

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

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## Abstract

The reaction of  $[\text{MoBr}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$  (dppe =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) with  $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$  and  $\text{Na}[\text{BPh}_4]$  in 1:1  $\text{NHEt}_2/\text{thf}$  as solvent, yields the aminoallenylidene complex  $[\text{Mo}\{\text{C}=\text{C}=\text{C}(\text{Me})\text{NEt}_2\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\text{BPh}_4$ , **[1]** $\text{BPh}_4$ . The reaction likely proceeds via nucleophilic addition of  $\text{NHEt}_2$  at  $\text{C}_\gamma$  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  $\text{Mo-C}_\alpha$  bond length of 2.077(3) Å, intermediate between that of the cumulenic diphenylallenylidene analogue  $[\text{Mo}(\text{C}=\text{C}=\text{CPh}_2)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\text{PF}_6$  (1.994(3)Å) and the alkynyl  $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$  (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  $\text{FeCp}_2/\text{FeCp}_2^+$  couple and the stable 17-electron radical dication **[1]**<sup>2+</sup> 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  $\text{cm}^{-1}$ ) as a result of oxidation of **[1]**<sup>+</sup> to **[1]**<sup>2+</sup>, consistent with a strongly metal-centred redox process and an enhancement in the alkynyl character of the allenylidene ligand following one-electron oxidation.

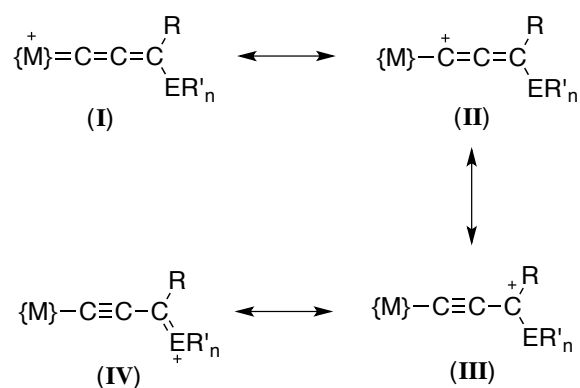
## Keywords

Molybdenum, Allenylidene, Alkynyl, Redox chemistry, Spectroelectrochemistry

## Introduction

Investigations on the synthesis, structure and reactivity of metal cumulenic complexes [1] have developed significantly since the early reports on the synthesis of metal allenylidenes by Fischer [2], Berke [3] and Selegue [4]. Allenylidene complexes are now accessible by a range of synthetic routes including dehydration of 2-propyn-1-ols, [5], alkylation of acyl substituted metal alkynyl complexes [6] and nucleophilic addition at  $C_\gamma$  of a butatrienylidene intermediate [7]. This latter method provides a versatile synthesis of heteroatom substituted allenylidene ligands [8] leading to a wide range of amino-, [9] alkoxy-, [7b,10] and thio-allenylidene [11] systems.

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  $\{M\}=C=C=C(R)ER'_n\}^+$  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  $C_\gamma$  (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  $\nu(\text{CCC})$  stretch of the allenylidene ligand and crystallographically determined  $M-C_\alpha$ ,  $C_\alpha-C_\beta$  and  $C_\beta-C_\gamma$  distances [8a].



**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  $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{R})\text{ER}'_n\}\text{Cl}(\text{dppm})_2]^+$  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  $[\text{MoX}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^{n+}$  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  $\{\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}$  and resultant symmetry attenuated interaction with ligand X. A few examples of stable 17-electron dications of the type  $[\text{MoX}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^{2+}$  are known [16a], including the heteroatom substituted cyclic oxacarbene  $[\text{Mo}\{\text{C}(\text{CH}_2)_3\text{O}\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^{2+}$  and this suggested that a related heteroatom substituted allenylidene could also exhibit the requisite stability. The diphenylallenylidene complex  $[\text{Mo}(\text{C}=\text{C}=\text{CPh}_2)(\text{dppe})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$  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  $[\text{Mo}\{\text{C}=\text{C}=\text{C}(\text{R})\text{NR}'_2\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$  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

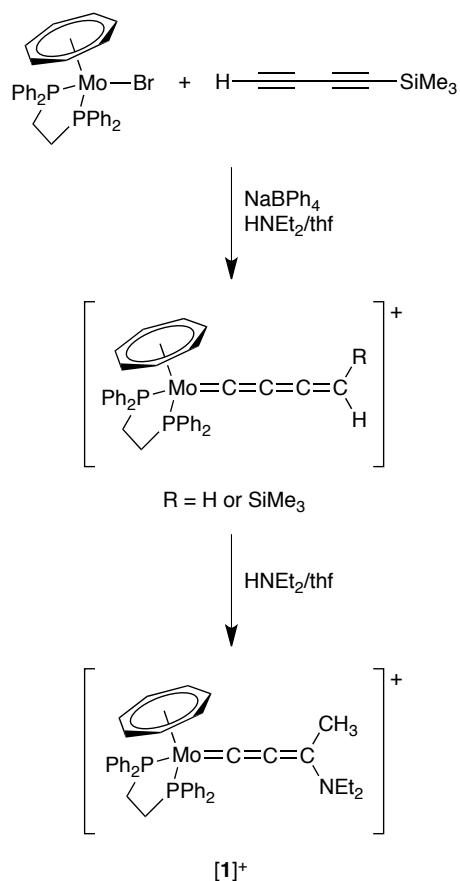
### 1. Synthetic Studies.

The synthetic protocol selected for generation of  $[\text{Mo}\{\text{C}=\text{C}=\text{C}(\text{R})\text{NR}'_2\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$

follows the principle of nucleophilic addition at  $C_\gamma$  of an intermediate cationic butatrienylidene. For example, treatment of *cis*-[RuCl<sub>2</sub>(dppm)<sub>2</sub>] with buta-1,3-diyne (HC≡CC≡CH) and NaSbF<sub>6</sub> followed by addition of a secondary amine NHR<sub>2</sub> results in the formation of the aminoallenylidene complexes *trans*-[Ru{C=C=C(Me)NR<sub>2</sub>}Cl(dppm)<sub>2</sub>]SbF<sub>6</sub> via the butatrienylidene *trans*-[Ru(C=C=C=CH<sub>2</sub>)Cl(dppm)<sub>2</sub>]<sup>+</sup> [9c]. Alternatively the buta-1,3-diyne synthon HC≡CC≡CSiMe<sub>3</sub> which is considerably easier to handle has been employed [10] in the synthesis of the alkoxy-allenylidene [Fe{C=C=C(Me)OMe}(dppe)Cp\*]PF<sub>6</sub> and this synthetic method provided a conceptual basis for the current work.

The reaction of [MoBr(dppe)(η-C<sub>7</sub>H<sub>7</sub>)] with HC≡CC≡CSiMe<sub>3</sub> and Na[BPh<sub>4</sub>] dissolved in a 1:1 solvent mixture of NHEt<sub>2</sub>/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=C(Me)NEt<sub>2</sub>}(dppe)(η-C<sub>7</sub>H<sub>7</sub>)]BPh<sub>4</sub>, [**1**]BPh<sub>4</sub> 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 butatrienylidene intermediate [Mo{C=C=C=C(H)R}(dppe)(η-C<sub>7</sub>H<sub>7</sub>)]BPh<sub>4</sub> (R = H or SiMe<sub>3</sub>). Subsequent addition of the solvent-based nucleophile NHEt<sub>2</sub> at  $C_\gamma$  followed by proton migration to the neighbouring  $C_\delta$  terminal carbon gives the final product [**1**]<sup>+</sup>. There was no evidence for the presence of the SiMe<sub>3</sub> protecting group in the final product and therefore at some juncture in the reaction sequence, SiMe<sub>3</sub> is replaced by H as is widely reported for reactions of SiMe<sub>3</sub> protected alkynes with organometallics in methanol or dichloromethane [18]. The use of Na[BPh<sub>4</sub>] was essential to the success of the synthesis and attempts to isolate complex [**1**]<sup>+</sup> as a [PF<sub>6</sub>]<sup>-</sup> salt by replacement of Na[BPh<sub>4</sub>] with K[PF<sub>6</sub>] were unproductive.

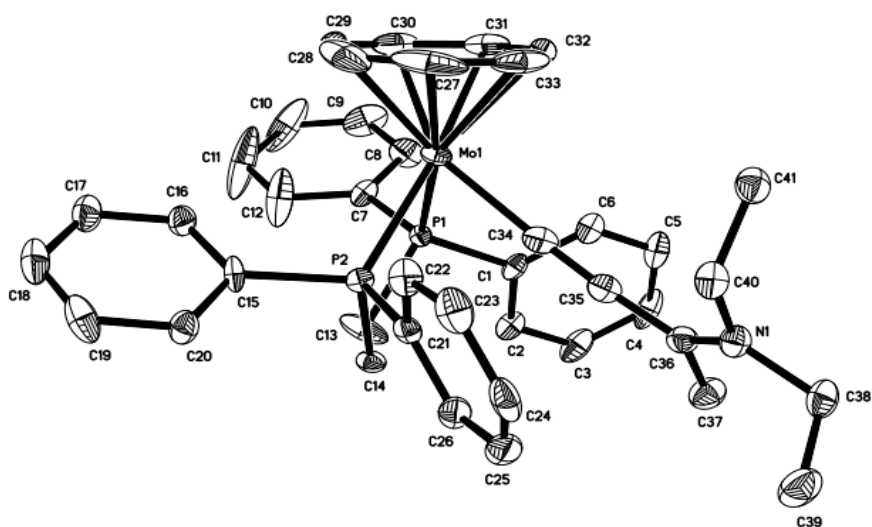
Complex [**1**]BPh<sub>4</sub> was fully characterised by microanalysis, mass spectrometry, IR and <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy (see Experimental Section) and by an X-ray structural determination. As discussed below, the structural and spectroscopic features of [**1**]BPh<sub>4</sub> 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  $[1]\text{BPh}_4$  were obtained by vapour diffusion of diethylether into an acetonitrile solution of the complex. The molecular structure of  $[1]\text{BPh}_4$ , 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,  $[\text{Mo}(\text{C}=\text{C}=\text{CPh}_2)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\text{PF}_6$ ,  $[2]\text{PF}_6$ , [17],  $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ , **3**, [19] and *Z-trans*- $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{Me})\text{N}(\text{Me})\text{CH}_2\text{Ph}\}\text{Cl}(\text{dppm})_2]\text{SbF}_6$ , **[4]** $\text{SbF}_6$ .<sup>[9c]</sup>



**Figure 2** Molecular structure of [1]BPh<sub>4</sub> with thermal ellipsoids plotted at 50% probability. H atoms and BPh<sub>4</sub> counter-ion omitted for clarity.

**Table 1:** Key structural data for [1]BPh<sub>4</sub> and structurally related allenylidene and alkynyl complexes.<sup>a</sup>

Complex	[1]BPh <sub>4</sub>	[2]PF <sub>6</sub>	3	[4]SbF <sub>6</sub>
Bond lengths (Å)				
M-C <sub>α</sub>	2.077(3)	1.994(3)	2.138(5)	1.947(6)
C <sub>α</sub> -C <sub>β</sub>	1.224(4)	1.258(5)	1.205(6)	1.217(9)
C <sub>β</sub> -C <sub>γ</sub>	1.391(4)	1.354(5)	-	1.398(9)
C <sub>γ</sub> -R	1.507(4) (R = Me)	1.479(5), 1.490(5) (R = Ph)	-	1.526(12) (R = Me)
C <sub>γ</sub> -N	1.318(4)	-	-	1.290(10)
M-P	2.4531(6) 2.499(2)	2.5132(9) 2.5102(9)	2.467(1) 2.477(1)	2.3446(19), 2.349(2) 2.3593(19), 2.3474(19)
Bond angles (°)				
M-C <sub>α</sub> -C <sub>β</sub>	176.4(2)	176.1(3)	178.5(4)	175.6(6)
C <sub>α</sub> -C <sub>β</sub> -C <sub>γ</sub>	175.9(3)	174.4(4)	-	170.8(8)
C <sub>β</sub> -C <sub>γ</sub> -R	118.9(3)	121.1(3), 119.1(3)	-	117.4(7)
C <sub>β</sub> -C <sub>γ</sub> -N	120.9(3)	-	-	123.6(8)

<sup>a</sup> [2]PF<sub>6</sub> = [Mo(C=C=CPh<sub>2</sub>)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)]PF<sub>6</sub>, **3** = [Mo(C≡CPh)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)], [4]SbF<sub>6</sub> = *Z-trans*-[Ru{C=C=C(Me)NMeCH<sub>2</sub>Ph}Cl(dppe)<sub>2</sub>]SbF<sub>6</sub>.

The structural data for [1]BPh<sub>4</sub> 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]<sup>+</sup> (which is well described in terms of a cumulenenic structure), complex [1]<sup>+</sup> exhibits elongated Mo-C<sub>α</sub> and C<sub>β</sub>-C<sub>γ</sub> distances and a shorter C<sub>α</sub>-C<sub>β</sub> separation, consistent with enhanced multiple bond character of the latter. The Mo-C<sub>α</sub> distance in [1]<sup>+</sup>, (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-C<sub>α</sub> distance in [2]<sup>+</sup> and the vinylidene complex [Mo(C=CHPh)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)]BF<sub>4</sub> (1.93(1) Å) [20].

In addition to the Mo-C<sub>α</sub> distance, the Mo-P bond lengths provide an indirect indicator of the character of the Mo-C<sub>α</sub> bond by acting as a monitor of electron density at the Mo centre. For the cumulenenic complex [Mo(C=C=CPh<sub>2</sub>)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)]PF<sub>6</sub>, [2]PF<sub>6</sub>, the average Mo-P distance is 2.51 Å, (*cf.* [Mo(C=CHPh)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)]BF<sub>4</sub>, 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 cumulenenic diphenylallenylidene ligand. By contrast, the average Mo-P distance in heteroatom stabilised [1]BPh<sub>4</sub> (2.48 Å) is rather shorter (*cf.* [Mo(C≡CPh)(dppe)(η-C<sub>7</sub>H<sub>7</sub>)]BF<sub>4</sub>, 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]BPh<sub>4</sub>, may be compared with that of *Z-trans*-[Ru{C=C=C(Me)NMeCH<sub>2</sub>Ph}Cl(dppe)<sub>2</sub>]SbF<sub>6</sub>, [4]SbF<sub>6</sub>. 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 C<sub>γ</sub>-N bond; the C<sub>γ</sub>-N bond lengths of [1]<sup>+</sup> and [4]<sup>+</sup> (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.* 1.47 Å) and also similar to the C<sub>α</sub>-N bond length determined for heteroatom stabilised aminocarbene complexes [M{C(Me)NH<sub>2</sub>}(dppe)Cp'<sup>+</sup>] (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]<sup>+</sup>.

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  $\{\text{RuCl}(\text{dppm})_2\}$ , *trans*- $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{Me})\text{NEt}_2\}\text{Cl}(\text{dppm})_2]\text{SbF}_6$ , **[5]** $\text{SbF}_6$  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  $[1]\text{BPh}_4$  and related complexes.<sup>a</sup>

Complex	$[1]\text{BPh}_4$	$[2]\text{PF}_6$	<b>3</b>	<b>[5]</b> $\text{SbF}_6$
IR <sup>b</sup> $\nu(\text{CCC})/(\text{C}\equiv\text{C})$	1959	1876	2045	1993 <sup>c</sup>
$\nu(\text{C}=\text{N})$	1542	-	-	1557 <sup>c</sup>
$^{31}\text{P}\{\text{H}\}$ NMR <sup>d</sup>	60.3	51.4	64.6	-8.7 <sup>e</sup>
$^{13}\text{C}\{\text{H}\}$ NMR <sup>d</sup>	$C_\alpha$ : 228.9, t {25} $C_\beta$ : 130.6 $C_\gamma$ : 146.2	$C_\alpha$ : 285.4, t {33} $C_\beta$ : 178.7, t, {10} $C_\gamma$ : 136.3, t, {6}	$C_\alpha$ : 141.4, t {26} $C_\beta$ : 121.6, br.	$C_\alpha$ : 204.3, q {14} $C_\beta$ : 119.1, q, {2} $C_\gamma$ : 154.2, q, {1} <sup>f</sup>

<sup>a</sup>  $[2]\text{PF}_6 = [\text{Mo}(\text{C}=\text{C}=\text{CPh}_2)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\text{PF}_6$ , **3** =  $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$ , **[5]** $\text{SbF}_6 = \textit{trans}$ - $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{Me})\text{NEt}_2\}\text{Cl}(\text{dppm})_2]\text{SbF}_6$ . <sup>b</sup> In  $\text{CH}_2\text{Cl}_2$  unless stated otherwise. <sup>c</sup> In 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$ . <sup>d</sup> In  $\text{CD}_2\text{Cl}_2$  unless stated otherwise, values in parentheses {} indicate  $J(\text{C}-\text{P})$  in Hz, t = triplet, q = quintet, br = broad. <sup>e</sup> In  $\text{CDCl}_3$ . <sup>f</sup> In  $\text{CD}_3\text{CN}$ .

The IR spectrum of complex  $[1]^+$  in  $\text{CH}_2\text{Cl}_2$  solution exhibits two key absorptions, one at  $1959\text{ cm}^{-1}$  attributable to the asymmetric  $\nu(\text{CCC})$  stretching mode and a second band at  $1542\text{ cm}^{-1}$  arising from the  $\text{C}_\gamma=\text{N}$  stretch. Consistent with the enhanced alkynyl character of the aminoallenylidene ligand of  $[1]^+$ , the position of the  $\nu(\text{CCC})$  band is to high wavenumber of the cumulenic diphenylallenylidene analogue  $[2]^+$ , although it is still much lower in wavenumber than the  $\nu(\text{C}\equiv\text{C})$  stretch of a typical alkynyl complex  $[\text{Mo}(\text{C}\equiv\text{CR})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$  ( $\nu(\text{C}\equiv\text{C})$  in the range  $2040\text{-}2060\text{ cm}^{-1}$ ).<sup>[16b]</sup> The  $^{31}\text{P}\{\text{H}\}$  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 cumulenyliene complexes such as  $[2]^+$  and the vinylidenes  $[\text{Mo}\{\text{C}=\text{C}(\text{H})\text{R}\}(\text{dppe})(\text{C}_7\text{H}_7)]^+$  which exhibit  $^{31}\text{P}\{^1\text{H}\}$  NMR shifts in the range 51-54 ppm. [17] The  $\nu(\text{C}_\gamma=\text{N})$  stretching frequency at  $1542\text{ cm}^{-1}$  is in the correct region for the  $\text{C}=\text{N}$  multiple bond of aminoallenylidenes and, in common with related complexes based on the  $\{\text{RuCl}(\text{dppm})_2\}$  moiety [9c], restricted rotation about the aminoallenylidene  $\text{C}=\text{N}$  bond results in inequivalence of the amino ethyl substituents in both  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  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  $\text{C}_\beta$  shifted to high field of  $\text{C}_\gamma$  [8a], consistent with increased alkynyl character at the beta carbon; the assignment of the resonance for  $\text{C}_\beta$  in  $[1]^+$  was assisted by a HMBC (Heteronuclear multiple bond correlation) experiment, exploiting the proximity of the methyl substituent on  $\text{C}_\gamma$ .

### 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  $\{\text{RuCl}(\text{dppm})_2\}$  unit have been reported previously [8a,9]. However in the current work the use of the  $\{\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)\}$  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 3.** Cyclic Voltammetric data and ligand parameters ( $P_L$ ) for compounds  $[1]^+$ ,  $[2]^+$ , **3**,  $[\text{Mo}\{\text{C}=\text{C}(\text{Me})\text{Bu}^t\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$  and  $[5]^+$ . <sup>a</sup>

Compound	$E_{1/2}$ (V)	$P_L$	ref.
$[1]^+$	-0.19	-0.86	this work
$[2]^+$	+0.41	-0.27	this work
<b>3</b>	-0.72	-1.26	16b
$[\text{Mo}\{\text{C}=\text{C}(\text{Me})\text{Bu}^t\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$	+0.49	-0.11	16a
$[5]^+$	+0.41	-0.84	9c

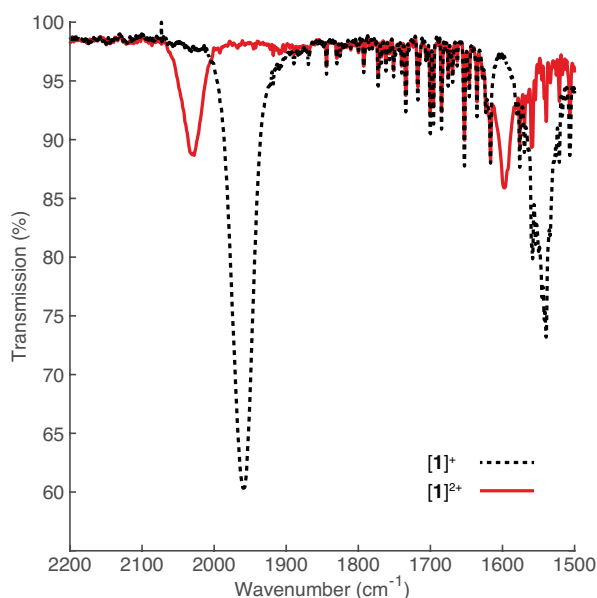
<sup>a</sup>All potentials are reported vs.  $\text{FeCp}_2/\text{FeCp}_2^+ = 0.00$  V. Data for complexes  $[1]^+$  and  $[2]^+$  from 0.2 M  $n\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$  solutions at ambient temperature at a glassy carbon working electrode.  $[2]^+ = [\text{Mo}(\text{C}=\text{C}=\text{CPh}_2)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$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

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 cumulenyl ligand of  $[2]^+$  for the heteroatom substituted ligand of  $[1]^+$ . For  $[2]^+$ , the  $E_{1/2}$  value of + 0.41 V vs.  $\text{FeCp}_2/\text{FeCp}_2^+$  is not significantly different to that of the vinylidene  $[\text{Mo}\{\text{C}=\text{C}(\text{Me})\text{Bu}^t\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ , and this serves to emphasise the strong acceptor cumulenyl character of the diphenylallenylidene ligand. By comparison the  $E_{1/2}$  value of -0.19 V vs.  $\text{FeCp}_2/\text{FeCp}_2^+$  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  $\{\text{RuCl}(\text{dppm})_2\}$  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  $\{\text{RuCl}(\text{dppm})_2\}$ -based diethylaminoallenylidene complex  $[5]^+$  and this relatively low potential

for the generation of 17-electron species  $[1]^{2+}$  indicated that the latter should be readily observable by spectroscopic methods. The oxidised species  $[1]^{2+}$  was generated in an OTTLE cell [23] from a solution in  $\text{CH}_2\text{Cl}_2$  / 0.1 M  $n\text{Bu}_4\text{NPF}_6$ , and the UV-Vis-NIR and IR spectra recorded *in situ*. The initial spectra corresponding to  $[1]^+$  were completely regenerated upon re-reduction of the sample during the spectroelectrochemical experiments indicating that the species observed was indeed  $[1]^{2+}$ . The electronic spectrum of  $[1]^+$  is characterised by MLCT absorption envelopes with apparent absorption maxima at 17440 and 22470  $\text{cm}^{-1}$ . Upon oxidation to  $[1]^{2+}$  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  $[1]^{2+}$  is the replacement of bands for  $[1]^+$  at 1959 ( $\nu(\text{CCC})$ , s) and 1542 ( $\nu(\text{C}=\text{N})$ , m)  $\text{cm}^{-1}$  with new bands at 2032 ( $\nu(\text{CCC})$ , w) and 1598 ( $\nu(\text{C}=\text{N})$ , m)  $\text{cm}^{-1}$  (Figure 3).



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

On oxidation of  $[1]^+$  to  $[1]^{2+}$ , the aminoallenylidene  $\nu(\text{CCC})$  band shifts to high wavenumber by approximately 70  $\text{cm}^{-1}$  and is also significantly decreased in intensity. The decrease in intensity in  $\nu(\text{CCC})$  following one-electron oxidation has been observed previously for *trans*- $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{Me})\text{NEt}_2\}\text{Cl}(\text{dppm})_2]^{n+}$  ( $n = 1, 2$ ),  $[5]^{n+}$  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 dicationic system [9b]. However the shift in  $\nu(\text{CCC})$  to higher wavenumber following one-electron oxidation of  $[\mathbf{1}]^+$  to  $[\mathbf{1}]^{2+}$  is in direct contrast to the observed decrease in the equivalent parameter reported to result from one-electron oxidation of  $[\mathbf{5}]^+$  to  $[\mathbf{5}]^{2+}$ . The result for the  $[\mathbf{5}]^+ / [\mathbf{5}]^{2+}$  couple is in common with several other heteroatom substituted allenylidene complexes supported by the  $\{\text{RuCl}(\text{dppm})_2\}$  system and, with one exception [9a], a shift in  $\nu(\text{CCC})$  to low wavenumber by 40-60  $\text{cm}^{-1}$  is observed following one-electron oxidation. A comparison of redox induced changes in  $\nu(\text{CCC})$  and  $\nu(\text{C=N})$  for the couple  $[\mathbf{1}]^+ / [\mathbf{1}]^{2+}$  with equivalent data for a series of closely related aminoallenylidene and phenylalkynyl 18- / 17- electron redox pairs is presented in Table 4.

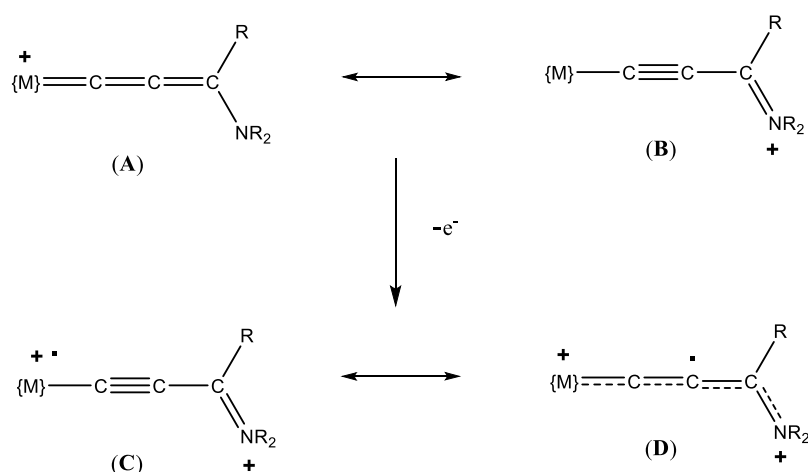
**Table 4** Redox induced changes in  $\nu(\text{CCC})/\nu(\text{C}\equiv\text{C})$  and  $\nu(\text{C=N})$  for selected aminoallenylidene and phenylalkynyl complexes.<sup>a</sup>

Complex	$\nu(\text{CCC})/\nu(\text{C}\equiv\text{C})$ ( $\text{cm}^{-1}$ )		$\Delta \nu(\text{CCC})/\nu(\text{C}\equiv\text{C})$ ( $\text{cm}^{-1}$ )	$\nu(\text{C=N})$ ( $\text{cm}^{-1}$ )		$\Delta \nu(\text{C=N})$ ( $\text{cm}^{-1}$ )	Ref.
	18 e <sup>-</sup>	17 e <sup>-</sup>		18 e <sup>-</sup>	17 e <sup>-</sup>		
$[\mathbf{1}]^+ / [\mathbf{1}]^{2+}$	1959	2032	+ 73	1542	1598	+ 56	t/w
$\mathbf{3} / [\mathbf{3}]^+$	2045	2032	- 13	-	-	-	16b
$[\mathbf{5}]^+ / [\mathbf{5}]^{2+}$	1993	1948	- 45	1557	1597	+ 40	9c
$\mathbf{6} / [\mathbf{6}]^+$	2075	1910	- 165	-	-	-	26

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

The apparently anomalous 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  $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$  and  $\text{RuCl}(\text{P-P})_2$  (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  $\nu(\text{CCC})$  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)( $\eta$ -C<sub>7</sub>H<sub>7</sub>), the metal centre has a high energy, metal based HOMO whereas, by contrast where {M} = RuCl(dppe)<sub>2</sub>, 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  $\nu(\text{CCC})$ .



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

Where {M} = Mo(dppe)( $\eta$ -C<sub>7</sub>H<sub>7</sub>), the monocation [**1**]<sup>+</sup> 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  $\nu(\text{CCC})$  stretching frequency in [**1**]<sup>+</sup> (a similar observation may also be made for the diphenylallenylidene derivative [**2**]PF<sub>6</sub>, see Table 2). This metal to ligand back bonding interaction is effectively eliminated following one-electron oxidation of [**1**]<sup>+</sup> to [**1**]<sup>2+</sup>. The strongly metal-centred character of the redox process [**1**]<sup>+</sup> / [**1**]<sup>2+</sup> 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 cumulenenic structure (**D**) may be inferred from the very small change in  $\nu(\text{C}\equiv\text{C})$  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 cumulenenic resonance forms to the overall structure and the enhanced iminium alkynyl character resulting from one-electron oxidation leads to a shift in  $\nu(\text{CCC})$  to higher wavenumber. Where  $\{\text{M}\} = \text{RuCl}(\text{dppm})_2$  the opposite arguments apply. In this case, by comparison with  $\{\text{M}\} = \text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$ , 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  $\text{Ru}(\text{dppe})\text{Cp}'$  and  $\text{RuCl}(\text{P-P})_2$  (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  $\text{cm}^{-1}$ , see Table 4) in the alkynyl  $\nu(\text{C}\equiv\text{C})$  stretching frequency [24,26]. The net effect of one-electron oxidation of  $[5]^+$  to  $[5]^{2+}$  is therefore to increase the cumulenenic character of the aminoallenylidene ligand and accordingly a shift in  $\nu(\text{CCC})$  to lower wavenumber is observed.

## Conclusions

The aminoallenylidene complex  $[\text{Mo}\{\text{C}=\text{C}=\text{C}(\text{Me})\text{NEt}_2\}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]\text{BPh}_4$ ,  $[1]\text{BPh}_4$ , has been obtained in a convenient, one-pot synthesis from the reaction of  $[\text{MoBr}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$  with  $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$  in a mixed  $\text{thf}/\text{NHET}_2$  solvent system. Spectroscopic and X-ray structural investigations indicate that the metal-ligand bonding in  $[1]\text{BPh}_4$  includes a significant contribution from an iminium-alkynyl resonance structure. The electrochemistry of  $[1]\text{BPh}_4$  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  $\nu(\text{CCC})$  stretching frequency of *ca.* 70  $\text{cm}^{-1}$  following one-electron oxidation in contrast to the redox-induced behaviour of the aminoallenylidene ligand in  $[\text{Ru}\{\text{C}=\text{C}=\text{C}(\text{Me})\text{NEt}_2\}\text{Cl}(\text{dppm})_2]^{n+}$  ( $n = 1, 2$ ), where a shift in  $\nu(\text{CCC})$  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  $\text{Mo}(\text{dppe})(\eta\text{-C}_7\text{H}_7)$  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  $\pi$ -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)( $\eta$ -C<sub>7</sub>H<sub>7</sub>)] was prepared by a published procedure [27]. NMR spectra were recorded on a Bruker Avance III HD (500 MHz <sup>1</sup>H, 125 MHz <sup>13</sup>C{<sup>1</sup>H}, 202 MHz <sup>31</sup>P{<sup>1</sup>H}) 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 *n*Bu<sub>4</sub>NPF<sub>6</sub>/ CH<sub>2</sub>Cl<sub>2</sub> solutions *ca.* 1 × 10<sup>-4</sup> 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 (FeCp<sub>2</sub>/FeCp<sub>2</sub><sup>+</sup> = 0.00 V). Spectroelectrochemistry was conducted in an OTTLE cell [23] using solutions in dichloromethane containing 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> 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 Emstat<sup>3+</sup> potentiostat at a scan rate of 10 mVs<sup>-1</sup>.

### Preparation of HC≡CC≡CSiMe<sub>3</sub>

The preparation of HC≡CC≡CSiMe<sub>3</sub> 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  $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$  to  $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$  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  $\nu(\text{CCC})$  band at  $2066\text{ cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ) (lit  $2065\text{ cm}^{-1}$  [29]) due to unreacted  $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$  in addition to product bands at  $2189$  and  $2034\text{ cm}^{-1}$  (lit.  $2190, 2035\text{ cm}^{-1}$  [30]).

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

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

A mixture of  $[\text{MoBr}(\text{dppe})(\eta\text{-C}_7\text{H}_7)]$  (0.762 g, 1.15 mmol),  $\text{HC}\equiv\text{CC}\equiv\text{CSiMe}_3$  (prepared as described above from  $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ , 1.00 g, 5.15 mmol and MeLi/LiBr,  $5\text{ cm}^3$  of a 1.5 M solution in diethylether, 7.5 mmol), and  $\text{Na}[\text{BPh}_4]$  (0.394 g, 1.15 mmol) was suspended in a 1:1  $\text{HNEt}_2/\text{thf}$  solvent mixture ( $40\text{ cm}^3$ ) 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  $\text{CH}_2\text{Cl}_2/\text{diethyl ether}$  to give the product as a deep green solid; yield 0.671 g, (57%).  $^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.65, 7.37, 7.30, 7.18, 7.05, 6.89, 6.73 (m, 40H, Ph, dppe and  $[\text{BPh}_4]$ ), 4.81 (s, 7H,  $\text{C}_7\text{H}_7$ ), 2.91 (q,  $J_{\text{H-H}}$  5 Hz, 2H,  $\text{CH}_2$ ,  $\text{NEt}_2$ ), 2.44 (q,  $J_{\text{H-H}}$  5 Hz, 2H,  $\text{CH}_2$ ,  $\text{NEt}_2$ ), 2.23, 2.20 (m, 4H,  $\text{CH}_2$ , dppe), 1.09 (s, 3H,  $\text{C}_\gamma\text{-CH}_3$ ), 0.81 (t,  $J_{\text{H-H}}$  5 Hz, 3H,  $\text{CH}_3, \text{NEt}_2$ ), 0.58 (t,  $J_{\text{H-H}}$  5 Hz, 3H,  $\text{CH}_3$ ,  $\text{NEt}_2$ ).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  228.9, t, ( $J_{\text{C-P}}$  25 Hz)  $\text{C}_\alpha$ ; 163.9, m,  $\text{C}_i$ ,  $\text{BPh}_4$ ; 146.2, s,  $\text{C}_\gamma$ ; 130.6, br,  $\text{C}_\beta$ ; 138.5 m,  $\text{C}_i$ ,  $\text{PPh}_2$ , dppe; 135.8, s, 125.6, s, 121.7, s, Ph,  $\text{BPh}_4$ ; 133.3, 130.9, 130.7, 129.8, 128.9, 128.7,



m, PPh<sub>2</sub>, dppe; 88.9, s, C<sub>7</sub>H<sub>7</sub>; 48.0, s, CH<sub>2</sub>, NEt<sub>2</sub>; 44.6, s, CH<sub>2</sub>, NEt<sub>2</sub>; 26.5, m, CH<sub>2</sub>, dppe; 21.2, s, CH<sub>3</sub>, C<sub>γ</sub>-CH<sub>3</sub>; 13.1, s, CH<sub>3</sub>, NEt<sub>2</sub>; 11.8, s, CH<sub>3</sub>, NEt<sub>2</sub>. <sup>31</sup>P{H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 60.3. IR (CH<sub>2</sub>Cl<sub>2</sub>; cm<sup>-1</sup>): ν(CCC) 1959, ν(CN) 1542. MS MALDI (*m/z*): 710 [M]<sup>+</sup>. Anal. Calcd. (%) for C<sub>65</sub>H<sub>64</sub>BMoNP<sub>2</sub>: C, 75.9; H, 6.2; N, 1.4. Found: C, 76.2; H, 6.4; N, 1.5.

## Crystallography

Single crystals of [1]BPh<sub>4</sub> were obtained as bronze-green blocks by vapour diffusion of diethyl ether into a CH<sub>3</sub>CN 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 F<sup>2</sup>. The non-hydrogen atoms were refined anisotropically and H atoms were included in calculated positions.

Crystal Data for [1]BPh<sub>4</sub>: C<sub>65</sub>H<sub>64</sub>BMoNP<sub>2</sub>, M<sub>r</sub> = 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) Å<sup>3</sup>, Z = 2, μ = 2.934 mm<sup>-1</sup>, 24284 reflections collected, final wR<sub>2</sub>(F<sup>2</sup>) = 0.0990 for all data, conventional R<sub>1</sub> = 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]BPh<sub>4</sub>. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Acknowledgements

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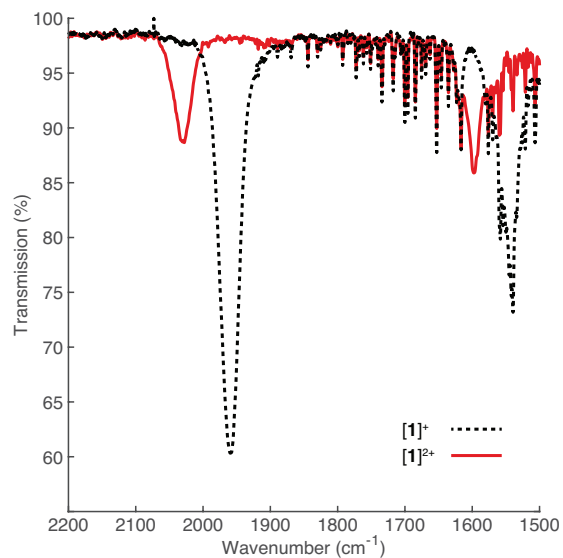
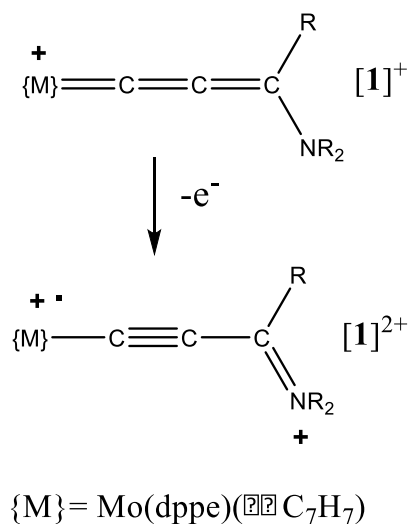
## References

1. (a) M.I. Bruce, *Chem. Rev.* 98 (1998) 2797. (b) M.I. Bruce, *Coord. Chem. Rev.* 248 (2004) 1603. (c) J.P. Selegue, *Coord. Chem. Rev.* 248 (2004) 1543. (d) H. Fischer and N. Szesni, *Coord. Chem. Rev.* 248 (2004) 1659. (e) V. Cadierno and J. Gimeno, *Chem. Rev.* 109 (2009) 3512.
2. E.O. Fischer, H.-J. Kalder, A. Frank, F.H. Köhler, and G. Huttner, *Angew. Chem., Int. Ed. Engl.* 15 (1976) 623.
3. H. Berke, *Angew. Chem., Int. Ed. Engl.* 15 (1976) 624.
4. J.P. Selegue, *Organometallics* 1 (1982) 217.
5. (a) V. Cadierno, M.P. Gamasa, J. Gimeno, M. González-Cueva, E. Lastra, J. Borge, S. Garcia-Granda, and E. Pérez-Carreño, *Organometallics* 15 (1996) 2137. (b) P. Crochet, M.A. Esteruelas, A.M. López, N. Ruiz, and J.I. Tolosa, *Organometallics* 17 (1998) 3479. (c) A.I.F. Venâncio, M.F.C. Guedes da Silva, L.M.D.R.S. Martins, J.J.R. Fraústo da Silva, and A.J.L. Pombeiro, *Organometallics* 24 (2005) 4654.
6. (a) F. Kessler, N. Szesni, K. Pöhako, B. Weibert, and H. Fischer, *Organometallics* 28 (2009) 348. (b) T. Haas, K. Kaspar, K. Forner, M. Drexler, and H. Fischer, *J. Organomet. Chem.* 696 (2011) 946.
7. (a) M.I. Bruce, P. Hinterding, P.J. Low, B.W. Skelton, and A.H. White, *J. Chem. Soc., Dalton Trans.* (1998) 467. (b) P. Haquette, D. Touchard, L. Toupet, and P. Dixneuf, *J. Organomet. Chem.* 565 (1998) 63.
8. (a) R.F. Winter and S. Záliš, *Coord. Chem. Rev.* 248 (2004) 1565. (b) V. Cadierno and S.E. García-Garrido, *Top. Organomet. Chem.* 30 (2010) 219.
9. (a) R.F. Winter, *Chem. Comm.* (1998) 2209. (b) R.F. Winter, K.W. Klinkhammer, and S. Záliš, *Organometallics* 20 (2001) 1317. (c) R.F. Winter, S. Hartmann, S. Záliš and K.W. Klinkhammer, *J. Chem. Soc., Dalton Trans.* (2003) 2342. (d) S. Hartmann, R.F. Winter, B. Sarkar, and F. Lissner, *J. Chem. Soc., Dalton Trans.* (2004) 3273.
10. V. Guillaume, P. Thomino, F. Coat, A. Mari, and C. Lapinte, *J. Organomet. Chem.* 565 (1998) 75.
11. R.F. Winter, *Eur. J. Inorg. Chem.* (1999) 2121.
12. I. García de la Arada, J. Díez, M.P. Gamasa, and E. Lastra, *Organometallics* 34 (2015) 1345.

13. R. Castarlenas, C. Fischmeister, C. Bruneau, and P.H. Dixneuf, *J. Mol. Catal. A: Chem.* 213 (2004) 31.
14. C. Coletti, A. Marrone, and N. Re, *Acc. Chem. Res.* 45 (2012) 139.
15. (a) W.E. Geiger, *Organometallics* 30 (2011) 28. (b) P.J. Low, S. Bock, *Electrochim. Acta* 110 (2013) 681. (c) M.I. Bruce, B.G. Ellis, P.J. Low, B.W. Skelton, and A.H. White, *Organometallics* 22 (2003) 3184. (d) M.J. Shaw, J. Hyde, C. White, and W.E. Geiger, *Organometallics* 23 (2004) 2205. (e) C.J. Adams, I.M. Bartlett, S. Boonyuen, N.G. Connelly, D.J. Harding, O.D. Hayward, E.J.L. McInnes, A.G. Orpen, M.J. Quayle, and P.H. Rieger, *Dalton Trans.* (2006) 3466.
16. (a) G.M. Aston, S. Badriya, R.D. Farley, R.W. Grime, S.J. Ledger, F.E. Mabbs, E.J.L. McInnes, H.W. Morris, A. Ricalton, C.C. Rowlands, K. Wagner, and M.W. Whiteley, *J. Chem. Soc., Dalton Trans.* (1999) 4379. (b) N.J. Brown, D. Collison, R. Edge, E.C. Fitzgerald, M. Helliwell, J.A.K. Howard, H.N. Lancashire, P.J. Low, J.J.W. McDouall, J. Raftery, C.A. Smith, D.S. Yufit, and M.W. Whiteley, *Organometallics*, 29 (2010) 1261. (c) N.J. Brown, D. Collison, R. Edge, E.C. Fitzgerald, P.J. Low, M. Helliwell, Y.T. Ta, and M.W. Whiteley, *Chem. Comm.* 46 (2010) 2253.
17. R.W. Grime, M. Helliwell, Z.I. Hussain, H.N. Lancashire, C.R. Mason, J.J.W. McDouall, C.M. Mydlowski, and M.W. Whiteley, *Organometallics* 27 (2008) 857.
18. (a) R.M. Bullock, *Chem. Comm.* (1989) 165. (b) M.I. Bruce and G.A. Koutsantonis, *Aust. J. Chem.* 44 (1991) 207.
19. R.L. Beddoes, C. Bitcon, and M.W. Whiteley, *J. Organomet. Chem.* 402 (1991) 85.
20. R.L. Beddoes, C. Bitcon, R.W. Grime, A. Ricalton, and M.W. Whiteley, *J. Chem. Soc., Dalton Trans.* (1995) 2873.
21. S.G. Eaves, D.S. Yufit, B.W. Skelton, J.A.K. Howard, and P.J. Low, *Dalton Trans.* 44 (2015) 14341.
22. A.J.L. Pombeiro, *J. Organomet. Chem.* 690 (2005) 6021.
23. M. Krejčík, M. Daněk, and F. J. Hartl, *J. Electroanal. Chem.* 317 (1991) 179.
24. (a) F. Paul, B.G. Ellis, M.I. Bruce, L. Toupet, T. Roisnel, K. Costuas, and C. Lapinte, *Organometallics* 25 (2006) 649. (b) M.A. Fox, R.L. Roberts, W.M. Khairul, F. Hartl, and P.J. Low, *J. Organomet. Chem.* 692 (2007) 3277.
25. (a) C.E. Powell, M.P. Ciuentes, J.P. Morrall, B. Luther-Davies, and G.A. Heath, *J. Am. Chem. Soc.*, 125 (2003) 602. (b) N. Gauthier, N. Tchouar, F. Justaud, G. Argouarch,

- M.P. Cifuentes, L. Toupet, D. Touchard, J.-F. Halet, S. Rigaut, M.G. Humphrey, K. Costuas, and F. Paul, *Organometallics* 28 (2009) 2253. (c) E. Kulasekera, S. Petrie, R. Stranger, and M.G. Humphrey, *Organometallics*, 33 (2014) 2434.
26. M.A. Fox, J.D. Farmer, R.L. Roberts, M.G. Humphrey, and P.J. Low, *Organometallics* 28 (2009) 5266.
27. S. El-Tarhuni, M. Ho, M.H. Kawser, S. Shi, and M.W. Whiteley, *J. Organomet. Chem.* 752 (2014) 30.
28. (a) K. Semba, T. Fujihara, T. Xu, J. Terao, and Y. Tsuji, *Adv. Synth. Catal.* 354 (2012) 1542. (b) B.C. Doak, M.J. Scanlon, and J.S. Simpson, *Org. Lett.* 13 (2011) 537.
29. (a) S. Delgado, D. Corripio, and C. Moreno, *Inorg. Chim. Acta* 357 (2004) 3205. (b) K. Kude, S. Hayase, M. Kawatsura, and T. Itoh, *Heteroatom Chem.* 22 (2011) 397.
30. D.R.M. Walton and F. Waugh, *J. Organomet. Chem.* 37 (1972) 45.
31. G.M. Sheldrick, *SHELXS-97*, Program for Crystal Structure Solution, Universität Göttingen, Germany, 1997.
32. G.M. Sheldrick, *SHELXL-2014/7*, Program for Crystal Structure Refinement, Universität Göttingen, Germany, 2014.

## Graphical Abstract: Pictogram



## Graphical Abstract: Synopsis

Spectroelectrochemical IR investigations on the aminoallenylidene complex

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