Table VI. Rh-Rh and Rh-L Distances (Å) in $Rh_2(O_2CR)_4L_2$ Molecules[a]

compd no.	R	L	Rh-Rh	Rh-L	ref
1	CMe_3	H_2O	2.371 (1)	2.295 (2)	14
2	CH_3	H_2O	2.3855 (5)	2.310 (3)	15
3	CH_3	py	2.3963 (2)	2.227 (3)	16
4	CH_3	Me_2SO	2.406 (1)	2.451 (1)	14
5	C_2H_5	Me_2SO	2.407 (1)	2.445 (1)	17
6	CH_3	THT	2.413 (1)	2.517 (1)	14
7	CH_3	CO	2.4191 (3)	2.091 (3)	18
8	CH_3	PPh_3	2.4505 (2)	2.477 (1)	4
9	CH_3	$P(OPh)_3$	2.4434 (6)	2.412 (1)	4
10	CF_3	PPh_3	2.486 (1)	2.494 (2)	this work
11	CF_3	$P(OPh)_3$	2.470 (1)	2.422 (2)	this work
12	CF_3	Me_2SO	2.420 (1)	2.240 (3)	17
13	CF_3	EtOH	2.403 (6)	2.27 (1)	19

[a] Equivalent distances and angles have been averaged where appropriate.

We thus focus attention on the decreases in the Rh–P bond lengths, by ca. 0.07 Å, upon replacing PPh_3 by $P(OPh)_3$.

We believe that steric factors alone may account for this. The steric repulsions between the atoms of the central $Rh_2(O_2CCF_3)_4$ unit and the PY_3 ligands are expected to be considerably greater at a given Rh–P distance for Y = C_6H_5 than for Y = OC_6H_5. This is apparent qualitatively by comparing Figures 1 and 2; the phenyl groups in **2** are directed outward by the orientations around the P–OC_6H_5 bonds, whereas the phenyl groups in **1** are required to approach the $Rh_2(O_2CCF_3)_4$ unit rather closely. This great steric difference between PPh_3 and $P(OPh_3)_3$ was described semiquantitatively some time ago by Tolman[13] in terms of his cone-angle criterion. On a scale ranging from about 100° to 200° for the commonly used PY_3 ligands, PPh_3 and $P(OPh_3)_3$ have cone angles of 145 and 121°, respectively. Thus, the ~0.07 Å greater Rh–PPh_3 distance could well be caused by the greater steric demand of PPh_3 compared to that of $P(OPh)_3$. It is also possible that, as suggested by Christoph et al.,[4] the bond radius of phosphorus is smaller in $P(OPh)_3$ than in PPh_3.

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Registry No. **1**, 77966-16-6; **2**, 77966-17-7; $Rh_2(O_2CCF_3)_4$, 31126-95-1.

Supplementary Material Available: Table V (least-squares planes and dihedral angles) and tables of observed and calculated structure factors for the two compounds (25 pages). Ordering information is given on any masthead page.

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Electronic Structure of Phosphine Adducts of Tetrakis(carboxylato)dirhodium(II). Pronounced Influence of Axial Ligands

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The electronic structure of phosphine adducts of $Rh_2(O_2CR)_4$ has been investigated by means of an Xα–SW molecular orbital calculation on the model compound $Rh_2(O_2CH)_4(PH_3)_2$. The method used to perform a calculation on this low-symmetry (C_{2h}) molecule containing a fragment of high symmetry (D_{4h}) is described in detail. The qualitative nature of the interactions between the phosphine ligands and the $Rh_2(O_2CH)_4$ moiety are very similar to those reported for $Rh_2(O_2CH)_4(H_2O)_2$; the magnitudes of these interactions are far different, however, resulting in a very different electronic structure. Strong σ donation by the phosphine ligands results in a highest occupied molecular orbital of Rh–Rh σ and Rh–P σ^* symmetry, consistent with the ESR spectra of the radical cations of phosphine adducts. Contrary to previous assertions, no Rh→P back-bonding is evident. The radical cations of the phosphine adducts are predicted to have longer Rh–Rh bonds than those found in the neutral adducts, in contrast to the decrease in Rh–Rh bond length found for $[Rh_2(O_2CCH_3)_4(H_2O)_2]^+$.

Introduction

The rapid growth in the synthetic and structural chemistry of dinuclear transition-metal complexes containing strong metal–metal bonds has provided a wealth of information about the nature of metal–ligand and metal–metal interactions.[1] These systems provide interesting challenges to quantum chemical methods in that they afford compounds having a great variety of metals and ligands within a common structural genre. Discussions of the electronic structural aspects of dinuclear transition-metal complexes have not been without controversy, as in the case of the $Cr_2(O_2CR)_4L_2$ systems in which SCF-HF calculations without CI[2] have been found to give conclusions inconsistent with structural and more complete theoretical results.[3-5] Discussions of the electronic structures

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and spectra of other compounds containing quadruple bonds between pairs of group 6 or group 7 metal atoms have been marked by controversies on some aspects.[6-9]

The chemistry of rhodium(II) tetracarboxylato species of general formula $Rh_2(O_2CR)_4L_2$ has received much attention in recent years, largely through the structural efforts of Christoph and Koh[10-12] and of Cotton and Felthouse.[13-16] The bonding in these d^7–d^7 dimers has also been the subject of much discussion, and there has been disagreement concerning the nature of the metal–metal and, more recently, of the metal–ligand interactions as well. It was originally suggested that $Rh_2(O_2CCH_3)_4(H_2O)_2$ might have a formal Rh–Rh triple bond in which the six electrons in excess of the quadruply bonded $\sigma^2\pi^4\delta^2$ configuration occupy the δ^* and two nonbonding σ orbitals.[17] However, Norman and co-workers subsequently carried out an Xα–SW molecular orbital calculation that indicates a Rh–Rh single bond arising from a $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$ configuration.[18,19] A similar proposal had also been made by Dubicki and Martin[20] on the basis of extended Hückel calculations. Christoph and Koh have attempted to answer this bond-order question by employing the propensity of the rhodium carboxylates to bind in the axial positions strong π acids such as carbon monoxide, phosphines, and phosphites. Their results do not provide an unambiguous description of the Rh–Rh bonding and pose the further question of how much back-bonding, if any, occurs in the π-acid adducts.

Recently Kawamura and co-workers have succeeded in obtaining ESR spectra of a number of radical cations of general formula $[Rh_2(O_2CR)_4(PY_3)_2]^+$.[21,22] They propose that their results are most consistently explained by assuming, first, a formal Rh–Rh single bond and, second, that the unpaired electron resides in an orbital of σ symmetry. The second of these assumptions is seemingly at odds with Xα–SW calculations on $Rh_2(O_2CH)_4(H_2O)_2$ and $[Rh_2(O_2CH)_4(H_2O)_2]^+$,[18,19] which would appear to suggest that the unpaired electron should have diatomic δ^* symmetry. Attention is thus focused on the need to investigate quantitatively the electronic differences between dirhodium complexes with "traditional" σ-donor axial ligands such as water, ethers, and amines and those complexes with ligands in which π acceptance as well as σ donation can occur.

In response to the situation just outlined we have carried out, and report here, an Xα–SW calculation on $Rh_2(O_2CH)_4(PH_3)_2$, a model of the structurally characterized[23] $Rh_2(O_2CR)_4(PY_3)_2$ species. The details of performing a calculation on such a low-symmetry (C_{2h}) species will be presented, and the results will be shown to be quite consistent with the ESR spectra, leading to a Rh–Rh single bond formulation in which the strongly σ-donating PH_3 groups cause an orbital of Rh–Rh σ and Rh–P σ^* character to become the highest occupied orbital. It will further be shown that the phosphine ligand does not π back-bond to any significant degree, a result that is consistent with structural work on a variety of phosphine and phosphite adducts. Finally, we will comment on the relation of our calculation to those previously reported for rhodium carboxylate systems and try to formulate some general conclusions about the bonding in these and related systems.

Table I. Bond Lengths and Angles, Atomic Sphere Radii, and Statistical Exchange Parameters for $Rh_2(O_2CH)_4(PH_3)_2$

atoms	lengths, Å	atoms	angles, deg
Rh–Rh	2.45	Rh–Rh–O	87.4
Rh–P	2.48	Rh–O–C	119.6
Rh–O	2.04	O–C–H	117.0
O–C	1.27	Rh–Rh–P	180.0
C–H	1.08	Rh–P–H	115.4
P–H	1.42	H–P–H	103.0

atom	sphere radius, Å	α
outer sphere	5.2648	0.74075
Rh	1.3004	0.70217
O	0.9223	0.74447
C	0.8495	0.75728
H(C)	0.6841	0.77725
P	1.2869	0.72620
H(P)	0.7683	0.77725

Computational Section

The Rh–Rh and Rh–P bond lengths used in the calculation of the electronic structure of $Rh_2(O_2CH)_4(PH_3)_2$ were taken from the crystal structure of $Rh_2(O_2CCH_3)_4(PPh_3)_2$.[23] The Rh–O distances and the bond lengths and angles of the formate ligands were identical with those used by Norman and Kolari in their calculation on $Rh_2(O_2CH)_4$[18] and are within the ranges of structural parameters generally found in dirhodium tetracarboxylate systems. The P–H distance was taken from the gas-phase electron diffraction study of PH_3,[24] and the H–P–H angle was chosen to be consistent with the observed C–P–C angles found in coordinated trialkyl- or triarylphosphines. The $Rh_2(O_2CH)_4$ fragment was idealized to D_{4h} point symmetry while the whole complex was idealized to C_{2h} point symmetry with the two PH_3 groups in an axially staggered geometry. The assumed bond lengths and angles are summarized in Table I.

Overlapping atomic sphere radii were taken to be 89% of the atomic number radii for a superposition of neutral atomic Herman–Skillman charge densities,[25] a value that generally leads to results in accord with Norman's nonempirical criterion for sphere radius selection.[26] α values were taken from the compilation of Schwarz.[27] The sphere radii and α parameters used are summarized in Table I.

The potential numerical difficulties of performing an Xα–SW calculation on a low-symmetry (C_{2h}) species containing a high-local-symmetry (D_{4h}) fragment were circumvented in the following manner. The $Rh_2(O_2CH)_4$ fragment was converged under D_{4h} symmetry in analogy with other dimetal

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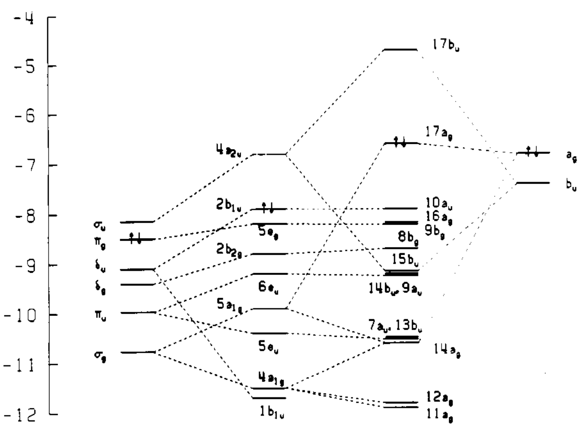

Figure 1. Molecular orbital diagram of the correlation of the orbitals of $Rh_2(O_2CH)_4(PH_3)_2$ to those of Rh_2, $Rh_2(O_2CH)_4$, and $(PH_3)_2$. Only those levels involved in Rh–Rh and Rh–P bonding or antibonding are shown. Arrows indicate the highest occupied orbital. The $4a_{2u}$ orbital of $Rh_2(O_2CH)_4$ is the lowest unoccupied orbital while the $17b_u$ MO of $Rh_2(O_2CH)_4(PH_3)_2$ is the second lowest unoccupied orbital (see text).

tetracarboxylate calculations. The converged potential of this calculation was used as a starting potential for the $Rh_2(O_2CH)_4$ fragment in $Rh_2(O_2CH)_4(PH_3)_2$, in which a minimal basis of partial waves in C_{2h} was used. Following convergence in this basis, more basis functions were added to include all spherical harmonics through $l = 6$ on the outer sphere, through $l = 3$ on Rh, through $l = 2$ on P, through $l = 1$ on C and O, and $l = 0$ on H.

It is both economical and convenient to perform the calculation in this fashion. Calculation of the structure of the $Rh_2(O_2CH)_4$ fragment under higher symmetry is computationally much cheaper than starting the calculation under C_{2h} symmetry since many of the D_{4h} energy levels transfer to the lower symmetry with only a very small change in value. More important, though, is the ease of establishing a one-to-one correspondence of the energy levels of $Rh_2(O_2CH)_4$ from higher to lower symmetry; this minimizes the possibility of "missing" an energy level in the energy search, a pervasive problem in Xα–SW calculations on low-symmetry systems.

The energy levels for Rh_2 and $(PH_3)_2$ were obtained from the appropriate parts of the converged potential of $Rh_2(O_2CH)_4(PH_3)_2$. They were not converged further; i.e., they are not the self-consistent energies which would be obtained from calculations on these species but rather represent the energies of these fragments within the whole molecule. Electronic transition energies were calculated in the usual fashion with the use of Slater's transition-state formalism.[28]

Results and Discussion

The correlation of the molecular orbitals of $Rh_2(O_2CH)_4(PH_3)_2$ with those of its component fragments is shown in Figure 1. The energy levels of Rh_2 do *not* represent the self-consistent levels of the neutral diatomic molecule; it has been recognized recently that the energetics of neutral transition-metal diatomic molecules are significantly different from those of the higher formal oxidation-state dimetal units to which ligands are bound.[29-32] Rather, we have obtained orbitals of Rh_2 appropriate for direct comparison to those in ligated complexes in the following manner. Following convergence of the potential of $Rh_2(O_2CH)_4(PH_3)_2$, the Rh and outer sphere portions of it were searched for energy levels under $D_{\infty h}$ symmetry. The resulting energy levels, shown in Figure 1, were not converged further, as they represent the levels of Rh_2 "in situ". As such they correspond to $Rh_2{}^{q+}$, $0 < q < 4$, in which the formal $Rh_2{}^{4+}$ unit has had its positive charge reduced by acceptance from the ligands. The π_g orbital is shown as the doubly occupied HOMO, but this is for convenient analogy to $Rh_2{}^{4+}$ only. The energy levels of Rh_2 calculated in this manner correspond to the usual manifold of metal-metal bonding levels derived from the 4d atomic orbitals, i.e., $\sigma_g < \pi_u < \delta_g < \delta_u < \pi_g < \sigma_u$. The 5s- and 5p-based molecular orbitals which are so prevalent and important to the discussion of *neutral* metal diatomics[29-32] are still at a much higher energy.

The interaction of the four formate ligands with Rh_2 produces the energy levels depicted for $Rh_2(O_2CH)_4$. The bonding characteristics of these orbitals have been discussed at length by Norman et al.[18] When the levels obtained for $Rh_2(O_2CH)_4(PH_3)_2$ are compared to those of $Rh_2(O_2CH)_4$, it is noted that those of the latter which are derived from the π_u, δ_g, δ_u, and π_g orbitals of Rh_2 are energetically unperturbed by the addition of axial phosphine ligands. Analysis of these orbitals indicates that they contain essentially no phosphine character and are indeed identical with the π, δ, δ^*, and π^* levels of $Rh_2(O_2CH)_4$. Therefore, we shall at present focus only on the orbitals of Rh–Rh of σ_g and σ_u symmetry.

The nearly pure d_{z^2} σ_g orbital of Rh_2 mixes with the lone pairs of the formate ligands, resulting in the formation of the $4a_{1g}$ and $5a_{1g}$ MO's of $Rh_2(O_2CH)_4$ which are Rh–O bonding and antibonding, respectively (cf. Figure 3 of ref 18). It should be noted that to a first approximation, since both the $4a_{1g}$ and $5a_{1g}$ MO's of $Rh_2(O_2CH)_4$ are fully occupied, this interaction will have no effect on the Rh–Rh σ bond. It is expected that these two orbitals, being of the same symmetry and necessarily orthogonal, would be induced to mix strongly in the presence of strong axial donors. The unoccupied $4a_{2u}$ MO of $Rh_2(O_2CH)_4$ is derived from the σ_u orbital of Rh_2, and, being more energetically removed from the formate lone pair levels, it has greater Rh character (76%) than either the $5a_{1g}$ (53%) or $4a_{1g}$ (48%) MO's. In the absence of axial ligands, the $4a_{2u}$ orbital is the LUMO of the complex.

The energetics of the $(PH_3)_2$ ligand group were obtained in a manner analogous to that used for Rh_2, except that C_{2h} symmetry was maintained. The six P–H bonding levels ($2\ a_g + a_u + b_g + 2\ b_u$) were found to be entirely noninteracting with the rest of the molecule and will be discussed no further. This leaves two lone-pair orbitals of a_g and b_u symmetry to interact with the metal. The relevance of virtual P 3d orbitals will be discussed later. These lone pairs are expected to be nearly degenerate because of their spatial separation; in fact, the a_g orbital is at slightly higher energy. This may be because of greater mixing of P–H antibonding character in this level, or it may be an artifact of our method for determining their energies.

The $(PH_3)_2$ a_g lone-pair orbital is expected to, and does, interact most strongly with the $5a_{1g}$ orbital of $Rh_2(O_2CH)_4$; it is both energetically and spatially favored over the $4a_{1g}$ MO. From this interaction come the $14a_g$ and $17a_g$ MO's of $Rh_2(O_2CH)_4(PH_3)_2$ which are Rh–P bonding and antibonding, respectively (Figures 2 and 3). The characters of these orbitals (Table II) indicate that the Rh–P interaction is a strong one as was seen for the Rh–O interaction in $Rh_2(O_2CH)_4(H_2O)_2$. We shall return to the comparative energetics of the Rh–P and Rh–O interactions presently.

The $(PH_3)_2$ b_u lone-pair orbital strongly interacts with the empty $4a_{2u}$ (σ^*) orbital of $Rh_2(O_2CH)_4$, generating the Rh–P

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Table II. Comparison of the Energetics and MO Contributions of the L-Rh-Rh-L σ Framework in $Rh_2(O_2CH)_4(PH_3)_2$ (This Work) and $Rh_2(O_2CH)_4(H_2O)_2$[18]

modes of interaction		$Rh_2(O_2CH)_4(PH_3)_2$					$Rh_2(O_2CH)_4(H_2O)_2$				
Rh-Rh	Rh-L	MO	ε, eV	% Rh	% $(O_2CH)_4$	% $(PH_3)_2$	MO	ε, eV	% Rh	% $(O_2CH)_4$	% $(H_2O)_2$
σ*	σ*	$17b_u$[a]	−4.72	62	11	27	$8b_{1u}$[a]	−3.70	78	14	8
σ	σ*	$17a_g$	−6.58	31	4	65	$8a_g$	−7.29	57	15	28
σ*	σ	$15b_u$	−9.15	34	11	55	$4b_{1u}$	−10.10	16	6	78
σ	σ	$14a_g$	−10.62	35	49	16	$6a_g$	−10.70	44	3	53

[a] This orbital is unoccupied.

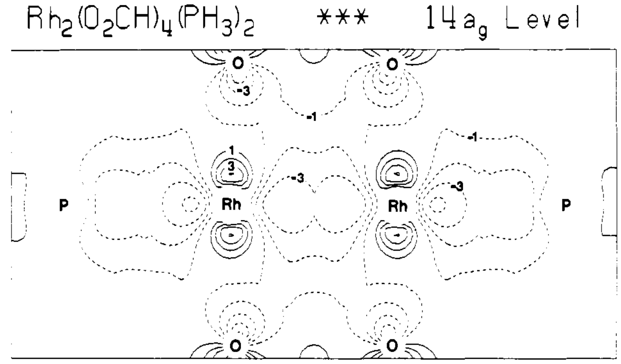

Figure 2. Contour map of the $14a_g$ molecular orbital of $Rh_2(O_2CH)_4(PH_3)_2$. The map is in the horizontal mirror plane containing the Rh atoms, the P atoms, two of the formate ligands, and two of the P-H bonds. Contour values for this and subsequent plots are ±1, ±2, ±3, ±4, ±5 = ±0.03, ±0.06, ±0.09, ±0.12, ±0.15 e/Å^3, respectively.

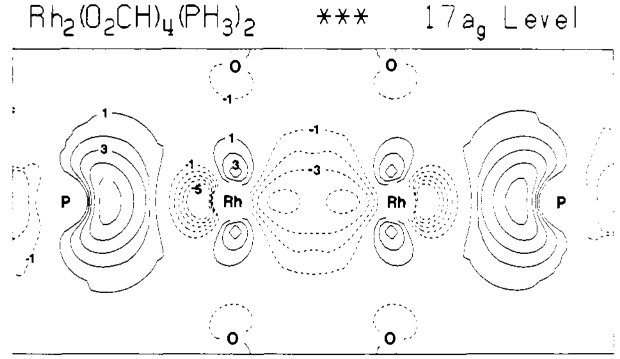

Figure 3. Contour map of the $17a_g$ molecular orbital of $Rh_2(O_2CH)_4(PH_3)_2$. This orbital is the HOMO of the complex.

bonding $15b_u$ and antibonding $17b_u$ levels, which are occupied and unoccupied, respectively (Figures 4 and 5; Table II). It is interesting to note that the $17b_u$ orbital is destabilized to such an extent that it is not the LUMO of the complex (the analogous $8b_{1u}$ MO of $Rh_2(O_2CH)_4(H_2O)_2$ is the LUMO of that complex[18]). Rather, the lowest virtual orbital is the $16b_u$ MO (not shown in Figure 1) which is $Rh-O_2CH$ antibonding and lies ~0.4 eV lower in energy than the $17b_u$ MO. As was the case for the dihydrate complex, it is these $15b_u$ and $17b_u$ levels which primarily account for Rh-L bonding by allowing donation from the lone pairs of the axial ligands into the formally empty σ* orbital of $Rh_2(O_2CH)_4$. Inspection of Table II clearly indicates that the phosphine ligands donate charge more effectively than do water ligands. The greater introduction of Rh-Rh σ* character by phosphine ligands is consistent with the longer Rh-Rh bond found for $Rh_2(O_2CCH_3)_4(PPh_3)_2$ (2.45 Å)[23] than for $Rh_2(O_2CCH_3)_4(H_2O)_2$ (2.39 Å).[17]

PH_3 vs. H_2O as an Axial Ligand. The description of the Rh-Rh and Rh-P bonding presented above is analogous to the analysis of the bonding in $Rh_2(O_2CH)_4(H_2O)_2$ put forth by Norman and Kolari.[18] The Rh-Rh bond is still derived from the formally singly bonded $\sigma^2\pi^4\delta^2\pi^{*4}\delta^{*2}$ configuration of Rh_2, and there are no surprising new interactions induced by the PH_3 ligands. It is clear, however, from structural and spectroscopic studies that there are large differences between the effects of PR_3 and H_2O on the $Rh_2(O_2CH)_4$ framework, and these must be due to the magnitude and energetics of the $Rh-PH_3$ interaction relative to the $Rh-OH_2$ one. In particular, if a consistent, believable bonding scheme is to be achieved, it is essential to explain the axially symmetric ESR spectrum of $[Rh_2(O_2(CH_3))(PPh_3)_2]^{+}$[22] vis-à-vis the prediction of a half-filled orbital of Rh-Rh δ* symmetry in $[Rh_2(O_2CH)_4(H_2O)_2]^{+}$.[19] In this section we will address the differences between phosphines and water as axial ligands in greater detail.

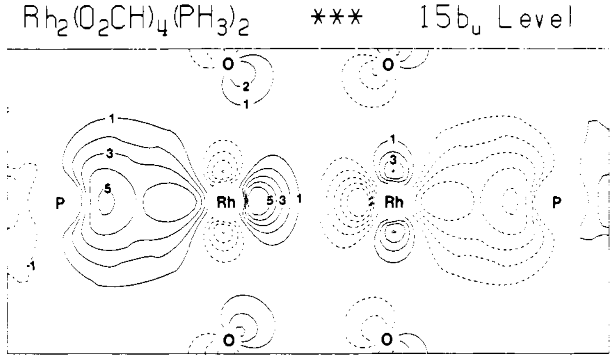

Figure 4. Contour map of the $15b_u$ molecular orbital of $Rh_2(O_2CH)_4(PH_3)_2$.

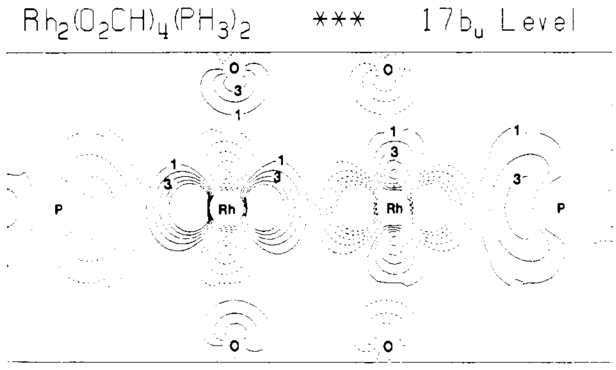

Figure 5. Contour map of the $17b_u$ molecular orbital of $Rh_2(O_2CH)_4(PH_3)_2$. This orbital is unoccupied.

In the absence of severe orbital rearrangement, the interaction between the Rh-Rh σ and σ* MO's of $Rh_2(O_2CH)_4$ and axial lone pairs will be a function of both the spatial overlap and the energetic difference of the interacting orbitals; Christoph and Koh[11] have used these criteria in attempting an elucidation of σ vs. π bonding. In order to assess the differences between PR_3 and H_2O as axial ligands, it is therefore necessary to gauge the spatial extent of the lone pairs and their energetic closeness to the $4a_{1g}$, $5a_{1g}$, and $4a_{2u}$ MO's of $Rh_2(O_2CH)_4$. It has been demonstrated that, within the series of usual axial ligands (i.e., H_2O, NR_3, PR_3, CO), energetic differences dominate, and we shall concentrate on these.

Norman and Kolari have compared the calculated orbital energies of the lone pairs of free H_2O with those of $Rh_2(O_2CH)_4$ (cf. Figure 1 of ref 18). It is found that the H_2O σ lone pair is roughly at the same energy as the $4a_{1g}$ MO of $Rh_2(O_2CH)_4$, and as such should interact with the orbitals of $Rh_2(O_2CH)_4$ in the order $4a_{1g} > 5a_{1g} > 4a_{2u}$. Table III of ref 18 indicates that this is indeed the case. The $6a_g$ MO of $Rh_2(O_2CH)_4(H_2O)_2$ contains nearly equal contributions from the Rh atoms and the H_2O ligands, and the Rh–O_2CH interaction, although quite small, is Rh–O bonding as is the $4a_{1g}$ orbital of $Rh_2(O_2CH)_4$. The $8a_g$ MO of $Rh_2(O_2CH)_4(H_2O)_2$ represents weaker mixing of the Rh atoms and H_2O ligands, and it is Rh–O_2CH antibonding, indicative of interaction primarily with the $5a_{1g}$ MO of $Rh_2(O_2CH)_4$. The lone pairs of the water ligands do not interact strongly with the $4a_{2u}$ MO of $Rh_2(O_2CH)_4$ from which they are energetically far removed, and the resulting $4b_{1u}$ and $8b_{1u}$ MO's of $Rh_2(O_2CH)_4(H_2O)_2$ are localized to a high degree on the water ligands and Rh atoms, respectively.

The situation is very different for axial phosphine ligands. Our "in situ" method of determining the energy of the phosphine lone-pair orbitals places them much closer in energy to the $4a_{2u}$ MO of $Rh_2(O_2CH)_4$, and as such the interaction order is expected to be $4a_{2u} > 5a_{1g} > 4a_{1g}$. To a large extent this is the case. The $14a_g$ MO of $Rh_2(O_2CH)_4(PH_3)_2$ contains a comparatively small contribution from the phosphine ligands. As mentioned earlier, the $15b_u$ and $17b_u$ MO's of $Rh_2(O_2CH)_4(PH_3)_2$ indicate much stronger donation from the axial ligands into the $4a_{2u}$ MO of $Rh_2(O_2CH)_4$ than do their counterparts in the dihydrate complex, consistent with the observed structural parameters. This energetically induced increase in donation upon replacing water ligands by phosphine ligands has been recognized by Christoph and Koh[11] and by Norman and Kolari.[19] The most pertinent electronic structural change induced upon ligand change, however, is that the much higher ligand lone-pair energy of PH_3 has forced the $17a_g$ MO of $Rh_2(O_2CH)_4(PH_3)_2$ to become the highest occupied orbital of the complex. Thus, we arrive at a picture in which the highest occupied orbital is axially symmetric and yet the Rh–Rh bond is still best described as single, in complete accord with the ESR results of Kawamura et al.[22]

It should be remarked that the comparison of orbital energies obtained for free H_2O to those of $(PH_3)_2$ in the complex is not entirely valid. However, a comparison of the lone-pair ionization energy of free PH_3 (10.6 eV)[33] to those of H_2O (b_2 12.6 eV, a_1 14.7 eV)[34] indicates that the supposed orbital energy difference is real and comparable to the $4a_{1g}$–$4a_{2u}$ splitting of 4.5 eV in $Rh_2(O_2CH)_4$. It should be emphasized that the results for the $Rh_2(O_2CH)_4(H_2O)_2$ and $Rh_2(O_2CH)_4(PH_3)_2$ molecules depend in no way upon the orbital energies assigned to the free axial ligands; the latter are used for convenience in discussion only.

The use of PH_3 as a model of PPh_3 does not cause any problems with the preceding arguments. The lone pair of PPh_3 is more easily ionized than that of PH_3 (PPh_3's first ionization potential 7.9 eV).[35] Hence, the interaction of the b_u lone-pair orbital of $(PPh_3)_2$ with the $4a_{2u}$ MO of $Rh_2(O_2CH)_4$ should be increased, i.e., there should be more donation than was seen for PH_3. The effect of the greater donation will be to lower the "in situ" orbital energies of $(PPh_3)_2$ to probably about the same value as found $(PH_3)_2$; it is for this reason that when possible, ligand orbital energies calculated within the complex are preferred to those obtained for the free ligand. The HOMO of $Rh_2(O_2CCH_3)_4(PPh_3)_2$ will undoubtedly still be of a_g symmetry, because of both the self-limiting charge donation described above and because of the energetic isolation of the $17a_g$ orbitals in $Rh_2(O_2CH)_4(PH_3)_2$.

The higher energy of the phosphine ligands also has interesting ramifications concerning the mutual trans influence of Rh–Rh and Rh–L bonding. Norman and Kolari[18] have argued that the unusually long Rh–OH_2 bond in $Rh_2(O_2CH)_4(H_2O)_2$ results from two effects: (1) the strongly bonding Rh–Rh σ bonding orbital remains filled upon axial ligand interaction and, hence, no net Rh–L bonding can result from this interaction; (2) the destabilization of the Rh–Rh σ^* level makes donation to it from the lower energy H_2O lone pairs an unfavorable process. The first of these effects also pertains upon replacement of H_2O by PH_3; both the $14a_g$ (Rh–P bonding) and $17a_g$ (Rh–P antibonding) orbitals are filled, and no net Rh–P bonding occurs from these interactions. However, the much higher energy of the PH_3 lone pairs means that the second argument does not apply in the present case. The $4a_{2u}$ MO of $Rh_2(O_2CH)_4$ and the b_u MO of $(PH_3)_2$ are nearly equal in energy, and the result is a much more covalent interaction in the $15b_u$ MO of $Rh_2(O_2CH)_4(PH_3)_2$ than that of the corresponding $4b_{1u}$ orbital of $Rh_2(O_2CH)_4(H_2O)_2$. It is to be noted that, in the presence of strong Rh–Rh σ bonding, the maximum order (in a Mulliken sense)[36] of the Rh–L bond is 0.5, and it would appear that the Rh–P bond comes close to achieving this "half-bond" upper limit.

The Question of Back-Bonding. The ability of the $Rh_2(O_2CR)_4$ framework to bind traditionally π-acidic ligands such as carbon monoxide, phosphines, and phosphites as axial ligands has raised the question of whether there is significant charge back-donated from the dimetal system to the axial ligands. Were Rh → L π donation occurring, it would most likely involve the Rh–Rh π^* orbital which is polarized away from the center of the molecule and is presumably high enough in energy to interact with the empty $2\pi^*$ orbital of CO or with the empty P 3d orbitals in phosphines or phosphites. Such an interaction would be expected to decrease both the Rh–Rh and Rh–L bond lengths via transfer of Rh–Rh π^* density into a Rh–L bond.

Experimental evidence on the occurrence of π bonding is neither extensive nor straightforward. For $Rh_2(O_2CR)_4(CO)_2$ compounds, the results are decidedly ambivalent,[37] and since the CO ligand is dissimilar in many ways to R_3P ligands, we shall not discuss these systems further in the absence of pertinent computational results.

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(37) A low-temperature crystal structure (Koh, Y.-B. Ph.D. Thesis, The Ohio State University, 1979) for $Rh_2(O_2CCH_3)_4(CO)_2$ gave the following bond lengths in Å: Rh–Rh, 2.4191 (3); Rh–C, 2.095 (2); C–O, 1.096 (3). The Rh–Rh bond is longer than that found with water or amines, the Rh–C bond is significantly (>0.2 Å) longer than those typically found for rhodium carbonyl compounds, and the C–O bond is shorter than that in free CO (1.128 Å). All of these data point to a description of the Rh–CO bond which is devoid of back-bonding; CO appears to be acting as a σ donor only. Sherwood and Hall[38] have recently investigated the dependence of the CO bond length upon the Cr–C bond length in $(CO)_5Cr$–C–O by using the generalized molecular orbital method. Their results substantiate the above views as they find that at long Cr–C distances, CO interacts with the metal through the weakly C–O antibonding 5σ orbital only, and a concomitant decrease in CO bond length is predicted. On the other hand, infrared spectral studies appear to indicate that at least a little Rh→CO 2π donation is occurring. Darensbourg[39] has obtained accurate ^{12}CO and ^{13}CO IR stretching frequencies in $Rh_2(O_2CC(CH_3)_3)(CO)_2$ and $Rh_2(mhp)_4CO$ (mhp = the anion of 2-methyl-6-hydroxypyridine) and finds that ν_{CO} decreases by ca. 50 cm^{-1} upon axial ligation. Although this shift is not large, it is opposite in direction to that which would be predicted by CO 5σ donation only.

(38) Sherwood, D. E., Jr.; Hall, M. B., private communication.

(39) Darensbourg, D. J., private communication.

Drago and co-workers[40] have proposed that there is extensive π back-bonding in several adducts of dirhodium tetrabutyrate, including a caged phosphite adduct. They base this proposal on the following observations. (1) The $\pi^* \rightarrow \sigma^*$ electronic transition in $Rh_2(\text{butyrate})_4$ at 15.34×10^3 cm^{-1} is claimed to exhibit large blue shifts upon successive formation of mono- and bisadducts. (2) Thermodynamic data from calorimetry and spectrophotometric titration of $Rh_2(\text{butyrate})_4$ are said not to be simply explainable by Drago's empirical E and C model. (3) The free energies and redox potentials for the formation of the neutral mono- and bisadducts from the corresponding monocations are said to support the proposal of π bonding.

Points 2 and 3 do not provide positive evidence for π bonding, and the correctness of Drago's conclusion depends critically on the spectral data and his interpretation thereof, namely, that the lowest energy strong electronic transition in all of the bisadducts is the $\pi^* \rightarrow \sigma^*$ transition as is the case for the unsubstituted and dihydrate complexes. However, this interpretation is inconsistent with the ESR work of Kawamura et al.[22] and with the theoretical work presented here. The energy of destabilization of the σ^* orbital by coordination of two axial PH_3 groups is $\sim 16 \times 10^3$ cm^{-1}, much larger than the blue shift observed upon addition of any of the bases. In fact, the lowest allowed strong transition should be the $^1B_u \leftarrow {}^1A_g$ transition resulting from excitation of an electron from the $17a_g$ to the $17b_u$ MO. This transition should have a high oscillator strength owing to the similarity in atomic orbital characters of the $17a_g$ and $17b_u$ MO's. A calculation of the energy of this excitation using Slater's transition-state formalism predicts it to be at 16.4×10^3 cm^{-1}, about 1000 cm^{-1} higher in energy than the $\pi^* \rightarrow \sigma^*$ transition in $Rh_2(O_2CC_3H_8)_4$. The extrapolated value for the $\pi^* \rightarrow \sigma^*$ ($16a_g$, $9b_g \rightarrow 17b_u$) transition in $Rh_2(O_2CH)_4(PH_3)_2$ is 29.5×10^3 cm^{-1}, which means it is expected to appear in the UV region.

The data of Drago et al., in fact, indicate that a change in the nature of the axial ligand does induce a drastic change in the nature of the first electronic transition. With the use of the example of caged phosphite as an axial ligand, a 2200-cm^{-1} blue shift is observed upon formation of $Rh_2(\text{butyrate})_4$(caged phosphite) from $Rh_2(\text{butyrate})_4$. An additional 5200-cm^{-1} blue shift is observed upon the addition of a second axial caged phosphite. If these observed bands were all due to the same electronic transition, it does not seem reasonable that the second ligand should produce an additional shift more than twice as large as that induced by the first ligand; it would be more reasonable to expect that the presence of the first ligand would mitigate the effect of the second. The most plausible explanation is that the observed transition in $Rh_2(\text{butyrate})_4(\text{caged phosphite})_2$ is *not* the $\pi^* \rightarrow \sigma^*$ transition.

We see no indication in the results of our calculation for back-bonding in $Rh_2(O_2CH)_4(PH_3)_2$. Although d spherical harmonics were included on the P atoms, they contribute no more than 1% to any MO in the molecule. This results in the excellent transferability of the MO's of Rh–Rh π, δ, π^*, and δ^* symmetry from $Rh_2(O_2CH)_4$ to $Rh_2(O_2CH)_4(PH_3)_2$. It should be noted that Norman has observed sizable P 3d AO participation in calculations on Pt(0) complexes in which PPh_3 was modeled by PH_3 as a ligand.[41] Thus, if we may extrapolate our results on the PH_3 adduct to π acids somewhat stronger than PH_3 such as PF_3, PPh_3, and $P(OR)_3$, we are inclined to believe that there is little or no back-bonding in adducts of these either, as supported by the long Rh–P and Rh–Rh bonds.

Future Considerations. The above analysis of the effects of replacing water by PH_3 as an axial ligand in tetrakis(carboxylato)dirhodium systems has led to a consistent explanation of the source of different HOMO symmetries in the two species. It is important to reemphasize that no new interactions have been introduced by the axial phosphine ligands; rather, the magnitudes of the Rh–L interactions have been altered. It is therefore expected that a continuum of electronic structures could be produced for $Rh_2(O_2CR)_4L_2$ by variation of the ligand L and that, at some intermediate donor strength, a crossover of the HOMO from Rh–Rh δ^* to Rh–Rh σ, Rh–L σ^* would be observed. Such an energetic dependence on the axial ligands may have important implications concerning the photochemical activity of these and related Rh systems.[42]

The calculations presented here also lead to some important predictions concerning the spectroscopic properties of the phosphino (or phosphito) adducts as well as the structural changes induced by removal of an electron. The electronic spectrum of $Rh_2(O_2CCH_3)_4(H_2O)_2$ has been investigated with use of single-crystal polarized absorption spectroscopy.[43,44] The first strong band ($\bar{\nu}_{max} = 16.8 \times 10^3$ cm^{-1}) was found to be x,y polarized with a Franck–Condon progression of 297 ± 5 cm^{-1}, clearly attributable to an excited-state Rh–Rh stretch. These data provide persuasive evidence for the assignment of this band to a $\pi^* \rightarrow \sigma^*$ transition, as predicted by Norman and Kolari.[18] Nearly superimposed on this strong x,y-polarized band is a much weaker z-polarized transition at $\bar{\nu}_{max} = 16.1 \times 10^3$ cm^{-1}. This transition was tentatively assigned as a Rh–Rh σ to Rh–Rh σ^* transition although there was no theoretical support for this assignment. A subsequent assignment[19] of this band as the dipole-forbidden, vibronically allowed $\delta^* \rightarrow \sigma^*$ transition is more consistent with the observed low intensity and with the calculations.

The electronic spectrum we would predict for $Rh_2(O_2CH)_4(PH_3)_2$ is very different from that observed for $Rh_2(O_2CCH_3)_4(H_2O)_2$. The destabilization of the $17a_g$ and $17b_u$ MO's results in the former becoming the HOMO of the complex and the latter being pushed above the $16b_u$ (Rh–O σ^*) MO, which is the LUMO of the complex. Thus the lowest energy transitions predicted for $Rh_2(O_2CH)_4(PH_3)_2$ are the $A^1B_u \leftarrow X^1A_g$ ($17a_g \rightarrow 16b_u$; Rh–Rh σ, Rh–P $\sigma^* \rightarrow$ Rh–O σ^*) at 14.8×10^3 cm^{-1} and the $B^1B_u \leftarrow X^1A_g$ ($17a_g \rightarrow 17b_u$; Rh–Rh σ, Rh–P $\sigma^* \rightarrow$ Rh–Rh σ^*, Rh–P σ^*) at 16.4×10^3 cm^{-1}. Both of these transitions are dipole allowed and will be strongly polarized along the Rh–Rh bond (the z direction under D_{2h} or D_{4h} symmetry). They are also predicted to be isolated from other allowed transitions by about 10×10^3 cm^{-1} which leads us to believe that these will be the two lowest transitions observed for $Rh_2(O_2CCH_3)_4(PPh_3)_2$ and other real compounds, although the energies will no doubt be somewhat different from those calculated for the model compound $Rh_2(O_2CH)_4(PH_3)_2$. Thus, we would expect that the x,y component observed at $\sim 17 \times 10^3$ cm^{-1} in $Rh_2(O_2CCH_3)_4(H_2O)_2$ will be absent from the single-crystal polarized spectrum of the phosphine or phosphite adducts. It is also expected that a vibrational progression on the $17a_g \rightarrow 17b_u$ band, if observable, should reflect the bond-weakening influence of a $\sigma \rightarrow \sigma^*$ transition. Such transitions are generally far into the UV and, as such, are not amenable to easy observation. Although the full effect of transferring an electron from a Rh–Rh σ to a Rh–Rh σ^* orbital would be mitigated by the high ligand character in the $17a_g$ and $17b_u$ MO's, we would still expect a great reduction in the Rh–Rh stretching frequency from the 320-cm^{-1} value

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found for the ground state of $Rh_2(O_2CCH_3)_4(H_2O)_2$.[45]

The nature of the HOMO in $Rh_2(O_2CH)_4(PH_3)_2$ also leads to our making a prediction concerning the structural changes upon the formation of cationic species $[Rh_2(O_2CR)_4(PR_3)_2]^+$. A crystal structure of $[Rh_2(O_2CCH_3)_4(H_2O)_2]ClO_4{\cdot}H_2O$ has been reported.[46,47] The Rh–Rh and Rh–OH_2 bonds in the dihydrate cation are 2.317 (2) and 2.22 (1) Å long, respectively, both much shorter than in the neutral species. Even after allowing for a decrease in the effective radius of Rh upon oxidation, the net changes in bond lengths are still negative, viz., Δ(Rh–Rh) = –0.02 Å and Δ(Rh–OH_2) = –0.06 Å, upon forming the cation.[19] The shortening of the Rh–OH_2 bond upon removal of a δ^* electron localized on the Rh atoms is easily rationalized as being due to the now smaller energetic difference of the water lone pairs and the acceptor orbital of the $Rh_2(O_2CCH_3)_4$ framework. The decrease in the Rh–Rh bond length has been attributed to the antibonding nature of the electron involved, although the impact of the antibonding character in a δ^* MO has come under question.[31,32]

We would expect much more pronounced changes in the Rh–Rh and Rh–L bond lengths upon oxidation of, for example, $Rh_2(O_2CCH_3)_4(PPh_3)_2$ to the corresponding cation. The Rh–P bond is expected to shorten considerably upon the removal of an electron from the strongly Rh–P antibonding $17a_g$ MO. The Rh–Rh bond would be expected to lengthen substantially for two reasons. First, electron density would be removed from the Rh–Rh σ-bond framework which is primarily responsible for the shortness of the Rh–Rh bond. Second, the decrease in the Rh–P bond length will be accompanied by increased donation from the phosphine lone pairs into the Rh–Rh σ^* orbital. Thus, from the perspective of the Rh–Rh bond, the oxidation of the system will accomplish a partial charge transfer from the σ to the σ^* orbital. Finally, it is appropriate to address the question of back-bonding once again. To reiterate, we find no evidence in our theoretical results for Rh → P donation in $Rh_2(O_2CH)_4(PH_3)_2$, although the applicability of this result to other systems may be considered a moot point. If our prediction that the Rh–P bond will shorten considerably upon oxidation is correct, however, it is expected that the overlap of the Rh–Rh π^* and P 3d orbitals would increase despite the higher formal oxidation state of the Rh atoms. Thus it is not unreasonable to predict more back-bonding in the oxidized cationic species than in the neutral molecule. If the electronic structure of the bis(carbonyl) adduct parallels that of the bis(phosphine) adducts, this prediction would be particularly easy to test, and we eagerly await experimental results.

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Tetrachlorotetraethoxodi-μ-ethoxo-ditungsten(*W*–*W*). Structure, Bonding, and Improved Preparation

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New methods of preparing the title compound by oxidizing $W_2Cl_4(\mu\text{-}OEt)_2(OEt)_2(HOEt)_2$ with silver nitrate or molecular oxygen are described. The crystal and molecular structure have been determined. The molecules, which consist of two distorted octahedra sharing an edge, reside on crystallographic centers of inversion but approximate to D_{2h} symmetry. There is a central $Cl_2W(\mu\text{-}OEt)_2WCl_2$ unit which is planar except for the Et groups. Four more EtO groups, two on each tungsten atom above and below this plane, complete the distorted octahedra about each metal atom. The W–W distance is 2.715 (1) Å. The structure and the diamagnetism can be best explained by postulating a single bond between the tungsten atoms. The crystals belong to space group $P2_1/n$ with a = 8.469 (1) Å, b = 9.344 (1) Å, c = 14.815 (1) Å, β = 93.850 (8)°, V = 1169.7 (5) Å^3, and Z = 2. The structure, with hydrogen atoms included but not refined, was refined to R_1 = 0.019 and R_2 = 0.028.

Introduction

A compound of formula $W_2Cl_4(OEt)_6$ appears to have been first reported by Klejnot[2] in 1965. It was later made also by Brubaker et al.,[3] and the *n*-propoxide was reported in 1970 by Reagan and Brubaker.[4] The report by these last workers of NMR spectra with normal characteristics (which we have confirmed for the ethoxide) provided evidence that these are diamagnetic compounds. From the composition, the NMR spectrum, and the diamagnetism, it is a reasonable conjecture that the molecule has OEt bridges between two octahedrally coordinated metal atoms and that the two d electrons supplied by the W^V ions become paired.

However, as the field of binuclear compounds with metal–metal bonds has developed in recent years, this compound took on new interest since it may be regarded as a kind of prototype. We therefore deemed it worthwhile to examine its chemistry further and to provide a definitive structural characterization of it, as a basis for discussing the bonding.

Experimental Section

Reagents. Samples of the tungsten(IV) complex $W_2Cl_4(OEt)_4(EtOH)_2$ were prepared from tungsten(IV) chloride with use of the procedure of Reagan and Brubaker.[4] All solvents were dried and purged with nitrogen prior to use.

Preparation of $W_2Cl_4(OEt)_6$. Method A. A 0.75-g (0.958-mmol), sample of $W_2Cl_4(OEt)_4(EtOH)_2$ and 0.325 g (1.91 mmol) of freshly ground silver nitrate were placed in 75 mL of acetone. The resulting suspension was stirred for 40 min, by which time the color had turned from brown to red. The solution was filtered, and the filtrate was

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