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Electronic structure and spectroscopy of the cycloheptatrienyl molybdenum halide complexes $[MoBrL_2(\eta\text{-}C_7H_7)]^{n+}$ (L_2 = 2CO, $n = 0$; 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.

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ABSTRACT

DFT calculations at the B3LYP/Def2-SVP level have been conducted on the half-sandwich cycloheptatrienyl molybdenum complexes $[Mo(CO)_3(\eta\text{-}C_7H_7)]^+$, [**1**]$^+$ and $[MoBrL_2(\eta\text{-}C_7H_7)]^{n+}$ (L_2 = 2 CO, $n = 0$, **2**; L_2 = bpy, $n = 0$, **3**; L_2 = bpy, $n = 1$, [**3**]$^+$; 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–Vis spectra of [**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**[PF_6] 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.

1. Introduction

The cycloheptatrienyl ligand, C_7H_7, has occupied an important role in the development of the organometallic chemistry of metal-sandwich and half-sandwich systems such as $[M(\eta\text{-}C_5H_5)(\eta\text{-}C_7H_7)]$ (M = Ti, Zr, Hf, V, Cr, Mo, W) and $[ML_3(\eta\text{-}C_7H_7)]^{n+}$ (M = Cr, Mo or W) [1–6] and offers the potential for advances in f-block organometallic chemistry, where the large size of the C_7H_7 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 (C_5H_5) 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 C_7H_7 by comparison with C_5H_5 results in a lowering in the energy of the ring e_2 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 $[ML_3(\eta\text{-}C_7H_7)]^{n+}$ where potentially the impact on the tripodal L_3 ligand set could be even more pronounced. In this context, a recent series of investigations on half-sandwich vinylidene $[Mo(C{=}CHR)(dppe)(\eta\text{-}C_7H_7)]^+$ [17] (dppe = $Ph_2PCH_2CH_2PPh_2$) and carbon chain complexes $[Mo\{(C{\equiv}C)_x{-}C{\equiv}CR)L_2(\eta\text{-}C_7H_7)]^{n+}$ ($n = 0$ or 1; $x = 0$ or 1, L_2 = dppe; $x = 1$, L_2 = 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_{z^2} character. This in turn is reflected in the novel structural and redox chemistry of these systems [18–21].

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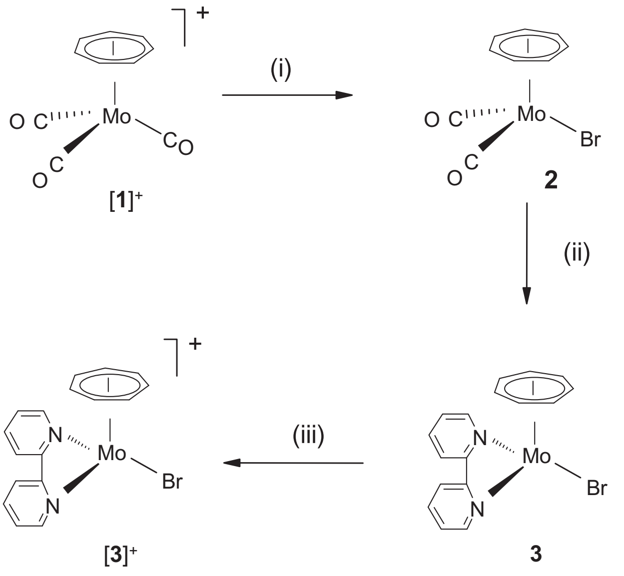
A further distinction between C_7H_7 and cyclopentadienyl ligands is a difference in formal charge of the co-ordinated ligand. Although the assignment of a formal charge to the C_7H_7 ligand, ranging from +1 to −3, remains an issue of debate [3b,7a,9, 10,22], the positive charge formalism, $C_7H_7^+$, may have some validity in the half-sandwich series $[ML_3(\eta\text{-}C_7H_7)]^{n+}$ (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, $[Mo(CO)_3(\eta\text{-}C_7H_7)][PF_6]$ and the bromide complexes $[MoBrL_2(\eta\text{-}C_7H_7)]^{n+}$ (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 $[Mo(CO)_3(\eta\text{-}C_7H_7)][PF_6]$ and $[MoX(CO)_2(\eta\text{-}C_7H_7)]$ (X = halide) are fundamental examples of organometallic cycloheptatrienyl derivatives, the work presented here details the first full DFT treatment of these important half-sandwich systems.

2. Results and discussion

2.1. Synthetic and structural Investigations

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

To facilitate optimisation of calculated structures, experimentally determined structural data for the series of complexes under investigation was examined. Structural data for **1**$[BF_4]$ 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**$[PF_6]$, was obtained in the current work; the molecular geometry of **3**$[PF_6]$ is illustrated in Fig. 1 together with important bond lengths and angles. The data for **3**$[PF_6]$ complement previous investigations on the structural effects of one-electron oxidation within the $[MoX(bpy)(\eta\text{-}C_7H_7)]^{n+}$ family of complexes and the Mo–N distances in **3**$[PF_6]$ (2.187(5), 2.193(6) Å) appear to correspond more closely with those determined for 17-electron $[Mo(C{\equiv}C\text{–}C{\equiv}CR)(bpy)(\eta\text{-}C_7H_7)]^+$ (2.19(1), 2.15(2) Å) than for 18-electron $[Mo(C{\equiv}C\text{–}C{\equiv}CR)(bpy)(\eta\text{-}C_7H_7)]$ (2.134(2), 2.142(2) Å) [19].



Scheme 1. *Reagents and conditions* (i) NaBr in acetone; (ii) 2,2′-bipyridyl in toluene, reflux 3 h. (iii) $[FeCp_2][PF_6]$ in CH_2Cl_2.

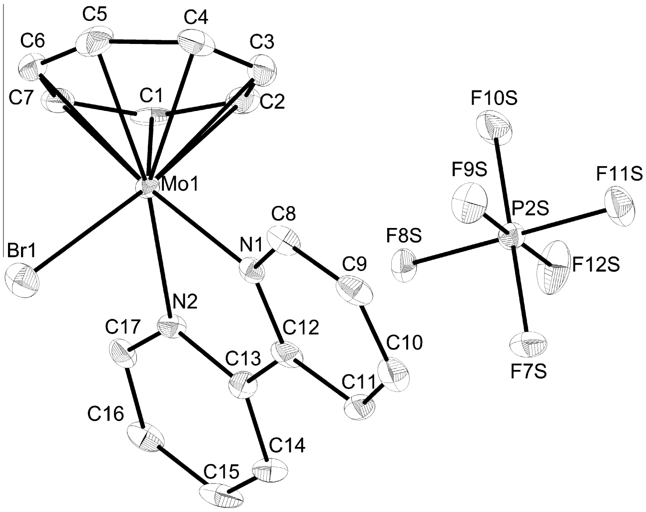


Fig. 1. Molecular structure of complex **3**$[PF_6]$, with thermal ellipsoids plotted at 50% probability. Hydrogen atoms are omitted for clarity. Key bond lengths (Å) and angles (°): Mo(1)–Br(1), 2.568(1); Mo(1)–N(1), 2.187(5); Mo(1)–N(2), 2.193(6); N(1)–Mo(1)–N(2), 73.3(2); N(1)–Mo(1)–Br(1), 82.9(2); N(2)–Mo(1)–Br(1), 86.2(2).

2.2. Electronic structure calculations

A computational study of the electronic structure of the model systems $[Mo(CO)_3(\eta\text{-}C_7H_7)]^+$, [**1A**]$^+$, $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$, **2A**, $[MoBr(bpy)(\eta\text{-}C_7H_7)]$, **3A**, and the open-shell, 17-electron radical $[MoBr(bpy)(\eta\text{-}C_7H_7)]^+$, [**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**$[BF_4]$, **2**, and **3**$[PF_6]$, 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 = $SiMe_3$) and calculated (R = H) data for the related redox pair $[Mo(C{\equiv}C\text{–}C{\equiv}CR)(bpy)(\eta\text{-}C_7H_7)]^{n+}$ (n = 0 or 1) [19]. Figs. 2–4 illustrate the plots of the key frontier orbitals for [**1A**]$^+$, **2A**, and **3A**, (HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1).

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