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NONPARAMETERIZED MO CALCULATIONS OF LIGAND-BRIDGED $M_2(CO)_8$-$(\mu_2\text{-}X)_2$-TYPE DIMERS CONTAINING METAL—METAL INTERACTIONS: EVIDENCE FOR DICTATION OF STEREOCHEMISTRY BY ONE-ELECTRON AND TWO-ELECTRON METAL—METAL σ-TYPE BONDS*

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Summary

Nonparameterized MO calculations performed on the (edge-bridged)-bioctahedral metal dimers of the Dessy-characterized $[Cr_2(CO)_8(\mu_2\text{-}PR_2)_2]^{(n-2)}$ series and of the $[Mn_2(CO)_8(\mu_2\text{-}PR_2)_2]^n$ series (n = 0, +1, +2) have revealed that the corresponding dimeric pairs with n = 0, +1, and +2 have two, one, and no electrons, respectively, in the antibonding $2b_{3u}$ MO corresponding to a "net" no-electron metal—metal bond, a "net" one-electron metal—metal bond, and a two electron metal—metal bond. Of prime significance is that this $2b_{3u}$ MO, which is the LUMO in both electron-pair (metal—metal)-bonded dimers (n = +2) and the HOMO in the corresponding dimers to which one or two electrons have been added, is found to be largely composed of in-plane antibonding σ^*-type dimetal orbital character rather than either out-of-plane π^*-type dimetal antibonding orbital character or bridging-ligand orbital character. These MO results are also shown to be completely compatible with the available spectral and X-ray data.

The stereochemical influence of strong metal—metal interactions on the molecular geometries of low-spin ligand-bridged binuclear metal cluster systems has been the subject of many studies. However, different physical measurements of such complexes containing M_2X_2-bridged systems have led (at least initially) to different conclusions about their electronic structures. For example, from their comprehensive characterization by NMR and EPR spectra of the electrochemical reduction of the (edge-bridged)-bioctahedral metal dimers, $M_2(CO)_8$-$[\mu_2\text{-}P(CH_3)_2]_2$ (M = Cr, Mo, W), Dessy and coworkers [2a] originally suggested

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for these complexes (each of which must contain an electron-pair metal—metal interaction in order to account for its diamagnetic behavior) that upon reduction to the radical anion and to the singlet-state dianion the electron(s) go into an MO comprised mainly of bridging ligand orbitals. This proposal disagrees with that previously advocated by us [3a] and others [3b-d] who have attributed the deformations in corresponding ligand-bridged bioctahedral metal dimers to the two added electrons in each dianion of the above molecules instead occupying an MO largely composed of antibonding $\sigma^\star$-type dimetal orbital character thereby resulting in a nonbonding M···M distance. A recent reinterpretation by Dessy and Bares [2b] of the spectral data on the above anions in favor of this $\sigma^\star$ dimetal orbital occupation stems in part from X-ray structural studies [4, 5] on the electronically-equivalent and structurally-resembling pseudo-bioctahedral dimers $[cis\text{-}Fe_2(h^5\text{-}C_5H_5)_2(CO)_2(\mu_2\text{-}SR)_2]^n$ ($n = 0$ [4a], + 1[4b]) and $[cis\text{-}Fe_2(h^5\text{-}C_5H_5)_2(CO)_2(\mu_2\text{-}P(C_6H_5)_2)_2]^n$ ($n = 0, +1, +2$) [5]. The much smaller Fe—Fe distance of 2.925(4) Å in the di-μ-methylmercapto monocation compared to the non-bonding value of 3.39 Å in the neutral di-μ-phenylmercapto analog together with the drastic stepwise decrease of the Fe—Fe distance by 0.36 and 0.38 Å from the nonbonding value of 3.498(4) Å in the neutral di-μ-diphenylphosphido iron parent by successive oxidation to the monocation and dication has provided convincing evidence that the electrons were removed from an MO of predominantly antibonding metal character (which was proposed to be of $\sigma^\star$ symmetry) corresponding in simple valence bond terms to a metal—metal bond order being spanned in a ligand-bridged dimer from zero, to one-half, to one.

A recent article by Mason and Mingos [6], which attempts to rationalize on a broad basis the geometries of ligand-bridged binuclear and polynuclear transition metal complexes in terms of MO symmetry arguments (arising from an extension of their qualitative bonding model applied to ligand-bridged, (so-called) electron-deficient species of main group metals), has raised a controversy concerning the specific orbital nature of the metal—metal bond. Mason and Mingos [6] proposed that the electron-pair metal—metal bonds present in various M_2X_2-bridged systems including the above bioctahedral configurations are of π- rather than σ-type symmetry. For either the phosphido-bridged dichromium (neutral) molecule or the phosphido-bridged diiron dication, their proposed π-type electron-pair metal—metal bond would arise from the particular antibonding $\pi^\star$ dimetal symmetry orbital (which is oriented out of the plane of the M_2P_2 bridging fragment) being empty (with the other bonding and corresponding antibonding dimetal orbitals filled), in contradistinction to the widely-accepted model that the antibonding $\sigma^\star$ combination is empty.

Their arbitrarily presumed MO energy-level ordering scheme prompts us to outline the results of our parameter-free MO calculations via the Fenske—Hall model [7] on the Dessy-studied $[Cr_2(CO)_8(\mu_2\text{-}PR_2)_2]^{(n-2)}$ complexes ($n = 0, +1, +2$) and on the manganese analogs, $[Mn_2(CO)_8(\mu_2\text{-}PR_2)_2]^n$ ($n = 0, +1, +2$)*

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*The unknown dimanganese cations ($n = +1, +2$) were included in the MO calculations for the sake of completeness. To simplify the calculations, the R substituents attached to the bridging phosphorus atoms were replaced by hydrogen atoms. Strong evidence that the MO energy levels and corresponding orbital character (especially those associated mainly with metallic character) are essentially invariant to whether R is C_6H_5, CH_3, or H is given by analogous MO calculations carried out [1] on the dimeric metal cluster system $[Fe_2(CO)_6(\mu_2\text{-}X)_2]^n$ (with $n = 0$ for X = NH_2, SCH_3, ½$[N_2(CH_3)_2]$, and ½$[S_2]$ and with $n = -2, -1, 0, +1, +2$ for X = PH_2)showing a close similarity in the Fe—Fe interactions (in terms of orbital character) for the above different electronically-equivalent, non-(π-acidic) bridging ligands.

which clearly support the σ-rather than the π-type of metal--metal bond when present. The distinction between these bonding models is particularly simplified for the (edge-bridged)-bioctahedral geometry because of the clear-cut separation (within the single-configuration approximation) of the σ- and π-type dimetal orbitals into different irreducible representations based on the reasonable assumption of D_{2h} molecular symmetry.

The basis functions chosen are described elsewhere [1, 8]. Only 1s to 3p atomic orbitals (corresponding to zero oxidation state) were used for phosphorus [9a]. However, inclusion of the phosphorus virtual 3d orbitals (i.e., a 3d single ζ function was used with an exponent of 1.4, a value used previously in other calculations [9b-d]) in a trial calculation on $Cr_2(CO)_8(\mu_2\text{-}PH_2)_2$ expectedly did not change the eigenvalues or wavefunctions to any appreciable extent. It should be mentioned that the calculations are invariant to the rotation of any of the local atomic coordinate systems.

The utilized molecular parameters given elsewhere [1] for $[Mn_2(CO)_8(\mu_2\text{-}PH_2)_2]^n$ and $[Cr_2(CO)_8(\mu_2\text{-}PH_2)_2]^{(n-2)}$ (where n = 0, +1, +2) were based on those determined from structurally-analogous complexes, viz., $Mn_2(CO)_8\text{-}(\mu_2\text{-}P(C_6H_5)_2)_2$ [10a], $Mn_2(h^5\text{-}C_5H_4CH_3)_2(CO)_2(\mu_2\text{-}P(C_6H_5)_2)_2$ [10b], $Cr_2(CO)_8\text{-}(\mu_2\text{-}P(C_6H_5)_2)_2$ [10a], and *trans*-$Cr_2(h^5\text{-}C_5H_5)_2(NO)_2(\mu_2\text{-}SC_6H_5)_2$ [10c]; in particular, the metal—metal distance was assumed to decrease proportionately to the values found [5] in $[cis\text{-}Fe_2(h^5\text{-}C_5H_5)_2(CO)_2(\mu_2\text{-}P(C_6H_5)_2)_2]^n$ (n = 0, +1, +2)*.

The calculated one-electron MO energy diagrams are shown in Fig. 1 with the symmetry representations (i.e., for clarity only MO levels with predominant M_2P_2 orbital character are shown) corresponding to the coordinate systems portrayed in Fig. 2. Examination of these MO diagrams reveals that for all species there are six MO's which span an energy range of about 1 - 4 eV in the vicinity of the diagonal metal 3d levels. The percent characters of these MO's show that they are primarily metallic (50 ~ 80%) in nature. In particular, they are the bonding and antibonding dimetal combinations of the $3d_{x^2-y^2}$ ($3a_g$ and $2b_{3u}$), $3d_{xz}$ ($1b_{1u}$ and $2b_{2g}$), and $3d_{yz}$ ($1b_{3g}$ and $1a_u$) orbitals which can be considered as σ-**, π-, and δ-type orbitals, respectively. Well below these "metallic" orbitals, there are in general four orbitals of symmetry representation $a_g+b_{2u}+b_{3u}+b_{1g}$ which are responsible for metal—ligand(bridge) bonding and which utilize primarily metal $3d_{z^2}$, $3d_{xy}$, and virtual 4s and 4p orbitals. It is immediately obvious that as electrons are added (Cr series) or removed (Mn series), only the antibonding $\sigma^\star$-type $2b_{3u}$ MO level is drastically affected in accord with the metal—metal interaction being of σ-type symmetry with maximum overlap in the M_2X_2

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*It should be mentioned that trial calculations of the chromium mono- and di-anions at the bonding Cr—Cr distance (identical to that of 2.92 Å utilized for the neutral species) expectedly gave rise to essentially the same orbital ordering as the neutral compound (except that all levels were destabilized due to the negative charges); in particular, the $2b_{3u}$—$3a_g$ separation in each of the anions is ca. 3 eV. The strong perturbation on the metal—metal distance arises from the injection of antibonding electrons into the highly repulsive $2b_{3u}$ orbital which inevitably leads to successive lengthening of the metal—metal distance (with the other distances relatively unaffected) thereby stabilizing this antibonding MO (i.e., relieving the repulsive interaction) and lowering the relative total energy.

** Although the bonding and antibonding combinations of the two $3d_{x^2-y^2}$ orbitals also have a δ-type component, the σ-type component will be the most important for the metal—metal bond, and hence we will refer to this orbital as being of σ-type symmetry. It is noteworthy that the bonding combination has also been classified as a "schedo-σ" or "pretty-nearly-σ" bond [11a] and as a "ξ-type" bond [11b].

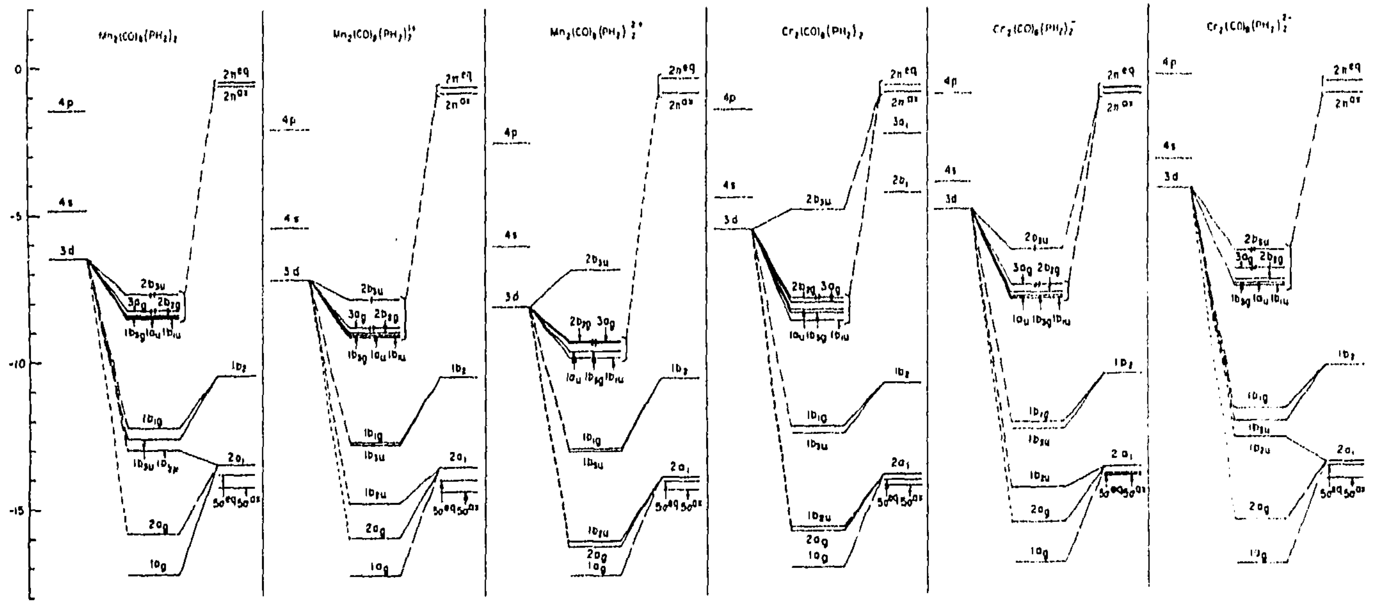

Fig. 1. Molecular orbital energy diagrams for $[Mn_2(CO)_8(\mu_2\text{-}PH_2)_2]^n$ and $[Cr_2(CO)_8(\mu_2\text{-}PH_2)_2]^{(n-2)}$ (where n = 0, +1, +2). The pairs of metal dimers with n = 0, +1, and +2 have two, one, and no electrons respectively, in the antibonding $2b_{3u}$ orbital corresponding to a "net" no-electron metal—metal bond, a "net" one-electron metal—metal σ-type bond, and a two-electron metal—metal σ-type bond, respectively.

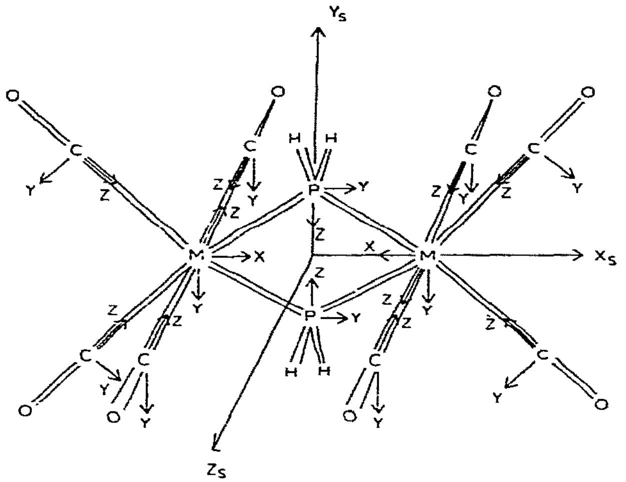

Fig. 2. The master coordinate system ($X_SY_SZ_S$) used in the orbital symmetry classification under the D_{2h} point group and the local atomic coordinate systems (xyz). The directions of the local axes not shown in this figure are each defined by a right-handed coordinate system.

plane and between the M—X bonds. More specifically, since the lowest unoccupied MO (i.e., LUMO) in the neutral molecule (n = +2) of the series $[Cr_2(CO)_8(\mu_2\text{-}PH_2)_2]^{(n-2)}$ is comprised mainly of antibonding $3d_{x^2-y^2}$ orbitals, a short Cr—Cr distance which corresponds to a single covalent bond is to be expected (in agreement with that of 2.93 Å found [10a] for $Cr_2(CO)_8[\mu_2\text{-}P(C_6H_5)_2]_2$). The addition of one or two electrons to this antibonding orbital should result in successive increases in metal—metal distance from a two-electron bonding value (n = +2) to a "net" one-electron bonding value (n = +1)* to a nonbonding value (n = 0) in harmony with the spectral observations of Dessy and co-workers [2]. Similarly, as electrons are removed from the antibonding $\sigma^\star$-type MO in the Mn series, the metal—metal distance should decrease substantially from a nonbonding value (n = 0) to a "net" one-electron bonding value (n = +1) to a two-electron bonding value (n = +2). The series $[cis\text{-}Fe_2(h^5\text{-}C_5H_5)_2(CO)_2(\mu_2\text{-}P(C_6H_5)_2)_2]^n$ (where n = 0, +1, +2), which is both electronically- and structurally-analogous to the Mn series, provides an operational test of the above predictions, i.e., in the course of oxidation, the Fe—Fe distance decreases from 3.498(4) to 3.14(2) to 2.764(4) Å.

From the calculated MO energies, it is apparent that the low-spin behavior (singlet ground state for n = 0, 2 and doublet ground state for n = 1) of these two series can primarily be attributed from an energetic viewpoint to strong metal—metal interactions rather than weak spin—spin exchange and/or superexchange coupling.

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[*] The utilized description [4b, 5] of a "net" one-electron metal—metal σ-type bond arises from the proposed bonding model (based upon structural data and theoretically substantiated here) that the $[Fe_2(h^5\text{-}C_5H_5)_2(CO)_2(\mu_2\text{-}X)_2]^+$ monocations (X = SR, PR_2) may be simply regarded [4b, 5] as possessing two electrons in a bonding dimetal σ-like orbital combination and one electron in the corresponding antibonding combination, formally analogous to the "net" one-electron bond described for the helium molecule ion, He_2^+, in its ground-state electronic configuration represented as $(\sigma_{1s})^2(\sigma_{1s}^\star)^1$.

Several correlations between calculated orbital-character occupancies and physical observables can be made. To a first approximation, one can relate the percent character of the half-filled molecular orbital of a radical anion or cation to the spin density indicated by the EPR hyperfine splitting due to each nucleus. The calculated $2b_{3u}$ MO for the $[Cr_2(CO)_8(\mu_2\text{-}PH_2)_2]^-$ monoanion ($n = +1$) is comprised of a total of 64.0% $3d_{x^2-y^2}$ and 2.6% $3d_{z^2}$ for the two Cr atoms*, 22% of equatorial carbonyl $2\pi_y$ for the eight terminal carbonyl groups, and 3.0% of bridging phosphido $1b_2$ character for the two bridging phosphorus ligands in fair agreement** with the small hyperfine splitting observed [2] in the EPR spectrum of the $[Cr_2(CO)_8(\mu_2\text{-}P(CH_3)_2)_2]^-$ anion which shows a 1/2/1 triplet with a hyperfine coupling constant of 13.0 G due to two equivalent phosphorus nuclei with each member of the triplet being further split into a 13-fold multiplet with a hyperfine coupling constant of 1.2 G due to 12 equivalent methyl protons.

The carbonyl stretching force constants (obtained from the Cotton—Kraihanzel model) can be correlated with the changes in carbonyl 5σ and 2π occupancies.*** A comparison of the axial vs. equatorial carbonyl orbital occupancies shows a pronounced *trans*-influence due to the relatively poorer π-backbonding ability of the bridging phosphido groups in comparison to that of the carbonyl ligands. This is reflected in the larger 2π but smaller 5σ occupancies for the equatorial carbonyls. More intriguingly, as electron(s) are added to the highly metallic LUMO in $Cr_2(CO)_8(\mu_2\text{-}PH_2)_2$, the Cr $3d$ orbitals are destabilized (Fig. 1) such that they become closer to the carbonyl 2π orbitals and further away from the carbonyl 5σ orbitals. This leads to a steady increase in both the carbonyl 2π and 5σ populations which result in large decreases in the carbonyl force constants. In addition, since the electrons are injected into the in-plane $3d_{x^2-y^2}$ orbitals, the increase (through direct π backdonation) in equatorial carbonyl 2π orbital populations is larger than the increase (through indirect π backdonation) in axial carbonyl 2π orbital populations; it follows that the decrease in equatorial carbonyl k's should be larger than in the axial carbonyl k's. This prediction is completely compatible with the experimental data of Dessy et al. [2] that the decrease in k^{eq} is larger than that of k^{ax} in going from the neutral species to the dianion (viz., $\Delta k^{eq} = 2.44$ mdyn/Å vs $\Delta k^{ax} = 1.55$ mdyn/Å) [2].

Finally, it should be pointed out that despite the addition or removal of the electrons during a redox reaction from a highly metallic orbital, the overall

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*The corresponding total percent orbital character in the $2b_{3u}$ MO is 60.2% Cr $3d_{x^2-y^2}$ and 4.8% Cr $3d_{z^2}$ for the neutral chromium dimer ($n = +2$) and 63.6% $3d_{x^2-y^2}$ and 0.6% Cr $3d_{z^2}$ for the chromium dianion ($n = 0$). A conversion to the standard diatomic coordinate system (obtained by an interchange of the local x and z coordinate systems on the two metal atoms) gave the following total percent metal orbital character for the three chromium dimers: 61.0% $3d_{z^2}$ and 4.0% $3d_{x^2-y^2}$ for the neutral molecule ($n = +2$); 60.0% $3d_{z^2}$ and 7.0% $3d_{x^2-y^2}$ for the monoanion ($n = +1$); and 53.2% $3d_{z^2}$ and 11.2% $3d_{x^2-y^2}$ for the dianion ($n = +2$). These proportions of metal d_{z^2} to $d_{x^2-y^2}$ orbital character in the $2b_{3u}$ MO for the three chromium dimers also hold in the counterpart $3a_g$ MO which largely contains the in-plane bonding σ-type dimetal orbital character.

**Note that the $2b_{3u}$ orbital in the series $[Cr_2(CO)_8(\mu_2\text{-}PH_2)_2]^{(2-n)}$ cannot acquire hydrogen character under D_{2h} symmetry; however, the substitution of methyl groups in place of hydrogens will breakdown the D_{2h} constraint regarding substituent character for this orbital. This effect together with the inclusion of phosphorus $3d$ orbitals in the calculations will increase to some extent the bridging phosphido ligand $1b_2$ participation in the $2b_{3u}$ orbital of the $[Cr_2(CO)_8(\mu_2\text{-}P(CH_3)_2)_2]^{(2-n)}$ complexes which would improve the agreement with the EPR results.

***The carbonyl 5σ electron-pair donor orbital and carbonyl 2π (or π^*) acceptor orbital are the highest occupied and lowest unoccupied MO's, respectively, of the free carbon monoxide ligand [8].

charge on the metal atoms remains essentially unchanged. This is primarily a consequence of the carbonyl ligands being excellent electrons reservoirs which can absorb excessive negative charge (on reduction) or donate charge (on oxidation) via the method discussed in the preceding paragraph. This phenomenon also presumably occurs in the series $[cis\text{-}Fe_2(h^5\text{-}C_5H_5)_2(CO)_2(\mu_2\text{-}P(C_6H_5)_2)_2]^n$ ($n = 0, +1, +2$) where only a small variation in the iron Mössbauer isomer shift has been observed [12].

A qualitative rationale for the calculated energy ordering of the "metallic" levels may be developed from an examination of the strong π-backbonding interactions between each metal atom and its four carbonyl ligands. The $3d_{xz}$ and $3d_{yz}$ metal AO's each interact with three carbonyl 2π orbitals, while the $3d_{x^2-y^2}$ metal AO interacts with only two. Thus, the MO's containing mainly $3d_{xz}$ and $3d_{yz}$ metal AO's (viz., the $1b_{1u}$, $2b_{2g}$, $1b_{3g}$, and $1a_u$) will be stabilized to a greater extent by the 2π carbonyl orbitals than those containing the $3d_{x^2-y^2}$ (viz., the $3a_g$ and $2b_{3u}$). The $3d_{z^2}$ and $3d_{xy}$ metal AO's are σ-bonding with respect to the terminal carbonyls and bridging ligands, respectively, and therefore the antibonding metal—ligand MO's lie much higher in energy than the above-mentioned π-bonding metal—ligand orbitals. On the basis that these symmetry arguments dominate the resulting energetics, the π-bonding metal—ligand MO of highest energy, which is involved in the oxidation (or reduction) of these (edge-bridged)-bioctahedral species, will be the $2b_{3u}$ MO possessing the antibonding σ^*-type combination of the $3d_{x^2-y^2}$ metal AO's. The $2b_{3u}$ MO being depressed much nearer the other "metallic" MO's as electrons are added to this orbital is primarily due to the large increase in the metal—metal distance greatly reducing the antibonding σ^*-type dimetal interaction.

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