

tween the ring and the N=N double bond, has been observed in both free³⁰ and complexed azobenzene.¹² These trans diazenes displayed twist angles up to 17.1°. The structure of *cis*-azobenzene³¹ displays a twist angle of 34° because of the steric interaction of the two phenyl rings. The attempt to relieve the H(2)–H(N1) close contact is also reflected in the N(1)–C(1)–C(2) and N(1)–C(1)–C(6) bond angles which are 123.3 (9) and 114.6 (9)°, respectively.

The nitrogen–hydrogen bond, N(1)–H(N1), of 1.12 (10) Å is normal. The N(1)–O(3) distance suggests a potential interaction, but the N(1)–H(N1)–O(3) angle of 128 (6)° precludes description of this interaction as a hydrogen bond.

It is clear that the complexation, two-electron reduction, and protonation of an aryldiazonium cation has reduced the N–N bond order from a triple bond to a double bond. The resulting aryldiazene complex represents a model for the intermediate diazene complex in the proposed mechanism for biological nitrogen

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fixation. Further reduction of the N–N bond order would eventually lead to the desired cleavage of the N–N bond. Though this model is appealing because it does not necessitate any unusual separation of charge, the 1,1-diazene complex found in the rhenium system⁸ cannot be ruled out as a model nor can the symmetrical, π -bonded type of 1,2-diazene complex found in several Ni(0) systems.^{12,13}

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Supplementary Material Available. Tables II–IV and Figure 3 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$6.00 for photocopy or \$2.00 for microfiche, referring to code number JACS 74-4804.

Tetraphenylporphinecobalt(II) Complexes as a Probe for the Nature of Phosphine σ -Donor Orbitals. Electron Paramagnetic Resonance Studies of Phosphine and Dioxygen Complexes

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Abstract: Tetraphenylporphinecobalt(II) forms 1:1 complexes with trivalent phosphorus ligands. All of the 1:1 complexes have effective axial symmetry with a $(d_{zz}, d_{yz}, d_{xy})^6(d_z^2)^1$ ground configuration. Cobalt-59 and phosphorus-31 hyperfine coupling constants are utilized in evaluating the odd electron spin distribution and the phosphorus 3s and 3p character in the coordinated phosphine σ -donor orbital. The 3s character in the coordinated phosphorus σ -donor orbital is found to increase substantially with increased electron withdrawing ability of the substituents. Phosphorus ligand spin densities are found to decrease as the donor orbital P_{3s} character increases. Properties of the M–P σ bonding are discussed and compared with results on the corresponding CO, CH₃NC, and C₅H₅N complexes. Dioxygen complexes (Co^{II}TTPP·PX₃·O₂) which exhibit ³¹P hyperfine coupling are reported and discussed.

Descriptions of the bonding of trivalent phosphorus ligands with metallo species have resulted in controversies centered on the relative importance of σ -donor and π -acceptor effects on observed properties such as metal–phosphorus (M–P) bond distances,^{1,2} vibrational frequencies,^{3–6} and ³¹P nmr shifts and coupling constants.^{7–10}

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A problem encountered in previous studies of metal–phosphorus bonding is that the observed properties do not definitively separate σ - and π -electronic effects. The only experiments which can clearly separate these effects involve observations that specifically probe the individual molecular orbitals involved in the σ and π bonding. Epr studies of metallophosphine complexes which have an odd electron isolated in either the σ or π molecular orbitals can provide this direct bonding probe.

This paper reports on epr studies for a series of 1:1 trivalent phosphorus ligand complexes of tetraphenylporphyrincobalt(II), [Co^{II}TTPP], where the unpaired electron is principally confined in a cobalt–phosphorus σ molecular orbital. Cobalt-59 and phosphorus-31 hyperfine coupling constants are utilized in evaluating the odd electron spin distribution and the phosphorus 3s and 3p character in the ligand σ -donor orbital.

Table I. Epr Parameters for CoTPP·B Complexes^a

B	g_{\parallel}	g_{\perp}	$A_{\parallel},^b \text{ cm}^{-1} (\text{G})$	$-A_{\perp}, \text{ cm}^{-1} (\text{G})$	$P,^c \text{ cm}^{-1}$	K	$\Delta E_{xz, yz \rightarrow z^2}, \text{ cm}^{-1}$
P(Et) ₃	2.020	2.243	0.00628 (67)	0.0028 (27)	0.0162	0.150	9,000
P(<i>n</i> -Bu) ₃	2.025	2.242	0.00654 (69)	0.0031 (29)	0.0171	0.153	9,500
P(Me) ₃	2.028	2.210	0.00615 (65)	0.0043 (42)	0.0175	0.187	11,200
P(OBu) ₃	2.032	2.250	0.00682 (72)	0.0028 (26)	0.0174	0.142	9,500
P(OEt) ₃	2.025	2.242	0.00666 (71)	0.0029 (27.5)	0.0171	0.143	9,600
P(OMe) ₃	2.024	2.244	0.00692 (73)	0.0028 (26.6)	0.0174	0.137	9,600
PF ₃	2.04	2.23	0.00809 (85)	0.0017 (16)	0.0169	0.060	9,900
PPh(Me) ₂	2.023	2.222	0.00629 (67)	0.0035 (34)	0.0168	0.163	10,200
Ph(Me) ₂	2.028	2.243	0.00667 (71)	0.0028 (27)	0.0170	0.141	9,400
CO ^d	2.017	2.217	0.00736 (77.6)	0.0034 (33)	0.0181	0.137	11,200
CNCH ₃	2.025	2.247	0.00670 (70.9)	0.0037 (35.6)	0.0187	0.176	10,200
C ₆ H ₅ N ^e	2.027	2.324	0.00789	0.0013	0.0198	0.127	8,200

^a Values for P , K , and $\Delta E_{xz, yz \rightarrow z^2}$ are based upon a $(xz, yz)^4(xy)^2(z^2)^1$ ground configuration of cobalt(II). ^b A_{\parallel} and A_{\perp} are the cobalt hyperfine coupling components along and normal to the principal magnetic axis. ^c $P = g_e \beta_e g_n \beta_n (r^{-3})_d \approx 0.023$ for cobalt(II) free ion. ^d Reference 19. ^e Reference 17.

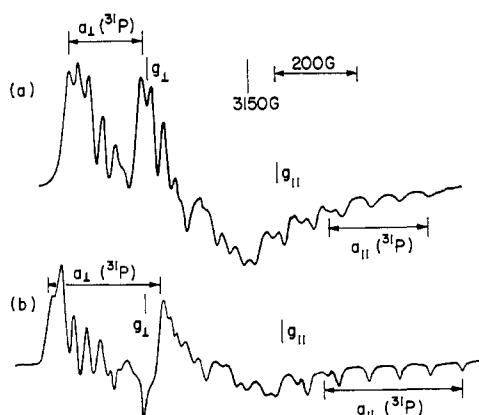


Figure 1. Epr spectra for 1:1 phosphorus donor adducts of Co^{II} TPP in toluene glass (-140°) ($\nu = 9137 \text{ MHz}$): (a) P(Et)₃, (b) P(OEt)₃.

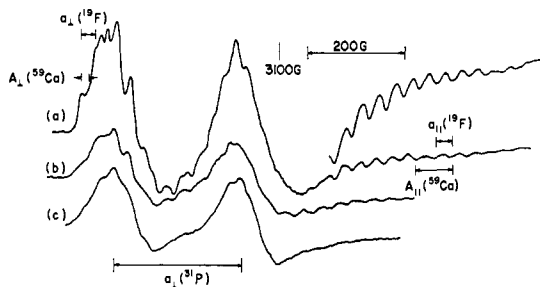


Figure 2. Epr spectra for a 1:1 PF₃ adduct of Co^{II} TPP in toluene: (a) -140° , (b) -100° , (c) -80° .

Dioxygen adducts of CoTPP·PX₃ complexes are reported and found to have well-defined ³¹P hyperfine splittings.

Experimental Section

Materials and Samples. Tetraphenylporphyrincobalt(II), [Co^{II}-TPP], was prepared according to the procedure of Rothmund and

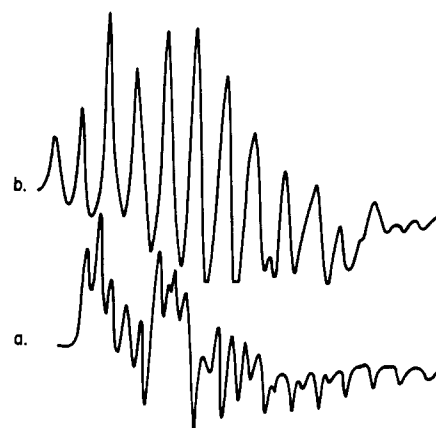


Figure 3. Epr spectra for phenyldimethylphosphine adducts of Co^{II} TPP in toluene glass (-140°) ($\nu = 9137 \text{ MHz}$): (a) 1:1 adduct, (b) 2:1 adduct.

Menotti.¹¹ The impure product was then chromatographed on aluminum oxide (Woelm, neutral, activity grade 1) purchased from Waters Associates Inc., Framingham, Mass., using benzene as the eluent. The Co^{II}TPP was stored under vacuum and used in subsequent studies. Phosphine ligands were in general obtained from Matheson Coleman and Bell. PF₃ was purchased from Strem Chemicals.

Samples were prepared by introducing Co^{II}TPP into the epr tube either as the solid or a toluene solution. The toluene solutions of Co^{II}TPP were then degassed by the usual freeze-pump-thaw method. When working with solid Co^{II}TPP, the epr tube was evacuated, and degassed toluene was distilled from P₂O₅ into the tube. Liquid ligands were degassed and then distilled into the epr tube containing Co^{II}TPP. Trialkylphosphines were mixed in 1:1 stoichiometry to avoid 2:1 adduct formation. Gaseous ligands were allowed to react with the Co^{II}TPP solution at pressures of 200–500 mm.

Instrumentation. Spectra were taken on a Varian Model V-4502 X-band spectrometer at 100°K, equipped with a Field Dial Mark I, Hewlett-Packard Model 7001 AM x-y recorder, and a Hewlett-

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Table II. Cobalt Spin Densities Calculated from Epr Parameters for CoTPP·B Complexes

B	$-A_o,^a \text{ cm}^{-1} (\text{G})$	$A_d, \text{ cm}^{-1} (\text{G})$	ρ_{3d}^b	ρ_{4s}	$\rho_{3d} + \rho_{4s}$	ρ_L^c	$\rho_L + \rho_{Co}$
P(Et) ₃	0.00241 (25.9)	0.0093 (100)	0.705	0.028	0.73	0.207	0.94
P(<i>n</i> -Bu) ₃	0.00261 (28)	0.0098 (105)	0.744	0.030	0.77	0.188	0.96
P(Me) ₃	0.00327 (35.1)	0.0100 (107)	0.753	0.025	0.78	0.179	0.96
P(OBu) ₃	0.00246 (26.4)	0.0099 (107)	0.757	0.032	0.79	0.169	0.96
P(OEt) ₃	0.00244 (26.1)	0.0097 (104)	0.741	0.031	0.77	0.159	0.93
P(OMe) ₃	0.00238 (25.6)	0.0099 (106)	0.754	0.032	0.79	0.151	0.94
PF ₃	0.00101 (10.9)	0.0097 (104)	0.735	0.042	0.78	0.148	0.93
PPh(Me) ₂	0.00273 (29.3)	0.0096 (103)	0.731	0.028	0.76	0.210	0.97
PH(Me) ₂	0.00240 (25.8)	0.0097 (104)	0.739	0.031	0.77	0.182	0.95
CO ^d	0.00247 (26.5)	0.0103 (111)	0.744	0.034	0.82	0.103	0.92
CNCH ₃ ^d	0.00329 (35.3)	0.0107 (115)	0.787	0.029	0.84		
C ₆ H ₅ N	0.00251	0.0113	0.860	0.038	0.90		

^a A_o and A_d are the cobalt contact and dipolar hyperfine coupling constants corrected for orbital magnetism ($A_o = PK$, $A_d = 4/7P$). ^b ρ_{3d} and ρ_{4s} are the calculated spin densities on the 3d and 4s atomic orbitals of cobalt(II). ^c ρ_L is the spin density on the ligand donor atom (P, C, N). ^d Reference 19.

Packard frequency meter, Model 532 B. Cooling was provided by using cold nitrogen gas and the temperature was controlled to $\pm 2^\circ$ using a Varian V-4557 variable-temperature accessory. The field and frequency calibrations were made using DPPH powder ($G = 2.0036$), field dial, and X532B frequency meter.

Results

Epr Spectra for 1:1 Adducts of Co^{II}TPP. Representative epr spectra for tetraphenylporphyrincobalt(II), (Co^{II}TPP), complexes with trivalent phosphorus ligands are shown in Figures 1–3. Phosphorus-31 hyperfine splitting demonstrates that the complexes are 1:1 adducts. The g values and cobalt-59 hyperfine parameters for CoTPP·PX₃ complexes are found in Table I along with the corresponding data for adducts with CO, CH₃NC, and C₅H₅N. All of these 1:1 complexes are found to have effective axial symmetry and accurately conform to the $(d_{xz}, d_{yz}, d_{xy})^6(d_{z^2})^1$ ground configuration. The first-order relationships between electronic structure and magnetic parameters for the $(d_{xz}, d_{yz}, d_{xy})^6(d_{z^2})^1$ configuration are¹²

$$g_{\parallel} = 2.002; g_{\perp} = 2.002 - 6\xi_{\text{eff}}/\Delta E_{xz,yz \rightarrow z^2}$$

$$A_{\parallel}(^{59}\text{Co}) = P[-K + 4/7 - 1/7(g_{\perp} - 2.002)]$$

$$A_{\perp}(^{59}\text{Co}) = P[-K - 2/7 + 15/14(g_{\perp} - 2.002)]$$

$$\langle A \rangle(^{59}\text{Co}) = P[-K + 2/3(g_{\perp} - 2.002)]$$

Second-order effects are not significant for CoTPP·B adducts where $\Delta E_{xz,yz \rightarrow z^2} \gg \xi_{\text{eff}}$. Results from solving these expressions for the series of 1:1 complexes are found in Table I. Signs for the cobalt coupling constants ($A_{\parallel} > 0$, $A_{\perp} < 0$) are established from the condition that P must be positive. Reduction of the cobalt P value and effective spin-orbit coupling constant by 20–30% from the free ion value of $P_0 \sim 0.023$ ¹³ is largely caused by redistribution of odd electron pop-

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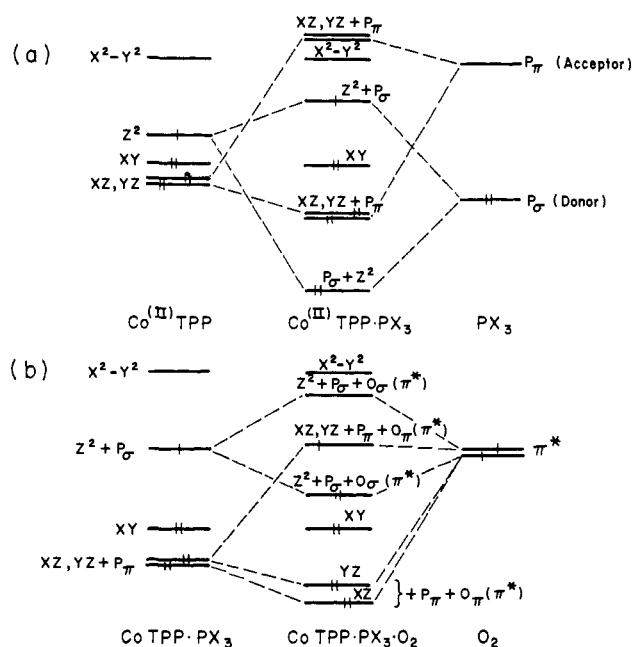


Figure 4. Schematic molecular orbital diagrams for Co^{II}TPP·PX₃ and dioxygen complexes: (a) an illustration of the M-P σ and π interactions in Co^{II}TPP·PX₃, (b) an illustration of the oxygen π^* interactions with the metal d orbitals in Co^{II}TPP·PX₃·O₂.

ulation from the cobalt d_{z^2} to the ligand σ donor orbital.

Using the observed g_{\perp} and an effective spin-orbit coupling constant (ξ_{eff}) reduced from the free ion value ($\xi_0 = 515 \text{ cm}^{-1}$) by the same fraction as the P value permits the estimation of the $d_{xz,yz} \rightarrow d_{z^2}$ energy separation ($\Delta E_{xz,yz \rightarrow z^2}$) (Table II). Ligand σ -donor interactions elevate the d_{z^2} acceptor orbital, and ligand π -acceptor interactions lower the $d_{xz,yz}$, such that they produce additive contributions to $\Delta E_{xz,yz \rightarrow z^2}$ (Figure 4a). The combined σ -donor and π -acceptor properties for

Table III. Phosphorus Hyperfine Parameters in Spin Densities for CoTPP·B Complexes

B	$a_{ },^a \text{ cm}^{-1}$ (G)	$a_{\perp}, \text{ cm}^{-1}$ (G)	$a_c,^b \text{ cm}^{-1}$	$2a_d,^c \text{ cm}^{-1}$	ρ_{3p}^d	ρ_{3s}	$\rho_{3p} + \rho_{3s}$	ρ_{3p}/ρ_{3s}^e	% s ^f
P(Et) ₃	0.0219 (232)	0.0176 (168)	0.0190	0.0029	0.151	0.056	0.207	2.70	27
P(<i>n</i> -Bu) ₃	0.0221 (234)	0.0184 (176)	0.0196	0.0025	0.130	0.058	0.188	2.24	31
P(Me) ₃	0.0244 (258)	0.0211 (205)	0.0222	0.0022	0.114	0.065	0.179	1.75	36
P(OBu) ₃	0.0291 (307)	0.0266 (253)	0.0274	0.0017	0.088	0.081	0.169	1.09	48
P(OEt) ₃	0.0291 (308)	0.0268 (256)	0.0276	0.0015	0.078	0.081	0.159	0.96	51
P(OMe) ₃	0.0295 (312)	0.0276 (264)	0.0282	0.0013	0.068	0.083	0.151	0.82	55
PF ₃	0.0352 (370)	0.0339 (326)	0.0343	0.0009	0.047	0.101	0.148	0.47	68
PPh(Me) ₃	0.0229 (243)	0.0185 (178)	0.0200	0.0029	0.151	0.059	0.210	2.56	28
PH(Me) ₂	0.0234 (247)	0.0200 (191)	0.0211	0.0023	0.120	0.062	0.182	1.94	34

^a $a_{||}$ and a_{\perp} are the ligand hyperfine coupling constants along and normal to the principal magnetic axis. ^b a_c is the contact coupling constant; $a_c = (a_{||} + 2a_{\perp})/3$. ^c $2a_d$ is the dipolar coupling constant $2a_d = a_{||} - a_c$. ^d ρ_{3s} and ρ_{3p} are the spin densities in the s and p atomic orbitals of the ligand donor species: $\rho_{3s} = a_c/a_{3s}^*$ ($a_{3s}^* = 3640 \text{ G} = 0.33963 \text{ cm}^{-1}$); $\rho_{3p} = 2a_d/2a_{3p}^*$ ($2a_{3p}^* = 206 \text{ G} = 0.01922 \text{ cm}^{-1}$). ^e Ratio of ρ_{3p}/ρ_{3s} character in the ligand donor orbital. ^f Per cent s character in the ligand donor orbital.

PX₃, CO, and CH₃NC ligands result in larger d orbital splitting ($\Delta E_{xz, yz \rightarrow z^2}$) than that for pyridine (Table I).

Cobalt Spin Densities. Results for the cobalt spin density analysis are found in Table II. Cobalt 3d_{z²} spin densities (ρ_{3d}) are evaluated from comparison of the observed *A* dipolar value with the theoretical value of (⁴/₇ $P_0 = 0.01314 \text{ cm}^{-1}$) for a cobalt 3d electron. Cobalt 4s spin densities are estimated from the relationship [*A* contact = $\rho_{4s}A(\text{Co } 4s) + \rho_{3d}A(\text{Co } 3d)$, where $A(\text{Co } 4s) = 1320 \text{ G} (0.1232 \text{ cm}^{-1})$ and $A(\text{Co } 3d) = -90 \text{ G} (-0.00840 \text{ cm}^{-1})$].¹⁴ The 3d spin densities fall in the range 0.71–0.86 while the 4s spin densities are ~ 0.025 – 0.042 . Co^{II}TPP·pyridine has a larger total cobalt spin density than the PX₃, CO, or CH₃NC ligands in the corresponding 1:1 adducts with Co^{II}TPP which is an indication that pyridine has the smallest ligand σ -donor orbital spin density (Table II).

Ligand Hyperfine Coupling in Phosphorus Donor Adducts of Co^{II}TPP. Co^{II}TPP has a single unpaired electron in the cobalt d_{z²} orbital, which is a primary acceptor orbital used in σ bonding with ligands (Figure 4). The overlap and mixing of the ligand σ -donor orbital with the cobalt d_{z²} directly places spin density in the ligand σ system and results in ligand nuclear hyperfine coupling. Phosphites and PF₃ ligands form only 1:1 complexes with Co^{II}TPP as shown by ³¹P hyperfine coupling. In these complexes each epr component is split into two lines by coupling with one phosphorus irrespective of the ligand to metal mole ratio. Phosphorus-31 coupling shows that trialkylphosphine ligands form both 1:1 and 2:1 adducts (Figure 3).

Ligand hyperfine coupling constants and donor atom spin densities are found in Table III. Analysis of the epr spectra for the ³¹P coupling constants is straightforward in most cases as shown in Figure 1. Fluorine hyperfine in the PF₃ adduct complicates the spectrum and the analysis for the ³¹P coupling constant. Analysis of the g_{\perp} region was assisted by changing the sample temperature so as to permit diffusion and rota-

tion to partially average the spectrum (Figure 2). Loss of resolution of the ⁵⁹Co and ¹⁹F hyperfine permits identification of A_{\perp} ³¹P. The hyperfine splittings of 40 G in the $g_{||}$ and 36 G in g_{\perp} regions are assigned to ¹⁹F.

Phosphorus-31 hyperfine splittings in CoTPP·PX₃ complexes are found to be very large and indicative of substantial spin density in the trivalent phosphorus σ -donor orbital (Table III). The ligand donor atom hyperfine coupling is larger in the $g_{||}$ than in the g_{\perp} region which is a characteristic for near coincidence of the *g* and ligand hyperfine tensors. Maintenance of effective fourfold rotational symmetry is an important property of this cobalt(II) porphyrin system. Analysis of the anisotropic ³¹P hyperfine coupling from glass spectra for this case provides good experimental estimates for the phosphorus 3s and 3p spin densities. Isotropic ³¹P coupling constants yield the 3s spin densities and the anisotropic couplings give the 3p spin densities.¹⁵ The 3p to 3s spin density ratio for the phosphorus donor atom in the series of CoTPP·PX complexes is given in Table III. This ratio (ρ_{3p}/ρ_{3s}) is found to be very sensitive to the electronegativity of the substituents on phosphorus. The s character in the coordinated phosphine ligand donor orbital increases regularly with substituent electronegativity from $\sim 27\%$ in P(Et)₃ to $\sim 68\%$ in PF₃. The total phosphorus spin densities and thus the cobalt d_{z²}-phosphorus σ donor orbital mixing are found to decrease regularly as the donor orbital 3s character increases. Summing the cobalt and phosphorus spin densities accounts for ~ 92 – 98% of the odd electron density (Table II).

Dioxygen Complexes of CoTPP·PX₃. Complexes of CoTPP with various phosphorus ligands form 1:1 dioxygen adducts (Figure 5, Table IV). Phosphorus-31 hyperfine splitting in the dioxygen adducts demonstrates that the phosphorus ligand remains coordinated in solution and glass media.

Nitrogen-14 hyperfine is not resolved in the corresponding dioxygen adducts with Co^{II}TPP nitrogen

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Table IV. Epr Parameters for Dioxygen Adducts of $\text{Co}^{\text{II}}\text{TPP}\cdot\text{PR}_3$

	$\langle g \rangle$	$\langle A \rangle$ (^{60}Co) ^a	$\langle a \rangle$ (^{31}P), cm^{-1} (G)	$\rho_{\text{P}_{3s}}$ ^b
P(Et) ₃	2.023	7.8	0.00148 (15.7)	0.0044
P(<i>n</i> -Bu) ₃	2.022	8.5	0.00173 (18.3)	0.0051
P(Me) ₂ Ph	2.025	7.8	0.00197 (20.9)	0.0058
P(OBu) ₃	2.016	7.3	0.00295 (31.4)	0.0087
P(OEt) ₃	2.020	7.2	0.00274 (29.1)	0.0081
P(OMe) ₃	2.020	7.5	0.00277 (29.4)	0.0082

^a Cobalt hyperfine splittings in gauss. ^b $\rho_{\text{P}_{3s}}$ is the spin density in 3s atomic orbital of the phosphorus atoms. $\rho_{\text{P}_{3s}} = a_{\text{iso}}/a_{3s}^*$, where $a_{3s}^* = 0.33963 \text{ cm}^{-1}, 3640 \text{ G}$.

donor complexes^{16,17} or in (coboglobin O₂).¹⁸ Atomic hyperfine values for phosphorus ($a_{\text{P}_{3s}} = 0.3396$, $a_{\text{P}_{3p}} = 0.01922 \text{ cm}^{-1}$) are much larger than those for nitrogen ($a_{\text{N}_{2s}} = 0.0515$, $a_{\text{N}_{2p}} = 0.0032 \text{ cm}^{-1}$)¹⁵ and permit detection of relatively small spin densities.

Cobalt(II) dioxygen complexes have the single odd electron predominantly in the oxygen π^* ^{16,17,19} (Figure 4b). Spin density can reach the phosphorus through π bonding with the cobalt $d_{xz,yz}$ or by a spin exchange mechanism. As expected, the ^{31}P hyperfine coupling constants in $\text{Co}^{\text{II}}\text{TPP}\cdot\text{PX}_3$ are reduced by an order of magnitude in forming the dioxygen adduct consistent with an odd electron occupying a molecular orbital that is largely oxygen π^* in character. The trend in isotropic ^{31}P coupling constants parallels the phosphine donor orbital s character in the corresponding $\text{Co}^{\text{II}}\text{TPP}\cdot\text{PX}_3$ complexes (Tables III, IV) and provides evidence that spin exchange between the ($\text{O}_{\pi^*} + xz, yz + \text{P}_{\pi}$) molecular orbital (Figure 4b) and the close lying fully occupied σ bonding orbital ($\text{P}_{\sigma} + \text{Co}_{d_{z^2}} + \text{O}_{\sigma}$) is primarily responsible for the ^{31}P hyperfine coupling. The ^{31}P coupling constant should be negative for this case. Phosphorus-31 nmr contact shifts could provide a direct test for this prediction, but attempts to observe the ^{31}P nmr have not yet been successful.

Discussion

Properties of the Metal-Ligand Interaction. Analysis of the epr parameters for $\text{Co}^{\text{II}}\text{TPP}\cdot\text{B}$ adducts provide details of the metal-ligand interaction. The order of cobalt spin densities (phosphines < CO \sim CH₃NC < pyridine) and ligand donor atom spin densities (phosphines > CO > pyridine) indicate that phosphines, CO, and CH₃NC have a larger d_{z^2} σ -donor orbital mixing than does pyridine. This is an interesting result considering the emphasis placed on the π acceptor bonding properties of CO and phosphines.²⁰ Within the series of phosphorus ligands the donor atom spin densities decrease as the s character of

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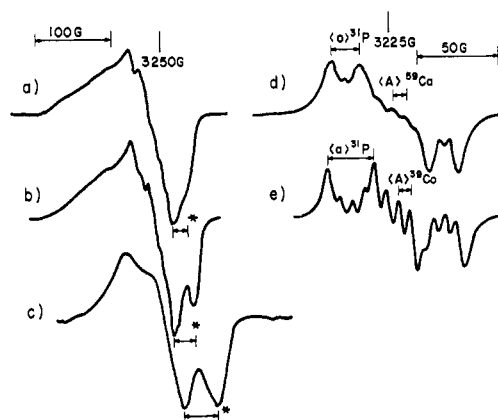


Figure 5. Epr spectra of $\text{Co}^{\text{II}}\text{TPP}\cdot\text{PX}_3\cdot\text{O}_2$ in toluene ($\nu = 9137 \text{ MHz}$): a, b, and c are frozen solution spectra (-140°) for X = (*n*-Bu), (OMe), and F, respectively; d and e are solution spectra (-60°) for X = (*n*-Bu) and (OMe), respectively. Asterisk (*) is the presumed ^{31}P hyperfine splitting in the g_{\perp} region.

the donor orbital increases (Table III). The superior σ -donor properties of the trialkylphosphines compared to phosphites and PF_3 probably has its origin in the cobalt $d_{xz,yz}$ -phosphorus donor orbital energy difference. This is supported by the phosphorus donor orbital energies determined by photo electron spectra.²¹ The occurrence of both 1:1 and 2:1 complexes with trialkylphosphines but only 1:1 complexes with phosphites and PF_3 can be attributed to better M-P σ -bonding properties of trialkylphosphine ligands.

In addition to details of the spin distribution, the epr data provide estimates of the $d_{xz,yz} \rightarrow d_{z^2}$ energy separation. This energy separation ($\Delta E_{xz,yz \rightarrow z^2}$) is subject to additive influences of ligand σ -donor and π -acceptor interactions which respectively elevate the d_{z^2} and lower $d_{xz,yz}$. The general trend in $\Delta E_{xz,yz \rightarrow z^2}$ is $\text{CO} \leq \text{CH}_3\text{HC} \sim \text{phosphines} > \text{pyridine}$. The combined influences of σ -donor and π -acceptor interactions have a larger effect on $\Delta E_{xz,yz \rightarrow z^2}$ for the CO, CH₃NC, and phosphine complexes compared to that for the pyridine adduct.

Nature of the σ -Donor Orbital in Coordinated Phosphorus Ligands. The s character in the donor orbitals of phosphorus ligands coordinated to $\text{Co}^{\text{II}}\text{TPP}$ is found to vary from 27 to 68% with changes in the phosphorus substituents (Table III). The order of increasing donor orbital s character is $\text{PF}_3 > \text{P}(\text{OR})_3 > \text{PR}_3$. The more electronegative substituents utilize a larger fraction of the available phosphorus 3p orbitals in bonding, and the σ -donor orbital (lone pair) is thus left with a larger fraction of phosphorus 3s character.

The donor orbital s character observed for the coordinated phosphines is probably smaller than or equal to the value for the free ligand. Bonding the phosphine ligand with a metal is expected to perturb the free ligand donor orbital so as to induce more p character and approach sp^3 hybridization.²² The limiting example of this process would be $\text{PH}_3 + \text{H}^+ \rightarrow \text{PH}_4^+$, which has four equivalent bonds. Coordination effects on the donor orbital rehybridization undoubtedly con-

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tributes to the observed trend in donor orbital *s* character. Any ligand rehybridization should be minimized in the PF₃ complex where the difference in electronegativities (Co *vs.* F) is maximized. Structural studies of Co(H)(PF₃)₄ have shown that the PF₃ bond angles and distances are little affected by coordination.²³ In contrast the C–P–C angles in P(Me)₃ are 98.1° in the free ligand²⁴ and change to an average of ~104° when coordinated in an Ir(I) complex.²⁵ The variation in donor orbital *s* character for coordinated phosphines can thus be ascribed in part to the ease of rehybridization occurring on coordination. The difficulty in rehybridizing PF₃ by coordination and the resulting retention of large donor orbital *s* character must contribute to the unique bonding properties of PF₃.²⁰

Results of this study pertain exclusively to the metal–phosphorus σ system and may provide new insight into M–P bonding. The observed wide variation in donor orbital *s* character for coordinated phosphines undoubtedly has profound effects on physical properties such as M–P bond distances and ³¹P nmr coupling constants. The M–P bond distance is expected to decrease as the phosphorus donor orbital *s* character increases. The M–P bond distance in (C₆H₅O)₃PCr(CO)₃ is 0.11 Å shorter than in the (C₆H₅)₃P derivative,^{1,2} which is consistent with the proposed trend. Short M–P distances in PF₃ complexes are generally ascribed to π back-bonding effects, but our results suggest that the large donor orbital *s* character will have an important if not the dominant influence. The factors contributing to M–³¹P nmr coupling constants have been itemized and discussed by Nixon and Pidcock.²⁶ The extent of mixing and *s* characters of the metal and ligand orbitals responsible for the M–P bonding were assigned the dominant role in determining the nmr coupling constants. Although experimental data provide good support for this model, the nmr experiment cannot definitively separate the terms contributing to

the M–³¹P nmr coupling constants.²⁶ The epr experiments reported here provide a direct evaluation of the phosphorus *s* and *p* orbital character for the ligand orbital used in binding the metal d_{z²}, and the extent of orbital mixing is given independently by the metal and ligand spin densities. The ratio of M–³¹P nmr coupling constants in *cis*-[PtCl₂(Bu₃P)₂] and *cis*-[PtCl₂{EtO)₃P}₂]} (3508/5698 Hz = 0.614), is virtually the same as the ratio of donor orbital *s* character for these ligands (0.31/0.51 = 0.61) in Co^{II}TPP complexes (Table III). This observation provides evidence that the M–³¹P nmr coupling constants for a series of phosphine complexes may be dominated by changes in the phosphine donor orbital *s* character. Observation of a M–³¹P nmr coupling constant M–P bond distance correlation⁸ is probably also influenced by the interrelationship of donor orbital *s* character with these properties. The large variation in donor orbital hybridization should also influence other physical properties such as the controversial phosphorus ligand induced changes in CO vibrational frequencies in PX₃Ni(CO)₃ and related complexes.^{3–6}

This study experimentally demonstrates that the nature of the coordinated phosphorus σ -donor orbital is highly sensitive to the substituents present. Donor orbital *s* character increases with the electron withdrawing ability of the substituents and thus follows a parallel trend with the presumed ligand π -acceptor properties. The demonstrated changes in the σ -donor orbital character can be used in rationalizing properties such as substituents effects on M–P bond distances which have been associated with trends in ligand π -acceptor properties. A parallel study involving complexes where the odd electron is in a π molecular orbital may prove useful in putting the relative importance of phosphorus σ -donor and π -acceptor properties in perspective.

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