contained in the above sample, was converted to give the concentration of the hydride species on the basis of a calibration obtained from a series of solutions of known concentration.

trans-$\mathrm{PtDBr(PPh_2Me)_2}$ was prepared in a manner essentially similar to that for *trans*-$\mathrm{PtDCl(PEt_3)_2}$[22] where *trans*-$\mathrm{PtHBr(PPh_2Me)_2}$[18] (1 g) was heated in 15 ml of acetone and 3 ml of $\mathrm{D_2O}$ containing 0.07 mmol of HCl for 4 hr. The same procedure was repeated three times using fresh samples of the solvent mixture. The deuterium content in *trans*-$\mathrm{PtDBr(PPh_2Me)_2}$ (85 ± 5%) was determined as for *trans*-$\mathrm{[PtD(PPh_3)_2(CO)]^+ClO_4^-}$ by observing the infrared peak size of ν(Pt–H) (2210 $\mathrm{cm^{-1}}$) for *trans*-$\mathrm{PtHBr(PPh_2Me)_2}$ contained in the above deuterido sample. *trans*-$\mathrm{PtD(NO_3)(PPh_2Me)_2}$ (IIId) was prepared in $\mathrm{D_2O}$–$\mathrm{CH_3OD}$–benzene solution.

Proton nmr spectra were obtained on Varian T-60 and HA-100 spectrometers using TMS as internal standard (τ 10.00). Infrared spectra were recorded using a Beckman IR-10 spectrophotometer, and mass spectra on a Varian M-66 spectrometer.

Reaction of Deuterido–Platinum(II) Species with $\mathbf{(CH_2{=}CHCH_2)_2O}$ (See Table I). The same procedure was employed in all cases. Diallyl ether was allowed to react with IId or IIId in methylene chloride (0.4 ml) at room temperature for 1.5 hr. Volatile compounds were then distilled out under vacuum at room temperature. A methanol solution of 2,4-dinitrophenylhydrazine prepared by the standard method[23] was added to this distillate to give the propionaldehyde–2,4-dinitrophenylhydrazone adduct (70–80% yield). Nmr spectra examined in $\mathrm{CDCl_3}$ at 50° showed complex absorptions at τ 8.8 for methyl and τ 7.55 for methylene protons and two separate triplets at τ 3.06 and 2.40 for methine protons corresponding to two different stereoisomers. Other resonances due to aromatic protons and the N proton appeared at lower than τ 2.12 and could be used as a reference for estimating the deuterium content in the $\mathrm{CH_3CH_2CH{=}}$ moiety (within ±0.05 atom unit). The mass spectrum of the adduct was run at a probe temperature of 90° under 3×10^{-7} Torr with an electron energy of 70 eV to give a high intensity of a parent ion peak.

Isomerization of Allyl Methyl Ether and Allyl Phenyl Ether. All the reactions were carried out in nmr sample tubes at room temperature. The calculations of product yields were based on relative peak areas. The assignments for the *cis*- and *trans*-propenyl alkyl ethers have already been reported.[7,8] Allyl phenyl ether (0.15 mmol) was almost completely converted to *cis*-propenyl phenyl ether in benzene (0.3 ml, 0.003 mmol of II for 10 min), $\mathrm{CD_2Cl_2}$ (0.3 ml, 0.006 mmol of II for 10 min), or acetone-d_6 (0.3 ml, 0.006 mmol of II or *trans*-$\mathrm{[PtH(PPh_3)_2(acetone)]^+BF_4^-}$ for 12 hr). The reaction of $\mathrm{CH_2{=}CDCH_2OMe}$ was carried out in benzene-d_6 and $\mathrm{CDCl_3}$. The ether (40 mg) and 5 mg of II were mixed in 0.3 ml of benzene-d_6 at room temperature. After 1 hr, the reaction was stopped by adding triphenylphosphine (2 mg), and the precipitate was filtered off. In $\mathrm{CDCl_3}$ (0.3 ml), after allowing 40 mg of the ether to react with 10 mg of II for 10 min, the volatile compounds were distilled off under vacuum at room temperature. The determination of the deuterium content by nmr spectroscopy is believed to be correct within ±0.05 atom unit. The reaction of allyl methyl ether with II was also performed under conditions similar to those in Table II except that 40 mg of methanol was added to the benzene or $\mathrm{CH_2Cl_2}$ solution. After 10 min, weak peaks due to propenyl methyl ethers began to appear gradually in the proton nmr spectrum. However, they were all replaced by weak resonances due to $\mathrm{CH_3CH_2CH(OMe)_2}$ after 3–6 hr.

Reaction of Butene-1. All the reactions were performed in nmr sample tubes. Butene-1 (1 mmol) in 0.4 ml of $\mathrm{CH_2Cl_2}$ was allowed to react with 3–5 mg of a platinum(II) hydride such as II, III, or IX at room temperature. After 1 hr in the case of II and IX and 24 hr in the case of III, nmr spectra showed almost complete conversion of the butene-1 to butene-2 with a trans:cis ratio ranging from 3:1 to 2:1. The reaction was also carried out using 60 mg of IX and 1 mmol of butene-1 in 0.4 ml of $\mathrm{CH_2Cl_2}$ at room temperature for 1 hr. Pyridine (7 mg) was added to the solution, and the solvents were evaporated under vacuum. The infrared spectrum of the solid mixture showed a weak band at 2180 $\mathrm{cm^{-1}}$ due to ν(Pt–H) of *trans*-$\mathrm{[PtH(PPh_2Me)_2(py)]^+BF_4^-}$.[14] The nmr spectrum in $\mathrm{CH_2Cl_2}$ showed the presence of *trans*-$\mathrm{[Pt\text{-}}$*n*$\mathrm{\text{-}Bu(PPh_2Me)_2(py)]^+BF_4^-}$.[2]

Registry No. *trans*-$\mathrm{PtD(ClO_4)(PPh_3)_2}$, 39494-96-7; *trans*-$\mathrm{PtD(NO_3)(PPh_2Me)_2}$, 39494-97-8; $\mathrm{(CH_2{=}CHCH_2)_2O}$, 557-40-4; *trans*-$\mathrm{PtH(ClO_4)(PPh_3)_2}$, 3219-29-8; *trans*-$\mathrm{[PtH(PPh_3)_2(CH_3COCH_3)]^+BF_4^-}$, 37036-05-8; *trans*-$\mathrm{PtH(SnCl_3)(PPh_3)_2}$, 18117-31-2; *trans*-$\mathrm{PtH(NO_3)(PPh_2Me)_2}$, 36464-75-2; $\mathrm{CH_2{=}CHCH_2OMe}$, 627-40-7; $\mathrm{CH_2{=}CHCH_2OC_6H_5}$, 1746-13-0; $\mathrm{CH_2{=}CDCH_2OMe}$, 35960-70-4; $\mathrm{CH_2{=}CH{-}CH_2{-}CH_3}$, 106-98-9.

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(22) P. Uguagliati and W. H. Baddley, *J. Amer. Chem. Soc.*, **90**, 5446 (1968).

(23) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley-Maruzen, New York, N. Y., 1956, p 219.

Contribution from the Space Sciences Division, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91103, and the Department of Chemistry, University of Southern California, Los Angeles, California 90007

Microwave Spectrum, Structure, and Dipole Moment of *N,N*-Dimethylaminodiborane

EDWARD A. COHEN and ROBERT A. BEAUDET*

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The microwave spectra of seven isotopic species of $\mathrm{(CH_3)_2NB_2H_5}$ have been assigned. The molecular structure including the boron-bonded hydrogen coordinates has been determined. Structural parameters other than those of the hydrogens are in close agreement with earlier electron diffraction results. No internal rotation splittings were detected. Also, the dipole moment was measured to be 2.77 ± 0.02 D.

Introduction

The microwave spectral study of *N,N*-dimethylaminodiborane, $\mathrm{(CH_3)_2NB_2H_5}$ (DMADB), was undertaken in order to determine the magnitude of the potential barrier to internal rotation of the methyl groups about the C–N bonds and to complement the existing electron diffraction structural study[1] which was unable to determine the B–H structure and which had relatively large probable errors for the bond lengths. The structure of this molecule as well as the numbering of the atoms which we use is given in Figure 1. We also refer to the terminal boron hydrogens by $\mathrm{H_t}$ to differentiate them from the bridge hydrogen, $\mathrm{H_{br}}$. A value of 3.7

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* To whom correspondence should be addressed at the University of Southern California.

(1) K. Hedberg and A. J. Stosick, *J. Amer. Chem. Soc.*, **74**, 954 (1952).

Table I. Frequencies of Assigned Low-*J* Transitions in $(CH_3)_2NB_2H_5$ (MHz)[a]

	Normal ^{11}B		1-^{10}B		1,2,3,4,5-d_5		1,2,3,4,5-d_5, ^{10}B		2,3,4,5-d_4	
Transitions	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$
$1_{01} \leftarrow 0_{00}$	8,923.06	−0.16	9,067.34	+0.49						
$2_{02} \leftarrow 1_{01}$	17,452.20	+0.11	17,678.71	−0.21	15,295.17	+0.04	15,454.47	0.00	15,648.14	+0.11
$2_{11} \leftarrow 1_{10}$	18,700.49	+0.19	19,052.69	−0.18	15,951.98	−0.26	16,177.97	−0.03	16,416.26	+0.23
$2_{12} \leftarrow 1_{11}$	16,992.45	−0.11	17,214.54	+0.02	14,959.0	+0.3	15,103.8	+0.2	15,272.26	−0.11
$3_{21} \leftarrow 2_{20}$	27,991.22	+0.04	28,571.02	+0.13	23,738.51	−0.04	24,094.80	+0.02	24,435.32	+0.07
$3_{03} \leftarrow 2_{02}$	25,548.15	+0.03	25,830.40	+0.21	22,627.85	−0.05	22,827.68	+0.02	23,097.40	+0.05
$3_{12} \leftarrow 2_{11}$	27,712.14	+0.01	28,177.26	−0.06	23,805.73	+0.02	24,121.82	+0.02	24,471.67	+0.03
$3_{13} \leftarrow 2_{12}$	25,279.77	+0.03	25,582.28	−0.10	22,349.90	+0.02	22,553.68	+0.02	22,801.32	+0.03
$3_{22} \leftarrow 2_{21}$	26,769.55	−0.10	27,200.38	−0.16	23,183.31	+0.08	23,461.15	−0.07	23,766.16	−0.14
$4_{22} \leftarrow 3_{21}$					31,861.37	−0.05	32,335.65	−0.65	32,806.39	−0.46
$4_{04} \leftarrow 3_{03}$	33,541.78	−0.03	33,900.55	−0.37	29,826.14	−0.32	30,069.26	−0.07	30,404.20	−0.12
$4_{31} \leftarrow 3_{30}$					31,344.81	+0.09	31,795.5	−0.3	32,227.71	−0.34
$4_{13} \leftarrow 3_{12}$	36,218.82	−0.17	36,716.79	−0.42	31,470.38	−0.36	31,841.38	−0.41	32,292.48	+0.07
$4_{32} \leftarrow 3_{31}$	36,233.0	−0.2			31,154.60	+0.44	31,559.0	−0.1	31,981.32	−0.03
$4_{14} \leftarrow 3_{13}$	33,444.62	−0.22	33,819.63	−0.25	29,673.88	−0.38	29,929.86	+0.09	30,251.56	−0.23
$4_{23} \leftarrow 3_{22}$	35,369.50	+0.06			30,782.75	−0.24	31,131.98	−0.32	31,530.82	+0.48

[a] Lines reported to 0.01 MHz have been measured to ±0.05 MHz. Lines reported to 0.1 MHz have been measured to ±0.2 MHz. Uncertainties do not reflect unresolved quadrupole splittings.

Table II. Transition Frequencies for the ^{15}N Isotopes of $(CH_3)_2NBH_5$ (MHz)

	^{15}N-^{11}B		^{15}N-^{10}B-^{11}B	
Transition	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$	ν_{obsd}	$\nu_{obsd} - \nu_{calcd}$
$3_{21} \leftarrow 2_{20}$	27,989.64	0.00	28,571.00	+0.19
$3_{03} \leftarrow 2_{02}$	25,547.95	+0.03	25,830.39	+0.18
$3_{12} \leftarrow 2_{11}$	27,711.21	−0.02	28,177.11	+0.02
$3_{13} \leftarrow 2_{12}$	25,279.32	−0.03	25,582.53	+0.02
$3_{22} \leftarrow 2_{21}$	26,768.83	+0.05	27,200.13	−0.38

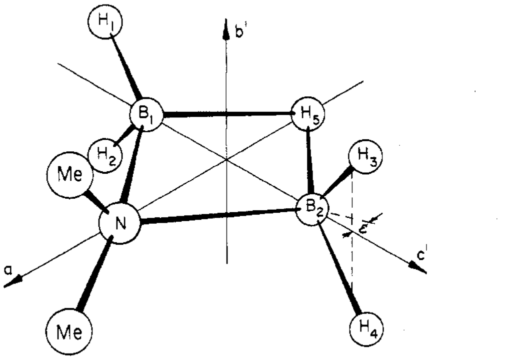

Figure 1. The orientation of the axes in *N,N*-dimethylaminodiborane. Two axes parallel to *b* and *c* are given for clarity. The center of mass is approximately through the nitrogen atom.

kcal/mol was obtained for the barrier to internal rotation of the methyl groups from the ir and Raman spectra[2-4] and from a calorimetric determination of the total entropy.[5] However, the ground-state rotational transitions that we have observed are insensitive to a barrier in this range, and an assignment of the excited torsional states could not be achieved. Therefore, we have been unable to determine the barrier height from the pure rotational spectrum. However, we were able to determine the bond distances and angles more accurately than in the original electron diffraction study. Also, the boron-hydrogen bond lengths which were assumed in the original work have been measured.

Experimental Section

A sample of $(CH_3)_2NB_2H_5$ was supplied by Dr. J. Basi and Professor A. Burg. Burg also prepared the ^{15}N-labeled sample by conventional methods. Deuterated samples were prepared by exchanging the normal species with deuterium gas for 24 hr at 80–90° in a sealed tube. All spectra were observed with a conventional 100-kHz Stark modulated spectrometer with the sample cell at −78°.

Spectrum Assignment

Model calculations indicated that the molecule would have an *a* dipole moment. Assuming C_{2v} symmetry, the other two dipole moment components are zero. The spectrum was very intense and rich. The low-*J* R branch transitions and numerous Q branch series were readily assigned by observation of their Stark effects. A dense background of weak absorption lines, probably due to numerous vibrational satellites, less abundant isotopic species, and unassigned high *J* transitions, prevented an assignment of the torsional satellites and of the less abundant deuterated species.

The spectra of seven isotopic species of $(CH_3)_2NB_2H_5$ and one excited state of the normal species were easily assigned with *a*-type selection rules as predicted. Attempts to find the spectrum of 1,2,3,4-d_4-DMADB were unsuccessful. The frequencies of the assigned low-*J* lines are listed in Tables I and II. Q branch transitions up to $J = 41$ have been assigned. The frequencies of these lines are available from the authors. The values of the ground-state rotational constants were calculated by a least-squares fitting of the five $J = 3 \leftarrow 2$ transitions. The final values of the rotational constants and moments of inertia for all isotopes are given in Table III.

Dipole Moment

The dipole moment has been determined from the Stark displacements of the $3_{03} \leftarrow 2_{02}, M = 2$; $3_{13} \leftarrow 2_{12}, M = 2$ and $M = 1$ transitions. The effective Stark cell spacing was measured using the $J = 2 \leftarrow 1$ line of OCS with Muenter's[6] value of 0.71521 D for the dipole moment. Since the molecule is known to have C_{2v} symmetry, the dipole moment is entirely along the *a* axis. Therefore, holding $\mu_b = \mu_c = 0$, one obtains for the dipole moment the values given in Table IV from each of the three lines. The dipole moment is thus 2.78 ± 0.02 D.

Molecular Structure

The coordinates of the boron atoms were independently determined in the principal axis system by using the Kraitchman method[7] with the normal, deuterated and ^{15}N-

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(2) D. E. Mann, *J. Chem. Phys.*, **22**, 70 (1954).
(3) D. E. Mann, *J. Chem. Phys.*, **22**, 762 (1954).
(4) J. E. Stewart, *J. Chem. Phys.*, **23**, 2204 (1955).
(5) G. T. Furukawa, *et al.*, *J. Res. Nat. Bur. Stand.*, **55**, 201 (1955).
(6) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).
(7) J. Kraitchman, *Amer. J. Phys.*, **21**, 17 (1953).

Table III. Rotational Constants and Moments of Inertia of the Isotopic Species of $(CH_3)_2NB_2H_5$[a]

Isotopic species	*A*, MHz	*B*, MHz	*C*, MHz	I_a, amu Å^2	I_b, amu Å^2	I_c, amu Å^2
$^{10}B^{11}BH_5$	5813.08	4993.011	4073.837	86.9377	101.2167	124.0541
$^{11}B^{11}BH_5$	5749.66	4888.543	4034.675	87.8967	103.3797	125.2582
$^{11}B^{11}BD_5$	4977.96	4112.250	3615.493	101.5227	122.8953	139.7807
$^{10}B^{11}BD_5$	5025.09	4178.799	3641.608	100.5705	120.9381	138.7783
$^{11}B^{11}BD_4H_t$	5162.15	4246.965	3675.136	97.9003	118.9970	137.5122
$^{15}N^{10}B^{11}BH_5$	5812.72	4992.952	4073.886	86.9431	101.2179	124.0526
$^{15}N^{11}B^{11}BH_5$	5749.87	4888.287	4034.642	87.8934	103.3851	125.2592

[a] Estimated errors in the rotational constants are $\Delta A = \pm 0.2$ MHz, $\Delta B = \Delta C = \pm 0.02$ MHz. The conversion factor to convert MHz to amu Å^2 was 5.05376×10^5 MHz amu Å^2.

Table IV. Stark Effect in $(CH_3)_2NB_2H_5$

Transition	$10^5 \Delta\nu/E^2$, MHz(cm/V)^2		μ_a, D
$3_{03} \leftarrow 2_{02}, M = 2$	1.414		2.78 ± 0.03
$3_{13} \leftarrow 2_{12}, M = 1$	1.915		2.77 ± 0.03
$3_{13} \leftarrow 2_{12}, M = 2$	8.265		2.79 ± 0.03
		Av	2.78 ± 0.02

substituted molecules as reference species and with the assumption that the molecule has C_{2v} symmetry. The B-B distance obtained in all three cases agreed to within ±0.002 Å. No change is noted in the B-B distances on deuteration. Bartell and Carroll's[8] results for diborane similarly showed no measurable change in the B-B distance upon deuteration. Since the nitrogen atom was very close to the center of mass, this atom was not precisely located. The coordinates are given in Table V.

The moments of inertia of the normal, 1,2,3,4,5-d_5, and 2,3,4,5-d_4 species were used to locate the hydrogen atoms. Again C_{2v} symmetry was assumed. The abundance of the bridge-substituted species is optimally only 5% and could not be assigned since the region of predicted low-*J* transitions was cluttered with numerous weak lines.

The terminal hydrogen positions were determined by the Kraitchman method from the d_5 and 2,3,4,5-d_4 species. The bridge hydrogen position may be determined from these two species and the normal species using the following relationships.

If C_{2v} symmetry is assumed

$$\frac{\Delta I_b + \Delta I_c - \Delta I_a}{2} = \Delta m(4a_t^2 + a_{br}^2) + \frac{(\Delta m)^2}{M - 5\Delta m}[4a_t + a_{br}]^2 \quad (1)$$

$$\frac{\Delta I_a + \Delta I_c - \Delta I_b}{2} = 4\Delta m b_t^2 \quad (2)$$

$$\frac{\Delta I_a + \Delta I_b - \Delta I_c}{2} = 4\Delta m c_t^2 \quad (3)$$

where the ΔI's are changes in moments of inertia; Δm is the change in isotopic mass; M is the total mass of the reference species; a_t, b_t, c_t are the coordinates of the terminal hydrogens; and a_{br} is the only nonzero coordinate of the bridge hydrogen. From the first of these equations and the *a* coordinate of the terminal hydrogen, the bridge hydrogen position may be determined. The perdeuterated molecule is used as the reference species. The *b* and *c* coordinates of the terminal hydrogens may be determined independently from eq 2 and 3 and these values also given in Table V are respectively 0.005 Å greater and 0.01 Å smaller than those determined by the single substitution.

Table V. Coordinates Determined for $(CH_3)_2NB_2H_5$[a]

Atom	Isotopic species used	*a*, Å	*b*, Å	*c*, Å
H_t	$^{11}B_2D_5$ and $^{11}B_2D_4H_t$	1.181 ± 0.001	1.030 ± 0.002	1.531 ± 0.001
	$^{11}B_2D_5$ and $^{11}B_2H_5$		1.036 ± 0.001	1.521 ± 0.001
H_{br}	$^{11}B_2D_5$, $^{11}B_2H_5$ and $^{11}B_2D_4H_t$	1.981 ± 0.005[b]	0.00[b]	0.00[b]
B	$^{11}B_2D_5$ and $^{10}B^{11}BD_5$	1.105 ± 0.002	0.00[b]	0.959 ± 0.002
	$^{11}B_2H_5$ and $^{10}B^{11}BH_5$	1.009 ± 0.002	0.00[b]	0.958 ± 0.002

[a] The errors given result from assuming uncertainties in the rotational constants of $\Delta A = \pm 0.2$ MHz and $\Delta B = \Delta C = \pm 0.02$ MHz for all species. [b] C_{2v} symmetry assumed.

This discrepancy is very likely due to the fact that zero-point vibrational effects on b^2 and c^2 of the bridge hydrogen are neither taken into account in eq 2 and 3 nor canceled out. It is felt that the effects of zero-point vibrations are minimized by using a single substitution in the d_5 species. Thus, values of *b* and *c* for the terminal hydrogens which are used in the final structure determination are those derived from the single substitution.

With the positions of the hydrogens and borons known, the carbon and nitrogen were determined by fitting the moments of inertia with an assumed methyl group structure. All the calculated coordinates are given in Table V.

Discussion

The structural parameters are compared to those of related compounds in Table VI. The listed uncertainties in the substitution parameters include consideration of the effects of zero-point vibrations. In addition, uncertainties in the structural parameters determined by fitting the moments of inertia include effects of varying the assumed structure of the methyl group. For those parameters which have been determined by both microwave and electron diffraction techniques the agreement is well within experimental uncertainties, but the microwave results are probably more accurate. The boron-hydrogen bond lengths and angles have been determined for the first time. In spite of the fact that the $(CH_3)_2N$ group contributes an additional electron pair to the diborane structure, the structure of the terminal BH_2 group is only slightly altered. The H_t-B distance and H_t-B-H_t angle are the same as in diborane to within the combined experimental uncertainties. It can be shown that the shrinking of the B-H distance on deuteration leads to the calculation of a short B-H distance if the Kraitchman equations are used. Such changes may be expected to be in the range of 0.003-0.005 Å. The value in Table VI is the result of using Kraitchman's equations. The uncertainty takes into consideration the changes in length on deuteration. Although the B-B distance

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(8) L. S. Bartell and B. L. Carroll, *J. Chem. Phys.*, **42**, 1135 (1965).

Table VI. Final Molecular Parameters for $(CH_3)_2NB_2H_5$

Parameter	$(CH_3)_2NB_2H_5$ This work	$(CH_3)_2NB_2H_5$ Ref 1	$H_2NB_2H_5$ Ref 2	B_2H_6 Ref 7
B-B, Å	1.916 ± 0.004	1.92 ± 0.11	1.93 ± 0.10	1.775 ± 0.003
$B-H_t$, Å	$1.191 \begin{smallmatrix}+0.010\\-0.003\end{smallmatrix}$		1.15 ± 0.09	$1.196 \begin{smallmatrix}+0.008\\-0.006\end{smallmatrix}$
$B-H_{br}$, Å	1.365 ± 0.006			$1.339_3 \begin{smallmatrix}+0.002\\-0.006\end{smallmatrix}$
B-N, Å	1.544 ± 0.010[a]	1.554 ± 0.026	1.564 ± 0.026	
C-N, Å	1.488 ± 0.010[a]	1.483 ± 0.029		
H_tBH_t, deg	119.6 ± 0.5			120.2 ± 1.8
$BH_{br}B$, deg	89.1 ± 0.9			83.0 ± 0.3
BNB, deg	76.8 ± 1[a]	76.4 ± 5.5	76.2 ± 2.8	
CNC, deg	110.0 ± 1[a]	111.5 ± 2.5		
ϵ,[b] deg	16.7 ± 1		15 ± 20	

[a] A tetrahedral methyl group with a C-H bond length of 1.091 Å has been assumed. The uncertainty in these parameters includes a ±0.01-Å uncertainty in the C-H length as well as those listed in the table. [b] ϵ is the angle made by the BH_2 plane and the plane perpendicular to the C_{2v} symmetry axis.

is 0.14 Å greater than that in diborane the $B-H_{br}$ distance is increased by only 0.03 Å.

The B-H-B angle, however, is increased by 6.1°. The primary effect of the increase in B-B distance is thus an increase of the B-H-B angle rathen than an increase in the B-H bond length. In order for the B_2H_5 group to accommodate the large nitrogen atom the B-H-B angle must increase. The overall effect is similar to opening a rigid molecule in the BNB plane using the bridge hydrogen as a hinge. As a result the BH_2 groups are tilted from the plane perpendicular to the symmetry axis by 16.7 ± 1°. This tilt is called ϵ in Table IV and is illustrated in Figure 1.

While the C-N-C angle is very close to tetrahedral, the B-N-B angle on the other hand is only 76.8°. Hence the B-N bonding orbitals probably lie in the BNBH plane, but subtend a larger angle than the B-N-B angle of 76.8°. This is similar to the "banana bonds" hypothesized in cyclopropane.

Registry No. $(CH_3)_2NB_2H_5$, 23273-02-1; $(CH_3)_2N^{10}B^{11}BH_5$, 39526-76-6; $(CH_3)_2N^{11}B^{11}BH_5$, 39526-77-7; $(CH_3)_2N^{11}B^{11}BD_5$, 39561-27-8; $(CH_3)_2N^{10}B^{11}BD_5$, 39561-28-9; $(CH_3)_2N^{11}B^{11}BD_4H_t$, 39526-78-8; $(CH_3)_2{}^{15}N^{10}B^{11}BH_5$, 39526-79-9; $(CH_3)_2{}^{15}N^{11}B^{11}BH_5$, 39526-80-2.

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E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Reaction of Phosphine with Some Transition Metal Complexes[1]

R. A. SCHUNN

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The syntheses and properties of the new phosphine complexes $Ni(PH_3)_x[P(OC_6H_5)_3]_{4-x}$ (x = 1-4), $Ni(PH_3)[P(C_6H_5)_3]_3$, $Ni(PH_3)_2[P(C_6H_5)_3]_2$, and $MnBr(CO)_3(PH_3)_2$ are described. The reaction of phosphine with $\{Ir[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$ (X = Cl, $B(C_6H_5)_4$) gives $\{Ir(PH_3)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]\}X$ at −70°, but a reversible, oxidative addition occurs at room temperature to give the hydridophosphide complexes $\{cis\text{-}IrH(PH_2)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2\}X$. The syntheses of the related complexes $\{trans\text{-}IrH(PH_2)[(CH_3)_2PCH_2CH_2P(CH_3)_2]\}X$ are also described. Infrared and nuclear magnetic resonance spectra of the new complexes are presented.

Introduction

The discovery[2,3] that phosphine (PH_3) forms stable complexes with transition metals has led to the isolation and characterization of many novel species. Examples of transition metal-phosphine complexes include $V(\pi\text{-}C_5H_5)(CO)_3(PH_3)$,[2,4] $Cr(CO)_{6-x}(PH_3)_x$ (x = 1,[2,4] 2,[3,5] 3,[6] 4[7]), $Mo(CO)_{6-x}(PH_3)_x$ (x = 1,[2,4] 2,[3,5,8] 3[8]), $W(CO)_{6-x}(PH_3)_x$ (x = 1,[2,4] 2,[3,5] 3[9]), $Mn(CO)_9PH_3$,[10] $cis\text{-}Mn(\pi\text{-}C_5H_5)(CO)_2\text{-}$

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[1] This work was presented in part at The Chemical Society of London symposium "Structure and Reactivity of Complexes of Transition Metals in Low Valence States," University of Sheffield, Aug 1969.

[2] E. O. Fischer, E. Louis, and R. J. J. Schneider, *Angew. Chem.*, **80**, 122 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 136 (1968).

[3] F. Klanberg and E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 3296 (1968). Many of the nickel and manganese complexes described here are covered by the claims of F. K. Klanberg, U. S. Patent 3,695,853 (Oct 3, 1972).

[4] E. O. Fischer, E. Louis, W. Bathelt, and J. Muller, *Chem. Ber.*, **102**, 2547 (1969).

[5] E. O. Fischer, E. Louis, and W. Bathelt, *J. Organometal. Chem.*, **20**, 147 (1969).

[6] E. O. Fischer, E. Louis, and C. G. Kreiter, *Angew. Chem., Int. Ed. Engl.*, **8**, 377 (1969).

[7] E. O. Fischer and E. Louis, *J. Organometal. Chem.*, **18**, P26 (1969).

[8] C. G. Barlow and G. C. Holywell, *J. Organometal. Chem.*, **16**, 439 (1969).

[9] L. J. Guggenberger, U. Klabunde, and R. A. Schunn, *Inorg. Chem.*, **12**, 1143 (1973).