

suggest a formal partitioning of oxidation states within the cation as $(\text{Au}^0)_6\text{Pt}^{\text{II}}$.

The ^{31}P NMR spectrum was inconsistent with the static structure of Figure 1 since it contained only two resonances,⁵ a septet for the PtPPh_3 atom and a doublet for the AuPPh_3 atoms due to PP coupling.¹¹ Hence the cation is fluxional and the time-averaged structure appears to be a hexagonal pyramid with equivalent AuPPh_3 units at the base and the $\text{Pt}(\text{PPh}_3)(\text{CC-}t\text{-Bu})$ unit, rapidly rotating with respect to the Au_6 hexagon, at the apex. The mechanism of fluxionality most reasonably involves rotation of the $\text{Pt}(\text{PPh}_3)(\text{CC-}t\text{-Bu})$ unit with respect to the Au_6 unit (Figure 1) in 60° steps, which, with flexing of the Au_6 unit, interconverts pairs of bridgehead and peripheral gold atoms. Both the structure of the cluster and the nature of the fluxionality appear to be unprecedented.

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Supplementary Material Available: Atom coordinates (Table I), thermal parameters (Table II), interatomic distances (Table III), and interbond angles (Table IV) (6 pages). Ordering information is given on any current masthead page.

- (11) This observation, together with the easy assignment of PtP and AuP resonances from the different magnitudes of $^1J(\text{PtP})$ and $^2J(\text{PtAuP})$ couplings², allows the number of AuPPh_3 and PtPPh_3 groups in a cluster to be determined. It also shows that the fluxional process does not involve reversible fragmentation of the cluster cation.

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Reversible Double Addition of H_2 on a Bis(μ -sulfido) Binuclear Rhodium Complex

Sir:

We report on a dinuclear rhodium species with a central Rh_2S_2 ring that may alternatively add or release 2 mol of molecular hydrogen.

Reaction of H_2S with $(\text{triphos})\text{RhCl}(\text{C}_2\text{H}_4)^1$ (1) in $\text{CH}_2\text{Cl}_2/\text{DMF}$ solution (triphos = $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$) followed by addition of NaBPh_4 in *n*-butanol gives pink crystals of $[(\text{triphos})\text{HRh}(\mu\text{-SH})_2\text{RhH}(\text{triphos})](\text{BPh}_4)_2 \cdot 3\text{DMF}$ (2) in 95% yield (IR (Nujol mull) 2540 ($\nu(\text{S-H})$), 2010 cm^{-1} ($\nu(\text{Rh-H})$); ^1H NMR (Me_2SO , 293 K) δ 2.12 (multiplet, S-H), 6.06 ($J(\text{H-P}_{\text{trans}}) = 95$ Hz, doublet of multiplets, Rh-H)) (Scheme I). Compound 2 is fluxional in solution as evidenced by its $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in DMF/ CD_3COCD_3 for the temperature range 223–328 K. In any case, the resonance of the P atom trans to H consists of a doublet of triplets at -4.04 ppm ($J(\text{P-P}) = 23.0$ Hz, $J(\text{P-Rh}) = 71.3$ Hz), -5.23 ppm ($J(\text{P-P}) = 22.0$ Hz, $J(\text{P-Rh}) = 71.8$ Hz), and -5.77 ppm ($J(\text{P-P}) = 22.1$ Hz, $J(\text{P-Rh}) = 71.5$ Hz) for the spectra recorded at 223, 293, and 328 K, respectively. At 293 K the resonances of the phosphorus atoms cis to H appear as a broad, unique band centered at ca. 23 ppm, which is split into two unresolved multiplets at 23.04 and 19.94 ppm at 328 K. Each of the last two resonances is further split into two multiplets at 31.55 and 9.97 ppm when the temperature is lowered to 223 K.

(1) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* 1986, 778.

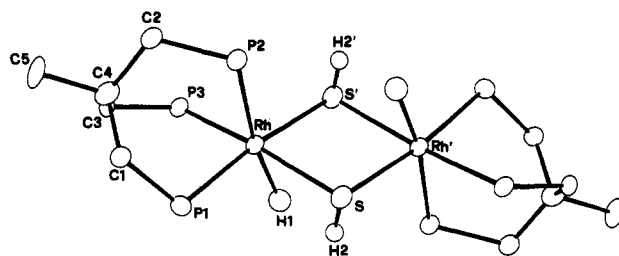
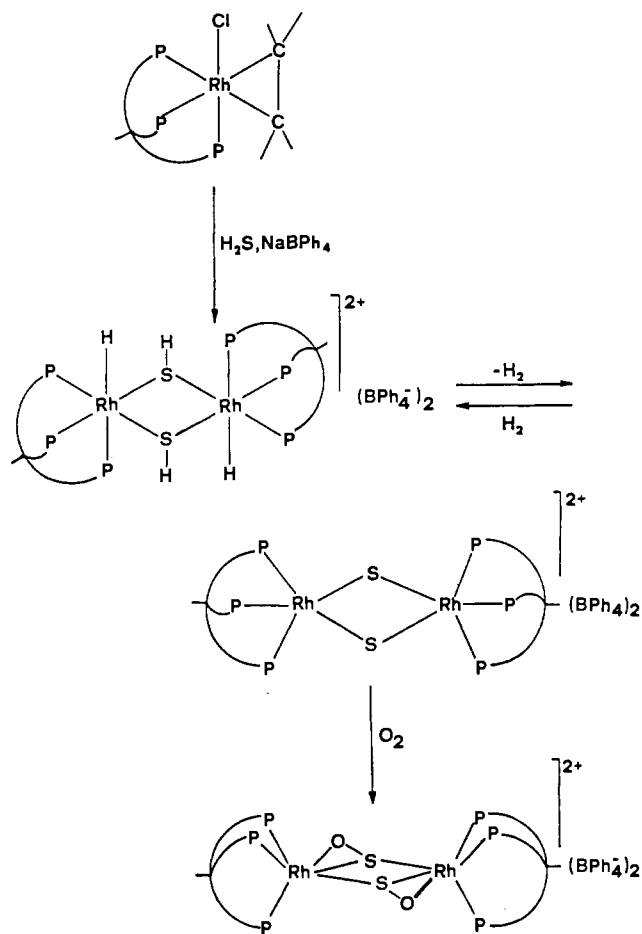


Figure 1. ORTEP drawing of the $[(\text{triphos})\text{HRh}(\mu\text{-SH})_2\text{RhH}(\text{triphos})]^{2+}$ complex cation. Some pertinent bond lengths (\AA) and angles (deg) are as follows: $\text{Rh-Rh}' = 3.617$ (2), $\text{Rh-S} = 2.395$ (3), $\text{Rh-S}' = 2.390$ (3), $\text{Rh-P}(1) = 2.288$ (3), $\text{Rh-P}(2) = 2.407$ (3), $\text{Rh-P}(3) = 2.312$ (3), $\text{Rh-H}(1) = 1.70$ (11); $\text{S-Rh-S}' = 81.9$ (1), $\text{Rh-S-Rh} = 98.2$ (2), $\text{Rh-S-H}(\text{av}) = 92$ (6).

Scheme I



In the X-ray structure of 2^{2+} each rhodium atom of the dimeric cation is coordinated by three terminal phosphine ligands, one hydride ligand, and two shared SH groups (see Figure 1). The Rh-S-Rh-S ring is planar, similar to analogous dimers having the $[(\text{triphos})\text{M}(\mu\text{-S})_2\text{M}(\text{triphos})]$ framework ($\text{M} = \text{Co}, \text{Ni}$)^{3,4} or to the closely related complex $(\text{PPh}_3)_2\text{ClHRh}(\mu\text{-SH})_2\text{RhHCl}(\text{PPh}_3)_2$.⁵ In the latter complex, as well as in 2, the S-H vectors are almost perpendicular to the Rh_2S_2 plane and are almost parallel with the Rh-H vectors (the torsion angles H-

(2) Crystal data: $\text{C}_{130}\text{H}_{122}\text{B}_2\text{P}_6\text{Rh}_2\text{S}_2 \cdot 3(\text{CH}_3)_2\text{NCHO}$; $M_r = 2381.1$; monoclinic, $P2_1/n$; $a = 14.848$ (4), $b = 31.145$ (9), $c = 14.244$ (3) \AA ; $\beta = 105.17$ (2) $^\circ$; $Z = 2$; $D_{\text{calcd}} = 1.24$ g cm^{-3} ; $\mu(\text{Mo K}\alpha) = 4.1$ cm^{-1} . X-ray data were collected on a Philips PW1100 diffractometer. Structure solution and least-squares refinement were based on 3715 absorption-corrected reflections with $I > 3\sigma(I)$ ($2\theta = 45^\circ$). The current R factor is 0.071 ($R_w = 0.077$). The hydride and SH hydrogen atoms, located from a ΔF map, behaved well during refinement.

Rh-S-H are -14.5° in **2**). Thus, the hydrogens linked to one metal and to one sulfur remain in close proximity.

A CH_2Cl_2 solution of **2** under a stream of argon loses 2 mol of H_2 (as determined by GC) and transforms into [(triphos)Rh($\mu\text{-S}$) $_2$ Rh(triphos)](BPh $_4$) $_2$ (**3**) ($^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3COCD_3 , 293 K) 24.02 ppm ($J(\text{P-Rh}) = 102$ Hz, doublet, triphos)). Brown crystals are precipitated by addition of ethanol. A stream of H_2 turns a solution of **3** to the original pink color, and the complex **2** is obtained quantitatively in 4 h. A preliminary X-ray analysis on **3** has confirmed the structural formulation given in Scheme I.

The ability of **3** to activate homodinuclear molecules shows up in the reaction with oxygen. When O_2 is bubbled throughout a CH_2Cl_2 solution of **3**, red crystals of the $\mu\text{-SO}$ complex [(triphos)Rh($\mu\text{-SO}$) $_2$ Rh(triphos)](BPh $_4$) $_2$ (**4**) are obtained quantitatively. The crystal structure and characterization of **4**, prepared by a different synthetic strategy, have recently been reported by us.⁶

- (3) Ghilardi, C. A.; Mealli, C.; Midollini, S.; Nefedov, V. I.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1980**, *19*, 2454.
 (4) Mealli, C.; Midollini, S. *Inorg. Chem.* **1983**, *22*, 2785.
 (5) Mueting, A. M.; Boyle, P.; Pignolet, L. H. *Inorg. Chem.* **1984**, *23*, 44.

Current studies are under way to try to elucidate the mechanism of the present H_2 activation. This might be helpful in understanding some enzymatic hydrogenation processes that have been postulated to proceed via intermediates containing metal-hydride and protonated metal-coordinated thiolates.⁷

Registry No. **1**, 105139-41-1; **2**, 105162-41-2; **3**, 105139-43-3; **4**, 105162-43-4; S^{2-} , 18496-25-8.

Supplementary Material Available: Tables of final fractional coordinates, thermal parameters, and bond distances and angles (4 pages); a table of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

- (6) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1024.
 (7) Yamamura, T.; Christou, G.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 939. Spiro, T. G. *Iron-Sulfur Proteins*; Wiley: New York, 1982; p 177.

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Articles

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Structural Characterization and Cage-Condensation Reactions of the Coupled-Cage Borane 1:2'-[B $_5$ H $_8$] $_2$: New Routes to Higher Single-Cage Boranes and Carboranes

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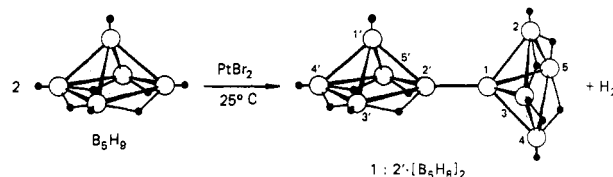
A single-crystal X-ray structure determination of 1:2'-[B $_5$ H $_8$] $_2$ has confirmed that the compound has a coupled-cage structure composed of two pentaborane clusters joined apex to base by means of a two-center two-electron boron-boron bond. The utility of 1:2'-[B $_5$ H $_8$] $_2$ as a precursor to larger single-cage boranes and carboranes has also been explored. It has been found that under appropriate conditions 1:2'-[B $_5$ H $_8$] $_2$ will undergo coupled-cage to single-cage condensations producing important higher cage materials, such as B $_9$ H $_{14}$, B $_9$ H $_{13}$ SMe $_2$, B $_8$ H $_{10}$ NEt $_3$, 1,2-R $_2$ C $_2$ B $_8$ H $_8$, and B $_{12}$ H $_{12}^{2-}$. Crystal data for 1:2'-[B $_5$ H $_8$] $_2$: space group $Pna2_1$; $Z = 4$; $a = 11.020$ (4) Å, $b = 5.870$ (6) Å, $c = 14.988$ (6) Å; $V = 969.5$ Å 3 . The structure was refined by full-matrix least squares to final R of 0.049 and R_w of 0.048 for the 406 unique reflections that had $F_o^2 > 3\sigma(F_o^2)$.

Introduction

We recently reported^{1,2} the development of high-yield, catalytic synthetic routes to boron-boron-coupled polyhedral boranes and carboranes via transition-metal-promoted dehydrocondensation reactions. The facile formation of multicage systems is potentially of great significance in polyhedral borane chemistry since the procedures used for their syntheses provide new pathways to higher boron content materials, which avoid the problems inherent in traditional thermally induced cage growth reactions. Furthermore, if these multicage compounds could be converted to fused-cage boranes or carboranes, then this would represent an alternative to decaborane(14)-based synthetic procedures for the formation of large-cage materials.³

One coupled-cage system of particular interest is the coupled-pentaborane dimer 1:2'-[B $_5$ H $_8$] $_2$, since the compound can now

be made catalytically, in nearly quantitative yields, from the readily available small boron hydride pentaborane(9).



We report here the first structural characterization, by means of a single-crystal X-ray study, of 1:2'-[B $_5$ H $_8$] $_2$ and that furthermore, under appropriate conditions, 1:2'-[B $_5$ H $_8$] $_2$ will undergo multicage to single-cage rearrangements to produce a number of important higher polyhedral boranes.

Experimental Section

Materials. 1:2'-[B $_5$ H $_8$] $_2$ was made by a platinum(II) bromide catalyzed dehydrodimerization reaction previously reported.^{1,2} Pentaborane(9) was obtained from laboratory stock. Platinum(II) bromide, lithium triethylborohydride, and dimethyl sulfide were obtained from Aldrich Chemicals, and 2-butyne, obtained from Farchan Labs, was used as received. Decane and 2,6-lutidine were obtained from Aldrich and dried with P_2O_5 and BaO, respectively. Triethylamine was obtained from

- (1) Corcoran, E. W., Jr.; Sneddon, L. G. *J. Am. Chem. Soc.* **1984**, *106*, 7793-7800.
 (2) Corcoran, E. W., Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182.
 (3) Early work by Grimes and Lipscomb demonstrated, in fact, that a coupled cage compound, 1:1'-[B $_5$ H $_8$] $_2$, can undergo such a conversion (to yield decaborane(14)). See: Grimes, R. N.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, *48*, 496-499.