per dimers so that the bond length effect can be separated from the bridge angle effect.

Acknowledgments. This research was supported by the National Science Foundation through grant GP-22887 and by the Materials Research Center of the University of North Carolina under Grant No. GH-33632 from the National Science Foundation. The authors wish to thank R. P. Scaringe for many helpful discussions.

Registry No. $[Co(en)_3]_2[Cu_2Cl_8]Cl_2 \cdot 2H_2O$, 28852-88-2.

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Electron Paramagnetic Resonance of Tetrakis(1-norbornyl)vanadium and -cobalt[1]

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Received August 23, 1973

Many soluble transition metal peralkyls display inconvenient degrees of thermal, oxidative, and hydrolytic stability. Pure $(Me)_4Ti$ thermally decomposes at room temperature, and $(Et)_4Ti$ is less stable. Peralkyl transition metal compounds which must pass through relatively high energy transition states in order to decompose by metal hydride elimination,[3-5] such as $(benzyl)_4V$,[6] $(Me_3SiCH_2)_4Cr$,[7] $(Me)_6W$,[8] $(Me_3CCH_2)_4Ti$,[9] $(benzyl)_4Zr$,[10] and $(t\text{-}Bu)_4Cr$,[11] are more thermally stable. However reactions of the above-mentioned compounds with moisture and oxygen are facile. By far the most stable known transition metal peralkyls are 1-norbornyls of first row transition elements. The absence of hydrogen on α carbons and the inability to form a reasonable π bond at the bridgehead preclude metal hydride elimination, while the bulky norbornyl groups shield the metal and the metal-carbon bonds from attack by external reagents.[12]

$(nor)_4Cr$ has a $3d^2$ configuration and its epr spectra in various environments have been described.[13] In this paper we describe the epr results of $(nor)_4V$ and $(nor)_4Co$.

Experimental Section

The synthesis of $(nor)_4V$ and $(nor)_4Co$ follow procedures analogous to that given for $(nor)_4Cr$.[11-13] The epr spectra were obtained with a Varian E-9 spectrometer operating in the X-band frequency. Other aspects of the experimental methods have been given previously.[13]

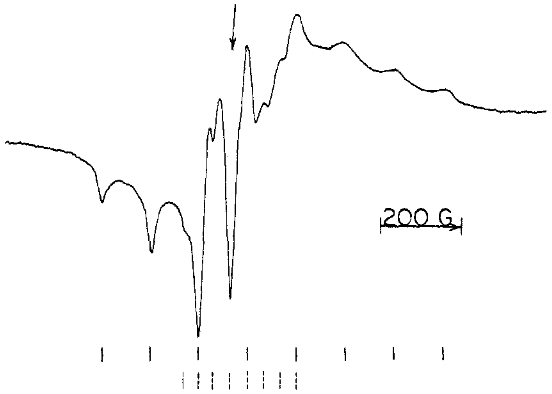

Figure 1. Epr spectrum of $(nor)_4V$ 60 mM in pentane at 77°K. Marker is for DPPH.

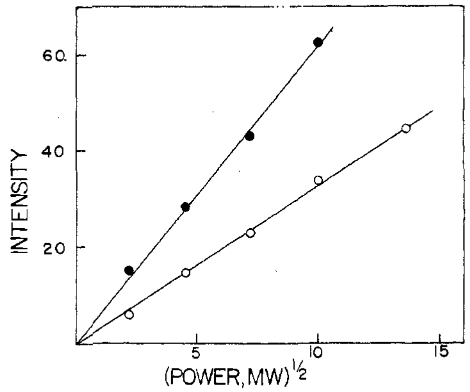

Figure 2. Saturation curve: ●, $(nor)_4V$ 60 mM in pentane at 77°K; ○, $(nor)_4Co$ 10.4 mM in benzene at 298°K.

The $(nor)_4V$ solutions used were 50 mM in isooctane and 60 mM in n-pentane. The $(nor)_4Co$ solutions studied were 10.4 mM in benzene, 12.5 mM in isooctane, 7.3 mM in n-heptane, and 9.3 mM in cyclohexane.

Results and Discussion

$(nor)_4V$ has a $3d^1$ configuration. Its ground state in a tetrahedral ligand field is ^2E. A distortion of trigonal symmetry does not split levels of e symmetry. However, with a distortion of tetragonal symmetry or lower, the ground state is ^2B for an elongated tetrahedron and ^2A for compressed tetragonal symmetry. $(nor)_4Co$ was shown to be a low-spin complex.[12] It has a ^2T ground state which becomes ^2E under a tetragonal compression or $^2B_2$ under a tetragonal elongation.

$(nor)_4V$ has no detectable epr signal at temperatures down to 143°K. Below this temperature an epr signal becomes discernible. Figure 1 shows the spectrum obtained at 77°K; it is the same in all the solvents studied. The spectral parameters are $g_\perp = 1.984$, $g_\parallel = 2.036$, $|A_\perp| = 120$ G, and $|A_\parallel| = 40$ G. The relaxation time of $(nor)_4V$ is still quite short at 77°K; the resonance is not saturated at 200-mW microwave power (Figure 2).

The spin-lattice relaxation time of $(nor)_4Co$ is much longer than that of $(nor)_4V$. A room-temperature epr spectrum was observed with $g = 2.1316$ and ΔH (line width) = 135-140 G. Though the spectrum is the same in all the solvents studied at room temperature, the low-temperature spectrum is dependent on the medium. In benzene, the 298 and 77°K epr spectra are the same aside from the expected (2-3)-fold increase in intensity. In n-heptane and isooctane, the spec-

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[1] Presented at the Sixth International Conference on Organometallic Chemistry, Amherst, Mass., Aug 15, 1973.

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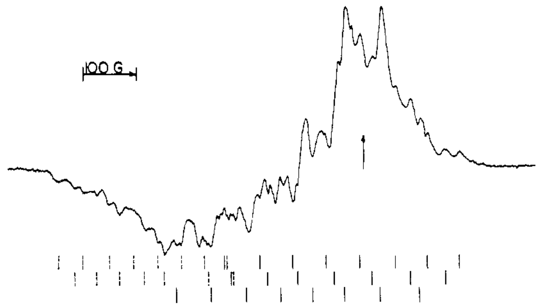

Figure 3. Epr spectrum of (nor)$_4$Co 93 m*M* in cyclohexane at 77°K. Marker is for DPPH.

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

Conform	$g_\parallel$	$g_\perp$	$\lvert A_\parallel \rvert$, G	$\lvert A_\perp \rvert$, 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 10*Dq* 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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