Cl^-/Zn^{2+} ratio equals 4 ($X = 0.67$). The appearance and behavior of the 292-cm^{-1} peak in Figure 7 indicate the presence of a certain kind of oscillator that is different from the above-mentioned $(ZnCl_2)_n$ polymer or the isolated $ZnCl_4^{2-}$ complex ion. It is surprising that this unknown oscillator has an appreciable thermal stability as is indicated by Figure 5.

Acknowledgment. The authors wish to express their sincere thanks to Professor Shirō Maeda and Mr. Shunsuke Kobinata, Research Laboratory of Resources Utilization, Tokyo Institute of Technology, for their kind instructions and permission to use their laser-Raman spectrophotometer. We also thank Dr. Noriko Itoh of our laboratory for her helpful discussions.

Registry No. $ZnCl_2$, 7646-85-7; KCl, 7447-40-7.

Contribution from the Department of Chemistry,
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Peroxo-Metal Bonding in $M(PH_3)_4(O_2)^+$, M = Co, Rh, Ir

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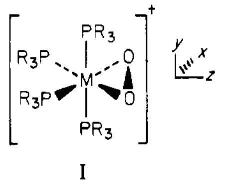
Previously we presented a comparison of the electronic structures of $Pt(PH_3)_2(O_2)$ and $Pt(PH_3)_2(C_2H_4)$—theoretical models for archetypal group 8 peroxo and d^{10} ethylene complexes with PPh_3 ligands—based on SCF–Xα–SW calculations.[1] Though extremely well characterized, $Pt(PPh_3)_2(O_2)$ is somewhat special in that most group 8 peroxo complexes contain Co(III), Rh(III), or Ir(III)—i.e., d^6 rather than d^8 metals.[2] Typical are six complexes $M(PR_3)_4(O_2)^+$ with general structure depicted by I.[3] We undertook SCF–Xα–SW



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calculations on $M(PH_3)_4(O_2)^+$ and $M(PH_3)_4^{3+}$, M = Co, Rh, Ir, using averaged dimensions from these structures,[4] in order to help answer the following questions: (1) Why do the observed rate of formation from $M(PR_3)_4^+ + O_2$ and the final stability of the peroxo complexes vary in the order Co ≫ Ir > Rh?[5] Coordination of O_2 is reversible for Rh but essentially irreversible for Co and Ir. (2) How do the frontier orbitals, and d vs. s vs. p character of the metal's contribution to bonding, change down the column and compare to $Pt(PH_3)_2(O_2)$? (3) What orbital transitions account for the observed electronic spectrum?[6,7]

Results and Discussion

Figure 1 compares the calculated frontier orbitals of the d^6 complexes with those of $Pt(PH_3)_2(O_2)$. These orbitals are mainly either metal d or peroxo π^*.[8] The Pt and Ir complexes are very similar; they differ significantly only in the expected energy elevation of the d_{y^2}-like orbital in the latter due to addition of two y-axis PH_3 ligands and in the associated removal of two d-like electrons. When the d^6 complexes are viewed as perturbed octahedra, each has a filled triad of "t_{2g}" d-like orbitals (xy, yz, and $z^2 - x^2$) at low energy and an empty pair of "e_g" orbitals (xz, y^2) at high energy. For Rh and Ir, the two peroxo π^* orbitals lie between the two groups of d-like orbitals and are the HOMO's of the complex. The Co complex is unique in having two "t_{2g}" orbitals between the $\pi^*_{\parallel}$ and $\pi^*_{\perp}$ pair. This is mainly due to the decreasing ligand field splitting of the d-like orbitals as one moves up the column. One may calculate an effective Δ_0 as the difference in average "t_{2g}" and "e_g" orbital energies. The result is 2.74, 3.58, and 4.01 μm^{-1} for the Co, Rh, and Ir complexes, respectively.

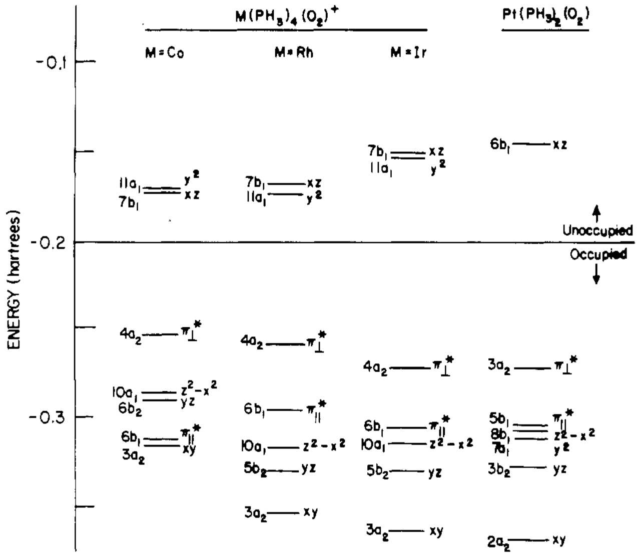

Figure 1. Highest occupied and lowest unoccupied SCF energy levels of $M(PH_3)_4(O_2)^+$, M = Co, Rh, Ir, and $Pt(PH_3)_2(O_2)$. Mainly metal d orbitals are designated by their subscripts (xy, yz, $z^2 - x^2$, xz, y^2) and mainly peroxide orbitals as either in the MP_2O_2 plane ($\pi^*_{\parallel}$) or perpendicular to it ($\pi^*_{\perp}$). There is one $M(PH_3)_4(O_2)^+$ orbital above −0.35 hartree, mainly $M-P_{axial}$ bonding, which is not shown here. For M = Co it is $5b_2$ and is at −0.33 hartree. For M = Rh and Ir it is $6b_2$ and is at −0.31 hartree.

Increasing ligand field splitting is often associated with increasing metal–ligand bond strength. However, here the total calculated bond energies[9] are found to follow the experimentally observed order of stability, i.e., Co ≫ Ir > Rh. This same trend is seen at the orbital level in the relative energies of the main $M-O_2$ bonding orbital, $6b_1$ (see Figure 1). The point is that Δ_0 reflects only the metal d component of the total bonding, while for these d^6 metals only one empty d orbital (xz) is available to accept electrons from the O_2^{2-} and two PH_3 ligands in the plane. Hence, the in-plane M–P and M–O bond strengths will be critically dependent on how effectively the metal can use its s, p_x, and p_z orbitals and hybridize them with d_{xz} for good overlap with the ligand orbitals.

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(4) Sphere radii, α values, basis functions, etc. were chosen as in our previous calculations.[1] Note that the coordinate system used here has the C_2 axis along z rather than along x as in ref 1; this interchanges b_1 and b_2 orbitals. A Fenske–Hall calculation on $Co(PH_3)_4(O_2)^+$ is described in: Teo, B. K.; Li, W.-K. *Inorg. Chem.* **1976**, *15*, 2005.
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(8) The occupied and unoccupied d-like orbitals are 54–89% and 41–52% metal, respectively; their metal character is 92–100% d. The peroxo π^*-like orbitals are 4–14% metal.
(9) Relative bond energies were obtained by subtracting from the calculated total energies the metal hyper-Hartree–Fock atomic energies[10] on which the choice of α values for the MO calculations is based. If the Rh-complex value thus obtained is taken as the zero point, the results for the complexes are −518, 0, and −40 kJ/mol for M = Co, Rh, and Ir, respectively. While Xα–SW total energies are well-known to be limited in accuracy, relative values for complexes as closely related as these should be meaningful.
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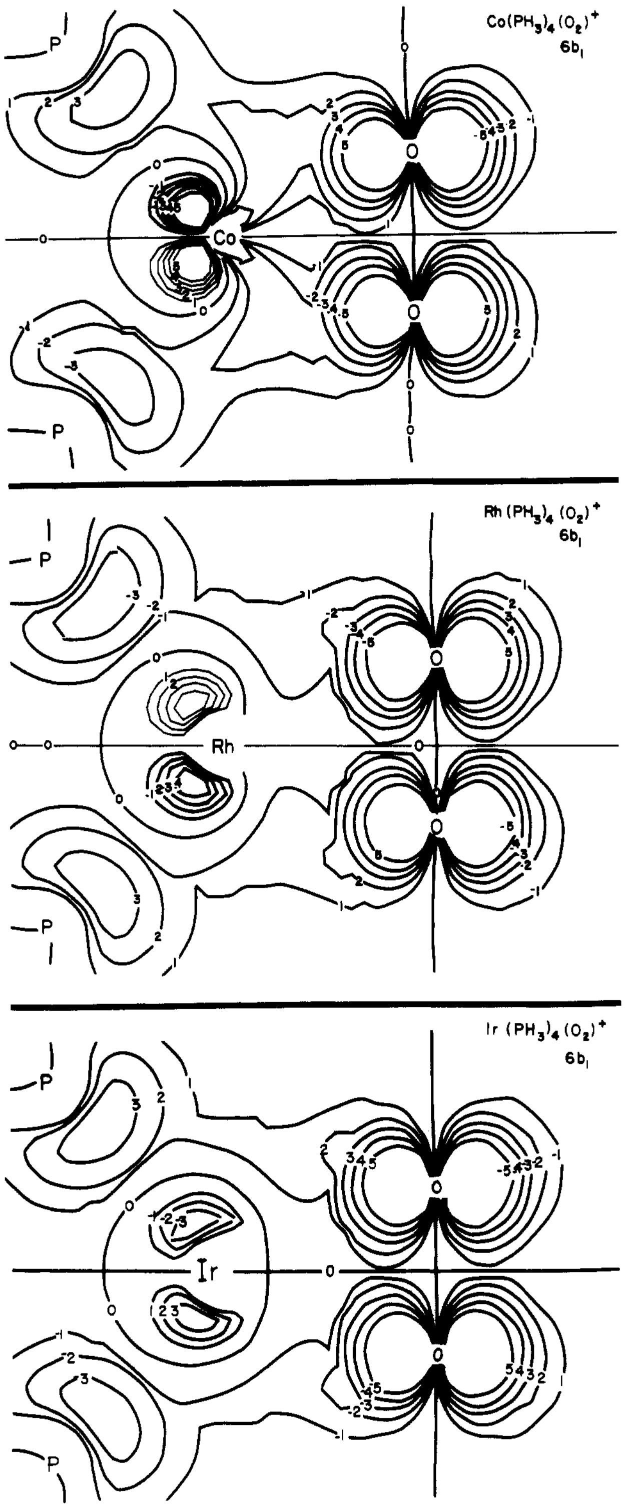

Figure 2. Contour maps of the 6b$_1$ orbital wave functions for M(PH$_3$)$_4$(O$_2$)$^+$, M = Co, Rh, Ir, in the xz plane. Contours close to atomic centers are omitted for clarity. The contour values are 0, ±1, ±2, ±3, ±4, ±5 = 0, ±0.05, ±0.075, ±0.10, ±0.125, ±0.16 (electron/bohr^3)$^{1/2}$, respectively.

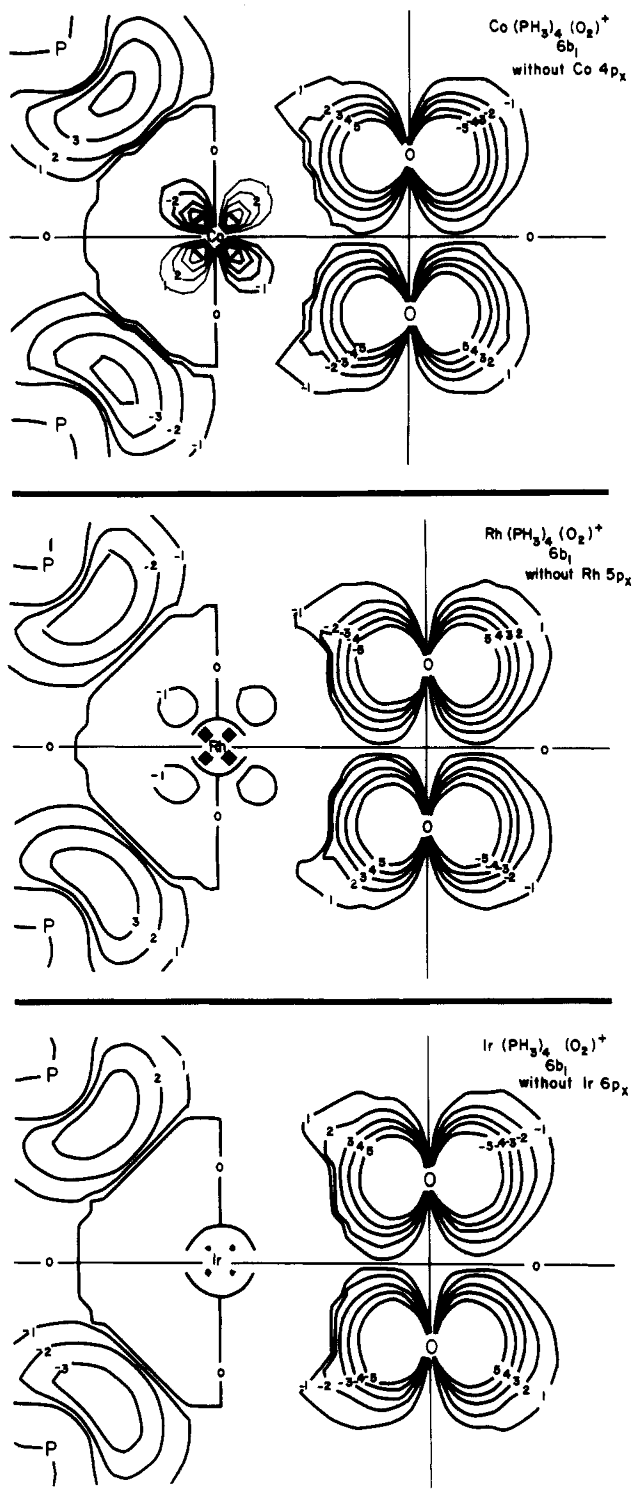

Figure 3. Maps of the 6b$_1$ wave functions under conditions identical with those in Figure 2 but with the metal p$_x$ functions removed from the basis set.

Careful comparisons among the calculations on M(PH$_3$)$_4$(O$_2$)$^+$ and M(PH$_3$)$_4{}^{3+}$ show that the metal d$_{xz}$ orbital is mainly used in bonding the PH$_3$ ligands, while the peroxo group is mainly bound through the metal p$_x$ orbital. This is sensible since the relative ligand- and metal-orbital energy orders are, respectively, PH$_3$ lone pair < peroxo π^* and d$_{xz}$ < p$_x$. The special stability of the Co complex comes about because Co is far superior to Rh and Ir at hybridizing into the p$_x$ orbital some d$_{xz}$ character, thereby improving its overlap with the O$_2$ $\pi^*_{\parallel}$ orbital. The crucial role of the p$_x$ orbital in M–O bonding and the more effective d–p hybridization by Co are seen in Figures 2 and 3. The superior hybridization ability of Co can be traced to the relative d, s, and p atomic energies. For model Co, Rh, and Ir atoms having the d, s, and p populations we calculate for the M(PH$_3$)$_4{}^{3+}$ fragments,[11] we find ΔE(d–p) = 4.34, 5.50, and 5.33 μm^{-1}, respectively. The order Co ≪ Ir < Rh is indeed the inverse of the observed orders of d–p hybridization effectiveness and overall complex stability.

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[11] For M = Co, Rh, and Ir, these are respectively 7.71 d/0.56 s/0.60 p, 7.79 d/0.45 s/0.43 p, and 7.73 d/0.52 s/0.52 p.

The electronic spectrum of [Co($Ph_2PCH{=}CHPPh_2$)$_2$(O_2)][PF_6] in frozen solution at 77 K has been reported and an assignment proposed from experimental comparisons.[6] Our assignment, based on transition energies for $Co(PH_3)_4(O_2)^+$ computed by the spin-polarized transition-state method,[12] is in general agreement. We ascribe the bands at 1.6 sh (ϵ 75), 2.16 (ϵ 1170), 2.6 sh (ϵ 1200), and 3.10 μm^{-1} (ϵ 24 500) to O_2^{2-} $\pi^*_\perp \rightarrow d_{xz}$, $d_{z^2-x^2} \rightarrow d_{xz}$, $d_{z^2-x^2} \rightarrow d_{y^2}$, and $\pi^*_\parallel \rightarrow d_{xz}$, d_{y^2} transitions, respectively, using the orbital designations in Figure 1.[13] Gray et al. denote the last transition as $\sigma(P) \rightarrow d\sigma^*(Co)$.[6] The $6b_1$ orbital, which we call O_2^{2-} $\pi^*_\parallel$, does have about 30% PH_3 lone-pair character (see Figure 2); alternatively, the difference between 2 PH_3 and $Ph_2PCH{=}CHPPh_2$ orbital energies may become significant this deep in the energy-level diagram.

Though these nonrelativistic calculations do qualitatively reproduce the observed order of stability, Co $\gg$ Ir > Rh, they quantitatively place the Ir and Rh complexes quite close in energy.[9] A good illustration at the orbital level is that the Rh- and Ir-complex $6b_1$ orbitals do differ in *energy* (Figure 1) but not significantly in M–O_2 *overlap* (Figure 2). The experimental difference in stability between the Ir and Rh complexes appears to be somewhat greater.[5,6] Relativistic corrections should preferentially decrease the atomic d–s and d–p energy splittings for Ir.[14] This is exactly what would be required to bring the calculated strength of peroxide bonding for Ir closer to that for Co. Very recent fully relativistic calculations on $Pt(PH_3)_2(O_2)$ explicitly support this hypothesis.[15]

Acknowledgment. We thank the NSF for support. We are grateful to Dr. Tom Ziegler for useful discussions and communication of unpublished results of Xα discrete variational calculations on $M(PH_3)_4(O_2)^+$. J.G.N. was a Fellow of the Alfred P. Sloan Foundation for 1978–1980.

Registry No. $Co(PH_3)_4(O_2)^+$, 59448-50-9; $Rh(PH_3)_4(O_2)^+$, 81987-93-1; $Ir(PH_3)_4(O_2)^+$, 81987-94-2.

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Two New Perchlorato Complexes. The Oxochloro(perchlorato)antimony Complexes $Sb_2Cl_6(OH)(O)(ClO_4)$ and $Sb_8Cl_{24}(O_5)(ClO_4)_6$: Synthesis, Vibrational Spectroscopy, and X-ray Structural Determination of (μ-Hydroxo)(μ-oxo)(perchlorato)bis[trichloroantimony(V)], $Sb_2Cl_6(OH)(O)(ClO_4)$

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In the course of systematic studies on the substitution of chlorine atoms by perchlorato ligands in nontransitional or transitional element chlorides, we have examined the behavior of $SbCl_5$ toward the strong perchlorating reagent Cl_2O_6.

For a long time, the very weak base ClO_4^- has been considered as a poor ligand despite the synthesis and spectroscopic studies of copper and iron perchlorates by Hathaway et al. in 1961.[2] In 1973, Rosenthal[3] underlined the lack of bibliography about perchlorate complexes. Overcoming the difficulties in the synthesis and handling of strong perchlorating reagents like anhydrous $HClO_4$, Cl_2O_6, and $ClOClO_3$ allowed Rosolvskii et al., ourselves, and Christe et al. to synthesize anhydrous perchlorato complexes of B,[4] Al,[5] Co,[6] Zr,[7] Hf,[8] Ti,[9] Cr,[10] Fe,[11] Ga,[12] Ni,[13,14] Pd,[14] and Sn.[15]

Although the isolated complexes crystallize poorly, their molecular structures could generally be deduced from infrared and Raman spectra. Fortunately, single crystals of a tin perchlorato complex were grown in $SnCl_4$, and their crystal structure determination gave the first evidence for an entirely inorganic perchlorato complex: $[Sn_3O_2Cl_4(ClO_4)_4]_2$.[15] Good agreement was obtained between X-ray and vibrational spectroscopy data.

Interesting results concerning the ClO_4 ligand can be expected from the well-known ability of $SbCl_5$ to react with basic ligands to form (i) addition complexes, $SbCl_5L$, and (ii) substitution complexes, $SbCl_4L$ and $SbCl_3L_2$; in the last 10 years, the $SbCl_5$–H_2O[16] and $SbCl_5$–Me_2SO[17] compounds have been reported. The carboxylate,[18,19] phosphate,[20] and sulfinate[21] ligands have been shown to be able to substitute Cl atoms.

So far, only $[(CH_3)_2Sb(ClO_4)]_2O$,[22] an antimony(V) perchlorato complex with the unidentate ClO_4, has been prepared and studied by X-ray diffraction.

In this paper are presented the syntheses of two new perchlorato complexes, $Sb_8Cl_{24}O_5(ClO_4)_6$ and $Sb_2Cl_6(OH)(O)(ClO_4)$, together with the spectroscopic investigations concerning both compounds and the crystal structure of the latter. For the first time, precise geometrical data for a strongly bonded bidentate ClO_4 group are given.

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