# A model for two-electron mixed valence in metal–metal bonded dirhodium compounds†

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**We propose that two-electron mixed valency in bimetallic complexes possessing three bridging ligands results from a second-order Jahn–Teller instability of the redox-symmetric state.**

Two-electron mixed valence in discrete molecules is uncommon, and much remains to be learned of its consequences for ground-state reactions and photochemistry. The most extensively characterised molecular two-electron mixed valence species thus far are the bridged $Au_2$(I,III) complexes of Fackler[1] and Grohmann and Schmidbauer,[2] and the phosphazane-bridged dirhodium and di-iridium species developed primarily in this laboratory.[3–6] The realisation of catalytic $H_2$ photoproduction from protic solutions, mediated by a $Rh_2$(0,II) complex,[7] illustrates that two-electron mixed valence bimetallics can enable significant transformations. Here, we propose a model that ascribes two-electron mixed valence in these rhodium complexes to a second-order Jahn–Teller effect, and we consider the model's implications for analogous compounds of other transition elements.

We have reported syntheses and crystal structures of homologous $Rh_2$(0,0) (**1**), $Rh_2$(0,II) (**2**), and $Rh_2$(II,II) (**3**) compounds, all triply bridged by the phosphazane ligand $F_2PN(Me)PF_2$ (dfpma).[3–6] Fig. 1a depicts, in skeletal form, the primary coordination spheres about rhodium. In all instances, the Rh–Rh bond is preserved. Redox asymmetric structure **2** is believed to be the thermodynamically favored isomeric form. Unlike most binuclear rhodium and iridium phosphine complexes,[8] no homovalent $Rh_2$(I,I) dinuclear complex has been obtained from **2** or any analogous two-electron mixed valence species.

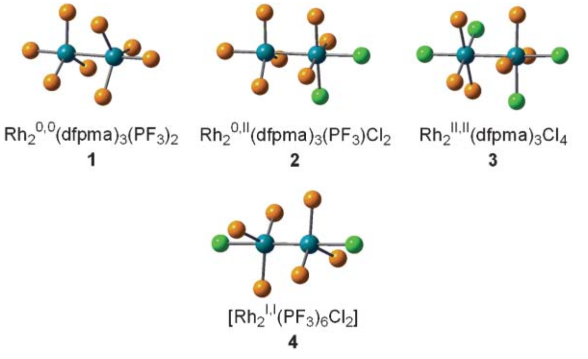

**Fig. 1** Primary coordination spheres of dirhodium compounds **1–3**, as determined crystallographically. Ball-and-stick model of hypothetical complex **4** ($D_{3d}$). Legend: dark blue, Rh; orange, P; green, Cl.

The quasi-trigonal symmetry of the $Rh_2$(0,0) complex **1** suggests an inroad to the redox asymmetry of **2**. Fig. 1 depicts a hypothetical, $D_{3d}$-symmetric entity $[Rh_2^{I,I}(PF_3)_6Cl_2]$, **4**. This structure is analogous to that proposed for $Rh_2(PF_3)_8$,[9] except that chlorides bind coaxially with the metal–metal bond. We sought to understand the electronic origins, if any, of the redox asymmetry in **2** by performing detailed electronic structure calculations of **4**.‡

An extended Hückel molecular-orbital energy-level diagram for **4** appears in Fig. 2. The singly occupied $e_g$-HOMOs are predominantly (44% by Mulliken population analysis[10]) rhodium d-orbitals, of mixed π/δ ($d_{xz}$,$d_{yz}$/$d_{x^2-y^2}$,$d_{xy}$) character. The $e_u$-second HOMOs are also have mixed π/δ parentage. The Rh–Rh σ($d_{z^2}$)-bonding orbital ($10a_{1g}$) lies lower in energy, and bears significant σ-antibonding character toward the axial chlorines.

Spin-unrestricted density-functional calculations, using relativistic effective core potentials,[11] support this picture. Fig. 3 depicts the Kohn–Sham orbital energy-level diagram so calculated for **4** (orbital images are included in ESI, Fig. S1). In the DFT calculations, the lowest unoccupied β-spin orbitals transform as $E_g$, and the extended Hückel calculation concurs with this finding. The DFT calculation predicts a set of $e_g$ spin-β HOMOs, and the $e_u$ orbitals that had been the second HOMOs (and formal spin-β HOMOs) in the extended Hückel model are now the β-second HOMOs. The DFT-calculated energy gap between the highest-occupied and lowest unoccupied spin-β orbitals is 0.48 eV.

Both spin-unrestricted DFT and the extended Hückel approximation predict **4** to be a spin-triplet ground state, which suffers a

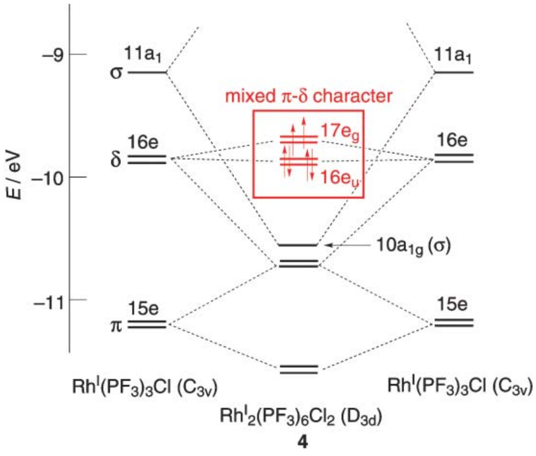

**Fig. 2** Extended Hückel orbital correlation diagram for **4**.

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† Electronic supplementary information (ESI) available: Computational details and Cartesian coordinates of optimised geometries. See http://www.rsc.org/suppdata/cc/b4/b410003d/

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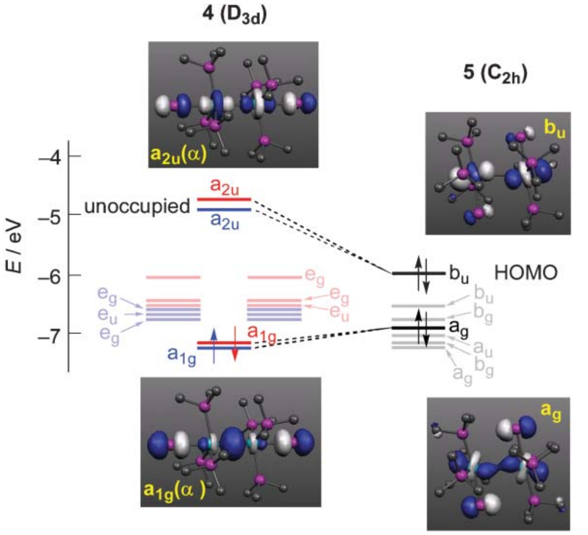

**Fig. 3** Orbital energy-level diagram for model complex **5** ($C_{2h}$). A partial orbital correlation with **4** is indicated. For compound **4**, blue indicates spin-$\alpha$, red, spin-$\beta$. Images of the Rh–Rh $\sigma$-bonding and antibonding orbitals for **4** and **5** are inset.

second-order Jahn–Teller instability.[12–14] Second-order instabilities of this type are potentially more destabilising than first-order Jahn–Teller instabilities, and the resulting deformations can exceed those of first-order or pseudo-Jahn–Teller effects. The DFT calculation predicts that the minority-spin HOMO and LUMO accidentally share the same irreducible representation $E_g$. They continue to do so if the complex degrades to any lower symmetry. The resulting states (in $D_{3d}$) intermix through configuration interaction, and this mixing persists upon distortion. The DFT calculation further predicts the $e_u$ spin-$\beta$ second HOMOs to be nearly degenerate with the $\beta$-HOMOs. If the complex distorts to a non-centrosymmetric geometry, this $e_u$ orbital can also intermix with the $\beta$-LUMOs, and augment the distortion. The result is that the $D_{3d}$ geometry of **4** is severely destabilised. Spin-unrestricted geometry optimisations indicate that $D_{3d}$-**4** is some 260 kJ mol$^{-1}$ less stable, in terms of electronic energy, than are two noninteracting, singlet $Rh(PF_3)_3Cl$ complexes.

It is generally difficult to predict the form that a stabilizing Jahn–Teller distortion will take, the moreso in large molecules with many vibrational modes. Figs. 2 and 3 show that the frontier orbitals of **4** differ in parity. Experimentally, compound **2** adopts a $C_s$-local symmetry that abolishes the inversion center and enables occupied and virtual spin orbitals near the frontier to mix configurationally. By breaking left–right symmetry, the stabilizing mixing is enhanced. The final distortion is such that the metal centers recognizably differ in oxidation state. Along these lines, there is no evidence that any such rhodium compound ever accesses a threefold-symmetric, homovalent geometry before distorting. Rather, we propose that a trigonally symmetric ground state is avoided, and that the two-electron mixed valence of **2** and related compounds results from this avoidance.

Redox-symmetric, dinuclear rhodium(I) species are known; the bis(diphenylphosphino)methane- and bis(diphenylarsino)methane-bridged dimers of Mague and Mitchener are entirely representative.[15] These compounds are dimers of square-planar rhodium(I) ions, not having a direct metal-to-metal bond; they are held together by bridging ligands. They also lack the trigonal disposition of ligands in **1** and **4**. The model complex **4** contains both a Rh–Rh single bond and axial ligands *trans* to it. The question follows whether these axial ligands promote metal–metal bonding.

Fig. 2 depicts a DFT-calculated one-electron orbital energy level diagram for the model compound $[Rh^{I}Cl(PF_3)_3]_2$ **5**, which is isomeric with **4** and has $C_{2h}$ symmetry. Compound **5** lacks terminal ligands coaxial with the Rh···Rh vector. A Rh···Rh distance of 3.12 Å has been assumed; this value lies in a metal–metal nonbonding range, and is representative of bridged $Rh_2$(I,I) dimers. A partial correlation with the orbital eigenvalues of **4** is indicated. The metal–metal bonding combination remains filled, and antibonding combination is stabilised, with that the $Rh_2$ $\sigma^*$-orbital becoming occupied. The direct metal–metal bond disappears as a consequence.

The model herein suggests new possibilities for synthesising two-electron mixed valent complexes. Figs. 3 and S1 indicate that CI between minority-spin HOMOs and LUMOs destabilises **4**. The same instability recurs for dimetal cores that are two-electrons (CI between spin-$\alpha$ and spin-$\beta$ frontier orbitals) and four electrons (CI between spin-$\beta$ orbitals) more oxidised. That is, potentially threefold-symmetric $d^7$–$d^7$ and $d^6$–$d^6$ dinuclear centres having bridging ligands may adopt two-electron mixed valence ground states to relieve instabilities brought by degeneracy. This prediction encompasses the $Rh_2$(I,III) entities characterised several years ago in this[3,5] and other laboratories.[16] Other plausible, mixed-valent cores include $Ir^{I}$–$Ir^{III}$,[4,6,17] $Pt^{II}$–$Pt^{IV}$; $Ru^{I}$–$Ru^{III}$, $Os^{I}$–$Os^{III}$, $Tc^{0}$–$Tc^{II}$, and $Re^{0}$–$Re^{II}$, among others. Second- and third-row transition elements may be advantageous for pursuing two-electron mixed valence, because of their substitutional inertness relative to first-row ions.[18,19] We note also that the more oxidised systems have fewer antibonding electrons, so the tendency toward intermetal bonding is enhanced.[20] We are not aware of metal–metal bonded two-electron mixed valence bimetallics for all of these metals, but the foregoing model suggests them to be credible synthesis targets.

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## Notes and references

‡ 1 eV = 96.48 kJ mol$^{-1}$. Abbreviations: CI, configuration interaction; DFT, density-functional theory; HOMO, highest-occupied molecular orbital or highest-occupied Kohn–Sham orbital; LUMO, lowest-occupied molecular orbital or lowest-occupied Kohn–Sham orbital.

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