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## Carbon-13 Nuclear Magnetic Resonance Studies on Cobaloximes

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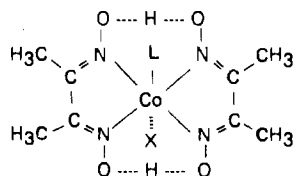
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The  $^{13}\text{C}$  NMR spectra of 51 cobaloxime complexes were measured and interpreted. Cobaloximes contain the moiety bis(dimethylglyoximato)cobalt(III),  $\text{Co}(\text{DH})_2$ , and, in this study, one of the two remaining coordination positions contained a neutral ligand L (either 4-*tert*-butylpyridine (Bupy), series I; trimethyl phosphite, series II; or tri-*n*-butylphosphine ( $\text{Bu}_3\text{P}$ ), series III) and the remaining position contained a negative ligand X. For all three ligands L, X =  $\text{NO}_3$ , Br, Cl,  $\text{N}_3$ ,  $\text{NO}_2$ , CN,  $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$ ,  $\text{P}(\text{O})(\text{OCH}_3)_2$ ,  $\text{CH}_2\text{Br}$ ,  $\text{C}_6\text{H}_5$ , and  $\text{CH}_3$ . For some of the L ligands, X = SCN, NCS, I, NCO,  $\text{S}_2\text{CO}-i\text{-C}_3\text{H}_7$ , *S*-*t*- $\text{C}_4\text{H}_9$ ,  $\text{CHBr}_2$ ,  $\text{C}_6\text{H}_4\text{Br}$ ,  $\text{CH}_2\text{Si}(\text{CH}_3)_3$ ,  $\text{CH}_2\text{C}_6\text{H}_4\text{CN}$ ,  $\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$ ,  $\text{C}_2\text{H}_5$ , and  $\text{CH}_2\text{C}_6\text{H}_5$ . Two hundred and thirty-one linear least-squares comparisons were made to determine the relationship between all the  $^{13}\text{C}$  shifts and  $^{31}\text{P}$ - $^{31}\text{C}$  coupling constants. Both *cis* and *trans*  $^{13}\text{C}$  NMR shifts were influenced similarly by X in all three series with the exception of the  $^{13}\text{C}$  NMR shifts of the  $\alpha$  C of Bupy in series I and C(1) of  $\text{Bu}_3\text{P}$  in series III. However, these shifts correlated well with each other. With the exception of these  $\alpha$ -C and C(1) shifts and the C(2) and C(3) shifts of  $\text{Bu}_3\text{P}$ , the dependence on X of the  $^{13}\text{C}$  NMR of axial ligands L is almost exactly opposite in order to the  $^1\text{H}$  NMR shifts of coordinated Bupy. The  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR shifts of the equatorial ligand follow essentially the same dependence on X and this dependence is similar to that for the  $^{13}\text{C}$  NMR shifts of the axial ligands. This pattern of shifts can be understood if the  $^{13}\text{C}$  NMR shifts are influenced primarily by through-bond effects of X and the  $^1\text{H}$  NMR shifts are influenced primarily by through-space effects of the near neighbor cobalt. This through-space effect in turn is influenced by the changes in cobalt magnetic anisotropy induced by the variation of X. The ordering of X generally observed is as follows: oxygen donors < halides or pseudohalides  $\sim$  CN  $\sim$  sulfur donors  $\sim$  phosphorus donors < alkyl or aryl groups. The position of CN in this series is variable and a comparison is made with similar variability observed in studies of organomercurials.

One of the major problems encountered in the understanding of the influence of the metal center on the chemical shifts of carbon atoms in attached ligands (as an aid in structural elucidation,<sup>1</sup> in the evaluation of electronic effects,<sup>2,4</sup> and in the identification of metal binding sites in labile systems<sup>3</sup>) is the assessment of the anisotropic effects of the metal or of other ligands.<sup>2,5</sup>

We have measured the  $^{13}\text{C}$  NMR spectra of over 50 different complexes containing the bis(dimethylglyoximato)-cobalt(III) (cobaloxime) moiety. The large number of possible axial groups<sup>4</sup> makes cobaloximes particularly suitable for a detailed study of the influence on  $^{13}\text{C}$  spectra of changing the metal coordination environment. These groups range from nitrate to methide and include neutral N donors, phosphines, and phosphites. Three series of cobaloximes,  $\text{LCo}(\text{DH})_2\text{X}$ , were chosen for study: (I) L = 4-*tert*-butylpyridine (Bupy),



- I. L = 4-*t*-Bupy  
 II. L =  $(\text{CH}_3\text{O})_3\text{P}$   
 III. L = (*n*-Bu) $_3\text{P}$

(II) L = trimethyl phosphite, and (III) L = tri-*n*-butylphosphine ( $\text{Bu}_3\text{P}$ ) [where X is a mononegative ligand and DH = dimethylglyoximate monoanion].

It has been possible to interpret<sup>6</sup> the  $^1\text{H}$  NMR shielding trends in these cobaloximes by assuming that, when ligand anisotropic effects are small or absent, the  $^1\text{H}$  NMR shifts are

dominated by the dipolar field about the cobalt center caused by currents induced in the d orbitals by the applied magnetic field. In such a case, knowing the geometry of the complexes, it is possible to estimate the anisotropic near-neighbor effect of the metal on the shifts ( $\Delta\sigma$ ) of the ligand atoms<sup>4,6,7,8</sup> with McConnell's equation, (1), for an axially symmetric anisotropic

$$\Delta\sigma = \Delta\chi \frac{(1 - 3 \cos^2 \theta)}{3R^3} \quad (1)$$

dipole.<sup>9</sup> The effect will drop off rapidly with distance,  $R$ , of the resonating nucleus from the metal and will depend on  $\theta$ , the angle between  $R$  and the symmetry axis of the dipole. Deviations from this estimate would then arise either from ligand anisotropies or from variations in local (mainly paramagnetic) shielding terms. The relatively large neutral ligands used in this study have carbon atoms which will be sufficiently distant from the metal to exclude any major anisotropic influence from the heavy atom. It should then be possible to determine whether systematic X-ligand-induced electronic changes in the metal center can cause changes in the shifts of  $^{13}\text{C}$  resonances in the neutral L and anionic (DH) ligands.

Cobaloximes containing phosphorus donor ligands allow the assessment of P-C coupling constants. Variations in coupling constants can be interpreted as possibly arising from rehybridization of one or both of the coupled nuclei.<sup>10</sup>

### Experimental Section

All of the complexes studied here either had been previously isolated and characterized for other studies or were prepared from known, isolated compounds by simple ligand-exchange reactions.<sup>11,12</sup> Spectra were measured in  $\text{CDCl}_3$  with respect to internal TMS (4%) at a probe temperature of 23  $^\circ\text{C}$ . Complex concentrations were 0.1 M or less depending on solubility. Chemical shifts and coupling constants appeared to be concentration independent in this range, although no

Table I. <sup>a</sup> <sup>13</sup>C NMR Data for (Bupy)Co(DH)<sub>2</sub>X Complexes (Series I), X = Common Ligands

X	Imine C	Oxime methyl C	α C	β C	γ C
NO <sub>3</sub>	153.89	13.22	150.82	123.14	164.33
Br	152.83	13.09	149.85	123.01	163.72
Cl	152.44	13.08	150.28	123.03	163.85
N <sub>3</sub>	151.98	12.89	150.49	123.02	163.68
NO <sub>2</sub>	152.43	12.79	149.94	122.94	163.81
CN	151.93	12.76	149.02	123.16	163.88
SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	152.39	12.57	149.59	122.87	163.28
P(O)(OCH <sub>3</sub> ) <sub>2</sub>	151.70	12.40	148.89	122.75 <sup>b</sup>	162.75
CH <sub>2</sub> Br	150.07	12.32	149.66	122.56	162.37
C <sub>6</sub> H <sub>5</sub>	150.15	12.20	149.61	122.50	162.08
CH <sub>3</sub>	148.84	12.00	149.43	122.36	161.84
Uncoordinated			149.51	120.51	159.66

<sup>a</sup> 0.1 M in CDCl<sub>3</sub>; ppm from TMS. The *t*-Bu methyl <sup>13</sup>C shift was essentially independent of X varying only 0.13 ppm, from 30.05 (X = NO<sub>3</sub>) to 30.18 ppm (X = CH<sub>3</sub>). The quaternary <sup>13</sup>C shift varied by 0.27 ppm, from 35.03 (X = NO<sub>3</sub>) to 34.76 ppm (X = CH<sub>3</sub>). <sup>b</sup> <sup>4</sup>J<sub>31P-13C</sub> = 3.6 Hz.

extensive concentration study was done.

Full spectral width (4000 Hz) random-noise <sup>1</sup>H-decoupled spectra were taken on the Varian CFT-20 spectrometer. The field:frequency ratio was stabilized by a time-shared deuterium lock on the solvent. The free induction decays of 13-μs pulses with an added 2-s pulse delay were accumulated during a 1.023-s acquisition in a full data table of 8192 increments. A sensitivity factor of -0.4 was applied to the data for further signal to noise enhancement prior to application of the Fourier transformation. A total of 2000-3000 transients were required for a good-quality spectrum of samples in the 0.1 M concentration range. For very dilute samples as many as 15000 transients were needed with an increased pulse delay for maximum nuclear Overhauser enhancement (NOE). Cr(acac)<sub>3</sub> was found to be useful for enhancing the signal strength of carbons lacking the NOE of a proton (e.g., C=O, C=N, quaternary carbons). No extensive study of its effectiveness was made, however. No attempt was made to observe the <sup>13</sup>C resonances of methide or CN.

## Results

**Acquisition and Treatment of Data.** <sup>13</sup>C chemical shifts and <sup>31</sup>P-<sup>13</sup>C coupling constants were found to be reproducible to within less than ±0.05 ppm even after many months. The influence of changing X on the shifts was generally greatly in excess of this reproducibility (Table I and supplementary material).<sup>14</sup> Assignment of ligand resonances was straightforward from literature values<sup>13,15</sup> for the uncomplexed L ligands, the differences in intensity based on the NOE effect, and trends in shift. We are uncertain as to the assignment of the C(2) and C(3) shifts of series III. All <sup>13</sup>C and <sup>1</sup>H shifts and couplings to <sup>31</sup>P were compared giving 231 least-squares plots and the results are tabularized in the supplementary material and a typical plot is illustrated by Figure 1.<sup>14</sup>

**Trends.** Several striking features emerged from the 231 comparisons. First, all sets of <sup>13</sup>C resonances and couplings correlate reasonably well (some much better than others)<sup>14</sup> except for the shifts of the α C of Bupy and of the C(1) of Bu<sub>3</sub>P. These two shifts, however, correlate very well with each other (Figure 2).

Second, cyanide often has an anomalous effect when comparisons are made between different spectroscopic parameters, either within a series or across series. Thus, in the comparison of imine-imine or oxime-oxime resonances only,<sup>14</sup> the point for cyanide falls on the line. However, in a plot of oxime-C shift (series I) with C(1) shift (series III), the point for CN is well off the line.<sup>14</sup> The shift of the γ C of Bupy for the CN complex is much further downfield than expected on the basis of other spectroscopic parameters. Also, it is not possible to assign rationally both the shifts and J<sub>PC</sub> of the C(2) and C(3) resonances of the Bu<sub>3</sub>PCo(DH)<sub>2</sub>CN complex.

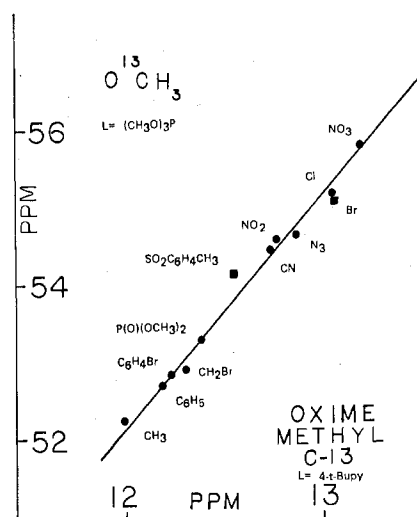


Figure 1. Plot of the <sup>13</sup>C NMR shifts of the (CH<sub>3</sub>O)<sub>3</sub>P ligand in series II vs. the oxime methyl <sup>13</sup>C NMR shift for (Bupy)Co(DH)<sub>2</sub>X, series I. The line was determined by a linear least-squares regression analysis, excluding ligands denoted by square points.

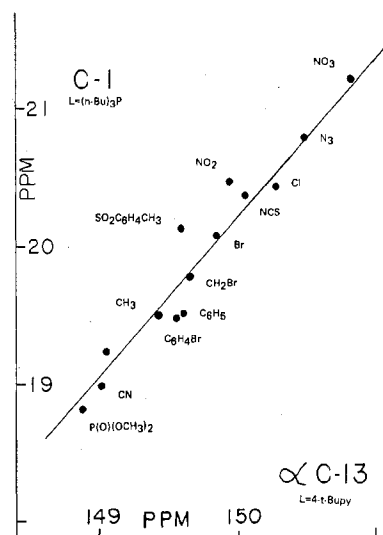


Figure 2. Plot of the <sup>13</sup>C NMR shift of C(1) of the Bu<sub>3</sub>P ligand in series III vs. the <sup>13</sup>C NMR shift of the α C of Bupy in series I. The line was determined by a linear least-squares regression analysis.

Third, correlations between <sup>13</sup>C data and <sup>1</sup>H data are usually relatively poor. The <sup>1</sup>H data are subject to changes both in the near-neighbor anisotropy in cobalt (induced by changing X) and in the anisotropy of X. It seems likely that the imine C of the DH ligand is also somewhat influenced by Co and X anisotropy.

Fourth, correlations involving only <sup>1</sup>H data generally lead to linear plots, when anisotropic effects of X are taken into account. This good agreement was noted previously for more limited data.<sup>4</sup>

## Discussion

Although there have been a number of moderately successful attempts to explain <sup>13</sup>C chemical shift information in terms of changes in π- and σ-electron density at the C center,<sup>16</sup> we shall limit this discussion to empirical considerations. We shall first try to demonstrate that the changes in <sup>13</sup>C shifts as a function of X are in fact caused for the most part by electronically induced (e.g., through-bond) changes in the electronic environment about the carbon center. Next, the bonding between X and the cobalt center will be discussed in terms of

Table II.<sup>a</sup> Comparison between the Observed and Calculated Chemical Shift Differences of <sup>13</sup>C Resonances for X = NO<sub>3</sub> and X = CH<sub>3</sub> in Series I

	σ, ppm	
	Calcd	Obsd
Oxime methyl C	-0.33	-1.22
Imine C	-1.16	-5.05
α C	1.40	-1.39
β C	0.56	-0.78
γ C	0.43	-2.49

<sup>a</sup> Crystallographic data obtained from ref 17, 18.

the trends observed in our data.

Some of the differences in shifts observed within each series for complexes with X = NO<sub>3</sub> and CH<sub>3</sub> are given in Table II. Calculated shifts which would arise from the change in cobalt anisotropy for the two X ligands are also included in Table II. These calculations assume that all of the spectral changes observed in the <sup>1</sup>H NMR spectrum of (Bupy)Co(DH)<sub>2</sub>X as a function of X arise from changes in cobalt anisotropy, and cobalt was treated as a point dipole according to eq 1.

Values of *R* and *θ* were estimated from x-ray crystallographic data<sup>17,18</sup> by application of the ORTEP computer program.<sup>19</sup> Δχ (the difference between the magnetic susceptibility parallel and perpendicular to the symmetry axis) was estimated to be equal to  $-7.3 \times 10^{-29}$  cm<sup>3</sup>/molecule, based on the difference in shielding between the α H's of series I for X = NO<sub>3</sub> and CH<sub>3</sub>. A C-H bond length of 1.08 Å was used.<sup>20</sup> For methyl groups 109.5° was used as the H-C-H bond angle.

The direction of the observed changes in shift when X is changed from NO<sub>3</sub> to CH<sub>3</sub> is correct for the C nuclei in the equatorial DH ligands (Table II). Within the limitations of our calculations, the observed shifts are too large to be solely a function of cobalt anisotropy. However, except for the C(2) and C(3) resonances of Bu<sub>3</sub>P in series III, the direction of the shifts in the trans L ligands as X is varied from nitrate to methide is opposite to that expected from cobalt anisotropy (Table II). This result is important in a number of ways. First, it shows that the <sup>13</sup>C shifts in axial ligands, at least, are responding to through-bond induced changes in the electronic properties at and near the resonating carbon nuclei. These changes very possibly reflect (σ + π)-electron density at the carbon.<sup>16</sup> Second, the trends in the proton shifts on the Bupy moiety are opposite to the trends in the <sup>13</sup>C shifts or, for the α C, do not correlate at all well. Proton shifts correlate with <sup>13</sup>C shifts in aromatic systems with both types of shifts reflecting changes in electron density at C.<sup>21</sup> The lack of correlation observed here supports our previous interpretation that <sup>1</sup>H NMR shifts are reflecting changes in cobalt anisotropy. Third, the excellent correlation between the shifts of C(1) in Bu<sub>3</sub>P and the α C of Bupy is difficult to understand solely in terms of transmission of electronic effects through bonds. In this connection, the P-C(1) coupling follows a normal pattern and correlates well with the other trends we observed for both cis and trans effects. It seems unlikely that C(1) is rehybridized in any unusual way with the rather different trans ligands CN, P(O)(OCH<sub>3</sub>)<sub>2</sub>, and I. Both the α C and C(1) occupy similar geometric positions, close to the metal center. Clearly, the anomalous effect probably arises from metal anisotropy. This result suggests that the estimation of through-bond electronic effects at nuclei close to a metal center using NMR shifts may be quite hazardous.

In a review<sup>22</sup> of the trans influence, it was concluded that different physical and spectroscopic properties of complexes could be regarded as being largely, but not exclusively, sensitive to the ability of the ligand being varied to rehybridize the metal center, whereas other properties were more sensitive to the overall (σ + π)-charge-donating ability of the ligand. In general, the ability of a ligand to rehybridize the metal center

will depend to a large extent on the nature of the donor atom in the ligand. The charge-donating ability of the ligand will depend also on the overall electronegativity of the ligand.

The general trends for the dependence of both cis and trans <sup>13</sup>C shifts (and <sup>31</sup>P-<sup>13</sup>C couplings) on X follow the order: oxygen donors < halides and pseudohalides < CN ~ sulfur donors ~ phosphorus donors < carbon donors. This order has been found for many spectroscopic properties of both transition metal complexes and organomercurials.<sup>4,22-25</sup> The <sup>13</sup>C data we report here suggest there is a close parallel between the ability of these X ligands to rehybridize the metal center and the charge-donating ability of these ligands. The most likely exception to this parallelism is the CN ligand. Our data generally suggest that this ligand's ability to rehybridize the metal center is more similar to sulfur donor ligands whereas the charge-donating ability of the ligand is more similar to that of halide ligands such as Cl.<sup>14</sup> The dual nature of the effect of the CN ligand on <sup>13</sup>C spectra has also been observed for organomercurials and was attributed to hyperconjugative effects.<sup>23</sup> We find we can obtain good linear correlations between our data for the shift of the α H in series I with the <sup>2</sup>J<sub>199Hg-13C</sub> constants in (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>HgX compounds. This latter coupling does not correlate well with the <sup>2</sup>J<sub>199Hg-1H</sub> or the <sup>1</sup>H NMR shift of the CH<sub>2</sub> group in these organomercurial compounds. However, the shift of the DH methyl C in series I does correlate well with these latter organomercurial spectroscopic trends. Thus, the dual nature of CN in the organomercurials correlates well with the dual nature of CN in cobaloximes.

It is our impression that the widely observed correlations between many spectroscopic parameters in several metal systems<sup>4</sup> arise from the close parallelism between the ability of X ligands to rehybridize the metal center and the ability of these ligands to donate charge into the metal species. Most spectroscopic trends will depend to some extent on both of these influences of the X ligand. When comparisons are made between two parameters, one which depends heavily on the rehybridizing ability of X and one which depends heavily on the charge-donating ability of X, deviation from linearity will be observed. Although we feel the number of systems which adhere closely to the ordering of the influence of X given above is impressive,<sup>4,22,25</sup> a truly detailed understanding of these effects is still lacking. In particular, whereas the through-metal influence of X in most metal systems bears little relationship to organic substituent constants for X, Coulson has found significant correlations of <sup>13</sup>C shifts of the aryl ligand in Pt(II) compounds with both Taft and Swain-Lupton substituent constants.<sup>27</sup>

**Registry No.** (Bupy)Co(DH)<sub>2</sub>NO<sub>3</sub>, 51194-55-9; (Bupy)Co(DH)<sub>2</sub>Br, 51194-57-1; (Bupy)Co(DH)<sub>2</sub>Cl, 38985-28-3; (Bupy)Co(DH)<sub>2</sub>N<sub>3</sub>, 51194-56-0; (Bupy)Co(DH)<sub>2</sub>NO<sub>2</sub>, 51194-34-4; (Bupy)Co(DH)<sub>2</sub>CN, 51212-02-3; (Bupy)Co(DH)<sub>2</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 55886-69-6; (Bupy)Co(DH)<sub>2</sub>P(O)(OCH<sub>3</sub>)<sub>2</sub>, 52896-11-4; (Bupy)Co(DH)<sub>2</sub>CH<sub>2</sub>Br, 55886-76-5; (Bupy)Co(DH)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, 55886-81-2; (Bupy)Co(DH)<sub>2</sub>CH<sub>3</sub>, 51194-36-6; (Bupy)Co(DH)<sub>2</sub>SCN, 51261-66-6; (Bupy)Co(DH)<sub>2</sub>I, 55886-66-3; (Bupy)Co(DH)<sub>2</sub>NCS, 51261-65-5; (Bupy)Co(DH)<sub>2</sub>NCO, 55886-67-4; (Bupy)Co(DH)<sub>2</sub>S<sub>2</sub>CO-*t*-C<sub>6</sub>H<sub>7</sub>, 51194-35-5; (Bupy)Co(DH)<sub>2</sub>S-*t*-C<sub>6</sub>H<sub>9</sub>, 55886-70-9; (Bupy)Co(DH)<sub>2</sub>CHBr<sub>2</sub>, 55886-72-1; (Bupy)Co(DH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Br, 55886-52-7; (Bupy)Co(DH)<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>, 55886-77-6; (Bupy)Co(DH)<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CN, 55886-74-3; (Bupy)Co(DH)<sub>2</sub>P(O)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 52880-68-9; (Bupy)Co(DH)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, 55886-79-8; (Bupy)Co(DH)<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, 55886-75-4; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>Br, 61024-81-5; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>NO<sub>3</sub>, 61024-82-6; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>Cl, 52654-86-1; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>N<sub>3</sub>, 61024-83-7; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>NO<sub>2</sub>, 61024-84-8; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>CN, 61024-85-9; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 61024-86-0; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>CH<sub>2</sub>Br, 42934-27-0; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>P(O)(OCH<sub>3</sub>)<sub>2</sub>, 61062-61-1; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Br, 61024-87-1; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, 61024-88-2; (CH<sub>3</sub>O)<sub>3</sub>PCo(DH)<sub>2</sub>CH<sub>3</sub>, 25586-92-9; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>SCN, 51194-41-3; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>I, 55886-53-8;

(Bu<sub>3</sub>P)Co(DH)<sub>2</sub>Br, 51194-40-2; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>NO<sub>3</sub>, 51194-37-7; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>Cl, 24501-27-7; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>NCS, 51194-38-8; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>C<sub>3</sub>H<sub>4</sub>N<sub>5</sub>, 61075-77-2; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N<sub>4</sub>O, 61024-89-3; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>N<sub>3</sub>, 51194-39-9; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>NO<sub>2</sub>, 51194-42-4; (Bu<sub>3</sub>P)Co(DH)CN, 51194-44-6; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 55886-56-1; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>P(O)(OCH<sub>3</sub>)<sub>2</sub>, 61024-90-6; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>CH<sub>2</sub>Br, 55886-62-9; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>, 55886-64-1; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, 55923-88-1; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Br, 55886-65-2; (Bu<sub>3</sub>P)Co(DH)<sub>2</sub>CH<sub>3</sub>, 51020-41-8; [(Bu<sub>3</sub>P)<sub>2</sub>Co(DH)<sub>2</sub>]As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, 61026-07-1; Bupy, 3978-81-2; (CH<sub>3</sub>O)<sub>3</sub>P, 121-45-9; Bu<sub>3</sub>P, 998-40-3; <sup>13</sup>C, 14762-74-4.

**Supplementary Material Available:** Tables of <sup>13</sup>C NMR shifts and P-C coupling constants for series II and III, for additional compounds in series I, and for the X ligands, a more extensive tabulation similar to Table II but for <sup>1</sup>H NMR and <sup>13</sup>C NMR for all three series, and a summary of the least-squares correlations (8 pages). Ordering information is given on any current masthead page.

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## Synthesis and Properties of Cobalt(I) Compounds. 4. Syntheses of Tris(triphenyl phosphite)cobalt(I) Halides

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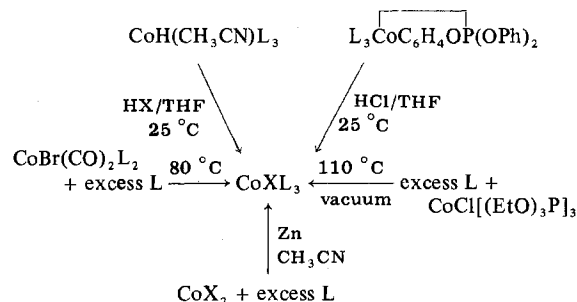
Three methods of preparation of CoX[(PhO)<sub>3</sub>P]<sub>3</sub> (X = Cl, Br) are given. Conversion to the known cobalt(I) compounds {Co[(EtO)<sub>3</sub>P]<sub>3</sub>}<sup>+</sup>Cl<sup>-</sup> and CoBr(CO)<sub>2</sub>[P(OPh)<sub>3</sub>]<sub>2</sub> is demonstrated.

The preparation of the four-coordinate cobalt(I) halide complexes, CoXL<sub>3</sub>, has been previously described in the cases where L is trimethylphosphine, triphenylphosphine, and triethyl phosphite.<sup>1</sup> The analogous triphenyl phosphite complexes, on the other hand, have not previously been isolated even though their use as catalysts with in situ formation has been disclosed.<sup>2</sup> The preparation and characterization of the complexes CoX[(PhO)<sub>3</sub>P]<sub>3</sub> has now been completed. Reaction of these complexes with triethyl phosphite gave the known cobalt(I) complexes {Co[(EtO)<sub>3</sub>P]<sub>3</sub>}<sup>+</sup>X<sup>-</sup>.<sup>1b</sup> Reaction of CoBr[P(OPh)<sub>3</sub>]<sub>3</sub> with excess carbon monoxide gave the known cobalt(I) halide complex, CoBr(CO)<sub>2</sub>[(PhO)<sub>3</sub>P]<sub>2</sub>.

The methods developed for the preparation of CoCl[(PhO)<sub>3</sub>P]<sub>3</sub> and CoBr[(PhO)<sub>3</sub>P]<sub>3</sub> are summarized in Scheme I. The two top routes use HX to react with a cobalt hydride or cobalt aryl. The center two routes are ligand-exchange reactions and do not require reduction or oxidation. The bottom route is a reduction of cobalt halide by metallic zinc. All of the routes work fairly well but have individual difficulties. The bottom route in particular is simple in materials and concept, but can easily go wrong.

The magnetic moments of the CoX[P(OPh)<sub>3</sub>]<sub>3</sub> complexes were found to be about 3.2–3.4 μ<sub>B</sub> at room temperature. This

Scheme I. Syntheses of CoX[(PhO)<sub>3</sub>P]<sub>3</sub> (L = (PhO)<sub>3</sub>P; X = Cl, Br)



is close to the values previously observed for the analogous complexes with tertiary phosphine<sup>8</sup> or triethyl phosphite<sup>1b</sup> ligands.

### Preparation from Cobalt Hydrides and HX

The triphenylphosphinecobalt hydride complexes CoHN<sub>2</sub>[Ph<sub>3</sub>P]<sub>3</sub> and CoH<sub>3</sub>[Ph<sub>3</sub>P]<sub>3</sub> are reported to produce the four-coordinate complex CoCl[Ph<sub>3</sub>P]<sub>3</sub> readily by reaction with HCl under mild conditions.<sup>4</sup> Several attempts were made to produce CoCl[(PhO)<sub>3</sub>P]<sub>3</sub> by the reaction of the well-known