Synthesis of [Mo(η^6-NC$_5$H$_3$Me$_2$-2,6)(η^6-C$_6$H$_5$Me)]: Photoelectron Spectra and Electronic Structure of some Transition-metal η^6-2,6-Dimethylpyridine Complexes†

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Synthesis of the mixed-ring sandwich compound [Mo(η^6-NC$_5$H$_3$Me$_2$-2,6)(η^6-C$_6$H$_5$Me)] is reported. Photoelectron spectroscopic studies of [M(η^6-NC$_5$H$_3$Me$_2$-2,6)$_2$], where M = Ti, V, Cr or Mo and [Mo(η^6-NC$_5$H$_3$Me$_2$-2,6)(η^6-C$_6$H$_5$Me)] established that these sandwich compounds are electronically very similar to the bis(arene) analogues, and that 2,6-dimethylpyridine is a better δ acceptor than benzene.

An increasing number of compounds have been reported where a heterocyclic aromatic ligand is bound to a metal through its ring π electrons forming a metal-sandwich compound. Examples include pyridine[1] and substituted pyridines such as 2,6-dimethylpyridine,[1–6] methylthiophenes,[1,7] arsabenzene,[8] tetramethylpyrazine,[9,10] phosphinine,[11] furan[1,6] and $C_4H_4E^-$ where E = P–Bi.[12]

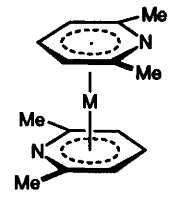
Often in these cases there is an alternative co-ordination mode whereby the ring can bind through a lone pair on the heteroatom.[6] For example, reaction of (η^6-arene)bis(trihalogenosilyl)nickel complexes with pyridines result in displacement of the arene by two or three N-co-ordinated pyridines the precise number depending on the steric requirements of the ligand.[13] Substituted pyridines have also been found to co-ordinate in an η^2-mode.[14–16]

Metal-bound pyridine complexes are proposed as intermediates in a number of reactions. A π-co-ordination mode has been proposed for the heterocyclic intermediates in hydrodesulfurization and hydrodenitrogenation processes.[17] An η^2-co-ordination mode is implicated in 2 + 2 + 2 cycloaddition to form pyridines, and also in some C–H activation processes.[14–16]

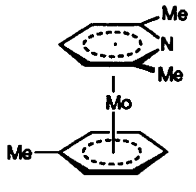
In order to compare the bonding of η^6-pyridines with that of η^6-benzene we have undertaken a photoelectron (PE) spectroscopic study of some 2,6-dimethylpyridine sandwich complexes of the early transition metals.

Bis(2,6-dimethylpyridine)metal sandwich compounds have been synthesized for the metals Cr,[2,3] Ti, V and Mo.[4,5] Here we report the synthesis of a mixed-ring sandwich compound containing 2,6-dimethylpyridine, [Mo(η^6-NC$_5$H$_3$Me$_2$-2,6)(η^6-C$_6$H$_5$Me)].

The spectral properties of the bis(2,6-dimethylpyridine) complexes indicate that they are electronically similar to the bis(benzene)metal sandwich complexes. Structural studies show a decrease in metal–ring distance in the series Ti > V > Cr > Cr$^+$, which is interpreted in terms of the increase in effective nuclear charge along the series favouring 2,6-dimethylpyridine to metal donation.[5] The non-eclipsed conformation of the two rings in the neutral Ti, V and Cr complexes is attributed to the metal-to-ring back-donation into the ring b_1 π* orbitals; torsional angles of 45 or 135° ensure that back donation from both the d_{xy} and $d_{x^2-y^2}$ orbitals is maximized. The Cr$^+$ complex, where back donation is expected to be at a minimum, has an eclipsed structure. Marked differences are reported between the d–d transitions of bis(2,6-dimethylpyridine)chromium and bis(benzene)chromium, the former having higher energy. This is attributed to a stabilization of the highest-occupied molecular orbital (HOMO) when benzene is replaced by pyridine. The absence of a similar energy shift in the d–d bands of the titanium analogues, which have two fewer electrons is consistent with this interpretation.[4] The photoelectron study reported here enables further elucidation and confirmation of such deductions.



M = Ti **1**, V **2**, Cr **3** or Mo **4**



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Experimental

All manipulations and reactions were carried out using standard Schlenk and vacuum-line techniques under an atmosphere of dinitrogen, which had been purified by passage over MnO (or BASF catalyst) and 4 Å molecular sieves, or in a dry-box containing dinitrogen. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled under an atmosphere of dinitrogen from phosphorus pentoxide (dichloromethane), potassium (tetrahydrofuran), sodium [toluene and triglyme,1,2-bis(2-methoxyethoxy)ethane] or sodium–potassium alloy (1 : 3 w/w) [light petroleum (b.p. 40–60 °C), diethyl ether and pentane]. Deuteriated solvents (Aldrich) for the NMR studies were stored in Young's ampoules under an atmosphere of dinitrogen over sodium–potassium alloy ([^{2}H$_6$]benzene) or dried using calcium hydride (CD$_2$Cl$_2$) and transferred by vacuum distillation. Proton, ^{13}C and ^{31}P spectra were recorded using a Brüker AM 300 (^{1}H 300, ^{13}C 75.5, ^{31}P 121.6 MHz) spectrometer. Spectra were referenced internally using residual protio solvent resonances (^{1}H and ^{13}C) relative to tetramethylsilane (δ = 0) or externally using trimethylphos-

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† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

phate in D_2O (^{31}P). All chemical shifts are quoted in ppm and coupling constants in Hz. Signals are expressed as position, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), relative integration, coupling constant and assignment. IR spectra were recorded on a Perkin-Elmer 1510 FT interferometer. Elemental analyses were performed by the Microanalytical Department of this laboratory.

Compounds **1**–**4** were prepared according to the literature method.[4,9]

Synthesis of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(\eta^6\text{-}C_6H_5Me)]$ **5**.—Molybdenum metal (4.84 g, 50.5 mmol) and toluene–2,6-dimethylpyridine (1 : 1, 200 cm^3) were co-condensed onto the surface of a glass bell-jar which was cooled by liquid nitrogen.[18] A dark red matrix developed over a 6 h period. The matrix was allowed to warm to room temperature and than washed from the reaction vessel using light petroleum (*ca.* 1.5 dm^3). The yellow-brown extract was filtered through a Celite bed at −30 °C and the filtrate was evaporated to dryness *in vacuo*. The residue was extracted with *n*-pentane, filtered through a Celite bed at −30 °C and the filtrate was evaporated to dryness under reduced pressure. The separation of the products was achieved by column chromatography on alumina at −25 °C. Elution with Et_2O–*n*-pentane (1 : 20) gave a green band, from which $[Mo(\eta^6\text{-}C_6H_5Me)_2]$ was isolated as green crystals after recrystallization from *n*-pentane at −80 °C. Yield: 340 mg (3%). Elution with Et_2O gave a bright orange fraction, from which the solvent was removed *in vacuo*. The resulting oil was extracted with *n*-pentane and cooled to −80 °C giving brown, air-sensitive crystals of compound **5**. Yield: 850 mg (6%). IR (Nujol): 3045m, 1321w, 1051w, 1024w, 981w, 945w, 795w, 772w, 707w and 637w cm^{-1}. NMR (C_6D_6): ^1H, δ 1.800 (s, 3 H, C_6H_5*Me*), 2.240 (s, 6 H, NC_5H_3*Me*$_2$), 4.590 (m, 4 H, *o,m*-H of C_6H_5Me), 4.626 (m, 1 H, *p*-H of C_6H_5Me), 4.703 [t, 1 H, ^3J(HH) 4.9, *p*-H of $NC_5H_3Me_2$], 4.838 [d, 2 H, ^3J(HH) 4.9, *m*-H of $NC_5H_3Me_2$]; ^{13}C, δ 21.26 (q, 1 C, C_6H_5*Me*), 23.76 (q, 2 C, NC_5H_3*Me*$_2$), 73.67 (d, 1C, *p*-C of C_6H_5Me), 77.73 (d, 2 C, *m*-C of C_6H_5Me), 79.42 (d, 2 C, *o*-C of C_6H_5Me), 80.36 (d, 1 C, *p*-C of $NC_5H_3Me_2$), 82.59 (d, 2 C, *m*-C of $NC_5H_3Me_2$), 93.30 (s, 1 C, *ipso*-C of C_6H_5Me), 104.67 (s, 2 C, *ipso*-C of $NC_5H_3Me_2$). (Found: C, 57.05; H, 5.70; N, 4.65. Calc. for $C_{14}H_{17}MoN$: C, 56.95; H, 5.80; N, 4.75%). The spectroscopic data for compound **5** were supportive of the suggested structure. The ^1H NMR spectrum of **5** showed that the resonances assignable to the aromatic protons on the co-ordinated 2,6-dimethylpyridine and toluene ligand were shifted substantially upfield from those in the free ligands (δ 7.00 and 6.56 for free 2,6-dimethylpyridine in C_6D_6, δ 7.10 for free toluene in C_6D_6). This upfield shift was also apparent in the recorded $^{13}C\text{-}\{^1H\}$ NMR spectra.

Table 1 Ionization energies (eV) and recording conditions for $[M(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)_2]$ (M = Ti **1**, V **2**, Cr **3** or Mo **4** and $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(\eta^6\text{-}C_6H_5Me)]$ **5**

	Compound (*T*/°C)				
Band	**1** (60–65)	**2** (70–80)	**3** (73–85)	**4** (80)	**5** (50)
A[a]	6.14 ($^2E_2$)	6.16 ($^3E_2$)	5.43 ($^2A_1$)	5.47 ($^2A_1$)	5.42 ($^2A_1$)
		6.3[b] ($^1A_1$)	6.54 ($^2E_2$)	6.83 ($^2E_2$)	6.59 ($^2E_2$)
		6.87 ($^1E_2$)			
B	9.10	9.37	9.25	(9.24)	9.09
			9.44		9.61
C[c]	10.18	10.21	10.29	(10.11)	10.27
	12.6	11.78	11.61		11.61
	13.7	12.75	12.61		
		13.71	13.72		13.88

[a] d Bands. [b] Shoulder. [c] Assigned to the nitrogen lone pair.

The photoelectron spectra were measured using a PES Laboratories 0078 photoelectron spectrometer which has a hollow-cathode helium discharge lamp capable of providing both He I and He II radiation. The samples were held at a constant temperature and data collected by repeated scans on an Atari microprocessor. Recording conditions are given in Table 1. The spectra were calibrated with reference to N_2, Xe and He. Ionization energies of the principal features are given in Table 1. Although $[M(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)_2]$ where M = V **2** or Cr **3** were thermally stable under the measurement conditions, the Ti **1** and Mo **4** compounds were prone to thermal decomposition as was $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(\eta^6\text{-}C_6H_5Me)]$ **5**. In these cases the vapour pressure of the samples were lower than ideal for a good signal-to-noise ratio. In the case of $[Mo(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)(\eta^6\text{-}C_6H_5Me)]$ a spectrum was obtained without any evidence of thermal decomposition but for $[M(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)_2]$ (M = Ti or Mo) the spectra obtained are probably contaminated with low levels of free 2,6-dimethylpyridine. This does not affect the validity of the data obtained at ionization energies less than 8.5 eV.

Results and Discussion

The He I and He II PE spectra of compounds **1**–**5** are shown in Figs. 1–5 and the vertical ionization energies of key low-energy features are tabulated (Table 1).

The PE spectra below 11 eV are conveniently divided into three regions, A, B and C. Assignment is readily achieved by comparison with the PE spectra of the bis(arene) analogues[19–21] and that of free 2,6-dimethylpyridine.[22,23] Bands labelled A result from ionization of the d orbitals, bands B from the top-filled π orbitals of the rings and C from the σ lone-pair ionization of the 2,6-dimethylpyridine. Though more features are noticeable in the 2,6-dimethylpyridine PE spectrum, bands B and C in the spectra of the bis(2,6-dimethylpyridine)

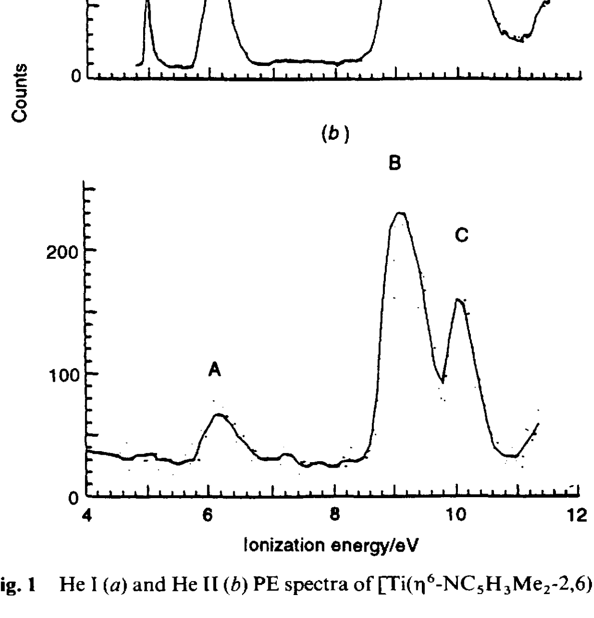

Fig. 1 He I (*a*) and He II (*b*) PE spectra of $[Ti(\eta^6\text{-}NC_5H_3Me_2\text{-}2,6)_2]$ **1**

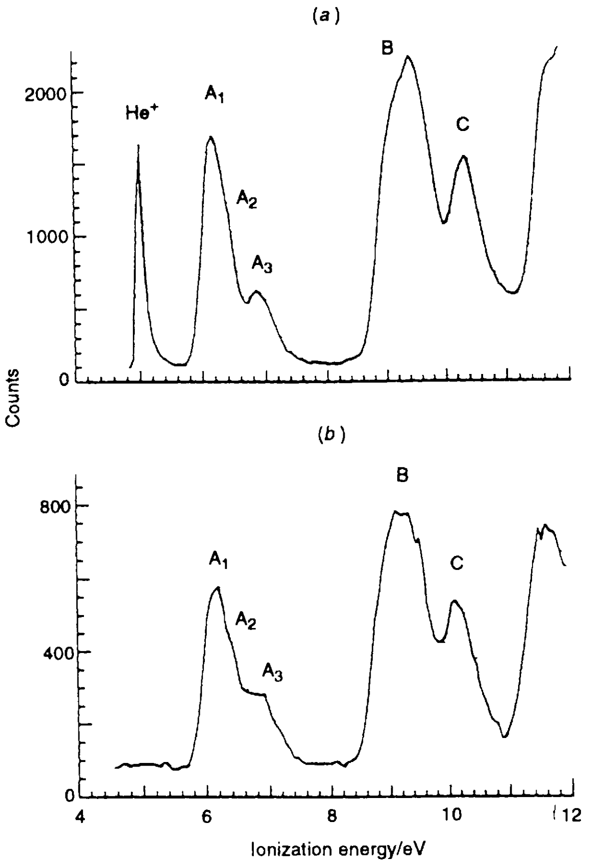

Fig. 2 He I (*a*) and He II (*b*) PE spectra of [V(η^6-NC$_5$H$_3$Me$_2$-2,6)$_2$] **2**

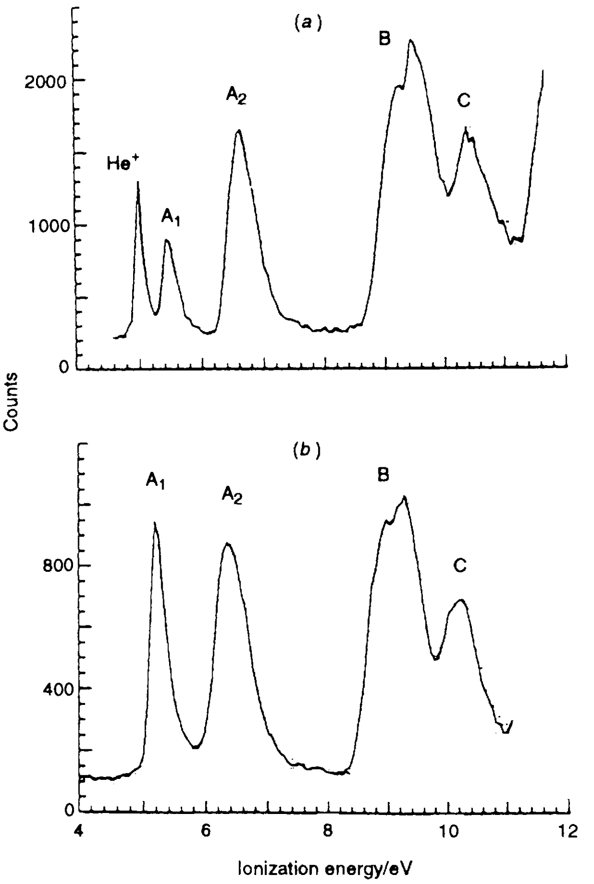

Fig. 3 He I (*a*) and He II (*b*) PE spectra of [Cr(η^6-NC$_5$H$_3$Me$_2$-2,6)$_2$] **3**

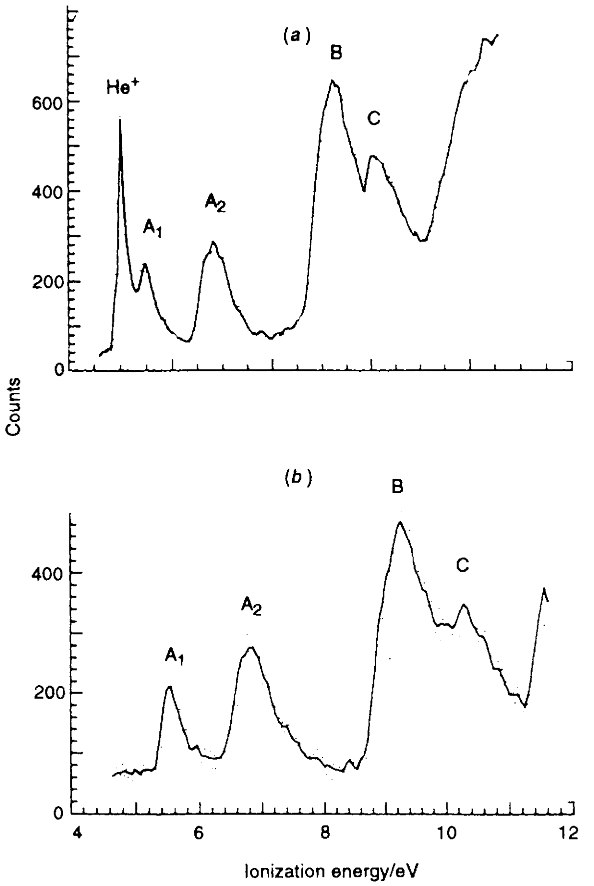

Fig. 4 He I (*a*) and He II (*b*) PE spectra of [Mo(η^6-NC$_5$H$_3$Me$_2$-2,6)$_2$] **4**

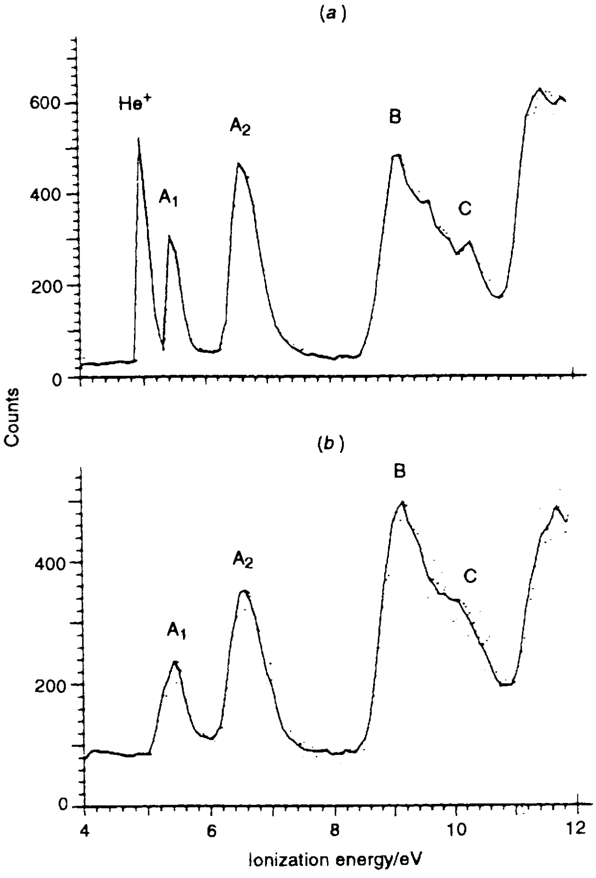

Fig. 5 He I (*a*) and He II (*b*) PE spectra of [Mo(η^6-NC$_5$H$_3$Me$_2$-2,6)(η^6-C$_6$H$_5$Me)] **5**

complexes seem largely unshifted in their energies. The mixed-ring compound **5** shows band C less well resolved from band B, due to the presence of the toluene π ionization in the same region.[23]

The bis complexes lack the high molecular symmetry of their bis(benzene) analogues,[5] but the absence of any effective barriers to ring rotation in solution and the similarity of the d-band structure in the PE spectra suggests that it is permissible to treat them as effectively having an infinite rotational symmetry axis. The d orbitals which are potentially occupied in these compounds are the d_{z^2} of a_1 symmetry which is expected to be non-bonding as a result of its nodal characteristics,[20] and the effectively degenerate pair, d_{xy} and $d_{x^2-y^2}$, of e_2 symmetry which are able to back-donate electron density to the ring. The resulting d configurations and accessible ion states are summarized in Table 2.

Assignment of the d bands to the ion states parallels closely the assignments of the bis(arene) analogues.[19,20] In the 18-electron, d^6 compounds **3**–**5**, band A_1 is assigned to the $^2A_1$ ion state resulting from ionization of the a_1 orbital, and band A_2 to the $^2E_2$ ion state resulting from ionization of the e_2 orbital. Band A_1 increases in intensity relative to band A_2 in the He II spectra. This is commonly found for a_1 ionizations of sandwich compounds. The increase is due to the presence of a strong shape resonance in the a_1 ^{1} ionizations at photon energies around 40 eV.[24–26]

The vanadium compound **2** has a 17-electron d^5 configuration, and, as a result of its open-shell nature, three bands are predicted from ionizing the $e_2{}^4a_1{}^1$ configuration. Though in the low-energy region of the PE spectrum of **2** only two maxima, A_1 and A_3, are evident, there is a shoulder, A_2, on the high-energy side of band A_1 which becomes more prominent in the He II spectrum. The intensity pattern is analogous to the bis(arene)vanadium PE spectra, so we are confident that this shoulder corresponds to the $^1A_1$ ion state resulting from ionization of the a_1 electron.

For the titanium compound **1** only one ion state is predicted for ionizing the closed-shell $e_2{}^4$ configuration so the single band, A_1, is assigned to a $^2E_2$ state.

The trends in ionization energies are plotted in Fig. 6 and compared with those of the bis(toluene) analogues. The similarities of the trends underlines the electronic similarities of these two classes of sandwich compounds. The increased ionization energy of the e_2 orbital across the series Ti, V, Cr can be attributed to the increase in nuclear charge of the metal.[27] The increase from Cr to Mo, in this case, is probably due to the lowering of electron–electron repulsion on descending the group.[27]

The ionization data for a series of bis(arene) complexes are given in Table 3. As the a_1 orbital is non-bonding in character its ionization energy is a good probe of the charge on a metal. For the Group 6 2,6-dimethylpyridine compounds the a_1 ionization energies are very similar to those of the bis(benzene) compounds and significantly larger than the toluene or mesitylene compounds. That this is the case, in spite of the presence of the two methyl groups, indicates that the pyridine ring is electron withdrawing compared to benzene. In contrast, the e_2 ionization energies are greater for the 2,6-dimethylpyridine complexes than the benzene analogues. The presence of the nitrogen atoms on the ring will in general stabilize the ring π orbitals; this should lead to a pyridine ring being a worse donor but a better acceptor than benzene.

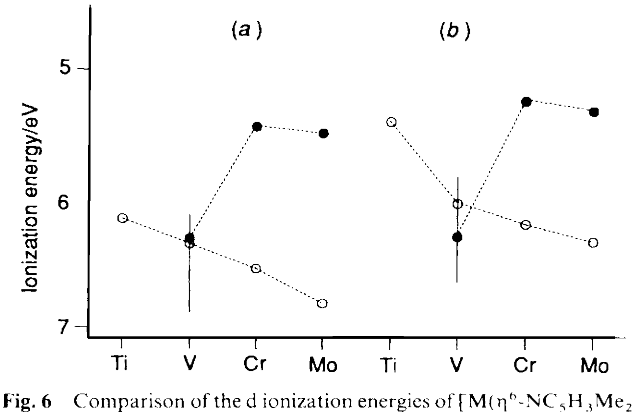

Fig. 6 Comparison of the d ionization energies of [$M(\eta^6-NC_5H_3Me_2-2,6)$] (*a*) and [$M(\eta-C_6H_5Me)_2$] (M = Ti, V, Cr or Mo); (*b*) ●, a_1 and ○, e_2 orbital

The energy separation of the singlet and triplet E_2 states in the PE spectrum of compound **2** is determined only by the electron–electron repulsion, and is given by 16*B* (taking $C = 4B$, where *B* and *C* are Racah parameters).[20] The similarity of the separation (0.71 eV) to that found for the bis(arene) compounds (0.75–0.83 eV) suggests that the Racah parameters are very similar. The uncertainty of the position of the $^1A_1$ ionization in the spectrum of **2** makes a complete ligand-field analysis to determine Δ_2 unrewarding. However, if we assume little variation in electron–electron repulsion throughout the series the larger $^2E_2$–$^2A_1$ separations found for the d^6 bis(2,6-dimethylpyridine) compounds indicate that Δ_2 is significantly larger for these compounds than for the bis(arene) derivatives. Thus 2,6-dimethylpyridine is a better δ acceptor than benzene, which is the best among the arenes studied, back donation being more effective in the bis(2,6-dimethylpyridine) sandwiches than the bis(arene) ones.

The a_1 and e_2 ionization energies of the mixed-ring compound **5** fall between those of compound **4** and bis(toluene)molybdenum, giving an additive model for ring substitution.

The results presented here suggest that a revaluation of the d–d spectra of the bis(2,6-dimethylpyridine) compounds is necessary. We note there is no significant stabilization of the HOMO between bis(benzene)chromium and compound **3** as predicted.[28] The contrast between the absorption spectra of the 2,6-dimethylpyridine and benzene chromium sandwiches is therefore unaccounted for. We also predict that compounds **1**, **2** and [$Cr(\eta^6-NC_5H_3Me_2-2,6)_2$]$^+$ will show bands in the IR region of the spectrum associated with e_2 to a_1 based transitions.

Conclusion

The PE spectra of the series of bis(2,6-dimethylpyridine) metal complexes examined here confirm that they are electronically

Table 2 Electronic configurations and accessible ion states for compounds **1**–**5**

Compound	Configuration	Ion states
1	$e_2{}^4$	$^2E_2$
2	$e_2{}^4a_1{}^1$	$^1A_1$, $^3E_2$, $^1E_2$
3–**5**	$e_2{}^4a_1{}^2$	$^2A_1$, $^2E_2$

Table 3 Ionization energies (eV) and ligand-field parameters (eV) for [$M(NC_5H_3Me_2-2,6)_2$] **I**, [$M(C_6H_6)_2$] **II**, [$M(C_6H_5Me)_2$] **III** and [$M(C_6H_3Me_3-1,3,5)_2$] **IV**

Metal		**I**	**II**	**III**	**IV**
Ti	$^2E_2$	6.14	5.5–6.0	5.4	
V	$^3E_2$	6.16	5.95	5.82	5.33
	$^1A_1$	6.3*	6.10	6.28	5.61
	$^1E_2$	6.87	6.70	6.65	6.08
Cr	$^2A_1$	5.43	5.45	5.24	5.01
	$^2E_2$	6.54	6.46	6.19	5.88
Mo	$^2A_1$	5.47	5.52	5.32	5.13
	$^2E_2$	6.83	6.59	6.33	6.03

* Shoulder.

very similar to bis(arene)metal complexes. 2,6-Dimethylpyridine is shown to be a better δ acceptor than benzene when co-ordinated in an η^6 mode. A similar charge on the metal is inferred for bis(2,6-dimethylpyridine)- and bis(benzene)-metal complexes. Thus 2,6-dimethylpyridine is deduced to be more strongly bound than benzene. Differences found in the reactivity of the two ligands may thus be attributed to the greater variety of co-ordination modes available to the pyridine ring.

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