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Synthesis, structure and redox chemistry of the aminoallenylidene complex [Mo{C$=$C$=$C(Me)NEt$_2$}(dppe)(η-C$_7$H$_7$)][BPh$_4$]

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ABSTRACT

The reaction of [MoBr(dppe)(η-C$_7$H$_7$)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with HC≡CC≡CSiMe$_3$ and Na[BPh$_4$] in 1:1 NHEt$_2$/THF as solvent yields the aminoallenylidene complex [Mo{C$=$C$=$C(Me)NEt$_2$}(dppe)(η-C$_7$H$_7$)][BPh$_4$], [**1**][BPh$_4$]. The reaction likely proceeds via nucleophilic addition of NHEt$_2$ at C$_\gamma$ of a butatrienylidene intermediate. Structural and spectroscopic characterisation of [**1**][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**][BPh$_4$] determines a Mo—C$_\alpha$ bond length of 2.077(3) Å, intermediate between that of the cumulenic diphenylallenylidene analogue [Mo(C$=$C$=$CPh$_2$)(dppe)(η-C$_7$H$_7$)][PF$_6$] (1.994(3) Å) and the alkynyl compound [Mo(C≡CPh)(dppe)(η-C$_7$H$_7$)] (2.138(5) Å). Complex [**1**][BPh$_4$] undergoes a reversible one-electron oxidation with $E_{½} = -0.19$ V with respect to the FeCp$_2$/FeCp$_2^+$ couple and the stable 17-electron radical dication [**1**]$^{2+}$ is readily observed by spectroelectrochemical methods. IR spectroelectrochemistry in CH$_2$Cl$_2$ demonstrates that the ν(CCC) stretch, characteristic of the allenylidene ligand, shifts to higher wavenumber (from 1959 to 2032 cm^{-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.

1. 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 (Fig. 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 ν(CCC) stretch of the allenylidene ligand, the chemical shift ordering of C$_\beta$ and C$_\gamma$ in the ^{13}C NMR spectrum and crystallographically determined M-C$_\alpha$, C$_\alpha$-C$_\beta$ and C$_\beta$-C$_\gamma$ distances [8a].

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

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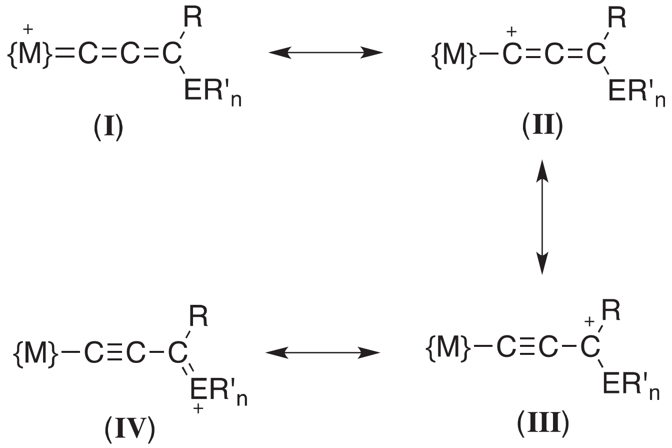


Fig. 1. Resonance structures of a cationic heteroatom (E) substituted allenylidene complex.

pair [15]. In this context, Winter and co-workers have investigated a series of heteroatom substituted allenylidene complexes of the type $[Ru\{C{=}C{=}C(R)ER'_n\}Cl(dppm)_2]^+$, and monitored the changes in the IR active ν(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 by spectroelectrochemistry [8a,9]. One limitation to these investigations is the high redox potential associated with the formal Ru(II)/Ru(III) couple for one-electron oxidation of these complexes and the associated relatively poor thermodynamic stability of the resulting 17-electron species.

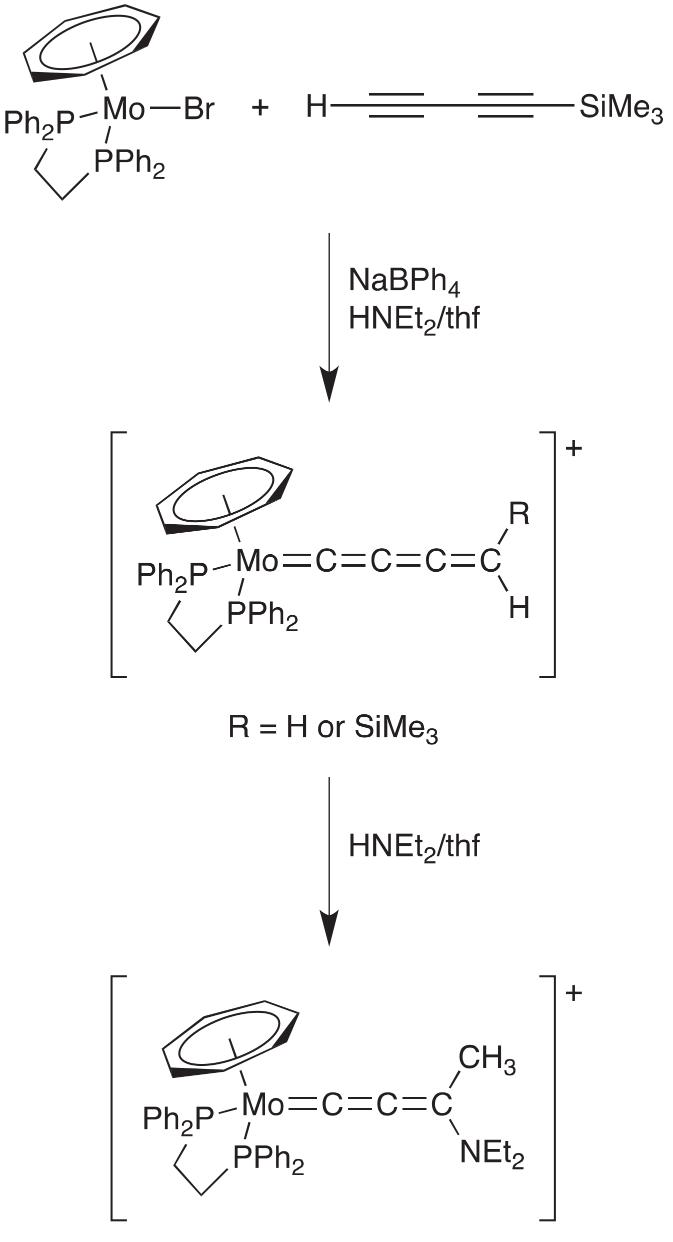
In a series of investigations, we have demonstrated that cycloheptatrienyl molybdenum complexes of the type $[MoX(dppe)(\eta\text{-}C_7H_7)]^{n+}$ exhibit an extensive oxidative redox chemistry of thermodynamically stable 17-electron radical systems [16]. These findings are attributable to a high energy, metal based d_z2 HOMO in the fragment $\{Mo(dppe)(\eta\text{-}C_7H_7)\}$ and resultant symmetry attenuated interaction with ligand X. A few examples of stable 17-electron dications of the type $[MoX(dppe)(\eta\text{-}C_7H_7)]^{2+}$ are known [16a], including the heteroatom substituted cyclic oxacarbene $[Mo\{C(CH_2)_3O\}(dppe)(\eta\text{-}C_7H_7)]^{2+}$ and this suggested that a related heteroatom substituted allenylidene could also exhibit the requisite stability for facile study. The diphenylallenylidene complex $[Mo(C{=}C{=}CPh_2)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ 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 $[Mo\{C{=}C{=}C(R)NR'_2\}(dppe)(\eta\text{-}C_7H_7)]^+$ for which the redox potential for one-electron oxidation may be expected to be significantly more thermodynamically favourable due to the electron donor properties of the heteroatom substituent and resulting enhanced contribution of alkynyl resonance forms (**III**) and (**IV**) to the structure.

2. Results and discussion

2.1. Synthetic studies

The synthetic protocol selected for generation of $[Mo\{C{=}C{=}C(R)NR'_2\}(dppe)(\eta\text{-}C_7H_7)]^+$ follows the principle of nucleophilic addition at C_γ of an intermediate cationic butatrienylidene. For example, treatment of *cis*-$[RuCl_2(dppm)_2]$ with buta-1,3-diyne (HC≡CC≡CH) and $Na[SbF_6]$ followed by addition of a secondary amine NHR_2 results in the formation of the aminoallenylidene complexes *trans*-$[Ru\{C{=}C{=}C(Me)NR_2\}Cl(dppm)_2][SbF_6]$ via the butatrienylidene *trans*-$[Ru(C{=}C{=}C{=}CH_2)Cl(dppm)_2]^+$ [9c]. Alternatively the buta-1,3-diyne synthon $HC{\equiv}CC{\equiv}CSiMe_3$ which is considerably easier to handle has been employed [10] in the synthesis of the alkoxyallenylidene $[Fe\{C{=}C{=}C(Me)OMe\}(dppe)Cp^*][PF_6]$ and this synthetic method provided a conceptual basis for the current work.

The reaction of $[MoBr(dppe)(\eta\text{-}C_7H_7)]$ with $HC{\equiv}CC{\equiv}CSiMe_3$ and $Na[BPh_4]$ dissolved in a 1:1 solvent mixture of $NHEt_2$/THF resulted in a colour change from brown-green to a deep purple colour and after stirring for 21 h the aminoallenylidene complex $[Mo\{C{=}C{=}C(Me)NEt_2\}(dppe)(\eta\text{-}C_7H_7)][BPh_4]$, [**1**]$[BPh_4]$ 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 $[Mo\{C{=}C{=}C{=}C(H)R\}(dppe)(\eta\text{-}C_7H_7)][BPh_4]$ (R = H or $SiMe_3$). Subsequent addition of the solvent-



[**1**]$^+$

Scheme 1. Synthetic route to [**1**]$[BPh_4]$.