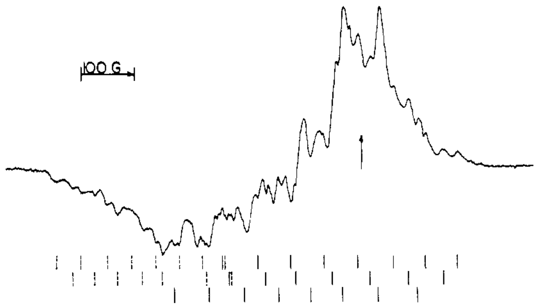

Figure 3. Epr spectrum of (nor)$_4$Co 93 mM in cyclohexane at 77°K. Marker is for DPPH.

Table I. Epr Spectral Parameters of (nor)$_4$Co in Cyclohexane at 77°K

Conform	$g_\parallel$	$g_\perp$	$\vert A_\parallel \vert$, G	$\vert A_\perp \vert$, G
I	2.288	2.028	45	62
II	2.277	2.061	42	66
III		2.085		65

trum is asymmetric at 77°K. The spectral parameters are $g_\perp = 2.062$ and $|A_\perp| = 40$ G; the parallel values cannot be estimated with certainty. The corresponding spectrum in cyclohexane (Figure 3) contains more lines than can be expected from one species even if it has only rhombic symmetry. In analogy to (nor)$_4$Cr,[13] we interpret the spectrum as arising from three conformations of (nor)$_4$Co each with an axial symmetry. The approximate spectral parameters according to this interpretation are given in Table I.

The spin-lattice relaxation imparts information regarding the magnitude and symmetry of ligand-field distortion. Let us consider the case of (nor)$_4$V first. A related 3d^1 molecule VCl$_4$ has 10Dq of about 9000 cm^{-1} from optical transition.[14-17] Consequently, there is no appreciable mixing between the ground ^{2}E state and the excited ^{2}T$_2$ state. The ground orbital degeneracy Δ_2 is split by Jahn-Teller distortion, but the splitting is only about 500 cm^{-1}.[18,19] Spin-lattice relaxation time is extremely short; epr was observable only at liquid He temperatures.[20,21] Increase in Δ_2 is accompanied by increase of relaxation time. This happens when one or more of the chlorines are replaced with -OR groups[22] or if VCl$_4$ is complexed with acetonitrile[22] or attached to metal oxide surfaces.[20] The epr spectral behavior of (nor)$_4$V suggests a Δ_2 to be intermediate between VCl$_4$ and the other cases. The ligand field distortion in (nor)$_4$V is tetragonal, as trigonal distortion would not lift the ground orbital degeneracy.

In the tetragonal distortion of a tetrahedral crystal field, an elongation splits t$_2$ orbitals into an e and a b$_2$ orbital with the latter lying lower by Δ_1. The orbital energies are reversed in the case of tetragonal compression. For 3d^5 (nor)$_4$Co, the relaxation time would be very short if the impaired electron is in the ^{2}E ground state. The observation of the room-temperature epr spectrum argues for a ^{2}B$_2$ ground state. That (nor)$_4$Co should have much longer relaxation time than (nor)$_4$V is due to much rapid increase of Δ_1 in comparison to increase of Δ_2 with crystal field distortion.

Acknowledgment. This work was supported by Grant GH 3911 from the National Science Foundation.

Registry No. (nor)$_4$V, 36333-77-4; (nor)$_4$Co, 36333-80-9.

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Bis(carbonyl)diborane(4)

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Received September 17, 1973

The synthesis of triborane(7) carbonyl has been reported by Paine and Parry.[1] By a different method we have prepared this compound in purer form and studied some of its properties.[2] In this paper we report its decomposition to give B$_2$H$_4$(CO)$_2$ and a study of the structure and properties of this latter material.

Experimental Section

General Data. All reactions were performed using standard high-vacuum techniques described elsewhere.[3] The ^{1}H and ^{11}B nmr spectra were measured on a Varian Associates HR-220 spectrometer at 220 and 70.6 MHz, respectively. Mass spectra were measured on an AEI Model MS-9 spectrometer. Infrared spectra were measured on a Perkin-Elmer Model 621 spectrometer.

Decomposition of B$_3$H$_7$CO. A sample of B$_3$H$_7$CO (1.60 mmol) in a 4.5-ml sealed tube was let stand at 0° for 2 hr. A mixture of H$_2$ (0.02 mmol) and CO (0.39 mmol) was removed at −196° and separated by oxidation with hot CuO.[3] Approximate quantities in millimoles of other materials formed in the reaction, identified by their infrared spectra, are B$_2$H$_4$(CO)$_2$ (0.092), B$_3$H$_7$CO (0.23), B$_2$H$_6$ (0.21), BH$_3$CO (0.42), B$_4$H$_{10}$ (0.49), and B$_5$H$_{11}$ (0.18). Smaller amounts of B$_5$H$_9$ and B$_8$H$_{18}$ were also observed as well as a liquid carbonyl borane of low volatility (2.7 mg) and a nonvolatile white solid (3.0 mg). We have found that B$_3$H$_7$CO and B$_4$H$_{10}$ cannot be completely separated by trap-to-trap distillation. Although B$_2$H$_4$(CO)$_2$ is intermediate in volatility between these materials, we obtained a clean separation with use of a low-temperature column described previously[4] wherein B$_2$H$_4$(CO)$_2$ sublimes at −110° as easily recognized needles with no observable decomposition. A vapor density determination at −21° gave a molecular weight value of 81.5; calcd for B$_2$H$_4$(CO)$_2$, 81.7. The ^{11}B nmr spectrum at −50° is a (1:3:1) triplet at +47.6 ppm relative to external boron fluoride etherate and the proton spectrum is a (1:1:1:1) quartet at −0.86 ppm relative to internal tetramethylsilane. Both spectra show a B-H coupling constant of 92 Hz. The infrared spectrum was measured near liquid nitrogen temperature using a modification of a low-temperature cell described by Shriver[3] with NaCl outer windows and an IRtran cold window. Bands were observed at 2436 (m), 2427 (s), 2343 (s), 752 (w), 743 (s), and 735 (m) cm^{-1}. A very strong carbonyl absorption was observed at 2153 cm^{-1} with a possible shoulder at 2118 cm^{-1}. The mass spectrum is summarized in Table I. Masses of 82.03843 and 81.03141 were measured by peak matching; calcd for ^{11}B$_2{}^1$H$_4$(^{12}C^{16}O)$_2$ and ^{11}B$_2{}^1$H$_3$(^{12}C^{16}O)$_2$ respectively 82.03974, 81.03193.

In another reaction a sample of B$_3$H$_7$CO was allowed to stand at 0° for 4 hr in a 100-ml bomb tube pressurized to 30 atm with

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Table I. Atomic Coordinates and Thermal Parameters

	X^a	Y	Z	$B_{11}{}^b$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	0.148 (0)	0.143 (1)	0.207 (0)	7.5 (5)	52 (3)	8.5 (6)	6 (2)	28 (8)	8 (2)
C	0.119 (0)	0.262 (1)	0.112 (0)	4.9 (6)	30 (3)	9.1 (8)	−1 (2)	5 (1)	−8 (3)
B	0.074 (0)	0.431 (2)	0.986 (0)	5.6 (7)	32 (4)	7.4 (8)	−4 (3)	5 (1)	0.6 (25)
H_1	0.428 (5)	0.23 (1)	0.97 (5)	*c*					
H_2	0.150 (5)	0.40 (1)	0.487 (5)	*c*					

[a] Uncertainties in the final digit are given in parentheses. [b] Anisotropic values $\times 10^3$. [c] Hydrogen isotropic B values held constant at $B = 2.00$.

carbon monoxide. Only a trace of decomposition products were isolated and almost all the B_3H_7CO was recovered.

Decomposition of $B_2H_4(CO)_2$. A 59.8-mg sample of $B_2H_4(CO)_2$ was allowed to stand at 27° for 15 min. Approximate quantitites in milligrams of the products formed in the decomposition identified by their infrared spectra are: CO (18.1), BH_3CO (13.7), and $B_2H_4(CO)_2$ (7.8). A small amount of B_6H_{12}, a nonvolatile solid (10.4), and a liquid carbonyl borane of low volatility (1.7) were also isolated. The infrared spectra of the latter two compounds agreed well with the spectra of the similar appearing compounds from the triborane carbonyl decomposition. The white solid is insoluble in chloroform and appeared to react with tetrahydrofuran. The infrared spectrum (Nujol mull) exhibits broad bands at 2540 (m), 2130 (m), and 1350 (s) cm^{-1}. The material is probably polymeric. The infrared spectrum of the liquid carbonyl borane shows a strong carbonyl band at 2150 cm^{-1} but could not be satisfactorily purified.

X-Ray Structure Determination. A purified sample of $B_2H_4(CO)_2$ in a thin-walled Pyrex capillary (0.5-mm o.d.) was mounted on a Picker FACS-1 diffractometer which was equipped with a gaseous N_2 cooling system.[5] At no time during mounting of the capillary was the sample allowed to reach its melting point. A single crystal (approximately 0.5 × 0.5 × 0.5 mm) was grown from the liquid phase (mp −100 to −110°) and then cooled to approximately −150°. A standardized reciprocal lattice search procedure[6] was used to characterize the crystal as monoclinic, C_2/c ($C_{2h}{}^6$). A least-squares fit of centered reflections gave the following cell parameters: $a = 10.82$ (2), $b = 4.437$ (5), $c = 10.41$ (1) Å, $\beta = 98.37$ (6)°, and $d_c = 1.1$ gm/cm^3 for $Z = 4$ at approximately −150°. Data were collected using Mo Kα radiation with a highly oriented graphite monochromator and a take-off angle of 2.2°. Reflections were scanned at 2°/min over a 2° + dispersion range and a 10 sec stationary background count was taken at both ends of the scan. Intensities of three standard reflections (100, 020, and −202) were measured every 30 readings. The standards showed a continuous decrease in intensity over a 4–5 hr period and the crystal was realigned when the decrease reached 10%. Several realignments were necessary to obtain a complete data set and each of these restored a smaller percentage of the original intensity of the standard reflections. When data collection was complete, realignment could restore only 80% of their original intensity. The crystal was then melted and regrown to form a second crystal, slightly smaller than the first. A second data set was near completion before fracture of the capillary occurred. Due to loss of the crystal, intense reflections could not be remeasured. It was felt that counter saturation was not severe, however, and these data were included in the calculations. Furthermore, no correction was made for the apparent decomposition of the sample in the X-ray beam as evidenced by the gradual decrease in intensity of the standards. Redundant data from the two crystals were scaled and averaged to yield a final set of 483 independent reflections of which 228 were greater than $\sigma(I)$ based on counting statistics and standard propagation of error. The latter were used in all subsequent calculations. The X and Z coordinates of the B, C, and O atoms were located by trial and error methods based on strong intensities in the $h0l$ zone. Trial Y coordinates were then calculated from the apparent shortening of the distances in the BCO moiety on a two-dimensional Fourier map relative to their expected three-dimensional values. Hydrogen atoms were located by standard difference Fourier techniques, after isotropic refinement.[7] Anisotropic least-squares refinement of the B, C, and O atom parameters and isotropic refinement of the H atom positional parameters using unit weights gives an overall R factor of 0.061. The molecule has a 1,2-disubstituted ethane-like structure with a center of inversion. Bond distances are: B–B, 1.78 (1); B–C, 1.52 (1); C–O, 1.125 (7); B–H_1, 1.14 (6); B–H_2, 1.11 (6) Å. Bond angles are: B–B–C, 102.3 (5); B–C–O, 177.5 (6); H_1–B–C, 108 (3); H_2–B–C, 100 (3); H_1–B–B, 115 (3); H_2–B–B, 117 (3); H_1–B–H_2, 112 (4)°. Atomic coordinates and anisotropic thermal parameters are given in Table I. See paragraph at end of paper regarding supplementary material.

Results and Discussion

Bis(carbonyl)diborane(4) is shown to have a 1,2-disubstituted ethane-like structure in which bond distances and angles appear normal.

The formation of $B_2H_4(CO)_2$ from decomposition of B_3H_7CO and the observation that added carbon monoxide stabilizes B_3H_7CO (and therefore probably does not cause its cleavage to the B_2H_4 derivative) is evidence for the intermediate existence of B_2H_4. We expect that B_2H_4 will be shown to be an important intermediate in small molecule borane interconversions. Indeed, we have already obtained evidence that it reacts with B_6H_{10} to form B_8H_{12}.

Acknowledgment. The authors wish to acknowledge J. C. Huffman and J. D. Glore for helpful discussions and the National Science Foundation for support through Grant No. 24266X.

Registry No. B_3H_7CO, 11126-92-4; $B_2H_4(CO)_2$, 49627-05-6.

Supplementary Material Available. A listing of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-760.

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(7) Preliminary data were processed using locally written programs. Least-squares, Fourier, and subsequent calculations were performed using programs written by Dr. A. Larson of Los Alamos Scientific Laboratory, Los Alamos, New Mexico.