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(5) The pure meso diacid was obtained by recrystallization from a mixture of *dl* and meso diacid in 10 N HCl. Treatment of the meso diacid, mp 209–210 °C, with diazomethane afforded the corresponding meso diester, dimethyl 2,3-dimethylsuccinate, 98% isomerically pure by analytical VPC.[8]

(6) The meso and *dl* diacid chlorides (bp 40–50 °C at 0.1 mm), both >97% isomerically pure,[7] were taken up in CH_2Cl_2 and added to sodium peroxide in water buffered with NaH_2PO_4 and Na_2HPO_4.[3b]

(7) The isomeric purities of the diacid chlorides were determined by quenching in methanol and analyzing the corresponding *meso-* and *dl*-dimethyl esters by analytical VPC.[8]

(8) *meso-* and *dl*-dimethyl 2,3-dimethylsuccinate were separated by VPC on UCON 550X stationary phase at 130 °C, relative retention times 1 and 1.14, respectively.

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(10) Controls show that the *dl* and meso peroxides **1** and **2** react with triphenylphosphine in CH_2Cl_2 at similar rates.

(11) *meso-* and *dl*-2,3-dimethylsuccinic anhydrides were separated by VPC on PMPE(6-R) stationary phase at 180 °C, relative retention times 1.14 and 1.0, respectively.

(12) However, these peroxides are extremely shock sensitive in the solid state and will explode upon rapid heating.

(13) Added O_2 had no effect on the product stereochemistry.

(14) Chamber pyrolysis, 5 s.

(15) The cis:trans ratios of 2-butenes were constant with time (10–40% conversion). Control experiments show that neither *cis*-4-octene nor *cis*-stilbene isomerize (<1% detectable) in the presence of decomposing peroxides **1** or **2**. A first-order rate constant for the appearance of 2-butenes from **1** was measured for 1 half-life ($k \sim 7.6 \times 10^{-4}$ s^{-1} in THF at 46.9 °C). We cannot rigorously rule out any competition from induced decomposition.

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(20) 3.4% 3-methoxy-1-butene (**8**), 3.8% 2-methoxybutane (**9**), 0.1% butane (**10**), 1.4% 1-butene (**11**).

(21) The identities of the ether and hydrocarbon products **9–11** from both the peroxide decompositions in methanol and the direct irradiation of 2-butenes in methanol were confirmed by gas chromatographic–mass spectroscopic analysis[22] and compared with authentic samples.

(22) ¼ in. × 6 ft 3% UCON 550X glass column interfaced to a Finnegan 9500 mass spectrometer. We thank Mr. Ray Haack for his assistance in carrying out these experiments.

(23) Using a Hanovia 450-W medium-pressure mercury arc and a water-cooled quartz immersion well.

(24) Alfred P. Sloan Research Fellow, 1977–1979.

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Framework Electron Count in Metalloheteroboranes. Platinathiadecaboranes

Sir:

Recent reports indicate that certain metalloheteroboranes formed from the more electron-rich transition elements have "exceptional" structures. For instance, 3-(Et_2NCS_2)-3,1,2-$AuC_2B_9H_{11}$[1] and 8,8-$(Me_3P)_2$-7,8,10-$CPtCB_8H_{10}$[2] have been found by x-ray crystallography to have open (nido) structures rather than the more symmetric closo structures anticipated on the basis of framework electron count.[3-5]

Our recent investigation of metallothiaboranes has led to the preparation of platinathiaboranes which could be characterized as closo L_2Pt (SB_8H_8) molecules with "exceptional" nido structures on the basis of x-ray crystallography alone.
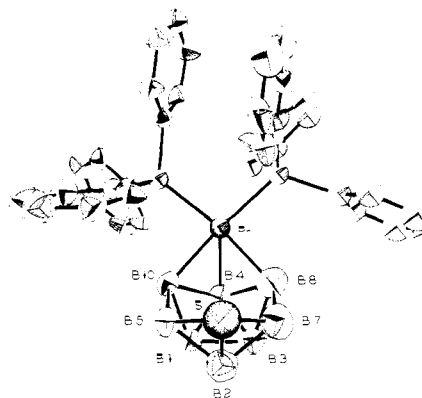

Figure 1. Molecular structure of 9,9-$(PPh_3)_2$-6,9-$SPtB_8H_{10}$. Hydrogen atoms not shown. The numbering convention for the platinathiaborane cluster is shown with the shaded atoms 6 and 9 being S and Pt, respectively.

However, additional evidence shows that they have nido framework electron counts and are correctly characterized as $(PMe_2Ph)_2Pt(SB_8H_{10})$ (I), $(PEt_3)_2Pt(SB_8H_{10})$ (II), $(PPh_3)_2Pt(SB_8H_{10})$ (III), and $(PPh_3)_2Pt(SB_8H_9 \cdot OEt)$ (IV). I–IV appear to be very similar to the $L_2M(SB_9H_9)$ [M = Pd, Pt] complexes reported previously.[6]

The reaction of L_4Pt (L = PMe_2Ph, PEt_3, PPh_3) with 1-SB_9H_9 in dry refluxing ethanol or methanol under nitrogen gives white to pale yellow crystals of I–III, respectively, in 75% yield. When $(PPh_3)_2Pt(C_2H_4)$ is used instead of L_4Pt, IV results. The products are air stable in crystalline form but were generally recrystallized from methylene chloride/alcohol in an inert atmosphere. The dimethylphenylphosphine and triethylphosphine derivatives (I and II) have been characterized by mass spectroscopy, IR, ^1H and ^{11}B NMR, and elemental analysis. However, we have been unable to obtain a mass spectral molecular weight of III and IV.

Single crystal x-ray studies of III and IV using conventional Patterson and Fourier difference techniques show that the framework structure is nido for both (Figure 1). Crystal data for III, 9,9-$(PPh_3)_2$-6,9-$SPtB_8H_{10}$: mol wt 848.3; monoclinic; space group $P2_1/n$; $a = 11.522$ (5), $b = 20.005$ (5), $c = 16.398$ (4) Å; $\beta = 95.74$ (3)°; $V = 3760$ (2) Å^3; $d_{obsd} = 1.49$ (1), $d_{calcd} = 1.498$ g cm^3; $Z = 4$; μ (Mo Kα) = 40.88 cm^{-1}; $R_1 = 0.043$ and $R_2 = 0.049$ for 5430 collected reflections (3211 with $I \geq 3\sigma(I)$). Crystal data for IV, 8-EtO-9,9-$(PPh_3)_2$-6,9-$SPtB_8H_9$: mol wt 892.4; monoclinic; space group $P2_1/n$; $a = 13.336$ (4), $b = 21.034$ (5), $c = 14.545$ (3) Å; $\beta = 103.04$ (2)°; $V = 3974$ (2) Å^3; $d_{obsd} = 1.48$ (1), $d_{calcd} = 1.491$ g cm^3; $Z = 4$, μ (Mo Kα) = 38.75 cm^{-1}; $R_1 = 0.54$ and $R_2 = 0.059$ at this stage for 5968 collected reflections (2962 with $I \geq 3\sigma(I)$). The skeletal structure shows that Pt achieves effective square-planar coordination in which three boron atoms of the thiaborane ligand (B-4, B-8, and B-10) act as a bidentate moiety: Pt–B distances for III (Å): 9-4 = 1.184 (16), 9-8 = 2.242 (15), 9-10 = 2.222 (17). A similar η^3 bonding was observed in $(Me_2PhP)_2PtB_3H_7$.[7] However, because of the disorder associated with the $B_3H_7^-$ ligand in the latter structure, the present one gives the clearest definition of η^3 bonding between Pt and a borane cluster.

The cluster structure is clearly open with nonbonding interactions between the Pt and boron atoms 5 and 7 (3.48 and 3.49 Å) and the sulfur (3.89 Å). In view of recent contentions that a nido structure is not confined to "electron-rich" systems, but appears to be related simply to the presence of a formal d^8 or d^9 metal,[1,8] we sought to establish firmly the framework electron count in III. The critical ambiguity revolves around the number of hydrogen atoms associated with the cluster which cannot be determined unambiguously by x-ray crystallography in this case because of the dominant scattering by
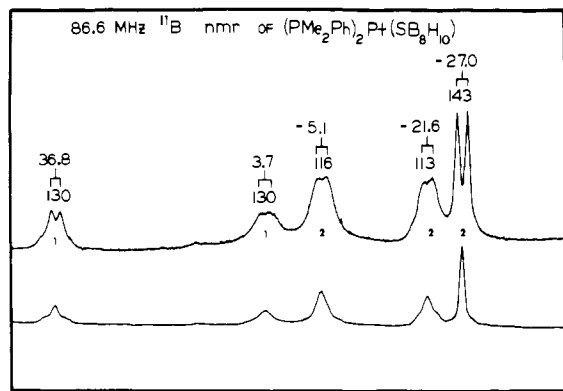
Figure 2. The 86.6-MHz ^{11}B NMR spectrum of 9,9-(PPhMe₂)₂-6,9-SPtB₈H₁₀. The lower spectrum is ^{1}H decoupled. Chemical shifts are in parts per million relative to Et₂O·BF₃ with negative values to high field. The J_{BH} is given below the bracket and the relative intensity under the peak.

Pt. If the thiaborane ligand is SB₈H₈, then according to the PERC formalism[5] the complex is closo (22 e⁻ = 2n + 2). However, the SB₈H₁₀ ligand with two "extra" hydrogens is predicted to be nido (24 e⁻ = 2n + 4) with an open structure. The evidence cited below clearly favors the SB₈H₁₀ formulation and thus the nido structure is not "unexpected". Those studies of d⁸ and d⁹ metalloheteroboranes which have uncovered unexpected structures are probably correct because of the mild reaction conditions used, but it should be noted that they have not confronted directly the possibility that extra hydrogen atoms could account for the observation of a nido structure.

The x-ray structure gives some indication of bridging hydrogens on the open face between borons 7,8 and 5,10. The average B–B distance between 7,8 and 5,10 in III and IV is 1.844 (28) Å. Other boranes with bridge hydrogens in the same place show the following distances (Å): 1.88 (1) in B₁₀H₁₂(SMe₂)₂[9] and 1.87 (1) in 6,6-(Et₃P)₂-5,9-Me₂-6,5,9-NiC₂B₇H₉.[10] With no bridge hydrogen this distance is significantly longer: 1.973 (4) in B₁₀H₁₄[11] and 2.037 (7) in 5-THF-6-(CO)₃-6-MnB₉H₁₂.[12]

Additional evidence favoring the SB₈H₁₀ ligand comes from the parent peak profiles in the mass spectra of I and II. Both spectra show excellent agreement between calculated and observed ion intensities for P through P − 7. (For II with P of 566 for ^{198}Pt^{11}B₈^{12}C₁₂^{1}H₄₀^{31}P₂^{34}S⁺ the calculated (observed) intensities are 0.003 (none), 0.006 (0.01), 0.07 (0.07), 0.14 (0.15), 0.31 (0.36), 0.65 (0.71), 1.00 (1.00), 0.99 (1.14).)

The ^{1}H NMR provides the best evidence for extra hydrogens. The spectra of I–IV show a broad peak at τ 11–12. In the case of III a ^{1}H-{^{11}B} spectrum was obtained and showed that the peak at τ 11.4 was due to bridge hydrogens since it was sharpened but not shifted by decoupling. The remainder of the spectrum is consistent with the phosphine ligands and unresolved terminal B–H signals.

The ^{11}B NMR spectra of I–IV are consistent with the x-ray structure, but give no evidence of bridge hydrogens; those of I–III are almost identical, and that of I is shown in Figure 2.[13] Since ^{195}Pt (I = ½) is 34% naturally abundant, observation of a 1:4:1 triplet for the signals at +36.8 and −21.6 upon {^{1}H}-^{11}B decoupling allows them to be assigned to atoms B-4 and B-8,10, respectively ($J_{^{11}B-^{195}Pt}$ = 260 and 240 Hz), those directly bonded to Pt.

We have found that L₂Pt(SB₈H₁₀) complexes also form when SB₁₁H₁₁ is substituted for SB₉H₉ as a starting material. Other experiments show that thiaboranes are degraded by ethanol. It appears that our synthetic method is a degradative insertion reaction where the Pt moiety is able to form a kinetically stable coordination complex after the thiaborane has been degraded to an SB₈ framework. The range of metal-

lothiaboranes which are susceptible to degradation by alcohol is not defined. However, since the previously reported L₂M(SB₉H₉) (M = Pd, Pt) complexes[6] were recrystallized from solutions containing ethanol and display ^{11}B NMR spectra strikingly similar to those which we find for the L₂Pt(SB₈H₁₀) complexes (Figure 2), they should be reinvestigated.

Supplementary Material Available. Tables of atomic coordinates and bond distances for III (18 pages). Ordering information is given on any current masthead page.

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Molecular Dynamics of Mixed-Metal Clusters. Carbon-13 Nuclear Magnetic Resonance Study of H₂FeRu₃(CO)₁₃ and H₂FeRuOs₂(CO)₁₃

Sir:

Metal surfaces undergo two basic types of dynamic processes: (1) The substrate (CO, H, etc.) moves on the surface, and (2) the metals themselves rearrange.[1,2] Studies of metal clusters aimed at modeling these surface dynamics have produced a variety of examples of the first type of mobility.[3,4] We present here evidence that the clusters H₂FeRu₃(CO)₁₃ and H₂FeRuOs₂(CO)₁₃ undergo dynamic processes not only involving ligand mobility but also a process in which the metals themselves move.

A previous ^{13}C DNMR study of H₂FeRu₃(CO)₁₃ (**1**) has been published.[5] In connection with our larger study of mixed-metal clusters, we reexamined the variable-temperature

1