solutions, evacuated, and then filled with ca. 700 mmHg D_2 before being sealed. The sealed tubes were immersed in a 65° oil bath for 1.5 hr. The gas phases were analyzed by mass spectrometry and the complexes were recovered as above for ^1H NMR analysis. The gas from the first tube containing just I was 97% H_2 and conversion of I was ca. 60%. In the second tube containing I and excess phosphite, the gas was still 85% D_2 and conversion of I was only ca. 10%. In the third tube, $CoH[P(OC_6H_5)_3]_4$, the gas was H_2 (8.6%), HD (34.4%), and D_2 (57%). Incorporation of that amount of deuterium corresponds to ca. 1.4 atom % excess deuterium in the hydride in the third tube.

Hydrogenation of 1-Butene. Two glass pressure bottles were prepared. One was charged with 0.13 g of I prepared from $Co(C_8H_{12})(C_8H_{13})$, and the other was charged with 0.16 g of a mixture of I and $CoH[P(OC_6H_5)_3]_4$ containing ca. 80% I (prepared by heating $CoH[P(OC_6H_5)_3]_4$). The bottles were then charged with 10 ml of benzene, ca. 30 mmol of 1-butene, and 30 psig H_2. The solutions were stirred magnetically and samples of the gas phase were withdrawn at intervals by syringe for gas chromatographic analysis on a $^1/_8$ in. × 8 ft column with silicone nitrile XE 60 packing. The rate of pressure drop and the rate of appearance of butane were the same for both bottles. After the conversion of ca. 12 mmol of 1-butene to butane at room temperature the temperature was raised to ca. 48°. After determining that the rate of appearance of butane was still the same for both bottles, 3 ml of degassed triphenyl phosphite was added by syringe to one bottle. No additional hydrogenation occurred in this bottle while ca. 20 mmol of 1-butene was consumed in the other during ca. 20 hr. There was no accumulation of isomeric butenes.

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Registry No. I, 54870-21-2; $Co(C_8H_{12})(C_8H_{13})$, 34829-55-5; $CoH[P(OC_6H_5)_3]_4$, 24651-64-7; triphenyl phosphite, 101-02-0; 1-butene, 106-98-9; ^{31}P, 7723-14-0.

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Contribution from the E. F. Smith Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter,
University of Pennsylvania, Philadelphia, Pennsylvania 19174

Low-Spin Cobalt(II)–Schiff Base and –Porphyrin Complexes of CO, MeNC, $AsMe_3$, and PX_3. Electron Paramagnetic Resonance Studies

B. B. WAYLAND,* M. E. ABD-ELMAGEED, and L. F. MEHNE

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Co^{II}(salen) forms 1:1 complexes with CO, MeNC, $AsMe_3$, and a series of trivalent phosphorus donors. All of the complexes have EPR spectra indicative of the $(d_{xz}, d_{yz}, d_{xy})^6(d_{z^2})^1$ ground configuration. Phosphorus-31 hyperfine coupling constants are used in estimating the coordinated phosphorus donor orbital s characters (PMe_3, 33% s; $P(OMe)_3$, 49% s; PPh_3, 24% s) which are consistent with results from studies of Co^{II}TPP complexes. Previous studies of Co^{II}TPP donors have been extended to $AsMe_3$. The donor orbital s character for the $AsMe_3$ (50%) complex of Co^{II}TPP is substantially larger than the value for PMe_3 (36%). Dioxygen complexes of $Co^{II}(salen)\cdot B$ (B = PX_3 or $AsMe_3$) which exhibit ^{31}P or ^{75}As hyperfine coupling are reported.

Introduction

(*N,N'*-Ethylenebis(salicylaldiminato))cobalt(II) [Co^{II}(salen)] has received considerable attention due to interest in the electronic structure[1–3] of low-spin cobalt(II) species and their property of dioxygen[4,5] and nitric oxide[6,7] complex formation. Electron paramagnetic resonance studies of Co^{II}(salen) complexes with nitrogen donor ligand are well documented,[8,9] but relatively little is known about the corresponding complexes with potential π-acceptor ligands such as CO, MeNC, and PR_3. With the exception of our study of the carbon monoxide adduct of tetraphenylporphyrincobalt(II)[10,11] [Co^{II}TPP], no low-spin cobalt(II) chelate complexes of CO have been documented. We have previously reported on EPR studies for $Co^{II}TPP\cdot PX_3$ complexes in which the cobalt-59 and phosphorus-31 hyperfine coupling constants were utilized in evaluating the odd-electron spin distribution and the phosphorus 3s and 3p character in the coordinated phosphine σ-donor orbital.[12,13] The 3s character in the coordinated phosphorus σ-donor orbital was found to increase by more than a factor of 2 for the series of ligands Me_3P, $(MeO)_3P$, and F_3P. This paper reports on the observation and EPR studies of Co^{II}(salen) complexes of CO, MeNC, $AsMe_3$, and a series of PX_3 ligands and several of the corresponding dioxygen adducts.

Experimental Section

Materials and Samples. Co^{II}(salen) was prepared according to the method of Bailes and Calvin.[14] The trialkylphosphine, trialkyl phosphite, and trialkylarsine ligands were obtained from Bell and Collman Co. Samples were prepared by introducing solid Co^{II}(salen) into an EPR tube with vacuum fittings and distilling degassed dichloromethane onto the solid. Volatile ligands were degassed and then distilled into the Co^{II}(salen) solution. Ligands with low vapor pressures were directly added to the Co^{II}(salen) solution in an inert-atmosphere box and then degassed on a vacuum line. Trimethylarsine was mixed in 1:1 stoichiometry with Co^{II}TPP to avoid 2:1 adduct formation.

Instrumentation. Spectra were taken on a Varian Model V-4502 X-band spectrometer equipped with a Fieldial Mark I, Hewlett-Packard Model 7001 Am X-Y recorder, and a Hewlett-Packard frequency meter, Model 532 B. Cooling was provided by using cold nitrogen gas and the temperature was controlled to ±2° using a Varian V-4557 variable-temperature accessory. The field and frequency calibrations were made using DPPH powder ($g = 2.0036$), fieldial, and X532B frequency meter.

Results and Discussion

EPR Studies of Co^{II}(salen) Complexes of CO, MeNC, and PX_3. A frozen toluene solution (−140°) of Co^{II}(salen) in the presence of carbon monoxide (500 mm) produces EPR spectra distinctly different from that of the parent Co^{II}(salen) and

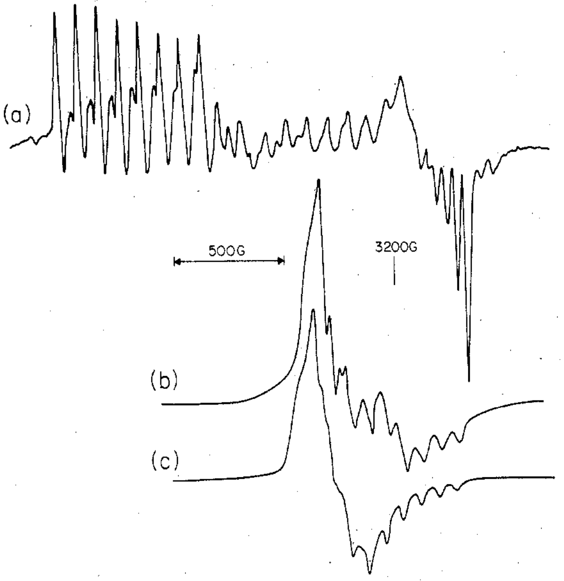

Figure 1. EPR spectra for Co^{II}(salen) complexes in CH_2Cl_2 glass (−140°, $\nu = 9.135$ MHz): (a) Co^{II}(salen); (b) Co^{II}(salen) + 500 Torr of CO; (c) Co^{II}(salen)·MeNC.

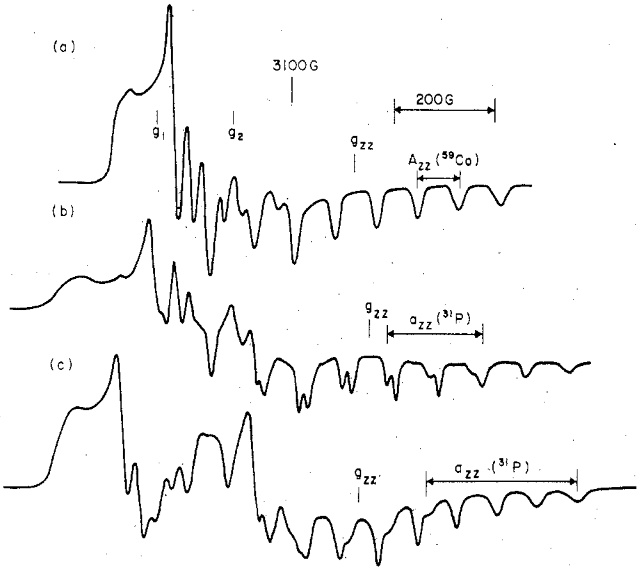

Figure 2. Frozen-solution EPR spectra for Co^{II}(salen)·B complexes (−140°): (a) B = MeNC in CH_2Cl_2; (b) B = PPh_3 in toluene; (c) B = $P(OMe)_3$ in CH_2Cl_2.

diagnostic for adduct formation (Figure 1, Table I). The carbon monoxide complex observed in toluene glass (−140°) is not detected in toluene solution down to −70°. No evidence for a six-coordinate complex containing CO has been obtained, which parallels observations with Co^{II}TPP[10,11] and is consistent with the absence of a CO adduct of coboglobin.[15] The corresponding MeNC complex can be isolated and fully characterized as the 1:1 complex and has EPR parameters closely related to the CO adduct (Figures 1 and 2, Table I). Co^{II}(salen) is shown to form only 1:1 adducts with a series of trivalent phosphorus donors by the ^{31}P hyperfine splitting (Figure 2, Tables I and II).

EPR parameters for Co^{II}(salen) diluted in Ni^{II}(salen) ($g_{xx} = 3.80$, $g_{xy} = 1.72$, $g_{zz} = 1.76$, $A_{xx}(^{59}Co) = 292 \times 10^{-4}$ cm^{-1}, $A_{yy} = 24 \times 16^{-4}$ cm^{-1}, $A_{zz} = 16 \times 10^{-4}$ cm^{-1}) have been used to demonstrate a $(d_{yz})^1$ ground configuration.[1] Interaction of Co^{II}(salen) with ligands (CO, MeNC, PX_3) moves the d_{z^2} clearly above the d_{yz} and yields EPR parameters which accurately conform to the $(d_{xy}, d_{xz}, d_{yz})^6(d_{z^2})^1$ ground configuration (Table I). The appropriate relationship between

Table I. EPR Parameters and Cobalt-59 Spin Densities for Co^{II}(salen)·B Complexes[a]

B	g_1	g_2	g_3	$\langle g \rangle$	$-A_1$, cm^{-1} (G)	$-A_2$, cm^{-1} (G)	A_3, cm^{-1} (G)	P,[b] cm^{-1}	K	$\Delta E_{yz\to z^2}$, cm^{-1}	$\Delta E_{yz\to z^2}$, cm^{-1}	$-A_c$,[c] cm^{-1} (G)	$-A_d$, cm^{-1} (G)	ρ_{3d}[d]	ρ_{4s}	ρ_{3d+4s}	ρ_L[e]
CO	2.28	2.17	2.02		0.0014 (13)	0.0035 (35)	0.00802 (85)	0.0179	0.090	8700	14,200	0.00162 (17.3)	0.0102 (109)	0.78	0.040	0.82	
MeNC	2.30	2.19	2.02		0.0021 (20)	0.0034 (33)	0.00754 (80)	0.0185	0.127	8300	13,000	0.00234 (25.0)	0.0106 (113)	0.81	0.036	0.84	
PPh_3	[2.40][f]	2.20	2.02	2.21	[8][g]	0.0025 (24)	0.00811 (86)	0.018	0.078	6000	12,100	0.00140 (15)	0.0103 (110)	0.78	0.042	0.82	0.18
PMe_3	[2.31]	2.18	2.02	2.17	[12]	0.0033 (32)	0.00717 (76)	0.0169	0.112	7300	12,500	0.00189 (20)	0.0097 (104)	0.74	0.066	0.81	0.18
$P(OMe)_3$	[2.31]	2.18	2.02	2.17	[12]	0.0033 (32)	0.00726 (77)	0.0170	0.111	7400	12,700	0.00189 (20)	0.0097 (104)	0.74	0.066	0.81	0.15

[a] Values for P, K, and ΔE are based upon a $(dxz, dyz, dxy)^6(dz^2)^1$ ground configuration for cobalt(II). [b] $P = g_e\beta_e g_n\beta_n\langle r^{-3}\rangle \approx 0.023$ for cobalt(II) free ion. [c] A_c and A_d are the cobalt-59 contact and dipolar hyperfine coupling constants corrected for orbital magnetism ($A_c = -PK$, $A_d = {}^4/_7P$). [d] ρ_{3d} and ρ_{4s} are the spin densities in the 3d and 4s atomic orbitals of cobalt(II) estimated from cobalt-59 hyperfine coupling.[13,19] [e] ρ_L is the spin density on the phosphorus donor atom. [f] g_1 values in brackets are calculated from the isotropic g values. [g] A_1 values in brackets are in gauss and calculated from the P and K values. A_1 values for these complexes have not been observed experimentally.

Table II. Phosphorus-31 Hyperfine Coupling Constants and Spin Densities for $Co^{II}(salen)\cdot PX_3$ Complexes

PX_3	a_1,[a] cm^{-1} (G)	a_2, cm^{-1} (G)	a_3, cm^{-1} (G)	$\langle a \rangle$,[b] cm^{-1}	$2a_d$,[c] cm^{-1}	ρ_{3p}[d]	ρ_{3s}	$\rho_{3p} + \rho_{3s}$	ρ_{3p}/ρ_{3s}[e]	% s[f]	$\rho_L + \rho_{Co}$
PPh_3	0.0110 (98)	0.0163 (159)	0.0177 (188)	0.0150 (145)	0.0027	0.14	0.044	0.18	3.07	24	1.00
PMe_3	0.0176 (163)	0.0189 (186)	0.0216 (229)	0.0193 (191)	0.0023	0.12	0.057	0.18	2.11	32	0.99
$P(OMe)_3$	0.0234 (217)	0.0253 (249)	0.0267 (283)	0.0252 (249)	0.0015	0.076	0.074	0.15	1.03	49	0.96

[a] a_1 and a_2 are the phosphorus-31 hyperfine coupling constants normal to the principal magnetic axis and a_3 is the value along the principal magnetic axis. a_1 is calculated from the relation $\langle a \rangle = (a_1 + a_2 + a_3)/3$. [b] $\langle a \rangle$ is the observed isotropic coupling constant. [c] $2a_d$ is the dipolar coupling constant $2a_d = a_3 - \langle a \rangle$. [d] ρ_{3s} and ρ_{3p} are the spin densities in the s and p atomic orbitals of the ligand donor species. $\rho_{3s} = \langle a \rangle / a^*_{3s}$ ($a^*_{3s} = 3640$ G $= 0.33963$ cm^{-1}); $\rho_{3p} = 2a_d/2a^*_{3p}$ ($2a^*_{3p} = 206$ G $= 0.01922$ cm^{-1}). [e] Ratio of ρ_{3p}/ρ_{3s} character in the ligand donor orbital. [f] Percent 3s character in the ligand donor orbital.

electronic structure and magnetic parameters for the (d_{xz}, d_{yz}, $d_{xy})^6(d_{z^2})^1$ configuration are[3]

$$g_{xx} = 2.002 - 6\lambda/\Delta E_{yz \to z^2}$$

$$g_{yy} = 2.002 - 6\lambda/\Delta E_{xz \to z^2}$$

$$A_{xx} = P[-K - {}^2/_7 + {}^1/_{14}(g_{yy} - 2.002) + (g_{xx} - 2.002)]$$

$$A_{yy} = P[-K - {}^2/_7 + {}^1/_{14}(g_{xx} - 2.002) + (g_{yy} - 2.002)]$$

$$A_{zz} = P[-K + {}^4/_7 - {}^1/_{14}(g_{xx} - 2.002) - {}^1/_{14}(g_{yy} - 2.002)]$$

where λ is the effective spin–orbit coupling constant in the complex. ΔE values are the energy separations of virtual states, P equals $g_n\beta_n g_e\beta_e(1/\langle r^3 \rangle_{3d})$ and is intrinsically positive, and PK is the Fermi contact term.

Results from solving these expressions for the series of 1:1 complexes are found in Table I. Signs for the cobalt coupling constants ($A_3 > 0$, A_1 and $A_2 < 0$) are established from the condition that P must be positive. Reduction of the cobalt P value by 20–30% from the free-ion value of $P_0 \approx 0.023$[16] is largely caused by redistribution of odd-electron population from the cobalt d_{z^2} to the ligand σ-donor orbital.

Using the observed g_{xx} and g_{yy} and an effective spin–orbit coupling constant (λ) reduced from the free-ion value ($\lambda_0 = -515$ cm^{-1})[17] by the same fraction as the P value permits the estimation of the d_{xz} and d_{yz} to d_{z^2} energy separations (Table I). Ligand σ-donor interactions elevate the d_{z^2} donor–acceptor orbital, and ligand π-acceptor interactions lower the d_{xz} and d_{yz} orbitals such that they produce additive contributions to $\Delta E_{xz \to z^2}$ and $\Delta E_{yz \to z^2}$. The estimated energy separations for the CO, MeNC, and PX_3 complexes are all similar ($\Delta E_{xz \to z^2} \approx 6000$–$8700$ cm^{-1}; $\Delta E_{yz \to z^2} \approx 12{,}100$–$14{,}200$ cm^{-1}) and generally larger than the corresponding values reported for the pyridine complex ($\Delta E_{xz \to z^2} \approx 6000$ cm^{-1}; $\Delta E_{yz \to z^2} \approx 9000$ cm^{-1}). The combined σ-donor and π-acceptor properties for PX_3, CO, and MeNC are thus more effective than pyridine in producing these d-orbital splittings.

Cobalt $3d_{z^2}$ spin densities (ρ_{3d}) are estimated from comparison of the observed values of the dipolar coupling constants, A_d, with the theoretical value ($A_d = {}^4/_7 P_0 = 0.01314$ cm^{-1}) for a cobalt 3d electron (Table I). The estimated 3d spin densities are all very similar ($\rho_{3d} \approx 0.74$–0.81) for this series of adducts (Table I) and are closely related to the values for $Co^{II}TPP$ adducts.[11]

Phosphorus-31 Hyperfine Coupling in $Co^{II}(salen)\cdot PX_3$ Complexes. $Co^{II}(salen)\cdot B$ adducts (B = CO, MeNC, PPh_3, PMe_3, and $P(OMe)_3$) have a single unpaired electron that is predominantly in the cobalt d_{z^2} orbital. The overlap and mixing of the ligand σ-donor orbital with the cobalt d_{z^2} directly places spin density in the ligand σ system and results in ligand nuclear hyperfine coupling. Trivalent phosphorus ligands observed in this study form only 1:1 complexes with $Co^{II}(salen)$ as shown by ^{31}P ($I = {}^1/_2$) hyperfine coupling (Figure 2). In these complexes each EPR component is split into two lines by coupling with one phosphorus donor atom.

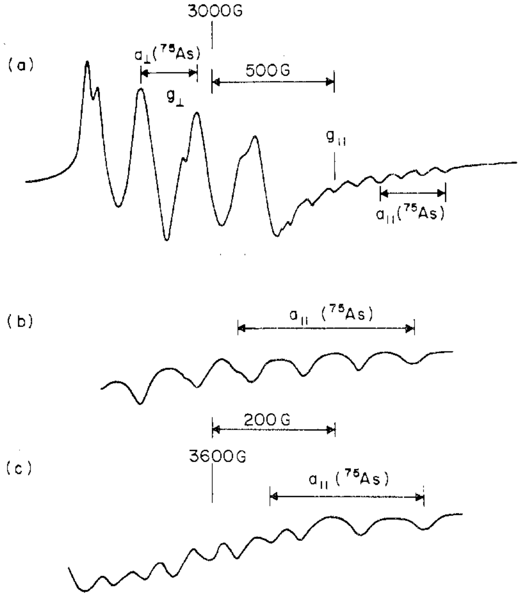

Figure 3. EPR spectra for trimethylarsine adducts in frozen solution (−140°): (a) $Co^{II}TPP\cdot AsMe_3$ in toluene; (b) expansion of high-field $g_\parallel$ region for $Co^{II}TPP\cdot AsMe_3$; (c) high-field portion of the $g_\parallel$ region for $Co^{II}(salen)\cdot AsMe_3$ in CH_2Cl_2.

The $A_{zz}(^{31}P)$ values for a series of phosphorus donor adducts [$P(n\text{-}Bu)_3$ (209 G), PMe_3 (229 G), PPh_3 (188 G), $P(OBu)_3$ (288 G), $P(OEt)_3$ (290 G), $P(OMe)_3$ (283 G), $P(OPh)_3$ (293 G)] are clearly defined in the EPR spectra. Analysis of the ^{31}P hyperfine in the g_{xx} and g_{yy} regions, however, is hampered by severe overlap which reduces confidence in the results. Only the PMe_3, $P(OMe)_3$, and PPh_3 complexes, where good isotropic spectra provided direct evaluation of the isotropic ^{31}P coupling, have been further analyzed in terms of the coordinated donor orbital s and p character. Isotropic ^{31}P coupling constants yield the 3s spin densities ($\rho_{3s} = \langle a \rangle / a^*_{3s}$; $a^*_{3s}(^{31}P) = 0.3396$ cm^{-1}) and the anisotropic coupling gives the 3p spin densities ($\rho_{3p} = (A_{zz} - \langle a \rangle)/2a^*_{3p}$; $2a^*_{3p}$ (^{31}P) $= 0.01922$ cm^{-1}).[18] The 3s and 3p spin densities for the phosphorus donor atom in $Co^{II}(salen)\cdot PX_3$ complexes are given in Table II. The 3s characters exhibited by the phosphorus donor orbital in $Co^{II}(salen)$ complexes (PMe_3, 33%; $P(OMe)_3$, 49%) parallel those estimated in the $Co^{II}TPP$ complexes (PMe_3, 36%; $P(OMe)_3$, 55%). The larger ^{31}P coupling constants in the trialkyl phosphite complexes compared to the trialkylphosphine donors is not the result of larger spin density but results from increased donor orbital s character (Table II). Triphenylphosphine has the smallest ^{31}P coupling constants ($A_{zz}(^{31}P) = 0.0177$ cm^{-1} (188 G), $\langle a \rangle(^{31}P) = 0.0150$ cm^{-1} (146 G)) and the smallest donor orbital s character (~24%).

Trimethylarsine Adducts of $Co^{II}(salen)$ and $Co^{II}TPP$. $Co^{II}(salen)$ forms only a 1:1 complex with trimethylarsine; however, CoTPP forms both 1:1 and 2:1 adducts, as shown

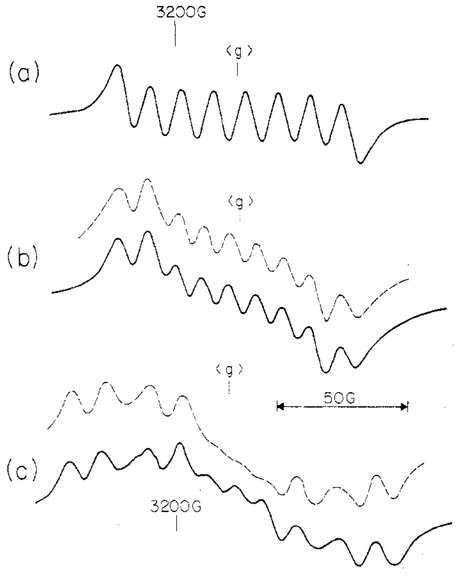

Figure 4. Solution EPR spectra for dioxygen adducts of Co^{II}(salen)·B complexes in CH_2Cl_2 (−60°) (——, observed; - - - -, simulated): (a) $B = C_5H_5N$, $\langle g\rangle = 2.027$, $\langle A(^{59}Co)\rangle = 12.4$ G; (b) $B = PPh_3$, $\langle g\rangle = 2.025$, $\langle A(^{59}Co)\rangle = 10.5$, $\langle a(^{31}P)\rangle = 10.5$; (c) $B = AsMe_3$, $\langle g\rangle = 2.028$, $\langle A(^{59}Co)\rangle = 11.0$; $\langle a(^{75}As)\rangle = 16.3$.

by the number of ^{75}As hyperfine lines (Figure 3). The anisotropic EPR spectrum of Co^{II}(salen)·$AsMe_3$ is complex due to the presence of three different g values and hyperfine splitting from arsenic-75 ($I = {}^3/_2$) and cobalt-59 ($I = {}^7/_2$). The g_{xx} and g_{yy} resonance areas overlap considerably and a unique assignment of all the transitions has not been successful. The g_{zz} region has been definitively assigned with $g_{zz} = 2.027$, $A_{zz}(^{59}Co) = 97$ G (0.0092 cm^{-1}), and $a_{zz}(^{75}As) = 246$ G (0.0232 cm^{-1}) (Figure 3).

The EPR spectrum of the 1:1 adduct of $Co^{II}TPP$ with trimethylarsine is closely related to the phosphine adducts. EPR parameters for $Co^{II}TPP\cdot AsMe_3$ ($g_{\|} = 2.04$; $g_{\perp} = 2.27$; $A_{\|}(^{59}Co) = 0.0084$ cm^{-1}; $A_{\perp}(^{59}Co) \approx 0.0013$ cm^{-1}) clearly indicate a $(d_{z^2})^1$ ground configuration. Analysis based on this configuration gives $P = 0.018$, $K = 0.065$, and $\rho_{3d} = 0.78$, which are comparable to values observed for the CO, MeNC, and PX_3 complexes of both $Co^{II}TPP$ and Co^{II}(salen).[10–13]

Arsenic-75 hyperfine coupling constants for CoTPP·$AsMe_3$ ($a_{\|}(^{75}As) = 267$ G (0.0254 cm^{-1}); $a_{\perp}(^{75}As) = 222$ G (0.0235 cm^{-1})) and the atomic hyperfine parameters ($a^*_{4s}(^{75}As) = 0.320$ cm^{-1}; $a^*_{4p}(^{75}As) = 0.0171$ cm^{-1})[18] permit estimation of the 4s and 4p spin densities in the coordinated arsine σ-donor orbital ($\rho_{4s} = 0.075$, $\rho_{4p} = 0.076$, $\rho_{As} = 0.15$). These results for the $AsMe_3$ adducts can be compared with the corresponding values in $Co^{II}TPP\cdot PMe_3$ ($\rho_{3s} = 0.065$, $\rho_{3p} = 0.114$, $\rho_P = 0.18$).[12,13] The percent s character in the coordinated donor orbitals of $AsMe_3$ (50%) and PMe_3 (36%) follow the expected trend with donor atom electronegativity.

Dioxygen Complexes of Co^{II}(salen)·B ($B = PX_3$, $AsMe_3$, and C_5H_5N) and $Co^{II}TPP\cdot AsMe_3$. Co^{II}(salen) and $Co^{II}TPP$ complexes with nitrogen donors are known to form monomeric dioxygen complexes. The unpaired electron in dioxygen complexes of this type occupies an MO that is predominantly oxygen π* in character.[4,11] (Representative isotropic EPR spectra for the dioxygen complexes of Co^{II}(salen)·B ($B = PPh_3$, $AsMe_3$, C_5H_5N) are shown in Figure 4.) Hyperfine splittings are observed for coordinated phosphorus and arsenic donors but not for nitrogen donors in the dioxygen complexes of Co^{II}(salen) (Figure 4). The atomic hyperfine parameters for ^{31}P and ^{75}As (see above) are much larger than those for nitrogen ($a^*_{2s}(^{14}N) = 0.0515$ cm^{-1}; $2a^*_{2p}(^{14}N) = 0.0032$ cm^{-1})[18] and provide a more sensitive probe for small spin densities. The magnitude of the ^{31}P hyperfine parameter (Co^{II}(salen)·$PPh_3\cdot O_2$, $\langle a\rangle(^{31}P) = 10.8$ G) should be approximately an order of magnitude larger than the ^{14}N hyperfine parameter, so that an ^{14}N coupling constant of ~1 G can be expected in the dioxygen complexes of nitrogen donor adducts. This explains why ^{14}N hyperfine splitting has not been easily observed in complexes such as the dioxygen adduct of cobaglobin but leaves open the possibility of eventually resolving this coupling. We have previously reported that the magnitude of the isotropic ^{31}P coupling constant in $Co^{II}TPP\cdot PX_3\cdot O_2$ complexes parallels the coordinated donor orbital s character.[13] The ^{75}As hyperfine coupling constant and associated s spin density in $Co^{II}TPP\cdot AsMe_3$ (~50% s) ($\langle a\rangle(^{75}As) = 25$ G, $\rho_{4s} = 0.0074$) compared to those of the Et_3P adduct (27% s) ($\langle a\rangle(^{31}P) = 15.7$ G, $\rho_{3s} = 0.0044$) are consistent with the trend in donor orbital s character. The same coupling constant trend is found for the Co^{II}(salen) complexes.

Summary

EPR studies demonstrate that the CO, MeNC, and R_3P complexes of Co^{II}(salen) all have the $(d_{xz}, d_{yz}, d_{xy})^6(d_{z^2})^1$ ground configuration and very similar metal and ligand spin density distributions. Dioxygen complexes of Co(salen)·B and CoTPP·B ($B = PX_3$, $AsMe_3$) are also closely related and show ^{31}P and ^{75}As hyperfine splitting. All features of the dioxygen complexes are consistent with a $Co^{III}O_2^-$ formulation. Analysis of the ^{31}P hyperfine splitting in the 1:1 Co^{II}(salen) adducts of PMe_3 and $P(OMe)_3$ demonstrates that the donor orbital s character is substantially larger in the coordinated phosphite ligand. These results corroborate our more extensive previous studies of phosphorus donors with $Co^{II}TPP$. Extension of this work to $Co^{II}TPP\cdot AsMe_3$ indicates that the arsine donor orbital has larger s character than the corresponding phosphorus ligand.

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Registry No. Co^{II}(salen)·CO, 54985-91-0; Co^{II}(salen)·MeNC, 54985-92-1; Co^{II}(salen)·PPh_3, 54985-93-2; Co^{II}(salen)·PMe_3, 54985-94-3; Co^{II}(salen)·$P(OMe)_3$, 54985-89-6; Co^{II}(salen), 36870-54-9; $Co^{II}TPP\cdot AsMe_3$, 54985-90-9; Co^{II}(salen)·$AsMe_3$, 54985-95-4; Co^{II}(salen)·$C_5H_5N\cdot O_2$, 28453-66-9; Co^{II}(salen)·$PPh_3\cdot O_2$, 54986-07-1; Co^{II}(salen)·$AsMe_3\cdot O_2$, 54986-08-2.

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Contribution from the Lash Miller Chemical Laboratories,
University of Toronto, Toronto, Ontario, Canada

Dissymmetric Arsine Complexes. Cobalt Hydrides

B. BOSNICH,* W. G. JACKSON, and S. T. D. LO

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General methods for the preparation of arsinecobalt hydrides are given and the problems associated with isolating them are discussed. It is shown that, electronically, all the derivatives are formally cobalt(III) complexes despite the dichotomous chemical properties observed with some of the hydrides. No correlation between the variations in the hydride chemical shifts and the ligand field strengths of the axial ligands is found and the possible reasons for this are suggested. An aquo group trans to a hydrido ligand is labilized to the extent that its exchange is observable on an NMR time scale. The presence of two hydrido ligands confers stereochemical nonrigidity to the *cis*-$[Co(diars)_2(H)_2]ClO_4$ system at room temperature.

Of the non-carbonyl-containing hydrido complexes of the elements Co, Rh, and Ir, those of the first have been the least studied even though the scattered data which exist[1-5] suggest that these, in a number of ways, may be more interesting than the species derived from Rh and Ir. One of the major problems associated with the study of cobalt–hydrido complexes is that no general methods for their preparation have been developed. It is well-known that three of the distinguishing features of cobalt complexes are, first, the stability of the labile Co(II) state, second, its involvement in the catalytic substitution of the stable and nonlabile Co(III) complexes and, third, the propensity of cobalt complexes in different oxidation states to undergo rapid redox disproportionation reactions. In addition, it is probable that most (formally) cobalt(III)–hydrido complexes are weakly acidic, releasing protons and the highly[5,6] reactive Co(I) species in basic media. Thus attempts at reducing Co(II) or Co(III) complexes with (basic) hydride ions in protic media, a procedure which is generally successful for Rh(III) complexes,[3,7] can give Co(I) species in equilibrium with the parent cobalt(III)–hydrido complex. A number of unwanted side reactions may then occur; a redox disproportionation reaction may ensue[8,9]

$$Co(I) + Co(III) \rightarrow 2Co(II)$$

the Co(II) species may catalyze the decomposition of the hydridocobalt(III) product,[10-12] and, in the presence of trace amounts of oxygen, the Co(I) species undergo rapid oxidative addition reactions to produce stable dioxygen adducts.[5,6]

We have encountered all these problems here, where we describe the preparation and properties of a series of cobalt–hydrido complexes containing tertiary arsine ligands. The three arsines employed are diars, *R*,*R*:*S*,*S*-tetars (and *R*,*R*-tetars), and *R*,*S*-tetars (Figure 1) where it will be noted that the chiral inner arsenic atoms of the tetars ligands are stable with respect to thermal inversion under the conditions employed. The one problem which we have not been able to avoid and which is inherent in some, but not all, of the pure species is their tendency to reduce "spontaneously" to the Co(II) state in various solvents, but this property appears to be characteristic of many cobalt(III)–arsine complexes[12] without hydrido ligands.

1. Preparations and Properties

When the Co(III) complexes *trans*-$[Co(diars)_2Cl_2]Cl$, *trans*-$[Co(R,S\text{-tetars})Cl_2]Cl$, and *cis*-α-$[Co(R,R{:}S,S\text{-tetars})Cl_2]Cl$ are treated with BH_4^- ions in methanol and/or water solutions, the complexes are reduced and become extremely sensitive to oxygen with which they react to form "sideways" bonded adducts *cis*-$[Co(As)_4O_2]^+$.[6] If, however, the solutions are kept acid, with acetic acid, throughout the reduction, the reduced complexes are no longer sensitive to oxygen and the *trans*-$[Co(As)_4(H)Cl]ClO_4$ compounds can be isolated. The bromo and iodo adducts are similarly prepared. All the hydrido species of the type *trans*-$[Co(As)_4(H)X]^{n+}$ described here are inert to oxygen in acidic or neutral solutions but, in the presence of base, they all react to give the dioxygen adducts. This suggests that the function of the base is to deprotonate the hydrido complexes and release a Co(I) species which is the entity reactive to oxygen. Thus the success of the hydrido complex preparations in mildly acidic conditions depends on constraining the equilibrium

$$[Co(As)_4(H)X]^{n+} \rightleftharpoons [Co(As)_4X]^{(n-1)+} + H^+$$

to the left, which not only suppresses the oxygen reaction but also the possible Co(I)–Co(III) redox reaction referred to earlier.

We have observed one apparent exception to this. When excess BH_4^- ions are added to solutions of *trans*-$[Co(diars)_2Cl_2]Cl$, under conditions where the resulting solutions are basic (pH ~8), then, provided BH_4^- ions are still present, a pale yellow, almost white complex *cis*-$[Co(diars)_2(H)_2]ClO_4$ can be isolated at this stage. This is a highly reactive complex and is stable as a solid in air for a few hours developing a pink coating of *cis*-$[Co(diars)_2O_2]ClO_4$ through reaction with oxygen. In neutral methanol suspensions or acetonitrile solutions the dihydrido complex spontaneously and rapidly reacts with oxygen and gives off 1 molar equiv of H_2. The same reaction occurs in basic media, although in solvents such as DMF and DMSO the complex is indefinitely stable at 0° if oxygen is excluded. Provided it is accepted that the Co(I) species is the reactive entity to oxygen, these reactions indicate that chemically one of the coordinated hydrogen atoms reacts as a proton, while the other behaves as a hydride, i.e.

$$cis\text{-}[Co(diars)_2(H)_2]^+ + O_2 \rightarrow cis\text{-}[Co(diars)_2O_2]^+ + H_2$$

This chemical dichotomy tends to be confirmed by the following observations.

The *cis*-$[Co(diars)_2(H)_2]ClO_4$ complex readily reacts with aqueous perchloric acid to liberate 1 molar equiv of hydrogen gas, and the yellow *trans*-$[Co(diars)_2(H)H_2O](ClO_4)_2$ complex is deposited

$$cis\text{-}[Co(diars)_2(H)_2]^+ + H_3O^+ \rightarrow trans\text{-}[Co(diars)_2(H)H_2O]^{2+} + H_2$$

The aquo group of this complex is exceedingly labile and can be displaced easily by other unidentate ligands. Thus we have prepared a series of *trans*-$[Co(diars)_2(H)X]^{n+}$ complexes, where X = Cl^-, Br^-, I^-, NCS^-, NO_3^-, CF_3COO^-, and CH_3CN.