Homolytic Cleavage of the S–S Bond in Dimethyl Disulfide by Cobalt Ions in Partially Co(II)-Exchanged Zeolite A, Co_4Na_4-A

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Abstract: Dehydrated partially Co(II)-exchanged zeolite A was exposed to dimethyl disulfide at 24 and at 200 °C in two separate experiments. From crystallographic analysis, it was learned that no reaction had occurred at 24 °C, but that after heating to 200 °C an S-bonded complex, stoichiometry $(CoSCH_3)_3CoNa_4Si_{12}Al_{12}O_{48}$ per unit cell, had formed. Crystallographic data for the complex, 326 reflections at the 3σ level collected at 24 °C using Mo $K\alpha$ radiation, were analyzed in the cubic space group $Pm3m$ (a = 12.198 (2) Å). The final weighted R index was 0.049. One and one-half molecules of dimethyl disulfide per unit cell undergo a homolytic cleavage of the S-S bond upon sorption. Three of the four Co(II) ions become tetrahedrally coordinated, to a sulfur atom and to three oxide ions of the framework; the fourth ion remains three coordinate and has near D_{3h} symmetry. Two of the four Na^+ ions are inside the sodalite unit and two are in the plane of the oxygen 8-rings. Some of the distances in the complex are Co–S = 2.52 (2) Å and Co–O = 2.249 (2) Å. Although these distances do not suggest that Co(II) has been oxidized, the black color of the complex and the presence of Na^+ ions in 8-rings suggest that at least a substantial transfer of charge from Co(II) to SCH_3 has occurred.

Introduction

The disulfide group has been found to react with transition-metal ions in several different ways. Examples indicate that disulfides can (a) form simple adducts or coordination complexes[1,2] and (b) undergo oxidative[3] or reductive[4] S–S bond cleavage reactions. Homolysis of the S–S bond has also been reported in chemical,[5] photochemical,[6] and thermal[7] studies of organic disulfides.

Dehydrated Co_4Na_4-A[8] has coordinatively unsaturated three-coordinate Co(II) ions.[9] Consequently, an unusual chemistry takes place within the voids of the zeolitic framework. The small molecules CO,[9] cyclopropane,[10] C_2H_4,[11] C_2H_2,[12] NO_2,[13] Cl_2,[14] Br_2,[15] and I_2[15] have been found to complex to the cobalt ions in the zeolite, and an oxidative addition reaction takes place when NO[13] is reacted with dry Co_4Na_4-A. This work was undertaken to investigate the reaction between dimethyl disulfide (DMDS) and the three-coordinate cobalt ions in partially Co(II)-exchanged zeolite A, Co_4Na_4-A.

Experimental Section

Single crystals of zeolite 4A were prepared by a modification of Charnell's method,[16] which included seeding with crystals obtained from an earlier synthesis. These were then exchanged with aqueous, 0.1 M $Co(NO_3)_2$ by methods described elsewhere.[9] The product, clear pink, hydrated crystals of approximate stoichiometry $Co_4Na_4Si_{12}Al_{12}O_{48}\cdot xH_2O$ per unit cell, will hereafter be referred to as Co_4Na_4-A.

Two single crystals of Co_4Na_4-A, each approximately 0.085 mm on an edge, were lodged in separate capillaries and were dehydrated at 300 °C for 48 h at 1×10^{-6} Torr. After they were returned to 24 °C, they were exposed to dry DMDS (vapor pressure = 27 Torr at 24 °C), which was prepared as follows.

DMDS (10 mL, K&K Laboratories) was repeatedly frozen and evacuated at 77 K to remove noncondensables, and was each time allowed to warm to 24 °C. It was distilled over a column of fully dehydrated (in situ) zeolite beads into ampules, each of which contained a few beads of fully dehydrated (in situ) zeolite 4A. One of these ampules, each with a vacuum break seal, was used for each sorption experiment.

Crystal 1. A fully dehydrated Co_4Na_4-A crystal was exposed to 27 Torr of DMDS at 200 °C for ca. 12 h. As a result, the crystal color darkened from blue (the color of dehydrated Co_4Na_4-A) to dark blue-black or nearly black.

Crystal 2. A similarly prepared crystal was exposed to 27 Torr of DMDS at 24 °C, also for ca. 12 h. This crystal retained the characteristic blue color of the dehydrated material.

X-ray Data Collection. The space group $Pm3m$ (no systematic absences) was used throughout this work for reasons discussed previously.[10] Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Syntex $P\overline{1}$ diffractometer, equipped with a graphite monochromator and a pulse-height analyzer. Molybdenum radiation was used for all experiments ($K\alpha_1$, λ = 0.709 30 Å; $K\alpha_2$, λ = 0.713 59 Å). The cubic unit cell constants at 24 °C, as determined by a least-squares refinement of 15 intense reflections for which $20° < 2\theta < 24°$, are 12.198 (2) Å for crystal 1 and 12.214 (1) Å for crystal 2.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \leq k \leq l$, and hlk, $h \leq l \leq k$) were examined using the θ–2θ scan technique, for $2\theta < 70°$. Each reflection was scanned at a constant rate of 1.0 deg min^{-1} over a symmetric range from 1° (in 2θ) below the calculated $K\alpha_1$ peak to 1° above the $K\alpha_2$ maximum. Background intensity was counted at each end of a scan range for a time equal to half the time required to measure the reflection. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 100 reflections to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection.

The raw data from each region were corrected for Lorentz and polarization effects (including that due to incident beam monochromatization), the reduced intensities were merged, and the resultant estimated standard deviations were assigned to each averaged reflection by the computer program COMPARE.[17] The mean intensity for a reflection was calculated as $I = (I_{hkl} + I_{hlk})/2$, where I_{hkl} = [CT $- 0.5(t_c/t_b)(B_1 + B_2)](\omega)$, CT is the total integrated count obtained in a scan time t_c, B_1 and B_2 are the background counts each measured in time t_b, and ω is the scan rate. Standard deviations of I were calculated as described previously.[10] The value of p was taken as 0.02, a value found to be appropriate for the instrumentation used.[10] No absorption correction was applied to the data; it was judged to be unnecessary (μR = 0.11). Of the 870 pairs of reflections examined for crystal 1 and 871 for crystal 2, only the 326 and 229, respectively, whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement.

A bulk sample of approximate composition Co_1Na_{10}-A was prepared, dehydrated under vacuum at 350 °C, and exposed to 27 Torr of dry DMDS. As before, its color changed from blue to black upon the addition of DMDS at 200 °C. At the same time, the EPR spectrum changed qualitatively. Further interpretation was hampered by the presence of EPR-active impurities in the starting material (Linde 4A, lot no. 494107701161).

Structure Determination. Full-matrix least-squares refinement of

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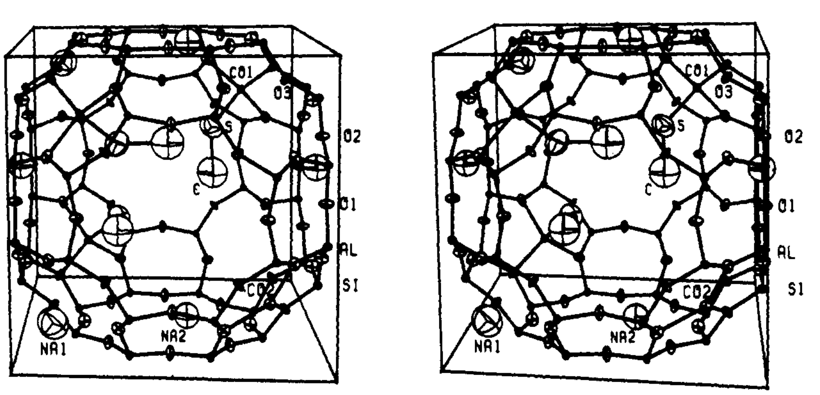

Figure 1. A stereoview of the $(CoSCH_3)_3CoNa_4$-A unit cell. Heavy bonds indicate the coordination sphere of the cobalt ions. Ellipsoids of 20% probability are used.

Table I. Positional, Thermal, and Occupancy Parameters for $(CoSCH_3)_3CoNa_4$-A[a]

	Wyckoff position	x	y	z	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	occupancy factor
(Si,Al)	24(*k*)	0	1823(2)	3691(2)	255(12)	190(10)	145(11)	0	0	25(9)	1[b]
O(1)	12(*h*)	0	2090(7)	½	816(68)	648(64)	227(43)	0	0	0	1
O(2)	12(*i*)	0	2971(4)	2971(4)	728(63)	293(30)	293(30)	0	0	207(38)	1
O(3)	24(*m*)	1133(3)	1133(3)	3322(5)	393(22)	393(22)	596(41)	192(29)	−89(23)	−89(23)	1
Co(1)	8(*g*)	2124(3)	2124(3)	2124(3)	233(12)	233(12)	233(12)	45(18)	45(18)	45(18)	⅜
S	8(*g*)	3318(43)	3318(43)	3318(43)	2330(145)	2330(145)	2330(145)	−443(132)	−443(132)	−443(132)	⅜
Na(1)	8(*g*)	1237(43)	1237(43)	1237(43)	3600(493)	3600(493)	3600(493)	−244(521)	−244(521)	−244(521)	¼
Na(2)	12(*i*)	0	4284(36)	4284(36)	2772(478)						⅙
Co(2)	8(*g*)	1806(11)	1806(11)	1806(11)	461(68)						⅛
C	12(*j*)	3285(85)	3285(85)	½	4272(1140)						¼

[a] All positional and thermal parameters are given ×10^4; standard deviations are in units of the least significant digit given for the corresponding parameters. The anisotropic temperature factor is $\exp[-2\pi^2(h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + l^2(c^*)^2U_{33} + 2hk(a^*b^*)U_{12} + 2hl(a^*c^*)U_{13} + 2kl(b^*c^*)U_{23})]$. [b] Occupancy factor for (Si) = ½; occupancy factor for (Al) = ½.

the structure of crystal 1 was initiated using the atomic coordinates of the framework ions ((Si,Al), O(1), O(2), and O(3)) and Co(II) obtained for a previously studied DMDS sorption complex of Co_4Na_4-A;[18] this model contained four equivalent Co(II) ions at 6-ring sites. Anisotropic refinement of these ions converged to $R_1 = (\sum|F_o - |F_c||)/\sum F_o = 0.087$ and $R_2 = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.084$.

A subsequent difference electron density function revealed a plausible S position on the threefold axis at $x = y = z = 0.33$ with a peak height of 2.4 e Å^{-3}. This difference function also indicated a Na^+ position on threefold axes inside the sodalite unit. Including them as four S atoms and two Na^+ ions further reduced R_1 to 0.081 and R_2 to 0.072.

The elongated thermal parameters of the cobalt ions suggested that these ions might not all be equivalent. A Fourier function indicated that the input cobalt position had a shoulder on its sodalite side and on the threefold axis. Accordingly the position was split into two with three ions at Co(1) and one at Co(2) (see Table I for the identities of these atoms). Subsequent least-squares refinement converged at $R_1 = 0.071$ and $R_2 = 0.061$. The peak at the sulfur position was symmetrical. Consistent with this, trial refinements with split S positions were unsuccessful.

The Fourier function also had a peak in the 8-ring (peak height = 2.7 e Å^{-3} at $x = 0, y = z = 0.42$). When this was included in least-squares refinement as Na^+, occupancy refinement at the site converged at 2.0 Na^+ ions. A subsequent Fourier had a peak at $x = y = 0.33$, $z = 1/2$ (height = 0.50 (7) e Å^{-3}). This was treated as three carbon atoms in least-squares refinement, and the final error indices $R_1 = 0.062$ and $R_2 = 0.049$ were obtained. Attempts to refine the Na(2) and carbon positions anisotropically were unsuccessful.

Occupancy refinements at the cobalt sites indicated 2.5 Co(II) ions at Co(1) and 1.4 at Co(2). However, this led to instability in least squares elsewhere in the structure. Hence the occupancies were fixed at whole numbers as indicated in Table I.

The goodness of fit, $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2}$, is 2.44; m (326) is the number of reflections and s (36) is the number of variables in least squares. All shifts in the final cycles of refinement were less than 1% of their respective standard deviations. The final difference function with an estimated standard deviation of 0.06 Å^{-3} was featureless except for residual peaks at the input S and Na(2) positions.

The final structural parameters are presented in Table I. Interatomic distances and angles are in Table II. A listing of observed and calculated structure factors is available; see paragraph at end of paper regarding supplementary material. A likely atomic arrangement consistent with the results of structure refinement is shown in Figure 1.

The quantity minimized in least squares is $[\sum w(F_o - |F_c|)^2]$ where each weight (w) was the reciprocal of the variance of the corresponding structure factor. Atomic scattering factors[19] for O^-, $(Si,Al)^{1.75+}$ (the average of Si^0, Si^{4+}, Al^0, and Al^{3+}), Co^{2+}, S^0, and C^{val}, modified to account for the real components (f') of the anomalous dispersion corrections,[20] were used.

Using the diffraction data for crystal 2, full-matrix least-squares refinement of the same initial trial structure (vide supra)[18] converged quickly to $R_1 = 0.069$ and $R_2 = 0.060$. An ensuing difference function, by being generally featureless in the region of the sulfur position of crystal 1 and elsewhere, except at the expected Na^+ position,[9] indicated that no sorption had occurred at 24 °C.

Discussion

The homolytic cleavage of the S-S bond in DMDS is quantitative at 200 °C upon sorption into Co_4Na_4-A. Each CH_3S group complexes to a cobalt ion in a bent manner, with a Co-S distance of 2.52 (2) Å (see Figure 2). A similar structure had been found, with Co-S = 2.50 (8) Å, when this experiment was first attempted.[18]

One and one-half disulfide molecules per unit cell of the zeolite undergo scission to give three CH_3S groups. Accordingly, three cobalt ions have moved outward from their respective 6-rings (see Table III) to become four coordinate upon complexation to CH_3S. The fourth cobalt ion remains three

Table II. Interatomic Distances (Å) and Angles (deg)[a]

(Si,Al)-O(1)	1.630(3)	O(1)-(Si,Al)-O(2)	110.5(4)
(Si,Al)-O(2)	1.653(3)	O(1)-(Si,Al)-O(3)	111.2(3)
(Si,Al)-O(3)	1.679(2)	O(2)-(Si,Al)-O(3)	106.4(3)
Co(1)-O(3)	2.249(5)	O(3) -(Si,Al)-O(3)	110.8(3)
Co(2)-O(3)	2.184(5)	(Si,Al)-O(1)-(Si,Al)	157.0(5)
Na(1)-O(3)	2.55(5)	(Si,Al)-O(2)-(Si,Al)	154.1(5)
Na(2)-O(1)	2.82(3)	(Si,Al)-O(3)-(Si,Al)	138.9(3)
Na(2)-O(2)	2.26(6)	O(3)-Co(1)-O(3)	114.2(4)
Co(1)-S	2.52(3)	O(3)-Co(1)-S	104(1)
S-C	2.05(2)[b]	C-S-Co(1)	124(3)[c]
C-O(3)	4.24(2)	O(3)-Co(2)-O(3)	120(1)
C-O(1)	4.26(2)		

[a] Numbers in parentheses are esd's in the units of the least significant digit given for the corresponding parameter. [b] This distance is likely to be inaccurately long, as is discussed in the text. [c] This angle is likely to be in error owing to the inaccurately determined carbon position.

Table III. Deviations of Atoms (Å) from the (111) Plane at O(3)[a]

Co(1)	0.55	Na(1)	−1.32
Co(2)	−0.12	O(2)	0.25
S	3.07		

[a] A negative deviation indicates that the atom lies on the same side of the plane as the origin.

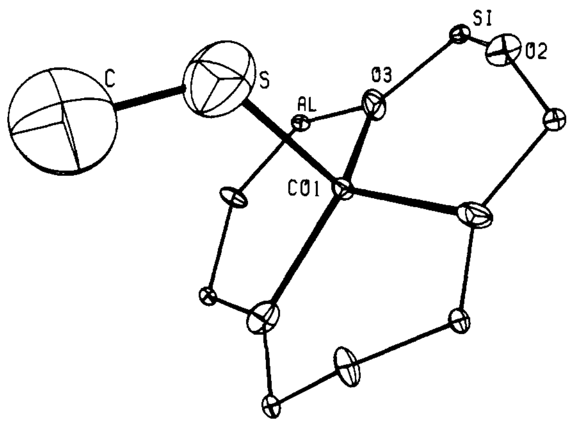

Figure 2. One of the three $[CoSCH_3]^{2+}$ complexes in the large cavity of each unit cell. Ellipsoids of 20% probability are used.

coordinate and retains the near D_{3h} site symmetry observed in the crystal structure of Co_4Na_4-A.[9] Why did only three of the four Co(II) ions per unit cell react with DMDS? The inclusion of a fourth CH_3S group would require an unreasonably close methyl-methyl distance of 2.96 Å, as can be seen in Figure 1. To avoid this destabilizing interaction, in part, the reaction halted at the stoichiometry observed.

Metal ion assisted scission of S-S bonds in disulfides (RSSR) is well documented.[4] Heterolytic cleavage yields RS^- and RS^+ fragments. If RS^- were to form, it would be expected to complex to cations in the zeolite, and a stoichiometric number of RS^+ ions should then be locatable elsewhere in the structure. Since none has been found, it can be inferred that the heterolysis of the S-S bond has not occurred.

DMDS did not react with intrazeolitic Co(II) at 24 °C. The requirement of an elevated temperature for reaction suggests a plausible reaction pathway. The S-S bond dissociation energy in DMDS has been found to be 73 kcal/mol.[21] There is evidence that the equilibrium

$$RSSR \rightleftharpoons 2RS\cdot$$

occurs at temperatures over 100 °C.[22] It is likely that the Co(II) ions have shifted this equilibrium to the right by complexing to $CH_3S\cdot$ radicals.

The four Na^+ ions in the structure occupy two distinct crystallographic sites: two at Na(1) are inside the sodalite unit, and two at Na(2) are in the planes of 8-rings. The Na(1)-O(3) distance, 2.55 (5) Å, is only virtually high: because of the structural disorder implied in refinements in the $Pm3m$ space group, only an average 6-ring conformation is learned. (Thus an accurate coordination situation is not learned for any particular 6-ring site.) The two Na^+ ions at Na(2) are in the plane of oxygen 8-rings but lie off their centers. The Na(2)-O(2) distance, 2.26 (3) Å, is consistent with Na-O distances reported in dehydrated 4A[23] and in the NO sorption complex[13] of Co_4Na_4-A for similarly situated Na^+ ions.

The nearly black color of the crystal suggests the presence of different absorbing species in the material. The uncomplexed cobalt ions at Co(2) transmit blue light; if the complexed cobalt ions were to absorb blue, the result would be a black crystal. The complexed Co(II) ions in the CO,[9] cyclopropane,[10] C_2H_4,[11] Cl_2,[14] and C_2H_2[12] sorption complexes of Co_4Na_4-A are all blue. The complexed cobalt ions in this structure, therefore, by absorbing blue, have a substantially modified electronic structure as compared to the ones listed above. It should be also noted that DMDS is colorless, so the black color is indicative of a charge redistribution along the Co-S bond.

It is possible that Co(II) has been oxidized to Co(III) by CH_3S. Colorless NO, upon sorption onto dehydrated Co_4Na_4-A, oxidized three of the Co(II) ions to Co(III), and the resulting material was brown-black.[13] Has such charge transfer occurred in this structure? The distance of the Co(1) ion from the (111) plane at O(3), 0.55 Å, is similar to the distances observed in the Co(II) sorption complexes of CO,[9] cyclopropane,[10] C_2H_4,[11] C_2H_2,[12] and Cl_2,[14] suggesting that Co(II) has not been oxidized by CH_3S radicals. Furthermore, the Co(1)-S distance, 2.52 (2) Å, is relatively long: a similar distance was reported in the thiourea complex of $CoCl_2$.[24] Similarly, the Co(1)-O(3) distance, 2.249 (5) Å, by being relatively long, does not suggest that an electron has been transferred from Co(II) to CH_3S. In the NO complex, however, three Na^+ ions (the maximum number possible) were promoted to 8-ring sites from 6-ring positions upon NO sorption to relieve the excessive charge buildup about the sodalite unit due to the formation of three Co(III) ions there. In this structure, two Na^+ ions have been promoted to 8-ring sites upon DMDS sorption, presumably for similar reasons; this suggests that a substantial, if not complete, transfer of charge from Co(II) to CH_3S has occurred.

The z coordinate of C is exactly $1/2$; this is unlikely to be correct because the symmetry (mm) of the site is not compatible with the local symmetry of the CH_3S group ($3m$). This may be responsible for the unreasonably elongated C-S bond, 2.05 (2) Å, observed in this structure (compared with 1.82 Å in DMDS).[25]

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Supplementary Material Available: Listings of the observed and calculated structure factors (supplementary Table I) (2 pages). Ordering information is given on any current masthead page.

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Five-Coordinate Dioxygen Adducts of Cobalt(II) Complexes

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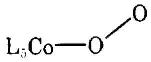
Abstract: A series of five-coordinate cobalt(II) trisphosphine complexes are reported and their electronic structures determined via EPR. Both distorted trigonal bipyramidal and tetragonal pyramidal geometries are obtained with ligand variation. Complexes with both geometries reversibly bind dioxygen but dissociate a phosphine in the process to form a novel series of five-coordinate terminally bound dioxygen complexes. The implication of this new type of adduct to the requirements for a ring-bonded mode of cobalt-dioxygen binding is discussed.

I. Introduction

Extensive research in recent years has enhanced our understanding of the binding of dioxygen to cobalt(II) complexes. However, many significant questions remain. For example, what properties of the cobalt determine the extent of electron transfer into and the nucleophilicity of the bound O_2? Several different geometries are possible for a bound dioxygen including end-on bonding[1] (I), bridging[1] (II), and a ring bonding[2] mode (III). The factors that determine the geometry which is obtained when dioxygen coordinates and the influences which these geometrical and electronic variations have on the reactivity of the bound O_2 remain as unanswered questions. A greater variety of systems need to be prepared and their electronic structures and chemical reactivity investigated before general patterns can be recognized. In this article the synthesis of a series of complexes in which rigid chelating structures are not attached to cobalt(II) is reported and their reactions with dioxygen are investigated. Five-coordinate complexes containing end-on bonded O_2, i.e., CoL_4O_2, are reported for the first time and the implications of this finding to the spin-pairing model of dioxygen binding are discussed.[3,4] Additional insight is provided regarding the requirements for forming structure III above.



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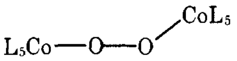

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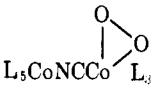

III

II. Experimental Section

A. General. All operations were carried out in oven-dried glassware in a dry N_2 atmosphere using Schlenk-type apparatus or in an inert atmosphere box, unless otherwise indicated. Heptane and medium petroleum ether were stirred vigorously over H_2SO_4 for 24 h, washed with dilute $NaHCO_3$ solution, and dried over $CaSO_4$. They were further purified before use by refluxing over $LiAlH_4$ for 24 h followed by distillation in a dry N_2 atmosphere. Toluene, benzene, and CH_2Cl_2 were refluxed over CaH_2 for 24 h and distilled under N_2 prior to use. Ethanol was treated with Na and distilled under N_2. Anhydrous $CoBr_2$ was prepared by heating $CoBr_2 \cdot 6H_2O$ in vacuo at 150 °C for 48 h. IR spectra were recorded on a Perkin-Elmer 467 grating infrared spectrophotometer. X-Band ESR spectra were recorded on a Varian Model E-9 spectrometer operating at ca. 9.1 GHz with a field sweep of 0–10 kG. A Varian E-15 Q band spectrometer was used to cover the range from 0 to 29 kG. Cooling was provided by a stream of cold (80 K) N_2 gas passing through the probe. Anisotropic EPR spectra were obtained in glasses formed from 3/2 (volume basis) toluene/CH_2Cl_2.

B. Preparation of Complexes. $Co(PMe_2Ph)_3Br_2$. Anhydrous $CoBr_2$ (2.2 g, 0.01 mol) was slurried in 50 mL of CH_2Cl_2 and PMe_2Ph (4.8 g, 0.035 mol) was added. The $CoBr_2$ slowly dissolved to yield a deep violet solution. The CH_2Cl_2 was removed in vacuo and the crude complex recrystallized from 50 mL of hot C_6H_6. The violet, crystalline solid was washed three times with 25-mL portions of heptane and dried in vacuo, yield 5.5 g (88%). The compound can be recrystallized from C_6H_6 in the presence of added phosphine.

Anal. Calcd for $CoC_{24}H_{33}P_3Br_2$: Co, 9.31; C, 45.52; H, 5.25; Br, 25.24. Found: Co, 9.19; C, 45.82; H, 5.30; Br, 25.54.

$Co(PMePh_2)_3Br_2$. An attempt to prepare this dibromotrisphosphine complex by the method used for $Co(PMe_2Ph)_3Br_2$ was unsuccessful. Only the green dibromobisphosphine complex, $Co(PMePh_2)_2Br_2$, was isolated.

Anal. Calcd for $CoC_{26}H_{26}P_2Br_2$: Co, 9.56; C, 50.43; H, 4.23; Br, 24.81. Found: Co, 9.52; C, 50.07; H, 4.14; Br, 25.76.

$Co(PMe_3)_3Br_2$. Anhydrous $CoBr_2$ (1.1 g, 5 mmol) was placed in a 50-mL round-bottom flask, and 25 mL of CH_2Cl_2 was added. The flask was attached to a vacuum line and the solution degassed. PMe_3 (2.5 g, 33 mmol) was vacuum transferred into the flask which had been cooled to liquid N_2 temperature. The solution was allowed to warm to ambient temperature and a dark violet solution resulted. The reaction was continued for 3 h, at which time the solvent and excess PMe_3 were vacuum transferred away, leaving a violet solid. This crude material was taken into an inert atmosphere box where it was dissolved in 10 mL of hot CH_2Cl_2 containing 1 equiv of PMe_3. Petroleum ether

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