to be in the ratio $^{13}CH_3/^{13}CO = 3.5 \pm 0.5$. Upon addition of ~0.05 *M* DTBN, this ratio was reduced to 2.1 ± 0.2, which is within experimental error of 2.0, the expected ratio in the absence of any Overhauser enhancement. Furthermore, the ^{13}CO intensity remained essentially unaltered, with only the $^{13}C\text{–}H_3$ intensity decreasing, which is consistent with the expectation[6] that the Overhauser enhancement is much larger for CH_3 than CO owing to the r_{C-H}^{-6} dependence of the dipolar coupling. This suggests that *A* for $^{13}C\text{–}H_3$ is ~0.7.

We have thus demonstrated that the presence of free radicals reduces the ^{13}C intensities of noise-decoupled spectra. From the limiting intensity as a function of radical concentration for *p*-dioxane and the ratio of the two intensities in acetone, we suggest that the Overhauser enhancement is eliminated. Most importantly, at the free-radical concentrations necessary to reach what we believe to be the "true" intensities, the ^{13}C line widths have *not increased* within experimental error over those in the neat samples. We therefore propose that this method may allow the use of noise-decoupled ^{13}C spectra for *quantitative* applications, although more extensive investigations, now in progress, are necessary before gauging the general utility of this technique.

Acknowledgment. Useful discussions with C. A. Reilly and D. F. S. Natusch are gratefully acknowledged.

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Received November 12, 1970

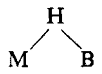
Metalloboranes. VI.[1] A $B_3H_7^{2-}$ Derivative of Platinum. A Possible π-Allyl Analog Based on Boron

Sir:

Metal complexes of the $B_3H_8^-$ ion have been described and their structures determined.[2,3] We wish to report the first example of a metal derivative of the previously unknown $B_3H_7^{2-}$ ion which may be a structural analog of π-allyl metal complexes.

Reaction of the cesium salt of $B_3H_8^-$ with bis(trialkyl- or -arylphosphino)platinum dichlorides in an acetonitrile–triethylamine solution yields compounds of the general composition $(R_3P)_2PtB_3H_7$. Complexes were prepared with triethylphosphine,[4] triphenylphosphine, ethyldiphenylphosphine, and tri-*p*-tolylphosphine ligands.

The platinum–B_3 complexes, although somewhat sensitive to air oxidation, are relatively resistant to hydrolysis in acidic media. This stability is substantially greater than that for $B_3H_8^-$ and metal complexes of $B_3H_8^-$. This hydrolytic stability does not seem consistent with



bridge bonding as found[1,2] in metal complexes of $B_3H_8^-$. The infrared spectra of all $B_3H_7^{2-}$ complexes have a complex BH stretching absorption at 2750 cm^{-1} as well as a sharp distinctive absorption at 1550 cm^{-1}. This latter absorption is absent in $B_3H_8^-$, $R_3NB_3H_7$, and metal complexes of $B_3H_8^-$.

A not implausible formulation of these new complexes is as platinum(0) derivatives of B_3H_7, with a Pt–B bond, analogous to the well-established $R_3N\text{–}B_3H_7$ complexes. However, X-ray photoelectron spectroscopic studies indicate that platinum(II) is present. The Pt $4f_{7/2}$ binding energy in $[(C_2H_5)_3P]_2PtB_3H_7$ is 72.9 eV, which compares well with a series of platinum(II) complexes,[5] *e.g.*, 73.3 eV for $[(C_2H_5)_3P]_2PtCl_2$ and 72.9 eV for $[(C_2H_5)_3P]_2PtB_8H_{12}$.[6] These values are significantly different from those of platinum(0) complexes: 71.6 and 71.6 eV for $[(C_6H_5)_3P]_3Pt$ and $[(C_6H_5)_3P]_4Pt$, respectively.

The proton nmr spectra (220 MHz) of the platinum–B_3 complexes[7] are especially suggestive of a unique bonding interaction. There are three major BH resonances of relative intensities of 3:2:2 at 25°. At lower temperatures, these peaks sharpen and the peak of intensity 3 shows apparent asymmetry, suggesting a 2:1:2:2 proton distribution. The multiple BH resonances are not structurally definitive. The spread of BH resonance is, however, very large, unlike all other $B_3H_8^-$ derivatives. At −26°, resonances are at −1.1, ~−0.9, −0.11, and +4.9 ppm (tetramethylsilane reference). Most importantly, the $B_3H_7^{2-}$ ligand appears to be stereochemically rigid; there are no spectral changes over the temperature range of −50 to +40° other than line-width decrease with temperature decrease.[8] In sharp contrast, $B_3H_8^-$ has a very low barrier to hydrogen tunneling so that all hydrogen nuclei and all boron nuclei are equivalent on the nmr time scale. Spin–spin coupling is preserved at 25° and hence for $B_3H_8^-$ the ^{11}B resonance is a nonet and the ^1H resonance is a decet.[11,12] In $(CH_3)_3NB_3H_7$, only a single broad BH resonance overlapping the CH_3 proton resonance was observed from −20 to +60°. Only in the quasi-tetrahedral $[(C_6H_5)_3P]_2CuB_3H_8$ complex has hydrogen inequivalence been detected.[10] The expected five BH proton resonances were observed at −110°;

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[1] Paper V: P. A. Wegner, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 3473 (1970).

[2] F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, 7, 2272 (1968).

[3] S. J. Lippard and K. M. Melmed, *ibid.*, **8**, 2755 (1969).

[4] Sample analytical data for the triethylphosphine derivative (colorless crystals, mp 93°). *Anal.* Calcd for $C_{12}H_{37}P_2PtB_3$: C, 30.61; H, 7.92; B, 6.89; P, 13.15; Pt, 41.43. Found: C, 30.89; H, 8.06; B, 7.13; P, 12.85; Pt, 41.13. Mass spectroscopic analysis of the diphenylethylphosphino analog showed the parent ion for $[(C_6H_5)_2C_2H_5P]_2PtB_3H_7$. Acid hydrolysis of this complex gave 271.2 cm^3/g of hydrogen gas *vs.* a theoretical yield of 270.4 cm^3/g.

[5] A complete report of the X-ray photoelectron spectroscopic studies on platinum will be presented separately by Dr. W. M. Riggs.

[6] A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 2571 (1970).

[7] Deuterated aromatic hydrocarbon or dichloromethane solutions.

[8] Presumably due to more effective quadrupole induced ^{10}B and ^{11}B spin relaxation.[9,10] Above +40°, the two low-field peaks broaden to the extent that overlap is complete. It is not known whether this reflects further broadening due to quadrupole relaxation effects or the onset of a $\pi \rightleftharpoons \sigma$ interconversion. The ^{11}B nmr spectra of the complexes were relatively broad and structureless, as has been the case[6] for other phosphine–transition metal borane complexes.

[9] M. Grace, H. Beall, and C. H. Bushweller, *Chem. Commun.*, 701 (1970).

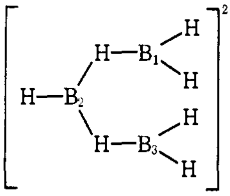
[10] H. Beall, C. H. Bushweller, W. J. Dewkett, and M. Grace, *J. Amer. Chem. Soc.*, **92**, 3484 (1960).

[11] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *ibid.*, **81**, 4496 (1959).

[12] W. N. Lipscomb, *Advan. Inorg. Chem. Radiochem.*, **1**, 132 (1959).

above ~−60° there was a single, broad BH proton resonance.[10] This higher barrier in the copper derivative is due to a second more activated process necessary in addition to hydrogen tunneling to achieve equilibration of boron atom environments. This was established in our ^{31}P nmr study of copper(I)–$B_3H_8^-$ complexes,[13] and it was proposed that the process comprised going from the ground state doubly hydrogen-bridged metal interaction to a single Cu–H–B interaction in the transition state.

The above data and the inferences derived strongly suggest a bonding framework in $B_3H_7^{2-}$ that differs substantially from the simple *closed* B_3 triangular model for $B_3H_8^-$ and its derivatives. The higher stereochemical rigidity in $[(C_2H_5)_3P]_2PtB_3H_7$ is especially supportive. In $B_3H_7^{2-}$, there may be *no bonding* between the B_1 and B_3 nuclei (1). This would be an isoelectronic analog of the allyl ion. We suggest then that the $L_2PtB_3H_7$ molecules may be π-borallyl complexes analogous to the well-established π-allyl complexes. The proton nmr of the $(C_6H_5)(CH_3)_2P$ derivative shows two methyl group resonances which would be required in a π-borallyl structure.[14] Precise characterization of the $B_3H_7^{2-}$ ligand in these metalloboranes will require a solid-state structural determination with location of all BH hydrogen atom positions. The X-ray study is in progress.



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Acknowledgment. We are deeply indebted to Dr. W. M. Riggs for the X-ray photoelectron spectroscopic data.

(13) E. L. Muetterties, W. G. Peet, P. A. Wegner, and C. W. Alegranti, *Inorg. Chem.*, **9**, 2447 (1970).

(14) This experiment was suggested by Professor H. C. Clark.

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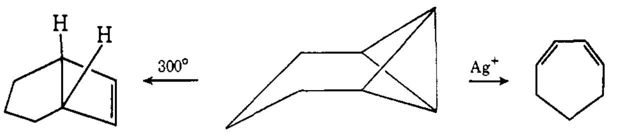
Received November 23, 1970

The Specificity of Metal Catalysts in the Opening of Highly Strained Polycyclic Molecules[1]

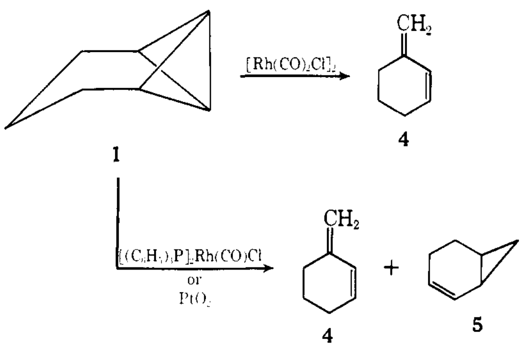
Sir:

The recent discussions of the thermal opening of tricyclo[4.1.0.0^{2,7}]heptane (**1**) to give **2** by Wilberg and Szeimies[2] and of the silver ion catalyzed opening of **1** to give **3** by Paquette and coworkers[3] prompt us to report that portion of our extensive investigation of the transition metal catalyzed rearrangement of highly strained polycyclic molecules related to **1**. We have found that the metal-catalyzed isomerization of **1** is a very general phenomenon which is readily accomplished by a wide variety of transition metal catalysts. In addition we wish to report at this time that the catalytic process is highly specific with different catalysts yielding different product mixtures.



2 **1** **3**

When an acetonitrile solution of tricyclo[4.1.0.0^{2,7}]heptane (**1**)[4] (2.8 *M*) was treated with 4 mol % of rhodium dicarbonyl chloride dimer at room temperature, a rapid reaction occurred which gave 98% 3-methylenecyclohexene[5] (**4**) after 15 min. This material was identical in all respects with an authentic sample of **4** prepared *via* the Wittig reaction of cyclohexenone with triphenylphosphinemethylene.[6,7] Replacement of the ligands on rhodium caused a significant change in the character of the reaction. A solution of **1** in acetonitrile reacted very slowly with *trans*-chlorocarbonylbis(triphenylphosphine)rhodium(**6**) at room temperature. Only after 48 hr at 65° with 5 mol % of **6** did **1** give 92% **4** and 5% 2-norcarene (**5**).[8] The failure of the reaction mixture to undergo any change on additional exposure to the reaction conditions coupled with the failure of pure **5** to isomerize under the reaction conditions indicated that **5** was not a precursor of **4**.



Platinum(IV) oxide served as a catalyst for the rearrangement of **1** under the same conditions as were used with **6**. With platinum(IV) oxide, **1** gave 62% **4** and 24% **5** after 48 hr at 65°. Certain noble metals also facilitate the rearrangement. In addition to **4** and **5**, the reaction of **1** with 5% palladium on carbon gave what has tentatively been identified as a mixture of methylcyclohexadienes. However, these products appear to be caused by isomerization of the 3-methylenecyclohexene.[9]

(1) Paper XV on "The Chemistry of Bent Bonds." For the previous paper in this series see P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970).

(2) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).

(3) L. A. Paquette, R. P. Henzel, and G. R. Allen, Jr., *J. Amer. Chem. Soc.*, **92**, 7002 (1970).

(4) W. R. Moore, H. R. Ward, and R. F. Merritt, *ibid.*, **83**, 2019 (1961).

(5) The use of chloroform instead of acetonitrile as the solvent gave 97% **4** after 15 min with 4 mol % of rhodium dicarbonyl chloride dimer.

(6) G. Wittig and U. Schoellkopf, *Org. Syn.*, **40**, 66 (1960).

(7) We wish to thank Mr. H. R. Drewes for preparing the authentic sample of **4**.

(8) The structure of the 2-norcarene was established by spectral and vpc comparison with an authentic sample.[4]

(9) In addition to those catalysts mentioned above, the isomerization of **1** is readily accomplished by rhenium decacarbonyl, manganese decacarbonyl, and dichlorotricarbonylruthenium dimer. These catalysts give complex mixtures which are currently under investigation.