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# Tetrahedral structure of the high-spin cobalt(I) complex (np3)CoBr. A symmetry-forbidden rearrangement to five-coordination

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found to decompose within several days in methylene chloride and several months in toluene at room temperature.

The  $^1\text{H}$  NMR spectrum of (methyl(trimethylsilyl)amino)-gallium dichloride in toluene (Figure 4) is temperature dependent and concentration independent. The intensities of the singlets at 2.62 and 0.23 ppm increase with respect to the intensities of the singlets at 2.55 and 0.24 ppm with an increase in temperature. The assignment of the former singlets to the protons of the methyl and trimethylsilyl groups in *cis*- $[\text{Cl}_2\text{GaN}(\text{Me})\text{SiMe}_3]_2$  and the latter singlets to the corresponding protons in *trans*- $[\text{Cl}_2\text{GaN}(\text{Me})\text{SiMe}_3]_2$  is based on the assumption that the *trans* isomer is the more thermodynamically stable dimer. The equilibrium constants ( $K_D = [\text{cis}]/[\text{trans}]$ ) for the *trans* to *cis* isomerization of  $[\text{Cl}_2\text{GaN}(\text{Me})\text{SiMe}_3]_2$  in toluene at various temperatures are listed in Table IV. The values of  $\Delta H$  and  $\Delta S$  (2.4 (2) kJ/mol, 0.08 (69) J/(mol K)) for the isomerization were obtained from a least-squares plot of  $\ln K_D$  vs.  $1/T$  ( $r^2 = 0.94$ ). In methylene chloride, the equilibrium is shifted to the right with  $K_D = 0.479$  at 19 °C (0.383 (calcd) in toluene at 19 °C). This result suggests that the *cis* isomer is more readily solvated by polar solvents.

In summary, equilibrium mixtures of the *trans* trimer and the *cis* and *trans* dimers have been observed in solutions of ((trimethylsilyl)amino)gallium dichloride. In solutions of (methyl(trimethylsilyl)amino)gallium dichloride, only the *cis* and *trans* dimers were identified. The position of the trimer-dimer equilibrium depends primarily on the steric strain of the substituents, entropy, and the valency angle strain in the dimer. Although the entropy favors the formation of the dimer in both systems, the valency angle strain in  $[\text{Cl}_2\text{GaN}(\text{H})\text{SiMe}_3]_2$  is greater than the steric strain in  $[\text{Cl}_2\text{GaN}(\text{H})\text{SiMe}_3]_3$ , and the trimer as well as the *cis* and *trans* isomers of the dimer is present in solutions of

((trimethylsilyl)amino)gallium dichloride. With both a methyl and a trimethylsilyl group on the nitrogen atoms, the steric strain in the trimer will be substantially larger than the valency angle strain in the dimer and, hence, only the *cis* and *trans* isomers of  $[\text{Cl}_2\text{GaN}(\text{Me})\text{SiMe}_3]_2$  are observed in solution. The equilibria do exhibit a solvent dependency, but the effects of the solvent on the positions of the equilibria are small. Although the trimer and the *cis* and *trans* isomers of the dimer are present in solutions of ((trimethylsilyl)amino)gallium dichloride, *trans*- $[\text{Cl}_2\text{GaN}(\text{H})\text{SiMe}_3]_2$  appears to be the only species in the solid state. Likewise, the *trans* isomer is the predominant if not the only isomer that precipitates from solutions of  $[\text{Cl}_2\text{GaN}(\text{Me})\text{SiMe}_3]_2$ . These results would suggest that the *trans* isomer of the dimer is the least soluble species in the polar solvents that were used in the syntheses and recrystallizations of these compounds.

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**Registry No.** *trans*- $[\text{Cl}_2\text{GaN}(\text{H})\text{SiMe}_3]_2$ , 93779-95-4; *cis*- $[\text{Cl}_2\text{GaN}(\text{H})\text{SiMe}_3]_2$ , 93779-96-5; *trans*- $[\text{Cl}_2\text{GaN}(\text{Me})\text{SiMe}_3]_2$ , 93683-64-8; *cis*- $[\text{Cl}_2\text{GaN}(\text{Me})\text{SiMe}_3]_2$ , 93780-86-0; *trans*- $[\text{Cl}_2\text{GaN}(\text{H})\text{SiMe}_3]_3$ , 93714-41-1.

**Supplementary Material Available:** Listings of hydrogen coordinates, anisotropic temperature factors, and observed and calculated structure factors as well as figures showing  $^1\text{H}$  NMR spectra of ((trimethylsilyl)amino)gallium dichloride and  $[\text{Cl}_2\text{GaN}(\text{Me})\text{SiMe}_3]_2$  in methylene chloride (33 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, 50132 Florence, Italy

## Tetrahedral Structure of the High-Spin Cobalt(I) Complex $(\text{np}_3)\text{CoBr}$ . A Symmetry-Forbidden Rearrangement to Five-Coordination

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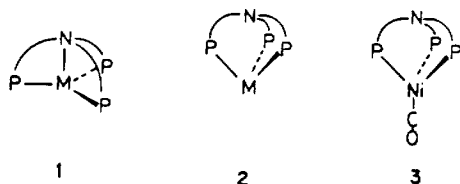
The crystal structure of  $(\text{np}_3)\text{CoBr}$ ,  $\text{np}_3 = \text{tris}(2\text{-(diphenylphosphino)ethyl})\text{amine}$ , has been examined by X-ray methods with the aim of determining whether the triplet ground state of the molecule depends on a particular stereochemistry. Analogous complexes of Co(I), where H and CN replace the bromine anion, are diamagnetic with a trigonal-bipyramidal structure. The application of the 18-electron rule easily rationalizes the latter geometry, where the amine group of  $\text{np}_3$  is apically coordinated to the  $d^8$  metal. On the other hand, the tripodal  $\text{np}_3$  ligand is known to be flexible enough to coordinate only through its phosphorus atoms, while retaining  $C_{3h}$  symmetry. This type of arrangement is found in the title compound, where the cobalt is tetrahedrally coordinated by the phosphorus and bromine atoms. The Co-N distance is 3.34 (1) Å, and the P-Co-Br and P-Co-P angles average 115.2 (20) and 103.2 (3)°, respectively. The space group is monoclinic  $P2_1$ ; the unit cell dimensions are  $a = 20.578$  (9) Å,  $b = 8.979$  (4) Å,  $c = 10.186$  (5) Å,  $\beta = 91.15$  (6)°,  $V = 1181.69$  Å<sup>3</sup>, and  $Z = 2$ . Qualitative MO arguments, supported by extended Hückel calculations, indicate that transformation to the trigonal-bipyramidal geometry, attainable by translation of the amine along the threefold axis, may be in some cases symmetry forbidden as a result of a level crossing that switches the nature of HOMO-LUMO

### Introduction

The ligand  $\text{tris}(2\text{-(diphenylphosphino)ethyl})\text{amine}$ ,  $\text{np}_3$ , has a very rich coordination chemistry in terms of both unusual stereochemical features and reactivity that it confers to its products. The ligand may use either all of its donor atoms (one N and three P) or only the phosphorus atoms to achieve coordination to the metal; there is no major steric obstacle to adoption of either conformation 1 or 2.<sup>1</sup> The electronic requirements imposed by

the metal and the coligands ultimately determine the coordination mode of  $\text{np}_3$ .

Generally the 18-electron rule is suited to predict or rationalize the presence of a *trans* axial ligand, for example in the case of a CO molecule as shown in 3.<sup>2</sup> On the other hand, the coordination of nitrogen and the stabilization of the unusual trigonal-pyramidal geometry (TP) is observed in the absence of other coligands (structure 1 is adopted by the complex  $(\text{np}_3)\text{Ni}$ ).<sup>3</sup> The  $d^8$  configuration predictably favors the trigonal-bipyramidal ge-



- (1) Experimental crystallographic data for a number of complexes containing  $\text{np}_3$  variously elongated show that the ligand easily allows the interconversion by simple torsions at the C-C bond of the chains.
- (2) Ghilardi, C. A.; Sabatini, A.; Sacconi, L. *Inorg. Chem.* 1976, 15, 2763.
- (3) Sacconi, L.; Ghilardi, C. A.; Mealli, C.; Zanobini, F. *Inorg. Chem.* 1975, 14, 1380.

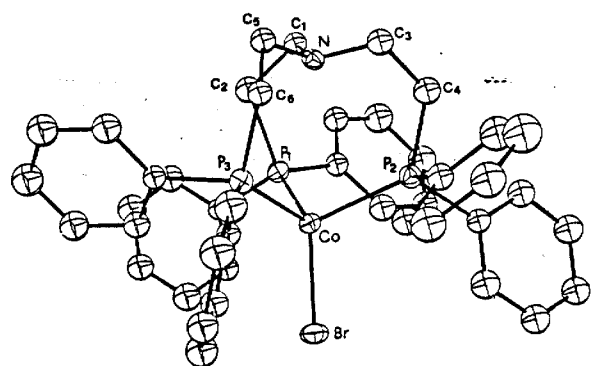
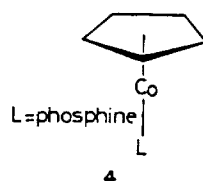


Figure 1. Perspective view of the (np<sub>3</sub>)CoBr complex molecule with 30% probability ellipsoids.

ometry (TBP), where the simultaneous presence of the nitrogen and another axial coligand satisfies the 18-electron count.

It seemed therefore quite reasonable, in a previous paper from this laboratory,<sup>4</sup> to assign the TBP structure to the diamagnetic [(np<sub>3</sub>)NiX]<sup>+</sup> complexes (X = Cl, Br, I) (an X-ray structure of the iodine derivative confirms the assignment).<sup>5</sup> The isoelectronic (np<sub>3</sub>)CoX complexes, X = Cl, Br, I, SCN, which are paramagnetic with two unpaired electrons, were also assigned a TBP coordination on the basis of the electronic UV spectra.<sup>3</sup> When X = CN or H, the corresponding compounds are diamagnetic and the crystal structure of the hydride complex reveals the TBP structure.<sup>3</sup> The different spin state was then attributed to the different electronegativity and nucleophilicity of the coligands rather than to a possible change of the coordination number. We are not aware of any other five-coordinated d<sup>8</sup> complex with a triplet ground state, but the triplet state is normal for pseudotetrahedral complexes of Ni(II) and Co(I) and has been ascertained in the presence of polyphosphine ligands.<sup>6</sup>

There has been a recent interest in the nature of d<sup>8</sup> Co(I) species of the type CpCoL (Cp = cyclopentadienyl), which are thought to be intermediates in ligand dissociation reactions of CpCoL complexes.<sup>7</sup> A detailed theoretical analysis and the suggestion that a pseudotetrahedrally coordinated Co(I) species (Cp is the equivalent of three separated ligands), as that shown in 4, would



4

be forced to have a pseudosymmetry-imposed high-spin state have prompted us to reconsider the structure of the paramagnetic (np<sub>3</sub>)CoX species. Were the nitrogen atom not coordinated, these complexes would be formally equivalent to 4.

## Results and Discussion

The molecular structure of (np<sub>3</sub>)CoBr (I) consists of mononuclear units. A perspective view of the molecule is shown in Figure 1. Selected bond distances and angles are given in Table I. The cobalt atom is four-coordinated by the three phosphorus atoms of np<sub>3</sub> and by a bromine atom, the central nitrogen atom being 3.34 (1) Å from the metal. The coordination geometry is distorted tetrahedral, the P-Co-Br angles, which average 115.2 (20)°, being significantly larger than the P-Co-P angles (average 103.2 (3)°). The complex is distorted from C<sub>3v</sub> symmetry by a slight shift of the bromine atom away from the threefold axis, since the Br-Co-P angles range between 113.0 (1) and 119.1 (1)°. The Co-Br distance of 2.366 (3) Å as well as the Co-P bonds (average

Table I. Selected Bond Distances (Å) and Angles (deg)

Co-Br	2.366 (3)	P2-C1,4	1.85 (1)
Co-P1	2.279 (5)	P3-C6	1.85 (1)
Co-P2	2.287 (4)	P3-C1,5	1.86 (1)
Co-P3	2.295 (4)	P3-C1,6	1.84 (1)
Co-N	3.34 (1)	N-C1	1.42 (2)
P1-C2	1.85 (2)	N-C3	1.43 (2)
P1-C1,1	1.83 (1)	N-C5	1.48 (2)
P1-C1,2	1.84 (1)	C1-C2	1.51 (2)
P2-C4	1.86 (2)	C3-C4	1.54 (2)
P2-C1,3	1.84 (1)	C5-C6	1.54 (2)
Br-Co-P1	113.0 (1)	C1,3-P2-C1,4	97.7 (5)
Br-Co-P2	113.4 (2)	Co-P3-C6	119.5 (5)
Br-Co-P3	119.1 (1)	Co-P3-C1,5	115.9 (3)
P1-Co-P2	103.6 (2)	Co-P3-C1,6	112.1 (3)
P1-Co-P3	102.7 (2)	C6-P3-C1,5	101.2 (5)
P2-Co-P3	103.4 (2)	C6-P3-C1,6	105.5 (6)
Co-P1-C2	118.5 (5)	C1,5-P3-C1,6	100.4 (5)
Co-P1-C1,1	113.5 (4)	C1-N-C3	113.4 (12)
Co-P1-C1,2	117.4 (4)	C1-N-C5	113.6 (12)
C2-P1-C1,1	103.6 (6)	C3-N-C5	115.0 (11)
C2-P1-C1,2	102.3 (6)	N-C1-C2	111.3 (12)
C1,1-P1-C1,2	99.0 (5)	C1-C2-P1	113.2 (10)
Co-P2-C4	119.9 (5)	N-C3-C4	111.6 (12)
Co-P2-C1,3	114.6 (3)	C3-C4-P2	109.8 (11)
Co-P2-C1,4	115.0 (3)	N-C5-C6	110.1 (12)
C4-P2-C1,3	104.4 (6)	C5-C6-P3	112.7 (10)
C4-P2-C1,4	102.1 (6)		

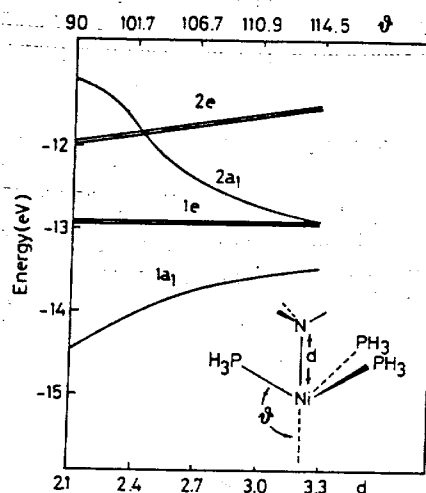


Figure 2. Evolution of the frontier orbitals for the interconversion process between the structures 1 and 2 in the case of a d<sup>10</sup> metal.

2.287 (5) Å) falls in the range of values found for related compounds<sup>8</sup> and reflects the difference of ca. 0.08 Å in the covalent radii of bromine and phosphorus atoms. An examination of the closely related [(np<sub>3</sub>)CoBr]<sup>+</sup> derivative shows that a d<sup>7</sup> species the elongation of the Co-N bond (2.73 (1) Å) is much less pronounced than in I but still suggestive of a nonbonding interaction between the atoms.<sup>9</sup>

The structure determination of I raises new questions about the origin of the different geometries and spin states between isoelectronic complexes such as [(np<sub>3</sub>)NiX]<sup>+</sup> and (np<sub>3</sub>)CoX or even between isometallic compounds such as (np<sub>3</sub>)CoY (Y = CN, H) and (np<sub>3</sub>)CoX (X = Cl, Br, I, SCN). In a previous paper<sup>10</sup> we constructed a Walsh diagram for the deformation process that interconverts structures 1 and 2. A small energy barrier of ca. 8 kcal/mol is calculated for the d<sup>10</sup> case. The diagram, reported in Figure 2, clearly indicates that the HOMO changes its nature in the two structures. In the former case the HOMO is the hybridized z<sup>2</sup> orbital (a<sub>1</sub>) but becomes an e level in 2 (xz, yz).

(4) Sacconi, L.; Bertini, I. *J. Am. Chem. Soc.* 1968, 90, 5443.

(5) Dapporto, P.; Sacconi, L. *J. Chem. Soc.* 1970, 1804.

(6) Sacconi, L.; Mani, F. *Transition Met. Chem. (N.Y.)* 1982, 8, 179.

(7) Hofmann, P.; Padmanabhan, M. *Organometallics* 1983, 2, 1273 and references therein.

(8) Orioli, P. L. *Coord. Chem. Rev.* 1971, 6, 285.

(9) Di Vaira, M. *J. Chem. Soc., Dalton Trans.* 1975, 1575.

(10) Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* 1984, 23, 922.

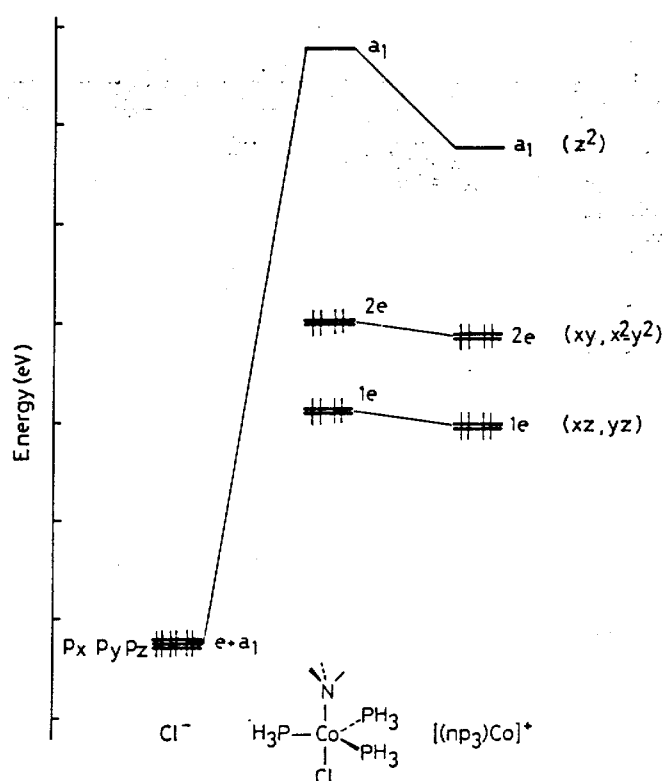
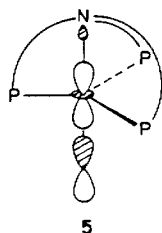


Figure 3. Diagram for the interaction between Cl and a TP fragment of the type  $(\text{NH}_3)(\text{PPh}_3)_3\text{Co}$ .

Since both levels are occupied, the interconversion is symmetry allowed. Now suppose the TP fragment 1 is allowed to interact with a trans ligand, such as chlorine. The interaction diagram, shown in Figure 3, reproduces the classical MO splitting in a TBP structure.<sup>11</sup> As seen, the strongest interaction involves the  $a_1$  levels, whereas the destabilizing  $\pi$  interactions are much weaker. 5 shows the HOMO as an antibonding combination between the chlorine  $p_z$  orbital and the metal hybrid of  $a_1$  symmetry.



Indeed the latter orbital, already the highest d level in the TP fragment, becomes even more destabilized from the interaction with the  $\sigma$  orbital of the ligand. For a  $d^8$  metal the  $a_1$  level is not populated. When the nitrogen atom is removed from the metal and the P atoms are raised above the equatorial plane, in a simulation of the constraints imposed by the  $\text{np}_3$  ligand,<sup>12</sup> the effect is that of a slight destabilization of the 2e level and a strong stabilization of the  $a_1$  level (see Figure 4). Within the limits imposed by  $\text{np}_3$  to the M–N distances (ca. 2.1–3.5 Å),<sup>13</sup> a crossing of these levels may or may not occur. If it does, a  $d^8$  complex would undergo a switch of the HOMO–LUMO character; the interconversion would be symmetry forbidden.<sup>14</sup> Figure 4 shows the different behavior of the  $(\text{np}_3)\text{CoX}$  species depending on the nature of X. Whereas a crossing is calculated for X = Cl, no

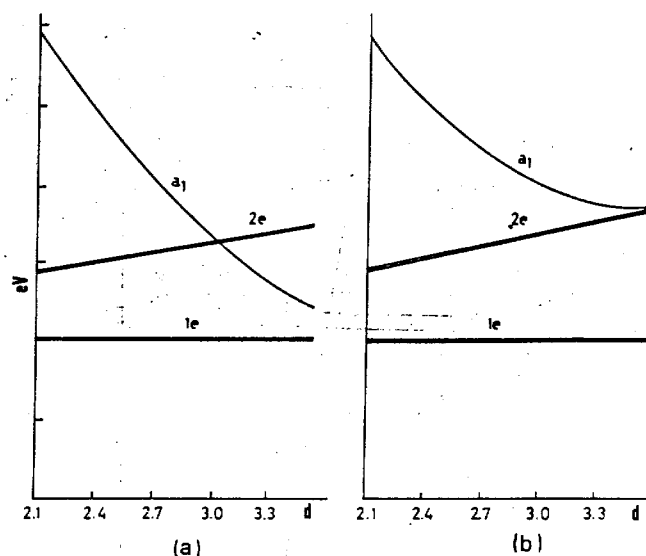


Figure 4. Walsh diagrams for removing the nitrogen atom from the coordination sphere of  $(\text{np}_3)\text{MX}$  complexes: (a) levels calculated for  $(\text{np}_3)\text{CoCl}$ ; (b) levels calculated for  $[(\text{np}_3)\text{NiH}]^+$ .

crossing occurs for X = H. Similar diagrams are presented in ref 9 and show comparable trends. However, no level crossing is observed since the range of M–N distances investigated is limited at 2.7–2.8 Å. Ultimately, for a given metal it will depend on the  $\sigma$ -donor capabilities of the ligand trans to the amine whether diamagnetic TBP or high-spin pseudotetrahedral complexes are observed. It is reasonable to assume that, in the formation of a complex with  $\text{np}_3$  and another coligand, the metal will be coordinated to the amine only at a late stage. If the strength of the coligand as  $\sigma$  donor is sufficient to keep the  $a_1$  level (5) above the 2e level, already at the initial pseudotetrahedral geometry, then the interconversion to a stable 18-electron TBP geometry ensues with a net energy gain (notice how the 2e levels stabilize for shorter M–N distances). On the other hand, if the 2e level is above the  $a_1$  level at the pseudotetrahedral coordination, a new M–N bond cannot be formed in a concerted reaction pathway that preserves  $C_{3v}$  symmetry. Hence the high-spin state results from the forced population of 2e with two electrons.

We recall here that the complex 1 is obtainable from the reduction with  $\text{BH}_4^-$  of the corresponding cationic  $\text{Co(II)}$  species.<sup>3</sup> The latter is paramagnetic with three unpaired electrons and, as already mentioned, exhibits little Co–N bonding. In the diagrams of Figure 4 it is clear that in any case the unpaired electrons will populate both  $a_1$  and 2e levels. However, the correct order of these levels is most likely that at the right of Figure 4a, since, upon reduction to obtain 1, the Co–N distance lengthens from 2.73 (1) to 3.34 (1) Å, whereas the  $C_{3v}$  symmetry is practically preserved. The extra electron populates the  $a_1$  level, which is not only antibonding between the metal and the halide but is also M–N antibonding. Occupation of the 2e level with three electrons would induce Jahn–Teller effects.

The fact that all the  $[(\text{np}_3)\text{NiX}]^+$  species are TBP diamagnetic is suggestive that only a Walsh diagram of the type reported in Figure 4b is applicable in this case. Although the differences between the diagrams of parts a and b of Figure 4 are clearly parameter dependent, we avoid any detailed discussion of the origin of the different behavior in  $\text{Ni(II)}$  and  $\text{Co(I)}$  species. The parameters used in the extended Hückel calculations are not very reliable, and arguments based on the different electronegativities ignore the fact that different nuclear charges must play an important role.<sup>15</sup>

The triplet state imposes high energy barriers for the thermal organometallic reactivity of the pseudotetrahedral  $\text{Co(I)}$  species, but it has been suggested<sup>7</sup> that in some cases a singlet state is

(11) Albright, T. A. *Tetrahedron* 1982, 38, 1339.

(12) A linear relationship between the N–M–P angles and the M–N distances was determined from a number of structures containing the  $\text{np}_3$  ligand variously elongated. An exhaustive list of these structures is given in ref 13.

(13) Mealli, C.; Sacconi, L. *Inorg. Chem.* 1982, 21, 2870.

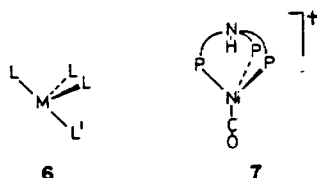
(14) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* 1969, 8, 781.

(15) Jørgensen, C. K. "Oxidation Numbers and Oxidation States"; Springer-Verlag: West Berlin, 1969; p 107.

Table II. Crystal Data and Data Collection Details

formula	C <sub>22</sub> H <sub>42</sub> BrCoNP <sub>3</sub>
mol wt	792.57
a, Å	20.578 (9)
b, Å	8.979 (4)
c, Å	10.186 (5)
β, deg	91.15 (6)
V, Å <sup>3</sup>	1881.69
space group	P2 <sub>1</sub>
Z	2
d <sub>calcd</sub> , g cm <sup>-3</sup>	1.398
habit	regular parallelepiped
dimens, mm	0.030 × 0.075 × 0.50
linear abs coeff, cm <sup>-1</sup>	16.6
transmission factors	0.88–0.95
radiation, Å	Mo Kα, 0.7107
monochromator	graphite
method	ω–2θ scan
scan speed, deg/s	0.07
scan width, deg	0.7 + 0.3 tan θ
bkgd time	half the scan time
stds	3 every 120 reflns
max dev stds, %	5
2θ limits, deg	5 < 2θ < 45
data collected	±h,k,l
no. of total data	2804
no. of data with I > 3σ(I)	1489
final no. of variables	152

achieved by shifting the coligand off the main axis of the fragment, to give intermediates of type 6. This possibility, which destroys



the ternary symmetry, was also previously considered by us for the migration of hydrogen over the amine group upon attack of CO on the [(np<sub>3</sub>)NiH]<sup>+</sup> species, to give the final product 7.<sup>10</sup>

It has been recently established<sup>7</sup> that the groups eligible for the rearrangement of type 6 must be good σ donors and π acceptors. Perhaps significantly our paramagnetic complexes contain halide anions that are σ donors and π donors at the same time, a situation that stabilizes the triplet ground state. On the other hand, a rich organometallic chemistry has been observed for species such as (np<sub>3</sub>)CoH, [(np<sub>3</sub>)NiH]<sup>+</sup>, [(np<sub>3</sub>)Co(CO)]<sup>+</sup>, etc., which allegedly form intermediates of type 6 easily.<sup>10,16</sup>

### Experimental Section

The complex (np<sub>3</sub>)CoBr was prepared by the method previously described.<sup>3</sup>

**Collection and Reduction of X-ray Data.** Data collection was carried out on a Philips PW 1100 automatic diffractometer, at 295 K. Unit cell parameters were determined from the least-squares refinement of 25 reflections. The crystals, which are isomorphous with those of (np<sub>3</sub>)NiCO,<sup>2</sup> are monoclinic. On the basis of the extinction 0k0 with k odd, the two space groups P2<sub>1</sub>/m and P2<sub>1</sub> were considered. The acentric P2<sub>1</sub> was confirmed by the successful refinement of the structure. Details of crystal data and data collection are given in Table II. After correction for background the intensities were assigned standard deviations σ(I) calculated by using the value of 0.03 for the instability factor p.<sup>17</sup> Intensity data were corrected for Lorentz–polarization effects and for absorption by a numerical integration method.<sup>18</sup>

**Solution and Refinement of the Structure.** All the calculations were carried out on a SEL 32/77 computer by using the SHELX-76<sup>18</sup> and ORTEP<sup>19</sup> programs. Atomic scattering factors of the appropriate neutral

Table III. Positional (×10<sup>4</sup>) Parameters

atom	x	y	z
Co	2372 (1)	2500	5346 (2)
Br	2098 (1)	4645 (3)	6564 (2)
P1	2140 (2)	336 (5)	6408 (5)
P2	3460 (2)	2312 (6)	4953 (4)
P3	1898 (2)	2142 (5)	3312 (4)
N	2839 (5)	–592 (14)	3804 (11)
C1	2685 (7)	–1753 (17)	4691 (14)
C2	2077 (7)	–1402 (18)	5434 (15)
C3	3524 (7)	–405 (21)	3632 (14)
C4	3842 (7)	443 (18)	4791 (15)
C5	2444 (7)	–618 (16)	2575 (13)
C6	2316 (7)	984 (15)	2088 (14)
C1,1	2729 (5)	–130 (10)	7713 (10)
C2,1	3076 (5)	1028 (10)	8311 (10)
C3,1	3523 (5)	722 (10)	9321 (10)
C4,1	3624 (5)	–743 (10)	9734 (10)
C5,1	3277 (5)	–1901 (10)	9136 (10)
C6,1	2829 (5)	–1595 (10)	8125 (10)
C1,2	1391 (4)	284 (10)	7371 (10)
C2,2	1284 (4)	1499 (10)	8192 (10)
C3,2	735 (4)	1533 (10)	8975 (10)
C4,2	295 (4)	353 (10)	8937 (10)
C5,2	402 (4)	–863 (10)	8116 (10)
C6,2	951 (4)	–897 (10)	7333 (10)
C1,3	3732 (4)	3351 (12)	3504 (11)
C2,3	3318 (4)	4425 (12)	2958 (11)
C3,3	3506 (4)	5227 (12)	1856 (11)
C4,3	4109 (4)	4955 (12)	1300 (11)
C5,3	4523 (4)	3882 (12)	1846 (11)
C6,3	4334 (4)	3080 (12)	2948 (11)
C1,4	3999 (4)	3221 (12)	6193 (9)
C2,4	3888 (4)	4736 (12)	6396 (9)
C3,4	4275 (4)	5525 (12)	7296 (9)
C4,4	4772 (4)	4800 (12)	7992 (9)
C5,4	4883 (4)	3286 (12)	7789 (9)
C6,4	4497 (4)	2496 (12)	6889 (9)
C1,5	1726 (5)	3862 (12)	2340 (7)
C2,5	1414 (5)	5017 (12)	2992 (7)
C3,5	1251 (5)	6324 (12)	2322 (7)
C4,5	1400 (5)	6476 (12)	998 (7)
C5,5	1712 (5)	5320 (12)	346 (7)
C6,5	1874 (5)	4014 (12)	1016 (7)
C1,6	1074 (5)	1362 (12)	3417 (9)
C2,6	720 (5)	1726 (12)	4526 (9)
C3,6	87 (5)	1201 (12)	4652 (9)
C4,6	–193 (5)	313 (12)	3670 (9)
C5,6	161 (5)	–51 (12)	2561 (9)
C6,6	795 (5)	474 (12)	2435 (9)

atoms were taken from ref 20 for the non-hydrogen atoms and from ref 21 for hydrogen atoms. Both the Δ<sup>f</sup> and Δ<sup>f'</sup> components of anomalous dispersion were included for all non-hydrogen atoms.<sup>22</sup> The refinement was based on F<sub>o</sub>, the function minimized being Σw(|F<sub>o</sub>| – |F<sub>c</sub>|)<sup>2</sup>, where w = 1/σ<sup>2</sup>(F<sub>o</sub>). Owing to the isomorphism of the title compound with (np<sub>3</sub>)NiCO, the final parameters of the latter structure were used as starting parameters (the y coordinate of the cobalt atom was fixed at 1/4). Refinements were carried out with assignment of anisotropic thermal parameters to the atoms of the coordinating polyhedron and isotropic thermal parameters to the remaining atoms. The phenyl rings of the np<sub>3</sub> ligand were treated as rigid groups, the carbon atoms being assigned an individual thermal parameters. The hydrogen atoms were introduced in calculated positions but not refined. The absolute configuration of the structure was determined by applying the anomalous dispersion correction. Because of the polarity of P2<sub>1</sub>, two possible enantiomeric structures must be considered, one being the image of the other reflected through a mirror plane at y = 1/4. The refinement of the model with parameters reported in Table III yielded R = 0.049 and R<sub>w</sub> = 0.044, whereas the refinement of the enantiomorph yielded R = 0.052 and R<sub>w</sub> = 0.047. R and R<sub>w</sub> factors are defined as Σ||F<sub>o</sub>| – |F<sub>c</sub>||/Σ|F<sub>o</sub>| and [Σw(|F<sub>o</sub>| – |F<sub>c</sub>|)<sup>2</sup>/Σw(F<sub>o</sub>)<sup>2</sup>]<sup>1/2</sup>. Final positional and thermal parameters are in Table

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III and Tables SI and SII (supplementary material).

**Extended Hückel MO Calculations.** The calculations on the model compound  $(\text{NH}_3)(\text{PH}_3)_2\text{MCl}$ ,  $\text{M} = \text{Co}, \text{Ni}$ , were performed by using the program ICON<sup>23</sup> and the routine FMO for the fragment orbital analysis.<sup>24</sup> The atomic parameters for N, C, H, Cl, Co, and Ni were taken from ref 25 and those for P from ref 26. M-P, M-Cl, N-H, and P-H were fixed

at 2.25, 2.30, 1.1, and 1.1 Å, respectively.

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**Registry No.**  $(\text{np}_3)\text{CoBr}$ , 93684-10-7.

**Supplementary Material Available:** Listings of observed and calculated structure factors, final thermal parameters (Table SI), and hydrogen coordinates (Table SII) (12 pages). Ordering information is given on any current masthead page.

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## $\text{Nb}_6\text{I}_8(\text{NH}_2\text{CH}_3)_6$ : The Lowest Oxidation State in a Niobium Cluster Compound and Its Topochemical Formation

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$\text{Nb}_6\text{I}_{11}$  reacts topochemically with a solution of methylamine in ethanol, yielding a product with the composition  $\text{Nb}_6\text{I}_8(\text{NH}_2\text{CH}_3)_6$ . The diamagnetic behavior as well as structural details and analytical data is consistent with a 22-electron cluster system containing the metal in the lowest oxidation state (1.33+) observed in niobium clusters until now.  $\text{Nb}_6\text{I}_8(\text{NH}_2\text{CH}_3)_6$  crystallizes in the triclinic space group  $P\bar{1}$ , with  $Z = 2$  and lattice constants  $a = 1031.5$  (5) pm,  $b = 1104.4$  (5) pm,  $c = 1522.0$  (10) pm,  $\alpha = 82.00$  (5)°,  $\beta = 80.17$  (5)°, and  $\gamma = 81.05$  (5)°. The structure contains two crystallographically independent clusters that exhibit distinctly different geometries. The mean Nb-Nb distances are identical for both clusters ( $\bar{d}(\text{Nb-Nb}) = 275$  pm).

### Introduction

The compound  $\text{Nb}_6\text{I}_{11}$  consists of a three-dimensional network of  $\text{Nb}_6\text{I}_8$  clusters linked via I bridges.<sup>1,2</sup> The structure has two interesting aspects: (a)  $\text{Nb}_6\text{I}_8$  clusters occur in spite of the pronounced electron deficiency. Only 19 instead of 24 electrons are available for M-M bonding in the  $\text{Nb}_6$  octahedron. (b) The I bridges are strained, especially those involved in bonding layers of the  $\text{MoX}_2$  type structure ( $\text{Mo}_6\text{X}_8\text{X}_{4/2}\text{X}_2$ ) according to  $\text{Nb}_6\text{I}_8\text{I}_{4/2}\text{I}_{2/2}$ .<sup>1,2</sup> Both characteristics are responsible for an interesting physical property of the compound, namely the spin-crossover transition occurring at 274 K.<sup>2-4</sup> Both characteristics are also reflected in a peculiar topochemical reaction.

Crystals of  $\text{Nb}_6\text{I}_{11}$  react with aqueous ammonia, gaining volume along the [0, 1, 0] direction and splitting into extremely thin lamellae within seconds. As the orientation of the lamellae is parallel to the  $\text{MoX}_2$  type layers in the crystal of  $\text{Nb}_6\text{I}_{11}$ , this "accordion" reaction has been interpreted in terms of a  $(\text{I}_{2/2})$  bond breakage.<sup>1</sup> To prove this assumption, it must be shown that intermediate or final products of the reaction still contain the same kind of clusters as  $\text{Nb}_6\text{I}_{11}$  itself.

Unfortunately, the reaction product of  $\text{Nb}_6\text{I}_{11}$  and aqueous ammonia quickly decomposes to yield a white amorphous precipitation. Working with liquid ammonia in closed ampoules obviously results in a similar topochemical reaction. After some weeks, large dark brown crystals form, but these easily become amorphous and cannot be characterized further.<sup>5</sup> Fortunately the topochemical reaction also occurs with amines. The primary product of the reaction of  $\text{Nb}_6\text{I}_{11}$  with a solution of  $\text{CH}_3\text{NH}_2$  in

ethanol gradually dissolves, and dark brown crystals form that are stable at room temperature and atmospheric pressure. Single-crystal X-ray and conventional chemical analyses result in a composition  $\text{Nb}_6\text{I}_8(\text{NH}_2\text{CH}_3)_6$  for this compound, which in fact still contains the  $\text{Nb}_6\text{I}_8$  cluster.

### Experimental Section

**Preparations.**  $\text{Nb}_6\text{I}_8(\text{NH}_2\text{CH}_3)_6$  is prepared from 0.5 g of  $\text{Nb}_6\text{I}_{11}$  and 20 mL of a 20% solution of  $\text{CH}_3\text{NH}_2$  in ethanol (dried and deoxygenated with Oxisorb<sup>6</sup> at room temperature. The reaction starts at once, leading to a suspension of brown lamellae (phase I) in a brown solution. The lamellae slowly vanish, and after about 6 days a mixture of two solids has formed that consists of black and in thin layers dark red platelets of hexagonal shape (title compound) covered by light brown amorphous solid (phase II). Frequent shaking of the solution during preparation helps to separate the two phases. The crystals of the title compounds are isolated by repeated washings with the mother liquor. Attention is necessary as the amorphous component (phase II) is pyrophoric when dry.

$\text{Nb}_6\text{I}_8(\text{NH}_2\text{CH}_3)_6$  is air sensitive and has to be handled under an inert atmosphere. It is only slightly soluble in alcohols, e.g. ethanol, slowly decomposing to light brown amorphous products. Analysis of C, H, N, and I was by combustion with  $\text{V}_2\text{O}_5$  and Nb by ICP. Anal. Found (calcd): C, 4.14 (4.10); H, 1.73 (1.72); N, 4.80 (4.78); I, 56.6 (57.7); Nb, 31.7 (31.7). Reaction of  $\text{Nb}_6\text{I}_{11}$  and propylamine leads to the analogous compound.

$\text{Nb}_6\text{I}_8(\text{NH}_2\text{C}_3\text{H}_7)_6$  is prepared from 2 g of  $\text{Nb}_6\text{I}_{11}$  and 10 mL of dry propylamine at room temperature. The reaction starts at once, leading to a dark red solution. After 4 days, the solution is decanted cautiously from a small amount of fine deposit. By diffusion of 2-propanol into the dark solution, brown crystals precipitate. No amorphous products are observed in the reaction with  $\text{C}_3\text{H}_7\text{NH}_2$ , but the oxidized product of the disproportionation reaction is soluble in the system. Anal. Found (calcd): C, 12.22 (11.22); H, 3.10 (2.82); N, 4.64 (4.36); I, 51.8 (52.7); Nb, 28.7 (28.9).

**Investigations of  $\text{Nb}_6\text{I}_8(\text{NH}_2\text{CH}_3)_6$ . Thermal Behavior.**  $\text{Nb}_6\text{I}_8(\text{NH}_2\text{CH}_3)_6$  was thermally decomposed at a basis pressure of  $10^{-6}$  torr

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