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He(I) AND He(II) PHOTOELECTRON SPECTRA OF THE FOUR METAL–METAL BONDED COMPLEXES [$(CO)_5M–M'(CO)_3$(1,4-i-Pr_2-1,4-diaza-1,3-butadiene)] (M = M′ = Mn or Re; M = Mn, M′ = Re; M = Re, M′ = Mn)

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Summary

The ultraviolet He(I) and He(II) photoelectron (UP) spectra have been recorded for the dinuclear d^7-metal carbonyl complexes [$(CO)_5M–M'(CO)_3$(i-PrN=CHCH=N-i-Pr)], where M = Mn, M′ = Re; M = Re, M′ = Mn; M = M′ = Mn; M = M′ = Re. The observed vertical ionization energies (IE's) of these four complexes are assigned to metal *d* orbitals, the ligand orbitals, the metal–metal σ_b orbital with the aid of semi-empirical molecular orbital (MO) calculations, consideration of He(I)/He(II) intensity ratios, and comparison with data for related complexes. The IE's of the σ_b (M–M′) orbital of these complexes are 6.95 eV (M = M′ = Mn), 7.19 eV (M = Re, M′ = Mn), 7.15 eV (M = Mn, M′ = Re) and 7.03 eV (M = M′ = Re), respectively. These data and other UP results are of importance for the interpretation of the photochemical behaviour of these complexes.

Introduction

Much attention has been given in our laboratory in the past decade to the chemistry [1], spectroscopy [2–4] and photochemistry [5–8] of transition metal carbonyl complexes containing an α-diimine ligand (see Fig. 1a–d).

In the course of our photochemical investigations of such complexes containing a chelate bonded α-diimine ligand (Fig. 1e) [2–8], we found the need for more detailed information about the electronic properties of the complexes in their ground states, and so an ultraviolet photoelectron spectroscopy (UPS) study was undertaken of a series of mononuclear transition metal carbonyls containing an 1,4-diaza-1,3-butadiene ligand RN=C(R′)C(R″)=NR (abbreviated as R-DAB {R′,R″} [9]). The UP spectra of [$M(CO)_4$(R-DAB)] (M = Cr, Mo, W), [$MX(CO)_3$(R-DAB)] (M = Mn,

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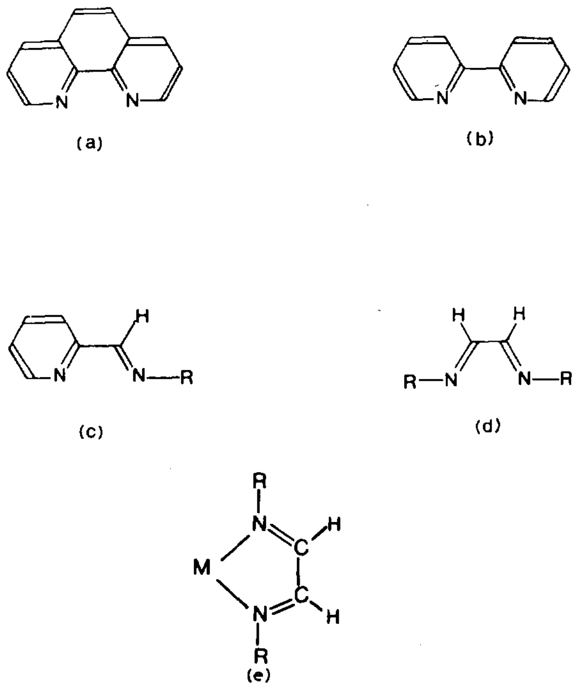


Fig. 1. Four α-diimines: (a) 1,10-phenanthroline, (b) 2,2′-bipyridine, (c) pyridine-2-carbaldehydeimine, (d) 1,4-diaza-1,3-butadiene (R-DAB) and the chelate bonding of R-DAB in metal carbonyl complexes (e).

Re; X = Cl, Br), [M(CO)$_3$(R-DAB)] (M = Fe, Ru) and [M(CO)$_2$(R-DAB)] (M = Ni) were recorded and correlated with those of the unsubstituted carbonyl complexes [10]. The valuable information derived from those spectra prompted us to extend the studies to the complexes [(CO)$_5$M–M′(CO)$_3$(i-Pr-DAB)] (i-Pr-DAB = i-PrN=CHCH=N-i-Pr) with M = Mn, M′ = Re; M = Re, M′ = Mn; M = M′ = Mn, or M = M′ = Re, which show a very interesting photochemical behaviour [11,12]. Figure 2 shows the molecular structure and C_s symmetry of these complexes.

Experimental

Syntheses

The ligand [13] and complexes [(CO)$_5$M–M′(CO)$_3$(i-Pr-DAB)] (M, M′ = Mn, Re) were prepared by literature methods [14,15]. The compounds were identified by spectroscopic measurements (^{1}H NMR, FT-IR and UV/VIS) and by elemental analysis. The thermal stabilities of the complexes in the gas phase were examined by thermoanalyses under high vacuum conditions.

Photoelectron spectra

The UP spectra were recorded on a Perkin–Elmer PS-18 photoelectron spectrometer, equipped with a Helectros Developments hollow cathode He(I)/He(II) light source. The spectra were calibrated with respect to He, Ar and Xe lines as internal references.

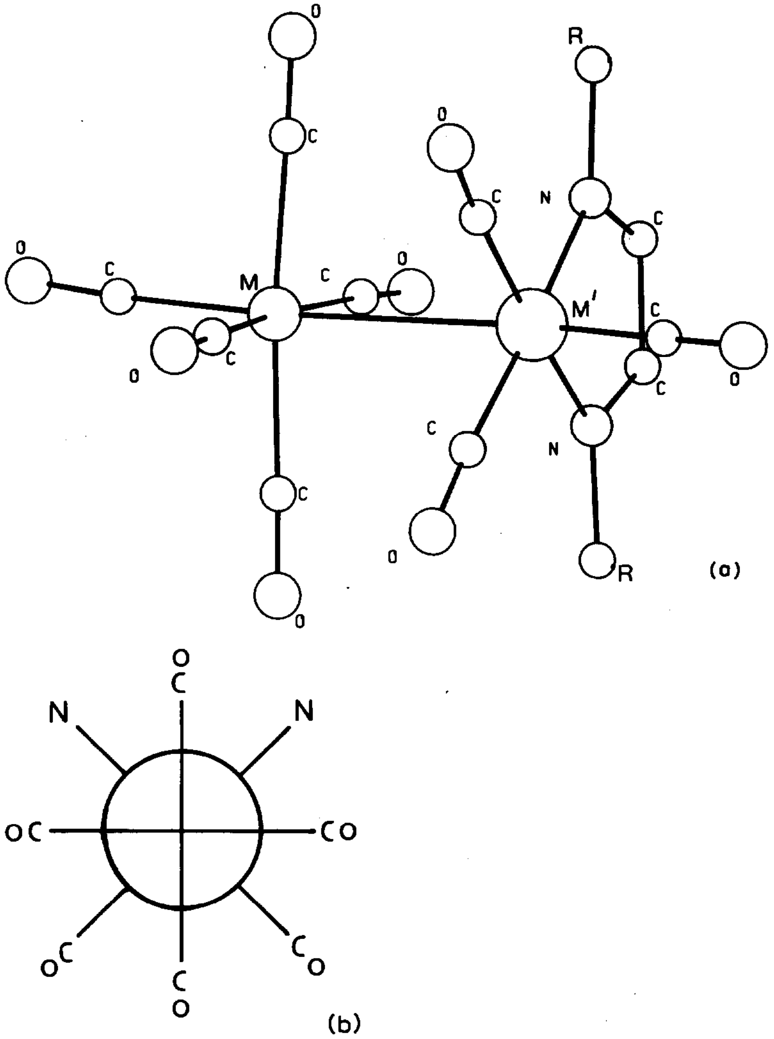


Fig. 2. Molecular structure of [$(CO)_5M$–$M'(CO)_3$(i-Pr-DAB)] (a) and a Newman projection along the M–M' bond (b).

Calculations and geometry

The MO calculations were performed with an extended version of the CNDO/S method using the parametrization of Del Bene and Jaffé [16] in which the repulsion integrals were approximated by the method of Nishimoto and Mataga [17]. Geometrical parameters were taken from an X-ray crystal structure determination of [$(CO)_5$Re-Mn$(CO)_3$(i-Pr-DAB)], which will be published in a forthcoming paper [12].

Results and discussion

He(I) and He(II) photoelectron (UP) spectra of the complexes [$(CO)_5$-M–$M'(CO)_3$(i-Pr-DAB)] (M, M' = Mn, Re) have been measured and will be discussed separately.

Throughout the discussion, for each ionization a canonical molecular orbital (MO) is assumed to exist that indicates the electron to be ejected by the ionization. In the CNDO LCAO-MO-SCF theory the eigenvalues of the canonical MOs are compared with ionization energies (IE) using Koopmans' theorem [18,19]: $IE = -\varepsilon_j$.

Breakdown into fragments

The complexes shown in Fig. 2 consist of two fragments, $M(CO)_5$ and $M'(CO)_3$(R-DAB), both containing a transition metal centre with a formal d^7 electron configuration.

The four occupied metal d orbitals of manganese and rhenium in $M(CO)_5$ transform as $a_1(d_z^2)$, $e(d_{xz},d_{yz})$ and $b_2(d_{xy})$ in local C_{4v} symmetry, which reduces to a', a'', a'' and a' in C_s symmetry of the complexes. The IE of these d-levels can be derived from the UP data of $[MX(CO)_5]$ (M = Mn, Re; X = H, Cl, Br, I, CH_3, etc.) and of $[M_2(CO)_{10}]$ (M = Mn, Re) [20–23]. The metal d orbitals of the substituted fragment $M'(CO)_3$(R-DAB) also transform as a', a'', a'' and a' in C_s symmetry.

We recently studied the effect of substituting two CO groups by an α-diimine ligand on the metal d ionizations [10]. From the results a shift of 1.7 eV was deduced for the weighted mean of the metal d ionizations of $M'(CO)_3$(R-DAB) with respect to the unsubstituted fragment $M(CO)_5$.

The bonding between the two fragments involves σ-overlap between the two half-filled d_{z^2} orbitals giving rise to an a' orbital (σ_b: M–M'). In addition to this σ-bonding, π-interaction will probably occur between the occupied d_{xz} and d_{yz} metal orbitals of both fragments. Such a π-interaction has e.g. been observed between the two $M(CO)_5$ fragments in the UP spectra of $[M_2(CO)_{10}]$ (M = Mn, Re). We have also explored how this π-interaction changes, when the two fragments contain different metals, this was done by comparing the UP spectra of $[M_2(CO)_{10}]$ (M = Mn, Re) with those of $[MnRe(CO)_{10}]$ [24], which showed that, although the metal d orbitals of the two fragments are of different energy in the latter complex due to the larger electronegativity of Re, the π-interaction between the two $e(d_{xz},d_{yz})$ levels is practically the same in both complexes [21–24].

A δ-interaction between the two remaining d_{xy} orbitals is not expected to involve large energy splittings and is impossible in a staggered molecular conformation (Fig. 2).

Ionizations from orbitals mainly localized on the R-DAB ligand i-Pr-N=CHCH=N-i-Pr have been observed and assigned before, by us [10,25] and by others [26]. The lowest IE are expected to arise from the π-system ($\pi_2(-)$ and $\pi_1(+)$) and from the nitrogen lone pair combinations n_+ and n_-. The low-lying empty π-orbitals ($\pi_3^\star$ and $\pi_4^\star$) are responsible for the strong π-backbonding between the metal and the chelate bonded ligand (Fig. 1e).

The eight carbonyl groups of the complexes give rise to ionizations from orbitals of 5σ, 1π and 4σ type at energies higher than 12 eV [27].

Assignment criteria

Crucial to the assignment of UP spectra of organometallic complexes are the He(I)/He(II) intensity ratio differences [27]. These arise from the differences in cross sections on ionization from molecular orbitals with He(I) or He(II) photons. In cases of highly localized orbitals in particular, qualitative arguments have proved to

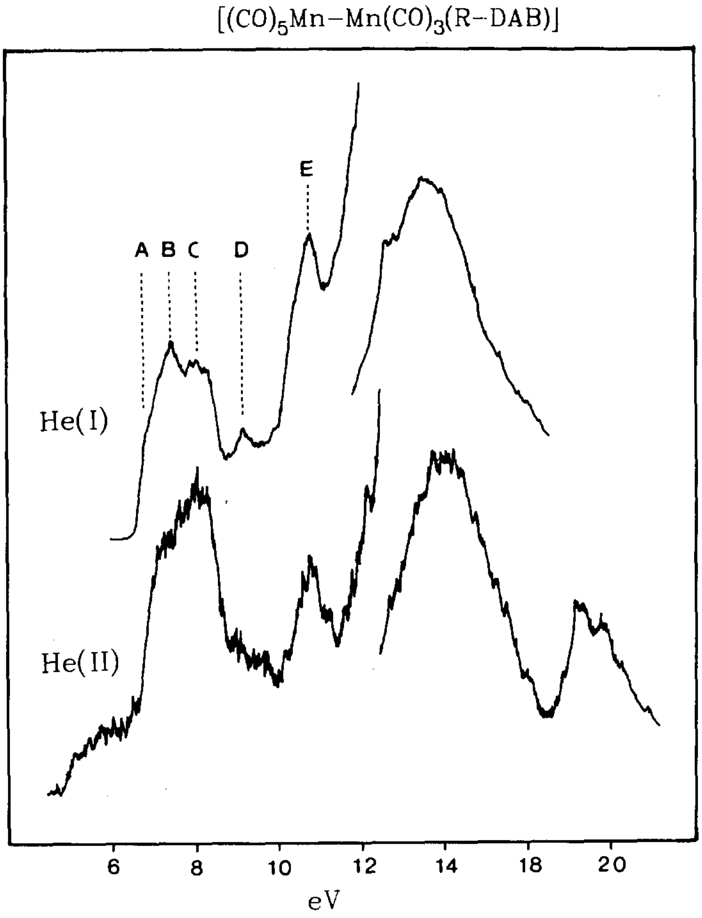


Fig. 3. He(I) and He(II) photoelectron spectra of [$(CO)_5Mn-Mn(CO)_3$(i-Pr-DAB)].

be very helpful [27] and the following rules apply [28]: (a) Metal *d* type orbitals are characterized by a strong enhancement in intensity upon going from He(I) to He(II) radiation; (b) σ-orbitals have low He(II) intensities, because of participation of C_{2s}, H_{1s} and N_{2s}; (c) C_{2p} and N_{2p} type orbitals have about the same cross sections in He(I) and He(II) which means, however, that they lose intensity on going from an He(I) to an He(II) UP spectrum with respect to transition metal *d* type ionization bands.

UP spectra of [$(CO)_5M-M'(CO)_3$(i-Pr-DAB)] *(M, M' = Mn, Re)*

All the spectra show a more or less resolved region between 7 and 11 eV, whereas very broad and unresolved bands are observed at higher IE. The latter bands arise from ionizations from the R-DAB σ- and carbonyl σ- and π-orbitals as discussed before.

The He(I) and He(II) UP spectra are displayed in Figs. 3–6 and the observed vertical ionization energies are listed in Table 1.

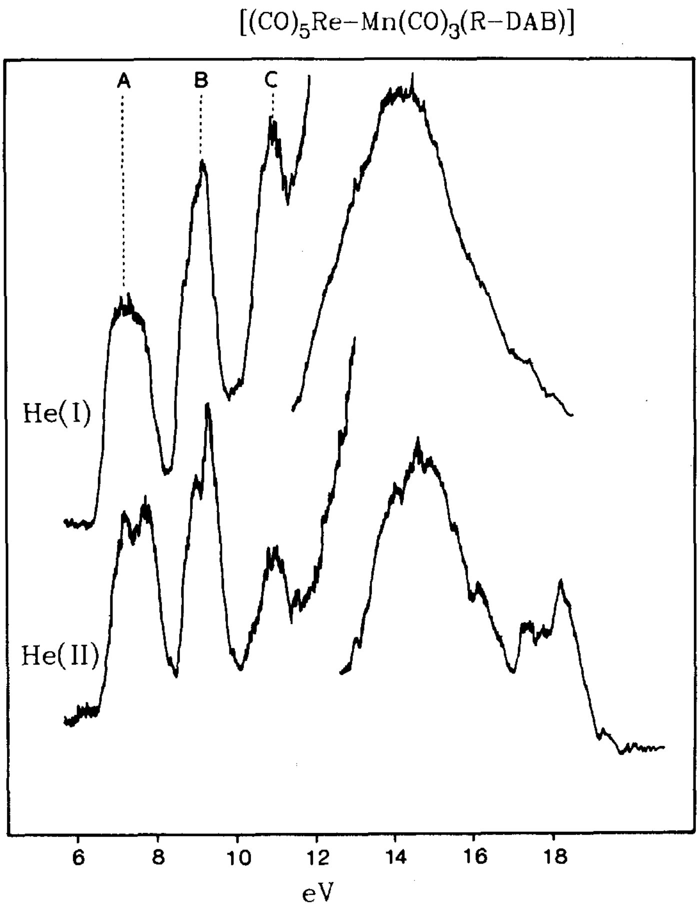


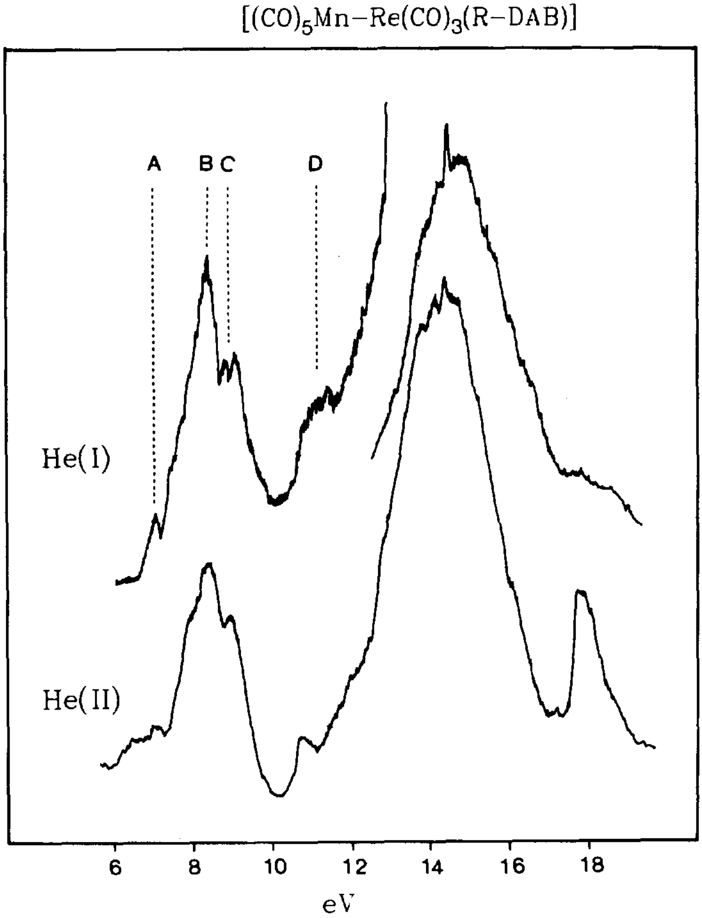
Fig. 4. He(I) and He(II) photoelectron spectra of [$(CO)_5Re$–$Mn(CO)_3$(i-Pr-DAB)].

M, M′ = Mn

The UP spectra of this complex, shown in Fig. 3, can be divided into three regions. The first region (6.8–9.0 eV) consists of a broad band with maxima **B** and **C** and a shoulder **A** on the low IE side. These bands show an increase of intensity with respect to those of the second region (9–11 eV) on changing from He(I) to He(II) excitation. In the latter region only two clearly resolved bands, **D** and **E**, appear.

The relatively large cross sections of bands **A**–**C** as well as their IE [27] indicate that they belong to ionizations from manganese localized *d* orbitals. The ordering of these *d* orbitals can be determined by use of (i) UP data for the unsubstituted carbonyl complex [$Mn_2(CO)_{10}$], (ii) data obtained from our earlier studies on mononuclear transition metal carbonyls containing a R-DAB ligand [24], (iii) CNDO/S MO calculations, and (iv) intensity ratio differences on going from He(I) to He(II) excitation.

From UP studies of [$MX(CO)_5$] (M = Mn, Re; X = H, Cl, Br, etc.) complexes [27] it is known that the energy separation between the *e* and b_2 (C_{4v}) metal *d* ionizations is rather small, and hardly visible in the spectra [29]. Thus, the three d_{xy},



$[(CO)_5Mn-Re(CO)_3(R-DAB)]$

Fig. 5. He(I) and He(II) photoelectron spectra of $[(CO)_5Mn-Re(CO)_3(i\text{-}Pr\text{-}DAB)]$.

d_{xz}, d_{yz} orbitals of the two metals separately in $[(CO)_5Mn-Mn(CO)_3(i\text{-}Pr\text{-}DAB)]$ are expected to coincide. Furthermore, replacement of two CO groups by R-DAB causes an increase of electron density at the metal centre, the value depending on the number of CO groups left. For the d^6 complexes $[M(CO)_4(R\text{-}DAB)]$ (M = Cr, Mo, W) a decrease of 1.54 eV was deduced from the UP spectra for the weighted mean IE of the metal *d*-orbitals with respect to the unsubstituted complexes $[M(CO)_6]$ ($\Delta\overline{IE}_d$) [10]. This value of $\Delta\overline{IE}_d$ appeared to increase to 1.80 eV for the d^8 complexes $[M(CO)_3(R\text{-}DAB)]$ (M = Fe, Ru) and to 2.09 eV for the d^{10} complex $[M(CO)_2(R\text{-}DAB)]$ (M = Ni) [10]. The constant increase of $\Delta\overline{IE}_d$ arises from the progressive reduction of the number of remaining CO groups. By interpolation a $\Delta\overline{IE}_d$ of about 1.7 eV is expected for the d^7 complexes under study.

From these observations it is clear that the ionizations from the three non-bonding *d* orbitals (d_{xy}, d_{xz}, d_{yz}) of the two different Mn fragments in the molecule will not coincide. The *d* orbitals of the substituted Mn (= M') will be destabilized with respect to the corresponding *d* orbitals of the unsubstituted Mn (= M). This shift is responsible for the two maxima **B** and **C** within the lowest energy band. Thus, band

B is assigned to ionizations from the *d* orbitals of Mn in the $Mn(CO)_3$(i-Pr-DAB) moiety and band **C** to ionizations from these orbitals in the $Mn(CO)_5$ fragment. Further support for this assignment comes from the He(I)/He(II) intensity ratios of bands **B** and **C**. Band **B** decreases with respect to **C** on going to He(II) excitation, indicating participation of the R-DAB ligand (esp. N_{sp^2} mixing) in the *d*-orbitals of the $Mn(CO)_3$(R-DAB) fragment.

In view of the discussion above and the shape of the UP spectra of $[Mn_2(CO)_{10}]$ [20–24], shoulder **A** is assigned to ionizations from the Mn–Mn bonding orbital (σ_b). The value of 6.95 eV is about 1 eV less than for $[Mn_2(CO)_{10}]$ [20] because of the R-DAB substitution (inductive charge effect).

The second region (9–11 eV) consists of two distinct bands **D** and **E**. These bands are due to ionizations from orbitals of the i-Pr-DAB ligand, as observed before [10,25,26]. The decrease of the cross section of **D** with respect to **E** on changing to He(II) excitation, and to a lesser extent their He(I) intensity ratio of about 1/2,

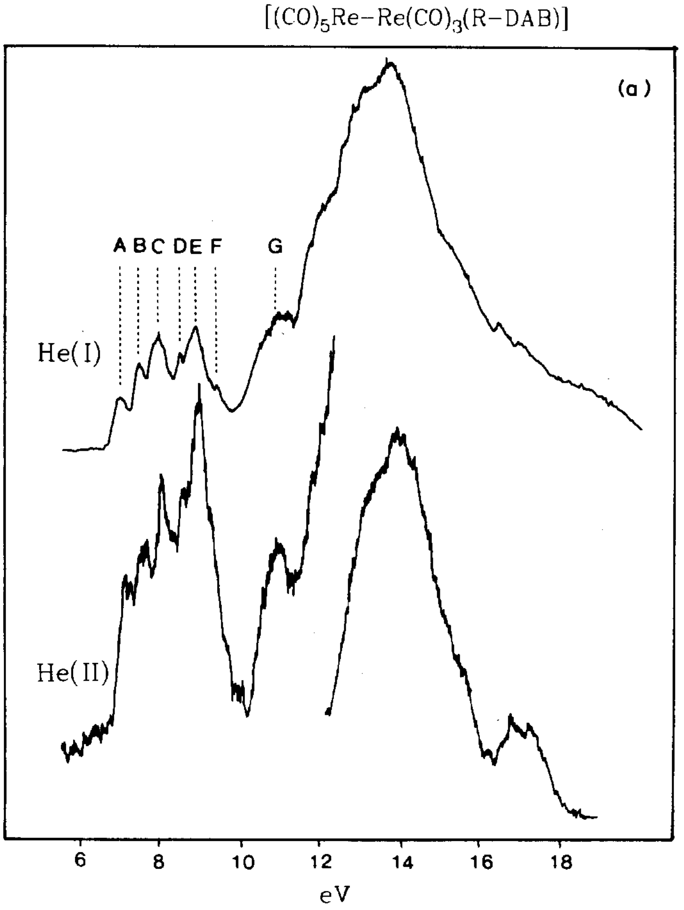
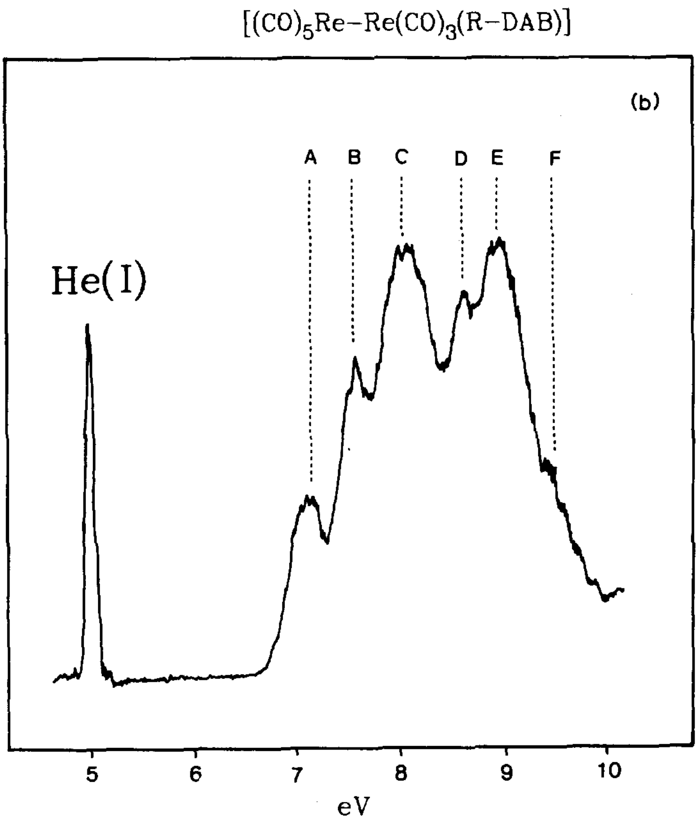


Fig. 6. Full He(I) and He(II) photoelectron spectra of $[(CO)_5Re–Re(CO)_3$(i-Pr-DAB) (part a) and expanded He(I) UP spectrum of the low IE region (part b).



support the assignment of band **D** to ionizations from the n_+ nitrogen lone pair orbital (n_- is stabilized by interaction with the metal) and band **E** to ionizations from the $\pi_2(-)$ and n_- orbitals.

The bands in the third region ($>$ 11 eV) belong to ionizations from 5σ, 1π and 4σ CO orbitals [27] and from several σ-i-Pr-DAB orbitals which will not be discussed here [10,25,27].

TABLE 1

OBSERVED VERTICAL IONIZATION ENERGIES (eV ± 0.05) FOR THE COMPLEXES [(CO)$_5$M-M'(CO)$_3$(i-Pr-DAB)]. BAND INDICES USED IN THE SPECTRA ARE IN BRACKETS

M	M'	IE					
Mn	Mn	6.95(a)		7.42(b)	8.10(c)	9.11(d)	10.73(e)
Re	Mn		7.31(a) [a]		8.81/9.10(b)		10.65(c)
Mn	Re	7.15(a)		8.41(b)	9.03(c)		10.94(d)
Re	Re	7.03(a)		7.54(b)/8.00(c)	8.66(d)/8.93(e)	9.5(f)	10.99(g)
Assignments		σ_b		metal *d*	metel *d*	ligand	
		M-M'		M'	M	n_+	$n_-\pi_2(-)$

[a] The onset IE of this band is found at ca. 7.19 eV.

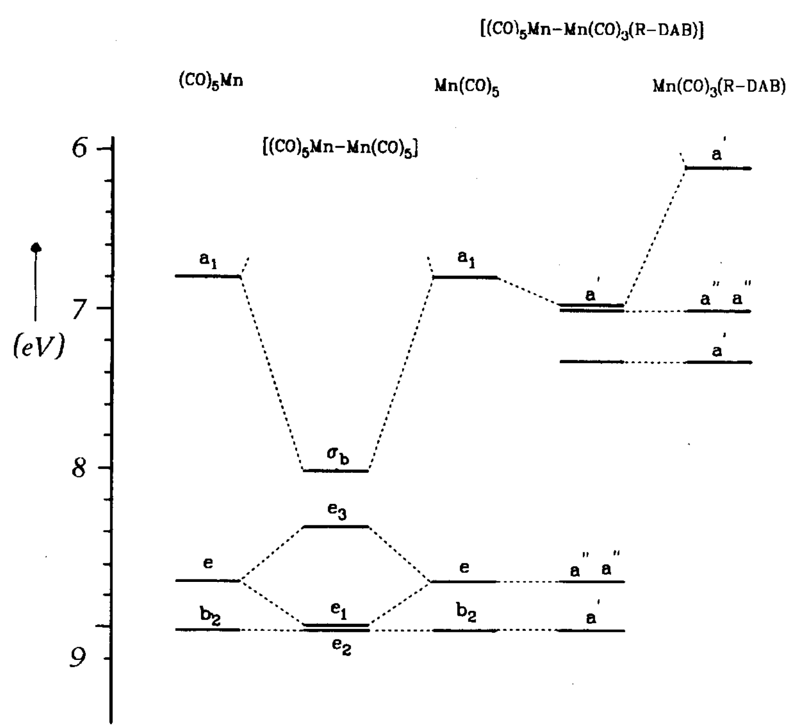


Fig. 7. Constructed interaction diagram of the various fragments.

On the basis of these qualitative assignments and CNDO/S semi-empirical MO calculations [30] an interaction diagram can be constructed for $[(CO)_5Mn-Mn(CO)_3(R\text{-}DAB)]$ (Fig. 7) based on those for $[M_2(CO)_{10}]$ (M = Mn, Re) [21,23,24,27].

M = Re, M′ = Mn

Figure 4 shows the UP spectra of the complex $[(CO)_5Re-Mn(CO)_3(i\text{-}Pr\text{-}DAB)]$. Changes in the spectra with respect to those of $[(CO)_5Mn-Mn(CO)_3(i\text{-}Pr\text{-}DAB)]$ discussed in the previous section are mainly expected for ionizations from the $M(CO)_5$ moiety. The assignments of these spectra are straightforward and can be made by using the same arguments as before. Band **A** now comprises ionizations from the σ_b orbital and the *d* orbitals of the $Mn(CO)_3(i\text{-}Pr\text{-}DAB)$ fragment. Band **B** results from ionizations from the rhenium metal *d*-orbitals.

The asymmetry of band **A** in the He(II) spectrum indicates the presence of σ_b(Re-Mn). The IE's of the Mn d-orbitals (band **A**) are more or less the same as for $[(CO)_5Mn-Mn(CO)_3(i\text{-}Pr\text{-}DAB)]$. On the other hand, the IE's of the metal *d* orbitals in the $Re(CO)_5$ fragment (band **B**) are higher than those of the $Mn(CO)_5$ fragment due to the larger electronegativity of Re. These values are comparable with those observed for other $[MX(CO)_5]$ (X = Cl, Br, etc.; M = Mn, Re) complexes [20–23,27]. From band **B** the spin-orbit (SO) coupling of the Re *e*-level ($e' + e''$ in local C_{4v}) is estimated at 0.3 eV, which is in agreement with results from other experiments [27]. This SO coupling results in a splitting of band **B** in the He(II) spectrum with an intensity ratio of $1/2$ $(= e'/(e'' + b_2))$.

In the case of the [(CO)$_5$Re–Mn(CO)$_3$(i-Pr-DAB)] complex the energy difference between the metal *d* orbitals of the two metal fragments is large because of the destabilization of the Mn *d* orbitals by R-DAB substitution and the stabilization of the Re *d* orbitals by its larger electronegativity. Both effects result in the two nicely separated bands **A** and **B** (Fig. 4).

Band **C** at 10.9 eV is assigned to ionizations from the $\pi_2(-)$ and n_- orbitals of the R-DAB ligand. Ionizations from the n_+ orbital, which have small cross sections in the He(I) spectrum of [(CO)$_5$Mn–Mn(CO)$_3$(i-Pr-DAB)], are obscured by the ionizations from the Re *d* orbitals (e', $e'' + b_2$) in the case of [(CO)$_5$Re–Mn(CO)$_3$(i-Pr-DAB)].

M = Mn, M′ = Re

The complex [(CO)$_5$Mn–Re(CO)$_3$(i-Pr-DAB)] represents the other extreme. In this case the energy difference between the ionizations from the metal *d* orbitals of the two metal fragments will be smallest. This is evident from the UP spectra in Fig. 5, which show, in addition to a small band **A** at 7.15 eV, a complex band centred at ca. 8.6 eV indicated by **B** and **C**. Ionizations from the *d* orbitals of Mn and Re will now coincide and no detailed assignment can be made. It is clear, however, from the intensity ratio changes on going to He(II) excitation and by adapting the MO diagram on Fig. 7 to the corresponding fragments that band **B** has mainly Mn and band **C** mainly Re character.

For this complex the ionizations from the $a'(\sigma_b$: Mn–Re) metal–metal orbital are now observed as a separate band (**A**) at 7.15 eV [31]. This IE is the same as measured for a′ (σ_b: Re–Mn), but larger by 0.15 eV (≡ 3 kcal/mole) than for the corresponding orbital a' (σ_b: Mn–Mn). This means that the metal–metal bond is weaker in [(CO)$_5$Mn–Mn(CO)$_3$(i-Pr-DAB)] than in the mixed Mn and Re complexes.

Ionizations from the n_+ orbital are again obscured by band **C** and only observed as a shoulder at the high energy side of this band. Ionizations from $\pi_2(-)$ and n_- of R-DAB are again observed at 10.94 eV.

M, M′ = Re

The last member of the series is [(CO)$_5$Re–Re(CO)$_3$(i-Pr-DAB)], which has an Re metal in both fragments. The He(I) and He(II) UP spectra are shown in Fig. 6 (a + b) and the observed vertical ionization energies are listed in Table 1.

At first glance, the general shape of the full and expanded UP spectrum looks quite different from that of the three other members of this series. In particular in the valence IE region (7–10 eV) several sharp bands (**A**–**E**) appear in the He(I) and He(II) spectra. This part of the He(I) spectrum has therefore been expanded in the second part of Fig. 6 in order to clarify the labels of the bands discussed below.

In this complex SO coupling has to be taken into account for both metal fragments. This SO coupling is also the reason why the UP spectra of [Re$_2$(CO)$_{10}$] are much more complex than those of [Mn$_2$(CO)$_{10}$] [21,23,27]. The ζ_{5d} value obtained for many other rhenium carbonyl complexes [27] is about 0.3 eV at a maximum. Bands **A**–**E** can be assigned by use of their intensity ratios in the He(I) spectrum and the intensity ratio changes on going from He(I) to He(II) excitation.

The weakest band **A** has a lowest IE of 7.03 eV, a value which is in agreement with those obtained for a' (σ_b: M–M′) for the other members of the series. The set of bands consisting of **B** and **C** can be related to **D** and **E**. Both sets of bands have

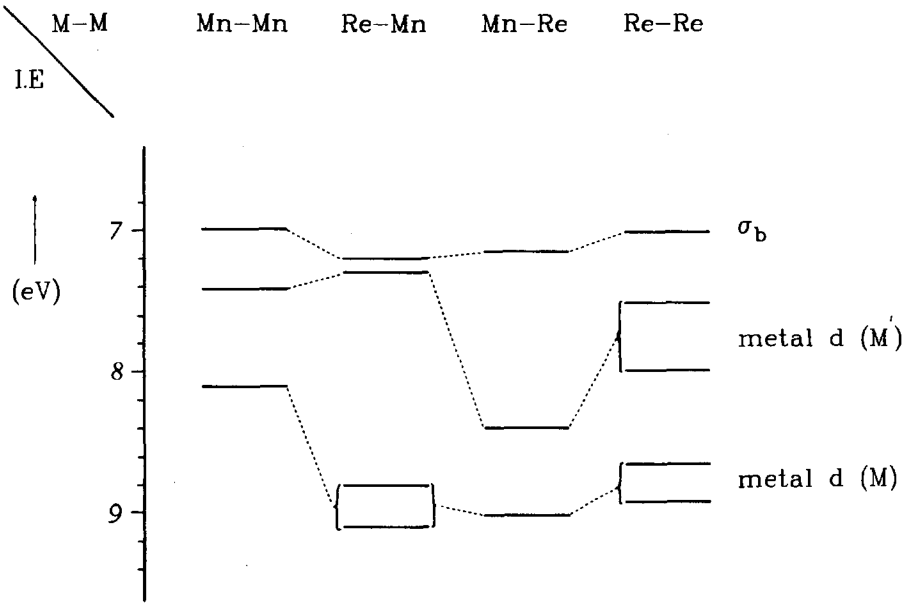


Fig. 8. Correlation diagram of the UP data of the series $[(CO)_5M\text{–}M'(CO)_3(i\text{-}Pr\text{-}DAB)]$ (M, M′ = Mn, Re).

mainly metal *d* character, as can be seen from the He(II) spectrum. Within one set the intensity ratio in the He(I) spectrum is about 1/2 (Fig. 6b). The energy separation between **B** and **C** is equal to that between **D** and **E** and is about 0.4 eV. From this it is evident that bands **B** and **D** arise from ionizations from the SO coupling components *e′* of Re′ and Re respectively (local C_{4v} symmetry). Bands **C** and **E** represent ionizations from the counterpart *e″* and b_2 (d_{xy}) orbitals of Re′ and Re respectively. There is hardly any mixing observed between the d_{xy}, d_{xz} or d_{yz} orbitals of the two fragments because of the large destabilization of the Re′ *d* orbitals by the R-DAB ligand (about 1.7 eV) [10].

Band **F** at the high energy side of **E** at ca. 9.5 eV is assigned to the n_+ orbital and band **G** to the remaining $\pi_2(-)$ and n_- orbitals of the R-DAB ligand.

Now that the UP spectra of the four metal–metal bonded complexes $[(CO)_5M\text{–}M'(CO)_3(i\text{-}Pr\text{-}DAB)]$ (M, M = Mn, Re) have been assigned, the results can be combined. This is normally done by constructing a correlation diagram, such as that in Fig. 8.

Two conclusions can be reached. First of all, the IE of the *a′* (σ_b: M–M′) orbital is lower for the homodinuclear complexes than for the mixed ones, which implies that the metal–metal bond is stronger in the latter. Secondly, in the case of M′ = Mn and M = Re the IE's of the metal *d*-orbitals of the two fragments, not involved in the metal–metal bond, are very different (1.9 eV), whereas they are nearly the same for the corresponding complex with M′ = Re and M = Mn. Such a difference in IE is closely related to the difference between both metal fragments caused by (i) electronegativity and (ii) R-DAB substitution. Both effects will influence the photochemical behaviour of these complexes. The homolytic splitting of the metal–metal bond will be influenced by its strength as reflected in the IE of *a′* (σ_b: M–M′), while the heterolytic splitting will mainly be determined by the difference in electronegativity of the two metal fragments. Both types of photochemical reactions have been observed [12] and discussed in the light of these UP results.

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9 Most 1,4-diaza-1,3-butadienes have the general formula RN=C(R')C(R")=NR and an important subgroup of this class is RN=CHCH=NR. For economy of space, if the R group is specifically stated, then the form R-substituent-DAB is used and this implies proton substitution at the α-diimine carbon atoms, e.g. i-PrN=CHCH=N-i-Pr becomes i-Pr-DAB. Abbreviation for the R group in R-DAB used is i-Pr = isopropyl.
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31 It is necessary to take account of the existence of ghosting in He(I) spectra due to He(I)-β radiation, formation of radicals, etc. This is excluded by recording UPE spectra at various sublimation rates by use of different temperatures and very low scan speeds. In this way the illustrated spectra in Fig. 5 and 6 retain the same shape. Thus, bands A are bands arising from ionizations of orbitals of the complexes (σ_b: M–M').