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Preparation and Spectroscopic Properties of Cobalt(III) Complexes Containing Phosphine Ligands. The Electronic Structural Description of Side-Bonded Dioxygen

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Abstract: The cobalt(III) complexes $[Co(2{=}phos)_2X_2]ClO_4$ ($X^- = Cl^-$, Br^-, NCO^-, N_3^-, NCS^-), where $2{=}phos$ is *cis*-1,2-bis(diphenylphosphino)ethylene, have been prepared. The infrared and electronic spectral properties of these complexes are consistent with an assignment of trans stereochemistry. The corresponding cobalt(III) complexes of $2{-}phos(1,2{-}bis(diphenylphosphino)ethane)$ are extremely unstable. Furthermore, several reactions of the $[Co(2{=}phos)_2X_2]^+$ complexes give unexpected products; thus, reaction with NO_2^- yields $[Co(2{=}phos)(NO)_2]^+$. Variations in the stabilities of the complexes of $2{=}phos$ and $2{-}phos$ apparently are related to differences in nonbonding interactions of phenyl groups with the axial ligands. Special attention has been paid to the formulation of the electronic structures of $[Co(2{=}phos)_2O_2]^+$ and related rhodium and iridium complexes. The PF_6^- salt of $[Co(2{=}phos)_2O_2]^+$ exhibits electronic absorption bands at 21.6 (ϵ 1170), 26 (ϵ 1200), and 31.4 (ϵ 24 500) kK at 77 K in a 12:1 EPA-CHCl₃ glass. As the spectrum is strikingly similar to that of the analogous Co(III)-carbonato complex, $[Co(2{=}phos)_2CO_3]^+$, assignment of the 21.6 and 26 kK bands to the two spin-allowed d–d transitions ($^1A_1 \rightarrow {}^1T_1$, $^1T_2$) expected for a $[Co^{III}P_4(O_2{}^{2-})]^+$ ground state is indicated. The intense band at 31.4 kK is attributed to an allowed $\sigma(P) \rightarrow d\sigma^*(Co)$ charge transfer transition. The electronic spectrum of $[Ir(2{=}phos)_2O_2]^+$ is also reported. The lowest energy feature, a broad shoulder in the 33–34-kK region, is attributed to $^1A_1 \rightarrow {}^1T_1$ in an $[Ir^{III}-P_4(O_2{}^{2-})]^+$ center.

In 1963, Vaska reported that *trans*-[Ir(PPh₃)₂(CO)Cl] reacts reversibly with dioxygen to give a 1:1 adduct complex.[1] The subsequent crystal structure determination showed the dioxygen to be side-bonded to the metal, the IrO_2 unit forming an isosceles triangle.[2] Similar dioxygen adducts have since been prepared with many other central metal ions.[3–5] Although the formation of such adducts is generally thought to involve oxidation of the central metal,[5] little detailed electronic structural information is available that bears on the point. For example, there have been very few attempts to analyze in any depth the electronic spectra of side-bonded dioxygen complexes.

The investigations outlined in this paper were prompted by the report[6] of a side-bonded dioxygen adduct of $[Co(2{=}phos)_2]^+$, where $2{=}phos$ is *cis*-1,2-bis(diphenylphosphino)ethylene. We have found that it is possible to prepare an extensive series of complexes of the type $[Co(2{=}phos)_2X_2]^+$, whereas all the $2{-}phos$ (1,2-bis(diphenylphosphino)ethane) analogues appear to be unstable. The chemistry of these $2{=}phos$ complexes has proved to include some surprising redox instability patterns, which we have attempted to analyze. We also have interpreted the electronic spectroscopic properties of $[Co(2{=}phos)_2X_2]^+$ by reference to other Co(III) complexes and to Rh(III) analogues. The spectrum of $[Co(2{=}phos)_2O_2]^+$ has been examined with particular care, as it contains information about the electronic structure of the CoO_2^+ unit. In addition, we have attempted to correlate the electronic spectroscopic properties of $[Co(2{=}phos)_2O_2]^+$ with those of the corresponding rhodium and iridium complexes.

Experimental Section

The phosphine ligands were obtained from Pressure Chemical Co. and were used as received. All other reagents and solvents were at least analytical reagent grade. The compounds $Co(2{-}phos)_2X_2$ ($X^- = Cl^-$, Br^-) were prepared by the method of Horrocks et al.[7] The compounds $Co(2{=}phos)_2X_2 \cdot CoX_2$ ($X^- = Cl^-$, Br^-, I^-) were prepared by the same procedure. The formulation given for the latter complexes is based on elemental analyses, which, assuming the stoichiometry $Co(2{=}phos)_2X_2 \cdot nCoX_2$, consistently gave $n = 0.9{-}1.2$. (Example analysis: Calcd for $Co(2{=}phos)_2Cl_2 \cdot CoCl_2$: C, 59.34; H, 4.22; Cl, 13.47; Co, 11.2. Found: C, 58.67; H, 3.69; Cl, 13.11; Co, 12.9.) The compounds presumably are $[Co_2X_6]^{2-}$ salts of $[Co(2{=}phos)_2X]^+$.

$[Co(2{=}phos)_2](ClO_4)_2$. A solution of 0.75 g of $Co(ClO_4)_2 \cdot 6H_2O$ in 15 ml of acetone was added under nitrogen to a solution of 0.65 g of $2{=}phos$ in 30 ml of acetone. The solution turned orange, and a yellow product began to form. After storage at 10° for 1 h, the solution was filtered under nitrogen. The bright-yellow crystalline product was washed with methanol and ether. It is indefinitely stable in air when dry. Anal. Calcd for $[Co(2{=}phos)_2](ClO_4)_2$: C, 59.22; H, 4.59; P, 11.75. Found: C, 58.62; H, 4.28; P, 11.72.

$[Co(2{=}phos)_2](BF_4)_2$ was prepared similarly, from $Co(BF_4)_2 \cdot 6H_2O$, and obtained as yellow crystals. Anal. Calcd for $[Co(2{=}phos)_2](BF_4)_2$: C, 60.91; H, 4.33. Found: C, 60.81; H, 4.33.

$[Co(2{=}phos)_2Cl_2]ClO_4$. Chlorine gas was bubbled through a solution of $Co(2{=}phos)_2Cl_2 \cdot CoCl_2$ (0.5 g) in 25 ml of CH_2Cl_2, in the dark. A green solid began to form almost immediately. After 15 min, the solution was flushed with nitrogen briefly to remove

excess chlorine, and the product was filtered off and washed first with a small amount of cold CH_2Cl_2, and then thoroughly with ether. This chloride salt was dissolved in absolute ethanol, and several drops of saturated ethanolic $NaClO_4$ were added. Storage at 0° overnight gave apple green crystals of the perchlorate salt, which were filtered off and washed with cold ethanol and ether. Analytical samples were prepared by removing small amounts of Co(II) impurities by chromatography on neutral alumina in methanol. Anal. Calcd for $[Co(2=phos)_2Cl_2]ClO_4$: C, 61.11; H, 4.34; Cl, 10.41; P, 12.12. Found: C, 61.34; H, 4.65; Cl, 10.61; P, 12.24. The complex $[Co(2=phos)_2Cl_2]^+$ may also be prepared by treatment of either $[Co(2=phos)_2CO_3]^+$ or $[Co(2=phos)_2O_2]^+$ (vide infra) with HCl in methanol.

$[Co(2=phos)_2Br_2]ClO_4$. This compound was prepared initially by a procedure similar to that employed for the analogous dichloro derivative, using a stoichiometric amount of liquid Br_2. However, elemental analyses consistently indicated considerable incorporation of chloride ion (presumably derived from solvent) in the product. A pure sample of the compound was obtained by refluxing a methanolic solution of $[Co(2=phos)_2CO_3]ClO_4$ (vide infra) with a few milliliters of concentrated aqueous HBr. The orange-brown precipitate was recrystallized from methanol by addition of concentrated methanolic $NaClO_4$, yielding orange crystals of the perchlorate salt. Anal. Calcd for $[Co(2=phos)_2Br_2]ClO_4$: C, 56.22; H, 3.99; Br + Cl, 17.57. Found: C, 55.43; H, 3.87; Br + Cl, 17.13. This compound is strongly thermochromic, reversibly changing color from yellow-green at liquid nitrogen temperature to bright red at 160°.

$[Co(2=phos)_2X_2]ClO_4$ $(X^- = N_3^-, NCO^-, NCS^-)$. These complexes were all prepared from $[Co(2=phos)_2Cl_2]Cl$ by stirring in methanol at ~50° with an excess of the sodium salt of the desired anionic ligand until the 630-nm absorption band of the starting material was undetectable (~0.5 h). The complexes were crystallized as perchlorate salts by addition of excess saturated methanolic $NaClO_4$ and cooling to 0°, and recrystallized in the same fashion from methanol. All were obtained as brown crystals. Anal. Calcd for $[Co(2=phos)_2(N_3)_2]ClO_4$: C, 60.56; H, 4.30; N, 8.15. Found: C, 59.73; H, 4.25; N, 8.02. Calcd for $[Co(2=phos)_2(NCO)_2]ClO_4$: C, 62.89; H, 4.30; N, 2.72; Found: C, 61.40; H, 4.30; N, 2.57. Calcd for $[Co(2=phos)_2(NCS)_2]ClO_4$: C, 60.76; H, 4.16; N, 2.62; S, 6.01; Cl, 3.32. Found: C, 59.31; H, 4.20; N, 2.97; S, 5.99; Cl, 3.61.

$[Co(2=phos)_2CO_3]ClO_4$. $[Co(2=phos)_2Cl_2]Cl$ (0.2 g) was agitated overnight with 1 g of Ag_2CO_3 in 3 ml of CH_3OH and 1 ml of H_2O, in the dark. The orange solution was filtered off. Addition of 1 ml of saturated methanolic $NaClO_4$ and cooling for several hours gave red-orange prisms of the product. Anal. Calcd for $[Co(2=phos)_2CO_3]ClO_4$: C, 62.96; H, 4.39; Cl, 3.51; P, 12.26. Found: C, 60.98; H, 4.38; Cl, 3.79; P, 12.17. The ir spectrum of the complex in a KBr disk exhibits an intense band at 1680 cm^{-1}, attributable[8] to bidentate carbonate.

$[Co(2=phos)(NO)_2]ClO_4$. (a) $[Co(2=phos)_2Cl_2]Cl$ (0.5 g) was dissolved in 100 ml of refluxing methanol under nitrogen, and solid $NaNO_2$ (2 g) was added. The solution gradually became deep orange during 3 h of refluxing. The solution was cooled and filtered, and 10 ml of saturated methanolic $NaClO_4$ was added. After cooling to 0° for ~0.5 h, any precipitate of $[Co(2=phos)_2Cl_2]ClO_4$ was filtered off, and the solution was maintained at 0° overnight, giving ~0.1 g of dark red crystals, which were washed with water and ether. (b) $Co(2=phos)_2Cl_2$ was stirred under nitrogen in methanol with excess $NaNO_2$, the solution rapidly becoming yellow brown. The solution was filtered and O_2 was bubbled through it, after which the solution darkened. After 15 min, a dark precipitate had begun to form. The precipitate was filtered off after 0.5 h, and was crystallized as the perchlorate salt from a methanolic solution containing $NaClO_4$. Anal. Calcd for $[Co(2=phos)(NO)_2]ClO_4$: C, 50.79; H, 3.61; N, 4.56; Cl, 5.77; P, 10.08. Found: C, 51.16; H, 3.75; N, 4.53; Cl, 6.64; P, 11.02. The ir spectrum of the product showed no bands attributable to NO_2^- or NO_3^-; however, very intense bands were observed at 1858 and 1800 cm^{-1}, evidencing the presence of coordinated NO.[9]

$[Co(2=phos)_2]BF_4$. To a solution of 4.5 g of 2=phos and 4.0 g of $NaBF_4$ in 350 ml of refluxing ethanol under nitrogen was added 2.5 g of $[Co(PPh_3)_3Cl]$ (prepared as an apple green powder by the zinc reduction method of Aresta et al.[10]) After refluxing for 1 h, the solution was cooled 1 h in an ice bath. Filtration under nitrogen

gave 3.5 g of glistening, dark green, crystalline product. (The product at this point contained impurities, mainly cobalt metal, which were difficult to remove from the sample. The product could be recrystallized from ethanol or CH_2Cl_2, but was found to be quite oxygen-sensitive.) Exposure of the green filtrate to air and addition of excess solid $NaBPh_4$ gave $[Co(2=phos)_2O_2]BPh_4$ as a light brown powder (yield $\simeq 1$ g), which was purified as described below.

$[Co(2=phos)_2O_2]X$ $(X^- = ClO_4^-, BF_4^-, BPh_4^-, PF_6^-)$. These complexes were prepared by three different methods. Details are given for $X^- = BF_4^-$. (a) Solid $[Co(2=phos)_2]BF_4$ was dissolved in CH_2Cl_2 in the presence of air. The initially bright green solution rapidly turned dark brown. After filtration to remove gray powdery impurities, the solution was evaporated in a stream of air to give a partly crystalline, dark brown solid. The solid was redissolved in methanol, the solution was filtered, and a large excess of a saturated solution of $NaBF_4$ in methanol was added. Storage at −5° overnight gave large, well-formed, dark brown plates of the product, which were filtered off, washed with cold methanol, and air-dried. The product could additionally be recrystallized from CH_2Cl_2-benzene, but solvent molecules were present in the resultant crystals. This recrystallization procedure was useful for the tetraphenylborate, which was otherwise difficultly crystallizable, but which formed large, shiny, blunt needles from CH_2Cl_2-benzene. (b) Solid 2=phos (1.20 g) was added slowly to a solution of 0.50 g of $Co(BF_4)_2\cdot6H_2O$ in 20 ml of acetone, with dioxygen being constantly bubbled through the solution. Acetone was periodically added to maintain the solvent level. The solution changed color, through gold, to dark brown. After completion of the addition, O_2 bubbling was continued for 0.5 h. Ether was then added, precipitating a light brown product. The precipitate was filtered off and washed with benzene (to remove unreacted 2=phos and its decomposition products) and ether. The product (yield $\simeq 1$ g) was recrystallized as described in (a). (c) $[Co(2=phos)_2](BF_4)_2$ (0.32 g) was dissolved in methanol (350 ml) and refluxed for 0.5 h, with air being constantly bubbled through the solution. The solution turned dark brown within a 20-min period. Reduction of the solution volume in a stream of air gave dark brown crystals of the product, with by-products of the reaction crystallizing when the mixture was nearly dry. The product could be recrystallized, as previously described.

$[Rh(2=phos)_2Cl_2]ClO_4$. Solid 2=phos (1.5 g) was added slowly to a boiling solution of 0.4 g of $RhCl_3\cdot3H_2O$ in 25 ml of absolute ethanol. The solution became lighter in color, and a yellow precipitate formed. The product was filtered off, dissolved in boiling ethanol, and precipitated by dropwise addition of saturated ethanolic $NaClO_4$, as a bright yellow powder. Anal. Calcd for $[Rh(2=phos)_2Cl_2]ClO_4$: C, 58.37; H, 4.52; Cl, 9.94; P, 11.56. Found: C, 57.1; H, 4.52; Cl, 10.3; P, 11.5.

$[Rh(2—phos)_2Cl_2]Cl\cdot3C_2H_5OH$. The crude chloride salt was obtained as for the 2=phos complex above. This salt was dissolved in a minimum amount of boiling ethanol, the solution was rapidly filtered, and ether was added (~0.5 volumes). After cooling the mixture to −5° for 2 h, large yellow crystals were filtered off and washed with ethanol and ether. Anal. Calcd for $[Rh(2—phos)_2Cl_2]Cl\cdot3C_2H_5OH$: C, 60.8; H, 5.81; Cl, 9.3; P, 10.8. Found: C, 60.8; H, 5.69; Cl, 9.4; P, 11.1.

Other Compounds. $[Rh(2-phos)_2]Cl$ was prepared by the method of Sacco and Ugo.[11] $[Rh(2=phos)_2]Cl$ was similarly prepared. These complexes were recrystallized from methanol under nitrogen. The ClO_4^-, BF_4^-, and PF_6^- salts of both complexes were also crystallized from methanol under nitrogen. Brown crystals of the dioxygen adduct $[Rh(2—phos)_2O_2]PF_6$ were prepared by a standard method.[3] An analyzed sample of $[Ir(2=phos)_2]Cl$ was furnished by G. L. Geoffroy and was converted to $[Ir(2=phos)_2O_2]ClO_4$ by addition of saturated methanolic $NaClO_4$ to an O_2-saturated methanol solution of the compound.

Spectroscopic Measurements. Ultraviolet, visible, and near-infrared spectra were measured using a Cary Model 17 spectrophotometer. Low-temperature spectra were obtained using a quartz Dewar with optical quality windows. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer.

Results and Discussion

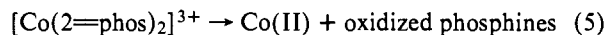We have prepared the complexes $[Co(2=phos)_2X_2]ClO_4$ by halogen (X_2) oxidation of $[Co(2=phos)_2X]^+$. The pseu-
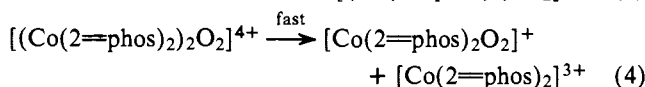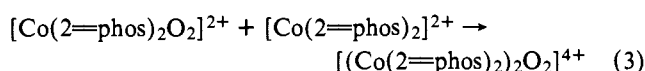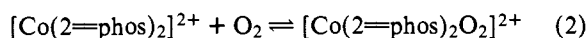
dohalide derivatives ($X^- = N_3^-$, NCO^-, NCS^-) and the carbonato complex ($X_2^{2-} = CO_3^{2-}$) were then prepared by substitution reactions. In each case only one isomer was obtained. Based on their electronic spectral properties, trans stereochemistry may be assigned to all the $[Co(2=phos)_2X_2]^+$ complexes (vide infra), except, of course, where X_2^{2-} is bidentate, as in the carbonato case. The trans formulation is additionally supported in each of the pseudohalide derivatives by the presence of a single, sharp ir band (KBr disk) attributable to a ligand stretching mode, as follows: 2028 (N_3^-); 2245 (NCO^-); and 2098 cm^{-1} (NCS^-).

Simple oxidative reaction procedures do not produce stable 2—phos analogues of $[Co(2=phos)_2X_2]^+$ [12] For example, even rapidly isolated and dried products from reactions of $Co(2-phos)_2X_2$ ($X^- = Cl^-$, Br^-) with their respective halogen molecules discolored and decomposed quickly in the solid state, and immediately upon dissolution in CH_2Cl_2 or CH_3OH. The fact that we were able to prepare and isolate $[Rh(2=phos)_2Cl_2]^+$ and $[Rh(2-phos)_2Cl_2]^+$, which are both very stable, suggests that steric effects may be important, as Rh(III) is larger than Co(III). Differences in steric effects may also explain the observation that the square pyramidal $[Ni(2-phos)_2X]^+$ complexes are less stable than their 2=phos analogues.[13,14] It is apparent from an examination of the crystal structures of $[Co(2=phos)_2O_2]^+$,[15] $[Rh(2-phos)_2O_2]^+$,[3] and $[Ir(2-phos)_2O_2]^+$ [3] salts that the puckered[3] P-C-C-P moiety of the 2—phos chelate ring necessarily causes rotation of PPh_2 units about P-M bonds, relative to their orientation in 2=phos complexes, thereby affecting nonbonding interactions between the phenyls and other groups in the coordination sphere. We suggest that the Ph···X repulsions in the trans disubstituted Co(III) complexes are large, thereby weakening the Co-X bonds and promoting redox decomposition processes.[16] These repulsions apparently are particularly severe in the case of 2—phos.

Straightforward attempts to prepare $[Co(2=phos)_2(NO_2)_2]^+$ from $[Co(2=phos)_2Cl_2]^+$ and NO_2^- gave $[Co(2=phos)(NO)_2]^+$,[17] and a ligand molecule was oxidized to cis-1,2-bis(diphenylphosphine oxide)ethylene, abbreviated 2=phosox.[18] We infer that $[Co(2=phos)_2(NO_2)_2]^+$ is unstable, owing to highly unfavorable steric interactions[19] involving NO_2^- and PPh_2 groups, and undergoes redox decomposition:

$$[Co(2=phos)_2(NO_2)_2]^+ \rightarrow [Co(2=phos)(NO)_2]^+ + 2=phosox \quad (1)$$
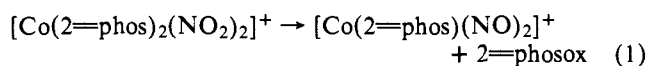
We have prepared $[Co(2=phos)_2O_2]^+$ both by dioxygen addition[6] to $[Co(2=phos)_2]^+$ and by oxidation of $[Co(2=phos)_2]^{2+}$. This latter complex may readily be crystallized either as a bright yellow tetrafluoroborate or perchlorate salt upon addition of the appropriate cobaltous salt to an acetone solution of 2=phos under anaerobic conditions. When the reaction is carried out aerobically, the solution turns dark brown and no product crystallizes. Work-up of the solution affords $[Co(2=phos)_2O_2]^+$, in somewhat less than 50% yield based on starting materials, as well as considerable amounts of cobalt(II). Reaction of $[Co(2=phos)_2]^{2+}$ with O_2 in various other polar organic solvents (e.g., methanol, acetonitrile, dichloromethane) similarly gives $[Co(2=phos)_2O_2]^+$. The reaction is quite slow and we observed no intermediates. In a quantitative experiment in which we forced the reaction to completion, the absorbance of the product solution at the low-energy peak of the dioxygen adduct (476 nm) indicated a yield of 50.5 ± 1.0% based on the amount of $[Co(2=phos)_2]^{2+}$ initially present. The remainder of the products were present in the form of Co(II) complexes. The following reaction sequence accounts for our observations:

$$[Co(2=phos)_2]^{2+} + O_2 \rightleftharpoons [Co(2=phos)_2O_2]^{2+} \quad (2)$$

$$[Co(2=phos)_2O_2]^{2+} + [Co(2=phos)_2]^{2+} \rightarrow [(Co(2=phos)_2)_2O_2]^{4+} \quad (3)$$

$$[(Co(2=phos)_2)_2O_2]^{4+} \xrightarrow{fast} [Co(2=phos)_2O_2]^+ + [Co(2=phos)_2]^{3+} \quad (4)$$

$$[Co(2=phos)_2]^{3+} \rightarrow Co(II) + \text{oxidized phosphines} \quad (5)$$

The fast step in the reaction (eq 4) may be viewed as a formal disproportionation of Co(II) into Co(I) and Co(III), with O_2 stabilizing the Co(I) (by irreversibly forming a strong complex). The instability of the Co(III) product $[Co(2=phos)_2]^{3+}$ (which is probably better represented as $[Co(2=phos)_2L_2]^{3+}$, where L is a solvent molecule) is consistent with our observations on such species (vide supra). The μ-peroxo intermediate is probably unstable for steric reasons. In order for this Co(III) complex to attain distorted octahedral coordination, solvent molecules must coordinate trans to the peroxide group.[20] Such solvent coordination should be unfavorable because of steric interactions with the phosphine ligands, and dissociation of one of the $[Co(2=phos)_2]^{3+}$ groups is a likely pathway.

The dioxygen adduct, $[Co(2=phos)_2O_2]^+$, is extremely stable. Acetonitrile solutions containing $[Co(2=phos)_2O_2]^+$ show very minor decomposition (from electronic spectral monitoring) over several days, and solutions in aqueous ethanol are fairly stable in the presence of strong acids, implying that the basicity of the complexed O_2 unit is low. As the "bite" of the coordinated dioxygen is small, steric interactions involving PPh_2 groups apparently are not severe.

Electronic Spectra of $[Co(2=phos)_2X_2]^+$ and Related Complexes. The electronic spectrum of 2=phos exhibits a broad, intense band at 39.1 kK (Figure 1). Assignment of this band to an $n \rightarrow \pi^*$ transition is suggested.[21] The energy of the lowest phenyl $\pi \rightarrow \pi^*$ transition can be estimated[22] to be ~35.5 kK from the position of the second $\pi \rightarrow \pi^*$ absorption at ~43.5 kK ($\epsilon \simeq 29\ 000$). Presumably, the lower $\pi \rightarrow \pi^*$ absorption contributes to the unsymmetrical tail of the $n \rightarrow \pi^*$ band. Both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions should be blue-shifted upon coordination of 2=phos, by analogy to the observed band positions in phosphine oxides.[23] These expectations are fulfilled, and phenyl $\pi \rightarrow \pi^*$ vibronic structure was observed near 38 kK for many of the metal complexes in the present study (particularly at low temperatures). We are confident, therefore, that any bands in $[Co(2=phos)_2X_2]^+$ at energies lower than 37 kK are not attributable to ligand-localized transitions.

The electronic spectra of the $[Co(2=phos)_2X_2]^+$ complexes are depicted in Figures 2 and 3. Spectral data are set out in Table I. The complexes trans-$[Co(en)_2Cl_2]^+$ and trans-$[Co(diars)_2Cl_2]^+$ show $^1A_{1g} \rightarrow {^1E_g}^a$ ligand-field (LF) transitions at 16.1[24] and 16.4 kK,[25] respectively, in remarkably close agreement with the position of the 15.9 kK band in $[Co(2=phos)_2Cl_2]^+$. The band in $[Co(2=phos)_2Br_2]^+$ at 14.9 kK is in similarly close agreement with the $^1A_{1g} \rightarrow {^1E_g}^a$ transition of trans-$[Co(en)_2Br_2]^+$ at 15.2 kK.[24] The fact that the intensities of the $^1A_{1g} \rightarrow {^1E_g}^a$ bands in the $[Co(2=phos)_2X_2]^+$ complexes are unexceptional for LF transitions is of interest, as intensification effects are often observed when phosphine ligands are present.[26] The relatively low intensities in the present case, however, are expected for an "axially localized" $^1A_{1g} \rightarrow {^1E_g}^a$ ($d_{xz}, d_{yz} \rightarrow d_{z^2}$) transition[27] in an effectively D_{4h} center. Thus both the positions and intensities of the lowest LF bands accord well with a formulation of trans stereochemistry for the $[Co(2=phos)_2X_2]^+$ complexes under consideration.

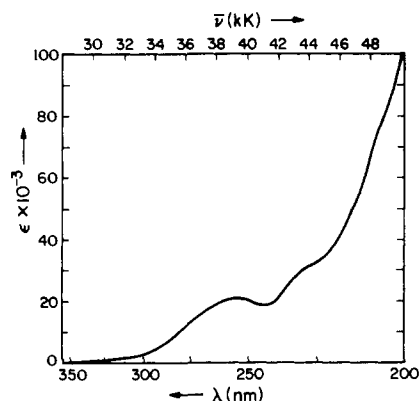The observed LF band at ~18 kK in $[Co(2=phos)_2(NCO)_2]^+$ is entirely consistent with the ranking of

Figure 1. Electronic spectrum of *cis*-1,2-bis(diphenylphosphino)ethylene (2=phos) in acetonitrile solution at 300 K.
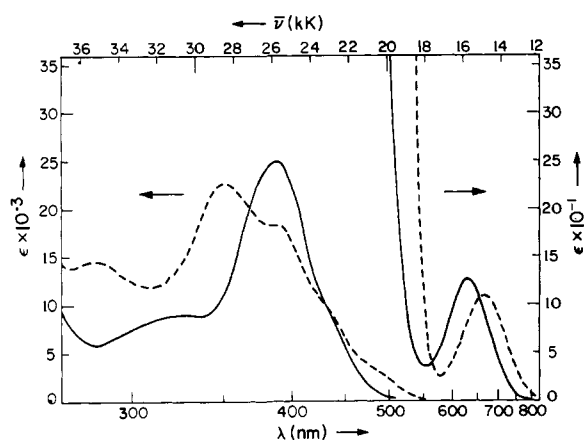

Figure 2. Electronic spectra in acetonitrile solution at 300 K of [Co(2=phos)$_2$Cl$_2$]ClO$_4$ (—) and [Co(2=phos)$_2$Br$_2$]ClO$_4$ (- - -).
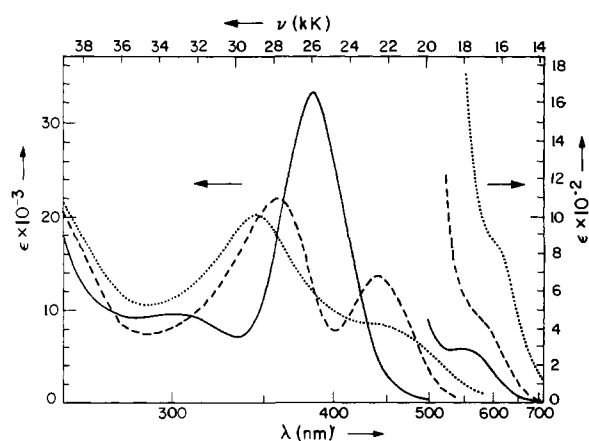
Figure 3. Electronic spectra in acetonitrile solution at 300 K of [Co(2=phos)$_2$X$_2$]ClO$_4$ complexes: X$^-$ = NCO$^-$ (—), NCS$^-$ (- - -), and N$_3$$^-$ (· · ·).

NCO$^-$ in the spectrochemical series for [CoX$_4$]$^{2-}$ complexes.[28] The LF bands of the N$_3$$^-$ and NCS$^-$ derivatives (Table I), on the other hand, appear at anomalously low energies, relative to the bands reported for *trans*-[Co(en)$_2$(N$_3$)$_2$]$^+$ (17.8 kK)[29] and *trans*-[Co(en)$_2$(NCS)$_2$]$^+$ (19.9 kK).[25] Yamada[25] noted a similar anomaly for *trans*-[Co(diars)$_2$(NCS)$_2$]$^+$, and proposed that the arsine complex contained S-bonded thiocyanato ligands, leading to a sharp decrease in ligand field strength relative to the N-bonded ethylenediamine complex. Although a formulation involving S-bonded thiocyanate helps explain the band position in [Co(2=phos)$_2$(NCS)$_2$]$^+$ as well, it is apparent that

Table I. Electronic Spectra of [Co(2=phos)$_2$X$_2$]ClO$_4$ in Acetonitrile Solution at 300 K

X$^-$	λ_{max} (nm)	$\bar{\nu}_{max}$ (kK)	ϵ	Assignment
Cl$^-$	630	15.9	128	$^1A_{1g} \rightarrow {}^1E_g$[a]
	~440	22.7	~7 800	$\sigma(P) \rightarrow d_{z^2}$
	388	25.8	25 200	$\sigma(P) \rightarrow d_{x^2-y^2}$
	325	31.0	9 000	$\pi(Cl) \rightarrow d_{z^2}$
Br$^-$	671	14.9	110	$^1A_{1g} \rightarrow {}^1E_g$[a]
	~490	20.5	3 000	a
	~435	23.0	9 000	a
	~390	25.7	18 000	a
	354	28.2	22 700	a
	284	35.1	14 300	$\sigma(Br) \rightarrow d_{z^2}$
NCO$^-$	~555	18.0	280	$^1A_{1g} \rightarrow {}^1E_g$[a]
	386	25.9	33 000	$\sigma(P) \rightarrow d_{x^2-y^2}$
	302	33.1	8 800	$\pi(NCO) \rightarrow d_{z^2}$
NCS$^-$	~595	16.8	~400 (sh)	$^1A_{1g} \rightarrow {}^1E_g$[a]
	442	22.6	13 400	$\sigma(P) \rightarrow d_{x^2-y^2}$
	360	27.8	21 900	b
N$_3$$^-$	~625	16.0	~750 (sh)	$^1A_{1g} \rightarrow {}^1E_g$[a]
	~465	21.5	8 400	$\sigma(P) \rightarrow d_{x^2-y^2}$
	346	28.9	19 200	b

[a] Overlapping $\sigma(P) \rightarrow d_{z^2}$, $\sigma(P) \rightarrow d_{x^2-y^2}$, and $\pi(Br) \rightarrow d_{z^2}$ absorptions. [b] Overlapping $\sigma(P) \rightarrow d_{x^2-y^2}$ and π(pseudohalide) $\rightarrow$ d$_{z^2}$ absorptions.

any anomalous features in the spectrum of [Co(2=phos)$_2$(N$_3$)$_2$]$^+$ cannot be accounted for in the same way.

All of the 2=phos complexes of Co(III) show intense bands between 20 and 37 kK, which may be assigned to ligand-to-metal charge transfer (LMCT) transitions.[30] The LMCT spectra are extremely similar to those of Co(III) arsine complexes,[31] and very similar optical electronegativities are inferred for arsenic and phosphorus ligands. As both cis and trans isomers are known for several of the arsine complexes,[32] the close similarity of the present spectra to those of known trans isomers accords with the ligand field analysis.

We shall attempt a detailed interpretation of the LMCT bands based on the assumption that the [CoP$_4$X$_2$]$^+$ core possesses D_{4h} symmetry. In D_{4h}, two allowed σ(phosphine)-to-metal transitions are expected, e$_u$(P) $\rightarrow$ d$_{z^2}$ and e$_u$(P) $\rightarrow$ d$_{x^2-y^2}$, both being $^1A_{1g} \rightarrow {}^1E_u$. Excitation to d$_{x^2-y^2}$ should be the higher energy of the two $^1A_{1g} \rightarrow {}^1E_u$ transitions, given the dσ* splitting implied by the LF spectra, and should also give rise to the more intense absorption band, owing to the larger overlap of the orbitals involved. The intense bands of [Co(2=phos)$_2$Cl$_2$]$^+$ at (25.8 kK) and [Co(2=phos)$_2$(NCO)$_2$]$^+$ (25.9 kK) are therefore assigned to this transition. The weak shoulder in the [Co(2=phos)$_2$Cl$_2$]$^+$ spectrum at 22.7 kK is assigned to the transition to d$_{z^2}$. The fact that no such shoulder is observable in the spectrum of the NCO$^-$ complex is reasonable, as this ligand would not be expected to produce a large dσ* splitting.

The lowest energy LMCT band in the spectrum of *trans*-[Co(en)$_2$Cl$_2$]$^+$ is a π(Cl) $\rightarrow$ d$_{z^2}$ transition at 32.5 kK (ϵ 1300).[24] Thus the band in [Co(2=phos)$_2$Cl$_2$]$^+$ at 31.0 kK can reasonably be assigned similarly. The conventional optical electronegativity of π(NCO) is the same as that of π(Cl),[33] and the [Co(2=phos)$_2$(NCO)$_2$]$^+$ band at 33 kK can therefore be assigned to π(NCO) $\rightarrow$ d$_{z^2}$ charge transfer. If, as seems reasonable from these assignments, the energies of the charge transfer transitions are assumed to fit into the series defined by *trans*-[Co(en)$_2$X$_2$]$^+$ complexes,

the inferred value of the optical electronegativity of $\sigma(P)$ is roughly equal to that of $\pi(Br)$, which is entirely consistent with other estimates.[33]

Bromide-to-cobalt(III) charge-transfer transitions are observed at 28.1 ($\pi(Br) \rightarrow d_{z^2}$) and 34.6 kK ($\sigma(Br) \rightarrow d_{z^2}$) in the spectrum of trans-$[Co(en)_2Br_2]^+$ [24] We can thus assign the 35.1-kK band of $[Co(2=phos)_2Br_2]^+$ to $\sigma(Br) \rightarrow d_{z^2}$, whereas $\pi(Br) \rightarrow d_{z^2}$ and $\sigma(P) \rightarrow d\sigma^*$ transitions evidently overlap to produce the extremely complicated absorption region between 20 and 32 kK.

The charge transfer spectra of $[Co(2=phos)_2(NCS)_2]^+$ and $[Co(2=phos)_2(N_3)_2]^+$ are also difficult to interpret, as two relatively intense bands between 20 and 30 kK are observed in each case. For comparison, bands attributable to π(pseudohalide)-to-cobalt(III) transitions are observed at 30.9 kK for trans-$[Co(en)_2(NCS)_2]^+$,[34] and at 32.3 kK for trans-$[Co(en)_2(N_3)_2]^+$ [29] One possibility is that the two bands in the 2=phos complexes represent transitions to two highly split components of ^1E_u ($\sigma(P) \rightarrow d_{x^2-y^2}$), and that the π(pseudohalide) $\rightarrow$ Co(III) transitions form part of the higher band system near 30 kK. Indeed, it could be argued that a large splitting of the ^1E_u excited state in the azido and thiocyanato derivatives should occur. Whereas M-NCO is generally linear or almost linear in isocyanato-metal complexes,[35] M-N_3 and M-SCN units are usually strongly bent.[36-38] Such bending will clearly remove the degeneracy of the ^1E_u excited state, and the effect could conceivably be very large in 2=phos complexes, in view of the steric hindrance to axial coordination. Furthermore, unusually low LF transition energies would be expected if the metal-pseudohalide bonds were forced to be somewhat longer than normal. It is also possible that the aforementioned broad absorption system of $[Co(2=phos)_2Br_2]^+$, consisting of at least four bands, has a related explanation, as the large radius of bromide could lead to distortions in the coordination sphere.

The spectrum of $[Rh(2=phos)_2Cl_2]^+$ (Figure 4) can be assigned completely by analogy to that of $[Co(2=phos)_2Cl_2]^+$. The $^1A_{1g} \rightarrow {}^1E_g{}^a$ ligand-field transition is observed at 24.6 kK (ϵ 420). For comparison, the same transition is found in trans-$[Rh(en)_2Cl_2]^+$ at 25.0 kK (ϵ 82.2).[39] The $^1A_{1g} \rightarrow {}^1E_u(\sigma(P) \rightarrow d_{x^2-y^2})$ transition of the 2=phos complex is at 31.2 kK (ϵ 35 000). The shifts of both the LF and LMCT transitions to higher energy relative to the Co(III) case accord well with experience.[40] It is especially noteworthy that the positions of the absorption bands in $[Rh(2=phos)_2Cl_2]^+$ and $[Rh(2—phos)_2Cl_2]^+$ are virtually identical,[41] which is consistent with observed similarities in the spectra of complexes of the two ligands with other central metals.[13,14,42] In the absence of severe steric interactions, therefore, it is apparent that there are no important electronic differences in M-P bonds between 2=phos and 2—phos complexes.

In Figure 5 we show the electronic spectra of $[Co(2=phos)_2O_2]^+$, as the PF_6^- salt, in 12:1 EPA-CHCl$_3$ solution at room temperature and 77 K. The room temperature spectrum is insensitive to both solvent and anion. The spectrum shows three absorption features, a poorly defined shoulder at ~16 ($\epsilon \simeq 75$), a sharp peak at 21.0 (ϵ 1020), and an intense band at 31.0 kK (ϵ 17 800). A broad feature at ~38 kK is ascribable to phenyl $\pi \rightarrow \pi^*$ absorption, with the very weakly structured higher energy portion of the spectrum being, as usual for aryl phosphine complexes, difficult to interpret.

The peak at 21 kK at room temperature blue-shifts strongly at 77 K and increases slightly in intensity. A shoulder is discernible at ~26 kK ($\epsilon \simeq 1200$). The band in the near-ultraviolet sharpens, intensifies considerably, and shifts moderately to higher energy. Finally, the phenyl $\pi \rightarrow$
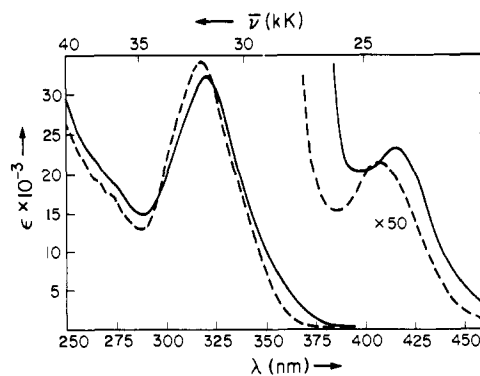

Figure 4. Electronic spectra of $[Rh(2=phos)_2Cl_2]ClO_4$ in 6:1 EPA-CH$_2$Cl$_2$ glass at 300 (—) and 77 K (- - -).
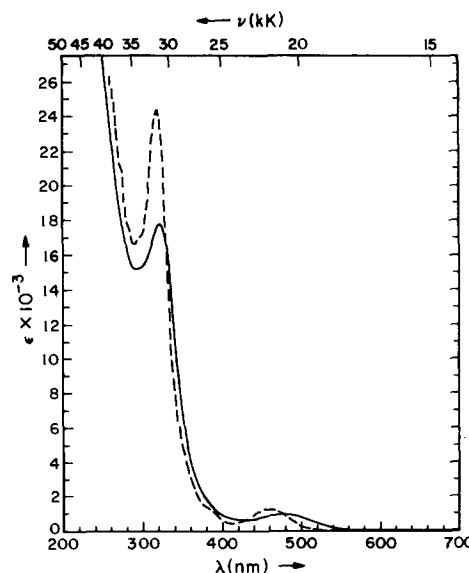

Figure 5. Electronic absorption spectra of $[Co(2=phos)_2O_2]PF_6$ in 12:1 EPA-CHCl$_3$ at 300 (—) and 77 K (- - -).

π^* band at higher energy shows increased resolution into individual vibronic transitions.

We initially remark that this spectrum is not consistent with a formulation involving either Co(I) or Co(II). Complexes of Co(I) have intense, low-energy electronic absorption bands. For example, the square planar, low-spin $[Co(2=phos)_2]^+$ complex exhibits a prominent band at 13.5 kK (ϵ 1300).[6] Complexes of Co(II) similarly show very low energy transitions, the square pyramidal low-spin [Co-(2—phos)$_2$Cl]$^+$ having bands at 16.7 (ϵ 600), 14.7 (ϵ 730), 0.72 (ϵ 120), and 0.48 kK (ϵ 80).[7]

However, the observed electronic spectrum of $[Co(2=phos)_2O_2]^+$ is exactly that expected for a cis-disubstituted cobalt(III) phosphine complex. In Figure 6 we present the electronic absorption spectrum of $[Co(2=phos)_2CO_3]^+$. The observed bands are compared to those exhibited by $[Co(2=phos)_2O_2]^+$ in Table II. The electronic spectral features of the two complexes are remarkably similar, both in energies and intensities.

The complex $[Co(en)_2CO_3]^+$ exhibits LF bands at 19.6 and 27.8 kK,[43] which are attributable to transitions to levels derived from the $^1T_{1g}$ and $^1T_{2g}$ states, respectively, of octahedral symmetry. Therefore the band near 20 kK in $[Co(2=phos)_2CO_3]^+$ and $[Co(2=phos)_2O_2]^+$ can immediately be assigned $^1A_1 \rightarrow {}^1T_1$, whereas the shoulder resolved at 26 kK (77K) for the dioxygen adduct is attributed to $^1A_1 \rightarrow {}^1T_2$. The relatively high molar extinction coefficients observed for the ligand field bands in these complexes are at-
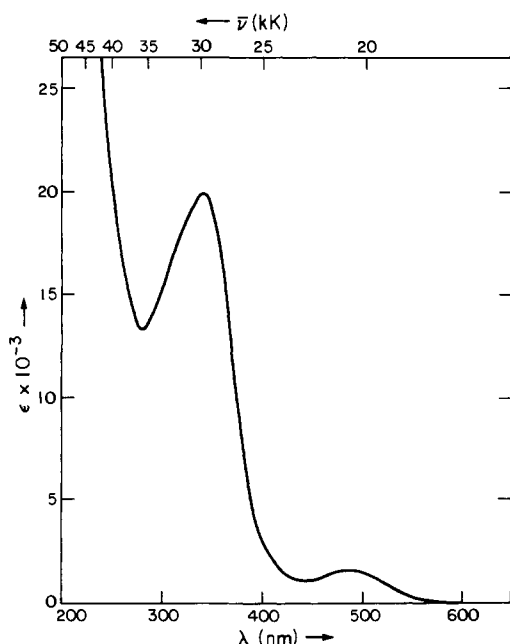
Figure 6. Electronic absorption spectrum of [Co(2=phos)₂CO₃]ClO₄ in acetonitrile solution at 300 K.

tributable to their low symmetry, in conjunction with the phosphine "intensification" effect.[26] The intense band observed near 30 kK in both complexes is assigned to an LMCT transition of the type $\sigma(P) \rightarrow d\sigma^*(Co)$. The observed bands are slightly blue-shifted from those of the [Co(2=phos)₂X₂]⁺ complexes of apparent trans stereochemistry (Table I), and are considerably broader.

It is apparent that the spectroscopic results strongly favor a ground-state electronic structure of [Co(2=phos)₂O₂]⁺ involving Co(III) and coordinated peroxide ion. Further, the spectrochemical properties of side-bonded O_2^{2-} appear to be quite normal for a bidentate, oxygen-donor ligand. No bands are observed that can be ascribed to transitions involving the dioxygen unit. The lowest energy LMCT transitions in the CoO_2^+ unit must originate in a filled π^* orbital of O_2^{2-}. In a side-bonded metal complex, the π^* level is split into an in-plane σ-bonding orbital and an out-of-plane π-bonding orbital. There are two allowed LMCT transitions from these $\pi^*(O_2^{2-})$ orbitals to the cobalt(III) $d\sigma^*$ orbital ("$d_{x^2-y^2}$") involved directly in the electronic structure of the CoO_2^+ group. It has been found[44] that μ-peroxodicobalt(III) complexes exhibit two broad LMCT bands between 25 and 35 kK, both of which are rather weak ($\epsilon \sim 3000$). In the μ-peroxo case, however, the $O_2^{2-} \rightarrow$ Co(III) σ-bonding is shared by both filled π^* orbitals. For a side-bonded peroxo complex, we expect the transition from the σ-bonding component to be shifted to higher energy;

hence, it is probably obscured in the [Co(2=phos)₂O₂]⁺ spectrum by intense ligand absorption above 35 kK. The transition from the out-of-plane π^* (O_2^{2-}) orbital, on the other hand, should be shifted to *lower* energy relative to a μ-peroxo case, and should become considerably weaker, as spatial overlap with $d\sigma^*$ orbitals is decreased. Thus, the out-of-plane $\pi^*(O_2^{2-}) \rightarrow$ Co(III) band could be masked by the moderately intense $^1A_1 \rightarrow \, ^1T_1$ absorption, or might even correspond to the weak shoulder at 16 kK.

Electronic spectral data for [Ir(2=phos)₂O₂]⁺ are also given in Table II. A shoulder at about 33 kK is assigned to the $^1A_1 \rightarrow \, ^1T_1$ LF transition. It may be noted that the shift to higher energy of ~12 kK relative to the cobalt complex is in accord with experience, as the lowest energy LF band in *trans*-[Ir(en)₂Cl₂]⁺, for example, is blue-shifted by 12.6 kK[45] from that observed for *trans*-[Co(en)₂Cl₂]⁺. An intense shoulder at ~43 kK ($\epsilon \simeq 70\,000$) in the spectrum of [Ir(2=phos)₂O₂]⁺ is evident, and has no counterpart at the same energy in the spectrum of [Co(2=phos)₂O₂]⁺. The energy is reasonable for $\sigma(P) \rightarrow d\sigma^*(Ir)$ charge-transfer, by arguments similar to those used for the ligand field band.

Comparison to the spectrum of [Rh(2=phos)₂O₂]⁺ would be instructive, as dioxygen addition to rhodium complexes is generally very reversible; thus, the ground state description of these complexes might conceivably *not* be analogous to the cobalt complex. Unfortunately, the equilibrium constant of the oxygenation reaction lies to the left in solution and we could not isolate any pure solids. The complex [Rh(2—phos)₂O₂]⁺ can be isolated as a crystalline salt,[3] but satisfactory spectral data could still not be obtained. Dissolution of [Rh(2—phos)₂O₂]X complexes in any solvent or preparation of a KBr pellet reversed the oxygenation reaction, whereas mull spectra were extremely poorly resolved. Difference spectral methods employed on the complex in solution indicate with certainty an intense band at ~36 kK, and this is tentatively assigned to the $\sigma(P) \rightarrow d\sigma^*(Rh)$ charge-transfer. The estimated intensity of the band, based on decreased Rh(I) absorption at lower energy, is comparable to that of the corresponding band in [Co(2=phos)₂O₂]⁺, whereas the energy is consistent with $\sigma(P) \rightarrow d\sigma^*(Rh)$ transitions in the bona fide Rh(III) phosphine complexes discussed earlier. The intense absorption of the Rh(I) complex made it impossible to detect a LF band. Some rhodium-dioxygen complexes are more stable,[46,47] but the ligand variations are too great to permit meaningful comparisons with the [M(2=phos)₂O₂]⁺ systems.

Conclusions and Additional Observations

The electronic spectroscopic properties of the dioxygen adduct [Co(2=phos)₂O₂]⁺ are those of a normal cobalt-(III) complex. Any unusual properties of this complex are thus due to the [Co(2=phos)₂]³⁺ moiety, and *not* to the dioxygen unit. The latter is well-defined as a chelating peroxide ligand, which in no way is more special than a biden-

Table II. Electronic Spectra of [MP₄O₂]⁺ Complexes

Compound	Conditions	λ_{max} (nm)	$\bar{\nu}_{max}$ (kK)	ϵ	Assignment
[Co(2=phos)₂- O₂]PF₆	12:1 EPA–CHCl₃ soln (300 K)	~620	~16	~75 (sh)	?
		475.5	21.03	1 020	$^1A_1 \rightarrow \, ^1T_1$
		322.5	31.00	17 800	$\sigma(P) \rightarrow d\sigma^*(Co)$
	12:1 EPA–CHCl₃ soln (77 K)	462	21.6	1 170	$^1A_1 \rightarrow \, ^1T_1$
		~385	~26	~1 200 (sh)	$^1A_1 \rightarrow \, ^1T_2$
		319	31.3	24 500	$\sigma(P) \rightarrow d\sigma^*(Co)$
[Co(2=phos)₂- CO₃]ClO₄	CH₃CN soln (300 K)	487.5	20.51	1 630	$^1A_1 \rightarrow \, ^1T_1$
		342	29.2	19 850	$\sigma(P) \rightarrow d\sigma^*(Co)$
[Ir(2=phos)₂- O₂]ClO₄	EPA soln (300 K)	~300	~33	~8 000 (sh)	$^1A_1 \rightarrow \, ^1T_1$
		~230	~43	70 000 (sh)	$\sigma(P) \rightarrow d\sigma^*(Ir)$

tate carbonato group. Additionally, it should be noted that the infrared spectra of $[M(2{=}phos)_2O_2]^+$ complexes are in excellent agreement with a bidentate peroxide formulation. Thus, $[Co(2{=}phos)_2O_2]^+$ exhibits an ir band at 909 cm^{-1}, whereas $[Rh(2{=}phos)_2O_2]^+$ and $[Ir(2{=}phos)_2O_2]^+$ have corresponding bands at 876 and 845 cm^{-1}.[6] The only reasonable interpretation of these bands is that they correspond to O–O stretching,[48-50] and their positions correspond well to the value of 880 cm^{-1} observed for H_2O_2.[51]

Similar conclusions to those we have reached regarding the $[Co^{III}(O_2{}^{2-})]^+$ formulation of $[Co(2{=}phos)_2O_2]^+$ have been put forward independently by Bosnich and co-workers[52] in the case of arsine analogues. It is interesting that, for the less-sterically-hindered arsine ligands, it was possible to prepare μ-peroxodicobalt(III) derivatives, by reaction of the cobalt(II) complexes with O_2. This observation adds support to our proposed mechanism for the reaction of $[Co(2{=}phos)_2]^{2+}$ with O_2.

Acknowledgments. We thank Dr. M. Kubota for helpful comments. This research was supported by the National Science Foundation.

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phos)$_2$]$(BF_4)_2$. The compound is unstable in solution, and attempted recrystallizations only served to lower the purity.
(17) We were also able to prepare $[Co(2{=}phos)(NO_2)_2]^+$ by direct reaction of $[Co(2{=}phos)_2NO_2]^+$ with dioxygen (see Experimental Section).
(18) In one preparation, the solvent was stripped from the deep orange product solution and the residue was extracted with hot toluene. The extract gave, after evaporation, approximately 1 equiv. relative to the starting Co(III) complex, of cis-1,2-bis(diphenylphosphine oxide)ethylene, contaminated with some 2$=$phos and other unidentified organic products. The di(phosphine oxide) product was identified by comparison (melting point and ir) to authentic material prepared by H_2O_2 oxidation of 2$=$phos (A. M. Aguiar and D. Daigle, J. Am. Chem. Soc., 86, 2299 (1964)).
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