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Synthesis and redox properties of the cycloheptatrienylmolybdenum complexes $[MoX(N-N)(\eta\text{-}C_7H_7)]^{z+}$, (N–N = 2,2′-bipyridine or 1,4-Bu^t_2-1,3-diazabutadiene; $z = 0$, X = Br or Me; $z = 1$, X = NCMe, $CNBu^t$ or CO)

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Abstract

The complexes $[MoBr(N-N)(\eta\text{-}C_7H_7)]$ (N–N = 2,2′-bipyridine (bipy), **1a**; N–N = 1,4-Bu^t_2-1,3-diazabutadiene (Bu^t-dab), (**1b**) have been prepared by reaction of $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ with N–N in refluxing toluene. Treatment of **1a** or **1b** with MeLi affords $[MoMe(N-N)(\eta\text{-}C_7H_7)]$ (N–N = bipy or Bu^t-dab). The acetonitrile complexes $[Mo(NCMe)(N-N)(\eta\text{-}C_7H_7)][PF_6]$, generated by reaction of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ with N–N in NCMe, are precursors to $[MoX(N-N)(\eta\text{-}C_7H_7)][PF_6]$ (X = $CNBu^t$ or CO; N–N = bipy or Bu^t-dab), through substitution of NCMe by X. Cyclic voltammetric studies reveal that each of the complexes $[MoX(N-N)(\eta\text{-}C_7H_7)]^{z+}$ (X = Me, Br, NCMe or $CNBu^t$; N–N = bipy or Bu^t-dab) exhibits a reversible one-electron oxidation and the 17-electron radicals derived from **1a**,**b** and $[Mo(CNBu^t)(bipy)(\eta\text{-}C_7H_7)][PF_6]$ have been isolated. $E°$ values for the complexes $[MoX(N-N)(\eta\text{-}C_7H_7)]^{z+}$, demonstrate that in each case the bipy derivative is more easily oxidised than the corresponding Bu^t-dab analogue. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

An expanding chemistry of the cycloheptatrienylmolybdenum auxiliary has evolved based upon complexes with phosphorus-donor supporting ligands [1] For example, we have reported a series of investigations on terminal alkyne transformations at a $Mo(dppe)(\eta\text{-}C_7H_7)$ centre (dppe = $Ph_2PCH_2CH_2PPh_2$) leading to vinylidene, alkynyl and carbene derivatives and further chemistry of the Mo–C bond has been developed starting from $[MoBr(CO)(PR_3)(\eta\text{-}C_7H_7)]$ (R = Me or Ph) [2–4]. Despite these advances, further progress is hindered by limitations on the range of supporting ligands L in the auxiliary $Mo(L)_2(\eta\text{-}C_7H_7)$ [5]. A recent development in the chemistry of the closely analogous $Ru(L)_2(\eta\text{-}C_5R_5)$ auxiliary (R = H or Me) has been to explore the synthesis of complexes of the chelate N-donor ligands, bipy [6,7] and 1,4-diisopropyl-1,3-diazabutadiene (Pr^i-dab) [8]. These ligands are reported to provide both electronically rich and flexible Ru centres which promote novel alkyne and alkene coordination chemistry. This paper explores the feasibility of extension of these principles to complexes of the cycloheptatrienylmolybdenum auxiliary with emphasis upon the elucidation of electronic properties conferred by bipy and Bu^t-dab ligands.

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Table 1
Microanalytical and mass spectroscopic data

Complex	Analysis (%)[a]			Mass spectral data[b]
	C	H	N	
$[MoBr(bipy)(\eta\text{-}C_7H_7)]$ **1a**	47.9 (48.2)	3.7 (3.5)	6.4 (6.6)	424 ($[M]^+$), 345 ($[M\text{–}Br]^+$)
$[MoBr(Bu^t\text{-}dab)(\eta\text{-}C_7H_7)]$ **1b**	46.9 (46.9)	6.1 (6.2)	6.3 (6.4)	436 ($[M]^+$), 357 ($[M\text{–}Br]^+$), 268 ($[M\text{–}(Bu^t\text{–}dab)]^+$)
$[MoMe(bipy)(\eta\text{-}C_7H_7)]$ **2a**	60.6 (60.3)	5.3 (5.0)	7.5 (7.8)	360 ($[M]^+$), 345 ($[M\text{–}Me]^+$)
$[MoMe(Bu^t\text{-}dab)(\eta\text{-}C_7H_7)]$ **2b**	58.7 (58.4)	8.5 (8.1)	7.4 (7.6)	372 ($[M]^+$), 357 ($[M\text{–}Me]^+$)
$[Mo(NCMe)(bipy)(\eta\text{-}C_7H_7)][PF_6]$ **3a**	43.4 (43.1)	3.5 (3.4)	7.9 (7.9)	345 ($[M\text{–}NCMe]^+$)
$[Mo(NCMe)(Bu^t\text{-}dab)(\eta\text{-}C_7H_7)][PF_6]$ **3b**	42.1 (42.1)	5.4 (5.5)	7.7 (7.8)	398 ($[M]^+$), 357 ($[M\text{–}NCMe]^+$)
$[Mo(CNBu^t)(bipy)(\eta\text{-}C_7H_7)][PF_6]^c$ **4a**	46.0 (46.2)	4.4 (4.2)	7.4 (7.4)	428 ($[M]^+$), 345 ($[M\text{–}CNBu^t]^+$)
$[Mo(CNBu^t)(Bu^t\text{-}dab)(\eta\text{-}C_7H_7)][PF_6]^d$ **4b**	45.0 (45.3)	6.2 (6.2)	7.0 (7.2)	440 ($[M]^+$), 357 ($[M\text{–}CNBu^t]^+$)
$[Mo(CO)(bipy)(\eta\text{-}C_7H_7)][PF_6]^e$ **5a**	42.0 (41.9)	2.8 (2.9)	5.1 (5.4)	373 ($[M]^+$), 345 ($[M\text{–}CO]^+$)
$[Mo(CO)(Bu^t\text{-}dab)(\eta\text{-}C_7H_7)][PF_6]^f$ **5b**	40.6 (40.9)	5.1 (5.1)	5.1 (5.3)	385 ($[M]^+$), 357 ($[M\text{–}CO]^+$)
$[MoBr(bipy)(\eta\text{-}C_7H_7)][PF_6]$ **6a**	36.2 (35.9)	2.7 (2.6)	5.0 (4.9)	424 ($[M]^+$), 345 ($[M\text{–}Br]^+$), 268 ($[M\text{–}bipy]^+$)
$[MoBr(Bu^t\text{-}dab)(\eta\text{-}C_7H_7)][PF_6]$ **6b**	35.2 (35.2)	4.7 (4.7)	4.7 (4.8)	436 ($[M]^+$), 357 ($[M\text{–}Br]^+$)
$[Mo(CNBu^t)(bipy)(\eta\text{-}C_7H_7)][PF_6]_2^g$ **7a**	37.0 (36.9)	3.3 (3.4)	5.7 (5.8)	428 ($[M]^+$), 345 ($[M\text{–}CNBu^t]^+$)

[a] Calculated values in parentheses.
[b] By FAB mass spectroscopy, m/z values based on ^{98}Mo.
[c] ν_{CN}, CH_2Cl_2, 2137 cm^{-1}, [d] ν_{CN}, CH_2Cl_2, 2161 cm^{-1}, [e] ν_{CO}, CH_2Cl_2, 1983 cm^{-1}, [f] ν_{CO}, CH_2Cl_2, 2009 cm^{-1}, [g] ν_{CN}, CH_2Cl_2, 2220 cm^{-1}.

2. Results and discussion

2.1. Synthetic studies

Prior to the current work, just two examples of complexes of the type $[MoX(N\text{–}N)(\eta\text{-}C_7H_7)]$ had been reported (X = I, N–N = bipy or *o*-phenanthroline), prepared by reaction of $[MoI(CO)_2(\eta\text{-}C_7H_7)]$ with N–N in refluxing benzene [9]. An analogous strategy was employed to prepare the new derivatives $[MoBr(N\text{–}N)(\eta\text{-}C_7H_7)]$ (N–N = bipy, **1a**; N–N = Bu^t-dab, **1b**) from $[MoBr(CO)_2(\eta\text{-}C_7H_7)]$ and N–N in refluxing toluene. The complexes **1a**, and **1b** were isolated as intensely coloured, deep purple, light sensitive solids; details of the characterisation of these, and subsequently described, complexes are presented in Table 1 (microanalytical and mass spectroscopic data) and Table 2 (^1H and $^{13}C\{^1H\}$-NMR data). The diazabutadiene complex **1b** gave well resolved ^1H and ^{13}C-NMR spectra with characteristic low field resonances for the CH=N units of the chelate ring but, in common with the halide complexes $[MoX(dppe)(\eta\text{-}C_7H_7)]$ [10], the bipyridine complex **1a** initially failed to give satisfactory NMR spectra, probably due to trace air oxidation of **1a** to the paramagnetic 17-electron radical $[MoBr(bipy)(\eta\text{-}C_7H_7)]^+$ (see later). However, good NMR data for **1a**, as presented in Table 2, was obtained by addition to the NMR sample of small quantities of the one-electron reducing agent $CoCp_2$.

We have previously developed the chemistry of the Mo–C σ-bond in cycloheptatrienyl molybdenum complexes by halide substitution in $[MoCl(dppe)(\eta\text{-}C_7H_7)]$ and $[MoBr(CO)(PR_3)(\eta\text{-}C_7H_7)]$ [4] and an analogous strategy was also successful starting from **1a** and **1b**. Thus treatment of THF solutions of **1a** or **1b** with MeLi followed by low temperature work up afforded the methyl derivatives $[MoMe(N\text{–}N)(\eta\text{-}C_7H_7)]$ (N–N = bipy, **2a**; N–N = Bu^t-dab, **2b**) which were isolated as light sensitive, intensely coloured blue and red solids, respectively. Each of the complexes **2a**, and **2b** provided informative ^1H and ^{13}C-NMR spectra and the chemical shifts associated with the bipy and Bu^t-dab ligands reflect the high electron density at the Mo centre. In the case of the bipy complex **2a**, the $^{13}C\{^1H\}$-NMR resonances for the bipyridine carbons C^B, C^C and C^D are shifted to exceptionally high field.

A further objective of this work was to establish an entry into the chemistry of cationic derivatives $[MoX(N\text{–}N)(\eta\text{-}C_7H_7)]^+$ (X = two-electron ligand). In the chemistry of the $Ru(Pr^i\text{-}dab)(\eta\text{-}C_5Me_5)$ auxiliary, Ag(I) promoted halide abstraction from a neutral halide precursor in the presence of a coordinating ligand and provides a good synthesis of cationic complexes [8] but this strategy is less suitable in the current work where Ag(I) salts effect one-electron oxidation of **1a** and **1b**. The alternative, successful strategy is analogous to the methods used in the synthesis of cationic *bis*-phosphine derivatives [11]. Reflux of a solution of $[Mo(\eta\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)][PF_6]$ in acetonitrile results in the formation of $[Mo(NCMe)_3(\eta\text{-}C_7H_7)]^+$, which, on treatment with N–N at room temperature (r.t.) affords $[Mo(NCMe)(N\text{–}N)(\eta\text{-}C_7H_7)][PF_6]$ (N–N = bipy, **3a**; N–N = Bu^t-dab, **3b**).

Complexes **3a** and **3b** incorporate a labile NCMe ligand which undergoes facile substitution by added ligands X. Indeed the lability of **3a** precluded its full characterisation but the identity of these complexes is supported by the products of subsequent reactions. Thus treatment of **3a** and **3b** with $CNBu^t$ in acetone or CH_2Cl_2, respectively led to immediate reaction and the

Table 2
^{1}H and $^{13}C\{^{1}H\}$-NMR spectral data[a]

$[MoX(bipy)(\eta\text{-}C_7H_7)]^{z+}$

Complex	^{1}H-NMR						^{13}C-NMR					
	H^A	H^B	H^C	H^D	C_7H_7	X	C^A	C^B,C^D	C^C	C^E	C_7H_7	X
1a[b]	9.33, d, (5.8)	7.01, m	7.33, m	7.94, d, (8.2)	4.89	—	150.1	121.1, 121.3	131.6	147.1	88.7	—
2a[c]	8.76, d, (6.2)	6.37, m	6.65, m	7.48, d, (8.4)	4.73	−0.10 (Me)	148.4	118.9, 121.8	127.3	145.5	88.8	9.7 (Me)
4a[d]	9.49, d, (5.2)	7.54, m	7.96, m	8.59, d, (8.1)	5.34, br	1.16 (CNBu^t)	151.4	122.7, 124.0	135.5	150.7	89.8	161.8, br, 57.8, 28.9 (CNBu^t)
5a[d]	9.45, d, (5.2)	7.65, m	8.15, m	8.65, d, (8.2)	5.67	—	153.9	124.4, 126.4	139.0	153.6	94.3	232.0 (CO)

$MoX(Bu^t\text{-}dab)(\eta\text{-}C_7H_7)]^{z+}$

	^{1}H-NMR				^{13}C-NMR			
	N*CH*	Bu^t-dab	C_7H_7	X	N*CH*	Bu^t-dab	C_7H_7	X
1b[e]	7.22	1.61	5.21	—	139.3	64.2, 32.0	90.1	—
2b[c]	7.07	1.41	4.88	−0.12 (Me)	136.4	62.2, 31.9	88.8	7.4 (Me)
3b[f]	7.44	1.54	5.35		144.1	64.9, 31.7	91.7	
4b[e]	7.61	1.46	5.30	1.43 (CNBu^t)	146.0	64.3, 31.8	91.3	58.6, 29.8 (CNBu^t)
5b	7.94	1.49	5.54	—	153.6	67.1, 32.6	94.8	207.0 (CO)

[a] 300 MHz ^{1}H-NMR spectra, 75 MHz $^{13}C\{^{1}H\}$-NMR spectra; all resonances singlets unless stated otherwise, d = doublet, m = multiplet, br = broad; coupling constants (in parentheses) in Hz; bipy ligand labelled consecutively from C^AH (adjacent to N) to C^E (bridgehead carbon); spectra recorded in CD_2Cl_2 unless stated otherwise.
[b] Spectra recorded after the addition of a trace quantity of cobaltocene.
[c] ^{1}H-NMR spectrum in C_6D_6, [d] In acetone-d_6, [e] In $CDCl_3$, [f] In CD_3CN.

Table 3
Cyclic voltammetric data[a] for the complexes $[MoX(L\text{-}L)(\eta\text{-}C_7H_7)]^{z+}$

Ligand L-L	Ligand X				
	Me [b]	Br[c]	NCMe[d]	CNBu^t[c]	CO[c]
bipy	−0.34 (−0.41[c])	−0.09	0.10 (0.23[f])	0.39	0.78[e]
Bu^t-dab	0.11 (0.08[f])	0.33	0.51 (0.63[c])	0.79	1.14
dppe	−0.37[c,g]	0.00[h]	0.37[i] (0.51[c])	0.71[h]	1.23[g]

[a] Potentials in V versus SCE, 0.2 M $[NBu^n_4][BF_4]$ supporting electrolyte, E° values unless stated otherwise.
[b] In THF, [c] In CH_2Cl_2, [d] In NCMe, [e] E_p^A at 100 mV s^{-1}.
[f] Estimated $E°$ in CH_2Cl_2 adjusted from data in THF or NCMe.
[g] Data from ref. [4], [h] Data from ref. [13], [i] data from ref. [5].

formation of $[Mo(CNBu^t)(N\text{–}N)(\eta\text{-}C_7H_7)][PF_6]$ (N–N = bipy, **4a**; N–N = Bu^t-dab, **4b**) which were isolated as intensely coloured, bottle green and dark red solids, respectively. Similarly, when carbon monoxide was bubbled through a refluxing acetone solution of **3a** or **3b** over a period of 2 h, purple–red $[Mo(CO)(N\text{–}N)(\eta\text{-}C_7H_7)][PF_6]$ (N–N = bipy, **5a**; N–N = Bu^t-dab, **5b**) were formed. Comparison of infrared active ν_{CN} and ν_{CO} stretching frequencies associated with the ligand X [ν_{CN}, cm^{-1}, (CH_2Cl_2): **4a**, 2137; **4b**, 2161; ν_{CO}, cm^{-1}, (CH_2Cl_2): **5a**, 1983; **5b**, 2009] suggests a lower electron density at the molybdenum centre in the diazabutadiene complexes by comparison with their bipyridine analogues. This observation is consistent with the superior π-acceptor capacity of diazabutadiene [12] by comparison with bipyridine ligands and also with the results of cyclic voltammetric investigations detailed in the following section.

2.2. Electrochemical investigations and synthetic redox chemistry

Our previous studies have demonstrated the capacity of the cycloheptatrienylmolybdenum auxiliary $Mo(dppe)(\eta\text{-}C_7H_7)$ to support reversible one-electron oxidation processes in its complexes with a wide range of ligands X and therefore analogous behaviour was predicted for the bipy and Bu^t-dab derivatives reported in the current work. The results of cyclic voltammetric studies, carried out on each of the complexes **1–5** in CH_2Cl_2, THF or acetonitrile are summarised in Table 3 together with comparative data for analogous complexes of the dppe ligand [4,5,13]. The trend in $E°$ values is reflected quite closely in some of the NMR chemical shift parameters reported in Table 2.

The electrochemical behaviour of $[MoX(L\text{-}L)(\eta\text{-}C_7H_7)]^{z+}$ is markedly X and L-L dependent. In common with their dppe analogues, each of the bromide and isocyanide complexes **1a**,**b** and **4a**,**b** undergoes a diffusion controlled ($i_p/v^{\frac{1}{2}}$ is constant for scan rates $v = 50$–500 mV s^{-1}) chemically reversible one-electron oxidation in CH_2Cl_2 with the separation between cathodic and anodic peak potentials comparable to that determined for ferrocene under identical conditions. The electrochemistry of the remaining examples (X = Me, NCMe or CO) was less straightforward and warrants more detailed discussion.

The cyclic voltammetry of the methyl complexes **2a** and **2b** was investigated in THF. The Bu^t-dab derivative **2b**, exhibited a one-electron oxidation process with the conditions for reversibility, enumerated above, fully satisfied. The bipyridine analogue **2a** also undergoes a reversible one-electron oxidation but, in both THF and CH_2Cl_2, a further, unidentified reversible process [$E°$(THF) −0.12 V] was observed, not definitively assigned to **2a** and with relatively small peak current values. The acetonitrile complex $[Mo(NCMe)(Bu^t\text{-}dab)(\eta\text{-}C_7H_7)][PF_6]$ **3b**, exhibits a fully reversible one-electron oxidation in both acetonitrile and CH_2Cl_2 but by contrast, the electrochemistry of the bipyridine derivative **3a**, is more complex. In acetonitrile, **3a** undergoes a reversible one-electron oxidation process but in CH_2Cl_2 this process is irreversible [$E_p^A = 0.29$ V (100 mV s^{-1})] and leads to the formation of a secondary product (tentatively assigned as $[MoCl(bipy)(\eta\text{-}C_7H_7)]^+$) which exhibits a reversible redox process [$E°(CH_2Cl_2) = -0.10$ V]. These results are consistent with the observed lability of the acetonitrile ligand in **3a**. The relatively poor stability of complexes of the $Mo(bipy)(\eta\text{-}C_7H_7)$ auxiliary towards oxidation is further demonstrated by the carbonyl derivative **5a** which exhibits an irreversible oxidation process [E_p^A (CH_2Cl_2) = 0.78 V (100 mV s^{-1})] with no evidence of a coupled reduction wave, even at scan rates of 500 mV s^{-1} at −20°C. By comparison, oxidation of the Bu^t-dab derivative **5b**, although chemically irreversible, is accompanied by a coupled reduction wave in the cyclic voltammogram at scan rates of 200 mV s^{-1} or greater so allowing estimation of the $E°$ value presented in Table 3.

Inspection of the formal reduction potentials $E°$, presented in Table 3, establishes that for any given ligand X, the $E°$ value for the bipyridine complex is shifted to negative potential by approximately 0.4 V by comparison with the Bu^t-dab analogue. This observation is in accord with the relative π-acceptor capacities of the two classes of ligand. Moreover, the distinctive capability of the cycloheptatrienylmolybdenum system to promote reversible one-electron oxidation processes, now provides three related series of complexes [MoX(L-L)(η-C_7H_7)] (L-L = bipy, Bu^t-dab and dppe) for which $E°$ values can be compared directly for five ligands X (X = Me, Br, NCMe, $CNBu^t$ or CO).

It is clear that, for a specific Mo(L-L)(η-C_7H_7) auxiliary, the magnitude of $E°$ is related to the σ-donor/π-acceptor properties of X with the strongest acceptor ligand, CO giving the most positive $E°$ value. The net donor/acceptor properties of the ligand X can be expressed in terms of a ligand constant P_L [14]. In the case of formally d^6 octahedral complexes of the type *trans*-[MoX(Y)$(dppe)_2$] (Y = CO, N_2 etc.), Chatt [14] developed a theory which relates the $E°$ value for a given complex M_SX to the ligand constant P_L for a specific X ligand according to the equation:

$$E°(M_SX) = E_S + \beta P_L$$

where E_S and β are constants inherent to the metal site M_S. Thus for a fixed metal site M_S, in which the ligand X was systematically varied, a plot of $E°$ versus P_L was found to give a good linear correlation of slope β and intercept E_S.

Eighteen-electron complexes of the type [MoX(L-L)(η-C_7H_7)$]^{z+}$ may also be considered to possess a d^6 molybdenum centre and the resemblance of these systems to those originally investigated by Chatt prompted us to explore the extension of ligand constant theory to metal sites, M_S, of the type Mo(L-L)(η-C_7H_7). The objective of this investigation was to provide a quantitative comparison between the electronic properties of the structurally related sites Mo(L-L)(η-C_7H_7) (L-L = bipy, Bu^t-dab or dppe). To furnish data suitable for comparison, all $E°$ values for [MoX(L-L)(η-C_7H_7)$]^{z+}$ were adjusted to CH_2Cl_2 solvent (either through direct measurement or by correction factors estimated from values for the [Fe(η-C_5H_5)$_2$]-[Fe(η-C_5H_5)$_2$]$^+$ couple in CH_2Cl_2, THF or acetonitrile). The adjusted values employed and their origin are detailed in Table 3. The P_L values [X, (P_L): Me, (−1.49); Br, (−1.17); NCMe, (−0.58); $CNBu^t$, (−0.43); CO, (0.00)] were taken from ref. [14] [X = Br, NCMe, $CNBu^t$ (assumed identical to CNMe), CO] or, in the case of X = Me, the P_L value was estimated from an extended study on complexes of the type [MoX(dppe)(η-C_7H_7)$]^{z+}$. Plots of the formal reduction potentials $E°$ against the ligand constant P_L for each of the systems [MoX(L-L)(η-C_7H_7)$]^{z+}$ (L-L = bipy, Bu^t-dab or dppe) gave, in each case, a reasonably linear relationship (Fig. 1) with estimated gradients, β, [L-L, β: Bu^t-dab, 0.68; bipy, 0.71; dppe, 1.04]. The gradient, β, is a measure of the polarisability of the metal site M_S, and may be considered as an indication of the ease of transmission of electronic effects from the ligand X to the highest occupied molecular orbital in the complex [14]. Our investigations suggest that the polarisability of the three sites Mo(L-L)(η-C_7H_7) lies in the order: L-L = dppe > bipy ≈ Bu^t-dab. Even from a very qualitative inspection of Fig. 1 and Table 3, it is clear that the Mo(dppe)(η-C_7H_7) site has a substantially greater polarisability than the analogous bipy and Bu^t-dab systems. Thus, whilst for X = Me, the dppe and bipy complexes exhibit similar $E°$ values, where X = $CNBu^t$ it is the Mo(dppe)(η-C_7H_7) and Mo(Bu^t-dab)(η-C_7H_7) sites which give rise to closely comparable $E°$ figures.

In summary, the three supporting ligands, bipy, Bu^t-dab and dppe confer quite different electronic properties upon the Mo(L-L)(η-C_7H_7) site. The bipyridine ligand provides a very electron rich molybdenum centre but bonding to the ligand X appears to be relatively weak (especially where X = NCMe, **3a**, or CO, **5a**). The Bu^t-dab ligand always acts as a good acceptor ligand and therefore moderates $E°$ values for good donor ligands such as X = Me or Br. However it is with dppe as supporting ligand that the electronic effects of X seem to be transmitted most directly to the highest occupied molecular orbital of the Mo(L-L)(η-C_7H_7) site and it may be that it is this latter property which is critical in the promotion of interesting reactivity. Certainly, whilst the Mo(dppe)(η-C_7H_7) auxiliary is extremely effective at promoting terminal alkyne transformations leading to carbene and vinylidene complexes, our efforts to effect analogous reactions at Mo(L-L)(η-C_7H_7) (L-L = bipy or Bu^t-dab) centres have been wholly unsuccessful.

The magnitudes of $E°$ and the reversibility of the redox processes suggested that, with appropriate chemical redox reagents, syntheses of the radical cations derived from complexes **1a**,**b**; **2a**,**b** and **4a** might be

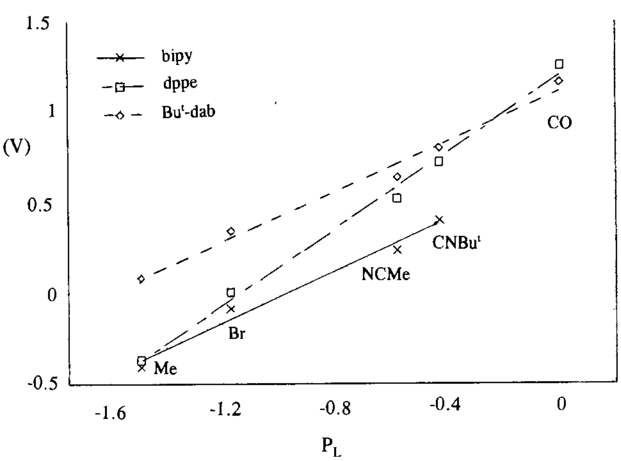

Fig. 1. Plots of $E°$ for the series of complexes [MoX(L-L)(η-C_7H_7)$]^{z+}$ (L-L = dppe, bipy or Bu^t-dab) against the ligand constants P_L of the variable ligands X as indicated on the plots.

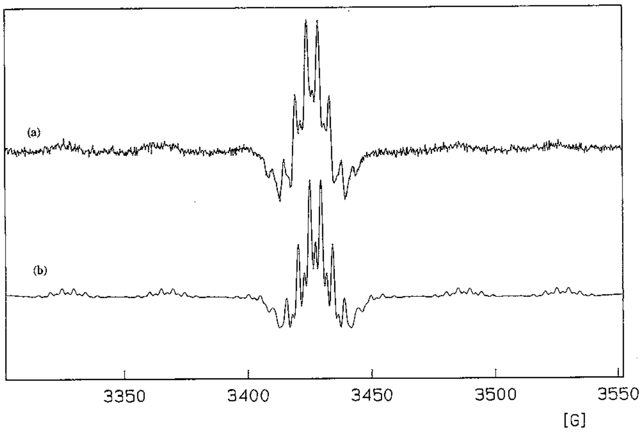

Fig. 2. X-band, acetone solution (−30°C), second derivative, EPR spectrum of [Mo(CNBu^t)(bipy)(η-C_7H_7)][PF_6]$_2$, **7a** (a) experimental spectrum and (b) simulated spectrum.

achieved. Treatment of CH_2Cl_2 solutions of the bromide complexes **1a** and **1b** with [$FeCp_2$][PF_6] resulted in the respective isolation of the stable radical cations [MoBr(N–N)(η-C_7H_7)][PF_6] (N–N = bipy, **6a**; N–N = Bu^t-dab, **6b**). The identity of **6a**,**b** as members of redox pairs with **1a**,**b** was established in each case by complementary cyclic voltammetry [$E°$(V) (CH_2Cl_2): **6a**, −0.07; **6b**, 0.32] and their identity as radicals was demonstrated by EPR spectroscopy [X-band solution spectra in CH_2Cl_2 recorded at ambient temperature: **6a**, $<g>$1.985, a(^{95,97}Mo) 41 G; **6b**, $<g>$1.988, a(^{95,97}Mo) 42 G]. In contrast with the EPR spectra of [MoX(dppe)(η-C_7H_7)]$^+$(X = Br, Cl or C≡CR) [2,10], those of **6a**,**b** are relatively broad and uninformative showing hyperfine coupling only to Mo-95/97.

Disappointingly, and in spite of the promising cyclic voltammetric results, attempts to synthesise the radicals derived from the methyl complexes **2a** and **2b** by chemical oxidation with [$FeCp_2$][PF_6] led to unstable products which eluded satisfactory characterisation. However the green isocyanide complex [Mo(CNBu^t)(bipy)(η-C_7H_7)][PF_6] **4a**, reacted with [$FeCp_2$][PF_6] in CH_2Cl_2 to give a yellow precipitate of the radical di-cation [Mo(CNBu^t)(bipy)(η-C_7H_7)][PF_6]$_2$ **7a**. The formation of **7a** from **4a** is accompanied by a shift to high wavenumber of the infrared active ν_{CN} stretch [ν_{CN}, cm^{-1}, (CH_2Cl_2): **4a**, 2137; **7a**, 2220; $\Delta\nu = 83$ cm^{-1}] consistent with the operation of CNBu^t as a good π-acceptor ligand. As with the bromide complexes, the identity of **7a** was established by complementary cyclic voltammetric data [$E°$(V) (CH_2Cl_2), 0.38] and by EPR spectroscopy. At −30°C, the X-band acetone solution EPR spectrum of **7a**, recorded as a second derivative spectrum, reveals well resolved hyperfine coupling (Fig. 2a) and, with the aid of spectral simulation (Fig. 2b), the EPR parameters for **7a** were determined as $<g>$ 1.975, a(H) 4.6 G, a(^{14}N) 2.4 G, a(^{95,97}Mo) 40 G. The magnitude of a(H) [a(H) is attributed to hyperfine coupling to the seven protons of the cycloheptatrienyl ligand] is comparable with typical a(H) values for complexes of the type [MoX(dppe)(η-C_7H_7)]$^{z+}$. However, consistent with data for isotropic hyperfine interactions for unit spin density [15], the hyperfine a(^{14}N), which originates from coupling to the two nitrogens of the 2,2′-bipyridine ligand, is substantially smaller than corresponding a(^{31}P) values (typically 20–25 G) determined for analogous [MoX(dppe)(η-C_7H_7)]$^{z+}$ complexes [2,4,5].

3. Experimental

3.1. 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 compounds [MoBr(CO)$_2$(η-C_7H_7)] [16], [Mo(η-C_6H_5Me)(η-C_7H_7)][PF_6] [17], [$FeCp_2$][PF_6] [18] and Bu^t-dab [19] were prepared by published procedures and the chemicals bipy and CNBu^t were supplied by Aldrich. 300 MHz ^{1}H and 75 MHz ^{13}C{^{1}H}-NMR spectra were recorded on Bruker AC 300 E, Varian Associates XL 300 or Varian Unity Inova 300 spectrometers. IR spectra were obtained on a Perkin Elmer FT 1710 spectrometer and FAB mass spectra using a Kratos Concept 1S instrument. X-band (ca. 9.6 GHz) EPR spectra were recorded on a Bruker ESP 300E spectrometer. Cyclic voltammetric studies were carried out, as described previously [2], at a carbon working electrode (area 0.28 cm^2) using 0.2 M [NBu^n_4][BF_4] as supporting electrolyte in solutions purged with nitrogen gas. All potentials are referenced to an aqueous calomel electrode and, under these conditions, $E°$ for the couple $FeCp_2$–$FeCp_2^+$ is 0.43 V in NCMe, 0.56 V in CH_2Cl_2 and 0.59 V in THF. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

3.2. Preparations

3.2.1. [MoBr(bipy)(η-C_7H_7)] *1a*

A mixture of [MoBr(CO)$_2$(η-C_7H_7)] (0.51 g, 1.58 mmol) and bipy (0.25 g, 1.60 mmol) in toluene (50 cm^3) was gently refluxed for 3 h, the solution turning from green to deep purple. The solvent was removed in vacuo and the residue recrystallised from CH_2Cl_2–diethyl ether to give **1a** as a light sensitive, deep purple solid; yield 0.51 g (76%).

3.2.2. [MoBr(Bu^t-dab)(η-C_7H_7)] *1b*

A mixture of [MoBr(CO)$_2$(η-C_7H_7)] (1.50 g, 4.64 mmol) and Bu^t-dab (0.80 g, 4.76 mmol) in toluene (100

cm^3) was heated at 110°C for 2 h to give a purple solution. The reaction mixture was filtered, reduced in volume to ca. 5 cm^3 and *n*-hexane added to precipitate **1b** as a purple solid; yield 1.63 g (81%).

3.2.3. [MoMe(bipy)(η-C_7H_7)] ***2a***

A purple solution of **1a** (0.30 g, 0.71 mmol) in THF (40 cm^3) was cooled to −78°C and treated with LiMe (5.60 mmol, 4.0 cm^3 of a 1.4 M dm^{-3} solution in diethyl ether). The reaction mixture was allowed to warm to −30°C, then maintained at this temperature for 2 h. The resulting blue solution was then re-cooled (−78°C) and transferred to an alumina-*n*-hexane chromatography column maintained at −78°C. Elution with *n*-hexane gave a blue band which was collected and the solution reduced in volume, treated with further *n*-hexane and cooled to give **2a** as a dark blue, light sensitive solid; yield 0.16 g (63%). The red, light sensitive complex [MoMe(Bu^t-dab)(η-C_7H_7)] **2b**, was prepared in 55% yield from **1b** (0.49 g, 1.13 mmol) and LiMe (7.0 mmol, 5.0 cm^3 of a 1.4 mol dm^{-3} solution in diethyl ether) in THF (50 cm^3). The procedure was analogous to the preparation of **2a** except that the reaction mixture was stirred at r.t. for 1 h (not 2 h at −30°C) and, after chromatography, the product was obtained by crystallisation from *n*-hexane at −78°C.

3.2.4. [Mo(NCMe)(bipy)(η-C_7H_7)][PF_6] ***3a***

A solution of [Mo(η-C_6H_5Me)(η-C_7H_7)][PF_6] (0.709 g, 1.67 mmol) was refluxed in NCMe (40 cm^3) for 20 min. The red solution so formed, was cooled to r.t., treated with bipy (0.298 g, 1.91 mmol) and the reaction mixture stirred at r.t. for 2 h. The resulting solution was filtered and the volume reduced to ca. 5 cm^3 and diethyl added to precipitate **3a** as a green–brown solid; yield 0.602 g (68%). Brown–violet [Mo(NCMe)(Bu^t-dab)(η-C_7H_7)][PF_6] **3b** was obtained in 70% yield by a similar procedure starting from [Mo(η-C_6H_5Me)(η-C_7H_7)][PF_6] (0.53g, 1.25 mmol) and Bu^t-dab (0.227 g, 1.35 mmol).

3.2.5. [Mo($CNBu^t$)(bipy)(η-C_7H_7)][PF_6] ***4a***

A green solution of [Mo(NCMe)(bipy)(η-C_7H_7)][PF_6] (0.602 g, 1.14 mmol) in acetone (30 cm^3) was treated with $CNBu^t$ (0.150 g, 1.81 mmol) resulting in an immediate colour change to an intense bottle green. After stirring at r.t. for 2 h, the solution was reduced in volume and diethyl ether added to precipitate the crude product which was subsequently recrystallised from CH_2Cl_2–diethyl ether then acetone–diethyl ether to give **4a** as a bottle green solid; yield 0.552 g (85%).

3.2.6. [Mo($CNBu^t$)(Bu^t-dab)(η-C_7H_7)][PF_6] ***4b***

A sample of [Mo(NCMe)(Bu^t-dab)(η-C_7H_7)][PF_6] (0.54 g, 1.00 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and the solution immediately treated with $CNBu^t$ (0.14 g, 1.69 mmol). The reaction mixture was then refluxed for 2 h resulting in a deep red solution which was evaporated to dryness. The residue was recrystallised from CH_2Cl_2–diethyl ether to give **4b** as a dark red solid; yield 0.547 g (94%).

3.2.7. [Mo(CO)(bipy)(η-C_7H_7)][PF_6] ***5a***

A slow stream of carbon monoxide was passed through a solution of [Mo(NCMe)(bipy)(η-C_7H_7)][PF_6] (0.411 g, 0.78 mmol) in acetone (30 cm^3) over a period of 2 h. Initially the reaction was carried out at r.t. but the reaction temperature was increased in stages to the boiling point of acetone. The resulting red-brown solution was filtered, reduced in volume and diethyl ether added to precipitate the crude product. Recrystallisation from acetone–diethyl ether gave **5a** as a purple–red solid; yield 0.170 g (42%). A sample of purple–red [Mo(CO)(Bu^t-dab)(η-C_7H_7)][PF_6] **5b** was prepared in 60% yield by an identical procedure starting from [Mo(NCMe)(Bu^t-dab)(η-C_7H_7)][PF_6] (0.40 g, 0.74 mmol).

3.2.8. [MoBr(Bu^t-dab)(η-C_7H_7)][PF_6] ***6b***

A purple solution of [MoBr(Bu^t-dab)(η-C_7H_7)] (0.31 g, 0.71 mmol) in CH_2Cl_2 (40 cm^3) was treated with [$FeCp_2$][PF_6] (0.24 g, 0.73 mmol) resulting in an immediate colour change to orange–brown. After stirring for 15 min, the product was precipitated by addition of diethyl ether and, after removal of the mother liquors, washed with toluene to remove residual $FeCp_2$. The remaining solid was recrystallised from CH_2Cl_2–diethyl ether to give **6b** as a red solid; yield 0.15 g (36%). The bipyridine analogue **6a** was obtained as an orange solid in 21% yield starting from [MoBr(-bipy)(η-C_7H_7)] (0.36 g, 0.85 mmol) and [$FeCp_2$][PF_6] (0.40 g, 1.21 mmol) in CH_2Cl_2 (30 cm^3) by an identical procedure except that recrystallisation was from acetone–diethyl ether.

3.2.9. [Mo($CNBu^t$)(bipy)(η-C_7H_7)][PF_6]$_2$ ***7a***

A green solution of [Mo($CNBu^t$)(bipy)(η-C_7H_7)][PF_6] (0.250 g, 0.44 mmol) in CH_2Cl_2 (15 cm^3) was treated with [$FeCp_2$][PF_6] (0.152 g, 0.46 mmol) and the solution stirred for 1.5 h resulting in the formation of a yellow precipitate of the product. The product was collected by filtration, washed with CH_2Cl_2 and recrystallised from acetone–diethyl ether to give **7a** as a yellow solid; yield 0.242 g (77%).

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