A Study of the Electronic Structure of the Dimers $[Co_2(\eta\text{-}C_5Me_5)_2(CO)_2]$, $[Rh_2(\eta\text{-}C_5Me_5)_2(CO)_2]$, $[Co_2(\eta\text{-}C_5Me_5)_2(NO)_2]$, and $[Co_2(\eta\text{-}C_5Me_5)_2(CO)(NO)]$ by He-I and He-II Photoelectron Spectroscopy *

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He-I and He-II photoelectron spectra have been obtained for the compounds $[M_2(\eta\text{-}C_5Me_5)_2(CO)_2]$ (M = Co or Rh), $[Co_2(\eta\text{-}C_5Me_5)_2(NO)_2]$, and $[Co_2(\eta\text{-}C_5Me_5)_2(CO)(NO)]$. The assignment presented is consistent with delocalized bonding in the bridge and, together with structural data, may be used to rule out alternative models where there is direct bonding between the metal atoms.

In recent years there have been a number of studies, both experimental and theoretical, of dimeric transition metal compounds with ligands bridging the two metal atoms, the aim of which was to elucidate the nature of the bridge.[1] Historically, it was common to postulate a metal–metal bond for compounds such as $[Co_2(CO)_8]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ to account for their observed diamagnetism,[2,3] the metal–metal distances being consistent with such a hypothesis. More recently, detailed *X*-ray and neutron scattering investigations have been used to study electron density in the bridging region. Mitschler *et al.*[4] concluded for $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ that there was no build-up of electron density in the region between the iron atoms compared to that due to the atoms themselves, rather that this central region appeared to be denuded. This conclusion was supported by the calculations of Bénard.[5] However, theoretical studies on $[Mn_2(CO)_{10}]$,[6] where the metals are directly bonded and unbridged, indicate that metal–metal bonds may not be observed in this way. They may only emerge as an accumulation of electron density when the total electron density is compared with that predicted from a calculation on two $Mn(CO)_5$ fragments, rather than with the electron density of the atoms themselves.

Most of the theoretical attempts to investigate such bridges [1,5,7] indicate that there is no direct metal–metal bond, and that the bonding in the bridge is delocalized and multicentred with the ligands mediating the interaction between the two centres.

Photoelectron (p.e.) spectroscopy has proved a useful technique for testing bonding models in this area of chemistry.[8] We have investigated the isostructural compounds $[M_2(\eta\text{-}C_5Me_5)_2(CO)_2]$ [M = Co (1) or Rh (2)], $[Co_2(\eta\text{-}C_5Me_5)_2(NO)_2]$ (3), and $[Co_2(\eta\text{-}C_5Me_5)_2(CO)(NO)]$ (4). These and related compounds have been the subject of a series of *X*-ray structural studies.[9–14] They provide a particularly interesting series as the electron occupancy varies though the basic structural unit remains the same. The variations found in the metal–metal distance remain somewhat puzzling [1] and provide no clear answer as to whether there is a metal–metal interaction or not. However, in a recent article, Bottomley [15] argues convincingly that the metal–metal distance is primarily controlled by the degree of back-donation to the bridging ligands.

A p.e. study of $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$ has been reported which has been interpreted in terms of the delocalized bridge-bonding model.[16]

Experimental

The compounds (1), (2), and (4) were prepared by reported routes.[17] Compound (3) was prepared by a modification of the method reported for $[Co_2(\eta\text{-}C_5H_5)_2(NO)_2]$.[18]

Preparation of $[Co_2(\eta\text{-}C_5Me_5)_2(NO)_2]$.—$[Co(\eta\text{-}C_5Me_5)(CO)_2]$ (2.57 g, 10.3 mmol) was dissolved in light petroleum (b.p. 40—60 °C; 30 cm^3) and NO gas was slowly bubbled through the solution for 1 h. The brown slurry produced was chromatographed on an alumina column: a yellow by-product was eluted with light petroleum (b.p. 40—60 °C), and then toluene was used to elute an olive-green and a brown band which were not separated but collected together. The toluene solvent was removed under reduced pressure to give a brown oil. More yellow oil and red unreacted starting material were removed from the brown oil by heating to 70 °C under reduced pressure, leaving a solid black residue. $[Co_2(\eta\text{-}C_5Me_5)_2(NO)_2]$ was obtained from this solid by sublimation (1.5×10^{-3} Torr, 119 °C). The product is air sensitive, decomposing with no noticeable colour change, and can be recrystallized from hexane as black, needle-shaped crystals. Yield 207 mg, 9%. I.r., bridging NO stretch at 1 510 cm^{-1}; ^1H n.m.r., δ 1.61 p.p.m. (s, $\eta\text{-}C_5Me_5$); mass spectrum, parent ion at *m/e* 448.

Photoelectron spectra were obtained on two instruments, a Perkin-Elmer PS 16/18 spectrometer and a PES Laboratories 0078. Spectra were calibrated using xenon, nitrogen, and the helium self-ionization band.

Results

The ionization energy (i.e.) and intensity data are given in Table 1 and the spectra obtained are shown in Figures 2—4. As many of the bands were overlapping, especially in the case of the cobalt compounds, it was not possible to estimate individual band intensities reliably, so only composite intensities are given where possible. Some indication of the intensity variation of individual bands was possible however by an inspection of peak heights. All intensity data given have been corrected by dividing the band areas by the kinetic energy of the associated electrons.

All spectra show a main band and some higher energy bands above 11 eV. These may be assigned to the lowest π level of the cyclopentadienyl ring, ionizations from its σ structure and from the 5σ, 1π, and 4σ orbitals of the bridging ligands: [8] they will not be discussed further.

Any further assignment is intimately involved with the proposed bonding model which is discussed below.

Discussion

Structural studies have been carried out on many compounds in this class, interest centring round the metal–metal distance as the 18-electron rule predicts a double metal–metal bond in the case of the d^8–d^8 dimers and a single metal–metal bond in the case of the d^9–d^9 dimers. The distances found are summarized in Table 2. Though the majority of the com-

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* *Non-S.I. units employed:* Torr ≈ 133 Pa; eV ≈ 1.60×10^{-19} J.

Table 1. Ionization energies (eV) and He-II/He-I intensity ratios in parentheses for the dimers $[Co_2(\eta\text{-}C_5Me_5)_2(CO)_2]$ (1), $[Rh_2(\eta\text{-}C_5Me_5)_2(CO)_2]$ (2), $[Co_2(\eta\text{-}C_5Me_5)_2(NO)_2]$ (3), $[Co_2(\eta\text{-}C_5Me_5)_2(CO)(NO)]$ (4), and $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$ (5)

Compound	b_{3g}	b_{2g}	b_{2u}	Other *d* bands			$b_{2g} + b_{3g} + b_{2u} + b_{3u}$
(1)		6.29	6.71	6.96	7.52		8.31
		(1.2)	(0.9)	(1.4)	(1.0)		(0.81)
(2)		6.07	6.40	7.40	7.81	8.15	8.85
		(0.76)		(1.1)	(1.3)		(0.8)
(3)	6.04	6.70		7.13	7.28		8.19, 8.55
	(1.3)	(0.7)		(1.2)			(0.8)
(4)	5.68	6.67		6.93	7.48		8.11, 8.29
	(1.2)			(1.0)			(0.9)
(5) *	6.97	7.45	8.03	8.60	9.0		9.50

* Ref. 16.

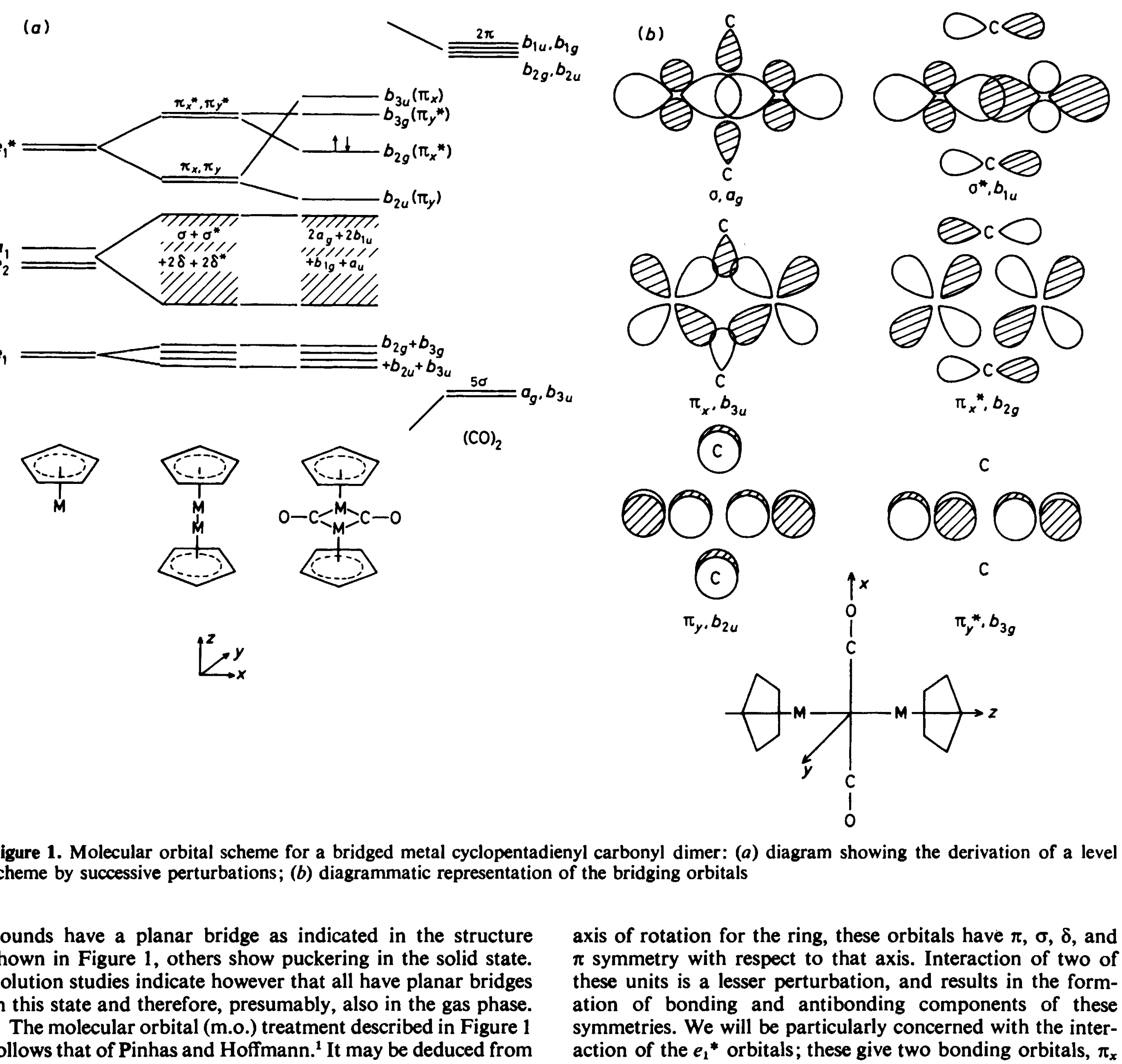

Figure 1. Molecular orbital scheme for a bridged metal cyclopentadienyl carbonyl dimer: (*a*) diagram showing the derivation of a level scheme by successive perturbations; (*b*) diagrammatic representation of the bridging orbitals

pounds have a planar bridge as indicated in the structure shown in Figure 1, others show puckering in the solid state. Solution studies indicate however that all have planar bridges in this state and therefore, presumably, also in the gas phase.

The molecular orbital (m.o.) treatment described in Figure 1 follows that of Pinhas and Hoffmann.[1] It may be deduced from their calculation that the most important factor in determining the ordering of the upper '*d*' levels is the interaction between the metal and the cyclopentadienyl ring. This results in the well known half-sandwich ordering $e_1^* < a_1 \sim e_2 > e_1$. If we take the metal–metal axis as the *z* axis and assume an infinite axis of rotation for the ring, these orbitals have π, σ, δ, and π symmetry with respect to that axis. Interaction of two of these units is a lesser perturbation, and results in the formation of bonding and antibonding components of these symmetries. We will be particularly concerned with the interaction of the e_1^* orbitals; these give two bonding orbitals, π_x and π_y, and two antibonding counterparts, π_x^* and π_y^*. In the d^8–d^8 dimers the two bonding orbitals are occupied, and it is this occupancy which would give the simple metal cyclopentadienyl dimers a double bond. Another way of achieving double bonding with this occupancy would be to allow the

Table 2. Metal–metal distances (Å) reported for the metal cyclopentadienyl–carbonyl and –nitrosyl dimers

Compound	M–M	*d* Configuration	Ref.
$[Fe_2(\eta\text{-}C_5H_5)_2(NO)_2]$	2.326(4)	8–8	11
$[Co_2(\eta\text{-}C_5Me_5)_2(CO)_2]$	2.327(2)	8–8	9
	2.338(2)		10
$[Co_2(\eta\text{-}C_5H_5)_2(CO)_2]^-$	2.372(2)	8–9	12
$[Co_2(\eta\text{-}C_5Me_5)_2(CO)_2]^-$	2.372(1)	8–9	10
$[Co_2(\eta\text{-}C_5H_5)_2(CO)(NO)]$	2.370(1)	8–9	13
$[Co_2(\eta\text{-}C_5H_5)_2(NO)_2]$	2.372	9–9	13
$[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$	2.357	9–9	14
$[Ni_2(\eta\text{-}C_5H_4Me)_2(CO)_2]$	2.390	9–9	14

perturbation involved in the metal–metal interaction to be much greater, in which case the σ^* orbital would be destabilized above the π^* orbitals. The overall occupation would then be $\sigma(2),\delta(4),\delta^*(4),\pi(4),\pi^*(2)$. This ordering results in one of the components being a metal–metal σ bond, that which is normally envisaged when a line is drawn between two metal atoms. Indeed the double bond would be formally similar to that of oxygen. In both models the addition of two extra electrons, the d^9–d^9 case, would lower the bond order to one.

The calculation predicts, however, that the further perturbation introduced by the bridging ligands is sufficient to change this occupancy. The interactions with the ligand 5σ and $2\pi^*$ orbitals are represented diagrammatically in Figure 1; the ligands in this diagram lie in the *xz* plane and D_{2h} symmetry is assumed for the molecule. The crucial interactions are that the π_x orbital is destabilized by an antibonding interaction with the σ-donor orbitals of the bridging ligands, whereas π_y and π_x^* are stabilized by back-donation [Figure 1(*b*)]. The π_y^* orbital is of such a symmetry that it remains unperturbed to a first approximation. The predicted occupancy is now $b_{2g}(\pi_x^*)^2,b_{2u}(\pi_y)^2$ for the d^8–d^8 case and in addition $b_{3g}(\pi_x^*)^2$ for the d^9–d^9 case. The simple picture of a direct metal–metal interaction, albeit of π symmetry, has been lost and replaced by a delocalized multicentre bond.

There is structural evidence to support these occupancies. Careful work by Byers and Dahl [19] on the structure of $[Co(\eta\text{-}C_5Me_5)(CO)_2]$ identified a distortion in the five-membered ring which could be traced back to unequal occupancy of orbitals of e_1 parentage. A similar distortion was observed for $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$ [14] which confirms that π_y type orbitals have a greater occupancy than π_x type orbitals, as is predicted by the model of Pinhas and Hoffmann.[1] If the orbitals of π_x parentage had higher occupancy than those of π_y parentage, the distortion pattern of C–C bond lengths would be different from that observed. It should also be the case that the d^8–d^8 compounds should have undistorted rings; however, in all cases examined so far, the data are insufficiently good to test whether such a distortion is absent.

In order for a p.e. investigation to provide a useful test of this model it is necessary for there to be a method of distinguishing the several ionization bands at lower i.e. Fortunately, examination of many monomeric cobalt and rhodium cyclopentadienyl compounds indicates that there are criteria that we can use to identify the orbital parentage of ionization bands in these cases.[17] For example, in the case of $[Rh(\eta\text{-}C_5Me_5)(CO)_2]$ the highest occupied molecular orbital (h.o.m.o.), b_1, is metal–ring antibonding (e_1^* parentage), and gives an ionization band well separated from the other *d* bands; it also shows a smaller He-II/He-I intensity ratio than the other *d* bands, though a larger one than the lower-lying metal–ring bonding b_1 and b_2 bands (e_1 parentage). These intensity characteristics indicate the proportion of *d*-orbital character contributing to a m.o., as the He-II/He-I intensity ratio is greater for a *d* orbital than a carbon 2*p* orbital.[8] In the case of $[Co(\eta\text{-}C_5Me_5)(CO)_2]$, both the separation of the b_1 band and the intensity characteristics are less marked. Granozzi *et al.*[61] have used similar intensity criteria for assigning the spectrum of $[Ni_2(\eta\text{-}C_5H_5)_2(CO)_2]$, where the intensity characteristics are more analogous to the rhodium pattern than the cobalt one.

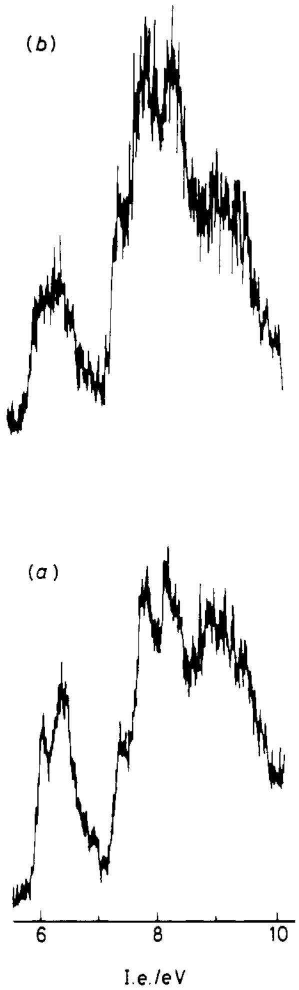

Figure 2. Low-energy region of (*a*) the He-I and (*b*) the He-II p.e. spectra of (2)

If we consider first the spectrum of the rhodium dimer (2) (see Figure 2) we see the two lowest ionization bands are separated from the rest by about 1 eV and also have an intermediate He-II/He-I intensity ratio. This suggests e_1 type parentage and suggests assignment to the b_{2g} and b_{2u} ionizations.

The cyclopentadienyl e_1 ionization may be assigned to the band at 8.85 eV on the grounds of its low He-II/He-I ratio. The comparable band in the spectrum of the rhodium monomer occurs at 8.51 eV. A complex pattern of bands with identifiable features at 7.40, 7.81, and 8.15 eV may be taken to have high *d* content and these are assigned to the σ, σ^*, δ, and δ^* ionizations. It is noteworthy that the shoulder at 7.40 eV rises in the He-II spectrum just as much as does the main *d* band. This fact weighs against a model in which the three highest occupied orbitals are of π type origin with a very destabilized unoccupied σ^* orbital. Also if the σ^* orbital were very destabilized there should be a parallel stabilization of the σ metal–metal bonding orbital; however, no single *d* band

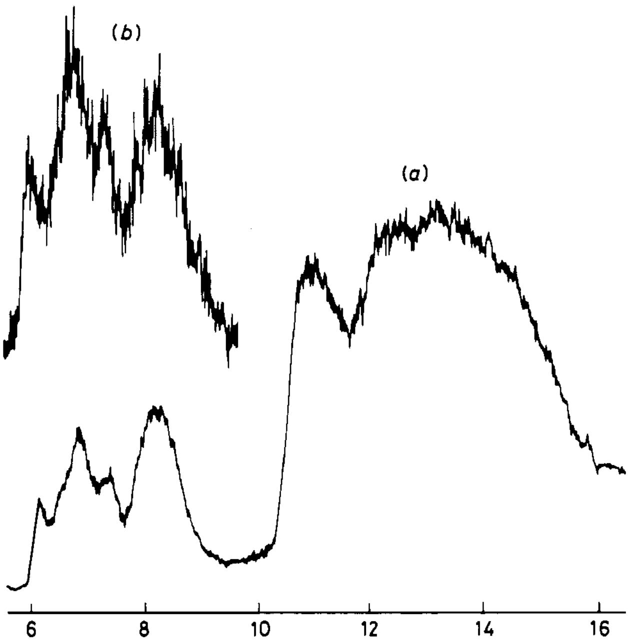

Figure 3. (*a*) He-I and (*b*) He-II p.e. spectra of (1)

appears at a significantly higher ionization energy than any other. Finally, a model of this type would predict a ring distortion in the d^8–d^8 complexes but an undistorted ring for the d^9–d^9 cases, so the weight of the evidence is against it.

The p.e. spectrum of the cobalt dimer (1) (see Figure 3) like the monomer shows a less clear-cut intensity pattern, and the separation of the first band from the rest is only *ca.* 0.4 eV. We assign the spectrum by extrapolation from the rhodium case as indicated in Table 1. The shoulder at 6.71 eV does appear to show a significantly smaller He-II/He-I ratio than the main *d* band so it is assigned to the b_{2u} ionization.

In the case of the nitrosyl dimers, we expect an extra ionization band as a consequence of occupancy of an additional orbital. Though Pinhas and Hoffmann [1] consider the possibility that the extra electrons might be located in orbitals of π^* NO character, they reject it on the grounds that the NO distances are not increased in the d^8–d^9 and d^9–d^9 cases over that found in the d^8–d^8 case of the iron–nitrosyl dimer.[1,11,13] In their model the extra electrons reside in a b_{3g} orbital, which has no back-bonding role to the bridging groups. In support of this, e.s.r. studies on the closely related [$Co_2(\eta\text{-}C_5Me_5)_2(CO)(NO)$] give a spectrum in which no hyperfine coupling due to nitrogen is evident but a 15-line spectrum due to coupling to two ^{59}Co ($I = \frac{7}{2}$) is found.[18] This confirms that the h.o.m.o. is not NO centred but is metal centred, consistent with the localization proposed for the b_{3u} (π_y^*) orbital.

The spectra of the two NO-bridged compounds are shown in Figure 4 and the ionization energy trends represented graphically in Figure 5.

It is reasonable for (3) and (4) to have lower first-ionization energies than (1) as the orbital from which the electron is ionizing in these cases is not involved in back-donation to the bridging ligands. In the case of (4), an open-shell molecule, the spectrum beyond 6 eV is expected to be broadened by multiplet splitting. Both the b_{2g} and the b_{2u} ionizations are raised on introduction of NO as a bridging ligand (see Figure 5), more so than is the main *d* band, consistent with these orbitals having a contribution from the $2\pi^*$ orbitals of the NO group. The NO ligand possesses lower lying $2\pi^*$ orbitals than CO; NO has one electron occupying these orbitals and has a first i.e. of 9.27 eV. Introduction of NO as the bridging ligand into the $M_2(\eta\text{-}C_5Me_5)_2$ dimer should produce a greater perturbation on the lower lying e_1 metal–

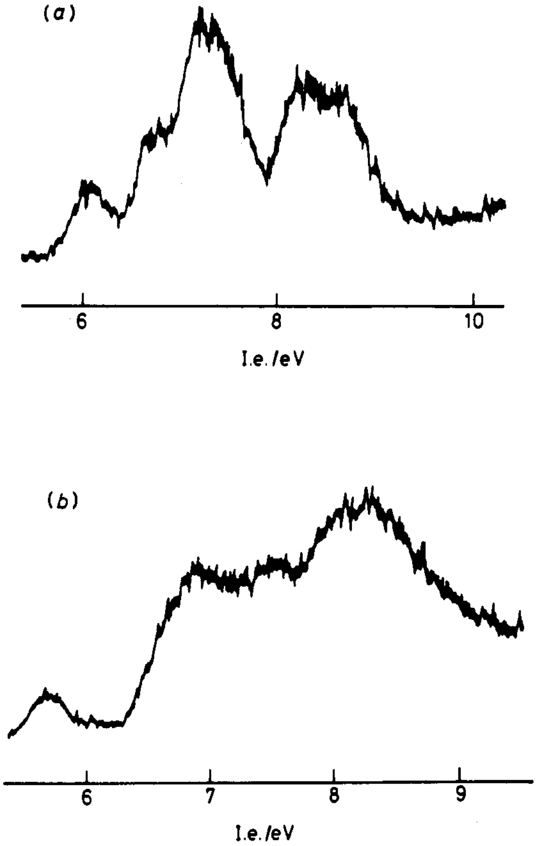

Figure 4. Low-energy region of the He-I p.e. spectra (*a*) of (3) and (*b*) of (4)

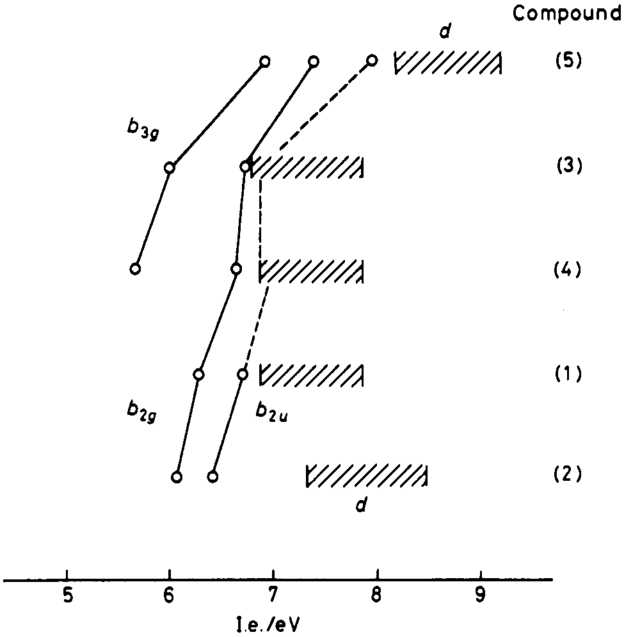

Figure 5. Graphical representation of the i.e. trends in compounds (1)—(5)

ring bonding orbitals than does CO. We would expect the b_{2g} and b_{2u} orbitals to acquire significant NO character, but the b_{3g} and b_{3u} orbitals should remain relatively unchanged. It is interesting in this context that a splitting of the associated bands [8.19 and 8.55 eV for (3) and 8.11 and 8.29 eV for (4)] is observed in the spectra of (3) and (4) (see Figure 4), whereas these four bands are unresolved for (1) and (2). Ionizations from the higher lying b_{2u} and b_{2g} orbitals, which are involved in back-donation to the more electronegative nitrosyl group, should give higher ionization energies. Introduction of NO also seems to lower the He-I intensity of these bands. These considerations are fully consistent with the assignments given in Table 1.

We had also measured the He-I and He-II spectra of $[Ni_2(\eta\text{-}C_5Me_5)_2(CO)_2]$ but as our results are fully in agreement with those of Granozzi *et al.*[16] they are not reported here. We differ though from these authors on a small point of assignment. The He-I spectrum shows two low lying bands at 6.97 and 7.45 eV and a further shoulder at 8.03 eV. Granozzi *et al.* assign the first band to the b_{3g} ionization and the second band to both the b_{2g} and b_{2u} ionizations. However, both these bands and the shoulder at 8.03 show a decrease in intensity in the He-II spectrum relative to the *d* bands at 8.60 and 9.0 eV. It therefore seems reasonable to us to assign the second band to just the b_{2g} ionization and the shoulder at 8.03 eV to the b_{2u} ionization. The separation of the b_{2g} and b_{2u} ionization bands would not be dissimilar to that found for the cobalt and rhodium complexes.

Conclusions

The p.e. spectra of this series of dimers are consistent with the bonding model proposed by Pinhas and Hoffmann[1] and, together with the structural distortions found by Byers and Dahl[19] in $[Ni_2(\eta\text{-}C_5Me_5)_2(CO)_2]$ may be used to rule out alternative models where direct bonding is present between the metal atoms. Spin pairing between the two metal atoms occurs *via* delocalized orbitals involving bridging ligands. In view of this, the $M_2(\mu\text{-}CO)_2$ system in these dimers is best regarded as a ring. The chemistry of the d^8–d^8 dimers should be dominated by the low lying vacant orbital of b_{3g} symmetry.

Acknowledgements

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