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Synthesis and Properties of Cobalt(I) Compounds. II. An Ortho-Metalated (Triphenyl phosphite)cobalt(I) Complex

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The preparation and properties of the ortho-metalated compound $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4}Co$ are described. This compound was prepared by reaction of triphenyl phosphite with $Co(C_8H_{12})(C_8H_{13})$ as well as by heating solutions of $CoH[(C_6H_5O)_3P]_4$. The ortho-metalated compound catalyzed the hydrogenation of 1-butene and exchanged ligand hydrogens with D_2 under mild conditions.

There has been increasing interest in ortho-metalation reactions of triaryl phosphite complexes of transition metals. A number of ortho-metalation products of triphenyl phosphite complexes of the later transition metals have been isolated.[1] The ortho-metalation compounds derived from triaryl phosphite complexes of the first-row transition elements have, however, been elusive. An ortho-metalated triphenyl phosphite complex of manganese has recently been reported.[2a] A coordinatively unsaturated ortho-metalation product was proposed as an intermediate in the ortho deuteration of hydridotetrakis(triphenyl phosphite)cobalt,[1a] and ortho metalation is said to be the reason for the formation of complex products in the reaction of (triaryl phosphito)cobalt hydrides with potassium hydride,[2b] but the ortho-metalated compounds have not previously been isolated. Because of the potential for interesting catalytic properties, a method for the preparation of an ortho-metalated triphenyl phosphite complex of cobalt was sought.

Preparation and Properties

The ortho-metalated compound $[(C_6H_5O)_3P]_3(C_6H_5O)_2\overline{POC_6H_4}Co$ (I) has now been prepared by two different methods. In the first method mixtures of I and the corresponding hydride, $CoH[P(OC_6H_5)_3]_4$, were prepared by heating solutions of the hydride (in accord with the earlier proposal that ortho-metalated intermediates participated in the ortho deuteration of the hydride[1a]). Compound I and the hydride had similar solubility properties, and since I was available by another procedure, the fractionation of the mixtures was not pursued. In the second method I was prepared by the reaction of $Co(C_8H_{12})(C_8H_{13})$[3] with triphenyl phosphite at room temperature. An earlier report[4] of the

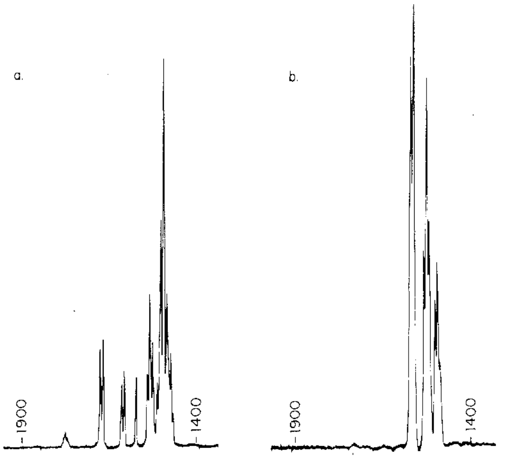


Figure 1. The 220-MHz ^1H NMR spectra with hertz from internal tetramethylsilane in C_6D_6 (low-field regions only): (a) $[(C_6H_5O)_3P]_3(C_6H_5O)_2POC_6H_4Co$; (b) $CoH[P(OC_6H_5)_3]_4$.

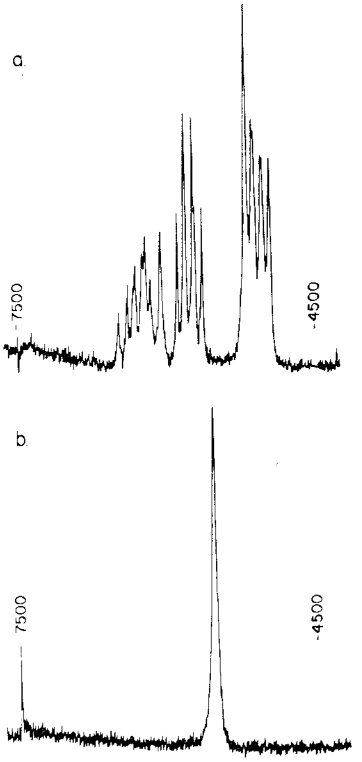


Figure 2. The 36.43-MHz ^{31}P NMR spectra in benzene with hertz from external 85% H_3PO_4: (a) $[(C_6H_5O)_3P]_3(C_6H_5O)_2POC_6H_4Co$; (b) $CoH[P(OC_6H_5)_3]_4$.

reaction of $Co(C_8H_{12})(C_8H_{13})$ with phosphorus ligands implied that this procedure should have produced the corresponding hydride, but there were no indications of more than traces of hydride product from this reaction.

Compound I (prepared from $Co(C_8H_{12})(C_8H_{13})$) and the hydride have quite different ^1H and ^{31}P NMR spectra as shown in Figures 1 and 2. A mixture of I and the hydride was prepared by heating a sample of the hydride prepared by borohydride reduction of cobalt nitrate in the presence of the ligand.[5] It was clear by comparison of the ^1H and ^{31}P spectra that this mixture was predominantly (ca. 80–90%) the same material (I) as produced by reaction of $Co(C_8H_{12})(C_8H_{13})$ with triphenyl phosphite. The ir spectra of I prepared by both methods have weak peaks at ca. 1100 cm^{-1} and medium-intensity peaks at ca. 800 cm^{-1} in accord with the spectra of the ortho-metalated complexes of the later transition metals.[1]

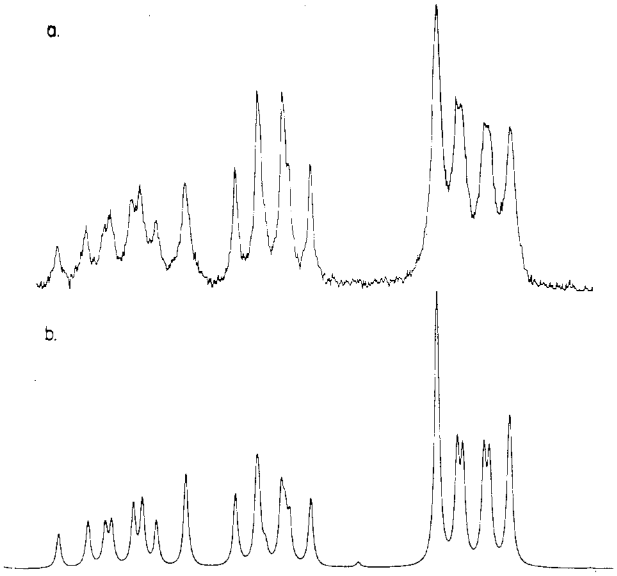


Figure 3. ^{31}P NMR spectrum of $[(C_6H_5O)_3P]_3(C_6H_5O)_2POC_6H_4Co$: (a) observed spectrum; (b) computer simulation.

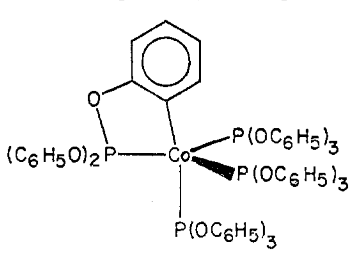


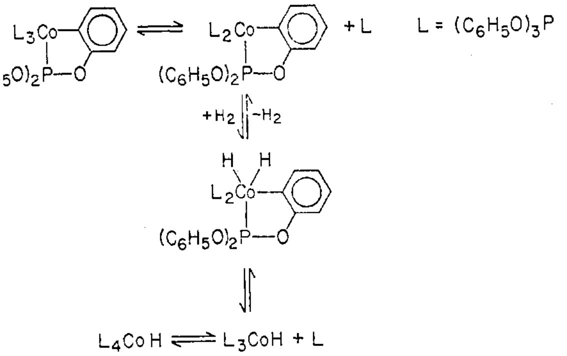
Figure 4. A possible structure for $[(C_6H_5O)_3P]_3(C_6H_5O)_2POC_6H_4Co$.

An expansion of the ^{31}P spectrum of I is shown in Figure 3 along with a computer simulation of a spectrum for an ABC_2 spin system.[6] The observed spectrum is clearly consistent with an ABC_2 spin system in contrast to the AB_3 pattern recently reported[2b] for the dimers $Co_2[P(OR)_3]_8$, R = CH_3 and C_2H_5. The parameters used in the simulation were as follows: A, 160 ppm; B, 144 ppm; C, 122 ppm (downfield from 85% H_3PO_4); $J_{AB} = -127$ Hz; $J_{AC} = +212$ Hz; $J_{BC} = -100$ Hz. These do not necessarily represent the best fit. Some other combinations of the relative signs provided fairly good fits, but J_{AC} and J_{BC} must have opposite relative signs. The acceptable relative sign combinations are J_{AB} ±, J_{AC} ∓, J_{BC} ± and J_{AB} ±, J_{AC} ±, J_{BC} ∓ The ^{31}P spectrum was obtained at room temperature and was substantially the same at 100°. Figure 4 shows one possible structure for I.

Catalytic Activity

Compound I prepared by both methods gave essentially identical behavior when treated with hydrogen or hydrogen and 1-butene. At room temperature with 50 psig hydrogen I was only slowly converted to $CoH[P(OC_6H_5)_3]_4$. About 10% conversion was obtained in 15 hr. Under otherwise identical conditions about 50% conversion could be obtained in $^1/_2$ hr at 55° or nearly complete conversion could be obtained in 1 hr at 65°. Solutions of I are efficient catalysts for the hydrogenation of 1-butene under mild conditions (25–50°, 30 psig H_2), while the hydride, $CoH[P(OC_6H_5)_3]_4$, is essentially inactive as a hydrogenation catalyst under these conditions. The conversion of 1-butene to butane is accompanied by almost no accumulation of isomeric butenes which is probably due to hydrogenation of 1-butene being much more rapid than isomerization. More than 30 mmol of butene was hydrogenated with only 0.1 mmol of I as catalyst, and at room

Scheme I



temperature ca. 12 mmol was hydrogenated in ca. 20 hr.

The reaction of I with deuterium could be pictured as a simple reaction between one molecule of I and one of D_2 to produce a cobalt deuteride, $[(C_6H_5O)_3P]_3(C_6H_4DO)P(OC_6H_5)_2CoD$, with one deuterium on cobalt and one deuterium in a ligand. This is clearly not the case. Compound I was treated with deuterium under conditions which gave essentially complete conversion of I to the hydride when hydrogen was used instead of deuterium. Examination of the ligand and high-field hydride portions of the ^1H NMR spectrum of the product showed that at least half of the product was present as a cobalt hydride rather than a deuteride. The gas phase was still ca. 85 atom % deuterium at the end of the experiment. Also, analysis of the recovered cobalt complex for deuterium[7] showed that it contained on the average more than six atoms of deuterium per molecule. Control experiments showed that the product $CoH[P(OC_6H_5)_3]_4$ underwent little or no exchange with deuterium gas under the same conditions.

Discussion

These observations are consistent with (*but do not prove*) a scheme (see Scheme I) for the interconversion of I and hydride (or deuteride) which is an elaboration of that proposed by Parshall et al.[1a] for ortho deuteration of the hydride. In terms of this scheme the observations suggest that the intermediates in the hydrogenation of I live long enough for some scrambling of the cobalt and ring hydrogens to occur before the intermediates are trapped by free triphenyl phosphite. The generally greater reactivity of I compared to the hydride could be due to greater ease of loss of ligand from I.

The activity of I as a hydrogenation catalyst presumably arises from competition between olefin and free triphenyl phosphite for some coordinatively unsaturated species. A compound closely related to the L_3CoH of Scheme I has been shown to be a very active catalyst for the hydrogenation of 1-butene,[8] but the evidence is not sufficient to determine whether it is this or a different species which interacts with the olefin.

The dissociative mechanism for the deuteration of the hydride, $CoH[P(OC_6H_5)_3]_4$, was indicated earlier[1a] by the observation that excess ligand inhibited the exchange between deuterium gas and the ortho-ligand hydrogens. In the course of the present work an increase in the rate of exchange was observed when the substrate concentration was decreased which is also consistent with the dissociative mechanism. The rate of exchange of the ligand hydrogens of I with deuterium appeared to be larger at a lower substrate concentration as well.

The suggestion that the hydrogenation of butene by I involves loss of ligand and competition between olefin and free triphenyl phosphite for a coordinatively unsaturated species is supported by the observation that addition of excess triphenyl phosphite to the reaction mixture essentially completely suppressed the hydrogenation reaction (at least a 20-fold rate reduction).

The conversion of I to the hydride and exchange with deuterium are also inhibited by excess ligand, but the situation is not simple. At ca. 0.08 *M* I and 50 psig the conversion of I to the hydride was only slightly slower in the presence of ca. 1 *M* triphenyl phosphite than with no added triphenyl phosphite. However, at ca. 0.02 *M* I and ca. 10 psig there was a large reduction in the rate of both conversion to hydride and deuterium exchange when the reaction mixture was made ca. 1 *M* in triphenyl phosphite.

Experimental Section

Commercially available materials were used without special preparation. Melting points are uncorrected. The ^1H NMR spectra were obtained with a Varian 220-MHz instrument. The ^{31}P NMR spectra were obtained with a Bruker 90-MHz instrument modified for Fourier transform operation.

All experiments were carried out in the absence of air. A nitrogen-filled glove box was used in most cases.

Preparation of $[(C_6H_5O)_3P]_3(C_6H_5O)_2POC_6H_4Co$ from $Co(C_8H_{12})(C_8H_{13})$. To a solution of 13 g of triphenyl phosphite in 20 ml of benzene was added 3.6 g of $Co(C_8H_{12})(C_8H_{13})$.[3] The resulting solution was left at room temperature overnight. The benzene was evaporated under reduced pressure and the residue was triturated with hexane. The hexane was evaporated and the crude solid product was collected and washed with hexane. Recrystallization from acetone gave 7.0 g of pale yellow solid, mp ca. 190–195° dec. Anal. Calcd for $C_{72}H_{58}O_{12}P_4Co$: C, 66.62; H, 4.50; Co, 4.54. Found: C, 66.38; H, 4.83; Co, 4.59. The ^1H and ^{31}P NMR spectra are presented in Figures 1 and 2.

Preparation of $[(C_6H_5O)_3P]_3(C_6H_5O)_2POC_6H_4Co$ from $CoH[P(OC_6H_5)_3]_4$. A solution of 5 g of $CoH[P(OC_6H_5)_3]_4$[5] in 200 ml of benzene was placed in a 350-ml glass pressure vessel. The pressure vessel was joined to a cold trap and vacuum pump via a needle valve. It was warmed in a 140° oil bath while the liquid was stirred magnetically. The needle valve was adjusted to maintain a steady flow of benzene vapor from the vessel such that ca. 150 ml of liquid was removed in 30 hr. About 150 ml of benzene was added to restore the lost liquid volume and ca. 70 ml of benzene was allowed to escape from the vessel during an additional 24 hr in the 140° bath. The resulting dark brown liquid was filtered through Celite and the benzene was evaporated from the filtrate. The residue was crystallized from 50 ml of methylcyclohexane, yielding 2.9 g of yellow solid, ca. 70% ortho-metalated product–30% hydride by ^1H NMR. Fractional recrystallization from toluene–hexane gave a small sample of material estimated to be ca. 90% ortho-bonded compound and 10% $CoH[P(OC_6H_5)_3]_4$ from the integration of the ^1H NMR spectrum. In a similar experiment 1.2 g of material containing ca. 80% compound I was obtained from 5 g of hydride by crystallizing the crude product from acetone.

Reaction of $[(C_6H_5O)_3P]_3(C_6H_5O)_2POC_6H_4Co$ with H_2 and D_2. Small glass pressure bottles were charged with ca. 0.08 *M* solutions of I in benzene or benzene and triphenyl phosphite. The bottles were evacuated briefly and then charged with ca. 50 psig H_2. After the specified reaction period the benzene was removed under vacuum. The residues were triturated with hexane and the recovered solid was hexane washed and dried. The extent of conversion was estimated from the relative areas of the peaks in the ca. 7–8-ppm region of the ^1H NMR spectra as well as by comparing the area in the 7–8-ppm region with that of the high-field (ca. 13.5 ppm) quintet from the cobalt hydride. The ca. 800-cm^{-1} ir peak intensity provided a quick initial indication of the extent of reaction. The extent of conversion was as follows: 15 hr, room temperature, ca. 10%; 0.5 hr, 55°, ca. 50%; 1 hr, 65°, 95+%.

The reaction of I with deuterium was carried out in just the same manner with a reaction period of 75 min at 65°. The spectra indicated complete conversion of I, and deuterium analysis[6] showed 10.1 atom % excess deuterium in the recovered product. The gas phase was shown by mass spectrometry to have H_2, HD, and D_2 in the ratio of 5.3:17.4:77.3. There was no detectable incorporation of deuterium into the benzene solvent. A sample of $CoH[P(OC_6H_5)_3]_4$ treated in just the same way contained only 0.17 atom % excess deuterium. Three additional experiments were carried out with a modified procedure. Glass tubes containing ca. 0.02 *M* I in benzene, ca. 0.02 *M* I in a 25 vol % solution of triphenyl phosphite in benzene, and ca. 0.02 *M* $CoH[P(OC_6H_5)_3]_4$ in benzene were chilled to freeze the 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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Low-Spin Cobalt(II)–Schiff Base and –Porphyrin Complexes of CO, MeNC, $AsMe_3$, and PX_3. Electron Paramagnetic Resonance Studies

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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)·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