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Synthesis and redox chemistry of cycloheptatrienyl molybdenum carbon-chain complexes featuring diimine support ligands: $[Mo\{(C{\equiv}C)_nC{\equiv}CR\}(R'N{=}CH{-}CH{=}NR')(\eta\text{-}C_7H_7)]$, ($n = 0$ or 1)

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The alkynyl complexes $[Mo(C{\equiv}CR)(R'\text{-dab})(\eta\text{-}C_7H_7)]$ (dab = diazabutadiene; $R' = {}^tBu$, R = Ph, **2a**; C_6H_4–4-Me, **3a**; ^{t}Bu, **4a**; $R' = C_6H_4$–4-Me, R = Ph, **2b**) have been synthesised by reaction of $[MoBr(R'\text{-dab})(\eta\text{-}C_7H_7)]$ with $LiC{\equiv}CR$ in thf. Crystallographic characterisation of $[Mo(C{\equiv}CC_6H_4\text{–}4\text{-}Me)({}^tBu\text{-dab})(\eta\text{-}C_7H_7)]$, **3a** determines a Mo-C_α bond distance of 2.154(3) Å. Cyclic voltammetric investigations on the alkynyl complexes **2a**, **2b**, **3a**, **4a** and the extended chain butadiynyl derivative $[Mo(C{\equiv}CC{\equiv}CSiMe_3)({}^tBu\text{-dab})(\eta\text{-}C_7H_7)]$, **5a**, reveal that each complex exhibits a chemically and electrochemically reversible one-electron oxidation to give the corresponding 17-electron radical cation. Characterisation of the radicals $[\mathbf{2a}]^+$, $[\mathbf{2b}]^+$, $[\mathbf{3a}]^+$, and $[\mathbf{5a}]^+$ by IR and EPR spectroscopic techniques indicates that the redox process is strongly metal centred. Spectroscopic and synthetic investigations establish that 17-electron radicals of the type $[Mo\{(C{\equiv}C)_nC{\equiv}CR)\}(R'\text{-dab})(\eta\text{-}C_7H_7)]^+$ ($n = 0$ or 1) have relatively low thermodynamic stability.

1. Introduction

Complexes of highly unsaturated carbon-chain ligands [1,2] are the focus of significant current activity in organometallic chemistry with the expectation of future applications as molecular materials in electronic [3], magnetic [4] and optical [5] devices. Many investigations have focussed on carbon chain complexes of redox-active, metal phosphine based support groups such as Fe(dppe)Cp* [6], $Ru(PPh_3)_2Cp$ and Ru(dppe)Cp* [7], $Mn(dmpe)_2$ [8], $Re(PPh_3)(NO)Cp^*$ [9], $RuCl(dppe)_2$ [10] and $Mo(dppe)(\eta\text{-}C_7H_7)$ [11–13], (dppe = $Ph_2PCH_2CH_2PPh_2$) leading to the development of carbon chain bridged bimetallic systems in a range of oxidation states [14]. An alternative line of enquiry has centred on complexes of the type $[Pt(C{\equiv}CR)_2(bpy)]$ [15], (bpy = 2,2′-bipyridine) $[Re\{(C{\equiv}C)_nC{\equiv}CR\}(CO)_3(bpy)]$ [16], and $[Ru(C{\equiv}CR)(bpy)L_3]$, ($L_3 = Cl(PPh_3)_2$, $(C{\equiv}CR)(PPh_3)_2$, 1,4,7-trithiacyclononane) [17], in which the combination of carbon-chain donor and diimine acceptor ligands promotes luminescence and photoinduced charge separation properties. However very few reports provide the opportunity for a direct comparison between the properties of phosphine and diimine supported systems [13,18,19].

Our investigations on the redox chemistry of carbon chain complexes have centred on the cycloheptatrienyl molybdenum systems $[Mo\{(C{\equiv}C)_nC{\equiv}CR\}(dppe)(\eta\text{-}C_7H_7)]^{z+}$, ($n = 0$ or 1; $z = 0$ or 1) [11–13]. The $Mo(dppe)(\eta\text{-}C_7H_7)$ support unit confers relatively high thermodynamic stability upon 17-electron radical cations ($z = 1$), an observation which may be rationalised by electronic structure calculations which reveal a largely metal-centred HOMO incorporating substantial metal d_z2 character [11]. In addition to dppe supported systems, examples of diimine halide complexes $[MoBrL_2(\eta\text{-}C_7H_7)]$ (L_2 = bpy, ^{t}Bu-dab; ^{t}Bu-dab = 1,4-^{t}Bu$_2$-1,3-diazabutadiene) [20] and the butadiynyl derivatives $[Mo(C{\equiv}C{-}C{\equiv}CSiMe_3)L_2(\eta\text{-}C_7H_7)]$ (L_2 = bpy, ^{t}Bu-dab) [12,13] have been described. These complexes exhibit well behaved, reversible one-electron oxidation processes and a few key results indicate that some diimine support ligands may enhance the stability of 17-electron radical cations (diimine = bpy) [13] and co-ordinatively unsaturated 16-electron species (diimine = bis(imidazolin-2-imine) [21]). The objective of the current work was therefore to develop an extended range of complexes $[Mo\{(C{\equiv}C)_nC{\equiv}CR\}L_2(\eta\text{-}C_7H_7)]^{z+}$ (L_2 = diimine) to explore the effect of substitution of dppe by a diimine ligand upon the reaction chemistry and redox properties of these complexes.

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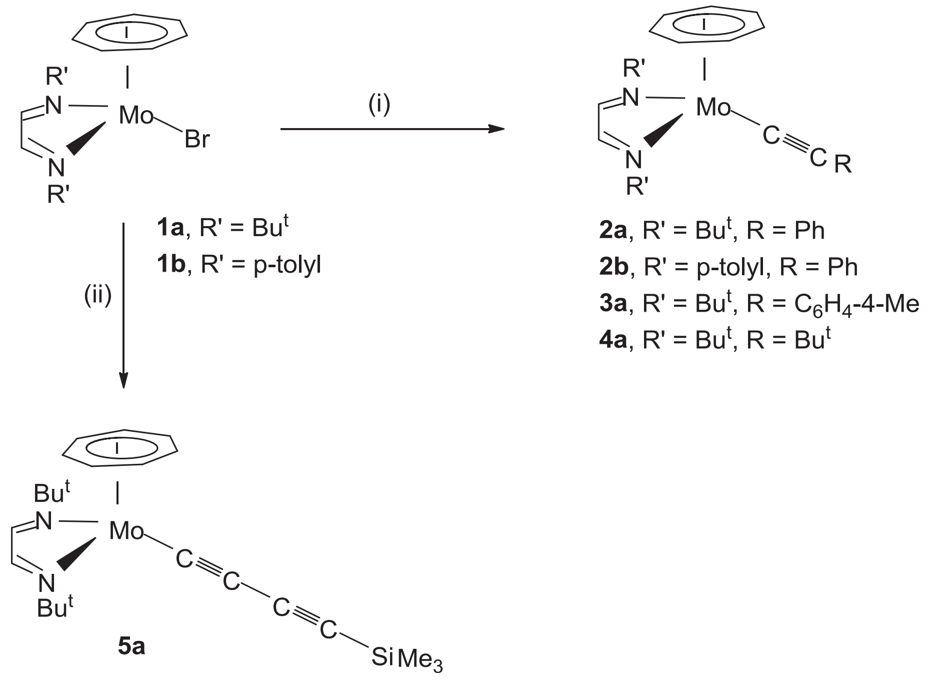

Scheme 1. *Reagents and conditions* (i) LiC≡CR, thf, −30 °C, 45 min; 20 °C, 1 h (ii) LiC≡C−C≡CSiMe$_3$, thf, −78 °C, 30 min; 20 °C, 1 h, 30 °C, 30 min.

2. Results and discussion

2.1. Synthetic and structural studies

The reaction of [MoBr(^{t}Bu-dab)(η-C_7H_7)], **1a** with LiC≡CR (R = Ph, C_6H_4−4-Me or ^{t}Bu) in thf resulted in a colour change from violet-purple to red-purple and formation of the new diimine alkynyl complexes [Mo(C≡CR)(^{t}Bu-dab)(η-C_7H_7)] (R = Ph, **2a**; C_6H_4−4-Me, **3a**; ^{t}Bu, **4a**, Scheme 1) which were isolated as purple solids following purification by chromatography on alumina. Similarly [Mo(C≡CPh)(p-tolyl-dab)(η-C_7H_7)], **2b**, (p-tolyl = C_6H_4−4-Me) was obtained by reaction of [MoBr(p-tolyl-dab)(η-C_7H_7)], **1b** with LiC≡CPh in thf. The extended chain butadiynyl complex [Mo(C≡CC≡CSiMe$_3$)(^{t}Bu-dab)(η-C_7H_7)], **5a** was also prepared as described previously [12], from the reaction of **1a** with LiC≡CC≡CSiMe$_3$ in thf.

In contrast with the diazabutadiene system, the chemistry of carbon-chain complexes of the Mo(bpy)(η-C_7H_7) support group is more limited. We have previously reported the synthesis and redox chemistry of the butadiynyl complex [13] [Mo(C≡CC≡CSiMe$_3$)(bpy)(η-C_7H_7)] but attempts to prepare bipyridyl supported alkynyl complexes [Mo(C≡CR)(bpy)(η-C_7H_7)] were unsuccessful. Thus reaction of [MoBr(bpy)(η-C_7H_7)] with LiC≡CPh in thf resulted in a deep green solution which exhibited an IR active stretch at 2057 cm^{-1} but subsequent work up led to decomposition.

Characterisation details for each of the new alkynyl complexes **2a**, **3a**, **4a** and **2b** are presented in Table 1 (^{1}H and ^{13}C NMR spectroscopy) and the Experimental section (IR spectroscopy, mass spectrometry and, with the exception of **4a**, microanalytical data). The very high solubility of **4a** in all common solvents impeded purification attempts by recrystallisation. Each of the alkynyl complexes exhibits a characteristic ν(C≡C) infra-red active stretching frequency around 2075 cm^{-1} (CH_2Cl_2) and in the ^{13}C{^{1}H} NMR spectrum the arylalkynyl derivatives exhibit a resonance for C_α in the region 135–140 ppm. These values are similar to the chelate phosphine analogues (for example [Mo(C≡CPh)(dppe)(η-C_7H_7)], ν(C≡C), (CH_2Cl_2) 2045 cm^{-1}; δ C_α (CD_2Cl_2), 141.4 ppm) [11] but by comparison with dppe analogues the diazabutadiene derivatives exhibit a small shift in ν(C≡C) to higher wavenumber and a high field shift in both δ C_α and δ C_β. These differences are indicative of decreased electron density at the metal centre in the diazabutadiene complexes; a similar trend is observed along the series

Table 1
^{1}H and ^{13}C{^{1}H} NMR data[a] for [Mo{(C≡C)$_n$C≡CR}(R′-dab)(η-C_7H_7)].

	^{1}H NMR			^{13}C{^{1}H} NMR				
	C≡C*R*	C_7H_7	R′-dab	C_α	C_β	C≡C*R*	C_7H_7	R′-dab
2a	7.04, 4H, m; 6.92, 1H, m	5.01	7.19, NC*H*; 1.45, ^{t}Bu	137.8	108.9	130.4, 129.1, 128.2, 124.5	90.2	139.7, NCH; 63.1, *C*Me$_3$; 32.0, C(*C*H$_3$)$_3$
2b	7.13, 2H, m, H$_o$; 7.06, 2H, m, H$_m$; 6.97, 1H, m, H$_p$	5.01	7.44, 2H, d (J_{H-H} 8); 7.20, 2H, d (J_{H-H} 8); C_6*H*$_4$Me; 7.19, NC*H*; 2.36, C_6H_4*Me*	136.5	109.2	131.1, 128.4, 128.3, 125.3	92.3	140.9, NCH; 154.9, 136.0, 129.4, 121.7, *C*$_6$H$_4$Me; 21.2, C_6H_4*Me*
3a	6.86, 2H, d (J_{H-H} 8); 6.82, 2H, d, (J_{H-H} 8); C_6*H*$_4$Me; 2.13, C_6H_4*Me*	4.98	7.20, NC*H*; 1.42, ^{t}Bu	134.2	108.7	132.3, 130.3, 128.9, 126.1, *C*$_6$H$_4$Me; 21.3, C_6H_4*Me*	90.2	139.6, NCH; 63.1, *C*Me$_3$; 32.0, C(*C*H$_3$)$_3$
4a	0.91	4.88	7.13, NC*H*; 1.39, ^{t}Bu	117.2; 115.6[b]		61.4, *C*Me$_3$; 32.6, C(*C*H$_3$)$_3$	89.9	138.6, NCH; 62.7, *C*Me$_3$; 31.9, C(*C*H$_3$)$_3$
5a[c]	0.12	5.07	7.32, NC*H*; 1.50, ^{t}Bu	134.6	92.0	91.6, C_γ; 74.5, C_δ; −0.2, SiMe$_3$	89.9	140.0, NCH; 62.7, *C*Me$_3$; 31.4, C(*C*H$_3$)$_3$

[a] 400 MHz ^{1}H, 100 MHz ^{13}C{^{1}H}, spectra; d = doublet, m = multiplet; chemical shifts downfield from SiMe$_4$, coupling constants in Hz; in CD_2Cl_2 solution. All spectra recorded at ambient temperature.

[b] C_α and C_β not distinguished.

[c] Data from Ref. [12].