electrolyte. Spectra were recorded on an Agilent Technologies Cary 660 FTIR or an Avantes diode array UV-Vis-NIR system comprising two light sources (UV-Vis: AvaLight-DH-S-Bal, Vis-NIR: AvaLight-Hal-S) and two spectrometers (UV-Vis: AvaSpec-ULS204-8L-USB2, NIR: AvaSpec-NIR256-2.5TEC) connected to a custom-built sample holder by bifurcated fibre optic cables. The Vis-NIR light source was attenuated with a band-pass filter transparent between ~900–4700 nm. Electrolysis in the cell was performed using a PalmSens Emstat³⁺ potentiostat at a scan rate of 10 mVs⁻¹.

**Preparation of HC≡CC≡CSiMe₃**

The preparation of HC≡CC≡CSiMe₃ was carried out by a modification of reported literature procedures [28]. Both diethylether and thf were investigated as reaction solvents but reactions in
diethylether appeared to progress only slowly and incompletely. Full conversion of 
Me$_3$SiC=CC=CSiMe$_3$ to HC=CC=CSiMe$_3$ was not achieved even in thf with a 1.5 molar excess 
of MeLi/LiBr as evidenced by IR spectra of isolated products which exhibited a ν(CCC) band at 
2066 cm$^{-1}$ (CH$_2$Cl$_2$) (lit 2065 cm$^{-1}$ [29]) due to unreacted Me$_3$SiC=CC=CSiMe$_3$ in addition to 
product bands at 2189 and 2034 cm$^{-1}$ (lit. 2190, 2035 cm$^{-1}$ [30]).

Me$_3$SiC=CC=CSiMe$_3$ (2.00 g, 10.3 mmol) was dissolved in distilled, degassed thf (25 cm$^3$) 
and stirred under N$_2$ forming a beige solution. The solution was cooled to -78 °C before 
MeLi/LiBr (10 cm$^3$ of a 1.5 M solution in diethylether, 15.0 mmol) was added dropwise over 
10 min. The reaction mixture was stirred at -78 °C for 1 h. and then allowed to warm to room 
temperature and stirring continued for a further 2.5 h. Saturated aqueous NH$_4$Cl solution (30 
cm$^3$) was added portion-wise with cooling and the mixture was then stirred for 1 h. The 
reaction mixture was extracted with pentane (40 cm$^3$) and the organic layer was washed with 
brine, dried with MgSO$_4$, filtered and evaporated to give the product as a yellow-brown oil; 
IR: ν(C≡C) (cm$^{-1}$), (CH$_2$Cl$_2$), 2189, 2066, 2034. The isolated product was used directly 
without further purification in subsequent reactions with an assumed yield of 
HC=CC=CSiMe$_3$ of ca. 50% consistent with previous reports [28b].

**Preparation of [Mo{C=C=C(NEt$_2$)CH$_3$}(dppe)(η-C$_7$H$_7$)]BPh$_4$**

A mixture of [MoBr(dppe)(η-C$_7$H$_7$)] (0.762 g, 1.15 mmol), HC=CC=CSiMe$_3$ (prepared as 
described above from Me$_3$SiC=CC=CSiMe$_3$, 1.00 g, 5.15 mmol and MeLi/LiBr, 5 cm$^3$ of a 
1.5 M solution in diethylether, 7.5 mmol), and Na[BPh$_4$] (0.394 g, 1.15 mmol) was 
suspended in a 1:1 HNEt$_2$/thf solvent mixture (40 cm$^3$) then stirred at room temperature for 
21 h. to give a deep purple solution. The solvent was removed under vacuum and the 
resulting residue was recrystallized from CH$_2$Cl$_2$/diethyl ether to give the product as a deep 
green solid; yield 0.671 g, (57%). $^1$H NMR (CD$_2$Cl$_2$): δ 7.65, 7.37, 7.30, 7.18, 7.05, 6.89, 
6.73 (m, 40H, Ph, dppe and [BPh$_4$]), 4.81 (s, 7H, C$_7$H$_7$), 2.91 (q, $J_{H-H}$ 5 Hz, 2H, CH$_2$, NEt$_2$), 
2.44 (q, $J_{H-H}$ 5 Hz, 2H, CH$_2$, NEt$_2$), 2.23, 2.20 (m, 4H, CH$_2$, dppe), 1.09 (s, 3H, C$_7$- CH$_3$), 
0.81 (t, $J_{H-H}$ 5 Hz, 3H, CH$_3$,NEt$_2$), 0.58 (t, $J_{H-H}$ 5 Hz, 3H, CH$_3$, NEt$_2$). $^{13}$C{H} NMR 
(CD$_2$Cl$_2$): δ 228.9, t, ($J_{C-P}$ 25 Hz) C$_{α}$; 163.9, m, C$_{β}$; 146.2, s, C$_{γ}$; 130.6, br, C$_{δ}$; 138.5 m, 
C$_{δ}$, PPh$_2$, dppe; 135.8, s, 125.6, s, 121.7, s, Ph, BPh$_4$; 133.3, 130.9, 130.7, 129.8, 128.9, 128.7,
m, PPh₂, dppe; 88.9, s, C₇H₇; 48.0, s, CH₂, NEt₂; 44.6, s, CH₂, NEt₂; 26.5, m, CH₂, dppe; 21.2, s, CH₃, Cγ-CH₃; 13.1, s, CH₃, NEt₂; 11.8, s, CH₃, NEt₂. ³¹P{H} NMR (CD₂Cl₂): δ 60.3.

IR (CH₂Cl₂; cm⁻¹): ν(CCC) 1959, ν(CN) 1542. MS MALDI (m/z): 710 [M⁺]. Anal. Calcd. (%): for C₆₅H₆₄BMoNP₂: C, 75.9; H, 6.2; N, 1.4. Found: C, 76.2; H, 6.4; N, 1.5.

Crystallography

Single crystals of [1]BPh₄ were obtained as bronze-green blocks by vapour diffusion of diethyl ether into a CH₃CN solution of the complex at 4°C. Single crystal X-ray data were collected at 100 K on a Bruker APEX-II CCD Diffractometer, by a means of Cu-Kα (λ = 1.54178 Å) radiation. SHELXS-97 [31] was employed for the computing structure solution and SHELXL-2014/7 [32] for the computing structure refinement. The structure was solved by direct methods with refinement based on F². The non-hydrogen atoms were refined anisotropically and H atoms were included in calculated positions.

Crystal Data for [1]BPh₄: C₆₅H₆₄BMoNP₂, Mr = 1027.86, triclinic, space group P-1, a = 10.0541(3) Å, b = 14.4743(4) Å, c = 19.2548(6) Å, α = 77.289(2)°, β = 86.325(2)°, γ = 73.589(2)°, U = 2622.04(14) Å³, Z = 2, μ = 2.934 mm⁻¹, 24284 reflections collected, final wR₂(F²) = 0.0990 for all data, conventional R₁ = 0.0410 for 9853 reflections with I>2σ(I), S = 1.039.

Appendix. Supplementary material

CCDC 1493834 contains the supplementary crystallographic data for complex [1]BPh₄. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the Government of Saudi Arabia for a research studentship (to H.A.A). We also gratefully acknowledge funding from the EPSRC and ARC (DP 140100855). PJL held an EPSRC leadership fellowship and now holds an ARC Future Fellowship (FT 120100073).
References


Spectroelectrochemical IR investigations on the aminoallenylidene complex
\([\text{Mo}\{\text{C}=\text{C}(\text{Me})\text{NET}_2\}\{\text{dppe}\}(\eta^1-\text{C}_7\text{H}_7)]\text{BPh}_4, [1]^+,\) reveal that a reversible one-electron oxidation to the 17-electron radical dication \([1]^{2+}\) results in an enhancement in the iminium alkynyl character of the ligand.