

Pyramidity Effect on Rh(II)–Rh(II) Single Bonds

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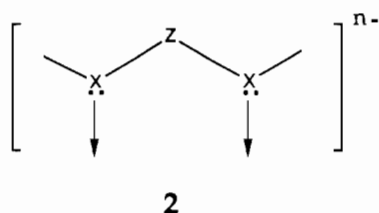
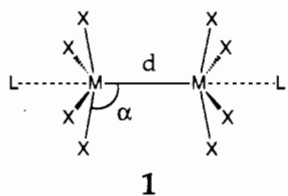
A structural database and molecular orbital study of the binuclear Rh(II) compounds of the type $Rh_2X_nL_n$ ($n = 0-2$), where X_2 may be one bridging bidentate ligand or two monodentate ligands, is presented. The structures of 139 crystallographically independent molecules from 130 compounds were analyzed in search for a structural correlation between the Rh–Rh bond distance and the Rh–Rh–X pyramidity angle, and the effect of the axial ligands on both structural parameters was studied. The largest family, of the tetrakis(chelate) compounds with N or O donor atoms (113 molecules), and the much smaller one with two carboxylato ligands and two metallated phosphines (6 molecules), both show a strong susceptibility of the Rh–Rh bond strength to pyramidalization. No clear correlation between bond distance and pyramidity angle was found for the family of complexes with two diamines and two carboxylato ligands (eight molecules). A theoretical study using extended Hückel methodology was carried out on model compounds. The effect of the chelating nature of the equatorial X ligands was analyzed, as well as the influence of axial ligands. A simple orbital model based on the hybridization of the p_z orbital of the RhX_4 moieties accounts for the pyramidity effect on the Rh–Rh bond strength.

The metal–metal bond distance in binuclear complexes of transition metals with triple and quadruple bonds has been found to depend not only on bond order and steric effects but also on other structural parameters, mainly the average pyramidity angle α .^{1,2} The correlation between the bond distance and the pyramidity angle, for a particular metal and a given type of ligands, can be summarized in eq 1, where b is the standard M–M

$$d(M-M) = b + c \cos \alpha \quad (1)$$

bond distance (i.e., for $\alpha = 90^\circ$) and c is a measure of the susceptibility of that M–M bond to pyramidalization around the metal atom. Although it has been stated that the δ metal–metal bond is not influenced by the pyramidity, it appears that both the σ and π components of the bond are affected by changes in that angle. It is therefore interesting to find out whether the compounds with single M–M bonds follow the same trend.

In this work we focus on the binuclear compounds of Rh(II) of type 1, with stoichiometry $Rh_2X_nL_n$ ($n = 0-2$), for which a



large amount of structural data is currently available and which have the added interest of their potential applications as catalysts in a number of processes or as substitutes of *cis*-platin in cancer

chemotherapy.³ First we will look for the structural correlation between the M–M bond distance and the pyramidity angle α and for the effect of the axial ligands on both parameters. Then, a theoretical (extended Hückel) study on model compounds without and with axial ligands will be presented. Finally, the effect of the chelating nature of the ligands will be theoretically analyzed. Several studies of the electronic structure of Rh(II) carboxylates have been previously published,⁴⁻⁷ at the EH, $X\alpha$ -SW, and SCF levels. However, these studies focused on the single bond nature of the Rh–Rh linkage and the effect of the axial ligands L, and no analysis of the effect of pyramidity or of the chelating nature of the ligands has been reported so far.

Methodological Aspects

Our theoretical study has been carried out first on a simplified $[Rh_2O_8]^{12-}$ model in which only the donor atoms of the carboxylato ligands are retained; in this way we can focus only on the effects of the Rh–Rh–O angle without the geometrical restrictions imposed by the chelating nature of the ligands. The total charge of the model molecule is adjusted to make all ligands O^{2-} and the metals Rh(II). One advantage of this approximate molecular orbital method is that it is not sensitive to the net molecular charges, thus the highly charged model compound causes no problems. The second model used is $[Rh_2O_8Cl_2]^{14-}$, in which the effect of the two axial chloride ligands is analyzed. Finally, the CH groups bridging the donor atoms are incorporated, resulting in the more realistic $[Rh_2(HCOO)_4]$ compound, which allows us to study the importance of the chelate nature of the ligands. All the molecular orbital calculations of the extended Hückel type⁸ were carried out using the modified Wolfsberg–Helmholz formula⁹ and the atomic parameters shown in Table I. The following bond distances (Å) were used and kept constant throughout: Rh–Rh = 2.39, Rh–O = 2.04, Rh–Cl_{ax} = 2.59, C–O = 1.26, and C–H = 1.09. The search of structural data was carried out with the help of the Cambridge Structural Database.¹⁰

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Table I. Atomic Parameters for Extended Hückel Calculations^a

atom	orbital	H _{ii}	ζ _{1i} (c ₁)	ζ _{2i} (c ₂)	ref
Rh	5s	-8.09	2.135		11
	5p	-4.57	2.100		
	4d	-12.50	4.290 (0.5807)	1.970 (0.5685)	
O	2s	-32.30	2.275		8
	2p	-14.80	2.275		
Cl	3s	-30.00	2.033		12
	3p	-15.00	2.033		
C	2s	-21.40	1.625		8
	2p	-11.40	1.625		
H	1s	-13.60	1.300		8

^a H_{ii}'s are the orbital ionization potentials, ζ_{ii} the exponents of the Slater orbitals, and c_i the coefficients in the double-ζ expansion of the d orbitals.

Structural Correlations in the Rh₂X₆ Core

In order to make our study as general as possible, we want to look at compounds belonging to different families (i.e., bearing different types of ligands). However, we have already seen in our previous studies that the standard M-M bond distance and the susceptibility to pyramidalization are different for each family of ligands. Consequently, as a compromise between generality and accuracy, we chose to analyze several closely related families of Rh(II) compounds, having four chelating ligands of the type represented in 2, where X is nitrogen or oxygen. The most common chelating ligands are carboxylates (RCOO⁻), amidates (R'CONR⁻), and derivatives of 2-hydroxypyridine (abbreviated hp⁻). There are a wide variety of axial ligands, such as chloride, water, ethanol, pyridine, caffeine, acetonitrile, dimethylsulfoxide, or tetrahydrofuran. A full list of the compounds included in our structural analysis is presented in the Appendix (Table II), together with the literature references for the crystal structure determination reports, the Cambridge reference code (when available), and the two structural parameters (*d* and α). In this family, the Rh-Rh bond distances vary in the range 2.36 < *d* < 2.49 Å, and the angles vary in the range 86.5 < α < 89.1°.

A least squares fitting of the structural data of 101 compounds (presented in the Appendix) to a linear equation yields the following expression:

$$d = 6.903 - 0.051\alpha \quad (2)$$

The regression coefficient (*r* = 0.84) is fair, given the large number and variety of compounds under consideration, and the standard error for the estimated distance is 0.014 Å. Although in most cases¹ the *d*(α) plot (Figure 1) is best represented by a second degree function, in this case the fitting is not improved by inclusion of the second-order term. From Figure 1 it is worth noting that the presence and number of axial ligands seems to be much less effective in determining the Rh-Rh bond distance than a change of a few degrees in the pyramidality angle.

In order to compare the data for Rh(II) with those of other metals and to analyze the importance of the geometrical constraints imposed by the chelate ligands, it is convenient to express the distance as a linear function of cos α. Since α and cos α are linearly related for a small interval of α, the fit obtained is as good as that of eq 2:

$$d = 2.299 + 2.934 \cos \alpha \quad (3)$$

The susceptibility of the Rh-Rh bond distance to pyramidalization is given by the slope of eq 3. This value (2.9) is surprisingly larger than those found for the molybdenum (2.2), tungsten (1.9), and rhenium (1.5) chelates with quadruple bonds, and only smaller

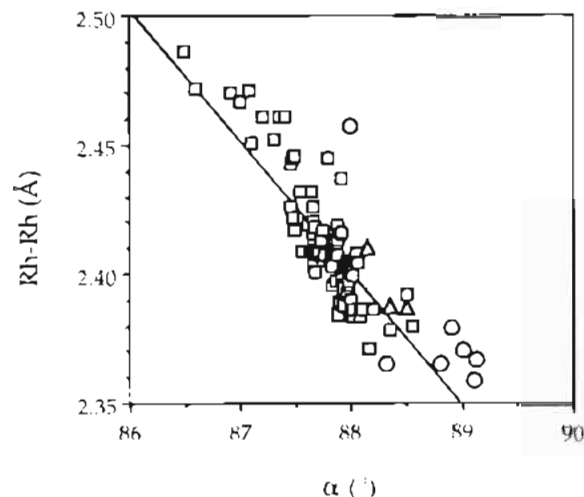


Figure 1. Rh-Rh bond distances plotted as a function of the average pyramidality angle α for the family of tetrakis(chelate) compounds of Rh(II) with two (squares), one (triangles), and no (circles) axial ligands. The line through the experimental data corresponds to the least-squares equation for 101 data pairs (eq 2).

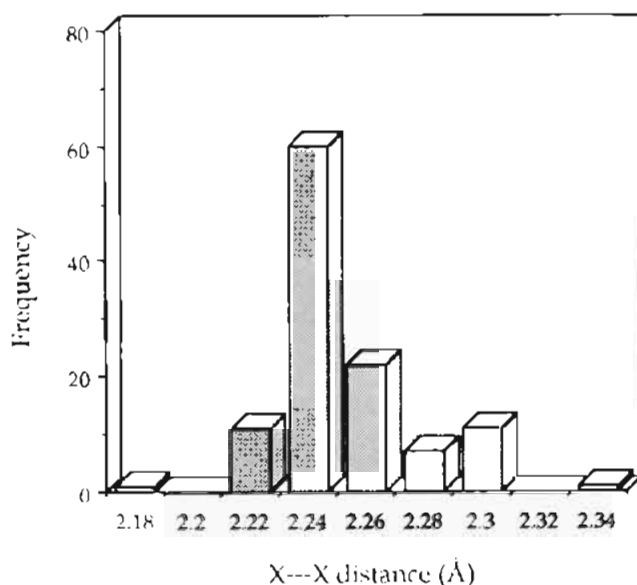


Figure 2. Distribution of the bite size for the chelating ligands (average of the nonbonded X-X distance for each compound) in the tetrakis(chelate) complexes of Rh(II).

than the susceptibility of Cr(II) complexes.^{1,2} The intercept (2.3 Å) gives the *standard* Rh-Rh distance, at α = 90°, coincident with the bite of the chelating ligands.

One can think that, as far as the chelating ligands are approximately rigid, a geometrical relationship exists between Rh-Rh-X bond angles and Rh-Rh bond distances:

$$d(\text{Rh-Rh}) = (\text{X-X}) + 2(\text{M-X}) \cos \alpha \quad (4)$$

There is an easy way to check whether the correlation of eq 3 corresponds *only* to the geometrical constraint of eq 4, or some electronic effect is at work. If the correlation is only geometrical, the following relationships should hold: (X-X) ≈ 2.3 and 2(M-X) ≈ 2.9. Practically all the experimental bites (X-X distances) in the compounds under study (Figure 2) are in the range 2.18 < (X-X) < 2.36, in good agreement with the geometrical requisite of eq 4. However, the M-X bond distances (see histogram in Figure 3) are far from the value of 1.47 expected if the geometrical constraint of eq 4 were the only responsible for the correlation between *d* and α.

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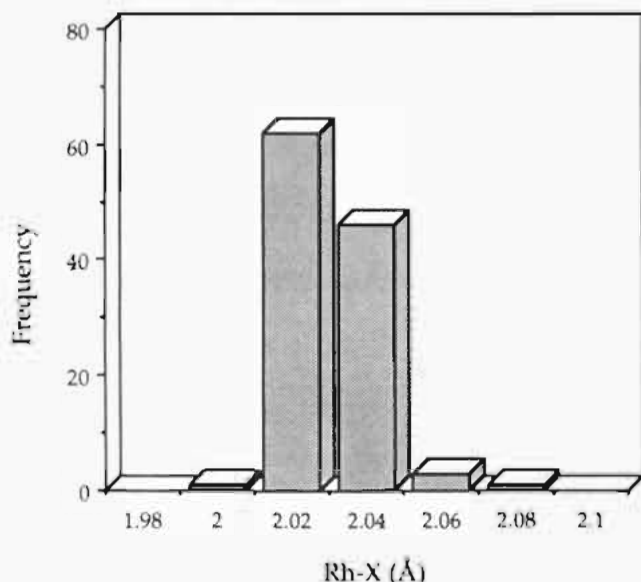


Figure 3. Distribution of the average Rh-X bond distances in the tetrakis(chelate) complexes of Rh(II).

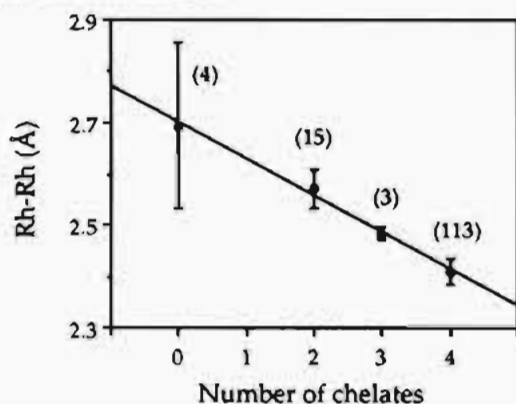


Figure 4. Average Rh-Rh bond distances for the families of dinuclear Rh(II) compounds as a function of the number of chelate rings present. The corresponding data and references to the structural literature are given in the Appendix (Tables II-V). The bars represent the standard deviation of the averages, and the number of compounds in each family is given in parentheses.

It thus appears that an electronic (or steric) effect is superimposed on top of the strict geometric relationship between d and α . But it is clear that the presence of chelate rings enhances the pyramidal effect. This can be nicely seen in the dependence of the Rh-Rh bond distances on the number of chelate groups present in a compound (Figure 4).

A much smaller family of Rh(II) compounds is that containing two carboxylato ligands and two metalated phosphines, bridging the two Rh atoms. The (d, α) pairs for this family are represented in Figure 5, in which the expected trend is apparent (for references to the structures of such compounds see Table VI in the Appendix). However, in the family of bis(carboxylato)-bis(diamine) complexes (eight compounds) no clear correlation is found between d and α (see Table IV in Appendix).

Theoretical Study of the Rh_2O_3 Core

With the Rh-Rh bond distance kept constant, the Rh-Rh overlap population is calculated to vary with α as shown in Figure 6 (top): the bond becomes stronger as the pyramidal angle increases, in excellent agreement with the experimental trend (Figure 1). On the other hand, the maximum bond strength is calculated at $\alpha \approx 96^\circ$, and the energy minimum at 94.6° , suggesting that the $d(\alpha)$ line of Figure 1 might be experimentally continued to lowest distances in the future, although the

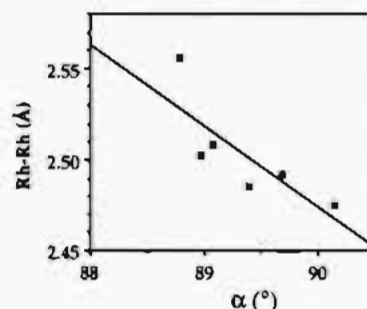


Figure 5. Rh-Rh bond distances plotted as a function of the average pyramidal angle α for the family of bis(carboxylato)-bis(metalated phosphine) compounds of Rh(II). The line through the experimental data (Appendix, Table VI) corresponds to the least-squares equation for six data pairs: $d = 6.506 - 0.045\alpha$ (regression coefficient, $r = 0.80$, and standard deviation for the estimated distance = 0.019).

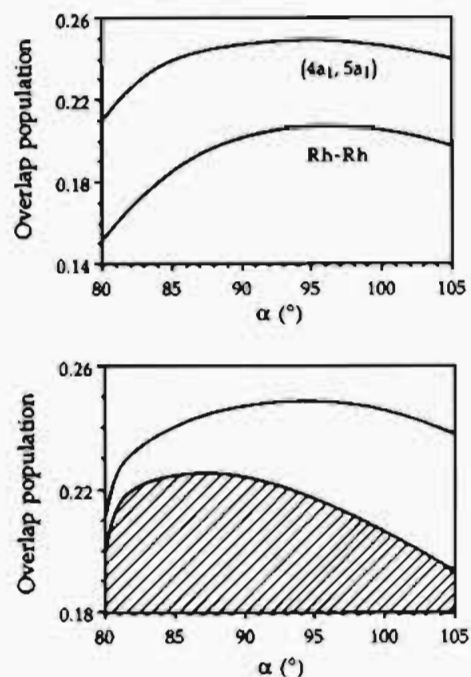


Figure 6. Top: Dependence of the Rh-Rh overlap population on α in the model compound $[\text{Rh}_2\text{O}_3]^{12-}$. Bottom: Pyramidal dependence of the overlap population between the $4a_1$ fragment orbitals of two $[\text{RhO}_4]^{6-}$ moieties (shaded area) and between the $4a_1$ orbital of one $[\text{RhO}_4]^{6-}$ fragment and the $5a_1$ orbital of the alternate $[\text{RhO}_4]^{6-}$ fragment (white area).

nonchelating nature of the oxo ligands in our model molecule may bias this prediction. Let us stress that the variation of the Rh-Rh overlap population with α parallels that of the overlap population between rhodium σ orbitals. The fact that the total Rh-Rh overlap population is smaller than its σ component is due to the negative contribution of the occupied d orbitals (electron pair repulsions).

As the calculated bond strength reproduces the experimental behavior, it is worthwhile to explore the electronic structure of the model compound in search for a simple explanation of such behavior. For that we focus on the relevant valence orbitals of each $[\text{RhO}_4]^{6-}$ fragment (approximately planar, C_{4v} symmetry) and how they interact in a dimer, as shown in Figure 7. The highest occupied orbital in $[\text{RhO}_4]^{6-}$ is d_{z^2} ($4a_1$), in which an unpaired electron is located, and the lowest unoccupied orbital pointing outside the RhO_4 plane is p_z ($5a_1$). The d_{z^2} orbitals of each RhO_4 moiety form bonding and antibonding combinations in the dimer, and so do the p_z orbitals. For Rh(II) the bonding combination of d_{z^2} ($4a_{1g}$) is occupied, and is therefore responsible for the Rh-Rh single bond. However, the overlap population between the $4a_1$ fragment orbitals (Figure 6, bottom) decreases

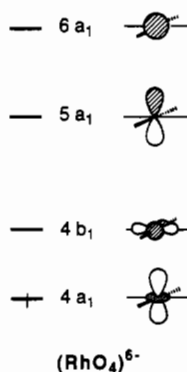


Figure 7. Valence orbitals of a square-planar $[\text{RhO}_4]^{6-}$ fragment. Symmetry labels correspond to the C_{4v} point group.

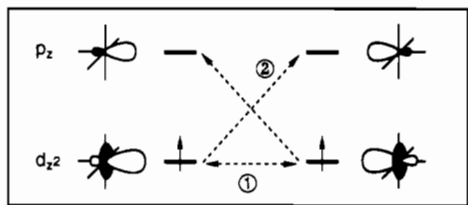


Figure 8. Schematic representation of the relevant interactions between the σ orbitals of two MX_4 fragments for d^7 metal ions. ① is a classical two-center-two-electron bond, and ② are one-electron donor-acceptor interactions.

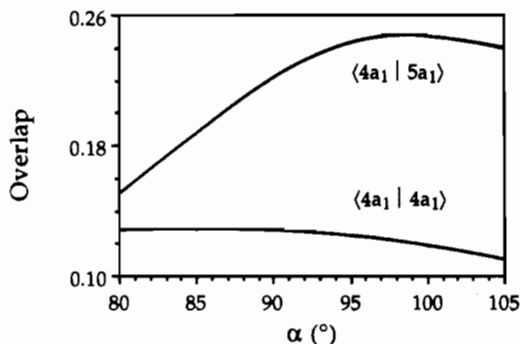
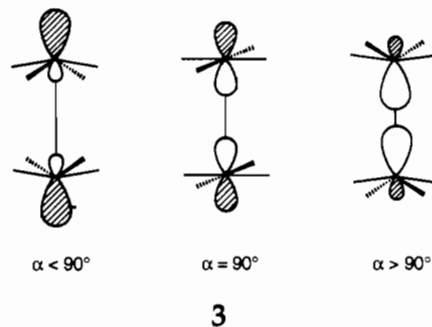


Figure 9. Variation of the overlap integrals between the σ metal orbitals of the RhO_4 fragments in a Rh_2O_8 core as a function of α .

with increasing α (except for very small angles), in sharp contrast with the behavior of the Rh–Rh overlap population (Figure 6, top) and with the experimental trend (Figure 1). It is obvious from Figure 6 that it is the $4a_1/5a_1$ interaction which is responsible for the increased bond strength at larger angles, but what is the meaning of such interaction? In a crude way one can say that on top of the single Rh–Rh bond associated to the $4a_1/4a_1$ interaction, there are two donor-acceptor interactions between the $4a_1$ and $5a_1$ orbitals, involving one electron each (Figure 8); the strength of the bond is determined by the $4a_1/4a_1$ interaction, whereas the pyramidal effect is produced by the $4a_1/5a_1$ interaction. This diagram is not only useful to understand the pyramidal effect in Rh(II) but also, by appropriately filling the $4a_1$ orbitals, to attempt predictions on the pyramidal behavior of d^8 – d^8 interactions.¹³

But why the interaction between the d_{z^2} orbitals is not improved with pyramidalization while that between d_{z^2} and p_z is strongly enhanced? Let us start by looking at the composition of these two orbitals ($4a_1$ and $5a_1$) of an RhO_4 fragment and how they change with α . The $4a_1$ orbital is roughly 90% d_{z^2} and 5% s of the Rh atom, with smaller contributions from the ligands, and its composition is practically constant for all values of α considered ($80^\circ < \alpha < 105^\circ$). In contrast, $5a_1$ is practically 100% p_z (Rh)

at $\alpha = 90^\circ$, but acquires increasing s (Rh) contribution upon pyramidalization, reaching contributions of $\sim 25\%$ at $\alpha = 105^\circ$ (or 75°). For the isolated RhO_4 fragment, the relative contributions of the Rh atomic orbitals depend on how much α deviates from 90° , but $5a_1$ is hybridized in the opposite direction to that of the ligands as shown in 3. As a consequence, the density of

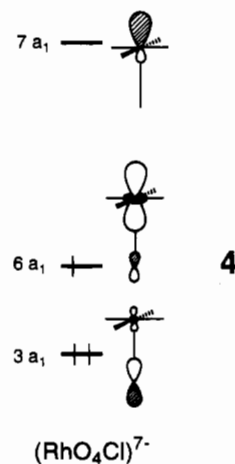


the $5a_1$ orbital in the intermetallic region is small for small α and increases continuously with this angle. The outcome of the changes in composition of these two orbitals with α is that their overlap integrals depend on the angle as shown in Figure 9. In few words, the two-orbital-two-electron bond is essentially insensitive to pyramidalization, whereas the one-electron donor-acceptor interactions are strongly enhanced when the degree of pyramidalization increases.

Theoretical Study of the Effect of Axial Ligands in a $\text{Rh}_2\text{O}_8\text{Cl}_2$ Core

The first qualitative effect to be noticed when two axial ligands are added, in a $[\text{Rh}_2\text{O}_8\text{Cl}_2]^{14-}$ model compound, is a decrease in the bond angle at the energy minimum ($\alpha = 92.6^\circ$, to be compared with 94.6° obtained for the model without axial ligands). This result, not anticipated in previous works^{4–7} in which the geometry was frozen and only the competition of the axial ligand for the σ orbitals was studied, reflects nothing but the tendency of the Rh atom to adopt an approximately octahedral coordination sphere. The behavior of the Rh–Rh overlap population with α , on the other hand, is analogous to that found for the model without axial ligands.

In this case there are three σ orbitals to be considered at each RhO_4Cl moiety, schematically depicted in 4. The behavior of



the Rh–Rh overlap population nicely parallels that of the $6a_1/7a_1$ interaction, in a manner similar to that discussed above for the interaction between RhO_4 fragments: $6a_1$ is essentially d_{z^2} (Rh) and insensitive to pyramidalization, and $7a_1$ is mostly p_z (Rh) and highly sensitive to α . Nevertheless, there are two differences with the previous case, (i) a larger energy difference between $6a_1$ and $7a_1$ than between $4a_1$ and $5a_1$, and (ii) a stronger hybridization

(13) Aullón, G.; Alvarez, S. To be submitted for publication.

of "p_z", produced through interaction with the axial ligand. The first factor results in a poorer donor-acceptor interaction (② in Figure 8), whereas the second one favors this interaction. The fact that the experimental data seem to be roughly insensitive to the presence of axial ligands can be due to a compensation of both factors.

Calculations were also carried out on a model with only one axial ligand, [Rh₂O₈Cl]¹³⁻, and the general trends are similar to those discussed above. The main difference is that the bond angle at the rhodium atom with only four ligands is optimized at 95.1° and that at the metal with an additional axial ligand at 91.6°.

Chelating Nature of the Ligands: Theoretical Study of a Rh₂(HCOO)₄ Core

Introduction of the CH bridges linking pairs of O donor atoms obviously diminishes the possibility of varying α . If the Rh-Rh, Rh-O, and C-O distances are kept constant, the OCO angle and α are not independent, and α cannot be made larger than 92° without introducing too much strain into the carboxylato ligands. The calculated energy minimum therefore appears at 85.9°, a much smaller angle than obtained with the monodentate ligands (94.6°). The calculated value is only slightly smaller than the experimental ones (see Figure 1). This result is also consistent with the dependence of the Rh-Rh bond distance on the number of chelate rings discussed above (Figure 4).

As found for the simpler models, the Rh-Rh overlap population increases with α , correctly reproducing the experimental behavior even if the maximum bond strength is calculated for a too small angle ($\alpha = 84.6^\circ$). Also the optimized OCO angle (112.7°) is smaller than the experimental ones (123° < OCO < 129°) and, consequently, the calculated bite (2.1 Å) is somewhat shorter than the experimental ones (X-X > 2.2 Å, see Figure 2). All in all the methodology used seems to reproduce well the trends, but fails to give good quantitative estimates of the bond angles in the chelate rings. It is interesting in this respect to compare these results with those obtained by Davy and Hall for the Cr(II) chelates using much more accurate calculations of the GVB type.¹⁴ These authors obtain optimized Cr-Cr distances too long as compared with the experimental data, but the corresponding theoretical values of α fit nicely in the $d(\alpha)$ plot of the experimental values.² Apparently, molecular orbital calculations at the extended Hückel and at the GVB levels have the same difficulties in calculating the angles of the chelate rings but can qualitatively predict the correlation between the M-M bond distance and α .

Another interesting result of our calculations is that the C-O overlap population of the carboxylato groups increases with the OCO angle (Figure 10, top), reaching a maximum for an angle of ~131°. An analysis of the structural data for the family of tetrakis(chelates), including carboxylates, amidinates, and the like, shows that these compounds follow the expected behavior (Figure 10, bottom), allowing us to estimate the shortest C-X distances to appear at angles close to 132°. The least-squares fit to the experimental data, shown in Figure 10 (bottom) illustrates that the general trend is similar to the calculated one, despite the variety of ligands under consideration and the large amount of available structural data.

Conclusions

The Rh-Rh bond distances in the family of the tetrakis(chelate) binuclear complexes (113 crystallographically independent molecules from 104 compounds) of Rh(II) decrease with increasing pyramidalization angles, and a least-squares linear equation reproduces the experimental distances of all the molecules (with or without axial ligands) in the eclipsed conformation with an estimated standard error of 0.014 Å. The susceptibility of the Rh-Rh bonds to changes in the average pyramidalization angle is comparable to that of the triple or quadruple bonds between

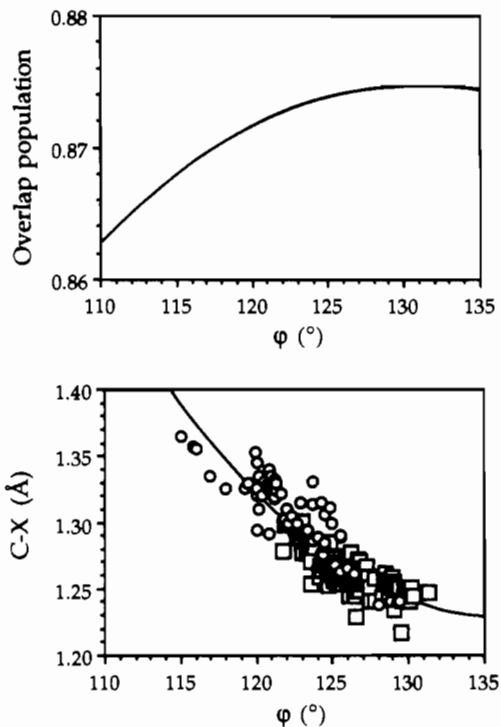


Figure 10. Top: Variation of the C-O overlap population as a function of the OCO bonding angle for the carboxylato ligands of [Rh₂(HCOO)₄]. Bottom: Plot of the C-X bond distances as a function of the XCX bond angles in the chelating groups of type 2 (X = O or N). The squares correspond to carboxylato groups and the circles to other chelates of type 2.

metal atoms of the earlier transition elements. The number of bridging bidentate ligands has been found to favor shorter distances for the same pyramidalization angle. The family of compounds having two carboxylato ligands and two metallated phosphines (six compounds) show the same trend in the $d(\alpha)$ plot, whereas the bis(diamine)-bis(carboxylato) complexes show no clear correlation (eight compounds).

The molecular orbital calculations show that the Rh-Rh overlap population increases upon increasing α , in good agreement with the structural data. The orbital explanation for the pyramidalization effect relies on the participation of the 4a₁ (d_{z²}) and 5a₁ (p_z) orbitals of the MX₄ fragments. The two-orbital-two-electron interaction between the 4a₁ orbitals is responsible for the largest part of the Rh-Rh σ bond, but is practically insensitive to pyramidalization. On the other hand, a weaker interaction between 4a₁ of one fragment and 5a₁ of the other one is strongly enhanced upon pyramidalization of the MX₄ groups in the direction opposite to the M-M bond. This result is seen to be related to the increased sp hybridization of the p_z orbital upon increasing α .

The addition of axial ligands has two opposite effects on the fragment orbitals. The d_{z²} and p_z orbitals have a poorer energy match, but at the same time p_z is more strongly hybridized toward the other Rh atom. The fact that the addition of axial ligands does not affect the Rh-Rh bond distance if the pyramidalization angle is unchanged indicates that the two effects have approximately equal weights. The chelating nature of the ligand introduces a geometrical constraint which forces shorter distances for the same pyramidalization angle, but the Rh-Rh bond strength depends on α if the ligands are kept roughly constant. Also a correlation between the CO bond distance and the OCO bond angle has been found in the carboxylato complexes.

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Appendix: Tables of Structural Data and References

Table II. Structural Data, Reference Codes for the Cambridge Structural Database, and References for Dinuclear Rh(II) Compounds with Four Chelate Rings

compd	Rh–Rh (Å)	RhRhX (deg)	refcode	ref	compd	Rh–Rh (Å)	RhRhX (deg)	refcode	ref
[Rh ₂ (mhp) ₄] ^a	2.359	89.1	mopyrh10	15	[Rh ₂ (PhCO ₂) ₄ (Me ₂ SO) ₂]	2.405	87.7	fammov	51
[Rh ₂ (PrCO ₂) ₄]	2.365	88.3	dukjoi	16	[Rh ₂ (MeCO ₂) ₄ (Me ₂ SO) ₂]	2.406	87.8	pvarhc	20
[Rh ₂ (mhp) ₄] ^{a,b}	2.365	88.8	mpyrha	17	[Rh ₂ (CF ₃ CO ₂) ₄ (nitme)]	2.407	87.8	fundib10	52,53
	2.370	89.0			[Rh ₂ (MeCO ₂) ₄ (S(CH ₂ Ph) ₂) ₂]	2.407	87.8	dehbib	54
[Rh ₂ (mhp) ₄] ^a	2.367	89.1	camjap	18	[Rh ₂ (EtCO ₂) ₄ (Me ₂ SO) ₂]	2.407	87.7	msorha	55
[Rh ₂ (1-adamantyl-CO ₂) ₄ (MeOH) ₂]	2.371	88.2	cidpek	19	[Rh ₂ (MeCO ₂) ₄ (PhNNHPh) ₂]	2.407	87.7	feztot	56
[Rh ₂ (Me ₃ CCO ₂) ₄ (H ₂ O) ₂]	2.371	88.1	pvarha	20	[Rh ₂ (CF ₃ CO ₂) ₄ (Me ₂ SO- <i>d</i> ₆) ₂] ^b	2.407	87.9	begfey	57
[Rh ₂ (mhp) ₄ (MeCN)] ^c	2.372	87.0	mpyrhb	17		2.409	87.9		
[Rh ₂ (ttb) ₄ (py) ₂] ^c	2.374	87.4	javsuu	21	[Rh ₂ (MeCO ₂) ₄ (ttf) ₂]	2.408	88.0	kabwoz	58
[Rh ₂ (CO ₃) ₄ (H ₂ O) ₂] ⁴⁺	2.378	88.3		22	[Rh ₂ (PrCO ₂) ₄ (dimenol) ₂]	2.408	87.7	didbex	59
[Rh ₂ (chp) ₄]	2.379	88.9	mpyrhf	17	[Rh ₂ (CF ₃ CO ₂) ₄ (H ₂ O) ₂]	2.409	87.8	biktuk	48
[Rh ₂ (CO ₃) ₄ Cl ₂] ⁶⁻	2.380	88.5		22	[Rh ₂ (MeCO ₂) ₄ (maac) ₂]	2.409	87.7	kabjay	49
[Rh ₂ (MeCO ₂) ₄ (Me ₂ NCHO) ₂] ^b	2.383	88.1	getjaq	23	[Rh ₂ (MeCO ₂) ₄ (trim) ₂]	2.409	87.7	femfei	50
	2.383	88.0			[Rh ₂ (MeCO ₂) ₄ (pyr) ₂]	2.409	87.7	femfim	60
[Rh ₂ (MeCO ₂) ₄ (MeCN) ₂]	2.384	88.0	barpit	24	[Rh ₂ (EtCO ₂) ₄ (phz) ₂] ^c	2.409	87.6	prnrhc	29
[Rh ₂ (o-HOC ₆ H ₄ CO ₂) ₄ (H ₂ O)(EtOH)]	2.384	87.9	colcel	25	[Rh ₂ (MeCO ₂) ₄ (dmtc) ₂]	2.409	87.6	gidfee	61
[Rh ₂ (mhp) ₄ (im)] ^c	2.384	87.4	mpyrhe	17	[Rh ₂ (fhp) ₄ (Me ₂ SO)]	2.410	88.1	cuwmem	62
[Rh ₂ (MeCO ₂) ₄ (H ₂ O) ₂]	2.385	88.1	acaqrh10	26	[Rh ₂ (MeCO ₂) ₄ (theophylline) ₂] ^c	2.411	87.0	racthe	37
[Rh ₂ (H ₃ NCH ₂ CH ₂ CO ₂) ₄ (H ₂ O) ₂] ⁴⁺	2.385	87.9	alarhp10	27	[Rh ₂ (CF ₃ CO ₂) ₄ (nitph) ₂]	2.412	87.9	fundat10	52,53
[Rh ₂ (chp) ₄ (im)] ^c	2.385	87.2	mpyrhg	17	[Rh ₂ (PhNpy) ₄ (PhCN)] ^c	2.412	87.5	valkuo	63
[Rh ₂ (S)-PhCH(OH)CO ₂] ₄ (EtOH) ₂] ^b	2.386	88.2	donnoj	28	[Rh ₂ (MeCO ₂) ₄ (tht) ₂]	2.413	87.8	pvarhb	20
	2.386	88.1			[Rh ₂ (Me ₃ NCH ₂ CO ₂) ₄ Cl ₂] ²⁺	2.413	87.7	visdak	64
[Rh ₂ (EtCO ₂) ₄ (dda)]	2.386	88.0	prnrhd	29	[Rh ₂ (MeCO ₂) ₄ (admp) ₂] ^a	2.414	87.6	jakjua	65
[Rh ₂ (MeCO ₂) ₂ (mhp) ₂ (im)] ^a	2.387	88.5	mpyrhd	17	[Rh ₂ (MeCONH) ₄ (H ₂ O) ₂]	2.415	87.9	dokjaa	66
[Rh ₂ (MeCO ₂) ₂ (mhp) ₂ (im)] ^a	2.388	88.3	mpyrhc	17	[Rh ₂ (MeCO ₂) ₄ (admp) ₂] ^a	2.415	87.6	jakkah	65
[Rh ₂ (MeCO ₂) ₄ (metro) ₂]	2.388	87.9	vemrio	30	[Rh ₂ (CF ₃ CO ₂) ₄ (tempo) ₂]	2.417	87.7	convoq10	67
[Rh ₂ (MeCO ₂) ₂ (Ph ₃ CCO ₂) ₂ (MeCN) ₂]	2.389	87.9	cidpio	19	[Rh ₂ (EtCO ₂) ₄ (acr) ₂]	2.417	87.5	prnrha	29
[Rh ₂ (dpb) ₄] ^c	2.389	87.4		31	[Rh ₂ (MeCO ₂) ₄ (dmtf) ₂]	2.418	87.7	gidfii	61
[Rh ₂ (R)-PhCH(OMe)CO ₂] ₄ (thf) ₂] ^b	2.389	87.9	donnup	28	[Rh ₂ (CF ₃ CO ₂) ₄ (imme)]	2.419	87.9	fundoh10	52,53
	2.390	88.0			[Rh ₂ (MeCO ₂) ₄ (CO) ₂]	2.419	87.6	cbacrh	44
[Rh ₂ (vall) ₄ (Hvall) ₂]	2.392	88.5	sahgud	32	[Rh ₂ (CF ₃ CO ₂) ₄ (Me ₂ SO) ₂]	2.420	87.6	msorhb10	55,57
[Rh ₂ (MeCO ₂) ₄ (4-NH-py) ₂]	2.393	88.0	cejkux	33	[Rh ₂ (MeCO ₂) ₄ (SbPh ₃) ₂]	2.422	87.5	dehbat	54
[Rh ₂ (CF ₃ CO ₂) ₄ (EtOH) ₂] ^b	2.393	87.9	tfaerh	34	[Rh ₂ (CF ₃ CO ₂) ₂ (form) ₂ (H ₂ O) ₂]	2.426	87.7	fazrih	68
	2.416	87.9			[Rh ₂ (MeCO ₂) ₄ (AsPh ₃) ₂]	2.426	87.4	dehbk	54
[Rh ₂ (Ph(CH ₂) ₃ CO ₂) ₄ (metro) ₂]	2.394	87.9	vemrou	30	[Rh ₂ (CF ₃ CF ₂ CO ₂) ₄ (tempo) ₂]	2.432	87.6	convo01	67
[Rh ₂ (MeCO ₂) ₄ (py) ₂]	2.396	88.0	pyachr	35	[Rh ₂ (CF ₃ CO ₂) ₄ (imme) ₂]	2.432	87.5	fundex10	52,53
[Rh ₂ (MeCO ₂) ₄ Cl ₂] ²⁻	2.396	87.9	accrgh01	36	[Rh ₂ (form) ₄] ^c	2.434	87.7	fivjoj	69
[Rh ₂ (MeCONPh) ₄ (Me ₂ SO)] ^c	2.397	87.4	fetcip	39	[Rh ₂ (dpb) ₄ (CO)] ^c	2.436	87.2		31
[Rh ₂ (o-PhC ₆ H ₄ CO ₂) ₄ (MeCN) ₂]	2.396	87.8	cidpag	29	[Rh ₂ (PhCONH) ₄ (py) ₂]	2.437	87.9	deywin	70
[Rh ₂ (MeCO ₂) ₄ (caffeine) ₂]	2.397	88.0	raccap	37	[Rh ₂ (MeCO ₂) ₄ (P(OPh) ₃) ₂]	2.443	87.4	poacr10	71,72
[Rh ₂ (MeCO ₂) ₄ (diphenylcarbazide) ₂]	2.397	87.9	cucbad	38	[Rh ₂ (pyro) ₄ (Hpyro) ₂]	2.445	87.8	sahgox	32
[Rh ₂ (MeCO ₂) ₄ Cl ₂] ²⁻	2.398	87.9	ciftoa	40	[Rh ₂ (MeCONH) ₄ (Me ₂ SO) ₂]	2.445	87.5	doxhiih	73
[Rh ₂ (MeCO ₂) ₄ (misonidazole) ₂]	2.399	87.9	faltjv	41	[Rh ₂ (MeCONH) ₃ (MeCO ₂)(Me ₂ SO) ₂]	2.446	87.5	duwgil	74
[Rh ₂ (CF ₃ CO ₂) ₄ (Me ₂ SO) ₂] ^b	2.399	88.0	basbom	42	[Rh ₂ (MeCO ₂) ₄ (PPh ₃) ₂]	2.451	87.1	bammeh	72
	2.401	88.0			[Rh ₂ (MeCONPh) ₄ (Me ₂ SO) ₂]	2.452	87.3	fetcow	39
[Rh ₂ (ttb) ₃ (MeCO ₂)(py) ₂]	2.401	87.7	javsou	21	[Rh ₂ (MeCO ₂) ₄ (NO)(NO ₂) ^d]	2.454	86.0		44
[Rh ₂ (PhCO ₂) ₄ (py) ₂]	2.402	88.0	boyvoa	43	[Rh ₂ (dpf) ₄]	2.457	88.0	kilfiu	75
[Rh ₂ (MeCO ₂) ₄ (Et ₂ NH) ₂]	2.402	87.9	eaacrh	44	[Rh ₂ (dpf) ₄ (MeCN)] ^c	2.459	86.8	kolfoa	75
[Rh ₂ (EtCO ₂) ₄ (aza) ₂]	2.403	87.8	prnrhb	29	[Rh ₂ (PhCONH) ₄ (SbPh ₃) ₂]	2.461	87.4	deywej	70
[Rh ₂ (MeCO ₂) ₄ (aamp)] ^b	2.403	87.7	citlum	45	[Rh ₂ (MeCONH) ₃ (MeCO ₂)(SbPh ₃) ₂]	2.461	87.3	kajroc	76
	2.404	87.6			[Rh ₂ (CF ₃ CO ₂) ₄ (cariophyllene) ₂]	2.461	87.2	jicsix	77
[Rh ₂ (MeCO ₂) ₄ (mhac)] ^b	2.403	87.8	jevaxj	46	[Rh ₂ (MeCONH) ₃ (MeCO ₂)(AsPh ₃) ₂]	2.467	87.0	kajriw	76
	2.407	87.8			[Rh ₂ (CF ₃ CO ₂) ₄ (P(OPh) ₃) ₂]	2.470	86.9	bamnuy	78
[Rh ₂ (MeCO ₂) ₄ (tmp) ₂]	2.404	88.1	dewray	47	[Rh ₂ (MeCONH) ₄ (AsPh ₃) ₂]	2.471	87.1	kajrex	76
[Rh ₂ (CF ₃ CO ₂) ₄ (tempol) ₂]	2.405	88.0	biktoe	48	[Rh ₂ (CF ₃ CONH) ₄ (py) ₂]	2.472	86.6	butmei	79
[Rh ₂ (EtCO ₂) ₄ (aac) ₂]	2.405	88.0	kabhok	49	[Rh ₂ (CF ₃ CO ₂) ₄ (PPh ₃) ₂]	2.486	86.5	bamnos	78
[Rh ₂ (MeCO ₂) ₃ (bpnp)] ⁺	2.405	88.0	bupbuj10	50					

^a Different crystallizations with varying counterion or solvation molecules. ^b Two independent molecules per unit cell. ^c These molecules are not in an eclipsed conformation and were not included in the least-squares fitting of eqs 2 and 3. Only structures with rotation angles smaller than 12° were considered. ^d This is probably a Rh(I)–Rh(III) mixed valence rather than a Rh(II) compound, and was not included in the least-squares fitting of eqs 2 and 3. ^e This compound deviates from the characteristic behavior, probably because of the unusual coordination of theophylline as compared to that of other puric bases such as caffeine or adenine, and was not included in the least-squares fitting of eqs 2 and 3.

Table III. Structural Data, Reference Codes for the Cambridge Structural Database, and References for Dinuclear Rh(II) Compounds with Three Chelate Rings

compd	Rh–Rh (Å)	RhRhX (deg)	refcode	ref	compd	Rh–Rh (Å)	RhRhX (deg)	refcode	ref
[Rh ₂ (MeCO ₂) ₃ (py) ₄] ⁺	2.474	89.7	commia10	80	[Rh ₂ (form) ₃ (NO ₃)(PPh ₃)]	2.498	90.7	kadgif	81
[Rh ₂ (form) ₃ (NO ₃)py]	2.476	89.1	kadgol	81					

Table IV. Structural Data, Reference Codes for the Cambridge Structural Database, and References for Dinuclear Rh(II) Compounds with Two Chelate Rings

compd	Rh–Rh (Å)	RhRhX (deg)	refcode	ref
[Rh ₂ (MeCO ₂) ₂ (CF ₃ CO) ₂ (CH) ₂ (py) ₂]	2.523	91.0	gawzej	82
[Rh ₂ (MeCO ₂) ₂ (CF ₃ COCHCOME) ₂ (py) ₂]	2.534	91.7	jezhur	83
[Rh ₂ (MeCO ₂) ₂ (MeCN) ₆] ²⁺	2.536	91.1	dorrux	84
[Rh ₂ (<i>p</i> -MeC ₆ H ₄) ₂ N ₃] ₂ (CO)(bipy)I] ₂ ²⁺	2.544	89.7	kawguk	85
[Rh ₂ (MeCO ₂) ₂ (MeCN) ₄ (py) ₂] ²⁺	2.547	91.4	dorsae	84
[Rh ₂ (MeCO ₂) ₂ (phen) ₂ (mim) ₂] ²⁺	2.556	90.5	fixraf	86
[Rh ₂ (MeCO ₂) ₂ (phen) ₂ (py) ₂] ²⁺	2.559	90.6	kofwad	87
[Rh ₂ (MeCO ₂) ₂ (Me ₄ phen) ₂ (mim) ₂] ²⁺	2.564	90.4	fixrin	86
[Rh ₂ (MeCO ₂) ₂ (Me ₂ phen) ₂ (mim) ₂] ²⁺	2.565	90.3	fixref	86
[Rh ₂ (pynp) ₃ Cl ₂] ²⁺	2.567	91.4	cozduq	88
[Rh ₂ (HCO ₂) ₂ (phen) ₂ Cl ₂]	2.576	90.8	fiskib	89
[Rh ₂ (HCO ₂) ₂ (bipy) ₂ Cl ₂]	2.584	91.8	bihjor10	90
[Rh ₂ (CF ₃ CONH) ₂ (phen) ₂ (py) ₂] ²⁺	2.612	90.2	kofvuw	87
[Rh ₂ (pncc) ₂ (CO) ₂ Cl ₂]	2.639	88.6	sergeb	91
[Rh ₂ (MeCO ₂) ₂ (py) ₆] ²⁺	2.653	90.5	commog10	80

Table V. Structural Data, Reference Codes for the Cambridge Structural Database, and References for Dinuclear Rh(II) Compounds without Chelate Rings

compd	Rh–Rh (Å)	RhRhX (deg)	refcode	ref
[Rh ₂ (CF ₃ COCHCOF ₃) ₄ (py) ₂]	2.590	91.6	kefjio	92
[Rh ₂ (MeCN) ₁₀] ⁴⁺	2.624	90.2	gojpok	93
[Rh ₂ (MeCN) ₈ (H ₂ O) ₂] ⁴⁺	2.625	90.5	kefjou	94
[Rh ₂ (Hdmg) ₄ (PPh ₃) ₂]	2.936	89.2	tpgyrh10	95

Table VI. Structural Data, Reference Codes for the Cambridge Structural Database, and References for Dinuclear Rh(II) Compounds with Two Chelate Rings and Two Metalated Phosphines

compd	Rh–Rh (Å)	RhRhX (deg)	refcode	ref
[Rh ₂ (MeCO ₂) ₂ (Ph{ <i>o</i> -BrC ₆ F ₄ }P{C ₆ H ₄ }) ₂]	2.475	90.1	fippid	96
[Rh ₂ (AcO) ₂ (Ph{ <i>o</i> -BrC ₆ F ₄ }P{C ₆ H ₄ }) ₂ (H ₂ O)]	2.485	89.4	fippep	96
[Rh ₂ (Me ₃ CCO ₂) ₂ (Me ₂ P{C ₆ H ₄ }) ₂ (H ₂ O) ₂]	2.492	89.7	takmoh	97
[Rh ₂ (AcO) ₂ (<i>m</i> -MeC ₆ H ₄) ₂ P{ <i>m</i> -MeC ₆ H ₃ }) ₂ (AcOH) ₂]	2.502	89.0	visbii	98
[Rh ₂ (AcO) ₂ (Ph ₂ P{C ₆ H ₄ }) ₂ (AcOH) ₂]	2.508	89.1	cesyaa10	99, 100
[Rh ₂ (AcO) ₂ (Ph ₂ P{C ₆ H ₄ }) ₂ (py) ₂]	2.556	88.8	cubdae	100
[Rh ₂ (AcO) ₂ (RR'P{C ₆ H ₄ }) ₂ (Ph ₂ P{C ₆ H ₄ })(PPh ₃) ^a	2.558	88.0	gamdaz	101
[Rh ₂ (AcO) ₂ (Ph ₂ P{C ₆ H ₄ }) ₂ (AcOH) ₂] ^a	2.493	88.6		102
[Rh ₂ (AcO) ₂ (<i>p</i> -ClCH ₂) ₂ P{ <i>p</i> -ClC ₆ H ₃ }) ₂ (AcOH) ₂] ^a	2.511	88.8		102

^a In these compounds, the Rh–C bonds correspond to the same Rh atom and do not conform to the general trend of the symmetric compounds represented in Figure 5.

Abbreviations Used for Ligands

aac	9-(2-aminoethyl)amino-6-chloro-2-methoxyacridine	mhac	<i>N</i> -(6-(dimethylamino)hexyl)-4-acridinecarboxamide
aamp	4-amino-5-(aminomethyl)-2-methylpyridine	mim	<i>N</i> -methylimidazole
AcOH	acetic acid	misonidazole	1-(2-hydroxy-3-methoxypropyl)-2-methyl-5-nitroimidazole
acr	acridine	Hmhp	6-methyl-2-hydroxypyridine
Hadamantane	tricyclo[3,3,1,1 ^{3,7}]decane	nitme	4,5-dihydro-2,4,4,5,5-pentamethyl- <i>N,N'</i> -dioximidazole
admp	2-amino-4,6-dimethylpyrimidine	nitph	4,5-dihydro-2-phenyl-4,4,5,5-tetramethyl- <i>N,N'</i> -dioximidazole
aza	7-azaindole	phen	1,10-phenantroline
bipy	2,2'-bipyridyl	phz	phenazine
bpnp	2,7-bis(2-pyridyl)-1,8-naphthopyridine	pncc	2-((α -methylbenzylidene)amino)pyridine
Hchp	6-chloro-2-hydroxypyridine	py	pyridine
dda	diaminedurene	pynp	2-(2-pyridyl)-1,8-naphthopyridine
dimenol	5,7-dimethyl-1,8-naphthopyridin-2-ol	pyr	2,4-diamino-5-(<i>p</i> -chlorophenyl)-6-ethylpyrimidine
H ₂ dmg	dimethylglyoxime	Hpyro	γ -butyrolactam
dmtc	<i>O</i> -ethyl <i>N,N</i> -dimethylthiocarbamate	Htcl	ω -caprolactam
dmtf	<i>N,N</i> -dimethylthioformamide	temp	2,2,6,6-tetramethylpiperidine <i>N</i> -oxide
Hdpc	<i>N,N'</i> -diphenylbenzamide	tempol	4-hydroxy-2,2,6,6-tetramethylpiperidine <i>N</i> -oxide
Hdpc	<i>N,N</i> -diphenylformamide	thf	tetrahydrofuran
Hfhp	6-fluoro-2-hydroxypyridine	tht	tetrahydrothiophene
Hform	<i>N,N</i> -di- <i>p</i> -tolylformamide	tmp	thiamine monophosphate
im	imidazole	trim	2,4-diamino-5-(3',4',5'-trimethoxybenzyl)pyrimidine
imme	4,5-dihydro-2,4,4,5,5-pentamethyl-1-oxoimidazole	Httb	2,4,6-tri- <i>p</i> -tolylbenzoic acid
maac	6-chloro-9-(2-(dimethylamino)ethyl)amino-2-methoxyacridine	tft	tetrathiofulvalene
metro	1-(2-hydroxyethyl)-2-methyl-5-nitroimidazole	Hvall	δ -valerolactam

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