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Electronic Structure and Spectroscopy of the Cycloheptatrienyl Molybdenum Halide Complexes $[\text{MoBrL}_2(\eta\text{-C}_7\text{H}_7)]^{n+}$ ($\text{L}_2 = 2\text{CO}$, $n = 0$; $\text{L}_2 = 2,2'$ -bipyridyl, $n = 0$ or 1).

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Dedicated to Professor Claude Lapinte on the occasion of his retirement and in celebration of his many contributions to our field.

Abstract

DFT calculations at the B3LYP/ Def2-SVP level have been conducted on the half-sandwich cycloheptatrienyl molybdenum complexes $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$, $[\mathbf{1}]^+$ and $[\text{MoBrL}_2(\eta\text{-C}_7\text{H}_7)]^{n+}$ ($\text{L}_2 = 2\text{CO}$, $n = 0$, **2**; $\text{L}_2 = \text{bpy}$, $n = 0$, **3**; $\text{L}_2 = \text{bpy}$, $n = 1$, $[\mathbf{3}]^+$; $\text{bpy} = 2,2'$ -bipyridyl). In all cases, strong δ -bonding interactions operate between the e_2 level of the C_7H_7 ring and metal d_{xy} and $d_{x^2-y^2}$ orbitals resulting in a metal-centred HOMO with substantial d_{z^2} character in the 18-electron, closed shell systems. The experimental electronic UV-visible spectra of $[\mathbf{1}]^+$, **2** and **3** are accurately reproduced by TD-DFT methods. For complexes **2** and **3**, assignments made with the assistance of calculated spectra indicate that absorptions in the region 390-770 nm originate from a series of MLCT (metal-ligand charge transfer) or ILCT (inter-ligand charge transfer) transitions in which carbonyl, C_7H_7 and 2,2'-bipyridyl ligands act as acceptor systems from the metal or mixed metal and bromide

donor groups. The metal-centred, one-electron oxidation of **3** to **3**[PF₆] results in almost complete quenching of the visible region MLCT/ILCT absorptions of **3** and replacement with weak transitions probably arising from bromide to metal LMCT (ligand to metal charge transfer) processes.

Key words: Molybdenum; Cycloheptatrienyl; DFT calculations; Visible spectroscopy

Introduction

The cycloheptatrienyl ligand, C₇H₇, has occupied an important role in the development of the organometallic chemistry of metal-sandwich and half-sandwich systems such as [M(η-C₅H₅)(η-C₇H₇)] (M = Ti, Zr, Hf, V, Cr, Mo, W) and [ML₃(η-C₇H₇)]ⁿ⁺ (M = Cr, Mo or W) [1-6] and offers the potential for advances in f-block organometallic chemistry, where the large size of the C₇H₇ ring is key to enhanced stability of lanthanide and actinide complexes relative to examples with smaller ring ligands [7-9]. By comparison with the more commonly encountered cyclopentadienyl (C₅H₅) ligand, the cycloheptatrienyl ligand is distinguished by its significant steric requirements [10], the facility of interconversion between hapticity modes [11-13] and more fundamentally, effects on electronic structure. Essentially the larger ring size of C₇H₇ by comparison with C₅H₅ results in a lowering in the energy of the ring e₂ MO's [14] leading to strong δ-interactions with metal valence d orbitals. The importance of metal-ring δ-interactions in the electronic structure of cycloheptatrienyl metal-sandwich complexes is well established [2-4, 8, 15] but very little attention has been given to the extension of this principle to half-sandwich systems [16] such as [ML₃(η-C₇H₇)]ⁿ⁺ where potentially the impact on the tripodal L₃ ligand set could be even more pronounced. In this context, a recent series of investigations on half-sandwich vinylidene [Mo(C=CHR)(dppe)(η-C₇H₇)]⁺ [17] (dppe = Ph₂PCH₂CH₂PPh₂) and carbon chain complexes [Mo{(C≡C)_x-C≡CR)L₂(η-C₇H₇)]ⁿ⁺ (n = 0 or 1; x = 0 or 1, L₂ = dppe; x = 1, L₂ = bpy) [18, 19], has demonstrated a re-ordering of the d-orbital manifold arising from metal-ring δ-bonding, leading to a metal-centred HOMO with significant d_{z²} character. This in turn is reflected in the novel structural and redox chemistry of these systems [18-21].

A further distinction between C₇H₇ and cyclopentadienyl ligands is a difference in formal charge of the co-ordinated ligand. Although the assignment of a formal charge to the C₇H₇ ligand, ranging

from +1 to -3, remains an issue of debate [3b, 7a, 9, 10, 22], the positive charge formalism, $C_7H_7^+$, may have some validity in the half-sandwich series $[ML_3(\eta-C_7H_7)]^{n+}$ ($M = Cr, Mo$ or W) for which selected examples exhibit properties typical of d^6 metal centres [17]. On this basis, it has been suggested that the cycloheptatrienyl ligand can act as a good acceptor group in MLCT and ILCT/LLCT processes [23, 24]. To examine this premise, and to explore further the control of electronic structure by metal- C_7H_7 δ -bonding over an extended series, $[Mo(CO)_3(\eta-C_7H_7)][PF_6]$ and the bromide complexes $[MoBrL_2(\eta-C_7H_7)]^{n+}$ ($L_2 = 2 CO, n = 0$; $L_2 = 2,2'$ -bipyridyl (bpy), $n = 0$ or 1 [25]) have been investigated by DFT and TD-DFT methods and the results correlated with experimental electronic spectra. The halide complexes feature a ligand set which combines the donor properties of the bromide ligand with a range of potential acceptor ligands, CO, C_7H_7 or 2,2'-bipyridyl, appropriate to the promotion of MLCT and ILCT excitations. Although the complexes $[Mo(CO)_3(\eta-C_7H_7)][PF_6]$ and $[MoX(CO)_2(\eta-C_7H_7)]$ ($X = \text{halide}$) are fundamental examples of organometallic cycloheptatrienyl derivatives, the work presented here details the first full DFT treatment of these important half-sandwich systems.

Results and discussion

Synthetic and Structural Investigations

The complexes $[MoBrL_2(\eta-C_7H_7)]^{n+}$ ($L_2 = 2 CO, n = 0$, **2**; $L_2 = \text{bpy}, n = 0$, **3**; $L_2 = \text{bpy}, n = 1$, [**3**]⁺) were obtained by previously reported synthetic protocols, starting from $[Mo(CO)_3(\eta-C_7H_7)][PF_6]$, **1**[PF₆], as outlined in Scheme 1. The conversions are accompanied by a sequence of colour changes from yellow (**1**[PF₆]) to green (**2**) to intense purple (**3**) and finally orange (**3**[PF₆]).

Scheme 1: *Reagents and conditions* (i) NaBr in acetone; (ii) 2,2'-bipyridyl in toluene, reflux 3 h. (iii) [FeCp₂][PF₆] in CH₂Cl₂.

To facilitate optimisation of calculated structures, experimentally determined structural data for the series of complexes under investigation was examined. Structural data for **1**[BF₄] and **2** are available in the literature [26, 27]. In addition, the X-ray crystal structure of the 17-electron, 2, 2'-bipyridyl complex, **3**[PF₆], was obtained in the current work; the molecular geometry of **3**[PF₆] is illustrated in Figure 1 together with important bond lengths and angles. The data for **3**[PF₆] complement previous investigations on the structural effects of one-electron oxidation within the [MoX(bpy)(η -C₇H₇)]ⁿ⁺ family of complexes and the Mo-N distances in **3**[PF₆] (2.187(5), 2.193(6) Å) appear to correspond more closely with those determined for 17-electron [Mo(C $\equiv$ C-C $\equiv$ CR)(bpy)(η -C₇H₇)]⁺ (2.19(1), 2.15(2) Å) than for 18-electron [Mo(C $\equiv$ C-C $\equiv$ CR)(bpy)(η -C₇H₇)] (2.134(2), 2.142(2) Å) [19].

Figure 1 Molecular structure of complex **3**[PF₆], with thermal ellipsoids plotted at 50% probability. Hydrogen atoms are omitted for clarity. Key bond lengths (Å) and angles (°): Mo(1)-Br(1), 2.568(1); Mo(1)-N(1), 2.187(5); Mo(1)-N(2), 2.193(6); N(1)-Mo(1)-N(2), 73.3(2); N(1)-Mo(1)-Br(1), 82.9(2); N(2)-Mo(1)-Br(1), 86.2(2).

Electronic Structure Calculations

A computational study of the electronic structure of the model systems [Mo(CO)₃(η-C₇H₇)]⁺, [**1A**]⁺, [MoBr(CO)₂(η-C₇H₇)], **2A**, [MoBr(bpy)(η-C₇H₇)], **3A**, and the open-shell, 17-electron radical [MoBr(bpy)(η-C₇H₇)]⁺, [**3A**]⁺, (denoted **A** to distinguish the computational and experimental systems) was conducted at the DFT level. Starting from the crystallographic structures of the experimental systems **1**[BF₄], **2**, and **3**[PF₆], full geometry optimisations were performed using the B3LYP functional [28] and the Def2-SVP basis obtained from the Turbomole library [29]. Time-dependent DFT (TD-DFT), as implemented in the Gaussian suite of programs [30], was used to obtain transition energies and oscillator strengths which were convoluted to produce absorption spectra using the GaussSum software [31].

There is generally good agreement between the crystallographically determined structures of the experimental systems and the DFT optimised geometries; metrical parameters from the DFT

optimised geometries and comparisons with experimental, crystallographic data are presented in Table 1. The one-electron oxidation of **3A** to **[3A]⁺** is predicted to result in a decrease in the Mo-Br bond length and corresponding increase in the Mo-N (bpy) distance in accord with experimental (R = SiMe₃) and calculated (R = H) data for the related redox pair [Mo(C≡C-C≡CR)(bpy)(η-C₇H₇)]ⁿ⁺ (n = 0 or 1) [19]. Figures 2 to 4 illustrate the plots of the key frontier orbitals for **[1A]⁺**, **2A**, and **3A**, (HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1).

Table 1. Selected bond lengths (Å) and bond angles (°) for **[1A]⁺**, **2A**, **3A** and **[3A]⁺** obtained at the B3LYP/SVP level compared with experimental systems [crystallographic data in parentheses].

	[1A]⁺ (1 [BF ₄])	2A (2)	3A	[3A]⁺ (3 [PF ₆])
Bond Lengths				
Mo-CO	2.054 [2.029(10), 2.036(9), 2.032(13)]	2.027 [2.10(3), 2.06(3)]	—	—
Mo-Br	—	2.639 [2.629(3)]	2.644	2.553 [2.568(1)]
Mo-N	—	—	2.159, 2.159	2.236 [2.187(5), 2.193(6)]
C≡O	1.139 [1.137(12), 1.120(12), 1.130(15)]	1.147 [1.08(4), 1.11(4)]	—	—
Bond Angles				
(OC)-Mo-(CO)	85.8 [85.2(4), 85.0(5), 85.1(4)]	82.1 [82.6(11)]	—	—
Br-Mo-(CO)	—	83.6 [87.9(8), 83.7(8)]	—	—
N-Mo-Br	—	—	85.8	83.3 [82.9(2), 86.2(2)]

Figure 2: LUMO+1, LUMO, HOMO, HOMO-1 and HOMO-2 of $[1A]^+$ at B3LYP/ Def2-SVP plotted as an isosurface of 0.04 au.

Figure 3: LUMO+1, LUMO, HOMO, HOMO-1 and HOMO-2 of **2A** at B3LYP/ Def2-SVP plotted as an isosurface of 0.04 au.

Figure 4: LUMO+1, LUMO, HOMO, HOMO-1 and HOMO-2 of **3A** at B3LYP/ Def2-SVP plotted as an isosurface of 0.04 au.

Before the specific effects of the tripodal ligand set are discussed, the general features of electronic structure, common to all of the systems investigated should be noted. For, $[1A]^+$, **2A**, and **3A**, the principal components of the frontier orbitals are similar throughout the series. Thus the LUMO and LUMO+1 incorporate substantial character of the π -acceptor ligands (CO, C_7H_7 or 2,2'-bipyridyl) whilst the HOMO is strongly metal centred, based on the d_{z^2} orbital (the z axis in these complexes is directed along the axis connecting Mo with the centroid of the C_7H_7 ring). By contrast, HOMO-1 and HOMO-2 feature a significant contribution from the metal and C_7H_7 ring as a result of the strong metal-ring δ -bonds between metal d_{xy} and $d_{x^2-y^2}$ orbitals and the e_2 molecular orbitals of the cycloheptatrienyl ligand. These results complement our previous DFT treatments of the alkynyl complex $[Mo(C\equiv CPh)(dppe)(\eta-C_7H_7)]^{n+}$ [18] and butadiynyl complexes $[Mo(C\equiv C-C\equiv CH)L_2(\eta-C_7H_7)]^{n+}$ ($L_2 = dppe, bpy$) [19] and confirm the importance of metal to C_7H_7 ring δ interactions in regulating electronic structure in these half-sandwich systems, independent of the identity of the tripodal L_3 ligand set.

Superimposed upon this basic description, the electronic structure of $[1A]^+$ is sequentially modified by the substitution of the tripodal carbonyl ligands with bromide and 2,2'-bipyridyl. Considering first the replacement of CO by bromide in the tricarbonyl cation, $[1A]^+$, the character of HOMO and HOMO-1 in **2A** is modified by strong, four-electron repulsive π -interactions between the filled halide p-orbitals and the metal d_{z^2} and d_{xy} orbitals; these orthogonal orbital overlaps are very similar to those described for the metal alkynyl bond in $[Mo(C\equiv CPh)(dppe)(\eta-C_7H_7)]$, [18] so endorsing comparisons between the two isolobal ligand types. Introduction of a strong π -acceptor 2,2'-bipyridyl ligand on conversion of **2A** to **3A** significantly alters the composition of LUMO and LUMO+1. In $[1A]^+$ and **2A**, the LUMO and LUMO+1 feature the dual acceptor character of CO and C_7H_7 ligands. However in **3A**, where CO is replaced by the 2,2'-bipyridyl ligand, the LUMO and LUMO+1 are essentially localised on the strongly π -accepting bipyridyl unit.

UV-Visible Electronic Absorption Spectroscopy

The UV-visible spectra of the experimental systems were taken from literature data (**1**[PF₆]) [23] or recorded in CH₂Cl₂ (**2**, **3**, and **3**[PF₆]) for comparison with calculated spectra obtained via TD-DFT methods. Experimental and calculated spectra for **2/2A** and **3/3A**, are shown in Figures 5 and 6 and visible region experimental and calculated data are summarised in Table 2.

(a)

(b)

Figure 5 UV-visible spectra of [MoBr(CO)₂(η-C₇H₇)], **2/2A** (a) experimental, CH₂Cl₂ solution, and (b) calculated TD-DFT oscillator strengths (green) and simulated absorption spectrum

(blue).

Figure 6 UV-visible spectra of $[\text{MoBr}(\text{bpy})(\eta\text{-C}_7\text{H}_7)]$, **3/3A** (a) experimental, in CH_2Cl_2 / 0.1M $\text{N}^n\text{Bu}_4\text{PF}_6$ solution, showing spectroelectrochemical, one-electron oxidation to $[\text{3}]^+$ and (b) calculated TD-DFT oscillator strengths (green) and simulated absorption spectrum (blue).

Table 2. Experimental and calculated (TD-DFT) electronic absorption spectra in the visible region for complexes **1**[PF₆], **2**, **3** and **3**[PF₆]

Complex	Experiment λ / nm (ϵ) /dm ³ mol ⁻¹ cm ⁻¹ ^a	Theory λ / nm (f) ^d	Assignment of principal transitions ^e
[Mo(CO) ₃ (η -C ₇ H ₇)] [PF ₆], 1 [PF ₆] ^b	379 (1200)	398 (0.003)	HOMO-2→LUMO (0.48) HOMO-1→LUMO+1 (0.51)
		390 (0.002)	HOMO-2→LUMO+1 (0.66) HOMO-1→LUMO (0.23)
	298 (22400)	287 (0.251)	HOMO-2→LUMO (0.40) HOMO-1→LUMO+1 (0.38)
[MoBr(CO) ₂ (η -C ₇ H ₇)], 2	648 (150)	673 (0.002)	HOMO→LUMO (0.68)
	458 (350)	505 (0.001)	HOMO→LUMO+1 (0.66)
	387 (920)	412 (0.006)	HOMO-2→LUMO (0.54) HOMO-1→LUMO+1 (0.41)
		370 (0.020)	HOMO-3→LUMO (0.52) HOMO-1→LUMO+1 (0.37)
[MoBr(bpy)(η -C ₇ H ₇)], 3 ^c	771 (15500)	715 (0.062)	HOMO→LUMO (0.60)
	544 (10300)	527 (0.031)	HOMO→LUMO+2 (0.64)
		521 (0.028)	HOMO-2→LUMO (0.23) HOMO→LUMO+1 (0.59)
	434 (10650)	397 (0.099)	HOMO-3→LUMO (0.55) HOMO-1→LUMO+2 (0.37)
[MoBr(bpy)(η -C ₇ H ₇)] [PF ₆], 3 [PF ₆] ^c	770 (890)	951 (0.001)	HOMO-2(β)→HOMO(β) (0.9) HOMO-2(β)→LUMO(β) (0.26)
	550 (850)	513 (0.017)	HOMO-3(β)→HOMO(β) (0.92)
		493 (0.008)	HOMO-1(α)→LUMO(α) (0.87)
		482 (0.007)	Multiple transitions
	408 (5630)	417 (0.002)	Multiple transitions
		415 (0.002)	HOMO-5(α)→LUMO(α) (0.57) HOMO-5(β)→HOMO(β) (0.64) HOMO-5(β)→LUMO(β) (0.44)

^a Experimental data recorded in solution in CH₂Cl₂ unless stated otherwise. ^b Data from ref. 23, recorded in EtOH solution. ^c In solution in CH₂Cl₂/ 0.1M NⁿBu₄PF₆ ^d Calculated absorptions in the gas phase by TD-DFT (B3LYP/Def2-SVP), figures in parentheses indicate oscillator strength. ^e Calculated transition assignments (see figures 2, 3 and 4 for orbital diagrams). Figures in parentheses indicate fractional contribution to calculated absorption, (α) = alpha spin manifold, (β) = beta spin manifold.

(i) [Mo(CO)₃(η-C₇H₇)] [PF₆] and [MoBr(CO)₂(η-C₇H₇)]

The calculated and experimental spectra for **1**[PF₆] and **2** (Figure 5) show good agreement, particularly in the region 400-800 nm. Starting with **1**[PF₆], inspection of Table 2 shows that the main calculated components of the experimental absorption at 379 nm arise from excitations from HOMO-1/ HOMO-2 to LUMO+1/ LUMO. The excited state therefore has a combination of C₇H₇ and CO π* character and this broadly concurs with the literature report for **1**[PF₆] which assigns the experimental absorption at 379 nm to a Mo→C₇H₇⁺ MLCT (metal to ligand charge transfer) transition [23]. In the bromide complex **2**, a related absorption involving HOMO-1/ HOMO-2 to LUMO+1/ LUMO transitions is also observed (387 nm) but additionally there are two broad, low intensity bands centred at 458 and 648 nm which give rise to the green colour of the complex. The origin of these low energy bands in the visible spectra of [MoX(CO)₂(η-C₇H₇)] (X = iodide) has been the focus of previous investigations [24] and the TD-DFT treatment here presented now provides a more detailed interpretation of this work.

On the basis of the calculated spectrum, the principal excitations giving rise to the low energy absorptions in the visible spectrum of [MoBr(CO)₂(η-C₇H₇)] are HOMO→LUMO (648 nm) and HOMO→LUMO+1 (458 nm). Examination of Figure 3 reveals that the HOMO of **2A** has significant metal and bromide character, whereas LUMO/ LUMO+1 incorporate mainly C₇H₇ and CO π* composition. The transitions can therefore be considered in terms of MLCT/ILCT processes in which charge transfer from the halide donor ligand to the acceptor C₇H₇ and CO ligands is mediated through the metal centre. It is not possible to exclude totally a direct LLCT process from the halide donor to the C₇H₇ acceptor as previously described [24] but the frontier MO's derived from the DFT work support substantial involvement of the metal centre in the charge transfer transitions. To demonstrate the importance of the contribution of the halide ligand to these processes, the UV-visible spectra of an extended series of complexes [MoX(CO)₂(η-C₇H₇)] (X = Cl, Br, I) were examined (see Table 3 for visible region data). The broad and weak nature of the visible region absorptions presents some limitations to precise measurements but progression along the series X = Cl, Br, I results in a small blue shift in absorption maximum of the low energy band and an increase in absorption intensity in all three bands consistent with the more intense green-black colour of the iodide derivative by comparison with the paler green colour of the chloride analogue.

Table 3 Electronic absorption data for [MoX(CO)₂(η -C₇H₇)] (X = Cl, Br, I) in the visible region

^a Extinction (dm ³ mol ⁻¹)	X	Absorption maxima (nm) ^a			coefficients ϵ cm ⁻¹) in parentheses.
	Cl	657 (130)	456 (283)	384 (818)	
	Br	648 (150)	458 (350)	387 (920)	
	I	645 (370)	463 (499)	387 (1984)	

(ii) [MoBr(bpy)(η -C₇H₇)]ⁿ⁺ (*n* = 0 or 1)

As shown in Figure 6, the visible region of the electronic absorption spectrum of 18-electron [MoBr(bpy)(η -C₇H₇)], **3**, exhibits three principal bands centred at 771, 544 and 434 nm. These are very similar to bands previously reported for the analogous butadiynyl complex [Mo(C $\equiv$ C-C $\equiv$ CSiMe₃)(bpy)(η -C₇H₇)], (777, 542, 452 nm) [19] with the distinction that the absorption intensities are larger for the bromide complex **3**. This spectral signature of **3** is well reproduced at the B3LYP level with three calculated absorptions in the visible region at 715, 527 and 397 nm, slightly blue shifted from experimental values. As evident from Table 2, the orbital components contributing to these absorptions in **3** correspond closely to those discussed for the dicarbonyl analogue **2** with both complexes exhibiting three bands in the region 390-770 nm. However the absorptions for **3** are red shifted and of much higher intensity than those of **2**; a rationalisation for these differences is apparent from a comparison of the electronic structures of the two complexes. In complex **2A**, the main acceptor components in the LUMO+N orbitals (N = 0, 1 or 2) consist of CO and C₇H₇ groups whereas in **3A**, their function is totally replaced by the strongly accepting 2,2'-bipyridyl ligand. This change in the character of the excited state orbitals lowers transition energies and enhances intensities resulting in strong absorptions across the visible region which give rise to the intense purple colour of the complex. As with complex **2**, the lowest energy excitations at 771 nm (HOMO→LUMO) and 544 nm (HOMO→LUMO+2) retain significant net charge transfer between donor and acceptor ligands with the distinction that in **3**, this is from the halide donor to a bipyridyl acceptor ligand. Therefore, whilst investigations on complex **2** confirm the capacity of the

C_7H_7 ligand to function as an acceptor in MLCT or ILCT processes, in complex **3** the C_7H_7 ring is unable to compete effectively as an acceptor with the 2,2'-bipyridyl ligand.

The one electron oxidation of **3** to **3**[PF₆] is accompanied by a colour change from intense purple to pale orange, evident in the visible region of the electronic absorption spectrum by a collapse of the bands at 771 and 544 nm and replacement with very weak ($\epsilon < 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) absorptions at 770 and 550 nm (see Figure 6(a)). The third visible region band around 408 nm retains significant intensity and, based on the DFT results, may originate from bpy $\pi \rightarrow \pi^*$ transitions. The calculated spectrum of the 17-electron open shell radical **[3A]⁺** (Figure 7) is much less successful than for closed shell **3A** in modelling the form of the experimental spectrum although the absence of any strong absorption over a major part of the visible region is successfully predicted.

Figure 7 Calculated (TD-DFT, B3LYP/ Def2-SVP) UV-visible spectrum of $[\text{MoBr}(\text{bpy})(\eta\text{-C}_7\text{H}_7)]^+$, **[3A]⁺**. TD-DFT oscillator strengths (green) and simulated absorption spectrum (blue).

Experimentally, the significant changes in the visible region of the spectrum resulting from one-electron oxidation of **3** to **3**[PF₆] can be rationalised by the quenching of low energy MLCT/ILCT processes as a result of oxidation at the metal centre. However conversely the redox process **3**→

$3[\text{PF}_6]$ should promote the operation of LMCT transitions as reported for $[\text{Mo}(\text{C}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3)(\text{bpy})(\eta\text{-C}_7\text{H}_7)]$ which exhibits new absorptions around 500 nm assigned to butadiynyl to metal LMCT processes. The calculated spectrum of the bromide complex $[\mathbf{3A}]^+$ predicts low intensity excitations centred at 951 nm (HOMO-2 $\rightarrow$ HOMO in the β -spin manifold) and 513 nm (HOMO-3 $\rightarrow$ HOMO in the β -spin manifold) which are in modestly good agreement with the principal features in the experimentally observed spectrum (Table 2); the orbital components of this latter transition are illustrated in Figure 8.

Figure 8: β -spin orbital transition (HOMO-3 $\rightarrow$ HOMO) in $[\mathbf{3A}]^+$ assigned to the calculated band at 513 nm.

The character of this HOMO-3 to HOMO β -spin transition is clearly LMCT from bromide to metal. Moreover the orbital components have a very close similarity to the corresponding LMCT (alkynyl ligand to metal) process in open shell $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$, [18] which is mainly responsible for the deep blue colour of the complex. For $[\text{Mo}(\text{C}\equiv\text{CPh})(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ the intensity ($\epsilon = 4800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) of the experimental LMCT transition at 592 nm is enhanced by the alkynyl phenyl substituent but the corresponding transition at 500 nm in the alkylalkynyl complex $[\text{Mo}(\text{C}\equiv\text{CBu}^t)(\text{dppe})(\eta\text{-C}_7\text{H}_7)]^+$ is much weaker ($\epsilon = 720 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and similar to the experimental extinction coefficients determined for candidate LMCT absorptions at 770 and 550 nm in the visible region of the spectrum of $[\text{MoBr}(\text{bpy})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$. Interestingly, a related comparison between LMCT transitions in analogous 17-electron alkynyl and halide complexes $[\text{FeX}(\text{dppe})\text{Cp}^*]^+$ ($\text{X} = \text{C}\equiv\text{CR}$ or Cl) has been noted by Lapinte and co-workers [32]. Here again, the effect of substitution of $\text{C}\equiv\text{CR}$ with a halide ligand is both a blue shift and reduction in extinction coefficient of the LMCT transition. In summary,

although the agreement between experimental and calculated electronic absorption spectra of $[\text{MoBr}(\text{bpy})(\eta\text{-C}_7\text{H}_7)][\text{PF}_6]$ is relatively poor, there is some evidence to suggest that the weak bands observed in the visible region originate from LMCT processes involving the bromide ligand. Finally it should be noted that the reversible interconversion of **3** and **3** $[\text{PF}_6]$ provides an example of redox switching between strong and weak absorption in the visible region. The redox switch is readily initiated ($E_{1/2} = -0.65 \text{ V vs. FeCp}_2/[\text{FeCp}_2]^+$) consistent with the low redox potentials conferred by the $\text{Mo}(\text{bpy})(\eta\text{-C}_7\text{H}_7)$ support unit [25].

Conclusions

DFT calculations at the B3LYP/ Def2-SVP level on the half-sandwich cycloheptatrienyl molybdenum complexes $[\text{Mo}(\text{CO})_3(\eta\text{-C}_7\text{H}_7)]^+$, **1A** $^+$ and $[\text{MoBrL}_2(\eta\text{-C}_7\text{H}_7)]$ ($\text{L}_2 = 2 \text{ CO}$, **2A**; $\text{L}_2 = \text{bpy}$, **3A**) reveal a common electronic structure for the frontier molecular orbitals. Strong δ interactions between the e_2 level of the C_7H_7 ring and metal d_{xy} and $d_{x^2-y^2}$ orbitals stabilise the HOMO-1 and HOMO-2, resulting in a HOMO with substantial metal d_{z^2} character. The composition of the LUMO and LUMO+1 is ligand dependent with $\text{CO}/\text{C}_7\text{H}_7$ character replaced by 2,2'-bipyridyl character on progression from **2A** to **3A**. In both **2A** and **3A**, filled-filled π -interactions between bromide and the metal centre are evident in the HOMO and HOMO-1. The electronic UV-visible spectra of the experimental systems **1** $^+$, **2** and **3** are accurately reproduced by TD-DFT methods. For complexes **2** and **3**, assignments made with the assistance of calculated spectra indicate that absorptions in the visible region 390-770 nm, originate from a series of MLCT/ILCT processes. The distinction between the dicarbonyl complex **2** and the 2,2'-bipyridyl complex **3** lies in the identity of the acceptor group. Whereas in **2**, the C_7H_7 ligand makes a substantial contribution to the LUMO and LUMO+1, in complex **3** its function as an acceptor group is totally overridden by the 2,2'-bipyridyl ligand resulting in absorptions which are also of lower energy and enhanced intensity. The metal-centred, one-electron oxidation of **3** to **3** $[\text{PF}_6]$ results in almost complete quenching of visible region MLCT/ILCT absorptions of **3** and replacement with low intensity absorptions which may likely be assigned to bromide to metal LMCT processes. As such the interconversion of **3** and **3** $[\text{PF}_6]$ represents a redox-switch for control of absorption intensity in the visible region.

The assignment of a formal charge to the cycloheptatrienyl ligand in the half-sandwich complexes

described in this paper remains a difficult issue. The MLCT transitions observed for complexes **1**[PF₆] and **2** do involve the cycloheptatrienyl ligand as an acceptor group but it is probably an oversimplification to attribute this property to a formal positive charge on the ligand. However a tri-negative charge for the C₇H₇ ligand (as generally proposed for mixed sandwich systems of the type [M(η-C₅H₅)(η-C₇H₇)], [1b]) resulting in the assignment of a Mo(IV), d² configuration also does not seem to be consistent with the reactivity of some Mo(C₇H₇) half-sandwich systems which can promote alkyne to vinylidene isomerisation typical of a d⁶ or d⁴ metal centre [18,33]. One useful approach may be the assignment of a covalent bond classification [22] which is intimately linked with the contribution of the δ-interaction to the metal-cycloheptatrienyl bond (see ref. 22, Table 1 and Fig. 4). Alternatively, the relative metal d and cycloheptatrienyl fragment contributions to the frontier MO's involving δ-interactions have been considered [1b]. For the sandwich complex [Zr(η-C₅H₅)(η-C₇H₇)], the relevant contributions are: (HOMO), Zr, 32%; C₇H₇, 64% and this distribution has been attributed to an orbital energy ordering in which the C₇H₇ e₂ level is of lower energy than the metal d orbitals consistent with a formal -3 charge on the C₇H₇ ligand [1b]. However for the half-sandwich complex [Mo(C≡CPh)(dppe)(η-C₇H₇)], the relative contributions of C₇H₇ and ML₃ fragments to the δ-interactions are very different with a much smaller overall contribution from the C₇H₇ ligand [18]; this result may be explained by an energy ordering in which the C₇H₇ e₂ level is of higher energy than the metal d orbitals. In summary it is probable that neither a tri-negative nor the opposite extreme of a positive charge formalism are fully appropriate for the cycloheptatrienyl ligand in the half-sandwich molybdenum complexes investigated in the current work but there is some evidence to suggest that the character of the metal to η⁷-C₇H₇ δ-interaction is modified on progression from a sandwich complex of an early d-block metal to a half-sandwich complex of a group 6 metal.

Experimental

General Procedures

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen using standard Schlenk techniques. The complexes [MoX(CO)₂(η-C₇H₇)] (M = Mo, X = I, Br, Cl) [34,35] and [MoBr(bpy)(η-C₇H₇)]ⁿ⁺ (n = 0 or 1) [25] were prepared by published procedures. UV-visible spectroelectrochemistry was performed at room temperature with an air-

tight OTTLE cell of Hartl design [36] at the University of Durham. The cell was equipped with Pt minigrid working and counter electrodes, a Ag wire reference electrode and CaF₂ windows and spectra obtained using either a Nicolet Avatar spectrometer or a Perkin Elmer Lambda 900 spectrophotometer.

Crystallography: X-ray crystal structure of [MoBr(bpy)(η -C₇H₇)](PF₆), **3**[PF₆]

Crystal Data for **3**[PF₆]: C₁₇H₁₅MoN₂BrPF₆, M_r = 568.13, monoclinic, space group P1 2₁ 1, a = 8.5063(3) Å, b = 14.3654(4) Å, c = 15.7993(4) Å, β = 103.981(3)°, U = 1873.42(10) Å³, Z = 4, μ = 2.981 mm⁻¹, 6323 reflections collected, final wR₂(F²) = 0.1033 for all data, conventional R₁ = 0.0411 for 4524 reflections with I > 2 σ (I), S = 1.014.

Single crystals of **3**[PF₆] were obtained as orange plates by vapour diffusion of diethylether into a MeCN solution of the complex and a crystal of dimensions 0.40 x 0.40 x 0.10 mm was selected for analysis. Single crystal X-ray data were collected at 100 K on an Oxford Diffraction X-Calibur 2 Diffractometer equipped with an Oxford-Cryosystems low temperature device, by a means of Mo-K α (λ = 0.71073 Å) radiation and ω scans. Data were corrected for Lorentz, polarisation and absorption factors. Data collection, cell refinement and data reduction were carried out with CrysAlis CCD and CrysAlis RED, Oxford Diffraction Ltd. software; SHELXS-97, [37] was employed for the computing structure solution and SHELXL-97, [38] for the computing structure refinement. The structure was solved by direct methods with refinement based on F². The asymmetric unit of **3**[PF₆] contains two independent molecules; no significant disorder was encountered and important bond lengths and angles in the two molecules are very similar.

Electronic Structure Calculations

DFT calculations were performed in the generalised gradient approximation (GGA) with the B3LYP hybrid exchange-correlation functional [28]. Starting from the crystallographic structures of the experimental systems **1**[BF₄], **2**, and **3**[PF₆], full geometry optimisations were performed using the Def2-SVP basis obtained from the Turbomole library [29]. For H, C and P atoms, this constitutes an all electron split valence plus polarisation basis, while for Mo an effective core potential is applied to account for 28 core electrons (*K*, *L* and *M* shells) with a split valence orbital set including a set of *f* type polarization functions. This basis was also used to obtain UV-

visible spectra (via time-dependent density functional theory, TD-DFT) as implemented in the Gaussian suite of programs [30]).

Appendix A. Supplementary data

CCDC 985841 contains the supplementary crystallographic data for complex **3**[PF₆]. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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Graphical Abstract

Graphical Summary

Electronic structure calculations (DFT, B3LYP/Def2-SVP) on the half-sandwich cycloheptatrienyl molybdenum complexes [MoBrL₂(η-C₇H₇)] (L₂ = 2 CO or 2,2'-bipyridyl) reveal that in each case the HOMO features significant metal d_{z²} character but the composition of the LUMO is L₂ dependent. TD-DFT methods have been employed to analyse the experimental UV-visible electronic absorption spectra of these complexes.