

Table I. Acetolysis Rates of *p*-Toluenesulfonates

| Tosylate | Temp, °C | k_1 , sec ⁻¹ | Rel rate 25° | | ΔH^\ddagger , kcal/mol | ΔS^\ddagger , eu, 25° |
|---|-------------------|---------------------------|-----------------|------|-----------------------------------|-------------------------------|
| IIb | 25.0 ^a | 7.10×10^{-9} | 1.0 | 0.15 | 29.2 | 2.07 |
| | 75.0 | 9.72×10^{-8} | | | | |
| | 90.0 | 5.85×10^{-6} | | | | |
| | 100.0 | 1.74×10^{-4} | | | | |
| IIIb | 25.0 ^a | 2.33×10^{-8} | 3.3 | 0.48 | 28.5 | 2.27 |
| | 75.0 | 2.73×10^{-6} | | | | |
| | 85.0 | 7.93×10^{-5} | | | | |
| | 100.0 | 4.59×10^{-4} | | | | |
| Cyclohexyl ^b | 25.0 | 4.88×10^{-8} | 1.00 | | | |
| <i>exo</i> -Norbonyl ^c | 25.0 | 2.33×10^{-8} | | | | |
| <i>Nendo</i> -orbonyl ^c | 25.0 | 8.28×10^{-8} | | | | |
| <i>endo</i> -5,6-Trimethylene- <i>endo</i> -2-norbonyl ^d | 25.0 | 8.60×10^{-9} | | | | |
| <i>exo</i> -Tricyclo[3.2.1.0 ^{3,6}]- <i>oct</i> -2-yl ^e | 25.0 | 9.12×10^{-8} | | | | |
| <i>endo</i> -Tricyclo[3.2.1.0 ^{3,6}]- <i>oct</i> -2-yl ^e | 25.0 | 4.75×10^{-10} | | | | |

^a Calculated from data at other temperatures. ^b S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1127 (1952). ^c Reference 2e. ^d H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci., U. S.*, **56**, 1653 (1966); H. C. Brown and W. G. Hammar, *J. Amer. Chem. Soc.*, **89**, 6378 (1967); H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6380 (1967). ^e Reference 2f.

show that the steric interactions seem to be approximately the same.

In Table I are the acetolysis rate results. The product of acetolysis of both IIb and IIIb after saponification is largely IIa. The absolute yield by vpc of IIa using dodecyl alcohol as internal standard was 83 and 85%, respectively, with less than 5% of IIIa present in both cases. Samples collected by preparative vpc were identical with authentic alcohol.

Included in Table I are the rates of tosylates of some other norbornyl type ring systems. Assessment of factors involved in the rates of IIb and IIIb is difficult by direct comparison with model compounds. For example, comparison of IIb with *exo*- and *endo*-norbornyl would suggest that IIb is solvolyzing much slower than would be expected for an *exo*-tosylate. Comparison of the rate of IIIb with *endo*-norbornyl and with *endo*-5,6-trimethylene-*endo*-2-norbonyl would indicate that IIIb is solvolyzing at a "normal rate." If *endo*-tricyclo[3.2.1.0^{3,6}]-*oct*-2-yl tosylate were used as the model, rate enhancement would appear to be present for both IIb and IIIb.

The Schleyer equation¹² was used in an attempt to evaluate the factors involved in the rates. The carbonyl frequency used was 1753 cm⁻¹. Torsional strain relief for IIb was estimated using angles of 27 and 60° for the C₃H-CO and C₁H-CO angles, respectively. For IIIb we used angles of 27 and 60° for the C₄C₃-CO and C₁C₂-CO interactions. The assumption was made that no nonbonded strain was relieved in the *exo* compound. The same assumption was made for the *endo* compound IIIb since in many rigid polycyclic ring systems this has been found to be true.¹³ The Schleyer equation predicts that both *exo* and *endo* isomers will solvolyze by a factor of 6.0×10^{-4} slower than cyclohexyl. Experimentally the results show that both isomers are solvolyzing more rapidly than predicted. The *exo* rate is faster by a factor of 250 and the *endo*

faster by a factor of 795 than predicted. This higher than predicted rate for an *exo* isomer has been widely found before, both where there are rearrangements and also where rearrangements do not take place.^{2,12,14} The high rate of the *endo* isomer could be largely explained if we assume that ground-state strain is relieved in the transition state. However, it is not clear why ground-state strain would be relieved in this case and not in others.¹³ The possibility exists that the *endo* compound is ionizing with anchimeric assistance. We find no direct evidence for this since the large majority of product is unrearranged. However, anchimeric assistance cannot be eliminated since it is possible that only one form of a resonance hybrid is reacting with solvent.

We are actively engaged in further examination of this and other ring systems in an attempt to clarify this unusual solvolytic behavior.

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(14) Among the possibilities for rearrangement of IIb would be C₁-C₂ bond migration leading to a different ring system and degenerate rearrangements such as C₄-C₃ bond migration and migration of *endo*-3-hydride to C₃. This will be considered in the full paper.

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Metalloboranes. IV. The B₉H₁₀S⁻, B₉H₁₁(L)²⁻, and B₈H₁₂²⁻ Ligands

Sir:

We report the syntheses of three new classes of *nido*-metalloboranes. These are metal complexes in which the metal-boron skeletons are icosahedral frag-

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(12) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1854, 1856 (1964).

(13) H. C. Brown, I. Rothberg, P. v. R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1653 (1966); H. C. Brown and W. J. Hammar, *J. Amer. Chem. Soc.*, **89**, 6378 (1967); H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6380 (1967).

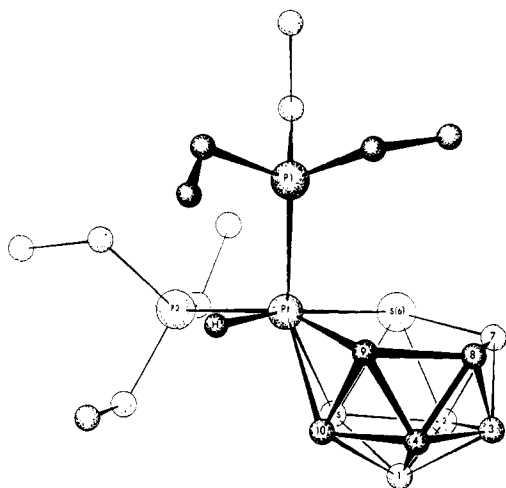


Figure 1. Structure of $[(C_2H_5)_3P]_2Pt(H)B_9H_{10}S$. Each of the nine boron atoms in this species has a terminal hydrogen atom which is not depicted in the drawing. The extra borane hydrogen, also not depicted, is probably associated with one or more atoms of the open face of the icosahedral fragment.

ments and the borane ligands are formally bidentate in character. This set of three comprises $(R_3P)_2Pt^{2+}$ derivatives of $B_9H_{10}S^-$, $B_9H_{11}(L)^{2-}$, and $B_9H_{12}^{2-}$.

Reaction of $CsB_9H_{12}S$ and $trans-[(C_2H_5)_3P]_2PtHCl$ yields H_2 , $CsCl$, and $[(C_2H_5)_3P]_2Pt(H)B_9H_{10}S$. The latter is monomolecular in solution, has a PtH infrared stretching frequency at 2214 cm^{-1} , and has nonequivalent phosphorus ligands by ^{31}P and 1H nmr.^{4,2} The structure of this metalloborane was determined from 2300 pieces of single-crystal data collected on an automatic diffractometer using $Cu\ K\alpha$ radiation. Crystals are monoclinic, space group $C2/c$, with $a = 16.387(6)$, $b = 10.138(5)$, $c = 29.276(8)$ Å, $\beta = 94.54(5)^\circ$, and with each unit cell containing eight molecules. The data were corrected for absorption effects. The structure was solved by a combination of Patterson and Fourier techniques and refined by least squares to an $R(\sum |F_o| - |F_c|) / \sum |F_o|$ of 0.048. The molecular structure (Figure 1) has a platinum atom completing an 11-atom icosahedral fragment and bonded to a sulfur atom (2.43 Å), three boron atoms (2.20–2.25 Å), two phosphorus atoms (2.36 and 2.39 Å), and one hydrogen atom.³ The average B–S and B–B bond lengths are 2.02 (5) and 1.81 (2) Å, respectively.

The $B_9H_{10}S^-$ ligand, isoelectronic with $B_{10}H_{12}^{2-}$, is formally analogous in this new metalloborane to the established bidentate $B_{10}H_{12}^{2-}$ ligand in the metalloborane $[(C_2H_5)_3P]_2PtB_{10}H_{12}$.⁴ There are three exopolyhedral Pt ligands,⁵ and we view the coordination about the platinum in this new complex as quasi five-

(1) The proton and phosphorus nmr data reported in this manuscript were obtained at 220 and 40.1 MHz, respectively.

(2) *Anal.* Calcd for $C_{12}H_{41}P_2PtB_9S$: C, 25.2; H, 7.23; B, 17.0; P, 10.8; Pt, 34.1; S, 5.61. Found: C, 25.2; H, 7.41; B, 16.9; P, 10.8; Pt, 34.1; S, 5.67.

(3) The largest peak on an electron density difference map, phased by a model including all the nonhydrogen atoms with anisotropic thermal parameters, was in the region of the expected hydrogen atom bonded to platinum. This hydrogen atom refined nicely giving a Pt–H bond of 1.66 Å.

(4) F. Klanberg, P. A. Wegner, G. W. Parshall, and E. L. Muetterties, *Inorg. Chem.*, **7**, 2072 (1968).

(5) We are attempting to abstract H^- to give $L_2PtB_9H_{10}S^+$ which would be strictly analogous to $L_2PtB_{10}H_{12}$.

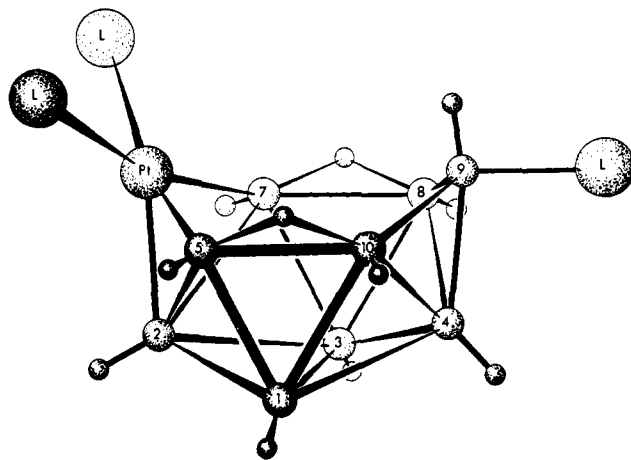


Figure 2. Proposed $[(C_2H_5)_3P]_2PtB_9H_{11}(L)$ structure.

coordinate with distorted square-pyramidal form: apical phosphine (P_1) and for the "square plane" hybridized Pt atomic orbitals directed at phosphorus (P_2) and hydrogen nuclei and at the B_5-S and B_9-B_{10} edges.⁶

The $B_9H_{12}^{2-}$ ion reacts with $trans-[(C_2H_5)_3P]_2PtHCl$ in the presence of donor molecules to give 1 mol of hydrogen, cesium chloride, and $[(C_2H_5)_3P]_2PtB_9H_{11}(L)$. Generally we found organic bases to function effectively as L, and complexes isolated include those based on amines, nitriles, phosphines, and sulfides.⁷ By ^{31}P and 1H nmr criteria, the phosphines bonded to platinum are equivalent.⁸ The most reasonable structure consistent with the spectral data and with general boron hydride bonding principles⁹ is one isoelectronic and isostructural with the $B_{10}H_{12}(base)_2$ species with L_2Pt^{2+} replacing a $6(9)BH(base)^{2+}$ unit as shown in Figure 2. We suggest that the $B_9H_{11}L^{2-}$ ligand is effectively bidentate with the square-planar platinum orbitals bisecting the B_2-B_5 and B_2-B_7 edges.

Alcohol degrades $[(C_2H_5)_3P]_2PtB_9H_{11}L$ to $[(C_2H_5)_3P]_2PtB_9H_{12}$.¹⁰ In this PtB_9 metalloborane, both phosphorus ligands are equivalent by nmr. The most plausible structure is simply derived from $[(C_2H_5)_3P]_2PtB_9H_{11}L$ (Figure 2) by elision of $BH(L)^{2+}$ and addition of $2H^+$ at edge-bridging positions to give a $B_9H_{13}L$ analog. The scope of this type of metalloborane chemistry is being investigated and a full report will be presented shortly.

(6) Consider the detailed arguments for $B_{10}H_{12}^{2-}$ as formally bidentate in the $Ni(B_{10}H_{12})_2^{2-}$ and $Zn(B_{10}H_{12})_2^{2-}$ ions.⁴ An alternative formulation of the platinum "coordination sphere" would be a distorted trigonal bipyramid with axial sulfur and hydrogen atoms, two equatorial phosphorus nuclei, and one equatorial multicenter interaction directed toward the boron atom labeled 10 in Figure 1.

(7) Sample analytical data: Calcd for $[(C_2H_5)_3P]_2PtB_9H_{11}(P-C_6H_5CH_3)_3$, $C_{33}H_{62}P_2PtB_9$: C, 46.2; H, 7.51; B, 11.7; P, 11.2; Pt, 23.4. Found: C, 46.0; H, 7.53; B, 11.8; P, 11.1; Pt, 23.4.

(8) The ^{11}B nmr spectra of phosphino metalloboranes are uniformly broad and uninformative.

(9) W. M. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(10) *Anal.* Calcd for $C_{12}H_{42}P_2PtB$: C, 27.2; H, 7.99; P, 11.7; Pt, 36.8; B, 16.3. Found: C, 27.1; H, 7.98; P, 11.7; Pt, 37.4; B, 16.0.

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