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# Synthesis, Properties, and Structure of Hydrido(cyanotrihydroborato)tris(triphenylphosphine)cobalt(II)

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The synthesis of CoH(BH$_3$CN)(PPh$_3$)$_3$, which is a rare example of a Co(II) hydride, is described. The terminal B–H infrared stretching frequency of 2340 cm$^{-1}$ is consistent with the solid-state structure. The observed C≡N stretching frequency at 2190 cm$^{-1}$ suggests that correlations between its variations and the M–N–C angle or the M–N bond length in M–NCBH$_3$ complexes should be used with caution. The compound crystallizes in the triclinic space group $P\bar{1}$, with $a$ = 13.074 (6) Å, $b$ = 10.346 (5) Å, $c$ = 19.722 (9) Å, $\alpha$ = 75.28 (4)°, $\beta$ = 78.75 (4)°, $\gamma$ = 65.42 (4)°, and $\rho$(calcd) = 1.260 g cm$^{-3}$ for $V$ = 2334 Å$^3$, mol wt 885.7, and $Z$ = 2. Diffraction data were collected on a modified Picker diffractometer using monochromated Mo K$\alpha$ radiation. The structure was solved by the heavy-atom method and refined by blocked full-matrix least squares to conventional and weighted $R$ factors of 0.067 and 0.056 for the 3252 independent reflections with $I > 2.0\sigma(I)$. The structure consists of discrete molecules of CoH(BH$_3$CN)(PPh$_3$)$_3$ with five-coordinate Co(II). The BH$_3$CN$^-$ ligand is bonded to Co(II) through the N atom. The molecule is described as a square pyramid distorted toward the trigonal bipyramid. The H and N atoms form the apical vertices of the trigonal bipyramid with bond lengths of 1.42 and 1.904 (8) Å to Co(II). The P atoms form the equatorial plane of the trigonal bipyramid, and one P atom forms the apical vertex of the square pyramid with a P–Co(II) bond length of 2.291 (3) Å. The other P–Co(II) bond lengths are 2.245 (2) and 2.234 (3) Å.

## Introduction

Reactions of sodium tetrahydroborate with Co(II) and Ni(II) salts in the presence of a wide variety of phosphines have been extensively studied.[2-5] Tricyclohexylphosphine (PCy$_3$) is apparently the only phosphine that stabilizes Co(II) in these reactions, and the well-characterized[5] CoH(BH$_4$)(PCy$_3$)$_2$ is the product obtained. With most other phosphines, reductions to metal(I) or metal(0) species are very rapid, which makes isolation of the numerous intermediates in the reductive sequence difficult. Sodium cyanotrihydroborate is a milder reducing agent than NaBH$_4$, and its use should allow easier control over the analogous reactions. This paper reports the synthesis, structure, and some properties of CoH(BH$_3$CN)(PPh$_3$)$_3$, which has been isolated[6] as one of several products from Co(II)/PPh$_3$/NaBH$_3$CN reactions and which is clearly related to the PCy$_3$ complex mentioned above. Of particular interest is the mode of attachment of the BH$_3$CN$^-$ group since, while most BH$_3$CN$^-$ complexes are assumed (from infrared data) to have N-coordinated cyanotrihydroborate units, the structures of only three such complexes have been determined by X-ray methods. Of these, two are binuclear systems which show[7,8] bridging of the type M–HBH$_2$CN–M while in the other[9] M–NCBH$_3$ is the arrangement.

## Experimental Section

**Reagents and Characterization.** Triphenylphosphine was recrystallized from ethanol and stored under nitrogen prior to use. Commercial (Aldrich) NaBH$_3$CN was used without further purification, But because of its hydroscopic nature, it was stored over CaCl$_2$. Solvents were reagent grade and were distilled, degassed with O$_2$-free N$_2$, and stored over molecular sieves (type 4-A) in a glovebox. Reactions and the growing of crystals for X-ray studies were carried out in a glovebox that was continuously flushed with dry N$_2$. Samples were protected from oxidation during data collection. Infrared spectra (Nujol mulls) were recorded on a Beckman IR-12 spectrophotometer (polystyrene reference film) using NaCl (650–4000 cm$^{-1}$) or polyethylene (200–600 cm$^{-1}$) plates while electronic spectra in the 16 000–3000-Å range (solution or reflectance) were obtained with a Cary 14 spectrophotometer. $^1$H (80 MHz) and $^{31}$P (32.3 MHz) NMR spectra were obtained with a Bruker WP-80 FT instrument with Me$_4$Si and 85% H$_3$PO$_4$ used as internal and external standards, respectively. In the $^{31}$P spectra, downfield shifts are positive. Solid-state magnetic moments were measured with use of the Gouy method. The double-ended Gouy tube was calibrated with Hg[Co(CNS)$_4$] and Ni (en)$_3$(S$_2$O$_3$) for different settings of a Varian Associates V-2900 regulated magnet power supply controlling a Varian V-4005 electromagnet. Microanalyses (C, H, N) were carried out in these laboratories with a Perkin-Elmer Model 240 analyzer.

**Synthesis of CoH(BH$_3$CN)(PPH$_3$)$_3$.** Co(ClO$_4$)$_2$·6H$_2$O (0.457 g, 1.25 mmol) and PPh$_3$ (1.74 g, 7.5 mmol) were dissolved in toluene/ethanol (1:1, 10 mL), and the resulting pale pink solution was stirred magnetically under N$_2$ for 10 min. A solution of NaBH$_3$CN (1.0 g, 16 mmol) in ethanol (10 mL) was then added dropwise with stirring over a period of 10 min, giving a red-violet solution at the end of the addition. This solution was stirred for 1 h and filtered and the filtrate allowed to stand at room temperature under N$_2$ for 18 h, during which time a wine red crystalline solid was deposited. This solid was separated by filtration, washed with ethanol (~10 mL) and *n*-hexane (~5 mL), and dried under reduced pressure to give the pure complex in ca. 30% yield.

The IR spectrum (Nujol mull) shows $\nu_{\max}$ at 2340 ($\nu_{\mathrm{B-H_t}}$), 2190 ($\nu_{\mathrm{CN}}$), and 1962 ($\nu_{\mathrm{Co-H}}$) cm$^{-1}$ while the solid-state electronic spectrum exhibits maxima at 8333 (broad) and 11 111 (shoulder) cm$^{-1}$. Anal. Calcd for C$_{55}$H$_{49}$BNCoP$_3$: C, 74.50; H, 5.57; N, 1.58. Found: C, 74.60; H, 5.67; N, 1.49.

With use of NaBD$_3$CN and the above synthetic procedure (scaled down), CoD(BD$_3$CN)(PPh$_3$)$_3$ was prepared. The IR spectrum (Nujol mull) of this complex shows $\nu_{\max}$ at 2190 ($\nu_{\mathrm{CN}}$), 1755 ($\nu_{\mathrm{B-D_t}}$), 1680, and 1635 cm$^{-1}$.

**Crystal Growth for X-ray Studies.** While the crystals obtained by the above method were pure, they were not suitable for X-ray studies. Furthermore, attempted simple recrystallization from a variety of solvents such as C$_6$H$_6$, PhMe, THF, CH$_2$Cl$_2$, MeCN, DMF, and Me$_2$SO was unsuccessful because of rapid (10–30 min) decomposition of the complex in these solvents even in the presence of free phosphine. Satisfactory crystals were, however, obtained by carrying out the synthetic procedure outlined above, with all weights and reaction conditions kept the same except that large solvent volumes (1:1 PhMe/EtOH, 40 mL) were used. After the reaction was complete, the mixture was stirred for 1 h before being filtered. The filtrate was kept at ca. 3 °C for 48 h with a slow stream of N$_2$ flowing over the

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Table I. Crystal Data and Intensity Collection

| | |
|---|---|
| mol formula | $C_{55}H_{49}BNCoP_3$ |
| mol wt | 885.7 |
| $a$ | 13.074 (6) Å |
| $b$ | 10.346 (5) Å |
| $c$ | 19.722 (6) Å |
| $\alpha$ | 75.28 (4)° |
| $\beta$ | 78.75 (4)° |
| $\gamma$ | 65.42 (4)° |
| $\rho$(calcd) | 1.260 g $cm^{-3}$ |
| $V$ | 2334.4 $Å^3$ |
| $Z$ | 2 |
| space group | $P\bar{1}$ |
| abs coeff | 5.2 $cm^{-1}$ |
| cryst dimens | 0.3 × 0.2 × 0.2 mm |
| radiation | Mo K$\alpha$ |
| monochromator type | flat graphite |
| take-off angle | 2° |
| data collection method | $\omega$-$2\theta$ scan |
| scan speed | 2° $min^{-1}$ |
| bkgd time | 0.4 × scan time |
| max dev of std | 4.6% |
| $2\theta$ limits | $3° < 2\theta \leqslant 45°$ |
| reflcns measd | $+h,\pm k,\pm l$ |
| no. of reflcns collected | 6136 |
| no. of reflcns used | 3252 |
| $I/\sigma(I)$ | 2.0 |

solution. Large red plate-shaped crystals were deposited together with some blue solid (the subject of a separate investigation). The mixture of solids was separated by repeated decantation with EtOH in which the blue solid forms a suspension while the red plates remain at the bottom of the flask. The red plates so obtained were washed with EtOH (10 mL) and *n*-hexane (5 mL) and dried under reduced pressure. Selected crystals were sealed in Lindemann capillaries (0.3-mm diameter) for the single-crystal X-ray diffraction studies.

**Collection of the X-ray Diffraction Data.** Accurate experimental density data could not be obtained for the crystals of the compound, but the density of the crystal is estimated to be between that of $CH_2Cl_2$ (1.317 g $cm^{-3}$) and water at room temperature. The Laue group and preliminary cell parameters were obtained from precession and cone-axis photographs. A thorough examination of the diffraction patterns and a computer search revealed no higher symmetry. Least-squares cell parameters were determined from the $2\theta$ settings of 100 reflections with $2\theta$ values between 37 and 40°, as measured on a modified Picker diffractometer with Mo K$\alpha_1$ radiation. This instrument was also used to collect intensity data. Further details appear in Table I.

Three reflections were monitored after the measurement of each group of 47 reflections, and no systematic changes in their intensities were observed. The intensities of 6136 independent reflections were measured at 18 ± 2 °C. Crystals of $CoH(BH_3CN)(PPh_3)_3$ do not diffract strongly, and only half the data gave $I > 2.0\sigma(I)$. Structure amplitudes, $|F_o|$, were extracted from the reduced intensities by application of Lorentz and polarization corrections. Absorption was not considered to be important because of the relatively small linear absorption coefficient and the small size of the crystal that was used for data collection. A solution of the structure was attempted, assuming one molecule per asymmetric unit, which fixed the space group as $P\bar{1}$. This choice of space group was confirmed by the successful refinement of the structure.

**Solution and Refinement of the Structure.** The cobalt atom and the three phosphorus atoms were located from an inspection of the Patterson function. The remaining non-hydrogen atoms were found from successive Fourier syntheses. The structure was refined by blocked full-matrix least squares, with use of weights defined as $w = (\sigma^2(F) + 6 \times 10^{-5}|F|^2)^{-1}$ and anisotropic temperature factors. The standard deviation of an individual reflection, $\sigma(F_o)$, was calculated from the counting statistics associated with the measurement of that reflection with an additional contribution determined from the extent to which the scatter of the values of the intensities of the standard reflections exceeded the scatter expected from their own counting statistics. This weighting scheme gave a distribution of $w\Delta^2$ ($\Delta = ||F_o| - |F_c||$), which was nearly a constant function of $|F_o|$. The hydroborate and hydride hydrogen atoms were located from a difference Fourier map. The positions of the 45 phenyl hydrogen atoms were then located with the assumption of $sp^2$ geometry and a C–H separation of 1.0 Å. Further refinement reduced $R_w$ (defined by $R_w = [\sum w\Delta^2/\sum w|F_o|^2]^{1/2}$) to 0.056, using individual isotropic temperature factors for the hydrogen atoms fixed equal to those of associated carbon atoms.

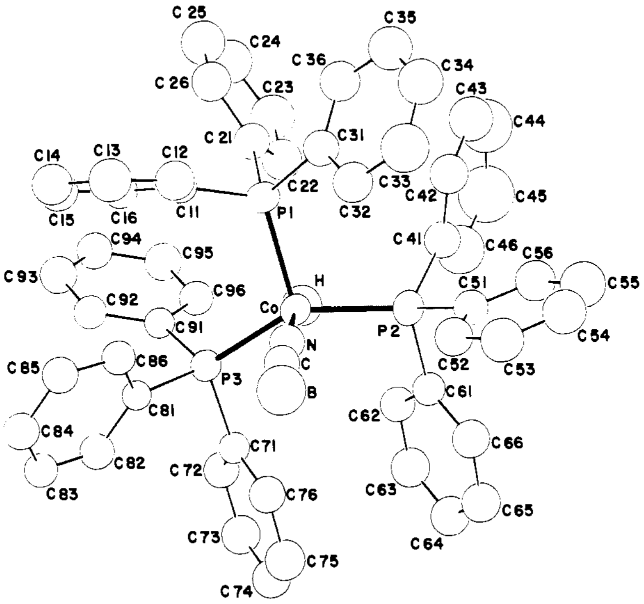

**Figure 1.** Atom labeling and view of the molecule of $CoH(BH_3CN)(PPh_3)_3$. Hydrogen atoms bonded to C and B atoms have been omitted for clarity.

The Co–H distance arrived at in this manner was unusually short, at 1.08 (8) Å. Furthermore, the shifts associated with the hydride ion remained relatively large and erratic, as a result of its high dependence on the positional parameters of the Co atom. The Co–H vector lies primarily along the *b* direction, and the correlation term between the *y* coordinates of the H and Co atoms is 0.25. Therefore, a further examination was made of the appropriate coordinates of the hydride ligand using a procedure suggested by La Placa and Ibers.[10] The hydride ligand was removed from the trial model, and a difference Fourier map was calculated by using only the data with $(\sin\theta)/\lambda < 0.30$ $Å^{-1}$. The maximum electron density (0.42 e $Å^{-3}$) was observed at a point 1.42 Å from the position of the Co atom. The H atom was then placed at that position with the temperature factor assigned as that obtained from the previous least-squares refinement of the position of the H atom. The position and temperature factor of the H atom were fixed, and the parameters of the remaining atoms were varied by blocked full-matrix least squares to convergence. The maximum shift over error ratio was 0.24. The final values of $R_w$, the conventional $R$ factor, and the "goodness-of-fit" (GOF) parameter were 0.056, 0.067, and 1.64, respectively.

Computer programs used in this work were the National Research Council of Canada PDP-8 system of programs[11] and the XRAY system (1976).[12] Final least-squares parameters are listed in Table II. Lists of observed and calculated structure amplitudes and individual anisotropic temperature factors and a stereographic projection are available as supplementary material.

## Results and Discussion

**Crystal and Molecular Structure.** The crystal is composed of discrete molecular units of $CoH(BH_3CN)(PPh_3)_3$. A view of the molecule is given in Figure 1. A selection of bond distances and angles, together with their estimated standard deviations in parentheses, is given in Table III. From Figure 1 it appears that the coordination polyhedron may be described to a first approximation as a distorted trigonal bipyramid (TBP) with triphenylphosphine ligands occupying the three

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**Table II.** Final Atomic Positional Parameters for $CoH(BH_3CN)(PPh_3)_3$

| atom | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$[a] | atom | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$[a] |
|---|---|---|---|---|---|---|---|---|---|
| Co | 0.25509 (9) | 0.10366 (11) | 0.22553 (6) | 3.96 (5) | C91 | 0.0491 (6) | 0.4273 (8) | 0.1542 (4) | 3.7 (2) |
| P1 | 0.1329 (2) | 0.1081 (2) | 0.3263 (1) | 4.46 (12) | C92 | −0.0635 (7) | 0.4778 (9) | 0.1434 (4) | 4.4 (2) |
| P2 | 0.4242 (2) | 0.0527 (2) | 0.2595 (1) | 4.36 (12) | C93 | −0.1402 (7) | 0.6112 (10) | 0.1616 (5) | 5.5 (3) |
| P3 | 0.1525 (2) | 0.2504 (2) | 0.1376 (1) | 3.78 (12) | C94 | −0.1050 (7) | 0.6910 (9) | 0.1881 (4) | 5.2 (3) |
| N | 0.2705 (5) | −0.0744 (7) | 0.2053 (3) | 5.1 (2) | C95 | 0.0064 (8) | 0.6459 (10) | 0.1980 (5) | 5.5 (3) |
| B | 0.3029 (14) | −0.3359 (17) | 0.1771 (8) | 9.9 (5) | C96 | 0.0843 (7) | 0.5111 (9) | 0.1810 (4) | 4.6 (2) |
| C | 0.2803 (7) | −0.1805 (9) | 0.1915 (4) | 5.3 (2) | H1 | 0.257 | 0.242 | 0.221 | 6.6 |
| C11[b] | 0.0042 (6) | 0.0857 (8) | 0.3176 (4) | 4.2 (2) | H2 | 0.274 (6) | −0.391 (8) | 0.231 (4) | 9.9 |
| C12 | −0.0037 (8) | −0.0491 (10) | 0.3322 (5) | 6.2 (3) | H3 | 0.389 (7) | −0.398 (9) | 0.184 (4) | 9.9 |
| C13 | −0.0998 (9) | −0.0614 (11) | 0.3175 (6) | 7.5 (3) | H4 | 0.277 (6) | −0.314 (8) | 0.129 (4) | 9.9 |
| C14 | −0.1880 (8) | 0.0590 (11) | 0.2896 (5) | 6.6 (3) | H12 | 0.052 (6) | −0.128 (7) | 0.357 (3) | 6.2 |
| C15 | −0.1793 (8) | 0.1896 (10) | 0.2747 (5) | 6.3 (3) | H13 | −0.092 (6) | −0.148 (8) | 0.331 (4) | 7.5 |
| C16 | −0.0869 (7) | 0.2061 (9) | 0.2890 (4) | 4.7 (2) | H14 | −0.246 (6) | 0.027 (7) | 0.276 (3) | 6.6 |
| C21 | 0.0735 (7) | 0.2721 (9) | 0.3655 (4) | 5.3 (2) | H15 | −0.235 (6) | 0.276 (7) | 0.251 (3) | 6.3 |
| C22 | 0.1266 (8) | 0.3651 (11) | 0.3484 (5) | 6.5 (3) | H16 | −0.076 (5) | 0.298 (7) | 0.276 (3) | 4.7 |
| C23 | 0.0805 (9) | 0.4964 (12) | 0.3770 (6) | 8.1 (3) | H22 | 0.195 (6) | 0.356 (7) | 0.319 (4) | 6.5 |
| C24 | −0.0193 (10) | 0.5214 (11) | 0.4188 (6) | 7.7 (3) | H23 | 0.145 (7) | 0.516 (8) | 0.362 (4) | 8.1 |
| C25 | −0.0697 (9) | 0.4339 (12) | 0.4371 (5) | 7.8 (3) | H24 | −0.027 (6) | 0.603 (8) | 0.426 (4) | 7.7 |
| C26 | −0.0269 (8) | 0.3040 (10) | 0.4109 (5) | 6.3 (3) | H25 | −0.116 (6) | 0.400 (8) | 0.466 (4) | 7.8 |
| C31 | 0.1929 (7) | −0.3916 (9) | 0.3998 (4) | 5.2 (2) | H26 | −0.053 (6) | 0.224 (7) | 0.429 (3) | 6.3 |
| C32 | 0.2673 (8) | −0.1704 (11) | 0.3846 (5) | 6.4 (3) | H32 | 0.268 (5) | −0.205 (7) | 0.343 (4) | 6.4 |
| C33 | 0.3264 (11) | −0.2874 (13) | 0.4398 (7) | 9.6 (4) | H33 | 0.307 (7) | −0.327 (10) | 0.421 (5) | 9.6 |
| C34 | 0.3051 (9) | −0.2603 (12) | 0.5062 (6) | 8.4 (4) | H34 | 0.355 (6) | −0.341 (8) | 0.537 (4) | 8.4 |
| C35 | 0.2335 (9) | −0.1311 (12) | 0.5217 (6) | 7.8 (3) | H35 | 0.237 (6) | −0.092 (7) | 0.565 (4) | 7.8 |
| C36 | 0.1761 (8) | −0.0193 (10) | 0.4681 (5) | 6.6 (3) | H36 | 0.139 (6) | 0.067 (7) | 0.482 (4) | 6.6 |
| C41 | 0.4265 (7) | 0.1418 (9) | 0.3276 (4) | 5.4 (2) | H42 | 0.383 (5) | 0.007 (7) | 0.409 (3) | 6.1 |
| C42 | 0.3952 (8) | 0.0932 (10) | 0.3968 (5) | 6.1 (3) | H43 | 0.380 (6) | 0.105 (8) | 0.496 (4) | 7.9 |
| C43 | 0.3895 (9) | 0.1588 (12) | 0.4510 (6) | 7.9 (3) | H44 | 0.470 (8) | 0.228 (11) | 0.443 (5) | 11.4 |
| C44 | 0.4118 (10) | 0.2821 (15) | 0.4385 (8) | 11.4 (5) | H45 | 0.386 (8) | 0.380 (11) | 0.365 (6) | 12.9 |
| C45 | 0.4554 (11) | 0.3316 (16) | 0.3685 (9) | 12.9 (5) | H46 | 0.455 (7) | 0.316 (9) | 0.277 (4) | 9.4 |
| C46 | 0.4558 (11) | 0.2595 (13) | 0.3136 (6) | 9.4 (4) | H52 | 0.480 (6) | −0.235 (7) | 0.231 (3) | 5.9 |
| C51 | 0.5240 (7) | −0.1339 (8) | 0.2898 (4) | 4.9 (2) | H53 | 0.583 (6) | −0.427 (8) | 0.257 (4) | 7.7 |
| C52 | 0.5218 (8) | −0.2443 (10) | 0.2656 (5) | 5.9 (3) | H54 | 0.696 (6) | −0.510 (8) | 0.339 (4) | 7.8 |
| C53 | 0.6016 (9) | −0.3912 (12) | 0.2857 (5) | 7.7 (3) | H55 | 0.721 (6) | −0.285 (8) | 0.385 (4) | 8.5 |
| C54 | 0.6767 (9) | −0.4125 (11) | 0.3303 (6) | 7.8 (3) | H56 | 0.605 (6) | −0.081 (7) | 0.351 (3) | 6.6 |
| C55 | 0.6824 (9) | −0.3078 (13) | 0.3536 (6) | 8.5 (4) | H62 | 0.399 (5) | 0.328 (7) | 0.170 (3) | 4.9 |
| C56 | 0.6037 (8) | −0.1623 (10) | 0.3344 (5) | 6.6 (3) | H63 | 0.484 (6) | 0.409 (7) | 0.067 (3) | 6.2 |
| C61 | 0.5054 (6) | 0.1151 (8) | 0.1814 (4) | 4.3 (2) | H64 | 0.650 (6) | 0.244 (7) | 0.012 (4) | 6.3 |
| C62 | 0.4632 (7) | 0.2612 (9) | 0.1476 (4) | 4.9 (2) | H65 | 0.729 (6) | −0.007 (7) | 0.073 (3) | 6.2 |
| C63 | 0.5220 (8) | 0.3084 (10) | 0.0862 (5) | 6.2 (3) | H66 | 0.633 (5) | −0.080 (7) | 0.173 (3) | 5.8 |
| C64 | 0.6169 (8) | 0.2138 (11) | 0.0562 (5) | 6.3 (3) | H72 | 0.176 (5) | 0.510 (7) | 0.047 (3) | 5.0 |
| C65 | 0.6597 (8) | 0.7084 (10) | 0.0879 (10) | 6.2 (3) | H73 | 0.281 (5) | 0.557 (7) | −0.062 (3) | 6.1 |
| C66 | 0.6047 (8) | 0.0208 (10) | 0.1509 (5) | 5.8 (3) | H74 | 0.433 (5) | 0.345 (7) | −0.102 (4) | 6.1 |
| C71 | 0.2468 (6) | 0.2906 (8) | 0.0619 (4) | 3.9 (2) | H75 | 0.450 (6) | 0.116 (7) | −0.034 (4) | 6.6 |
| C72 | 0.2369 (7) | 0.4308 (9) | 0.0269 (5) | 5.0 (2) | H76 | 0.332 (5) | 0.083 (7) | 0.053 (3) | 5.4 |
| C73 | 0.3077 (8) | 0.4525 (10) | −0.0330 (5) | 6.1 (3) | H82 | 0.044 (5) | 0.051 (6) | 0.181 (3) | 4.6 |
| C74 | 0.3865 (8) | 0.3394 (10) | −0.0593 (5) | 6.1 (3) | H83 | −0.085 (5) | −0.005 (7) | 0.135 (3) | 5.3 |
| C75 | 0.4001 (8) | 0.1996 (10) | −0.0275 (5) | 6.6 (3) | H84 | −0.124 (5) | 0.108 (7) | 0.015 (3) | 5.4 |
| C76 | 0.3310 (8) | 0.1743 (9) | 0.0340 (5) | 5.4 (3) | H85 | −0.028 (5) | 0.256 (6) | −0.050 (3) | 4.6 |
| C81 | 0.0708 (6) | 0.1909 (8) | 0.0960 (4) | 3.5 (2) | H86 | 0.085 (5) | 0.309 (7) | 0.002 (3) | 5.0 |
| C82 | 0.0230 (7) | 0.0946 (9) | 0.1351 (4) | 4.6 (2) | H92 | −0.086 (5) | 0.433 (7) | 0.126 (3) | 4.4 |
| C83 | −0.0522 (7) | 0.0652 (9) | 0.1060 (5) | 5.3 (3) | H93 | −0.205 (6) | 0.631 (7) | 0.144 (3) | 5.5 |
| C84 | −0.0757 (7) | 0.1277 (9) | 0.0370 (5) | 5.4 (3) | H94 | −0.152 (5) | 0.773 (7) | 0.207 (3) | 5.2 |
| C85 | −0.0245 (7) | 0.2176 (9) | −0.0025 (4) | 4.6 (2) | H95 | 0.046 (5) | 0.681 (7) | 0.215 (3) | 5.5 |
| C86 | 0.0461 (7) | 0.2496 (9) | 0.0271 (5) | 5.0 (2) | H96 | 0.162 (5) | 0.479 (6) | 0.191 (3) | 4.6 |

[a] $U_{eq}$ and $U_{iso}$ listed have been multiplied by 100 and are in Å². [b] C11 symbolizes carbon 1 of phenyl ring 1, and C21 symbolizes carbon 1 of phenyl ring 2, etc.

equatorial sites and the $BH_3CN$ and hydride ligands occupying axial positions. The hydride ion is effectively shielded from the external molecular environment by the triphenylphosphine ligands. The $BH_3CN^-$ ligand is bonded through the nitrogen atom.

The stereochemistry of five-coordinate compounds with unidentate ligands has recently been reviewed by Kepert.[13] The important five-vertex polyhedra are the aforementioned TBP, with symmetry $D_{3h}$, and the square pyramid (SP), with symmetry $C_{4v}$. In addition to the distortions to the geometry of the TBP and SP which are primarily a mixing of the two geometries, an additional distortion is important in five-coordinate metal hydrides. The hydride ion usually occupies an axial vertex of the TBP. The small radius of the hydride ligand allows a collapse of the equatorial ligands toward it. The resulting polyhedron has symmetry $C_{3v}$ and is referred to in the literature of five-coordinate polyhedra as the monocapped tetrahedron (MT).[14]

The nature of the pathway between two TBP coordinates, via the SP coordination as an intermediate (the Berry rearrangement[15]), has been discussed in detail by Burgi,[16] in terms of the same parameters as those used by Kepert.[13] In order to accommodate the effect of the distortion to the coordination polyhedron generated by the small steric requirements of the

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**Table III.** Important Intramolecular Bond Lengths (Å) and Bond Angles (deg)

| | | | |
|---|---|---|---|
| Co-H | 1.42 | P1-C21 | 1.849 (9) |
| Co-P1 | 2.291 (3) | P1-C31 | 1.836 (8) |
| Co-P2 | 2.245 (3) | P2-C41 | 1.822 (10) |
| Co-P3 | 2.234 (3) | P2-C51 | 1.847 (7) |
| Co-N | 1.904 (8) | P2-C61 | 1.829 (8) |
| N-C | 1.148 (13) | P3-C71 | 1.821 (8) |
| B-C | 1.599 (22) | P3-C81 | 1.827 (10) |
| P1-C11[a] | 1.830 (8) | P3-C91 | 1.832 (7) |
| H-Co-N | 164 | P1-Co-P2 | 106.3 (1) |
| H-Co-P1 | 96 | P2-Co-P3 | 137.1 (1) |
| H-Co-P2 | 76 | P3-Co-P1 | 107.0 (1) |
| H-Co-P3 | 74 | N-Co-P1 | 99.3 (2) |
| N-C-B | 174.8 (9) | N-Co-P2 | 103.4 (2) |
| Co-N-C | 178.4 (7) | N-Co-P3 | 97.1 (2) |
| Co-P1-C11 | 114.5 (3) | C11-P1-C21 | 101.6 (4) |
| Co-P1-C21 | 118.7 (3) | C21-P1-C31 | 103.7 (4) |
| Co-P1-C31 | 113.6 (3) | C31-P1-C11 | 102.8 (4) |
| Co-P2-C41 | 117.4 (3) | C41-P2-C51 | 100.8 (4) |
| Co-P2-C51 | 123.1 (4) | C51-P2-C61 | 101.9 (3) |
| Co-P2-C61 | 105.9 (3) | C61-P2-C41 | 105.6 (4) |
| Co-P3-C71 | 109.0 (2) | C71-P3-C81 | 100.2 (4) |
| Co-P3-C81 | 121.3 (2) | C81-P3-C91 | 102.1 (4) |
| Co-P3-C91 | 116.8 (3) | C91-P3-C71 | 105.2 (3) |

[a] C11 symbolizes carbon 1 of phenyl ring 1, and C21 symbolizes carbon 1 of phenyl ring 2, etc.

**Table IV.** Geometrical Angles for Five-Vertex Polytopes and $CoH(BH_3CH)(PPh_3)_3$ (Based on Constant Radii)

| | edge dihedral angles, deg | | | |
|---|---|---|---|---|
| | TBP | SP | MT | obsd |
| $P_2$-$P_3$ | 53.1 | 0.0 | 54.7 | 19.1 |
| $P_1$-$P_2$ | 53.1 | 75.7 | 54.7 | 71.4 |
| $P_1$-$P_3$ | 53.1 | 75.7 | 54.7 | 65.9 |
| N-$P_1$ | 101.5 | 75.7 | 109.5 | 94.6 |
| N-$P_2$ | 101.5 | 119.8 | 109.5 | 111.4 |
| N-$P_3$ | 101.5 | 119.8 | 109.5 | 113.8 |
| H-$P_1$ | 101.5 | 75.7 | 90.0 | 73 |
| H-$P_2$ | 101.5 | 119.8 | 90.0 | 112 |
| H-$P_3$ | 101.5 | 119.8 | 90.0 | 114 |

hydride ion, in our considerations of the TBP and SP character of the five-coordinate polyhedron, we will use the parameters first suggested by Porai-Koshits and Aslanov.[17] These are the family of dihedral angles, $\delta$, formed at each edge of the polyhedron. The $\delta$ parameters for the TBP and SP have been given by Muetterties and Guggenberger.[18] In order to focus on the symmetry of stellation about the central ion, all vertices may be assigned equal radii before calculating the $\delta$ parameters.

Table IV contains the $\delta$ parameters for $CoH(BH_3CN)(PPh_3)_3$ and the relevant idealized polyhedra, calculated at constant radii.[19] The collapse of the equatorial ligands toward the hydride ion leads to an average $\delta$ value for the N–P edges of 106.6° and 100° for the H–P edges, as opposed to 101.5 and 105.1° for the same edges in the TBP and SP, respectively. The $\delta$ of 19.1° for the $P_2$–$P_3$ edge and the division of the groups of N–P and H–P edges each into two large $\delta$ values and one small $\delta$ value clearly indicate that the polyhedron has more SP than TBP character.

The crystallography of transition-metal hydride complexes has been extensively reviewed by Teller and Bau.[20] Rossi and Hoffmann[21] have predicted that $d^7$ ions such as Co(II) should not show a strong preference for either the $D_{3h}$ symmetry of the TBP or the $C_{4v}$ symmetry of the SP. Analysis of the five-coordinate cobalt hydride complexes listed by Teller and Bau[20] (most of which involve Co(I)), using the $\delta$ parameters, shows that the full range of polyhedra from the TBP to the SP are possible. For instance, $CoH(N_2)(PPh_3)_3$[21] is chemically similar to the compound discussed here. Nevertheless, its coordination polyhedron approximates closely to the TBP with the characteristic effects of the hydride ions clearly present. The reason for the large differences between the stereochemistry of these two chemically similar compounds is not clear.

**Molecular Geometry.** The original position found for the hydride ion by least squares was unusually short. The reported coordinates are those found from the difference map. The two positions are essentially along the same radius vector from the Co(II) ion, and the foregoing analysis of the geometry of the polyhedron around the Co(II) ion would be unchanged if the least-squares position were chosen. The shortest known Co–H distance of 1.34 (8) Å occurs in $CoH(BH_4)(PCy_3)_2$, which is also the only other Co(II) hydride for which the structure has been determined.[5] Our results suggest that all Co–H distances determined from X-ray data may be unrealistically short, although the present case may be unique for reasons unknown. Neutron diffraction data might resolve the ambiguity.

The unique nature of the triphenylphosphine ligand containing P1 as the unique vertex associated with the SP geometry is also manifested by its unique bond length to Co(II), which is 0.051 Å longer than the average of the [P2–Co] and [P3–Co] distances. Rossi and Hoffmann[21] have predicted that for the SP with a $d^7$ central ion the basal bonds should be stronger.

**Infrared and Magnetic Studies.** On the basis of previous X-ray work,[7-9] Lippard et al. have shown how small variations in the infrared spectra of cyanotrihydroborate complexes in the B–H stretching region may be used to differentiate between N-coordinated monodentate ($\nu_{B-H_t}$ = 2320–2350 $cm^{-1}$) and bridging ($\nu_{B-H_t}$ = ca. 2380 $cm^{-1}$) $BH_3CN^-$ groups. The terminal $\nu_{B-H}$ mode occurs in the spectrum of $CoH(BH_3CN)(PPh_3)_3$ at 2340 $cm^{-1}$, which is within the range previously suggested [7-9] for monodentate N-coordination, and this vibration shifts to 1755 $cm^{-1}$ ($\nu_{B-H}/\nu_{B-D}$ = 0.75 compared with a calculated value of 0.736 based upon $^{11}B$) upon formation of $CoD(BD_3CN)(PPh_3)_3$. These data therefore reinforce Lippard's infrared criteria for distinguishing between these two bonding modes. This has very recently[23] become of some considerable importance since it now appears, from infrared data, that multiple bridging by $BH_3CN^-$, at least for binuclear Ni(II), is relatively common. Two additional peaks appear at 1680 and 1635 $cm^{-1}$ in the spectrum of $CoD(BD_3CN)(PPh_3)_3$, and similar peaks have been observed[8] in this region for related $Cu-BD_3CN$ systems.

One other point that should be discussed briefly concerns correlations between C≡N infrared stretching frequencies and the geometry of the $M—N≡CBH_3$ linkage in monodentate cyanotrihydroborate complexes. Infrared spectra of such complexes generally show[9] an increase in $\nu_{CN}$ of up to 30 $cm^{-1}$ from the value of 2179 $cm^{-1}$ observed in the spectrum of $NaBH_3CN$. This has been explained[9] in terms of some rehybridization about the N atom leading to an increased CN force constant. X-ray structural studies[9] have identified both linear and nonlinear M–N–C units using essentially sp orbitals (shorter C≡N bond) in the former while some $sp^2$ character (longer C≡N bond) would be present in the latter. For example, the structure of $Cu(BH_3CN)_2(Me_5dien)$ shows two different $BH_3CN$ groups.[9] The $\nu_{CN}$ with the smallest shift (13

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$cm^{-1}$) was assigned to the more strongly bound $BH_3CN^-$ group (i.e. the shorter Cu–N bond), which has a nonlinear Cu–N–C unit (with the longer of the two C–N bonds). The $\nu_{CN}$ with the larger shift (31 $cm^{-1}$) was assigned to the more weakly bound $BH_3CN^-$, which contains a linear Cu–N–C unit.

In $CoH(BH_3CN)(PPh_3)_3$, the Co–N–C unit is linear, the Co–N bond length is shorter than either of the two Cu–N bond lengths in the above-mentioned Cu compound, and the C–N bond is longer than in most other coordinated or uncoordinated –C≡N linkages.[9] It is difficult, therefore, to account for a shift in $\nu_{CN}$ of only 11 $cm^{-1}$ in the spectrum of this cobalt complex, and clearly, correlations between $\nu_{CN}$ and such features as the M–N–C angle and the M–N bond strength in $M{-}NCBH_3$ complexes should be made with caution.

No solution spectroscopic or magnetic studies could be carried out for $CoH(BH_3CN)(PPh_3)_3$ because of its very rapid decomposition in most solvents, even at −70 °C. However, in the solid state, the complex contains low-spin Co(II) ($\mu_{eff} = 1.9\ \mu_B$), as does the related[5] $CoH(BH_4)(PCy_3)_2$ previously mentioned, and this is consistent with a strong interaction between the Co and H atoms.

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**Registry No.** $CoH(BH_3CN)(PPh_3)_3$, 90605-24-6.

**Supplementary Material Available:** Table A, observed and calculated structure amplitudes, Table B, anisotropic temperature factors, and a stereoscopic view of the molecule $CoH(BH_3CN)(PPh_3)_3$ (15 pages). Ordering information is given on any current masthead page.

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# Two-Dimensional Short-Range Order in the Crystal Structure of (Tetraphenylporphinato)iron(III) 2,3,5,6-Tetrafluorobenzenethiolate. Analysis of the X-ray Diffuse Scattering and a Simulation of Crystal Growth

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The five-coordinate iron porphyrin complex (tetraphenylporphinato)iron(III) 2,3,5,6-tetrafluorobenzenethiolate, $Fe(TPP)(SC_6HF_4)$, crystallizes in the monoclinic space group $P2_1/a$ with $a = 13.272$ (4) Å, $b = 12.685$ (6) Å, $c = 22.46$ (1) Å, $\beta = 97.17$ (3)°, and $Z = 4$. The iron atom is displaced 0.395 (3) Å from the plane of the four nitrogen atoms, and the Fe–S distance is 2.298 (3) Å. The $hkl$, $k + l = 2n + 1$, reflections are observed to be diffuse. The diffuse intensity is in the form of circular disks perpendicular to the $a^*$ axis, indicating a lack of long-range order in the **b** and **c** directions. The specific nature of the disorder has been deduced, and potential mechanisms for its introduction have been examined in two-dimensional simulations of the crystal growth.

Recent investigations in this laboratory have focused on sulfur-ligated ferric porphyrin complexes. Single-crystal ESR and X-ray techniques have been used to characterize the electronic structure of these species and to provide quantitative descriptions of the axial ligand binding.[1-3] A series of isomorphous thiol/thiolate complexes displaying spin-state and structural equilibria in the solid state has been prepared. In this series, the free energy change associated with a structural transformation is strongly influenced by the $\sigma$-donor strength of the axial ligand. In an effort to extend the range of $\sigma$-donor strengths examined, syntheses of (tetraphenylporphinato)iron(III) complexes with the axial ligand 2,3,5,6-tetrafluorobenzenethiol have been undertaken. Isolated in the course of these syntheses was the five-coördinate thiolate complex $Fe(TPP)(SC_6HF_4)$ (I),[4] which is the subject of this report. Crystals of this material exhibit a relatively unusual kind of two-dimensional short-range order, the nature of which has been deduced from the observed diffuse scattering. The disorder in this structure has been mimicked in a two-dimensional simulation of the crystal growth.

Table I. Crystallographic Data

| | |
|---|---|
| formula | $FeSN_4C_{56}H_{31}F_4$ |
| cryst dimens, mm | 0.15 × 0.20 × 0.35 |
| space group | $P2_1/a$ |
| $Z$ | 4 |
| $a$, Å | 13.272 (4) |
| $b$, Å | 12.685 (6) |
| $c$, Å | 22.46 (1) |
| $\beta$, deg | 97.17 (3) |
| vol, $Å^3$ | 3752 (3) |
| density (calcd), $g/cm^3$ | 1.50 |
| radiation, Å | Mo Kα (0.7107), cryst monochromatized |
| temp, K | 117 |
| scan range | 1° < $K\alpha_1$ to 1° > $K\alpha_2$ |
| scan rate, deg/min | 2.0 |
| scan mode | $\theta/2\theta$ |
| $2\theta$ max, deg | 45 |
| unique data | 5453 |
| reflctns ($I > 3\sigma(I)$) | 1554 ($k + l = 2n$, only) |
| $\mu$, $cm^{-1}$ | 5.157 |
| transmission factors | 0.82–0.94 |
| data collcd | $+h,+k,\pm l$ |
| $R$ | 0.078 |
| $R_w$ | 0.088 |
| erf | 2.25 |
| no. of params refined | 159 |

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(4) Abbreviations used: TPP, tetraphenylporphyrin dianion; $SC_6HF_4$, 2,3,5,6-tetrafluorobenzenethiolate; PPIXDME, protoporphyrin IX dimethyl ester dianion; $SC_6H_4$-$p$-$NO_2$, $p$-nitrobenzenethiolate.

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