weeks earlier. Entry 12 in Table I indicates that dilution of the stock solution and an "equilibration" period of 45 min yields the same results as obtained without such an elapsed time. Entries 6 and 7 in the same table demonstrate that identical results are obtained when an aliquot of the concentrated Co(III) stock solution is introduced into the reaction mixture as when an aliquot of a sodium azide solution is injected into a dilute (*ca.* 7×10^{-4} *M*) Co(III) solution prepared from cobalt(III) carbonate.

All the results presented are correlated by the empirical form of the rate law presented in eq 1. Most of the results were obtained under experimental constraints of temperature, acidity, ionic strength, and initial concentrations of thereactants (Co(III) and HN_3) similar to those reported by Wells and Mays.[5] The empirical form of the rate law proposed by these authors, eq 2, however, is not consistent with the data that have been presented.

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Synthesis and Spectra of Sulfhydryltrimethylplatinum(IV)

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Structural conclusions have been made for tetrameric hydroxytrimethylplatinum(IV) on the basis of nmr and infrared spectra.[2,3] Neutron[4] and X-ray[5,6] diffraction have recently confirmed the tetrameric structure in the solid state. A most interesting feature of the nmr spectrum of this compound is the splitting pattern of the OH proton signal. Each oxygen is bound to three platinum atoms (33.8% ^{195}Pt, $I = {}^1/_2$) resulting in a seven-line pattern ($J_{Pt-O-H} = 11.2$ Hz, τ 11.53).

It was thought interesting to synthesize and examine the spectra of the sulfur analog.

Experimental Section

Sulfatobis(trimethylplatinum(IV)) tetrahydrate was prepared by the method of Pope and Peachey.[7] Sulfatobis(trimethylplatinum(IV)) is water soluble and insoluble in organic solvents, while it was presumed the sulfhydryl derivative would be water insoluble and soluble in organic solvents (similarly to the halo, thiocyanato,[8] and hydroxy derivatives). Benzene was added to an aqueous solution of the sulfato compound and a stream of gaseous hydrogen sulfide passed through the vigorously stirred mixture for 24 hr. The sulfhydryl derivative was extracted into the organic phase which was separated and evaporated to yield a small quantity of brown powder. A yellow crystalline material resulted upon recrystallization from benzene. *Anal.* Calcd for $C_3H_{10}PtS$: C, 13.18; H, 3.69; Pt, 71.38; S, 11.73. Found: C, 13.36; H, 3.64; Pt, 71.20; S, 11.84. Because of the extremely low solubility (and anticipated high molecular weight) an accurate molecular weight determination could not be made.

Sulfhydryltrimethylplatinum(IV) was also prepared by the hydrolysis of the thioacetamide adduct of iodotrimethylplatinum(IV) and the direct reaction of hydroxytrimethylplatinum(IV) with H_2S; but in both of these reactions the product was contaminated with starting materials.

Infrared spectra were recorded as Nujol and fluorocarbon mulls on a Perkin-Elmer Model 621 spectrophotometer. Cesium bromide plates were used for the region above 300 cm^{-1} and polyethylene film was used in the region 200–300 cm^{-1}.

Nmr data were obtained for benzene solutions using a Varian HA-100 spectrometer. Chemical shifts were referred to the solvent and converted to τ units having $\tau(C_6H_6)$ 2.74.

Results and Discussion

The nmr spectrum of $((CH_3)_3PtSH)_4$ is quite similar to that of $((CH_3)_3PtOH)_4$. The methyl proton resonance occurs at τ 8.52 with $J_{^{195}Pt-C-H_3} = 73.4$ Hz. Corresponding values for $((CH_3)_3PtOH)_4$ are τ 9.04 and 78.6 Hz. The SH proton signal occurs at τ 13.29 with $J_{^{195}Pt-S-H} = 15.2$ Hz. Corresponding values for $((CH_3)_3PtOH)_4$ are τ 11.53 with $J_{^{195}Pt-O-H} = 11.2$ Hz. Due to the low solubility of $((CH_3)_3PtSH)_4$ only the three strongest lines of the SH multiplet could be observed (comprising 85.7% of the theoretical total intensity[2]). We can formulate no reasonable alternative explanation for these data, however, without invoking unexpected five-coordinate platinum species. The most logical explanation is that the structure of $((CH_3)_3PtSH)_4$ is analogous to $((CH_3)_3PtOH)_4$.

The result of increasing the size of the bridging atom is an increase in the bonding interaction with the bridging ligand. This is reflected in the increased "s" character in the Pt–S–H region compared to the Pt–O–H region. The increased chemical shift ("shielding") of the SH proton supports this conclusion as does the *decreased* chemical shift of the methyl protons and the *decreased* value of $J_{^{195}Pt-C-H_3}$ on going from $((CH_3)_3PtOH)_4$ to $((CH_3)_3PtSH)_4$.

$((CH_3)_3PtOH)_4$ has elongated Pt–O bonds of 2.20 Å[4] compared with 1.96 Å from the sum of covalent radii. The increase in bond length implies a rehybridization in the tetramer to provide optimum overlap at the increased distance. The introduction of more directional (pd) character decreases the "s" character of the platinum–bridging atom bond and correspondingly increases it in the Pt–C bond. It would be expected that the effect of increasing the size of the bridging atom would be a lessening of this perturbation which, in turn, should affect the values of the chemical shifts and coupling constants. The values for the chemical shifts of the

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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.

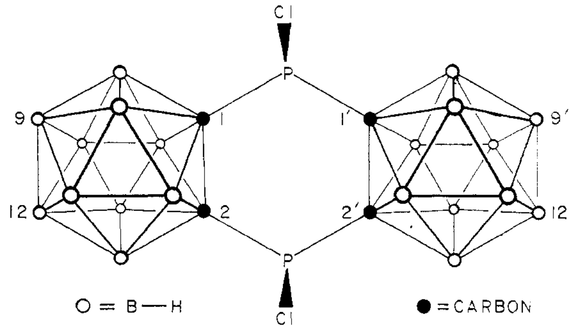

Figure 1.—*cis* isomer of dimeric chlorophospha(III)-*o*-carborane.

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