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CONTRIBUTION FROM CHEMISTRY HALL,
IOWA STATE UNIVERSITY, AMES, IOWA

Phosphorus Complexes of Group III Acids. II. Infrared Spectra of Boron Complexes of Polycyclic Phosphites

BY C. W. HEITSCH AND J. G. VERKADE

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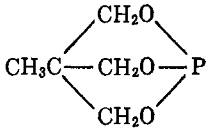
The infrared spectra from 650 to 5000 cm.$^{-1}$ of the polycyclic phosphites, 4-methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane ($C_5H_9O_3P$) and 1-phospha-2,8,9-trioxaadamantane ($C_6H_9O_3P$) as well as trimethylphosphite and some complexes of these ligands with BF_3, BH_3, BD_3, B_3H_7, and $B(CH_3)_3$ are reported and compared. The boron–phosphorus stretching frequency for these compounds falls in the region from 750 to 870 cm.$^{-1}$. It appears that the polycyclic ligands are better donors toward a BH_3 group than trimethylphosphite.

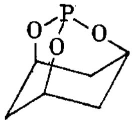
Introduction

While typical stretching modes have been reported for a variety of bond types, only one B–P stretching frequency has appeared in the literature, that of F_3PBH_3.[1] It was felt, therefore, that the following spectral study of some complexes of BH_3, BD_3, B_3H_7, BF_3, and $B(CH_3)_3$ would be of interest. The principal ligands used have been the polycyclic phosphites shown below.



$C_5H_9O_3P$

(4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane)



$C_6H_9O_3P$

(1-phospha-2,8,9-trioxa-adamantane)

Experimental

The preparation of the BH_3, BD_3, and B_3H_7 complexes of $C_5H_9O_3P$ are described elsewhere.[2] Details of the preparation of the corresponding adducts of $C_6H_9O_3P$ will be reported later.[3]

The boron trifluoride and boron trimethyl complexes were prepared by condensing a stoichiometric quantity of the acceptor onto a frozen 5–10% solution of the ligand in the appropriate solvent.[2,3] The mixtures so prepared were thawed, stirred, and scanned in the spectrometer. In the case of the $B(CH_3)_3$ complex with $C_5H_9O_3P$, a second solution, containing a tenfold excess of the acceptor, was scanned. Boron trimethyl was prepared as described by Brown.[4] Commercially available boron trifluoride from cylinders was purified after the fashion of Brown and Johannesen.[5]

The compound, $(CH_3O)_3PBH_3$, first reported by Reetz,[6] was prepared by the direct combination of diborane and trimethyl phosphite followed by vacuum distillation. A similar procedure was used for the preparation of $(CH_3O)_3PBD_3$.

Spectral grade solvents were used in all cases. For the BF_3 and $B(CH_3)_3$ complexes, the solvents were dried over P_4O_{10} and distilled *in vacuo* into the mixing vessel.

Spectra were scanned with a Perkin-Elmer Model 21 infrared spectrometer in the rock salt region. Where improved resolution was warranted, duplicate spectra were taken with a Beckman IR-7. The compound $C_5H_9O_3PBH_3$ also was examined with potassium bromide optics in a Perkin-Elmer Model 13 instrument.

Results and Discussion

It is significant that the vibrational frequencies of the polycyclic phosphites are relatively constant in their positions for the derivatives described here. This perhaps is due to the constraint imposed on the configuration of the skeleton in such polycyclic systems. The constancy of the bands of the ligand greatly facilitates the assignment of the new bands due to the acceptor moieties and to the B–P stretching mode. This point is illustrated in the spectra of $C_5H_9O_3P{=}O$ and $[Cu(C_5H_9O_3P)_4]NO_3$, which are shown in

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(1) R. C. Taylor and T. C. Bissot, *J. Chem. Phys.*, **25**, 780 (1956).

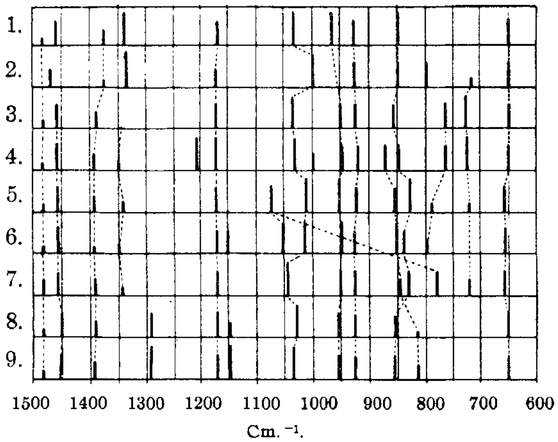
(2) C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962).

(3) J. G. Verkade and C. W. Heitsch, to be published.

(4) H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).

(5) H. C. Brown and R. B. Johannesen, *ibid.*, **72**, 2934 (1950).

(6) T. Reetz, *ibid.*, **82**, 5039 (1960).



1. $C_5H_9O_3P{=}O^a$
2. $[Cu(C_5H_9O_3P)_4]NO_3{}^f$
3. $C_5H_9O_3P^{a,e}$
4. $C_5H_9O_3PBF_3{}^{b,e}$
5. $C_5H_9O_3PBH_3{}^{a,c,d,f}$
6. $C_5H_9O_3PB_3H_7{}^{c,g}$
7. $C_5H_9O_3PBD_3{}^{a,c,d,f}$
8. $C_5H_9O_3P + B(CH_3)_3{}^a$ 1:1
9. $C_5H_9O_3P + B(CH_3)_3{}^a$ 1:10

[a] $CHCl_3$. [b] CH_2Cl_2. [c] CH_2Br_2. [d] CH_3CN. [e] CS_2. [f] Nujol mull. [g] KBr pellet.

Fig. 1.—Infrared spectra of $C_5H_9O_3P$ complexes.

Fig. 1 for purposes of comparison. It will be seen that the most significant differences between the phosphite on the one hand and the oxide and $CuNO_3$ derivatives on the other are bands in the region of 1340 cm.⁻¹. This has been assigned to the P=O stretch for the oxide.[7] For the cuprous nitrate derivative, a band is to be expected in this portion of the spectrum from the NO_3^- ion.[8]

In the case of trimethylphosphite and its derivatives, the lack of this same constancy is offset, somewhat, by the simplicity of the spectra. Thus, by comparison of spectra of the complexes with those of the ligands and with published reports of spectra of similar compounds, the assignments in Table I were made.

It can be seen from Table II that the values for the shift on deuteration reported here are consistent with those reported by other workers.

Table I

Spectra of Complexes[a]

Compound	ν (cm.⁻¹)	Assignment	Basis[b]
$C_5H_9O_3PBF_3$	1212, 1008	BF_3	$B^{9,12,13,14}$
	869	B–P stretch	A
$C_5H_9O_3PBH_3$	2400, 2355	B–H stretch	A, B^{10}
	1078	B–H def.	A, B^{10}, C
	855	B–P stretch	A, D
$C_5H_9O_3PBD_3$	1810, 1705	B–D stretch	A, B^{10}
	844	B–P stretch	A
	777	B–H def.	B^{10}
$C_5H_9O_3PB_3H_7$	2510, 2400	Term. B–H stretch	A, B^{10}
	2000	B–H–B stretch	B^{11}
	1053	B–H def.	B^{10}, C
	855	B–P stretch	A
$C_5H_9O_3PB(CH_3)_3$	1290, 1143	$B(CH_3)_3$	A, B^{12}
	811	B–P stretch	A
$C_6H_9O_3PBF_3$	1131	$B^{10}F_3$	$B^{9,12,13,14}$
	1115	$B^{11}F_3$	$B^{9,12,13,14}$
	939, 649	BF_3	$B^{9,12,13,14}$
	854	B–P stretch	A
$C_6H_9O_3PBH_3$	2400, 2350	B–H stretch	A, B^{10}
	1070	B–H def.	A, B^{10}
	860	B–P stretch	A
	665	BH_3 rock	B^{10}
$C_6H_9O_3PBD_3$	1827, 1719	B–D stretch	A, B^{10}
	865	B–D def.	A, B^{10}
	848	B–P stretch	A
$C_6H_9O_3PB_3H_7$	2530, 2470	Term. B–H stretch	A, B^{10}
	2000	Bridge B–H–B	A, B^{11}
	1153	B–H def.	A, B^{10}
	915	...	...
	868	B–P stretch	A
$C_6H_9O_3PB(CH_3)_3$	1295, 1147	$B(CH_3)_3$	A, B^{12}
	854	$B(CH_3)_3$	B^{12}
	833	B–P stretch	A
$(CH_3O)_3PBH_3$	2375, 2260	B–H stretch	A, B^{10}
	841, 827	...	...
	799	B–P stretch	A
$(CH_3O)_3PBD_3$	1795, 1691	B–D stretch	A, B^{10}
	975	...	...
	888	B–D def.	B^{10}
	835	...	...
	811	...	...
	759	B–P stretch	A

[a] Bands due to ligands have been omitted. [b] Basis: A = Internal consistency with other compounds included in this report. B = Comparison with similar compounds as reported by other authors. C = Fermi resonance. In both $C_5H_9O_3PBH_3$ and $C_5H_9O_3PB_3H_7$, a band usually found near 1035 cm.⁻¹ in the phosphite and other complexes appears at 1015 and 1012 cm.⁻¹, respectively. Accordingly, in $C_5H_9O_3PBD_3$, the isotopic substitution shifts the BH (or D) deformation mode to a lower frequency, breaking the resonance. The 1035 band of the phosphite appears normally in the BD_3 complex at 1040 cm.⁻¹. D = It will be noted that the 860 cm.⁻¹ band of $C_5H_9O_3P$ is somewhat sensitive to coördination, shifting varying amounts in the various derivatives. It is, however, of a

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[7] J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

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[9] J. Goubeau and H. Mitschelen, *Z. phys. Chem.* (Frankfurt) **14**, 61 (1958).

[10] (a) R. C. Taylor and C. L. Cluff, *Nature*, **182**, 390 (1958); (b) R. C. Taylor and C. L. Cluff in R. W. Parry, R. C. Taylor, and C. E. Nordman, "The Chemistry of Boron Hydrides and Related Hydrides," WADD Tech. Rept. 60-262, April, 1960, Univ. of Michigan.

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[12] W. J. Lehmann, C. O. Wilson, and I. Shapiro, *ibid.*, **28**, 777 (1958).

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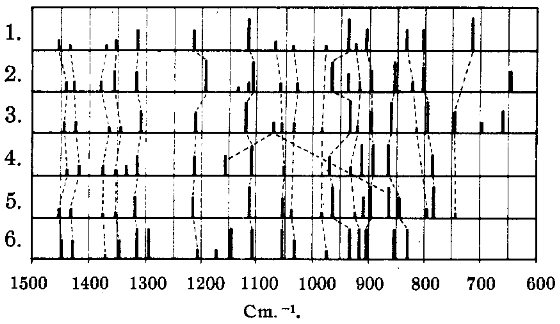
TABLE II

B–H STRETCHING FREQUENCIES

	Asymmetric			Symmetric		
Ligand	BH_3(cm.$^{-1}$)	BD_3(cm.$^{-1}$)	ν_H/ν_D	BH_3(cm.$^{-1}$)	BD_3(cm.$^{-1}$)	ν_H/ν_D
NH_3[10]	2316	1743	1.329	2263	1641	1.379
$N(CH_3)_3$[10]	2330	. . .	. . .	2268	. . .	. . .
$(CH_3O)_3P$	2375	1795	1.323	2260	1691	1.336
$C_5H_9O_3P$	2400	1810	1.326	2355	1705	1.381
$C_6H_9O_3P$	2400	1827	1.314	2350	1719	1.367
CO[16]	2434	1825	1.334	2380	~1700	. . .
PF_3[1]	2455	1845	1.331	2385	1717	1.389

characteristic shape, being quite sharp in a region of broad peaks, and is easily identified at 830 cm.$^{-1}$ in both $C_5H_9O_3PBH_3$ and $C_5H_9O_3PBD_3$.



1. $C_6H_9O_3P^{a,b,d,e}$
2. $C_6H_9O_3PBF_3{}^{b}$
3. $C_6H_9O_3PBH_3{}^{a,b,d,e}$
4. $C_6H_9O_3PB_3H_7{}^{a,c,e}$
5. $C_6H_9O_3PBD_3{}^{a,b,d,e}$
6. $C_6H_9O_3PB(CH_3)_3{}^{a}$

[a] $CHCl_3$. [b] CH_2Cl_2. [c] CH_2Br_2. [d] CH_3CN. [e] KBr pellet.

Fig. 2.—Infrared spectra of $C_6H_9O_3P$ complexes.

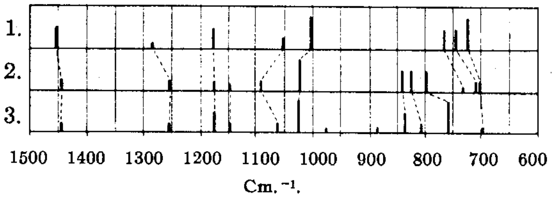
It has been observed that, to a first approximation, B–H stretching frequencies in BH_3 complexes can be used as a criterion of the donor–acceptor bond strength, decreasing as the donor ability of the ligand increases.[15] This rough rule of thumb seems to apply to the phosphite complexes in relation to the more stable nitrogen adducts and the highly dissociated complexes of CO and PF_3. However, small differences are not so easily correlated. The comparison is particularly poor in the case of the trimethylphosphite adduct. Generally speaking, however, the phosphite complexes seem to be intermediate in stability between the amine complexes and the relatively unstable adducts of PF_3 and CO. This is in agreement with earlier conclusions.[2] Thus, this criterion seems to be applicable in comparisons of ligands with large differences in donor abilities.

It is believed that B–P stretching frequency is a much more sensitive criterion of bond strength, if one of less applicability. These data are collected in Table III. It can be seen that the most probable values for this mode lie in the region from 750 to 870 cm.$^{-1}$ for phosphites. This is markedly higher than in the case of F_3PBH_3.[1] In this connection it is notable that the B–P stretching frequencies are lower for the $B(CH_3)_3$ complexes than for the better acceptors, BF_3, BH_3, and B_3H_7. Likewise, in the case of trimethylphosphite, where steric interaction between the methyl groups and the BH_3 moiety should weaken the B–P link, the stretching vibration appears at a lower frequency than in the case of the constrained, polycyclic phosphites.

TABLE III

PHOSPHORUS–BORON STRETCHING FREQUENCIES

Acceptor	$C_5H_9O_3P$ (cm.$^{-1}$)	$C_6H_9O_3P$ (cm.$^{-1}$)	$(CH_3O)_3P$ (cm.$^{-1}$)	PF_3[1] (cm.$^{-1}$)
BF_3	869	854	. . .	. . .
BH_3	855	860	799	607
BD_3	844	848	759	. . .
B_3H_7	855	868	. . .	. . .
$B(CH_3)_3$	811	833	. . .	. . .



1. $(CH_3O)_3P^{a}$
2. $(CH_3O)_3PBH_3{}^{b}$
3. $(CH_3O)_3PBD_3{}^{b}$

[a] Neat. [b] CH_3Br.

Fig. 3.—Infrared spectra of $(CH_3O)_3P$ complexes.

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(15) R. C. Taylor, private communication.

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