On the Nature of the Lowest Triplet Excited State of the [Rh$_2$(1,3-diisocyanopropane)$_4$]$^{2+}$ Ion

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The nature of the ground state and the lowest triplet excited state of the [Rh$_2$(1,3-diisocyanopropane)$_4$]$^{2+}$ ion have been investigated by the density functional theory. Two locally stable geometrical conformations are found on the potential energy surfaces of both the ground and excited states, corresponding to the eclipsed and twisted conformations, the eclipsed conformation being more stable and having the shorter Rh−Rh bond length. While the Rh−Rh distances of the two conformations differ by ~0.4 Å, they shorten to the same value upon excitation (~3.1 Å). The excited state originates from the d$_z^2$ (metal antibonding) to p$_z$ (ligand−metal bonding) electronic transition. The Mayer Rh−Rh bond order increases from ~0.2 to more than 0.8 upon excitation, while the Rh−C$_\text{aryl}$ bond order shows a slight decrease. A topological bond path between the Rh atoms is found in both the ground and excited states, while the electron localization function (ELF) indicates weak Rh−Rh covalent bonding for the excited state only.

Introduction

As part of our program of excited-state structure determination by time-resolved photocystallography, 1 we are performing theoretical calculations on isolated complexes to gain insight into the effect of the crystal matrix on geometry changes occurring during photoexcitation. We report here on a member of a series of d$_8$−d$_8$ binuclear complexes that show significant metal−metal bond shortening on excitation.

[Rh$_2$(I)(bridge)$_4$]$^{2+}$, bridge = 1,3-diisocyanopropane (further in the text abbreviated as [Rh$_2$(diprop)$_4$]$^{2+}$), has a paddle-wheel structure. The [Rh$_2$(diprop)$_4$]$^{2+}$ complex was first synthesized in 1976 by Gray et al., 2 who also reported on its excited-state reactivity.3 The 546-nm irradiation of [Rh$_2$(diprop)$_4$]$^{2+}$ in aqueous solutions of hydrohalic acids (HX) results in production of H$_2$ and formation of a d$_7$−d$_7$ [Rh$_2$(diprop)$_4$X$_2$]$^{2+}$ species. Since such binuclear complexes have relatively long phosphorescence lifetimes, they were among the first to be considered as candidates for solar energy conversion devices.3−5

Spectroscopic Properties

The polarized UV−vis absorption spectrum of a single crystal of the BPh$_4^-$ salt at 5 K exhibits a strong band at 565 nm attributable to a fully allowed 1A$_1$ → 1A$_2$ excitation (D$_1$ point group designations). The spectrum also shows a vibronically structured band (λ$_\text{max}$ ~ 670 nm), assigned to the 1A$_1$ → E (1A$_2$) transition, consisting of a very long progression with a separation of 143 cm$^{-1}$.6 In time-resolved Raman studies of the ground and excited states, this excited-state frequency was assigned to the ν(Rh$_2^+$) stretching, increased from the ground-state value of 85 cm$^{-1}$.7 From the Franck−Condon analysis of the vibrational fine-structure of the 670-nm band, a Rh−Rh shortening on excitation of 0.31 Å was derived, corresponding to an excited-state Rh−Rh distance of 2.93 Å, using the ground-state Rh−Rh distance of 3.242(1) Å from a room-temperature

**References**


The shortening that occurs on excitation of the d8
* orbital to a weakly bonding p
* orbital, similar to the correlation functional of Lee, Yang, and Parr (LYP). 17 The atomic orbitals of rhodium were described by a triple-
* Slater-type basis set (ADF database TZP, formerly IV). For the carbon,
nitrogen, and hydrogen atoms double-ζ Slater-type basis sets with one polarization function added (ADF database DZP, formerly III) were used. The (1s2s2p3s3p3d)28 core shell of Rh and the (1s) 2 core shells of C and N were treated in the frozen core (FC) approximation. Scalar relativistic effects were taken into account with the zeroth order regular approximation (ZORA). The integrals were evaluated numerically with an accuracy of 8 significant digits.

A set of auxiliary s, p, d, f, and g functions, centered on all nuclei, was used to fit the electron density, together with both Coulomb and exchange potentials in each SCF cycle. Geometry conversion was considered complete when the Cartesian gradients fell below the threshold of 10^{-4} Hartree/Å (compared to a 10^{-2} default value).

All optimized molecular geometries were confirmed as true energy minima by the positive eigenvalues in the Hessian matrices, from which IR frequencies were calculated. Time-dependent density functional theory (TD-DFT) calculations of vertical excitation energies were carried out with the same functionals and basis sets used in the geometry optimization. The Davidson algorithm was used, in which the error tolerances in the square of the excitation energies and trial-vector orthonormality criterion were set to 10^{-8} and 10^{-10}, respectively. The molecular orbitals were visualized with MOLDEN. The ADF output was converted to MOLDEN format using ADF2MOLDEN program. Deformation density maps were calculated with the ADF auxiliary program DENSF and converted to GNUPLOT format by the ADF auxiliary program CNTRS. The electron localization function (ELF) was calculated using the program written by J. Autschbach and T. Ziegler and implemented in the ADF auxiliary program DENSF. ELF and spin-density 3D-representations were prepared in MOLEKEL. Mayer bond orders were calculated with the program MAYER.

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Figure 2. 3D view of the eclipsed geometry corresponding to the global minimum on the ground-state PES of the [Rh2(diprop)4]^{2+} looking down the z-axis (a) and along the z-axis (b).

Figure 3. 3D view of the twisted geometry corresponding to the local minimum on the ground-state PES of the [Rh2(diprop)4]^{2+} looking down the z-axis (a) and along the z-axis (b).
Table 1. Selected Theoretical Bond Lengths (in Å) and Angles (in deg) of the Ground State in Comparison with the Experimental Structure, and Excited Triplet State of the [Rh2(diprop)4][BPh4]2+ Ion

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<tr>
<td></td>
<td>eclipsed</td>
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<tr>
<td></td>
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<tr>
<td>Rh–Rh</td>
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<td>Rh–CN</td>
<td>1.959(4), 1.960(4), 1.976(4), 1.960(4)</td>
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<td>C27–C23</td>
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<td>1.357(9)</td>
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<td>1.402(10), 1.429(8)</td>
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Table 2. Magnitude of the Rh–Rh and Rh–C12 Bond (in Å) Changes upon Singlet–Triplet Excitation in the [Rh2(diprop)4][BPh4]2+

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<th></th>
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<td></td>
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- Reference 6b. Franck–Condon value from polarized single-crystal absorption spectroscopy at 5 K, [Rh2(diprop)4][BPh4]2+CH3CN. b Reference 7. Empirical result from time-resolved resonance Raman spectrum in CH3CN solution.

Table 3. Selected Vibrational Modes of [Rh2(diprop)4][BPh4]2+

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<td>eclipsed</td>
<td>excited</td>
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<tr>
<td>ν(Rh2)</td>
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<td>144⁺⁺⁺⁺</td>
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<tr>
<td></td>
<td>85⁺⁺⁺⁺</td>
<td>149⁺⁺⁺⁺</td>
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<tr>
<td>ν(C==N)</td>
<td>2193⁺⁺⁺⁺</td>
<td>2177⁺⁺⁺⁺</td>
</tr>
<tr>
<td></td>
<td>2150⁺⁺⁺⁺</td>
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</tr>
</tbody>
</table>

- Reference 7a, CH3CN solution. b Reference 6b, [Rh2(diprop)4][BPh4]2+ CH3CN crystal. c There are a total of eight C==N vibrational modes. d Reference 7b, CH3CN solution.

Results and Discussion

Ground-State Geometry. The ground-state potential energy surface (PES) of the [Rh2(diprop)4][BPh4]2+ ion shows two minima corresponding, respectively, to nearly eclipsed (C4v symmetry) (Figure 2) and twisted (D2h symmetry) (Figure 3) conformations, the former being more stable by ~1.0 eV (because the C4v point group is not yet supported in ADF, the lower symmetry (C2) was used to optimize the eclipsed geometry). Selected geometrical parameters for both states are given in Table 1. The calculated Rh–Rh distance in the eclipsed structure is equal to 3.44 Å with a C–N–Rh–Rh–C angle of only ~2°, but it is longer by ~0.4 Å in the twisted conformation which has a twist angle of ~27°. This difference is opposite to the trend observed in published crystal structures, in which the larger twist angles correspond to shorter Rh–Rh distances (Figure 1). The difference may be related to the short length of the propane bridge, which necessitates a distortion of the ligand on twisting. This is confirmed by the theoretically optimized geometries, which show a reduction of the N11–C19–C27–C23 torsion angle from 68.0° to 41.9° and a decrease in the C3–N11–C19 angle from 177.6° to 164.2°. The energy change due to internal rotation around the C19–C27 bond of the ligand is calculated to be 4.2 kJ/mol (Scheme 1).

The eclipsed conformation of [Rh2(diprop)4][BPh4]2+ from theory agrees reasonably well with that of the [Rh2(diprop)4][BPh4]2+ ion in crystals of [Rh2(diprop)4][BPh4]2+ CH3CN (Table 1), though the calculated Rh–Rh distance is 0.2 Å longer than the observed value. The Rh–Rh potential is obviously very shallow as evidenced by the value of the stretching frequency, which is only 71 cm⁻¹ according to the calculation and 79 cm⁻¹ according to the experiment (Table 3). With the corresponding harmonic force constant, a lengthening of the Rh–Rh distance to 4.2 Å would only require 0.010 H, or 0.27 eV, a value considerably less than the calculated energy difference between the eclipsed and twisted conformations of the [Rh2(diprop)4]+ ion.

Attempts to optimize the twisted structure with Rh–Rh distances shorter than those in the eclipsed conformation were unsuccessful as the structure invariably returned to the geometry with the longer Rh–Rh distance.

There are no significant differences in other bond lengths or angles between the eclipsed and twisted conformations.

Excited-State Geometry. Selected structural parameters, as obtained by the optimization of the lowest-energy triplet excited state, are presented in Table 1. As in the ground state, both eclipsed (E^eclip) and twisted (E^twist) conformations are found to correspond to minima on the excited-state potential energy surface, the eclipsed conformation, ES^eclip, being more stable by 0.041 H, compared with 0.037 H for the ground state, GS^eclip. However, in contrast to the ground state, in the excited state the Rh–Rh distances of the two conformations differ by only 0.04 Å.
The calculations predict a Rh–Rh shortening for the eclipsed structure of 0.39 Å in reasonable agreement with the Franck–Condon value of 0.31 Å discussed earlier. For the twisted conformation, a Rh–Rh shortening of 0.76 Å is obtained (Table 2), leading to almost equal excited-state Rh–Rh distances for the two conformations. The shortening of the Rh–Rh bond in the excited state is also reflected in the calculated stretching frequency $\nu(\text{Rh}_2)$ which increases upon excitation in agreement with experimental results (Table 3).

The molecular orbitals in the ground and excited states are rather similar (Table S1). However, the occupied orbitals ligand, a limitation mentioned in the spectroscopic derivation of the bond length change. There are in fact ten calculated vibrational modes in the 420–500 cm$^{-1}$ region all involving displacements of Rh, C$_N$, and other ligand atoms, with some of the modes showing increasing and some decreasing frequencies upon excitation.

**Molecular Orbitals.** Consistent with the interpretation of the experimental observations, the HOMO consists mainly of d$_{z^2}$ atomic orbitals of the rhodium atoms and is antibonding in the metal–metal region (Figures 4 and 5). The LUMO, on the other hand, is bonding in the Rh–C$_N$ and Rh–Rh regions. According to the calculations (Table S1), the rhodium atomic orbital contribution to the LUMO amounts to only 18% (p$_z$ Rh), while the ligand p$_z$ atomic orbitals give a much larger contribution (44% for p$_z$ C$_N$ and 24% for p$_z$ N). This is manifested in the large overlapping regions with Rh atomic orbitals evident in Figures 4 and 5.

The molecular orbitals in the ground and excited states are rather similar (Table S1). However, the occupied orbitals ligand, a limitation mentioned in the spectroscopic derivation of the bond length change. There are in fact ten calculated vibrational modes in the 420–500 cm$^{-1}$ region all involving displacements of Rh, C$_N$, and other ligand atoms, with some of the modes showing increasing and some decreasing frequencies upon excitation.
The Rh spin delocalization over the CN groups is evident (Figure 7). The unpaired spin density is mainly localized on the Rh atoms (Table S2), though some degree of population. The unpaired spin density is mainly localized on the Rh and C atoms of the CN group, increase in the Rh 2304. Inorganic Chemistry, Vol. 43, No. 7, 2004


<table>
<thead>
<tr>
<th>∆P</th>
<th>s</th>
<th>p_α</th>
<th>p_β</th>
<th>p_γ</th>
<th>d_α</th>
<th>d_β</th>
<th>d_γ</th>
<th>d_δ</th>
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<td>n  = 4^+</td>
<td>−0.002</td>
<td>0.005</td>
<td>0.005</td>
<td>0.022</td>
<td>−0.009</td>
<td>0.045</td>
<td>0.059</td>
<td>0.009</td>
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<td>n  = 5^+</td>
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<td>0.005</td>
<td>0.005</td>
<td>0.114</td>
<td>−0.009</td>
<td>0.045</td>
<td>0.059</td>
<td>0.009</td>
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</table>

^* Similar values are obtained for the twisted geometry (Table S3). ^* n, the principal quantum number. ^* See Scheme 1 for atom numbering.

Hirshfeld and Bader Charge Analyses. The values of the difference between the atomic charges in the ground and excited states, (∆q(ES−GS)), for the Hirshfeld25 and Bader26 definitions agree remarkably well for all atoms, though, as is well-known, the two types of charges themselves differ widely. Comparison of the ground- and excited-state values (Table 4) reveals that upon excitation the rhodium atoms become more positive and the adjacent carbon atoms less positive. Changes in the charges of all other atoms are insignificant.

The Mulliken population analysis of the atomic orbitals (Table 5) shows a decrease in the population of the Rh d_α and 5s orbitals upon excitation, while the p orbitals of Rh, and the C and N atoms of the CN group, increase in population. The unpaired spin density is mainly localized on the rhodium atoms (Table S2), though some degree of spin delocalization over the CN groups is evident (Figure 7). The Rh−Rh bond order as defined by Mayer27 (Table 6) increases from a very small value to close to 1 (0.83), while the Rh−CN bond order decreases slightly, in agreement with the calculated bond length changes, and similar to the results obtained previously for the [Pt2(pop)4]4− ion.10

The excitation electron-density difference map defined as ρ_{excited} − ρ_{ground} with ρ_{excited} transferred to the ground-state geometry to eliminate the effect of atomic motion, is shown in Figure 8. As may be expected, the features are most pronounced in the Rh−CN regions.

Absorption Spectrum. The electronic transition energies of [Rh2(diprop)4]2+ calculated with TD-DFT are presented in Table 7, in which D3 symmetry notation is used to identify the transitions. The lowest-energy transition corresponds to the spin-forbidden singlet−triplet (1A2) excitation from the antibonding HOMO to the bonding LUMO. The calculated values of the excitation energy for this transition are 1.39 and 1.72 eV, for the eclipsed and twisted geometries, respectively, compared to the experimental (single crystal) value of 1.85 eV.6 The strong singlet−singlet HOMO−LUMO (1A1) transition is calculated at 1.84 and 2.13 eV, respectively, for the eclipsed and twisted geometries. In the twisted geometry, this 1A2 transition blue shifts compared with the eclipsed geometry, in agreement with the difference between experimental single-crystal values for twisted [Rh2(tmb)4]([PF6]2−2CH3CN and eclipsed [Rh2(diprop)4]−(BPh4)2•CH3CN.6,8

Our TD-DFT calculations are in accord with the experimental assignment of the HOMO to LUMO+1 (1A1 and 3A1) transitions as corresponding to d_α→p_α (metal antibonding) → p_α (ligand−metal antibonding) excitedations.

Topological Analysis of the Charge Density. The results of the topological analysis of theoretical charge density of [Rh2(diprop)4]2+, obtained with the program XAIM-1.0,28 are presented in Table 8. In both the ground state and excited

Figure 7. Representation of the spin density ("spin up" density minus "spin down" density) of the triplet [Rh2(diprop)4]2+. Eclipsed geometry is shown. Twisted geometry gives similar picture. Plotted isosurface value 0.003 au.

Figure 8. Excitation difference electron density of [Rh2(diprop)4]2+. The eclipsed geometry is shown. The twisted geometry gives similar picture. Plotted isosurface value 0.003 au, gray lobes are positive (accumulation of density).
shell classification based on the sign of involving metal atoms. It must be noted that in the case of critical point has been shown to be ambiguous, as it leads to a better description can be based on other properties such as the kinetic energy density at the bond critical point (BCP), as often observed for bonds involving metal atoms. It must be noted that in the case of bonds involving metal atoms the closed-shell versus open-shell classification based on the sign of the Laplacian of charge density at the bond critical point has been shown to be ambiguous, as it leads to the conclusion that all such bonds are of closed shell character, thus excluding any covalency. A better description can be based on other properties such as the kinetic energy density $G(r_c)$, the total electron energy density $H(r_c)$, and the ratio of these quantities to $\rho(r_c)$.

At the Rh–Rh BCP of the ground state, the kinetic energy density per electron $G(r_c)/\rho(r_c)$ is smaller than unity, while $V(r_c)$ and $G(r_c)$ have essentially equal values and, thus, $H(r_c)$ is zero. In the excited state, the kinetic energy density at the BCP $G(r_c)$ increases, but the negative value of $V(r_c)$ decreases more, in agreement with the increase in the total charge density $\rho(r_c)$ at the Rh–Rh BCP, leading to a more negative value of $H(r_c)$ and $H(r_c)/\rho(r_c)$. Thus, the potential energy density $V(r_c)$ dominates at the Rh–Rh BCP in the excited state indicating an increase in the open-shell character of the Rh–Rh interaction in the excited state. These

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**Table 7.** TD-DFT Electronic Transition Energies (in eV) for [Rh$_2$(diprop)$_4$]$_2^{2+}$

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<tr>
<th>$\Gamma_{Da}$</th>
<th>GS$^{\text{trip}}$ C$_2$</th>
<th>GS$^{\text{twist}}$ Da</th>
<th>one-electron excitation</th>
<th>MO character</th>
<th>% MO</th>
<th>% MO</th>
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<td>$^1A_2$</td>
<td>1.84 (0.0912)</td>
<td>2.13 (0.0739)</td>
<td>$12a_2 \rightarrow 13a_1$</td>
<td>$d_{x^2} \rightarrow p_z$</td>
<td>99</td>
<td>99</td>
<td>2.19</td>
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<tr>
<td>$^1A_1$</td>
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<td>$d_{x^2} \rightarrow p_z$</td>
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<td>75</td>
<td>415</td>
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<tr>
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<td>3.43 (0.0012)</td>
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<td>$d_{x^2} \rightarrow p_z$</td>
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<td>$^1A_2$</td>
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<td>1.72</td>
<td>$12a_2 \rightarrow 13a_1$</td>
<td>$d_{x^2} \rightarrow p_z$</td>
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* Nonzero oscillator strengths in parentheses. Only the lowest $d_{x^2}$, $d_{x^2}^{*}$ transitions are listed. b Reference 6b, [Rh$_2$(diprop)$_4$](BPh$_4$)$_2$-CH$_3$CN, polarized single-crystal absorption spectroscopy at 5 K.

**Table 8.** Topological Properties (in au) at the Rh–Rh and Rh–C$_B$ BCPs (3, -1) of the Ground State$^a$ and the Triplet State$^b$ of the Eclipsed [Rh$_2$(diprop)$_4$]$^{2+}$

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<td>-0.33</td>
<td>+0.14</td>
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</tbody>
</table>

* First line. b Second line. $V_2 \rho_\lambda$ = Laplacian of charge density at the BCP. $\lambda_1$, $\lambda_2$, $\lambda_3$ = eigenvalues of $V_2 \rho_\lambda$ ($V_2 \rho_\lambda = \lambda_1 + \lambda_2 + \lambda_3$). $\epsilon$ = bond ellipticity. $G(r_c)$ = electronic kinetic energy density at the BCP. $V(r_c)$ = electronic potential energy density at the BCP. $H(r_c)$ = the total electronic energy density ($H(r_c) = G(r_c) + V(r_c)$).

Figure 9. The trajectories of the gradient of the charge density in the plane defined by C$_9$, C$_{10}$, and Rh2 for the ground state (a) and excited triplet state (b) of eclipsed [Rh$_2$(diprop)$_4$]$^{2+}$. The bond paths are indicated by solid lines, and the bond critical points are denoted by filled circles. The graphs were generated with a locally modified version of TOPXD (Volkov, A.; Abramov, Y.; Coppens, P.; Gatti, C. Acta Crystallogr., Sect. A 2000, 56, 332–339).
observations are in agreement with the theoretical deformation electron density maps, which show that in the excited state there is an, albeit small, concentration of charge density in the Rh–Rh BCP region (Figure 10), similar to that observed for [Pt_2(pop)_4]^{2+} ion.^{10} No changes in the topological properties at the Rh–C_N bond critical points are observed upon excitation, in agreement with the very small changes of the Rh–C_N bond lengths in the excited state (Table 8).

The only pronounced difference for the twisted (Table S4) compared to the eclipsed geometry is found for the ground-state topological properties at the Rh–Rh BCP. The ground-state value of $\eta(r) = 0.77$. The Rh–C_N bonding region shows the localization domain close to the carbon atom, a feature previously described by Silvi et al.^{30} as typical for dative bonds.

The ELF isosurface of the excited triplet state at $\eta(r) = 0.77$ does not differ from that in the ground state for both eclipsed and twisted conformations and, thus, is not presented. However, at a lower ELF value $\eta(r) = 0.24$, we observe a compact almost spherical in shape ELF domain located between the two metal atoms.^{31} The formation of this ELF domain is consistent with the increase in Mayer bond order discussed above. The magnitude of the ELF value at which the metal–metal bonding is observed and the shape of the corresponding ELF domain resemble the ELF picture of Pt–Pt bonding in the [Pt_2(pop)_4]^{4+} ion,^{10} which similarly belongs to the family of d^8–d^8 complexes with paddle-wheel geometry. As in [Pt_2(pop)_4]^{4+}, we attribute the low value of the ELF for the Rh–Rh interaction to the small contribution of metal d-orbitals to the ELF.”

**Figure 10.** Theoretical deformation density maps of the ground state (a) and excited triplet state (b) of eclipsed [Rh_2(diprop)_4]^{2+} in the plane of Rh1, Rh2, and carbon atoms. Contour levels are drawn at ±0.0015 au, and positive levels are solid lines, zero contour omitted.

**Figure 11.** Electron localization function of [Rh_2(diprop)_4]^{2+} in the eclipsed and twisted conformations on the ground-state (a, b) and excited-state (c, d) PES. In parts a and b, the plotted ELF value is 0.77; for clarity, only the ELF isosurface for the upper part of the molecule is shown. In parts c and d, the plotted ELF value is 0.24, and the localization domains of the two rhodium atoms and the Rh–Rh bonding region are colored in solid gray, while all other regions of ELF are shown in transparent yellow.

**Conclusions**

The DFT study of the [Rh_2(diprop)_4]^{2+} ion reveals two energy minima on the ground-state and first excited-state potential energy surfaces corresponding to the eclipsed and twisted conformations, the eclipsed conformation being more stable by ~1 eV in both cases. The optimized geometry at the global energy minimum of the isolated [Rh_2(diprop)_4]^{2+} ion is similar to that determined in the low-temperature X-ray single crystal study, though the Rh–Rh distance is 3.1 Å. The Rh–Rh distance in the eclipsed ground-state structure is shorter by 0.4 Å than that in the twisted conformation, in contrast to the trend observed in a series of structure determinations in which a shorter Rh–Rh bond corresponds to a larger twist angle. The difference may be attributed to the shortness of the diisocyano ligand which is distorted on twisting.

The excited-state potential energy surface similarly exhibits two minima corresponding to the eclipsed and twisted conformations. But in this case, the Rh–Rh distance is 3.1 Å in both geometries.

The results of the TD-DFT calculation of the singlet–singlet and singlet–triplet excitation energies are in reasonable agreement with the experimental observations. The lowest energy state is the singlet $^1A_2$ followed by the triplet state of interest $^3A_2$, corresponding to $d_2^2$(metal antibonding) → $p_z$(ligand–metal bonding) transition.

The existence of Rh–Rh bond paths in the ground state and excited triplet state electron densities suggests weak...

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bonding metal–metal interaction in both states. However for the ground state, this observation is not supported by the electron localization function (ELF). In contrast to the ground state, the excited-state ELF at low values exhibits a low maximum in the Rh–Rh region, indicating Rh–Rh weak covalent bonding upon excitation of the complex, in agreement with the calculated Mayer Rh–Rh bond order which increases from a very low value to close to unity on excitation.

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**Supporting Information Available:** Tables of the atomic-orbital contributions to the frontier molecular orbitals (in %) and Mulliken spin populations for both eclipsed and twisted geometries. Tables of the difference in the population of the valence atomic orbitals and topological properties at the Rh–Rh and Rh–C N BCPs for the twisted geometry. Listing of Cartesian coordinates of the four optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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