

Supporting Information for

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

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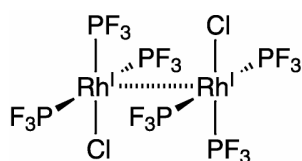
Computational Details. Calculations were performed within the Gaussian 98 Program suite.¹ DFT computations employed the exchange functional of Becke² and the correlation functional of Perdew.³ The default “extrafine” grid was used throughout. Self-consistent field convergence was achieved with direct methods. Equilibrium geometries were optimized or partially optimized in redundant internal coordinates.⁴ Relativistic effective core potentials were used for rhodium along with the standard Hay-Wadt double- ζ basis set,⁵⁻⁷ augmented by the optimized Rh 6p-function of Couty and Hall.⁸ The 6-31G(d,p) basis of Pople and co-workers^{9,10} was applied to all other atoms. Tight self-consistent field convergence criteria were maintained throughout. Reported energies and relative energies are electronic energies, and are not corrected for zero-point vibrational energies, since we deliberately consider structures that are not minima on the relevant potential energy hypersurface. Stability tests found all converged self-consistent fields to be stable to internal and external perturbations. Canonical Kohn-Sham orbitals were imaged with the program Molekel; default isodensity values were applied.¹¹ Extended Hückel calculations were carried out with the program Cacao, using default parameters.¹²

Model complex **4** was optimized within D_{3d} -symmetry. Being Jahn-Teller unstable, **4** is not expected to be a potential-energy minimum, and a harmonic frequency calculation indicates it is not, with seven imaginary frequencies corresponding to PF_3 librations or rotations.

The geometry of the singlet, square-planar complex $Rh(PF_3)_3Cl$ was first optimized with spin-unrestricted methods, and a harmonic frequency calculation indicated the converged structure to be a minimum. The structure was then re-optimized in a spin-unrestricted calculation; the optimizer converged on the first cycle. A spin-unrestricted frequency calculation was not attempted. The energy difference (260 kJ mol^{-1}) reported for $Rh(PF_3)_3Cl$ and **4** is the difference in calculated electronic energies; this difference more directly reflects the Jahn-Teller destabilization of **4**. As such, it has not been “corrected” for entropy or zero-point energy, and we therefore report this relative energy to two significant figures.

The geometry of model compound **5** was optimized in a spin-restricted fashion, with singlet multiplicity, and then re-optimized with a spin-unrestricted calculation. The Rh–Rh

distance was constrained to be 3.12 Å; consequently, neither optimized structure is an energy-minimum. Orbital eigenvalues depicted in Figure 3 are those of the spin-unrestricted calculation, to enable comparison to the eigenvalues of **4**. Because **5** is a spin-singlet, spin- α and spin- β eigenvalues are equal (the density does not break symmetry), and no distinction between spins is made in Figure 3.



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Table S1. Optimized Cartesian coordinates for triplet 4

<i>Atom</i>	<i>x</i>	<i>y</i>	<i>z</i>
Rh	0	0	1.2736521716
P	0	2.308275851	1.6859798662
F	0	2.8406714162	3.1804150726
F	-1.2206762546	3.1958324392	1.1603733671
F	1.2206762546	3.1958324392	1.1603733671
P	-1.9990255259	-1.1541379255	1.6859798662
F	-3.3780102059	-0.5407795733	1.1603733671
F	-2.1573339513	-2.6550528659	1.1603733671
F	-2.4600936102	-1.4203357081	3.1804150726
P	1.9990255259	-1.1541379255	1.6859798662
F	3.3780102059	-0.5407795733	1.1603733671
F	2.4600936102	-1.4203357081	3.1804150726
F	2.1573339513	-2.6550528659	1.1603733671
Cl	0	0	3.819471592
Rh	0	0	-1.2736521716
P	0	-2.308275851	-1.6859798662
F	0	-2.8406714162	-3.1804150726
F	1.2206762546	-3.1958324392	-1.1603733671
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F	2.1573339513	2.6550528659	-1.1603733671
F	3.3780102059	0.5407795733	-1.1603733671
F	2.4600936102	1.4203357081	-3.1804150726
Cl	0	0	-3.819471592

Table S2. Optimized Cartesian coordinates for singlet **5**

<i>Atom</i>	<i>x</i>	<i>y</i>	<i>z</i>
Rh	-0.475460963	0.	1.4790299493
Cl	1.8715238841	0.	1.9559552266
P	-0.3233308807	2.192446212	1.9799795325
P	-2.6601376565	0.	1.2667405208
P	-0.3233308807	-2.192446212	1.9799795325
Rh	0.475460963	0.	-1.4790299493
Cl	-1.8715238841	0.	-1.9559552266
P	0.3233308807	2.192446212	-1.9799795325
P	2.6601376565	0.	-1.2667405208
P	0.3233308807	-2.192446212	-1.9799795325
F	0.0574363905	2.4788656883	3.4968552537
F	-1.5778804427	3.1709255529	1.8528644729
F	0.7830382977	3.1006636991	1.2755267906
F	-3.4579682186	0.	2.6550121885
F	-3.412904211	-1.2249401342	0.5913786882
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F	0.0574363905	-2.4788656883	3.4968552537
F	0.7830382977	-3.1006636991	1.2755267906
F	-1.5778804427	-3.1709255529	1.8528644729
F	-0.0574363905	2.4788656883	-3.4968552537
F	1.5778804427	3.1709255529	-1.8528644729
F	-0.7830382977	3.1006636991	-1.2755267906
F	3.4579682186	0.	-2.6550121885
F	3.412904211	-1.2249401342	-0.5913786882
F	3.412904211	1.2249401342	-0.5913786882
F	-0.0574363905	-2.4788656883	-3.4968552537
F	-0.7830382977	-3.1006636991	-1.2755267906
F	1.5778804427	-3.1709255529	-1.8528644729

Table S3. Optimized Cartesian coordinates for square-planar, singlet Rh(PF₃)₃Cl

<i>Atom</i>	<i>x</i>	<i>y</i>	<i>z</i>
Rh	0.2369880467	0.	0.0672618637
Cl	2.4850540903	0.	0.8523070267
P	0.4325951238	2.2466006649	0.2194843461
P	-1.7722741247	0.	-0.747225381
P	0.4325951238	-2.2466006649	0.2194843461
F	0.8291363717	2.820044808	1.6443771589
F	-0.8113009492	3.1964662279	-0.0916215665
F	1.5255624608	2.9602843929	-0.6841336282
F	-3.0482637005	0.	0.2154801521
F	-2.2028284486	-1.2128105824	-1.6925927618
F	-2.2028284486	1.2128105824	-1.6925927618
F	0.8291363717	-2.820044808	1.6443771589
F	1.5255624608	-2.9602843929	-0.6841336282
F	-0.8113009492	-3.1964662279	-0.0916215665

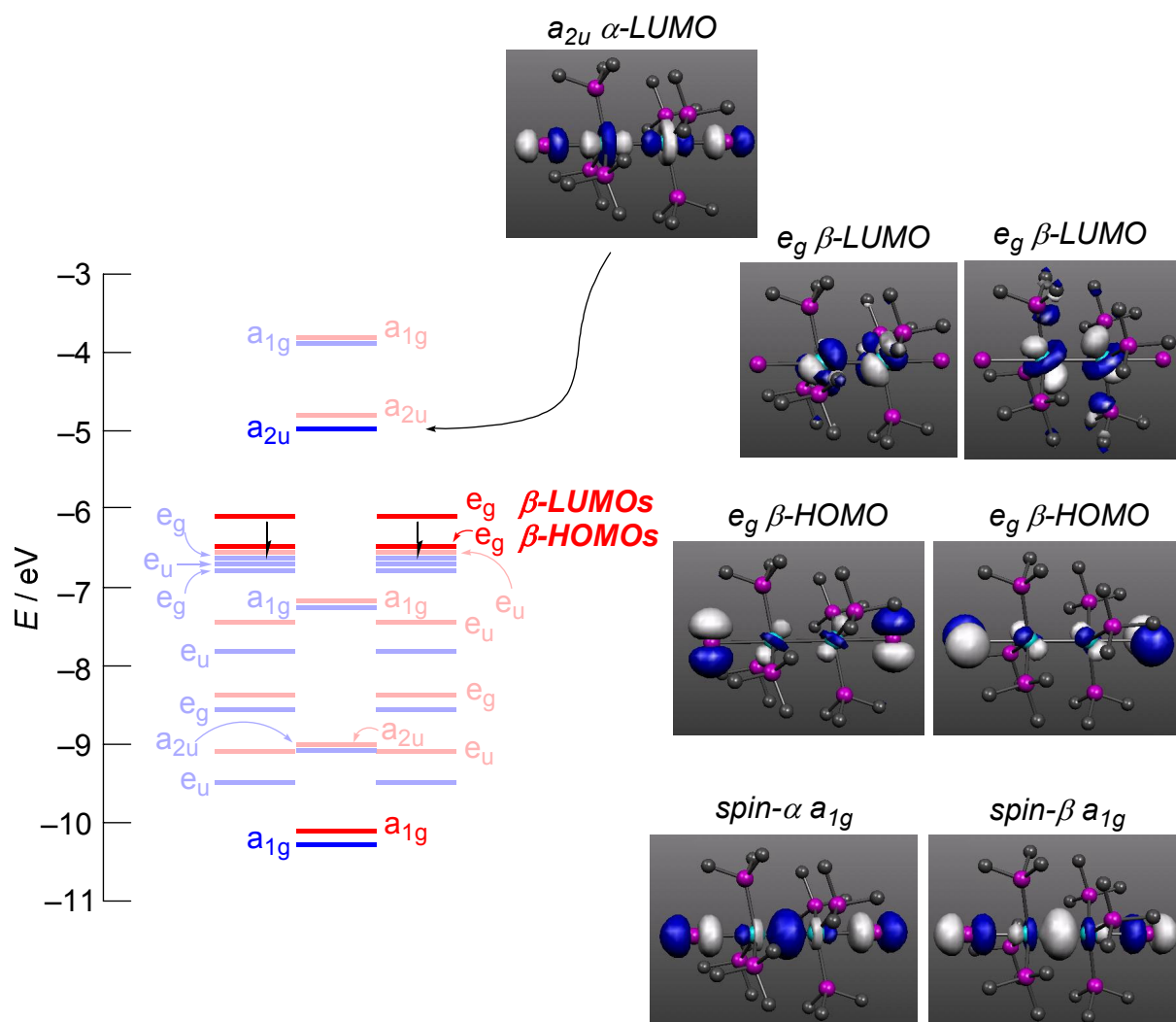


Figure S1. Kohn-Sham orbital energies of 4. Images of selected orbitals are inset. Blue indicates spin- α ; red, spin- β .