Explanation for the Bent Structure of $Rh_2Cl_2(CO)_4$

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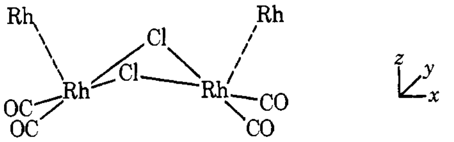
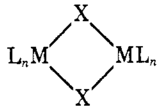
Abstract: SCF-Xα-SW calculations have been carried out on $Rh_2Cl_2(CO)_4$ in both the experimental bent conformation and a hypothetical planar one, in order to determine the reason for the bending. The reason is *not* enhancement of Rh-Rh bonding in the highest-occupied band of mainly Rh 4d levels. Such enhancement is completely absent, because an equal number of bonding and antibonding d-orbital combinations are occupied. However, in the next lowest band of mainly Cl 3p levels (4-23% Rh in character, the bonding orbitals of the Rh_2Cl_2 system) four of the orbitals are bonding and only two are antibonding with respect to *Rh-Rh* interaction. The molecule bends because the resultant lowering of symmetry converts a very weak Rh-Rh π interaction in one of these levels into a stronger one which is mainly σ in character. There is no corresponding antibonding effect in any other level. The resultant Rh-Rh "bond", much weaker than a two-electron interaction, *is* slightly bent below the Rh-Rh axis, but to a much smaller degree than orginally proposed by Dahl et al. Contour maps of the important molecular wave functions are presented, and the ordering of the mainly Rh 4d and Cl 3p levels is explained in detail. The character of the frontier orbitals is discussed.

Dichlorotetracarbonyldirhodium(I), $Rh_2Cl_2(CO)_4$, obtained by reduction of $RhCl_3 \cdot xH_2O$ with CO,[1,2] is perhaps the most important starting material for Rh^I chemistry. Its electronic structure has been widely discussed since publication of its crystal structure, which (see below) showed the molecule to be bent along the Cl-Cl axis, the two square-planar $RhCl_2(CO)_2$ units intersecting at an angle of 124°.[3] The Rh-Rh separation within the molecule is 3.12 Å, short enough to suggest some metal-metal interaction, but considerably longer than normal two-electron Rh-Rh bonds (compare Rh-Rh = 2.73 Å in $Rh_4(CO)_{12}$[4]). There are also fairly close intermolecular contacts to other metal atoms at 3.31 Å perpendicular to the coordination planes.



The overall structure led Dahl et al. to postulate octahedral hybridization of Rh orbitals and hence a "bent metal-metal bond", the bending of the molecule thus being necessary for efficient overlap of the orbitals on each Rh directed opposite the intermolecular-contact direction.[3] The structures of several other $Rh_2Cl_2L_4$ molecules have since appeared; for L_4 = $(CO)_2(PR_3)_2$,[5] $(C_8H_{12})(P(OR)_3)_2$,[6] $(C_2H_4)_4$,[7] and $(C_6H_{10})_4$,[8] the same general geometry is found, with bending angles and Rh-Rh distances in the ranges 116-123° and 3.09-3.17 Å, respectively. In none of these other cases, however, are ligands from other molecules found in analogous positions to the rhodium atoms in $Rh_2Cl_2(CO)_4$. Moreover, in solution, where the intermolecular contacts are certainly broken, elegant studies of the dipole moment[9] and IR spectrum[10] of $Rh_2Cl_2(CO)_4$ show that the molecule is bent with nearly the same angle (122°) as in the solid. The bending phenomenon is thus clearly a consequence of the molecular electronic structure rather than crystal packing. It seems likely, however, that the force responsible for it is comparable in magnitude to packing forces, since $Rh_2Cl_2(C_8H_{12})$ has a completely planar structure[11]—although the immediate Rh coordination sphere is identical with that in $Rh_2Cl_2(C_2H_4)_4$ and $Rh_2Cl_2(C_6H_{10})_4$.

These molecules are but a small subset of the very large number of transition metal complexes of the type I. Some are folded along the X-X line (e.g., $Co_2(CO)_8$); most are not (e.g., $Fe_2S_2(SR)_4^{2-}$ [12]); *n* and the geometry of the terminal ligands vary widely. There have been some notable attempts to provide a general qualitative bonding picture for such compounds.[13,14] Because of their structural diversity, and the varying possibilities for interaction between M-M and M-X bonds, we believe that thorough understanding of the relation of electronic structure to properties for these compounds will be achieved only through quantitative calculations on a number of representative examples. Such calculations have appeared for $Fe_2X_2(CO)_6$, X = S, SCH_3, PR_2, NR_2;[15] $Mn_2(PR_2)_2(CO)_8^{2+,+,0}$,[16] and $Cr_2(PR_2)_2(CO)_8^{0,-,2-}$.[16] In these cases, structure-determining, two-electron metal-metal bonds are found, concentrated in the highest-occupied molecular orbital, and resulting from overlap of d-like orbitals strongly localized on the metals. As will be shown below, the metal-metal interaction which causes $Rh_2Cl_2(CO)_4$ and its analogues to be bent is of a very different, more subtle type.



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Results

Our investigation of this problem has involved comparative SCF-Xα-SW calculations[17] on $Rh_2Cl_2(CO)_4$ in the bent configuration found in the crystal,[3] idealized to C_{2v} symmetry, and in a hypothetical planar configuration of D_{2h} symmetry, with the same bond lengths and Cl-Rh-Cl angle. The coordinate system is shown above; the correlation between representations of C_{2v} and D_{2h} in this coordinate system is given in Table I, along with the spherical-harmonic basis functions of the Rh_2 and Cl_2 units which contribute to each representation. Details of the calculations appear in the Appendix.

For both forms, the calculated energy levels in the range -1.25 to -0.43 hartrees correlate directly, in order of increasing energy, with CO 3σ, Cl 3s, CO 4σ, 5σ, and 1π levels. Only the four 5σ-like orbitals, in the range -0.57 to -0.52 hartree, have significant Rh character (33-45%); they thus represent the four Rh-C σ bonds. From -0.41 to -0.35 hartree there are six Rh-(Cl 3p) bonding levels, with 4-23% metal character. The Rh contribution to these levels is mainly 4d, but strongly hybridized with 5p in some cases for better overlap. From -0.33 to -0.27 hartree are eight mainly Rh 4d levels, representing plus and minus combinations of the d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{z^2} orbitals on the two metals. The maximum carbon character in these levels is 5%, indicating that *covalent* Rh-C π back-bonding is weak (however, the lower six orbitals have 7-16% oxygen character). Of the ten well-defined un-

Table I. Distribution of Rh_2 d and Cl_2 p Basis Functions among Representations of C_{2v} and D_{2h}[a]

Representation of C_{2v}	Representation of D_{2h}	Rh_2 d basis functions and Rh-Rh character[b]		Cl_2 p basis functions and Cl-Cl character[b]	
a_1	a_g	$z^2 + z^2$, $(x^2 - y^2) + (x^2 - y^2)$	(σ)	$p_y - p_y$	(σ)
	b_{1u}	$xz - xz$	$(\pi_\perp)$	$p_z + p_z$	$(\pi_\perp)$
b_1	b_{3u}	$z^2 - z^2$, $(x^2 - y^2) - (x^2 - y^2)$	(σ^*)	$p_x + p_x$	$(\pi_\parallel)$
	b_{2g}	$xz + xz$	$(\pi_\perp{}^*)$		
b_2	b_{2u}	$xy - xy$	$(\pi_\parallel)$	$p_y + p_y$	(σ^*)
	b_{3g}	$yz + yz$	(δ)	$p_z - p_z$	$(\pi_\perp{}^*)$
a_2	b_{1g}	$xy + xy$	$(\pi_\parallel{}^*)$	$p_x - p_x$	$(\pi_\parallel{}^*)$
	a_u	$yz - yz$	(δ^*)		

[a] See text for coordinate system. The bent and planar forms of $Rh_2Cl_2(CO)_4$ belong to C_{2v} and D_{2h}, respectively. [b] σ refers to a σ bonding interaction, σ^* to a σ antibonding interaction, etc. $\parallel$ and $\perp$ mean parallel and perpendicular, respectively, to the molecular plane of the planar form.

Table II. Valence Energy Levels of $Rh_2Cl_2(CO)_4$ between −0.43 and −0.09 hartree, and Their Charge Distributions[a]

		Planar form				Major Rh			Bent form				Major Rh
Level	Energy	%2Rh	2Cl	4C	4O	sph harm[b]	Level	Energy	%2Rh	2Cl	4C	4O	sph harm[b]
$6b_{1g}$	−0.0955	51	15	26	9	$d_{xy}{}^*$	$8a_2$	−0.1110	54	14	24	8	$d_{xy}{}^*$, $d_{yz}{}^*$
$3b_{2g}$	−0.1132	16		51	33	$d_{xz}{}^*$, $p_z{}^*$	$10b_1$	−0.1169	17	1	50	32	$d_{xz}{}^*$, $d_{z^2}{}^*$, $p_z{}^*$
$4b_{1u}$	−0.1200	17	10	42	31	d_{xz}, p_z	$10b_2$	−0.1276	53	12	23	12	d_{xy}, d_{yz}
$7b_{2u}$	−0.1252	57	9	23	11	d_{xy}	$12a_1$	−0.1354	20	7	39	34	d_{xz}, d_{z^2}, p_z
$8a_g$[c]	−0.2797	91	3	5	1	d_{z^2}	$9b_1$[c]	−0.2868	92	2	5	2	$d_{xz}{}^*$, $d_{z^2}{}^*$
$7b_{3u}$	−0.2804	92	2	5	1	$d_{z^2}{}^*$	$11a_1$	−0.2919	90	4	5	1	d_{z^2}, d_{xz}
$3b_{3g}$	−0.3059	72	21	1	7	d_{yz}	$8b_1$	−0.3121	74	14	2	9	$d_{x^2-y^2}{}^*$, $d_{z^2}{}^*$
$3b_{1u}$	−0.3082	73	18	1	9	d_{xz}	$10a_1$	−0.3128	67	22	1	10	d_{z^2}, d_{xz}
$6b_{3u}$	−0.3114	75	12	2	11	$d_{x^2-y^2}{}^*$	$9b_2$	−0.3177	70	22	0	7	d_{yz}, d_{xy}
$7a_g$	−0.3142	72	10	2	16	$d_{x^2-y^2}$	$7a_2$	−0.3277	86	4	1	10	$d_{yz}{}^*$, $d_{xy}{}^*$
$2b_{2g}$	−0.3213	90		0	10	$d_{xz}{}^*$	$9a_1$	−0.3295	72	12	2	14	$d_{x^2-y^2}$, d_{xz}
$2a_u$	−0.3235	90		0	10	$d_{yz}{}^*$	$7b_1$	−0.3300	86	0	0	13	$d_{xz}{}^*$, $d_{z^2}{}^*$
$6b_{2u}$	−0.3574	4	88	7	1	p_y, d_{xy}	$8b_2$	−0.3558	7	86	6	1	d_{yz}, p_y
$5b_{3u}$	−0.3720	10	69	8	13	$d_{x^2-y^2}{}^*$, $p_x{}^*$	$6b_1$	−0.3758	14	69	7	11	$d_{x^2-y^2}{}^*$, $p_x{}^*$
$2b_{3g}$	−0.3791	18	76	0	6	d_{yz}	$7b_2$	−0.3833	18	72	3	7	d_{yz}, d_{xy}
$5b_{1g}$	−0.3861	7	77	8	8	$p_y{}^*$, $d_{xy}{}^*$	$6a_2$	−0.3856	9	77	6	7	$d_{yz}{}^*$, $p_y{}^*$
$2b_{1u}$	−0.3889	18	79	0	3	d_{xz}	$8a_1$	−0.3882	23	70	2	5	d_{z^2}, d_{xz}
$6a_g$	−0.4054	14	74	5	8	$d_{x^2-y^2}$, p_x	$7a_1$	−0.4071	16	71	5	9	$d_{x^2-y^2}$, d_{xz}, p_x

[a] %2Rh, 4C, etc., are the relative amounts of charge within the two rhodium, four carbon, etc., spheres. They are the closest analogue of LCAO "atomic populations"; there is no analogue of "overlap populations". More than 65% (and usually more than 80%) of the charge is within the spheres for all levels except unoccupied $4b_{1u}$ and $3b_{2g}$ in the planar form (32 and 51%, respectively) and their analogues $12a_1$ and $10b_1$ in the bent form (29 and 51%). [b] Spherical-harmonic basis functions contributing more than 10% of the Rh charge are listed in order of decreasing importance. d_{z^2} means a bonding d_{z^2} combination, $d_{xz}{}^*$ an antibonding d_{xz} combination, etc. [c] The highest occupied levels.

occupied levels in the range −0.14 to −0.06 hartree, only two are mainly Rh (the plus and minus $4d_{xy}$ combinations). The rest correlate best with CO 2π antibonding orbitals; they have 10-27% Rh character.

The important orbitals for discussion of the bending phenomenon are the highest two occupied bands of mainly Cl 3p and Rh 4d character, respectively. They are diagrammed in Figure 1, along with the unoccupied mainly $4d_{xy}$ pair for completeness; the most reasonable correspondence between levels in the bent and planar forms, based on symmetry and character, is indicated by dotted lines. Their energies and charge distributions are given in Table II, along with those of the four lowest unoccupied levels (two of which are the mainly $4d_{xy}$ pair). Figures 2-6 depict the wave functions of critical orbitals in the *xz* plane.

Discussion

Reason for the Bending. Even the most cursory inspection of the calculated electronic structure shows that there is no simple, two-electron Rh-Rh bond in $Rh_2Cl_2(CO)_4$. Among the occupied mainly Rh 4d orbitals, there are four of bonding and four of antibonding Rh-Rh character. The bent and planar forms are no different in this respect, although considerably more mixing of the d orbitals occurs in the lower symmetry of the bent form. Any enhancement of Rh-Rh bonding character in particular levels brought about by this mixing is balanced by a corresponding enhancement of Rh-Rh antibonding character in other levels.

Of the six *Rh-Cl* bonding levels, however, four are of bonding and only two of antibonding character with respect to *Rh-Rh* interaction. Examination of wave function contour maps for these levels reveals the reason for the bending: enhanced Rh-Rh bonding in the $8a_1$ level of the bent form, compared to its $2b_{1u}$ analogue in the planar form. This effect is shown in Figure 2. Mixing of d_{z^2} character into the bonding d_{xz}-d_{xz} combination in the lower symmetry converts a very weak, purely π bond into a stronger interaction, mainly of σ type, between "tilted d_{xz}" orbitals. There is no corresponding increase in Rh-Rh antibonding character in any other level. Thus it *is* the d_{z^2} orbitals which bring about the enhanced Rh-Rh interaction which favors bending, but their role is rather different than originally postulated by Dahl et al. The Rh-Rh bond is bent below the Rh-Rh axis, but only slightly.

No other important *net* change in Rh-Rh bonding upon bending is observed, although naturally considerable rehybridization occurs. Mixing of d_{xz} character into the bonding $d_{x^2-y^2} + d_{x^2-y^2}$ combination in the $7a_1$ level ($6a_g$ in the planar

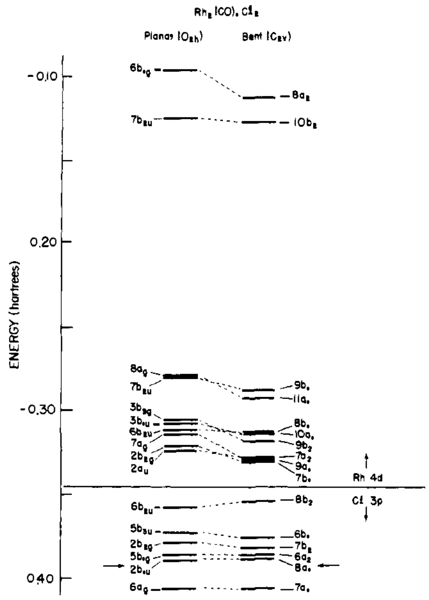

Figure 1. Valence energy levels of $Rh_2Cl_2(CO)_4$ with predominantly Rh 4d or Cl 3p character. The highest occupied levels are $8a_g$ and $9b_1$ for the planar and bent forms, respectively.

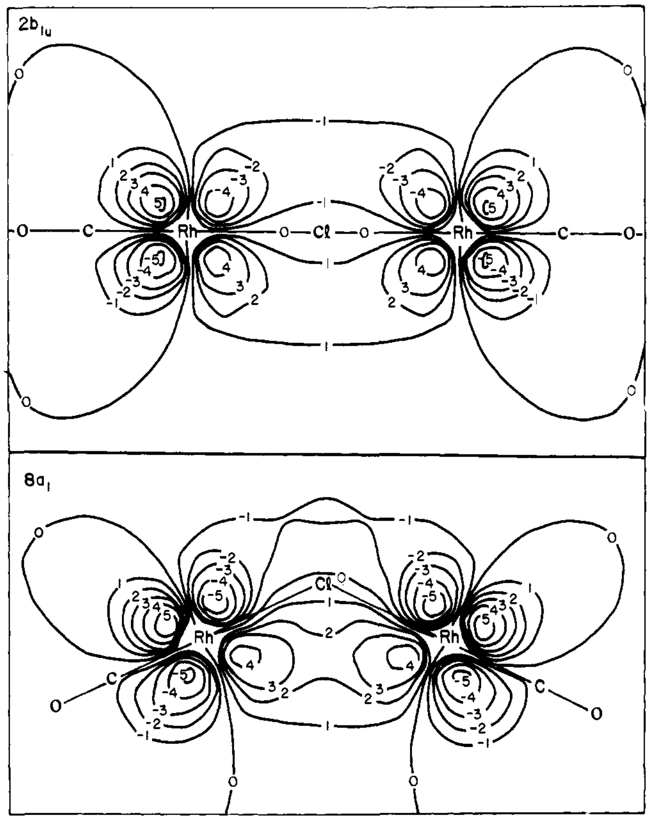

Figure 2. Contour maps of the wave functions for the $2b_{1u}$ and $8a_1$ levels of planar and bent $Rh_2Cl_2(CO)_4$, respectively, showing the enhancement of Rh-Rh bonding upon bending. This and all subsequent maps are in the *xz* plane, so that the molecules are seen in projection; interior contours around Rh are always omitted for clarity. The contour values for all the maps are 0, ±1, ±2, ±3, ±4, ±5 = 0, ±0.02, ±0.04, ±0.06, ±0.09, ±0.13.

form) does not, as shown in Figure 3, significantly enhance the Rh-Rh bonding. In any case, the bonding interaction in this level is essentially cancelled by analogous antibonding character in the $6b_1$ level ($5b_{3u}$ in the planar form). Similar increases in Rh-Rh bonding due to greater d_{xz} character in the

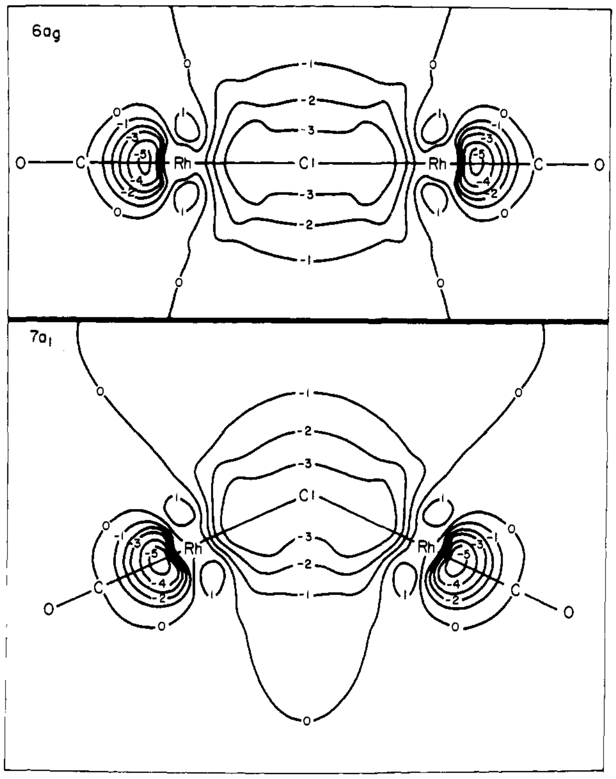

Figure 3. Contour maps of the $6a_g$ and $7a_1$ wave functions of planar and bent $Rh_2Cl_2(CO)_4$, respectively, showing that no significant change in Rh-Rh bonding occurs upon bending.

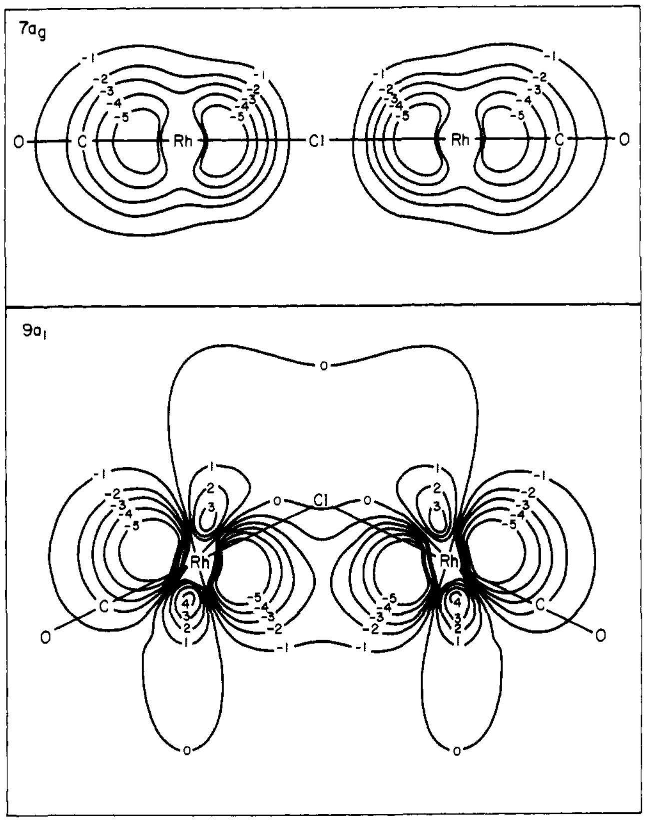

Figure 4. Contour maps of the $7a_g$ and $9a_1$ wave functions of planar and bent $Rh_2Cl_2(CO)_4$, respectively.

$9a_1$ and $11a_1$ levels ($7a_g$ and $8a_g$ in the planar form, respectively), shown in Figures 4 and 5, are likewise cancelled by increased antibonding in the $8b_1$ and $9b_1$ levels ($6b_{3u}$ and $7b_{3u}$ in the planar form, respectively).

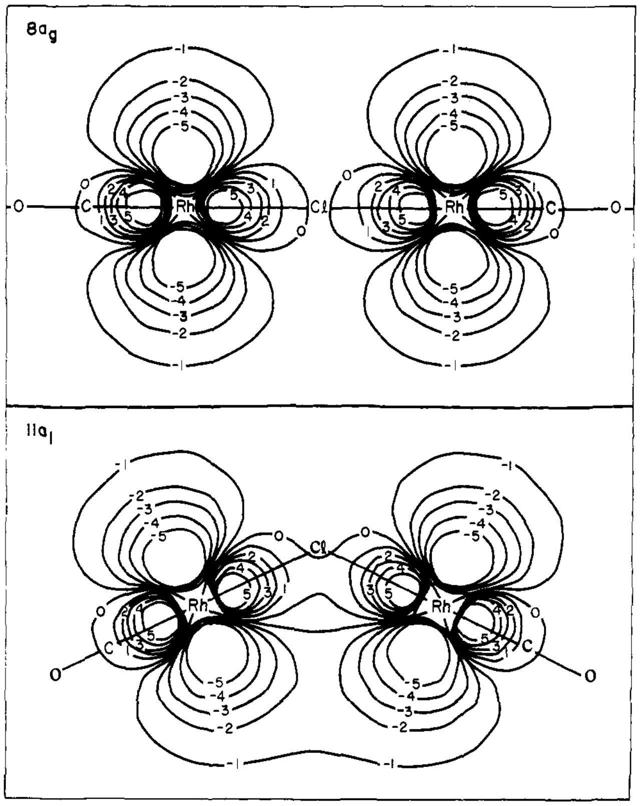

Figure 5. Contour maps of the $8a_g$ and $11a_1$ wave functions of planar and bent $Rh_2Cl_2(CO)_4$, respectively.

Ordering of the Energy Levels. In the planar form, the ordering of the Rh 4d-like orbitals corresponds closely to the predictions of a classical ligand-field treatment for a square-planar complex, very slightly perturbed by splitting between the plus and minus combinations of orbitals on the two metals. Averaging the energies of the plus and minus pairs gives the ordering (energies, in hartrees, in parentheses) xz,yz (-0.3147) $\approx x^2 - y^2$ (-0.3128) $< z^2$ (-0.2800) $\ll xy$ (-0.1103), the last being unoccupied as expected for a d^8 system. In three of the five cases the Rh-Rh antibonding combination lies lower than the bonding combination, indicating that the difference in energy is primarily due to differing interactions with ligand orbitals, and further illustrating the weakness of Rh-Rh bonding. In the bent molecule, there is no longer a single orbital corresponding to each d function, due to mixing in the lower symmetry, but there are still four occupied pairs of d-like orbitals fairly close in energy and one unoccupied pair at higher energy. The only qualitative change from the above discussion for the planar form is that the Rh-Rh bonding "d_{z^2}" combination ($11a_1$, now heavily mixed with d_{xz}) becomes slightly lower in energy than the antibonding combination ($9b_1$).

The ordering of the six mainly Cl 3p orbitals in the planar form is consistent with the simplest qualitative concept about relative effectiveness of Rh-Cl bonding; namely, the energies increase as the number of nodal surfaces passing through or near the Rh_2Cl_2 system increases. $6a_g$ has zero, $2b_{1u}$ one, $5b_{1g}$ and $2b_{3g}$ two, and $5b_{3u}$ and $6b_{2u}$ three such surfaces. Moreover, among the pairs with the same number of nodes the lower member represents σ- and the upper member π-type Rh-Cl bonding. The considerable rehybridization which occurs upon bending does not change this ordering. It is very different from the ordering proposed for complexes of type I in general by Mason and Mingos.[13] Their basic concept, that the M-M and M-X bonds strongly interact in such systems, is, however, certainly supported by our results.

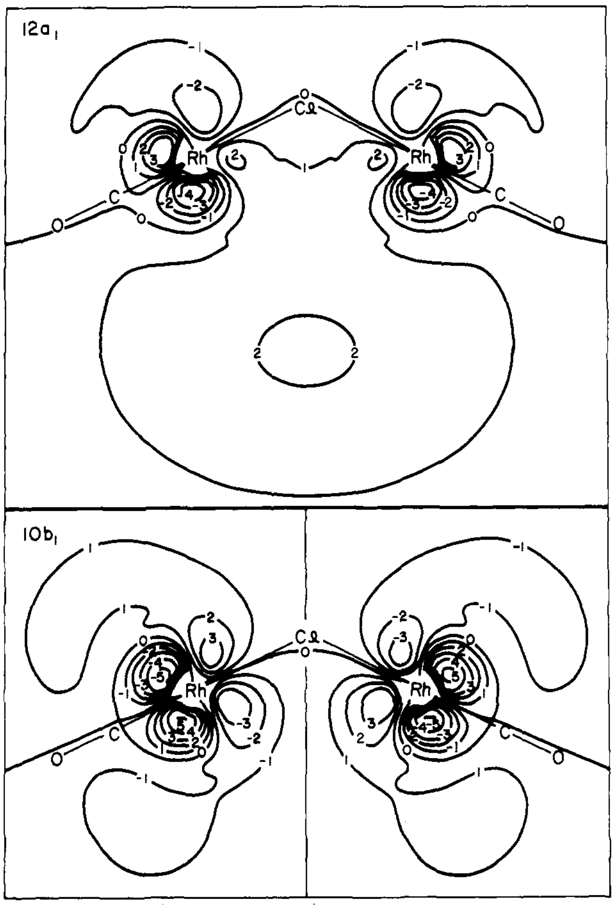

Figure 6. Contour maps of the wave functions for the unoccupied $12a_1$ and $10b_1$ orbitals of bent $Rh_2Cl_2(CO)_4$.

Table III. Atomic- and Outer-Sphere Radii (bohrs) used for $Rh_2Cl_2(CO)_4$

Region	Radius, planar form	Radius, bent form
Rh	2.280	2.270
Cl	2.347	2.329
C	1.583	1.577
O	1.609	1.603
Outer	9.430	8.890

Reactivity of $Rh_2Cl_2(CO)_4$. We conclude with a description of the frontier orbitals of the bent form. The predicted HOMO is $9b_1$. Contour maps show it to be a nearly exact antibonding counterpart of the $11a_1$ level depicted in Figure 5, i.e., a minus combination of "tilted d_{z^2}" orbitals. The Rh character of both $9b_1$ and $11a_1$ is about 90% 4d and 10% 5s; there is essentially no $5p_z$ contribution to either. Of the four lowest unoccupied orbitals, two ($10b_2$ and $8a_2$) are largely the plus and minus $4d_{xy}$ combinations, hybridized with $4d_{yz}$ to bring them into the $RhCl_2(CO)_2$ planes, and interacting with the ligands in an antibonding manner. The other two have mainly CO 2π character. Their ca. 20% Rh contribution is from plus (in $12a_1$) and minus (in $10b_1$) combinations of "tilted d_{xz}/p_z" functions. Of all the calculated orbitals, both occupied and unoccupied, these are the two with largest Rh $5p_z$ character; the form which the extremely diffuse $5p_z$ function gives them in the xz plane is shown by the contour maps in Figure 6. We emphasize, however, that the predominant CO 2π character of both levels lies out of the plane of these maps.

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Appendix: Details of the Calculations

Coordinates in atomic units to the nearest 0.000 01 bohr were derived from average crystallographic[3] bond parameters for $Rh_2Cl_2(CO)_4$, namely Rh-Cl = 2.36, Rh-C = 1.81, C-O = 1.18 Å, and angle Cl-Rh-Cl = 85°, using the relation 1 bohr = 0.529 177 Å. Schwarz's α_{HF} values[18] were used for the atomic exchange parameters; for the extramolecular and intersphere regions, a weighted average of the atomic α's was employed, the weights being the number of *valence* electrons in the neutral atoms. The outer-sphere center positions were computed using the same sort of average of the atomic positions. Overlapping sphere radii were obtained by our nonempirical procedure;[19] they are given in Table III.

The highest-order spherical harmonic basis functions used were $l = 4$ for the outer region, 2 for Rh, and 1 for Cl, C, and O. Core energy levels were never frozen; in each SCF iteration they were calculated explicitly using only the surrounding-atomic-sphere potential. Iterations were continued until convergence to ±0.0003 hartree or better was attained for all levels. The SCF potentials were used to search for excited-state levels up to −0.05 hartree. The final virial ratio was $-2T/V = 1.0006$ for both molecules.

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Electron Transfer Processes in Organoplatinum Complexes. Oxidation and Cleavage of Dialkylplatinum(II) with Hexachloroiridate(IV)

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Abstract: Dialkyl(bisphosphine)platinum(II) complexes are readily oxidized by hexachloroiridate(IV) to afford two principal types of products depending on the structure of the alkyl group and the coordinated phosphine. Thus, $Me_2Pt^{II}(PMe_2Ph)_2$ undergoes oxidation to dimethylplatinum(IV) species, whereas the diethyl analogue $Et_2Pt^{II}(PMe_2Ph)_2$ affords EtCl and monoethylplatinum(II) species by oxidative cleavage of one Et-Pt bond. The cleavage of the Me-Pt bond can be induced by replacement of the phosphine to $Me_2Pt^{II}(PPh_3)_2$, which competitively undergoes oxidation to dimethylplatinum(IV) species as well as oxidative cleavage to MeCl and methylplatinum(II) species. The stoichiometric requirement of 2 equiv of hexachloroiridate(IV) remains invariant for each dialkylplatinum(II), independent of the products of oxidation. The energetics and kinetics as well as the observation of alkyl radicals by spin trapping and oxygen scavenging support a mechanism involving the rate-limiting electron transfer from dialkylplatinum(II) to hexachloroiridate(IV). The selectivity in product formation leading to cleavage and/or further oxidation is associated directly with the paramagnetic intermediate $R_2PtL_2^+$ (formally a Pt(III) species), the stability of which is discussed in relationship to the strengths of the alkyl-platinum bonds and the phosphine ligands. These processes are compared to the reactions of related radical ions derived by electron transfer from alkylmercury(II), lead(IV), and cobalt(III) complexes.

Previous studies of the oxidation of organoplatinum(II) complexes have been concerned mainly with the synthesis of organoplatinum(IV) complexes by oxidative addition using halogens and alkyl halides.[1-3] The mechanism of these reactions has generally been considered to proceed through an S_N2 transition state such as that postulated for the reaction of alkyl halides with the more extensively studied Vaska-type complexes *trans*-$IrX(CO)L_2$.[4] Recently, there have been reports[5] suggesting the participation of free radical processes in the reaction of *trans*-$IrX(CO)L_2$ with alkyl halides, in addition to S_N2 processes.

We examined the oxidation of dialkylplatinum(II) complexes by the one-electron oxidant hexachloroiridate(IV)[6] in order to delineate free radical processes in organoplatinum intermediates in comparison with their nontransition metal counterparts, dialkylmercury and tetraalkyllead and -tin compounds, described earlier.[7] Retention as well as cleavage of the alkyl-platinum bonds are observed during the oxidation of dialkyl(bisphosphine)platinum(II) complexes, the extent of each depending on the structures of the alkyl group and the coordinated phosphine. The fate of the alkyl groups and the identity of the inorganic products, including platinum(II) and -(IV) complexes as well as reduced iridium(III), strongly implicate a paramagnetic dialkylplatinum(III) species as a prime intermediate following electron transfer. Factors involved in (a) the cleavage of this intermediate to alkyl radicals and alkylplatinum(II) or (b) the further oxidation to dialkylplatinum(IV) are important considerations in this study.