Uv	λ_{max}	E
Thermodynamic	225	1200
Kinetic	254	1400

$Pb(OAc)_4$ Oxidation of *threo*- and *erythro*-2,2'-Dimethylbenzopinacol. 2,2'-Dimethylbenzopinacol (0.432 mol) (55% thermodynamic, 45% kinetic) was allowed to react at room temperature with 0.158 mol of $Pb(OAc)_4$ in 10 ml of acetic acid for 3 days. After hydrolysis and normal workup, NMR analysis showed 34% kinetic, 55% thermodynamic, and 11% ketone (30% complete reaction).

References and Notes

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(2) E. C. Ashby, H. M. Neumann, and J. T. Laemmle, *Acc. Chem. Res.*, **7**, 272 (1974).
(3) E. C. Ashby, J. Laemmle, and H. M. Neumann, *J. Am. Chem. Soc.*, **94**, 5421 (1972).
(4) E. C. Ashby, L.-C. Chao, and H. M. Neumann, *J. Am. Chem. Soc.*, **95**, 4896 (1973).
(5) C. Blomberg, R. M. Sallinger, and H. S. Mosher, *J. Org. Chem.*, **34**, 2385 (1969).
(6) J. F. Fauvarque and E. Rouget, *C. R. Acad. Sci., Ser. C*, **267**, 1355 (1968).
(7) T. Holm and I. Crossland, *Acta Chem. Scand.*, **25**, 59 (1971).
(8) (a) E. C. Ashby, F. Walker, and H. M. Neumann, *Chem. Commun.*, 330 (1970); (b) E. C. Ashby, H. M. Neumann, F. W. Walker, J. Laemmle, and L. C. Chao, *J. Am. Chem. Soc.*, **95**, 3330 (1973).
(9) The "other" product is believed to be (2,6-dimethylphenyl)phenylmethylcarbinol.
(10) The "index of determination" is the explained variance divided by the total variance or (% explained variance)/100.
(11) E. C. Ashby and T. L. Wiesemann, *J. Am. Chem. Soc.*, **96**, 7117 (1974).
(12) It is possible that even $[Fe^0]$ is the "active catalyst" since $Fe(CO)_5$ is almost as effective as $Fe(acac)_3$ in catalyzing pinacol formation.
(13) I. A. Lopp, J. D. Buhler, and E. C. Ashby, *J. Am. Chem. Soc.*, **97**, 4966 (1975).
(14) The half-life for the disappearance of ketone in the noncatalyzed reaction was estimated from Figure 2 to be 9.3 h.
(15) Work in progress.
(16) Studies in this laboratory have shown that the kinetic product is also produced very early in reactions at room temperature, but conversion to thermodynamic pinacol occurs completely in less than 1 h.
(17) S. E. Rudolph and S. C. Smith, *J. Chem. Soc. D*, 1428 (1970).
(18) Since reaction at Grignard:ketone ratio of 400 gives hydrol in 36 to 72% yield.
(19) PPM trace elements in Dow doubly sublimed magnesium by spark source mass spectrometry: B-0.005, N-2.9, O-420, F-0.01, Na-8.9, Al-ND, Si-2, P-ND, S-1, Cl-25, K-0.85, Ca-1.8, Ti-ND, Cr-ND, Mn-ND, Fe-0.1, Co-ND, Cu-0.1, Zn-25, Ga-ND, Sr-ND, Y-ND, Zr-ND, Pb-ND. Analysis by MicroTrace Analytical Services, Industry, Calif., 91746 (ND = not detectable).
(20) (a) H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *Tetrahedron*, **31**, 1053 (1975); *ibid.*, 719 (1973); H. M. Walborsky and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3288 (1964); H. M. Walborsky and M. S. Aronoff, *J. Organomet. Chem.*, **51**, 31 (1973).
(21) J. Laemmle, E. C. Ashby, and H. M. Neumann, *J. Am. Chem. Soc.*, **93**, 5120 (1971).
(22) E. C. Ashby and R. G. Beach, *Inorg. Chem.*, **9**, 2300 (1970).
(23) E. C. Ashby and R. D. Schwartz, *J. Chem. Educ.*, **51**, 65 (1974).

Oxygen Activation by Transition Metal Complexes. 2. Bis(acetylacetonato)cobalt(II)-Catalyzed Oxidation of Tributylphosphine[1]

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Abstract: The oxidation of Bu_3P (**1**), catalyzed by $Co(acac)_2$ (**2**) is described. In MeCN under air at 0 °C the catalyzed oxidation of **1** gives mainly Bu_3PO, but $(BuO)Bu_2PO$ also forms in 20–30% yield, along with smaller amounts of other products. If Ph_2NH, or one of several other free-radical inhibitors, is added to the system, the oxidation proceeds rapidly and gives Bu_3PO as the *exclusive* product. Under these conditions the reaction is first order in cobalt species, one-half order in oxygen, and zero order in Bu_3P. However, spectroscopic studies showed that in solution most (≥80%) of the cobalt is present as $[(Bu_3P)Co(acac)_2]$ (**8**). The formation constant for **8** was estimated at room temperature to be $40 \pm 10\ M^{-1}$; thus the rate law for the reaction is given by rate $= k[(Bu_3P)Co(acac)_2][O_2]^{1/2}$. Complex **2** also catalyzed the oxidation of (*R*)-(−)-MePhPrP (**9**) to (*S*)-(−)-MePhPrPO with *retention* of configuration, as well as a slower conversion of $(BuO)_3P$ to $(BuO)_3PO$, but Ph_3P and $(PhO)_3P$ failed to undergo oxidation. By observing the catalytic activity of a number of other cobalt complexes, the importance of open coordination sites, as well as the redox potential of the complex, was noted. A mechanism is proposed to account for these results (Scheme I). It involves the reaction of **8** with O_2 to give a binuclear μ-peroxide **11**; the *reversible* dissociation of **11** via homolysis of the central O–O bond to give $[(Bu_3P)(acac)_2CoO]$ **12**; and the intramolecular rearrangement of **12** to give $[(Bu_3PO)Co(acac)_2]$ (**13**) in the product-forming step. The relationship of this reaction and mechanism to other metal-catalyzed oxygenations is discussed.

Under ordinary conditions most organic compounds are kinetically unreactive toward molecular oxygen. The major reasons for this lie in the properties of the oxygen molecule itself. Since oxygen has a triplet ground state, its direct combination with singlet organic molecules is a spin-forbidden process. Transition metals and their ions having multiple spin and oxidation states of suitable energy are not subject to the above restriction and can readily interact with the oxygen molecule, even to the extent of forming isolable oxygen adducts. In the complexed form the properties of the oxygen molecule are altered and the changes are often manifested as an increased reactivity of coordinated oxygen toward organic compounds. For example, π complexes of oxygen with d^6, d^8, and d^{10} metal centers are diamagnetic and catalyze several characteristic oxidations of organic phosphines,[2-5] isocyanides,[3] and olefins[5-7] by mechanisms which have been characterized as intracomplex rearrangements leading to the four-electron reduction of coordinated O_2 by two ligand molecules. On the other hand metal-superoxide complexes containing a paramagnetic Co(III)-O-O· moiety are free radical-like and are well known to react by one-electron steps or hydrogen abstractions. Thus these oxygen complexes catalyze the oxidation[8-10] or oxidative coupling[10,11] of phenols and thiols.[12] Metal-superoxide complexes are also intermediates in the

formation of a third major class of oxygen adducts, the binuclear μ-peroxides.[13] These diamagnetic complexes are generally less reactive than their superoxide precursors, but it is possible to envision a means of oxygen activation which might be open to certain binuclear μ-peroxides, i.e., the formation of reactive oxometal species via homolytic dissociation of the central O-O bond. In this paper we describe the $Co(acac)_2$-catalyzed oxidation of tributylphosphine and present evidence for the catalytic activation of molecular oxygen by such a "reductive-dissociation" process.

Results

In acetonitrile solution at 0 °C under air, tributylphosphine (**1**) remains stable for up to 3 h before detectable amounts of oxidation products are formed. However, addition of catalytic amounts of bis(acetylacetonato)cobalt(II), $Co(acac)_2$ (**2**), to this solution leads to a rapid oxidation of the phosphine. Under these conditions the principal oxidation product is tributylphosphine oxide, but varying amounts (20-30%) of butyl dibutylphosphinate, $(BuO)Bu_2PO$, and other oxidation products are also formed. Reactions run in the dark behaved similarly to those run in room light. Monitoring the concentration of **1** by GLC showed that it decreased linearly with time for up to 2 half-lives before slowing down. This enabled the determination of initial reaction rates and from a study of their concentration dependence, the kinetic rate law for the reaction: rate $= k[(Bu_3P)Co(acac)_2][O_2]^{1/2}$.

Effects of Additives on the Oxidation Process. Since the formation of phosphinate esters from trialkylphosphines is indicative of free-radical oxidation processes,[14] we tested the effects of several free-radical chain inhibitors in our reaction system. The inhibitors tested included diphenylamine, 2,6-di-*tert*-butyl-*p*-cresol, 2,6-di-*tert*-butylphenol, triphenylphosphine, and triphenyl phosphite. Upon addition to the reaction system of any of these inhibitors at concentrations as high as the Bu_3P concentration, it was observed that (1) the Bu_3P solutions were stable for days under air at room temperature, and (2) when catalytic amounts of $Co(acac)_2$ were added (0 °C under air) a very rapid oxidation commenced, giving Bu_3PO as the *sole* reaction product. In the absence of Bu_3P or in its presence, none of the above inhibitors were detectably oxidized or altered in any other way under the reaction conditions. Ultimately all kinetic studies were done with added diphenylamine, which served to block the noncatalyzed autoxidation of the phosphine and as an internal standard for GLC.

The effects of metal-binding additives were also studied. Water inhibited the reaction by about 50% when present at ten times the concentration of **2**, although $Co(acac)_2 \cdot 2H_2O$ was essentially equivalent to the anhydrous form of **2** in catalytic effectivity. The bis-pyridine adduct of **2** was only 25% as effective as **2** itself, and at a pyridine-[**2**] ratio of 10:1 the reaction was totally inhibited. The 2,2′-bipyridyl adduct of **2** had no catalytic effect, and if excess dipyridyl was added to a reaction in progress *all further oxidation was instantly stopped.* This effect proved useful for quenching aliquots which were withdrawn from the reaction for GLC analysis. Lithium perchlorate, but not tetraethylammonium perchlorate, strongly inhibited the reaction when added at ten times the concentration of **2**.

Other Catalysts and Substrates. Bis(benzoylacetonato)cobalt(II) (**3**) was approximately as active a catalyst as **2**, but bis(trifluoroacetylacetonato)cobalt(II) (**4**) was only about one-third as effective as **2** in catalyzing the oxidation of **1**. Tris(acetylacetonato)cobalt(III), $Co(acac)_3$ (**5**), was completely inactive as a catalyst. Interestingly, the well-known[13] oxygen carrier CoSalen (**6**) and a phosphine complex susceptible to oxidation in solution,[15] $(Ph_3P)_2CoI_2$ (**7**), both failed to show any activity for Bu_3P oxidation. The oxidation of $(BuO)_3P$ to $(BuO)_3PO$ was also catalyzed by **2**, but at a much slower rate than the Bu_3P oxidation. Ph_3P and $(PhO)_3P$ were not oxidized by **2**, either in the presence or absence of Bu_3P.

Spectroscopic Studies. The possibility that $Co(acac)_2$ forms an adduct with molecular oxygen was investigated by infrared difference spectroscopy using 1% solutions of **2** in acetonitrile, chloroform, and toluene. The solutions were prepared under nitrogen and the solution in the sample cell was purged with oxygen briefly before running the spectrum. In no case did we observe any spectral changes that could be associated with oxygen adduct formation.

We also investigated the interaction of $Co(acac)_2$ with Bu_3P in acetonitrile solution at room temperature using the method used by Fackler to study the complexation of **2** by pyridine.[16] Because the catalyzed oxidation was extremely fast at room temperature and even small amounts of Bu_3PO caused large perturbations in the visible spectrum of **2**, all solution preparation and cuvette-filling operations had to be carried out in an oxygen-free atmosphere. As the Bu_3P concentration was varied from 0 to 100%, with $[Co(acac)_2]$ constant at 0.005 M, there was a small but progressive shift in the spectrum of **2** from a broad maximum around 550 nm (ϵ 22) and a sharper minimum around 450 nm (ϵ 17) in pure acetonitrile to one with a maximum around 560 nm (ϵ 45) and a minimum around 460 nm (ϵ 31) at high ratios of phosphine to cobalt. It was evident that at phosphine concentrations between 0.2 M in MeCN and neat Bu_3P as solvent there was very little further change in the spectra. This suggested that a limiting 1:1 complex was being formed even at very high Bu_3P concentrations. Using the ϵ values from this limiting spectrum as representing the complex $[(Bu_3P)Co(acac)_2]$ (**8**), we could calculate the relative amounts of **8** and **2** as a function of added Bu_3P, which lead to an estimated value of $40 \pm 10\ M^{-1}$ for the equilibrium constant for formation of **8** from **1** and **2**. Thus under typical conditions of a catalytic oxidation ca. 80% of the cobalt is present as $(Bu_3P)Co(acac)_2$, which is assumed to be the catalytically-active species, since ligands which form bis adducts of **2** completely quench the catalysis.

Kinetic Studies. Acetonitrile solutions of the reactants were prepared under nitrogen at room temperature and cooled to 0 °C before replacing the nitrogen atmosphere with dry air or other oxygen-nitrogen mixtures to start the reactions. Each reaction mixture contained Ph_2NH (20-40 mM as an internal standard for GLC analysis and to inhibit the metal-independent autoxidation of **1**), $Co(acac)_2$ (2-10 mM), Bu_3P (20-100 mM), and in some cases other additives as mentioned above. Volumes (10 ml) of the reactant solutions were magnetically stirred at 0 °C, and at intervals of 30-120 s 0.5-ml aliquots were transferred to vials containing sufficient solid 2,2′-bipyridyl to convert all of the $Co(acac)_2$ to $(bpy)Co(acac)_2$ and quench the reaction. These samples were analyzed by GLC to determine the rate of phosphine oxidation. Plots of $[Bu_3P]$ vs. time were linear for up to 2 half-lives in some cases, but most rate data were collected at <25% conversion. Rates were obtained from least-squares analysis of six to ten data points per run.

Figures 1 and 2 show the oxygen dependence and cobalt dependence of the reaction rates as one-half order and first order, respectively. At several concentrations of catalyst the reaction was shown to be independent of the concentration of tributylphosphine.

Oxidation of (*R*)-(−)-MePhPrP with $Co(acac)_2$. Methylphenylpropylphosphine (**9**) was found to be cleanly and rapidly oxidized to MePhPrPO (**10**) in the presence of **2**. At 0 °C in MeCN the oxidation of **9** by catalytic amounts of **2** is faster than the oxidation of **1**, and the reaction is more sensitive to product inhibition as well. (*R*)-(−)-**9** was prepared according to Mislow's procedure[17] and had a specific rotation in methanol (384 mg/5 ml) of −10.7°, corresponding to 72% optical pu-

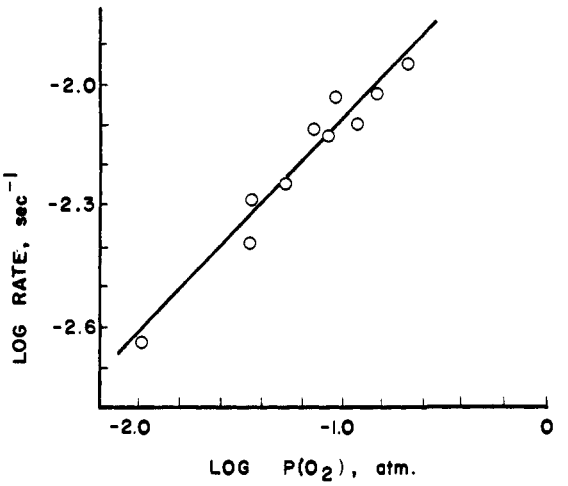


Figure 1. Dependence of Bu_3P oxidation rate on oxygen pressure. [Bu_3P] = 30 mM, [Ph_2NH] = 40 mM, [$Co(acac)_2$] = 5.3 mM in acetonitrile under 1 atm O_2/N_2 mixture at 0 °C; open circles are experimental points, the line is drawn to have a slope of 0.5.

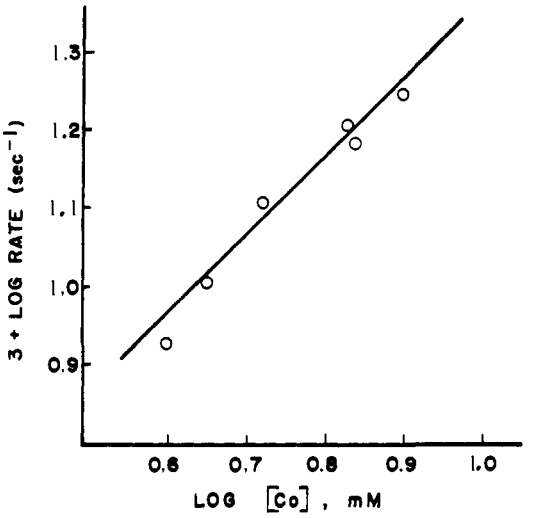


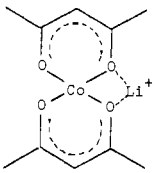
Figure 2. Dependence of Bu_3P oxidation rate on cobalt concentration. [Ph_2NH] = 40 mM, [Bu_3P] = 30 mM in acetonitrile under air at 0 °C; open circles are experimental points, the line is drawn to have a slope of 1.0.

rity.[18] Oxidation of 76 mg of this material with 1 ml of 30% H_2O_2 in 7 ml of methanol under nitrogen at 0 °C gave, after chromatography and sublimation, a 79% yield of **10** having a specific rotation in methanol (66 mg/2 ml) of −13 4°. This oxidation proceeds with 100% retention of configuration at phosphorus, which leads to a value of 67% (vs. 72% by direct polarimetry) for the optical purity of the starting (*R*)-(−)-**9**. Oxidation of 76 mg (0.457 mmol) of (*R*)-(−)-**9** with 20 mg (0.077 mmol) of **2** and 10 mg of Ph_2NH in 10 ml of acetonitrile at 0 °C for 1 h under air gave an 81% yield of **10**, having a specific rotation in methanol (68 mg/2 ml) of −11.4°. Thus the $Co(acac)_2$-catalyzed oxidation of (*R*)-(−)-**9** proceeds with *retention* of configuration at phosphorous.

Discussion

The free-radical autoxidation of trialkylphoshines produces characteristic mixtures of phosphinate, phosphonate, and phosphate esters in addition to the phosphine oxide.[14] Many transition metal ions and complexes are known to catalyze or promote free-radical chain autoxidations, but since the $Co(acac)_2$-catalyzed oxidation of tributylphosphine produces *only* the phosphine oxide and is not inhibited by a number of free-radical inhibitors, one is lead toward the conclusion that this reaction involves a specific metal-dependent oxygen activation and atom-transfer process. This conclusion is supported by the observation that the addition of ligands which coordinatively saturate the cobalt center (e.g., 2,2′-bipyridyl) instantly stops the catalyzed reaction by preventing the binding of phosphine and oxygen.

The interaction of oxygen with transition metal complexes is sensitive to the oxidation potential of the metal complex.[19,20] Thus increasing the electronegativity of the ligands on cobalt (cf. **2**, **3**, and **4**) raises the oxidation potential of the complex[1] and substantially decreases the efficiency of the complex as a catalyst. A similar effect is seen when lithium ions are added to solutions of **2**; the oxidation potential increases dramatically and catalytic activity is lost. This is attributable to the chelation of Li^+ by **2** to form bi- or trinuclear species such as **14** in anhydrous acetonitrile solution.[21,22] The inductive effects of the bound Li^+ make the electron density on cobalt less available for interaction with oxygen.

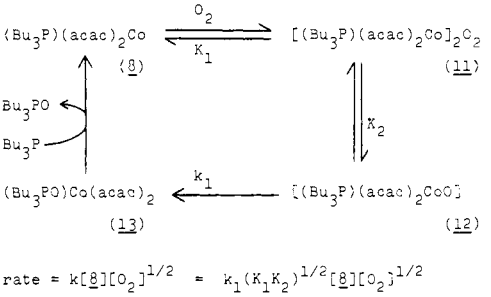


14

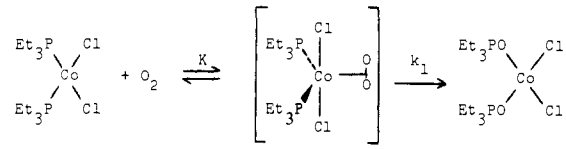
The rate of the $Co(acac)_2$-catalyzed oxidation of Bu_3P is independent of the Bu_3P concentration, but shows first-order dependence on cobalt concentration and one-half-order dependence on oxygen concentration. However, the spectroscopic studies showed that most of the cobalt in solution is present as **8** and not **2** and that oxygen does not interact significantly with **2** in the absence of Bu_3P. Thus the rate law for the reaction may be given by the expression: rate = $k[(Bu_3P)Co(acac)_2][O_2]^{1/2}$. This rate law is compatible with a reaction mechanism involving the steps shown in Scheme I. The oxidation of (*R*)-(−)-**9** with *retention* of configuration is in agreement with an intramolecular rearrangement (e.g., **12** → **13**) in the product-forming step and the half-order dependence on oxygen concentration can be explained if the formation of **12** is *reversible* and k_1 is rate limiting. The lack of catalytic activity (at 0 °C) of **2** for oxidation of Ph_3P and $(PhO)_3P$ and its reduced activity for oxidation of $(BuO)_3P$ may be explained in terms of their reduced tendency to form 1:1 adducts with **2**. However, Basolo and co-workers have shown[20] that Ph_3P serves very poorly compared to other axial bases for promoting oxygen uptake by Co(benacen). Thus trivalent phosphorus compounds with electronegative substituents may fail to undergo this catalytic oxygenation for the same basic reason that cobalt complexes with electronegative ligands fail to serve as efficient catalysts, i.e., unfavorable effects on K_1 mediated through changes in the redox potential of the cobalt complex.

The stoichiometric autoxidation of $(Et_3P)_2CoCl_2$ (**14**) has been reported[23] to produce only the phosphine oxide complex $(Et_3PO)_2CoCl_2$, which subsequently reacts with **14**, giving $(Et_3P)(Et_3PO)CoCl_2$.[24] Thls reaction also was not inhibited

Scheme I

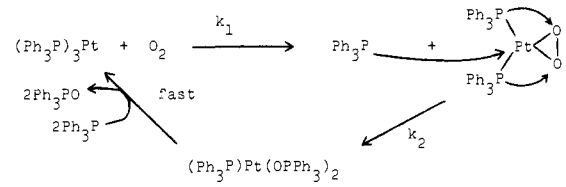


Scheme II



$$d[O_2]/dt = Kk_1[(Et_3P)_2CoCl_2][O_2]$$

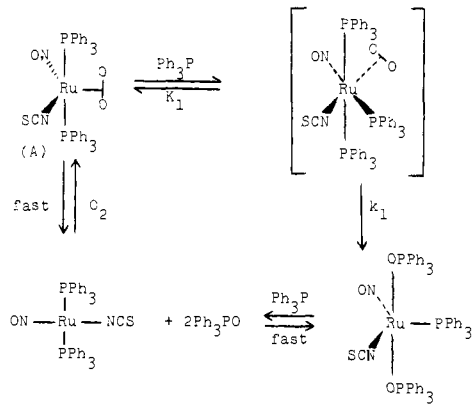
Scheme III



$$-d[(Ph_3P)_3Pt]/dt = k_1[(Ph_3P)_3Pt][O_2]$$

$$d[(Ph_3P)_3Pt]/dt = k_2[(Ph_3P)_2PtO_2][Ph_3P]$$

Scheme IV



$$\text{rate} = k_1K_1[Ph_3P][A] / (1 + K_1[Ph_3P])$$

by free-radial inhibitors and no evidence for an intermediate oxygen adduct was observed. The rate law and mechanism suggested for this reaction are given in Scheme II. It is interesting to compare the rate laws and suggested mechanisms of these reactions to other cases where isolable metal-oxygen complexes are involved (Schemes III[2] and IV[4]). In both of these cases the metal has coordination sites for *two* molecules of phosphine as well as for an oxygen molecule and the product-forming step involves an intramolecular rearrangement in which the coordinated oxygen apparently undergoes complete (i.e., four-electron) reduction with no involvement of intermediates. The same may be said for the mechanism of Scheme II, except that in this case the oxygen adduct is not isolable or detectable. In contrast, with $Co(acac)_2$ being four-coordinate[25] and forming a 1:1 adduct with Bu_3P, it is not possible to catalyze the reaction $2Bu_3P + O_2 + 2Bu_3PO$ within the coordination sphere of one metal complex as occurs in Schemes II-IV. Consequently, the activation of oxygen by $Co(acac)_2$ requires the cooperation of *two* metal centers in binding two molecules of phosphine and one molecule of oxygen. The most reasonable way for this to occur is via formation of the binuclear μ-peroxide **11** as shown in Scheme I.

Experimental Section

Tri-*n*-butylphosphine (Aldrich) was purified by chromatography over active silica gel *using deoxygenated solvents* (hexane containing 0-15% ether). The solvents were stripped on a rotary evaporator, breaking the vacuum with nitrogen to remove the neat phosphine, which was immediately sealed under nitrogen in glass ampules. This procedure was much more satisfactory than vacuum distillations. Acetonitrile was purified by successive distillations from NaH, P_2O_5, and CaH_2. Diphenylamine (Eastman) was recrystallized from 95% ethanol. $Co(acac)_2$ (**2**) was synthesized by the standard method[26] and sublimed (80-90 °C (0.02 Torr)) prior to use. Other cobalt complexes were available from a previous study.[1]

Reactions were run in 50-ml round-bottom flasks, which were connected with flexible tubing to a manifold for alternate evacuation and filling with nitrogen, air, or nitrogen-oxygen mixtures. The latter were prepared in a 2-l. filtration flask by displacing mineral oil with the appropriate gases. The mineral oil displaced was kept in a 2-l. separatory funnel reservoir and used to maintain a positive pressure slightly greater than 1 atm in the gas manifold and reaction flasks. The reaction solutions, prepared under nitrogen and cooled in a stirred ice-water bath, were stirred magnetically at a brisk speed, although the stirring speed did not seem to influence the rate of the reaction. Once the reactions were started (by replacing the nitrogen atmosphere by one containing oxygen), aliquots were removed and transferred to 13 × 100 mm Teflon-capped culture tubes containing 5 mg of *solid* 2,2′-bipyridyl adduct. These quenched samples were stored in a freezer for later analysis by GLC (5 ft × ⅛ in. 3% SE-30, 150 °C). The areas of the Bu_3P and Ph_2NH peaks were determined by electronic integration and from an appropriate calibration curve the concentration of Bu_3P in each aliquot was determined. Initial rates were determined by least-squares analysis of plots of $[Bu_3P]$ vs. time, using six to ten points per run.

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References and Notes

(1) Paper 1. R. P. Hanzlik and D. F. Smith, Jr., *J. Chem. Soc., Chem. Commun.*, 528 (1974).
(2) J. Halpern and A. L. Pickard, *Inorg. Chem.*, **9**, 2798 (1970).
(3) S. Otsuka, A. Nakamura, and Y. Tatsuno, *J. Am. Chem. Soc.*, **91**, 6994 (1969).
(4) B. W. Graham, K. R, Liang, C. J. O'Connor, and W. R. Roper, *Chem. Commun.*, 1272 (1970).
(5) C. Dudley and G. Read, *Tetrahedron Lett.*, 5273 (1972).
(6) J. E. Lyons and J. O. Turner, *J. Org. Chem.*, **37**, 2881 (1972).
(7) B. R. James and E. O. Ochiai, *Can. J. Chem.*, **49**, 975 (1971).
(8) E. W. Abel, J. M. Pratt, R. Whelan, and P. J. Wilkinson, *J. Am. Chem. Soc.*, **96**, 7119 (1974).
(9) A. Nishinaga, T. Tojo, and T. Matsuura, *J. Chem. Soc., Chem. Commun.*, 896 (1974).
(10) A. Nishinaga, K. Watanabe, and T. Matsuura, *Tetrahedron Lett.*, 1291 (1974).
(11) L. H. Vogt, Jr., J. G. Wirth, and H. L. Finkbeiner, *J. Org. Chem.*, **34**, 273 (1969).
(12) I. G. Dance, R. C. Conrad, and J. E. Cline, *J. Chem. Soc., Chem. Commun.* 13 (1974).
(13) R. G. Wilkins, *Adv. Chem. Ser.*, **No. 100**, 111 (1971).
(14) C. Walling and M. S. Pearson, *Top. Phosphorous Chem.*, **3**, 1 (1966).
(15) J. Rimbault and R. Hugel, *Inorg. Nucl. Chem. Lett.*, **9**, 1 (1966).
(16) J. P. Fackler, Jr., *Inorg. Chem.*, **2**, 266 (1963).
(17) K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).
(18) L. Horner et al., *Tetrahedron Lett.*, 161 (1961).
(19) M. J. Carter, L. M. Englehardt, D. P. Rillema, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, 810 (1973).
(20) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).
(21) M. Truter, *Chem. Br.*, 203 (1971).
(22) C. Floriana, F. Calderazzo, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 384 (1973).
(23) D. D. Schmidt and J. T. Yoke, *J. Am. Chem. Soc.*, **93**, 637 (1971).
(24) That the decrease in rate during *later* stages of this reaction is attributable to the intervention of a new mechanism involving a μ-peroxide, i.e.,

$$2CoCl_2(L)(LO) + O_2 \rightarrow (LO)(L)Cl_2CoOOCoCl_2(L)(LO) \rightarrow (LO)_2CoCl_2$$

could not be ruled out.[23] However, the *initial* stage of the reaction clearly proceeds according to Scheme II.
(25) It is unlikely that the acetylacetonate chelate rings would open to a monodentate form under the reaction conditions. If they did, and if it were kinetically significant, the rate law for the oxidation would simplify to that of Scheme II, where the ligands are strictly monodentate.
(26) J. B. Ellern and R. O. Ragsdale, *Inorg. Synth.*, **11**, 82 (1968).