methyl resonance signal increase in the order of decreasing size of the free anion in the series $((CH_3)_3PtX)_4$ (X = Cl, Br, I, OH).[9]

No nmr data are reported for compounds having a nonbridging Pt–O–H group; however we can compare our results with those of sulfhydrylhydridobis(triphenylphosphine)platinum(II)[10] which has a nonbridging Pt–S–H group. The SH proton resonance occurs at τ 11.44 with $J_{^{195}Pt-S-H} = 43.8$ Hz. This difference illustrates a reduction in the "s" character of the Pt–S–H orbitals in the tetrameric Pt(IV) compound compared to the monomeric Pt(II) compound. In general "s" character in Pt(IV) compounds should be about 0.67 of that in Pt(II) compounds.[11] The remaining difference is easily ascribed to the rehybridization discussed above.

Table I summarizes the vibrational frequencies of both tetrameric hydroxytrimethylplatinum(IV) and sulfhydryltrimethylplatinum(IV) and lists the corresponding assignments. The assignments are as reported by Rennick[2] as modified by the later work of Bulliner and Spiro[3] for hydroxytrimethylplatinum(IV). The peak at 541 cm^{-1} was assigned to the SH rocking mode by analogy to the assignment of the 719-cm^{-1} line of hydroxytrimethylplatinum(IV) by Spiro and coworkers to the OH bending mode and by consideration of the mass difference between oxygen and sulfur which would shift the rocking mode to lower wave number. The calculated position of this band is 497 cm^{-1}. The only peak of the required intensity in that region is the 541-cm^{-1} line. This band obscures the platinum–carbon stretching region; however the weak shoulder at 563 cm^{-1} may be assigned to the asymmetric PtC stretch. The symmetric PtC stretch is hidden beneath the SH rocking mode.

TABLE I

INFRARED SPECTRUM OF SULFHYDRYLTRIMETHYLPLATINUM(IV) (CM^{-1}) [a]

$((CH_3)_3PtSH)_4$	$((CH_3PtOH)_4$[2,3]	Assignment
(250 m)	365 vs	Pt–X str
(262 m)	382 m, sh	Pt–X str
541 m	721 vs	X–H bend
. . .	570 vw, sh	Sym Pt–C str
563 w, sh	590 w	Asym Pt–C str
850 w	854 b, m, sh	Pt–CH_3 rock
857 w	877 b, m	Pt–CH_3 rock
1108 vw	1160 mw	Combination
1218 s	1246 vvs	Nontotal sym CH def
1253 s	1280 w	Total sym CH def
. . .	1344 b, w, sh	
1383 vw	1381 b, m, sh	Sym CH def
1409 m	1411 m	Sym methyl def
1421 m	1427 b, m, sh	Asym methyl def
2450 vw	. . .	2 × 1218 = 2436
2513 w	. . .	2 × 1253 = 2506
2537 m	3584 m	X–H str
2796 w	2805 b, w	Overtone of asym methyl def
2894 s	2899 s	Sym C–H str
2954 s	2959 s	Unsym C–H str

[a] X is either S or O. Abbreviations: v, very; s, strong; m, medium; sh, shoulder; b, broad; w, weak. Parentheses indicate data taken on polyethylene plates below 300 cm^{-1}.

The medium peak at 2537 cm^{-1} was assigned to SH stretch since this vibration is usually seen as a weak to medium band between 2590 and 2540 cm^{-1} in mercaptans and thiophenols.[12] Incorporation of the sulfur atom as a tetracoordinate ligand would tend to weaken the sulfur–hydrogen bond and the vibration would occur at slightly lower wave number. The weak peak at 2513 cm^{-1} is assigned as the overtone of the Pt–CH_3 rock at 1253 cm^{-1}. The very weak peak at 2450 cm^{-1} could be the overtone of the 1218-cm^{-1} vibration. The other bands were assigned in strict analogy to the assignments reported by Rennick[2] for hydroxytrimethylplatinum(IV).

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The Dipole Moment of Dimeric Chlorophospha(III)-*o*-carborane

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The reaction of 1,2-dilithio-1,2-dicarbaclosododecaborane(12) with phosphorus trichloride yields dimeric chlorophospha(III)-*o*-carborane $(B_{10}H_{10}C_2PCl)_2$. This molecule contains two *o*-carborane icosahedral units with the carbon atoms of each incorporated in a six-membered ring containing the two phosphorus atoms (see Figure 1).[1] Boron atoms 9, 12, 9′, and 12′, the four carbon atoms (1, 2, 1′, 2′), and the two phosphorus atoms all appear to lie very nearly in a plane.[2] Therefore, when the positions of the chlorine atoms are considered, two isomers of the compound are possible.

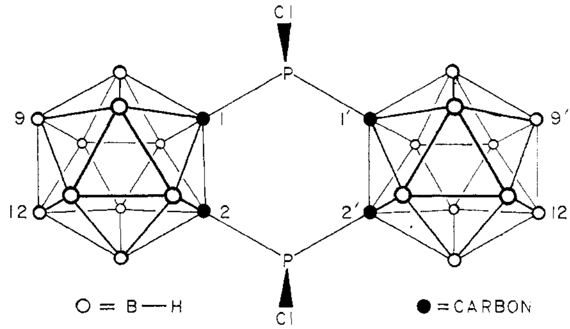

Figure 1.—*cis* isomer of dimeric chlorophospha(III)-*o*-carborane.

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[1] R. P. Alexander and H. Schroeder, *Inorg. Chem.*, **2**, 1107 (1963).

[2] R. Schaeffer, unpublished X-ray crystallographic data.

One has the chlorine atoms *cis* to this plane and the other has them *trans*. Furthermore, the *cis* isomer should have a permanent dipole moment while the *trans* isomer should not.

The physical properties of $(B_{10}H_{10}C_2PCl)_2$ indicate that only one isomer is isolated from the synthesis[1,3] and X-ray crystallographic data show this to be the *cis* isomer.[2] The dipole moment of this compound was determined to see if this isomer is also the one that exists in solution.

Experimental Section

The exact procedure for obtaining the data has been described previously.[4] For this investigation, ten independent solutions of the dimeric chlorophospha(III)-*o*-carborane in dry cyclohexane were prepared and the dielectric constant and refractive index of each solution was determined at 25.0°.

Results and Discussion

The dipole moment, given below, was calculated using eq 1, which is a modification of the Guggenheim method.[5] The error indicated is experimental. There is a possible error of up to 10% inherent in the method of calculation.[6] The values of ϵ_1, α_ϵ, and α_n are 2.0154, 0.507 ± 0.016, and 0.397 ± 0.011, respectively. The dipole moment calculated from these data is 0.73 ± 0.09 D.

$$\mu^2 = (\text{constant})\left(\frac{1}{d_1(\epsilon_1 + 2)^2}\right)(\alpha^\epsilon - \alpha_n)M_2 \qquad (1)$$

A dipole moment calculated by the above procedure is corrected for the electronic contribution to the total polarization. However, the atomic polarization has been neglected as is common practice.[5a]

The dipole moment of 0.73 D indicates that dimeric chlorophospha(III)-*c*-carborane exists in solution as the *cis* isomer in agreement with the results obtained in the crystallographic study of the solid. Of course, since the above dipole moment is rather small, there is a possibility that the *trans* isomer is also present in solution and that the *cis* isomer crystallizes out, preferentially, to give only one isomer in the solid phase.

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(4) R. Maruca, H. Schroeder, and A. W. Laubengayer, *Inorg. Chem.*, **6**, 572 (1967).

(5) (a) J. W. Smith, "Electric Dipole Moments," Butterworth and Co. Ltd., London, 1955; (b) F. Oehme and H. Wirth, "The Determination of the Molecular Dipole Moment," Kahl Scientific Instrument Corp., El Cajon, Calif.

(6) In eq 1, the constant equals 1.474×10^{-1} D^2 at 25.0°; d_1 is the density of the solvent and is 0.7742 g/ml at 25.0° for cyclohexane; ϵ_1 is the dielectric constant of the solvent and is taken as the limiting value of the dielectric constant of the solutions as the weight fraction solute approaches zero; α_ϵ and α_n are the slopes of the graph of the dielectric constant (ϵ) and refractive index squared ($(n_D)^2$) plotted as a function of weight fraction solute; and M_2 is the molecular weight of the solute.

Correspondence

On Vibrational Assignments in Pentacoordinated Molecules and Gillespie–Nyholm Theory[1]

Sir:

In several recent papers, Holmes, *et al.*,[2,3] have discussed the ambiguity in assigning the e′ bending modes in trigonal-bipyramidal molecules. Holmes weighed the evidence for alternative interpretations and concluded that available information does not allow a firm resolution of the problem. In diagnosing the situation, Holmes advanced certain physical arguments which he interpreted as favoring assignment A [ν(equatorial in-plane bend) > ν(axial bend)] over assignment B [ν(eq) < ν(ax.)]. We believe that assignment B is superior, on the basis of (largely unpublished) electron diffraction analyses. Furthermore, we suggest that the arguments offered by Holmes in support of assignment A, while plausible, bear further scrutiny, since they run contrary to implications of the rather successful Gillespie–Nyholm theory of directed valence.[4,5] Therefore, it seems worthwhile to present the diffraction results and to review the discrepant points, showing how the appealingly simple electron pair repulsion theory gives insight into the force field.

The experimental evidence consists of a comparison between rms amplitudes of vibration as measured by gas-phase electron diffraction[6-11] and corresponding amplitudes calculated by Holmes[2] and others[12,13] from vibrational frequencies. It turns out that the amplitudes l_{ae} and l_{ee} calculated for axial–equatorial and equatorial–equatorial nonbonded distances are sensitive to the choice of assignments for the e′ bending

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(1) Research supported by a grant from the National Science Foundation.

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(10) H. B. Thompson and L. S. Bartell, unpublished data.

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