measurable (~5 Hz), but only a single coupling is observed in **2** or **4**. We assume this to be the coupling between nitrogens which are trans to each other in the square-planar Pt(II) complex and that the cis coupling is too small to be observed (<0.5 Hz).[9] (4) The observation of the directly bonded $^{15}$N–H couplings for the amine nitrogens in **1** and **3** demonstrates that exchange of the amine protons with $H_2O$ is slow on the NMR time scale (i.e., a proton resides on an amine nitrogen for ~10 ms or longer between exchanges) when these amines are complexed by Pt(II). This is in contrast to dilute aqueous solutions of the free amine where proton exchange with $H_2O$ is very rapid. This may indicate that availability of the amine-nitrogen lone-pair electrons is important for rapid proton exchange with $H_2O$, as has been suggested earlier.[10]

Another interesting aspect of the data presented here is a consistent trend in the amine-nitrogen $^{15}$N shift and $^{195}$Pt–$^{15}$N coupling constant to lower values on substitution of $H_2O$ by the stronger ligand, $^{15}$N-MeIm, at the other Pt(II) sites. A similar effect is seen at the $N_3$ nitrogen of $^{15}$N-MeIm in going from **6** to **5** or **2**. This is consistent with the expectation that replacement of $H_2O$ by the stronger amine ligands would lead to a weakening of the trans Pt–N bond.

Addressing the question of the applicability of $^{15}$N NMR to studies of the interaction of *cis*-diamine-diaquoplatinum(II) with biological systems, the data in Table I clearly indicate that such association with imidazole-nitrogen sites would lead to substantial changes in both the $^{15}$N shift and the $^{15}$N–$^{195}$Pt coupling for the amine nitrogen in the Pt(II) complex. At the same time, the imidazole nitrogen at the biological site would be expected to undergo a large diamagnetic shift (relative to its resonant frequency in the absence of Pt(II) complexation) and to display $^{195}$Pt satellites due to $^{195}$Pt–$^{15}$N coupling. From an experimental point of view, the effects on the amine nitrogens of the Pt(II) complex may be more readily observed since those nitrogens are easily $^{15}$N labeled and could probably be observed at millimolar concentrations with state-of-the-art NMR equipment. A possible limitation of this approach might be a lack of specificity in determining the particular kind of biological site attacked by the *cis*-diamine-diaquoplatinum(II) species. We are pursuing this question further by studying the $^{15}$N NMR properties of the amine nitrogens in a series of $^{15}$N-en-Pt(II) complexes with a variety of ligands at the remaining two coordination sites and will report these results at a later date.

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of this assumption by examining the $^{15}$N NMR parameters of the species dienPtX$^{2+}$ (dien = diethylenetriamine = $H_2N(CH_2)_2NH(CH_2)_2NH_2$; X = $H_2O$, MeIm) in which all three dien nitrogens would be $^{15}$N labeled.
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## Reactions at the Rhodium Vertex of a Rhodacarborane Cluster. Preparation, Crystal and Solution Structure, and Reactions of 3,3-$(Ph_3P)_2$-3-$(HSO_4)$-3,1,2-$RhC_2B_9H_{11}$·$O(C_2H_5)_2$

*Sir:*

Since our discovery[1] that the hydridorhodacarborane 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ (I) is an active catalyst for the isomerization and hydrogenation of olefins, we have explored the extensive chemistry of this cluster in depth, particularly with regard to the Rh vertex. As an example, the reaction of I with sulfuric acid generates $H_2$[2] and a novel metallocarborane species $(Ph_3P)_2(HSO_4)RhC_2B_9H_{11}$ (II). The addition of hydrogen gas or primary alcohols to solutions of II regenerates I, with accompanying elimination of sulfuric acid from the cluster. We report here the synthesis, crystal and solution structure, and reactivity of 3,3-$(Ph_3P)_2$-3-$(HSO_4)$-3,1,2-$RhC_2B_9H_{11}$·$O(C_2H_5)_2$ (II). It is of note that II represents the first reported metallocarborane containing a metal-oxygen bond.

To a solution of 2.0 g (2.62 mmol) of I in 100 mL of dichloromethane, 3 mL of $H_2SO_4$ (50 mmol) was added with rapid stirring. Evolution of $H_2$ was evident within 30 s and an orange precipitate formed. After 15 min the precipitate was separated by filtration, washed with $CH_2Cl_2$, and triturated with diethyl ether to produce bright orange crystals of II in 56% yield. Recrystallization from tetrahydrofuran (THF)–heptane affords $(Ph_3P)_2(HSO_4)RhC_2B_9H_{11}$·$OC_4H_8$. Anal. Calcd for $C_{42}H_{50}B_9RhP_2SO_5$: C, 54.30; H, 5.42; B, 10.47; Rh, 11.08; P, 6.67; S, 3.45. Found: C, 54.51; H, 5.71; B, 10.66; Rh, 11.29; P, 6.47; S, 3.42.

The 200-MHz $^1$H NMR of II in $Me_2SO$-$d_6$ shows a complex multiplet centered at $\delta$ 7.6 (area 30) due to the $Ph_3P$ ligands and a singlet at 5.45 (2) assigned to carborane C–H. Multiplets present at 3.55 (4) and at 1.75 (4) are due to the two sets of methylene protons present in $OC_4H_8$.

The 80.5-MHz $^{11}$B{$^1$H} NMR is uninformative, consisting of two broad resonances centered at $-9$ and $+5$ ppm relative to $BF_3O(C_2H_5)_2$. The 81.02-MHz $^{31}$P{$^1$H} NMR in THF/$Me_2SO$ (Figure 1) is temperature dependent and is discussed below. The infrared spectrum of II (Nujol) exhibits a band characteristic of terminal B–H bonds at 2550 cm$^{-1}$ in addition to absorbtions due to the coordinated dicarbollide and triphenylphosphine ligands. Three bands at 1150, 1050, and 800 cm$^{-1}$ are assigned to the bisulfate ligand.

II was found to react readily with $H_2$ gas to regenerate I and $H_2SO_4$. A solution of II, 200 mg (0.215 mmol) in 100 mL of THF, was treated with hydrogen gas (1 atm) for 10 min. An equal volume of water was added and the acid liberated was titrated potentiometrically with NaOH, giving an equivalent weight of 963 for II, calcd 931. Evaporation of the THF provided crystals of I in 82% of isolated yield. When deuterium gas was used,[3] I could be isolated in high yield and contained only a trace of Rh–H by IR ($\nu_{RhD}$ 1520 cm$^{-1}$). Similarly, II reacted rapidly with ethanol or propanol at 50 °C to produce I in quantitative yield and acetaldehyde or propionaldehyde,[4] respectively.
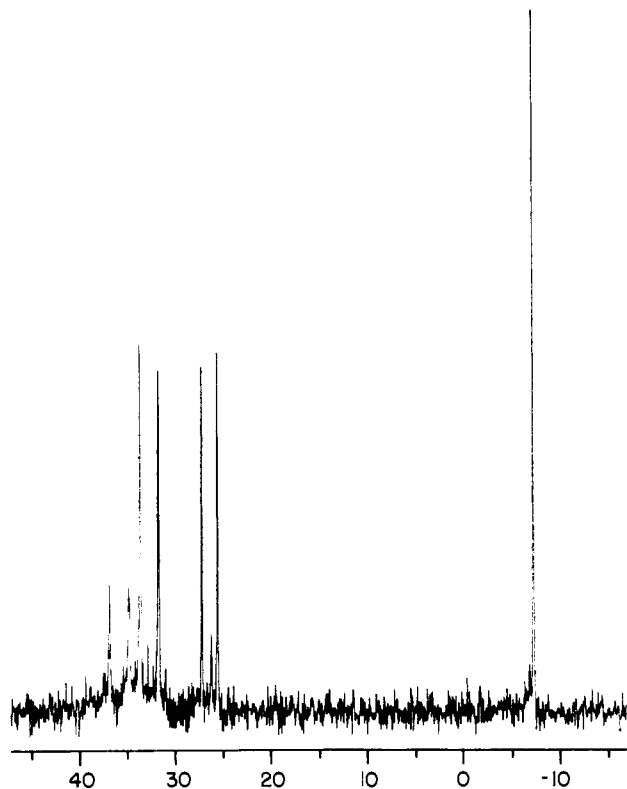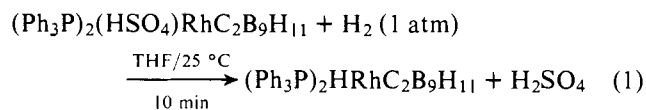
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Figure 1. The 81.02-MHz $^{31}P\{^1H\}$ NMR of II in THF/Me$_2$SO at $-32$ °C (refer to text for explanation).



Figure 2. The molecular geometry of 3,3-(Ph$_3$P)$_2$-3-(HSO$_4$)-3,1,2-RhC$_2$B$_9$H$_{11}$·O(C$_2$H$_5$)$_2$ with the ether molecule and hydrogen atoms omitted for clarity. Some pertinent bond distances and angles are Rh–B (av) = 2.243 (18), Rh–C (av) = 2.182 (14), Rh–P (av) = 2.387 (4), Rh–O = 2.243 (8), B–B (av) = 1.806 (8), C–B (av) = 1.723 (18), C–C(carborane) = 1.682 (17) Å; P–Rh–P = 98.7 (1)°.

$$(Ph_3P)_2(HSO_4)RhC_2B_9H_{11} + H_2 \text{ (1 atm)}$$

$$\xrightarrow[\text{10 min}]{\text{THF/25 °C}} (Ph_3P)_2HRhC_2B_9H_{11} + H_2SO_4 \quad (1)$$

Metathesis of II with NaCl or NaBr afforded the corresponding halogen complexes 3,3-(Ph$_3$P)$_2$-3-Cl-3,1,2-RhC$_2$B$_9$H$_{11}$[5] and 3,3-(Ph$_3$P)$_2$-3-Br-3,1,2-RhC$_2$B$_9$H$_{11}$ in >70% yield. Anal. Calcd for C$_{38}$H$_{41}$B$_9$RhP$_2$Br: C, 54.35; H, 4.92, B, 11.58; Rh, 12.25; P, 7.38; Br, 9.52. Found: C, 54.60; H, 5.21; B, 11.60; Rh, 12.02; P, 7.34; Br, 8.94.

**Crystal Data.** [P(C$_6$H$_5$)$_3$]$_2$HSO$_4$RhC$_2$B$_9$H$_{11}$·OC$_4$H$_{10}$ (II): M = 931.08; triclinic; space group $\bar{P}1$; $a$ = 13.049 (5); $b$ = 15.179 (8), $c$ = 11.378 (5) Å; $\alpha$ = 79.10 (3), $\beta$ = 92.30 (3), $\gamma$ = 94.51 (3)°; $Z$ = 2; $\mu$ (Mo K$\alpha$) = 5.53 cm$^{-1}$. Data were collected on a Picker FACS-I four-circle diffractometer at $-154$ °C and were corrected for Lorentz, polarization, absorption, and decay effects. The structure was solved by standard Patterson and Fourier techniques. At the present stage of refinement (all nonhydrogen atomic and thermal parameters varied in full-matrix least squares), the agreement factor stands at 0.086 (3694 reflections).

The molecule is illustrated in Figure 2 along with some pertinent interatomic distances. The structure consists of two triphenylphosphine ligands and a bisulfate moiety bound to the Rh vertex of a RhC$_2$B$_9$H$_{11}$ icosahedral cluster. The bisulfate fragment is bonded to the metal atom via an oxygen atom (Rh–O = 2.245 (8) Å), the only example of such a bond in the literature. This bond distance is significantly larger than Rh–O distances in various Rh(III) complexes[6] (Rh–O distances range from 2.049 to 2.151 Å in several complexes), but compares favorably with "long" Rh–O bonds in two Rh(III) aquo species (2.28 (1) and 2.24 (1) Å).[7] The length of this bond is not dictated by steric interactions between the bisulfate and triphenylphosphine ligands. The P–Rh–P angle of 98.7 (1)° is smaller than other reported P–Rh–P angles in d$^6$ metallocarboranes.[8] Whether this feature is indicative of a weak bond
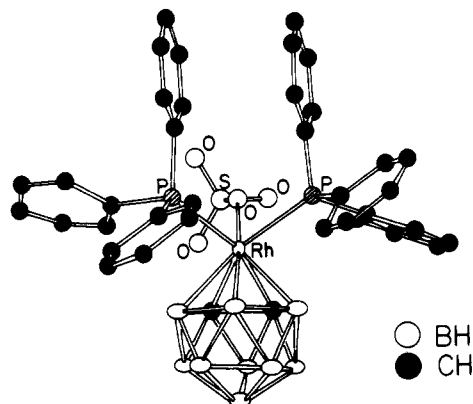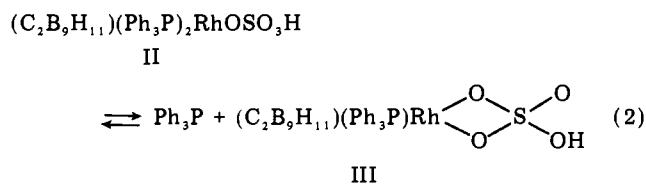
or merely a reflection of the effect of a carborane cage is unknown.

Although the hydrogen atoms have not been located in the structure the length of the S–O(3) bond, compared with the other S–O bonds, indicates that this oxygen is protonated. Also the proximity of this oxygen to O(2) of another molecule (O(3)–O(2)′ = 2.534 (12) Å) indicates its involvement in intermolecular hydrogen bonding.
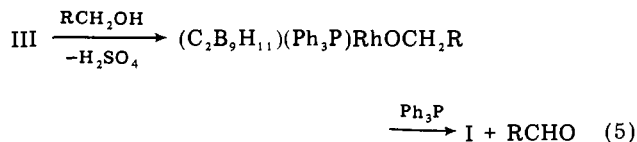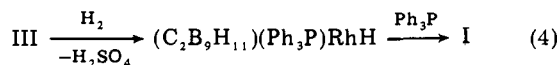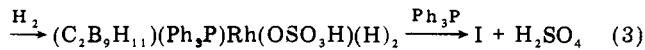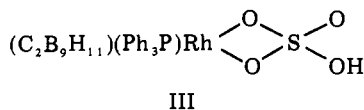
The room temperature 81.02-MHz $^{31}P\{^1H\}$ NMR in THF/Me$_2$SO revealed a doublet centered at 33.4 ppm relative to D$_3$PO$_4$ ($J_{P-Rh}$ = 152 Hz) and a singlet due to free Ph$_3$P.[9] Cooling to $-32$ °C provided a spectrum with three doublets centered at 36.2 ($J_{P-Rh}$ = 166 Hz), 33.0 ($J_{P-Rh}$ = 157 Hz), and 26.8 ($J_{P-Rh}$ = 132 Hz) in addition to the resonance for free Ph$_3$P. (The doublet at 26.8 ppm is equal in intensity to the free triphenylphosphine resonance.) We believe the low temperature spectrum indicates the equilibrium shown in eq 2. Ligand

$$(C_2B_9H_{11})(Ph_3P)_2RhOSO_3H$$
$$\text{II}$$

$$\rightleftharpoons Ph_3P + (C_2B_9H_{11})(Ph_3P)Rh\underbrace{\begin{array}{c} O \\ O \end{array}}_{} S\underbrace{\begin{array}{c} O \\ OH \end{array}}_{} \quad (2)$$
$$\text{III}$$

dissociation is well established for transition-metal phosphine complexes and in this instance is favored by the chelate effect of the formed bidentate bisulfate ligand. The doublet at 33.0 ppm was therefore assigned to the monodentate complex (II) while that at 26.8 ppm was attributed to the bidentate species. The remaining doublet at 36.2 ppm may be due to either bisulfate dissociation from II or an acid–base equilibrium involving the proton of the coordinated bisulfate ligand.

The reaction of II with H$_2$ could proceed by oxidative addition of H$_2$ to III followed by reductive elimination of H$_2$SO$_4$ (eq 3). Alternatively, a four-centered intermediate,[10] in which dihydrogen interacts simultaneously with both the Rh center and an oxygen atom of the bisulfate ligand, could collapse to produce I and H$_2$SO$_4$ (eq 4). We favor the latter mechanism insofar as oxidative addition of H$_2$ to III (formally Rh(III)) would yield a formal Rh(V) dihydride. The reaction of II with alcohols is most reasonably envisioned as proceeding through coordination of alcohol to III followed by loss of H$_2$SO$_4$. The resulting alkoxy rhodium species could then react via $\alpha$-hydride abstraction and addition of Ph$_3$P to produce I and the corresponding aldehyde (eq 5).

Further studies aimed at utilizing the complex II for cata-

$$(C_2B_9H_{11})(Ph_3P)Rh \overset{O}{\underset{O}{\diagdown}} S \overset{O}{\underset{OH}{\diagup}}$$

<div align="center">III</div>

$$\overset{H_2}{\longrightarrow} (C_2B_9H_{11})(Ph_3P)Rh(OSO_3H)(H)_2 \overset{Ph_3P}{\longrightarrow} I + H_2SO_4 \quad (3)$$

$$III \overset{H_2}{\underset{-H_2SO_4}{\longrightarrow}} (C_2B_9H_{11})(Ph_3P)RhH \overset{Ph_3P}{\longrightarrow} I \quad (4)$$

$$III \overset{RCH_2OH}{\underset{-H_2SO_4}{\longrightarrow}} (C_2B_9H_{11})(Ph_3P)RhOCH_2R$$

$$\overset{Ph_3P}{\longrightarrow} I + RCHO \quad (5)$$

lytic dehydrogenation of alcohols are currently underway in these laboratories. The reactions of II with cyanide ion[11] and with phenylacetylene[11] produce species quite unlike those discussed above and they will be reported at a later data.

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(3) One equivalent of triphenylphosphine was added to this reaction to suppress exchange of terminal B–H with D$_2$ catalyzed by I.
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**Novel Applications of Chiral Polymer and Liquid Crystalline Polymer Hosts for the Characterization of Intramolecular Charge-Transfer and Exciton Bands in Cs$_2$Pt(CN)$_4$ by Circular Dichroism Spectropolarimetry**

*Sir:*

Circular dichroism (CD) spectropolarimetry is an extremely useful tool for the characterization of optically isotropic chiral systems. CD provides both optical polarization information as well as the position of hidden transitions. Since CD can only be employed to probe chiral structures, its application is often
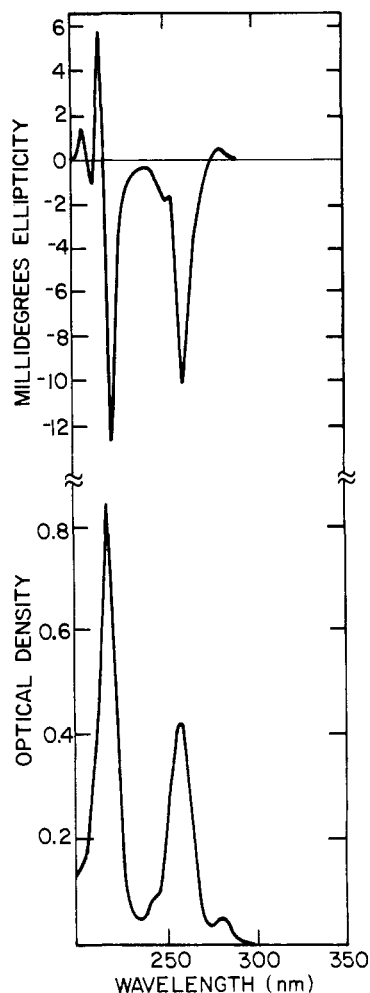


**Figure 1.** Absorption and circular dichroism spectra for dissolved Cs$_2$Pt(CN)$_4$ in hydroxypropyl cellulose ($\sim$20-$\mu$m film).

limited because resolutions of enantiomeric structures may be difficult, time consuming, or impractical.

We have reported previously that *achiral* molecules display CD when ordered in a chiral manner in a fluid thermotropic[1] or lyotropic[2] cholesteric liquid crystalline host. More recently we have reported an in situ optical resolution and CD of potentially chiral crystallites (J-aggregate species) of *achiral dyes* in a rigid chiral polymeric host.[3,4] In this latter case the chiral polymer provides both the chiral perturbation for the optical resolution of chiral crystallites and the rigid matrix for an array of uniformly dispersed submicron- to micron-sized particles. The rigid matrix allows then for the elimination of linear dichroism as previously described.[3,5] Highly intense optical transitions can be probed quite simply by this technique when conventional single-crystal absorption or reflection techniques may be ineffective. The chiral polymer spectroscopic technique requires that a good solvent for both the chiral polymer and the chromophoric molecule be employed to ensure growth of the crystallites subsequent to film formation.

To probe the application of these techniques to inorganic complexes we have investigated cesium tetracyanoplatinate (Cs$_2$Pt(CN)$_4$·H$_2$O, 1). This compound is unique among the tetracyanoplatinate salts which form one-dimensional stacks in the solid state because the Pt(CN)$_4^{2-}$ units, individually achiral, are organized into helical arrays which confer chirality on the crystal.[6,7] The optical properties of the one-dimensional tetracyanoplatinate salts are quite different from those of the individual Pt(CN)$_4^{2-}$ units. In dilute aqueous solution Pt(CN)$_4^{2-}$ has absorption bands at 280, 258, 242, and 218 nm which have been assigned by magnetic circular dichroism[8,9]