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## Complexes of Cobalt, Nickel, and Copper with the Tripod Ligand 1,1,1-Tris(diphenylphosphinomethyl)ethane ( $p_3$ ). Crystal Structures of the $[\text{Co}(p_3)(\text{BH}_4)]$ and $[\text{Ni}(p_3)(\text{SO}_2)]$ Complexes

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The 3d metal complexes  $[\text{Co}(p_3)(\text{BH}_4)]$ ,  $[\text{Cu}(p_3)(\text{BH}_4)]$ ,  $[\text{Co}(p_3)(\text{NO})]$ ,  $[\text{Ni}(p_3)(\text{SO}_2)]$ , and  $[\text{Ni}(p_3)(\text{CS}_2)]$  of the potentially tridentate tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane,  $p_3$ , have been prepared and characterized. The complexes are all isomorphous. The complexes  $[\text{Co}(p_3)(\text{BH}_4)]$  and  $[\text{Ni}(p_3)(\text{SO}_2)]$  have been characterized by complete x-ray structure analyses. These compounds are orthorhombic, space group  $Pn2_1a$ , with  $a = 20.530$  (6),  $b = 17.120$  (5),  $c = 10.316$  (3) Å (cobalt) and  $a = 20.451$  (5),  $b = 17.349$  (4),  $c = 10.246$  (3) Å (nickel). In both cases the ligand is found to be tridentate. The cobalt atom is bonded to the  $\text{BH}_4$  group via two bridging hydrogen atoms. An analogous structure is assigned to the compound  $[\text{Cu}(p_3)(\text{BH}_4)]$ . In the  $[\text{Ni}(p_3)(\text{SO}_2)]$  complex the nickel atom is bonded to the sulfur atom of the  $\text{SO}_2$  molecule, with which it is coplanar. A similar pseudotetrahedral structure is attributed to the complexes  $[\text{Co}(p_3)(\text{NO})]$  and  $[\text{Ni}(p_3)(\text{CS}_2)]$ , the latter containing a  $\pi$ -coordinated  $\text{CS}_2$  group.

### Introduction

The capacity of the potentially tridentate tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane,  $p_3$ , to form stable complexes with 3d metals in low oxidation states has been clearly demonstrated.<sup>1-4</sup> In particular it has been shown to stabilize the +1 oxidation state of both cobalt and nickel. In some cases, e.g. in the formation of the complexes  $[\text{M}(p_3)\text{I}]$  ( $\text{M} = \text{Co}, \text{Ni}$ ), reduction of the metal from the +2 state occurs without the use of obvious reducing agents.<sup>2</sup> What is more, the use of the reducing agent  $\text{NaBH}_4$  leads to different reactions. Thus we find (a) with cobalt(II) and nickel(II) halides the corresponding tetracoordinated halide complexes  $[\text{M}(p_3)\text{X}]$  ( $\text{X} = \text{Cl}, \text{Br}$ )<sup>2</sup> are formed, while (b) with iron(II) and cobalt(II) salts in the presence of poorly coordinating anions such as tetrafluoroborate or tetraphenylborate dimeric bioctahedral hydride complexes of formula  $[(p_3)\text{M}(\mu\text{-H}_3)\text{M}(p_3)]^+$  ( $\text{M} = \text{Fe}, \text{Co}$ ) are formed.<sup>4</sup>

We now find that under suitable conditions sodium tetrahydroborate gives the metal tetrahydroborates  $[\text{M}(p_3)(\text{BH}_4)]$  ( $\text{M} = \text{Co}, \text{Cu}$ ). Furthermore the neutral ligands  $\text{NO}$  and  $\text{SO}_2$  reacting respectively with cobalt(II) and nickel(II) salts of poorly coordinating anions and in the presence of  $p_3$  bind to the  $\text{M}(p_3)$  moiety to give the compounds  $[\text{Co}(p_3)(\text{NO})]$  and  $[\text{Ni}(p_3)(\text{SO}_2)]$ . Finally carbon disulfide is found to react with the compound  $[\text{Ni}(p_3)_2]$  to give the complex  $[\text{Ni}(p_3)(\text{CS}_2)]$ .

X-ray analysis shows that all five complexes are isomorphous, the unit cell parameters being very similar and also very close to those found previously for the pseudotetrahedral iodide compound  $[\text{Ni}(p_3)\text{I}]$ .<sup>3</sup> This shows clearly that the steric requirements of the moiety  $\text{M}(p_3)$  determine both the structure and the packing of these complexes regardless of the chemical nature and hindrance of the other ligand.

All of the compounds have been characterized using standard physical methods. The structures of the complexes  $[\text{Co}(p_3)(\text{BH}_4)]$  and  $[\text{Ni}(p_3)(\text{SO}_2)]$  have been determined by x-ray methods.

### Experimental Section

**Reagents.** All solvents were of reagent grade quality and were used without further purification. The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane,<sup>5</sup>  $p_3$ , and the complexes  $[\text{Ni}(p_3)_2]$ <sup>1</sup> and  $[\text{Cu}(p_3)\text{Cl}]$ <sup>2</sup> were prepared by methods previously described.

**Preparation of the Complexes.** All of the reactions were carried out under dry nitrogen, using deoxygenated solvents. The solid complexes were collected on a sintered-glass frit and dried in a stream of nitrogen.

**$[\text{Co}(p_3)(\text{BH}_4)]$ .**  $\text{Co}(\text{H}_2\text{O})_6(\text{BF}_4)_2$  (1 mmol), in 10 ml of ethanol, was added at room temperature to 1 mmol of  $p_3$  in 10 ml of THF. Sodium borohydride (2.5 mmol in 10 ml of ethanol) was added slowly,

with stirring, to the resulting solution. The green crystals that precipitated after about 10 min were washed with ethanol and petroleum ether. The product was recrystallized from DMF-1-butanol.

**$[\text{Cu}(p_3)(\text{BH}_4)]$ .**  $\text{NaBH}_4$  (1.5 mmol) in ethanol (10 ml) was added, at room temperature, to a solution of  $[\text{Cu}(p_3)\text{Cl}]$  (1 mmol) in methylene chloride (15 ml). The resulting solution, after filtration, was concentrated in a stream of cold nitrogen and white crystals quickly appeared. These were washed with ethanol and petroleum ether.

**$[\text{Co}(p_3)(\text{NO})]$ .**  $\text{Co}(\text{H}_2\text{O})_6(\text{BF}_4)_2$  (1 mmol in 10 ml of ethanol) was added to a solution of  $p_3$  (1 mmol in 40 ml of methylene chloride) and nitric oxide was bubbled through the solution until the color turned dark-brown (about 10 min). Concentration at room temperature led to precipitation of dark-brown crystals which were washed with ethanol and then petroleum ether.

**$[\text{Ni}(p_3)(\text{SO}_2)]$ .** **Method I.**  $\text{Ni}(\text{H}_2\text{O})_6(\text{BF}_4)_2$  (1 mmol in 10 ml of ethanol) was added to a solution of  $p_3$  (1 mmol in 30 ml of acetone). Sulfur dioxide was bubbled into this solution, held at 0 °C, until the color changed from orange to dark brown (about 5 min). Concentration of the solution under nitrogen at room temperature led to the precipitation of dark brown crystals which were washed with ethanol and petroleum ether.

**Method II.** A 1-mmol sample of  $[\text{Ni}(p_3)_2]$  was dissolved in 30 ml of methylene chloride and sulfur dioxide was bubbled through the solution until the color changed from yellow to dark brown. After dilution with ethanol (30 ml) and concentration, crystals precipitated and were washed as above.

**$[\text{Ni}(p_3)(\text{CS}_2)]$ .** A 20-ml portion of carbon disulfide was added at room temperature to a suspension of 1 mmol of  $[\text{Ni}(p_3)_2]$  in 20 ml of ethanol. Concentration of the resulting dark brown solution led to the precipitation of dark brown crystals which were washed with ethanol and petroleum ether.

**$[\text{Co}(p_3)(\text{BD}_4)]$ .** This compound was prepared in the same way as the corresponding proton-containing complex but by using  $\text{NaBD}_4$  and deuterated solvents.

The analytical data for the complexes are listed in Table I.

**Physical Measurements.** The methods used for the magnetic and molar conductance measurements and the recording of the infrared and uv-visible spectra have been described previously.<sup>6</sup>

**Collection and Reduction of the X-Ray Intensity Data.** The crystals of both complexes,  $[\text{Co}(p_3)(\text{BH}_4)]$  (I) and  $[\text{Ni}(p_3)(\text{SO}_2)]$  (II), are unstable in air and were sealed in glass capillaries to prevent decomposition.

Unit cell parameters for each complex were determined by carefully measuring the setting angles of 25 reflections at room temperature (about 22 °C) on a Philips PW 1100 diffractometer. Details of crystal data and data collection for the two compounds are given in Table II. After correction for background, the standard deviation  $\sigma(I)$  of the intensity,  $I$ , of a reflection was calculated as described elsewhere,<sup>7</sup> using values of the instability factor,  $k$ , of 0.02 and 0.03 for complexes I and II, respectively. The observed intensities were corrected for Lorentz and polarization effects. An absorption correction based upon numerical method was applied using Hamilton's GONO9 program.<sup>8</sup> The transmission coefficients were found to range from 0.90 to 0.98 for complex I and from 0.70 to 0.80 for complex II.

Table I. Analytical and Magnetic Data for the Complexes

Compd	Color	% calcd			% found			$\mu_{\text{eff}}$ , $\mu_B$ (293 K)
		C	H	M	C	H	M	
[Co(p <sub>3</sub> )(BH <sub>4</sub> )]	Green	70.49	6.22	8.44	69.52	6.21	8.27	3.1
[Co(p <sub>3</sub> )(NO)] <sup>a</sup>	Orange	68.98	5.51	8.26	69.22	5.76	8.25	Diam
[Ni(p <sub>3</sub> )(SO <sub>2</sub> )] <sup>b</sup>	Dark brown	65.87	5.26	7.86	66.27	5.31	7.41	Diam
[Ni(p <sub>3</sub> )(CS <sub>2</sub> )] <sup>c</sup>	Dark brown	66.41	5.18	7.73	65.85	5.38	7.34	Diam
[Cu(p <sub>3</sub> )(BH <sub>4</sub> )]	White	70	6.15	9.04	69.83	6.10	8.62	Diam

<sup>a</sup> Calcd: N, 1.96. Found: N, 2.05. <sup>b</sup> Calcd: S, 4.28. Found: S, 4.25. <sup>c</sup> Calcd: S, 8.45. Found: S, 8.04.

Table II. Crystal Data and Data Collection Details

	[Co(p <sub>3</sub> )(BH <sub>4</sub> )]	[Ni(p <sub>3</sub> )(SO <sub>2</sub> )]
Molecular formula	C <sub>41</sub> H <sub>23</sub> CoP <sub>3</sub> B	C <sub>41</sub> H <sub>23</sub> O <sub>2</sub> NiSP <sub>3</sub>
Mol wt	698.1	747.5
<i>a</i> , Å	20.530 (6)	20.451 (5)
<i>b</i> , Å	17.120 (5)	17.349 (4)
<i>c</i> , Å	10.316 (3)	10.246 (3)
<i>d</i> <sub>obsd</sub> (by flot), g cm <sup>-3</sup>	1.29	1.37
<i>d</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.28	1.36
<i>U</i> , Å <sup>3</sup>	3625.8	3635.3
<i>Z</i>	4	4
Space group	<i>Pn</i> 2 <sub>1</sub> <i>a</i>	<i>Pn</i> 2 <sub>1</sub> <i>a</i>
Abs coeff (Mo K $\alpha$ ), cm <sup>-1</sup>	6.14	7.54
Color	Green	Dark brown
Habit	Parallelepiped	Parallelepiped
Dimensions, mm	0.05 × 0.20 × 0.40	0.10 × 0.30 × 0.60
Diffractometer	Philips PW 1100	Philips PW 1100
$\lambda$ (Mo K $\alpha$ ), Å	0.7107	0.7107
Monochromator	Flat graphite crystal	Flat graphite crystal
Attenuator	Not used	Not used
Takeoff angle, deg	2	2
Method	$\omega$ -2 $\theta$ scan	$\omega$ -2 $\theta$ scan
Scan speed	0.07°/s in a range of 1° across the peak	0.07°/s in a range of 0.7° across the peak
Background time	7 s on each side of the peak	5 s on each side of the peak
Standards	3 every 100 readings	3 every 200 readings
Max dev of standards	5%	6%
2 $\theta$ limit	6° < 2 $\theta$ < 40°	4° < 2 $\theta$ < 46°
No. of total data	1956	2635
No. of data used in the calculations	1013 ( <i>I</i> > 2 $\sigma$ )	2133 ( <i>I</i> > 3 $\sigma$ )

Atomic scattering factors for Co, Ni, S, P, O, B, and C and those for hydrogen atoms were taken from ref 9 and 10, respectively. Corrections for anomalous dispersion effects for cobalt, nickel, sulfur, and phosphorus atoms were applied in the refinement stage.<sup>11</sup> The application of the  $\Delta F''$  corrections allowed the determination of the absolute structures. In fact, owing to the polar nature of the space group *Pn*2<sub>1</sub>*a*, two possible orientations of the structure for both complexes must be considered: the *x, y, z* structure and the inverted *x,  $\bar{y}, z$* .

**Solution and Refinement of the Structures.** On the assumption that the two complexes are nearly isomorphous with the [Ni(p<sub>3</sub>)I] compound,<sup>3</sup> the same acentric *Pn*2<sub>1</sub>*a* space group was assigned. The final parameters from the [Ni(p<sub>3</sub>)I] structure were taken as the starting values for the solution of the structures of [Co(p<sub>3</sub>)(BH<sub>4</sub>)] and [Ni(p<sub>3</sub>)(SO<sub>2</sub>)].  $\Delta F$  Fourier syntheses, calculated with these parameters, showed the position of the boron atom for complex I and of the sulfur and oxygen atoms for complex II. Refinements were performed by use of the full-matrix least-squares method of Busing and Levy as adapted by Stewart.<sup>12</sup> The minimized function was  $\sum w(|F_o| - |F_c|)^2$ , in which *w* is the weight assigned to the *F<sub>o</sub>* values, according to the expression  $w = 1/\sigma^2(F_o)$ .

**[Co(p<sub>3</sub>)(BH<sub>4</sub>)]**. Two cycles of refinement with individual isotropic temperature factors for all of the atoms reduced *R* to 0.09. The hydrogen atoms of the p<sub>3</sub> ligand were introduced in calculated positions (C-H = 0.9 Å). The hydrogen atoms of the methyl group were

introduced according to a "staggered" configuration. A  $\Delta F$  synthesis carried out at this stage revealed the positions of the four hydrogen atoms of the BH<sub>4</sub> group. The heights of these peaks range between 0.3 and 0.4 e/Å<sup>3</sup>. These peaks were more in evidence when the  $\Delta F$  Fourier synthesis used only the reflections having  $(\sin \theta)/\lambda \leq 0.30$  Å<sup>-1</sup>. Two of these hydrogen atoms are linked to the cobalt atom. Refinement was then continued using anisotropic temperature factors for cobalt and phosphorus atoms and isotropic factors for the carbon and boron atoms. The hydrogen atom positions were not refined at this stage (an overall *B* of 5 Å<sup>2</sup> was used). At this point the absolute structure was determined on the following basis: two mixed cycles on the two possible configurations, the second being obtained by changing the sign of the *y* coordinate of all the atoms, gave *R* values of 6.6 (for *x, y, z*) and 6.7 (for *x,  $\bar{y}, z$ )* respectively. Hamilton's test,<sup>13</sup> together with an analysis of the standard deviations of the parameters, confirmed that the *x, y, z* structure was the correct one.

At this point two refinement cycles, in which the four hydrogen atoms of the BH<sub>4</sub> group were also allowed to vary, were executed. The positional and thermal parameters of these hydrogen atoms converged to realistic values. It is interesting to note that the thermal parameters of the two hydrogen atoms linked to the metal atom assumed values very much lower than those of the other two hydrogen atoms.

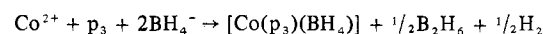
The final conventional *R* factor, obtained after this refinement, is again 0.066, while the *R*<sub>2</sub> factor, defined as  $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , is 0.046. The final values of the parameters and their standard deviations are reported in Tables III and IV.

**[Ni(p<sub>3</sub>)(SO<sub>2</sub>)]**. Least-squares refinement of the positional and thermal isotropic parameters of all atoms except hydrogen converged to a discrepancy factor of 0.08. Least-squares refinement was then continued with anisotropic temperature factors for atoms heavier than carbon. Hydrogen atoms were introduced in their calculated positions (C-H = 1.0 Å), with *B* = 5.0 Å<sup>2</sup> in the last set of cycles, and were not refined. A difference Fourier synthesis carried out at this point showed no particular features, except a few peaks of height 0.4 e/Å<sup>3</sup> close to the oxygen positions. This observation can be suggestive of some inadequacy of the simple anisotropic model used in the refinement to fully describe the electron density distribution. The absolute configuration of the structure was determined by applying the anomalous dispersion corrections, and for two possible structures *x, y, z* and *x,  $\bar{y}, z$*  gave *R* values of 0.053 and 0.057, respectively. The analysis of the standard deviations which are lower in the structure *x, y, z* confirmed that this structure is the correct one. The final conventional *R* factor is 0.053 and the weighted *R* factor is 0.047.

Lists of the atomic positional and thermal parameters together with their estimated standard deviations are given in Tables V and VI. Lists of observed and calculated structure factors of both complexes are available as supplementary material.

## Results and Discussion

The reactions which lead to the formation of [Co(p<sub>3</sub>)(BH<sub>4</sub>)], [Co(p<sub>3</sub>)(NO)], and [Ni(p<sub>3</sub>)(SO<sub>2</sub>)] involve the reduction of the bivalent cobalt and nickel ions. In the case of the tetrahydroborate complex a scheme of the present type can be proposed



In the reactions leading to the nitrosyl and sulfur dioxide complexes the potential reducing agents are NO, SO<sub>2</sub>, and p<sub>3</sub>. This last ligand, which has been previously found engaged in the reduction of cobalt(II) and nickel(II) to the oxidation state +1,<sup>2</sup> can both induce the reduction of the metal with the

**Table III.** [Co(p<sub>3</sub>)(BH<sub>4</sub>)] Positional Parameters (×10<sup>4</sup>) and Isotropic Temperature Factors with Estimated Standard Deviations in Parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (×10 <sup>3</sup> ), Å <sup>2</sup>
Co	-684 (1)	-1321 <sup>a</sup>	735 (2)	<i>b</i>
P(1)	378 (2)	-1266 (4)	1309 (5)	<i>b</i>
P(2)	-593 (3)	-137 (3)	-183 (5)	<i>b</i>
P(3)	-990 (2)	-830 (3)	2660 (5)	<i>b</i>
C(1)	358 (9)	992 (10)	2876 (19)	49 (7)
C(2)	42 (8)	265 (10)	2239 (18)	28 (5)
C(3)	588 (10)	-269 (11)	1718 (18)	44 (6)
C(4)	-418 (8)	560 (10)	1091 (17)	38 (6)
C(5)	-352 (8)	-180 (11)	3261 (19)	43 (6)
C(6)	646 (12)	-1851 (12)	2738 (20)	59 (6)
C(7)	1228 (12)	-1702 (13)	3313 (25)	87 (9)
C(8)	1427 (12)	-2130 (17)	4367 (27)	98 (9)
C(9)	1047 (12)	-2786 (14)	4721 (22)	72 (8)
C(10)	491 (12)	-2966 (12)	4158 (26)	74 (8)
C(11)	266 (11)	-2496 (13)	3142 (22)	65 (7)
C(12)	993 (9)	-1584 (11)	162 (19)	42 (6)
C(13)	1612 (9)	-1249 (14)	63 (18)	52 (6)
C(14)	2076 (9)	-1499 (12)	-801 (21)	58 (7)
C(15)	1914 (10)	-2098 (12)	-1644 (20)	56 (7)
C(16)	1290 (11)	-2429 (12)	-1635 (22)	62 (7)
C(17)	856 (9)	-2160 (11)	-692 (22)	55 (7)
C(18)	36 (8)	-40 (11)	-1408 (18)	39 (6)
C(19)	391 (9)	667 (12)	-1613 (19)	52 (6)
C(20)	846 (12)	737 (14)	-2605 (24)	86 (8)
C(21)	932 (10)	100 (14)	-3428 (21)	69 (8)
C(22)	611 (12)	-582 (13)	-3236 (23)	82 (8)
C(23)	173 (9)	-623 (11)	-2253 (22)	50 (6)
C(24)	-1259 (9)	296 (11)	-1032 (18)	38 (6)
C(25)	-1337 (10)	1143 (11)	-1045 (19)	47 (6)
C(26)	-1826 (11)	1460 (12)	-1781 (22)	53 (7)
C(27)	-2293 (12)	1028 (15)	-2304 (26)	88 (9)
C(28)	-2237 (11)	253 (12)	-2337 (22)	57 (7)
C(29)	-1749 (10)	-115 (12)	-1606 (20)	47 (6)
C(30)	-1150 (8)	-1509 (11)	4007 (17)	45 (6)
C(31)	-931 (8)	-1403 (14)	5234 (18)	46 (6)
C(32)	-1055 (10)	-1922 (12)	6190 (20)	59 (7)
C(33)	-1417 (9)	-2557 (11)	5955 (19)	38 (6)
C(34)	-1629 (10)	-2699 (12)	4737 (23)	56 (7)
C(35)	-1476 (10)	-2172 (13)	3749 (21)	58 (7)
C(36)	-1735 (8)	-212 (10)	2793 (17)	34 (6)
C(37)	-1841 (10)	172 (11)	3908 (21)	50 (7)
C(38)	-2378 (10)	689 (12)	3987 (20)	54 (6)
C(39)	-2803 (10)	752 (12)	2912 (20)	47 (6)
C(40)	-2676 (11)	340 (13)	1823 (23)	75 (8)
C(41)	-2140 (8)	-157 (10)	1721 (19)	51 (6)
B	-1202 (14)	-2347 (16)	-61 (28)	59 (9)
H(1) <sup>c</sup>	-95 (7)	-215 (9)	102 (16)	83 (32)
H(2)	-123 (7)	-154 (10)	-7 (15)	85 (34)
H(3)	-56 (8)	-278 (9)	-64 (18)	148 (36)
H(4)	-179 (9)	-262 (9)	49 (18)	149 (38)

<sup>a</sup> This value was chosen to have accordance with the *y* coordinate of the [Ni(p<sub>3</sub>)I] complex. <sup>b</sup> These atoms were refined anisotropically. <sup>c</sup> The hydrogen positional parameters are multiplied by 10<sup>3</sup>.

**Table IV.** [Co(p<sub>3</sub>)(BH<sub>4</sub>)] Anisotropic Thermal Parameters<sup>a</sup> (×10<sup>3</sup>, Å<sup>2</sup>) with Estimated Standard Deviations in Parentheses

Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Co	44 (2)	35 (2)	38 (2)	-7 (2)	-3 (2)	-3 (2)
P(1)	42 (4)	29 (3)	42 (4)	-3 (4)	0 (3)	4 (5)
P(2)	37 (4)	40 (4)	35 (4)	6 (4)	4 (4)	3 (3)
P(3)	43 (4)	33 (3)	29 (4)	3 (3)	-2 (4)	-4 (3)

<sup>a</sup> Form of the anisotropic thermal parameters is  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos \gamma^* + 2U_{13}hla^*c^* \cos \beta^* + 2U_{23}klb^*c^* \cos \alpha^*)]$ .

formation of pentavalent phosphorus compounds and stabilize the low oxidation state of the metal, probably because of the moderate  $\pi$  acidity of the phosphorus donor atoms. The formation of phosphine oxides in the reducing process of transition metals by tertiary phosphines has been reported.<sup>14</sup>

**Table V.** [Ni(p<sub>3</sub>)(SO<sub>2</sub>)] Positional Parameters (×10<sup>4</sup>) and Isotropic Temperature Factors with Estimated Standard Deviations in Parentheses

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (×10 <sup>3</sup> ), Å <sup>2</sup>
Ni	-686 (1)	-1321 <sup>a</sup>	788 (1)	<i>b</i>
S	-1140 (1)	-2257 (2)	65 (3)	<i>b</i>
P(1)	371 (1)	-1346 (2)	1296 (2)	<i>b</i>
P(2)	-605 (1)	-194 (2)	-160 (3)	<i>b</i>
P(3)	-1014 (1)	-888 (2)	2701 (2)	<i>b</i>
O(1)	-833 (5)	-2885 (6)	-475 (11)	<i>b</i>
O(2)	-1799 (5)	-2378 (7)	56 (14)	<i>b</i>
C(1)	360 (5)	869 (6)	2924 (10)	49 (3)
C(2)	40 (5)	181 (6)	2257 (9)	35 (2)
C(3)	602 (5)	-327 (6)	1715 (9)	42 (3)
C(4)	-382 (5)	501 (6)	1106 (8)	38 (2)
C(5)	-360 (5)	-254 (6)	3321 (9)	44 (3)
C(6)	639 (5)	-1920 (6)	2687 (10)	43 (3)
C(7)	264 (6)	-2524 (7)	3070 (10)	57 (3)
C(8)	467 (7)	-3030 (8)	4110 (13)	78 (4)
C(9)	1033 (7)	-2875 (8)	4714 (12)	73 (4)
C(10)	1414 (7)	-2277 (9)	4374 (12)	76 (4)
C(11)	1229 (6)	-1799 (7)	3356 (11)	64 (3)
C(12)	1001 (5)	-1641 (6)	101 (9)	44 (3)
C(13)	1612 (5)	-1299 (8)	54 (9)	55 (3)
C(14)	2063 (6)	-1544 (7)	-860 (11)	66 (4)
C(15)	1910 (6)	-2120 (8)	-1723 (12)	74 (4)
C(16)	1286 (6)	-2470 (7)	-1653 (12)	68 (4)
C(17)	847 (5)	-2225 (7)	-741 (10)	51 (3)
C(18)	37 (5)	-84 (6)	-1423 (10)	45 (3)
C(19)	380 (6)	606 (8)	-1589 (12)	71 (4)
C(20)	809 (7)	633 (10)	-2653 (14)	92 (5)
C(21)	919 (7)	39 (8)	-3404 (12)	77 (4)
C(22)	609 (6)	-651 (8)	-3235 (12)	70 (4)
C(23)	159 (5)	-715 (7)	-2193 (11)	54 (3)
C(24)	-1302 (5)	283 (6)	-968 (10)	45 (3)
C(25)	-1338 (6)	1078 (7)	-1042 (11)	58 (3)
C(26)	-1855 (7)	1435 (8)	-1736 (13)	72 (4)
C(27)	-2306 (7)	941 (8)	-2344 (13)	72 (4)
C(28)	-2265 (6)	179 (8)	-2299 (12)	68 (4)
C(29)	-1766 (6)	170 (7)	-1582 (11)	62 (3)
C(30)	-1153 (5)	-1556 (5)	4034 (9)	38 (3)
C(31)	-942 (5)	-1421 (7)	5281 (10)	57 (3)
C(32)	-1067 (7)	-1987 (8)	6246 (12)	73 (4)
C(33)	-1424 (6)	-2628 (7)	5992 (11)	61 (3)
C(34)	-1627 (6)	-2739 (7)	4759 (12)	65 (4)
C(35)	-1517 (6)	-2207 (7)	3761 (11)	54 (3)
C(36)	-1747 (5)	-255 (6)	2844 (9)	44 (3)
C(37)	-1875 (5)	161 (7)	4014 (10)	53 (3)
C(38)	-2399 (6)	648 (8)	4078 (11)	65 (3)
C(39)	-2794 (6)	717 (8)	3024 (11)	70 (4)
C(40)	-2703 (7)	312 (8)	1906 (12)	77 (4)
C(41)	-2168 (5)	-201 (7)	1805 (10)	55 (3)

<sup>a</sup> This value was chosen to have accordance with the *y* coordinate of the [Ni(p<sub>3</sub>)I] complex. <sup>b</sup> These atoms were refined anisotropically.

**Table VI.** [Ni(p<sub>3</sub>)(SO<sub>2</sub>)] Anisotropic Thermal Parameters (×10<sup>3</sup>, Å<sup>2</sup>) with Estimated Standard Deviations in Parentheses

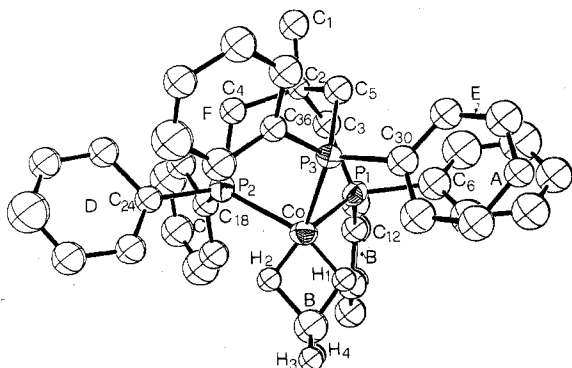
Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Ni	34 (1)	32 (1)	42 (1)	-4 (1)	0 (1)	-1 (1)
S	53 (2)	41 (2)	52 (2)	-12 (2)	0 (2)	-8 (2)
P(1)	34 (1)	33 (1)	47 (1)	-1 (2)	-2 (1)	2 (2)
P(2)	33 (2)	33 (2)	42 (2)	-1 (1)	0 (1)	2 (1)
P(3)	32 (1)	39 (2)	41 (2)	-1 (1)	1 (1)	0 (1)
O(1)	97 (8)	71 (7)	183 (11)	-7 (6)	-3 (7)	-64 (8)
O(2)	68 (7)	153 (12)	350 (16)	-56 (8)	13 (10)	-143 (12)

All four of the compounds reported in the present work are strictly isomorphous and the unit cell parameters, determined from single crystals, are very similar. They are also isomorphous with the previously studied pseudotetrahedral complexes [M(p<sub>3</sub>)X] (M = Co, Ni, Cu; X = Cl, Br, I).<sup>2,3</sup>

[Co(p<sub>3</sub>)(BH<sub>4</sub>)] and [Cu(p<sub>3</sub>)(BH<sub>4</sub>)]. While the white copper derivative appears to be insensitive to air, the green cobalt compound, [Co(p<sub>3</sub>)(BH<sub>4</sub>)], is highly unstable and in the

**Table VII.** Distances (Å) and Angles (deg) in the Coordination Groups with Estimated Standard Deviations in Parentheses

Co		Ni	
Distances			
Co-P(1)	2.261 (5)	Ni-S	2.013 (3)
Co-P(2)	2.245 (6)	Ni-P(1)	2.225 (3)
Co-P(3)	2.245 (6)	Ni-P(2)	2.188 (3)
Co-B	2.21 (3)	Ni-P(3)	2.203 (3)
Co-H(1)	1.55 (15)	S-O(1)	1.37 (1)
Co-H(2)	1.45 (15)	S-O(2)	1.36 (1)
B-H(1)	1.27 (16)		
B-H(2)	1.38 (17)		
B-H(3)	1.63 (17)		
B-H(4)	1.41 (18)		
Angles			
P(1)-Co-P(2)	89.6 (2)	S-Ni-P(1)	121.2 (1)
P(1)-Co-P(3)	91.3 (2)	S-Ni-P(2)	126.3 (1)
P(1)-Co-B	126.4 (8)	S-Ni-P(3)	117.5 (1)
P(1)-Co-H(1)	109.1 (55)	P(1)-Ni-P(2)	92.7 (1)
P(1)-Co-H(2)	155.7 (61)	P(1)-Ni-P(3)	95.4 (1)
P(2)-Co-P(3)	93.3 (2)	P(2)-Ni-P(3)	96.5 (1)
P(2)-Co-B	126.9 (8)	Ni-S-O(1)	125.3 (5)
P(2)-Co-H(1)	159.5 (57)	Ni-S-O(2)	125.6 (6)
P(2)-Co-H(2)	93.3 (67)	O(1)-S-O(2)	109.1 (7)
P(3)-Co-B	119.4 (8)		
P(3)-Co-H(1)	94.5 (60)		
P(3)-Co-H(2)	112.6 (60)		
H(1)-Co-H(2)	66.3 (88)		
H(1)-B-H(2)	76.2 (95)		

**Figure 1.** Perspective view of the [Co(p<sub>3</sub>)(BH<sub>4</sub>)] complex. Isotropic *B* temperature factors of 2 Å<sup>2</sup> were assigned to hydrogen atoms. The full lines joining the cobalt atom to the hydrogen atoms do not imply any conclusion on the nature of the Co-BH<sub>4</sub> bonding.

microcrystalline form is spontaneously inflammable. Both compounds have low volatility and low solubility in benzene but they do dissolve fairly readily in methylene chloride and in 1,2-dichloroethane, in which they are nonelectrolytes.

The copper complex is diamagnetic while the cobalt compound has  $\mu_{\text{eff}} = 3.1 \mu_{\text{B}}$  at room temperature as expected for high-spin *d*<sup>8</sup> configuration.

The molecular structure of [Co(p<sub>3</sub>)(BH<sub>4</sub>)] shows it to consist of monomolecular units. Bond lengths and bond angles together with their estimated standard deviations are summarized in Tables VII and VIII and Figure 1 shows a perspective view of the molecule. The cobalt atom is linked to the three phosphorus atoms of the p<sub>3</sub> ligand and to two of the hydrogen atoms of the BH<sub>4</sub> group. The coordination geometry of the cobalt atom may be described as a very distorted square pyramid with the P(3) atom at the apex of the pyramid (Figure 1). The Co, B, H(1), and H(2) atoms are coplanar to within 0.17 Å. If we ignore the hydrogen atoms, the boron atom can be described as occupying one apex of a tetrahedron in which the cobalt atom is at the center and the three phosphorus atoms occupy the other three apices. The Co-B distance (2.21 Å) is a little larger than the sum of the

**Table VIII.** Selected Bond Lengths (Å) and Angles (deg) in the p<sub>3</sub> Molecules with Estimated Standard Deviations in Parentheses

Co		Ni	
Distances			
P(1)-C(3)	1.81 (2)	1.88 (1)	
P(1)-C(6)	1.87 (2)	1.82 (1)	
P(1)-C(12)	1.81 (2)	1.85 (1)	
P(2)-C(4)	1.81 (2)	1.83 (1)	
P(2)-C(18)	1.81 (2)	1.84 (1)	
P(2)-C(24)	1.79 (2)	1.84 (1)	
P(3)-C(5)	1.83 (2)	1.84 (1)	
P(3)-C(30)	1.84 (2)	1.81 (1)	
P(3)-C(36)	1.87 (2)	1.86 (1)	
C(1)-C(2)	1.55 (2)	1.52 (1)	
C(2)-C(3)	1.54 (3)	1.55 (1)	
C(2)-C(4)	1.60 (2)	1.56 (1)	
C(2)-C(5)	1.53 (3)	1.56 (1)	
Angles			
M-P(1)-C(3)	109.3 (7)	106.2 (3)	
M-P(1)-C(6)	118.0 (8)	119.0 (3)	
M-P(1)-C(12)	119.2 (7)	121.8 (3)	
C(3)-P(1)-C(6)	104.6 (9)	105.0 (4)	
C(3)-P(1)-C(12)	105.6 (9)	103.7 (4)	
C(6)-P(1)-C(12)	98.5 (9)	99.0 (5)	
M-P(2)-C(4)	107.7 (6)	107.0 (3)	
M-P(2)-C(18)	115.9 (6)	117.1 (3)	
M-P(2)-C(24)	121.2 (7)	122.7 (4)	
C(4)-P(2)-C(18)	107.7 (8)	104.5 (4)	
C(4)-P(2)-C(24)	103.5 (8)	102.5 (5)	
C(18)-P(2)-C(24)	99.5 (8)	100.8 (5)	
M-P(3)-C(5)	109.2 (6)	106.8 (3)	
M-P(3)-C(30)	118.7 (6)	120.0 (3)	
M-P(3)-C(36)	120.5 (6)	121.0 (3)	
C(5)-P(3)-C(30)	104.8 (9)	103.6 (4)	
C(5)-P(3)-C(36)	102.6 (8)	101.9 (5)	
C(30)-P(3)-C(36)	99.0 (8)	101.0 (5)	
C(1)-C(2)-C(3)	108.6 (14)	106.8 (8)	
C(1)-C(2)-C(4)	108.0 (14)	107.3 (8)	
C(1)-C(2)-C(5)	109.2 (15)	106.9 (7)	
C(3)-C(2)-C(4)	111.0 (14)	110.0 (7)	
C(3)-C(2)-C(5)	109.2 (14)	111.4 (8)	
C(4)-C(2)-C(5)	110.8 (14)	114.1 (8)	
P(1)-C(3)-C(2)	117.8 (13)	115.5 (7)	
P(2)-C(4)-C(2)	116.6 (11)	116.0 (7)	
P(3)-C(5)-C(2)	116.6 (13)	115.4 (6)	
P(1)-C(6)-C(7)	120.3 (17)	118.6 (8)	
P(1)-C(6)-C(11)	119.3 (17)	124.0 (8)	
P(1)-C(12)-C(13)	123.9 (15)	122.1 (8)	
P(1)-C(12)-C(17)	120.0 (15)	117.5 (8)	
P(2)-C(18)-C(19)	122.9 (14)	121.8 (8)	
P(2)-C(18)-C(23)	121.8 (14)	116.6 (8)	
P(2)-C(24)-C(25)	120.1 (14)	120.8 (8)	
P(2)-C(24)-C(29)	124.4 (15)	118.7 (8)	
P(3)-C(30)-C(31)	124.2 (15)	122.9 (8)	
P(3)-C(30)-C(35)	118.2 (15)	117.1 (7)	
P(3)-C(36)-C(37)	118.3 (14)	120.8 (7)	
P(3)-C(36)-C(41)	118.1 (13)	119.0 (8)	

covalent radii of cobalt and boron (1.98 Å).<sup>15</sup> The four hydrogen atoms of the BH<sub>4</sub> group are tetrahedrally arranged around the boron. The two Co-H<sub>b</sub> (*b* = bridged) distances (1.55 and 1.45 Å) are in good agreement with the sum of the covalent radii (1.48 Å).<sup>15</sup>

The bond angles and distances relative to the metal-tetrahydroborate linkage in the complex [Co(p<sub>3</sub>)(BH<sub>4</sub>)] are compared in Table IX with the corresponding data for other metal complexes in which the BH<sub>4</sub> group is linked to the metal via two bridging hydrogen atoms. The Co-B distance in [Co(p<sub>3</sub>)(BH<sub>4</sub>)] is comparable to the M-B distance in other complexes when allowance is made for the different single-bond metallic radii. As far as the bond distances and angles involving hydrogen atoms are concerned, the observed differences, due in part to inaccuracies in the determination of the hydrogen atom positions, are not significant in terms of M-BH<sub>4</sub> bonding and probably result, insofar as they are

**Table IX.** Geometry of Some Metal Tetrahydroborate Compounds (Distances in Å; Angles in deg)

Compd	M-B	M-H <sub>b</sub>	B-H <sub>b</sub>	H <sub>b</sub> -M-H <sub>b</sub>	M-H <sub>b</sub> -B	H <sub>b</sub> -B-H <sub>b</sub>	Ref
[Co(p <sub>3</sub> )(BH <sub>4</sub> )]	2.21	1.48 (av)	1.31 (av)	67	105 (av)	77	This work
[Co(P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ) <sub>2</sub> H(BH <sub>4</sub> )]	2.13	1.83 (av)	1.35 (av)				16
[Cu(PPh <sub>3</sub> ) <sub>2</sub> (BH <sub>4</sub> )]	2.18	2.02	1.26	69	80	132	17
[Al(BH <sub>4</sub> ) <sub>3</sub> ]	2.14	1.80	1.28	73		114	18
[Ti(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (BH <sub>4</sub> )]	2.37	1.75	1.23	60	104	91	19

**Table X.** Infrared Vibrational Data (cm<sup>-1</sup>) for Borohydride Compounds<sup>a</sup>

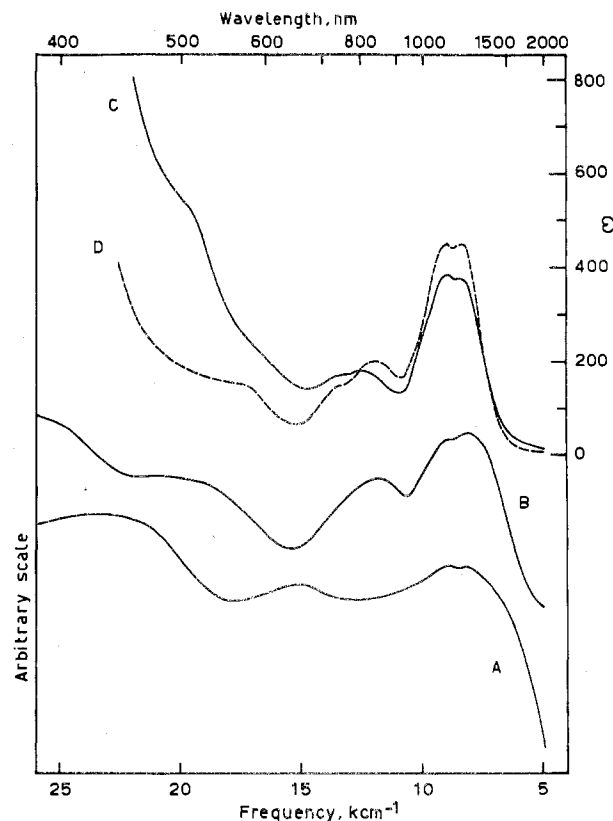
Compd	ν(B-H <sub>t</sub> )	ν(B-H <sub>b</sub> )	Ref
[Co(p <sub>3</sub> )(BH <sub>4</sub> )]	2370 mw, 2330 m	2015 w	This work
[Cu(p <sub>3</sub> )(BH <sub>4</sub> )]	2300 s	1980 w	This work
[Co(P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub> ) <sub>2</sub> H(BH <sub>4</sub> )]	2390, 2368	1958, 1379	16
[Cu(PPh <sub>3</sub> ) <sub>2</sub> (BH <sub>4</sub> )]	2420 vs, 2400 s	2010 s	21
[Ti(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> (BH <sub>4</sub> )]	2438 s, 2400 vs	2050 m, 1940	22

<sup>a</sup> Key: m, medium; s, strong; w, weak.

real, from the different geometries of the compounds. For example, the shorter Co-H<sub>b</sub> distances (1.55, 1.45 Å) found in [Co(p<sub>3</sub>)(BH<sub>4</sub>)] compared with the 1.80, 1.87 Å found in [Co(P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>)<sub>2</sub>H(BH<sub>4</sub>)],<sup>16</sup> which contains only two monodentate phosphine ligands, can be explained by the fact that, because of the steric requirements of the tripod ligand p<sub>3</sub>, the P-Co-P angles in the former complex are much smaller (91° on average instead of 157.8°) thus allowing the BH<sub>4</sub> group to get much closer to the metal. A structure similar to that of [Co(p<sub>3</sub>)(BH<sub>4</sub>)] can be assigned to the isomorphous [Cu(p<sub>3</sub>)(BH<sub>4</sub>)] complex, also in view of the ir results (vide infra).

The electronic spectrum of the complex [Co(p<sub>3</sub>)(BH<sub>4</sub>)] is shown in Figure 2 together with that of the isomorphous tetrahedral compound [Co(p<sub>3</sub>)Cl].<sup>2</sup> The close similarity of the absorption spectra of the two complexes, which have a band in the region 0.87–0.90 μm<sup>-1</sup>, another in the region 1.20–1.22 μm<sup>-1</sup> and a shoulder in the 1.74–2.00-μm<sup>-1</sup> region, favors an interpretation as that suggested by Cotton et al. for some nitratocobaltate(II) complexes.<sup>20</sup> According to this approach the "perturbing" effect by a bidentate ligand of a short "bite" on the metal ion is similar to that obtained by the replacement of the two donor atoms with a single atom located at their center of gravity. Thus the complex [Co(p<sub>3</sub>)(BH<sub>4</sub>)] can be considered essentially pseudotetrahedral with the BH<sub>4</sub><sup>-</sup> anion equivalent to a spherical negative charge.

In the ir spectrum of [Co(p<sub>3</sub>)(BH<sub>4</sub>)] there are bands at 2300 (together with a shoulder at 2370) and 2015 cm<sup>-1</sup> while in the ir spectrum of [Cu(p<sub>3</sub>)(BH<sub>4</sub>)] the corresponding bands occur at 2300 and 1980 cm<sup>-1</sup> (Table X). In the spectrum of the deuterated compound [Co(p<sub>3</sub>)(BD<sub>4</sub>)] the two bands are shifted to 1775 and 1720 cm<sup>-1</sup> corresponding to ν<sub>H</sub>/ν<sub>D</sub> ratios of 1.31 and 1.17, respectively. The higher frequency band is assigned to the terminal B-H<sub>t</sub> (t = terminal) stretching vibration while the lower frequency band is assigned to the bridging B-H<sub>b</sub> stretching vibration. These data are comparable to those found for other metal-tetrahydroborate compounds in which the BH<sub>4</sub> group coordinates via two hydrogen atoms (Table X). The low values found for the frequencies of the B-H<sub>t</sub> stretching vibrations of [Co(p<sub>3</sub>)(BH<sub>4</sub>)] and [Cu(p<sub>3</sub>)(BH<sub>4</sub>)] (and also for the other phosphine-borohydride complexes shown in the table), compared with the corresponding values found for the essentially covalent complex [Ti(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(BH<sub>4</sub>)],<sup>22</sup> are indicative of an appreciable amount of ionic character in the M-BH<sub>4</sub> bonding in the former. The low volatility and low solubility in protonic solvents shown by the two complexes support this view.



**Figure 2.** Solid-state spectra (arbitrary scale) of [Co(p<sub>3</sub>)(BH<sub>4</sub>)] (curve A) and [Co(p<sub>3</sub>)Cl] (curve B) and absorption spectra (arbitrary scale) of [Co(p<sub>3</sub>)(BH<sub>4</sub>)] (curve C) and [Co(p<sub>3</sub>)Cl] (curve D).

A recently adopted approach to the bonding between the BH<sub>4</sub> group and the central metal in a borohydride complex is to consider it as resulting from two two-electron three-center bonds involving the use of empty metal orbitals and appropriate BH orbitals. According to this scheme the borohydride ion behaves as a four-electron donor.<sup>22</sup> However, while this approach has shown itself to be useful in the study of various covalent tetrahydroborate metal complexes, it does not appear to be applicable to the complex [Co(p<sub>3</sub>)(BH<sub>4</sub>)] since it would make the cobalt atom an 18-electron diamagnetic system. It seems rather more reasonable to consider the BH<sub>4</sub><sup>-</sup> ion equivalent to a spherical anion and assume an appreciable amount of ionic character in the bonding between the borohydride ion and the metal atom than to use the scheme suggested for essentially covalent borohydride-metal complexes. This point of view can be considered valid, despite the shortness of the observed Co-H distances, for which the degree of uncertainties is very high.

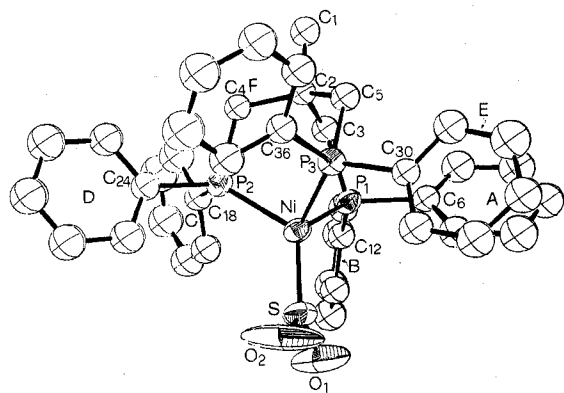
[Co(p<sub>3</sub>)(NO)]. This compound is orange, moderately stable in air, and soluble in benzene and 1,2-dichloroethane in both of which it is a nonelectrolyte.

A pseudotetrahedral structure with the NO group as the fourth ligand can be assigned to this compound, which is isomorphous with the other [M(p<sub>3</sub>)X] complexes, i.e., a structure corresponding to that of the isoelectronic, pseudotetrahedral nitrosyl complex [Ni(tep)(NO)]<sup>+</sup> in which tep = CH<sub>3</sub>C(CH<sub>2</sub>PEt<sub>2</sub>)<sub>3</sub>.<sup>23</sup>

Table XI. Maxima and Extinction Coefficients for the Electronic Spectra of the Cobalt and Nickel Complexes

Compd	Absorption max, <sup>a</sup> μm <sup>-1</sup> (ε <sub>M</sub> for soln)
[Co(p <sub>3</sub> )(BH <sub>4</sub> )]	a: 0.87, 1.525, 2.355 sh b: 0.835 sh, 0.895 (379), 1.22 (172), 2.00 sh
[Co(p <sub>3</sub> )(NO)]	a: 2.22 sh b: —
[Ni(p <sub>3</sub> )(SO <sub>2</sub> )]	a: 1.539 sh, 2.04, 2.855 sh b: 1.539 sh, 2.13 (1950)
[Ni(p <sub>3</sub> )(CS <sub>2</sub> )]	a: 1.725, 2.50 sh b: 1.85 (1062)

<sup>a</sup> Key: a, solid at room temperature; b, 1,2-dichloroethane solution.

Figure 3. Perspective view of the [Ni(p<sub>3</sub>)(SO<sub>2</sub>)] complex.

The ir spectrum of this complex has a very intense band at 1628 cm<sup>-1</sup> which can be assigned to the NO stretching vibration. Such a value for ν(NO) is very similar to that found for the pseudotetrahedral complex [Co(np<sub>3</sub>)(NO)], 1620 cm<sup>-1</sup>,<sup>24</sup> in which np<sub>3</sub> = tris(2-diphenylphosphinoethyl)amine, but it is lower than the value found for the isoelectronic [Ni(tep)(NO)]<sup>+</sup>, 1750 cm<sup>-1</sup>, probably because of the greater extent of back-donation in the neutral complexes.

[Ni(p<sub>3</sub>)(SO<sub>2</sub>)]. This compound, which is dark brown and unstable in air, is diamagnetic and is a nonconductor in 1,2-dichloroethane. Its electronic spectra, identical in the solid state and in 1,2-dichloroethane solution, have a shoulder at 1.54 μm<sup>-1</sup> and a peak at 2.10 μm<sup>-1</sup> (Table XI). The compound decomposes, reacting with molecular oxygen in 1,2-dichloroethane solution, and all attempts to isolate a solid compound were unsuccessful.

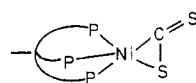
This compound has a structure consisting of monomolecular units of [Ni(p<sub>3</sub>)(SO<sub>2</sub>)]. The bond lengths and angles with their estimated standard deviations are summarized in Tables VII and VIII. Figure 3 shows a perspective view of the molecule. The coordination polyhedron shows the complex to be a distorted tetrahedron with the three phosphorus atoms of the p<sub>3</sub> ligand and the sulfur atom at the vertices. The Ni-S bond, which lies in the SO<sub>2</sub> plane, has a length of 2.013 (3) Å. This bond distance which is shorter than the sum of the covalent radii of the nickel and sulfur atoms, 2.19 Å,<sup>15</sup> suggests some multiple-bonding character between the nickel and sulfur atoms. An M-S distance shorter than the sum of the covalent radii has also been found for the complexes [RuCl(NH<sub>3</sub>)<sub>4</sub>(SO<sub>2</sub>)]<sup>+</sup>,<sup>25</sup> [CpMn(CO)<sub>2</sub>(SO<sub>2</sub>)],<sup>26</sup> and [CpRh(C<sub>2</sub>H<sub>4</sub>)(SO<sub>2</sub>)]<sup>27</sup> in which the M-SO<sub>2</sub> geometry is again planar.

The S-O bond distances are somewhat shorter than the values reported for free solid SO<sub>2</sub> and for coordinated SO<sub>2</sub>.<sup>27</sup> This is probably due to a not very precise description of the thermal motion of the oxygen atoms of the SO<sub>2</sub> group. The use of a more complicated model other than the simple single-atom anisotropic one would probably result in longer S-O bond distances.

Recently a bonding model for transition metal-sulfur dioxide complexes has been proposed which is fully analogous to that previously used for the corresponding nitrosyl derivatives.<sup>28</sup> This approach considers the M-SO<sub>2</sub> bond as resulting from interaction of a σ and a π\* orbital of the ligand SO<sub>2</sub> with the d<sub>z<sup>2</sup></sub> (z = M-S axis) and d<sub>xz</sub> metal orbitals, respectively, and accounts for the geometry of the M-SO<sub>2</sub> moiety (planar or bent) in terms of the number of d electrons in the system and of the coordination polyhedron. According to this approach the d<sup>10</sup> tetrahedral L<sub>3</sub>M(SO<sub>2</sub>) model systems favor a bent geometry for SO<sub>2</sub>; however when L is a strong π-acceptor ligand (e.g., CO), a planar geometry for the M-SO<sub>2</sub> moiety has been predicted. The x-ray structure determinations of the two pseudotetrahedral complexes [Pt(PPh<sub>3</sub>)<sub>3</sub>(SO<sub>2</sub>)]<sup>29</sup> and [Pt(PPh<sub>3</sub>)<sub>2</sub>(SO<sub>2</sub>)<sub>2</sub>]<sup>30</sup> have shown that the geometry of the M-SO<sub>2</sub> group is bent for both complexes. However, it should be noticed that the geometry of the coordination polyhedron in the complex [Pt(PPh<sub>3</sub>)<sub>3</sub>(SO<sub>2</sub>)] is closer to trigonal pyramidal than to tetrahedral, due to the large P-Pt-P angles (118° (average)). As has been pointed out by Hoffmann et al.,<sup>31</sup> the L-M-L angles for L<sub>3</sub>MX model systems are expected to be low when a strong π interaction between the metal and the X ligand is established. Conversely, low values of these angles, imposed by such a ligand as p<sub>3</sub> in the present complex, favor π metal-sulfur interaction and may determine the planar geometry of the M-SO<sub>2</sub> moiety.

The ir spectrum of the complex [Ni(p<sub>3</sub>)(SO<sub>2</sub>)] has a strong band at 1190 cm<sup>-1</sup>, a pair of strong bands at 1055 and 1045 cm<sup>-1</sup>, and a band of medium intensity at 540 cm<sup>-1</sup>. These are assigned respectively to the asymmetric stretching, to the symmetric stretching, and to the bending vibrations of the coordinated SO<sub>2</sub>. The frequencies of the stretching modes which are appreciably lower than the values found in uncoordinated solid SO<sub>2</sub> (ν<sub>asym</sub> 1330, 1308 cm<sup>-1</sup>; ν<sub>sym</sub> 1147 cm<sup>-1</sup>)<sup>32</sup> are in agreement with the assumption of a back-donation from the metal to the SO<sub>2</sub> ligand.

[Ni(p<sub>3</sub>)(CS<sub>2</sub>)]. This dark brown complex is reasonably stable in air and is soluble in benzene and 1,2-dichloroethane in both of which it is a nonconductor. The compound is diamagnetic and its electronic spectrum has a band at 1.725 μm<sup>-1</sup> with a shoulder at 2.50 μm<sup>-1</sup> (Table XI). The ir spectrum has strong bands at 1145 and 631 cm<sup>-1</sup>, characteristic of a CS<sub>2</sub> group π-coordinated to the metal,<sup>33</sup> which are assigned respectively to the out-of-ring ν(C=S) and to the ring ν(C-S) stretching vibrations. The isomorphism of this complex with the others suggests that all three phosphorus atoms in the p<sub>3</sub> ligand are bound to nickel to give a structure of the type



An analogous geometry was already found in the complex [Rh(PPh<sub>3</sub>)<sub>2</sub>(NO)(SO<sub>2</sub>)]<sup>34</sup> containing the SO<sub>2</sub> S,O-bonded to the metal.

Coordination of CS<sub>2</sub> to the nickel atom has only previously been reported for a few square-planar complexes.<sup>35</sup> If the addition of the CS<sub>2</sub> molecule to the Ni(p<sub>3</sub>) moiety is considered as an oxidative reaction,<sup>36</sup> then [Ni(p<sub>3</sub>)(CS<sub>2</sub>)] may be regarded formally as a nickel(II) complex, and its electronic spectrum is more compatible with this formulation than with any alternative assignment. However, it should be pointed out that in a situation involving essentially covalent bonds, an ionic formulation which necessitates the assignment of oxidation numbers should be avoided.

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**Registry No.** I, 58689-52-4; II, 58657-89-9; [Cu(p<sub>3</sub>)(BH<sub>4</sub>)], 60294-97-5; [Co(p<sub>3</sub>)(NO)], 60294-98-6; [Ni(p<sub>3</sub>)(CS<sub>2</sub>)], 60294-99-7; [Co(p<sub>3</sub>)(BD<sub>4</sub>)], 60295-00-3; [Cu(p<sub>3</sub>)Cl], 37701-76-1; [Ni(p<sub>3</sub>)<sub>2</sub>], 60295-01-4.

**Supplementary Material Available:** Listings of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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## Synthesis and Characterization of the Mixed-Valence Copper Complex Trichlorobis(4-methyl-1,8-naphthyridine)dicopper

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The binuclear complex trichlorobis(4-methyl-1,8-naphthyridine)dicopper has been prepared and characterized by x-ray diffraction and ESR spectroscopy. The emerald green crystals conform to monoclinic space group  $P2_1/c$  with  $a = 11.795$  (5),  $b = 14.850$  (5),  $c = 11.320$  (5) Å,  $\beta = 99.20$  (9)°,  $Z = 4$ . The structure, refined to a final conventional  $R$  value of 0.051 on 2815 counter data, consists of dimeric molecules containing two equivalent copper atoms in pseudotetrahedral environments, bridged by one chlorine atom and by two 4-methyl-1,8-naphthyridine ligands, which act as bidentate bimetallic ligands. The equivalence of the two copper atoms is substantiated by the ESR spectra. The electronic structure of the complex is also discussed.

### Introduction

Recently we have reported that the potentially bidentate ligand 1,8-naphthyridine (NN) and its 4-methyl-substituted derivative (MeNN) form binuclear complexes  $[\text{Ni}_2\text{X}_2(\text{NN})_4]\text{Y}$  and  $[\text{Ni}_2\text{X}_2(\text{MeNN})_4]\text{Y}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{NCS}$ ;  $\text{Y} = \text{PF}_6, \text{B}(\text{C}_6\text{H}_5)_4$ ) in which the oxidation number of the nickel atoms is +1.5.<sup>1,2</sup> These complexes have been found to have a dimeric structure of the copper acetate type, with the nonlinear triatomic group N-C-N of NN and MeNN acting as a syn-syn bridge between two equivalent nickel atoms.

Encouraged by these results we have investigated the behavior of naphthyridine ligands toward copper(II) salts. Several copper(I) and copper(II) complexes with NN and some methyl derivatives have been reported,<sup>3-7</sup> but in no instance were the ligands found to bridge two metal atoms. We have now found that by reaction of copper(II) chloride with MeNN in alcoholic medium a mixed valence compound of formula  $[\text{Cu}_2\text{Cl}_3(\text{MeNN})_2]$  is formed, and we wish to report its characterization by single-crystal x-ray diffractometry and by ESR spectroscopy.

### Experimental Section

**Preparation of the Complex.** The materials and solvents were reagent grade and were used without further purification. The ligand MeNN was prepared according to the reported procedure.<sup>8</sup> To a hot (50 °C) solution of 1 mmol of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in 20 cm<sup>3</sup> of *n*-butyl alcohol a solution containing 2 mmol of the ligand in 5 cm<sup>3</sup> of the same solvent was added and the reaction mixture was brought to the boiling point. A green emerald crystalline precipitate was formed, which was filtered, washed with *n*-butyl alcohol and petroleum ether, recrystallized from a mixture of *n*-butyl alcohol and dichloromethane, and dried in a vacuum oven at 60 °C. *Anal.* Calcd for  $\text{C}_{22}\text{H}_{16}\text{Cl}_3\text{Cu}_2\text{N}_4$ : C, 41.63; H, 3.24; Cl, 20.85; Cu, 24.06; N, 10.76. Found: C, 41.43; H, 3.08; Cl, 20.38; Cu, 24.36; N, 10.73.

**Collection and Reduction of the X-Ray Intensity Data.** The compound  $[\text{Cu}_2\text{Cl}_3(\text{MeNN})_2]$  crystallizes as dark green prisms, which are ill-shaped, showing large cavities at least on one side. One crystal of dimensions  $0.52 \times 0.16 \times 0.14$  mm<sup>3</sup> was chosen for the preliminary work of orientation, lattice constants, and space group determination and finally for data collection. These routines were executed by a Philips PW 1100 automated diffractometer. The compound was found to be monoclinic with space group  $P2_1/c$ . The cell constants were determined (at ca. 22 °C) as  $a = 11.795$  (5),  $b = 14.850$  (5),  $c =$