

the respective scavengings of $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{17}(\text{O}^*)^{3-}$ and $\text{Mo}_7\text{O}_{23}(\text{O}^*)^{6-}$ are nearly complete. Corrections of the $\text{Cr}(\text{III})$, $\text{Ni}(\text{II})$, $\text{Rh}(\text{III})$, and $\text{Fe}(\text{III})$ quantum yields in Table II for incomplete scavenging of the ligand-radical intermediates give values that are very close to those determined with $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}^{3-}$. This observation suggests that population of the dd states by various paths, eqs 6 and 9, does not appear to diminish, to a large extent, the yield of the ligand-radical formation. In this regard, the 2-fold difference between the quantum yields measured respectively at 300 and 254 nm, Table II with $\text{Mo}_7\text{O}_{24}^{6-}$ and $\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}^{3-}$ is likely related to an intrinsic dependence of ϕ_1 , eq 5, on λ_{exc} .²³

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- (23) Preliminary results (Kraut, B.; Ferraudi, B., Work in progress) from extended Huckel MO calculations suggest that there are several LMCT excited states with close energies but centered on different metal ions. These states can be populated with photonic energies within those of the absorption bands in the spectra of the polyoxomolybdates and have characteristic photochemistries, eqs 7-9. These results also indicate that the thermal stability of the intermediates listed in Table I may also be related to the characteristics of the LUMO in such species.

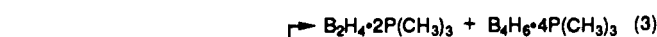
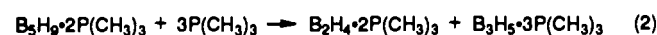
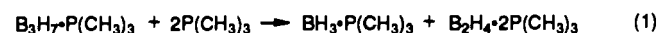
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Reaction of Bis(trimethylphosphine)-Tetraborane(8) with Trimethylphosphine

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Smaller boranes undergo fast, primary reactions with trimethylphosphine. Diborane(6), tetraborane(10), and pentaborane(11) undergo rapid cleavage reactions at low temperatures to give BH_3 , B_3H_7 , and B_4H_8 adducts of $\text{P}(\text{CH}_3)_3$, respectively.^{1,2,3} Pentaborane(9) and hexaborane(10) readily form adducts with $\text{P}(\text{CH}_3)_3$.^{4,5} All of these adducts, except $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$, further react with $\text{P}(\text{CH}_3)_3$ to finally give cleavage products which are electron precise. Thus, eqs 1-4 have been established.^{3,6,7}



Similarly, $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$, the primary cleavage product of B_5H_{11} , was known to further undergo reactions with $\text{P}(\text{CH}_3)_3$.³ However, the exact nature of the reaction products was not established; one of the possible products, $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$, had not been known, and the ^{11}B NMR signals of the products were too broad and close together to be resolved by the instruments that were commonly used at that time. Now that higher field NMR

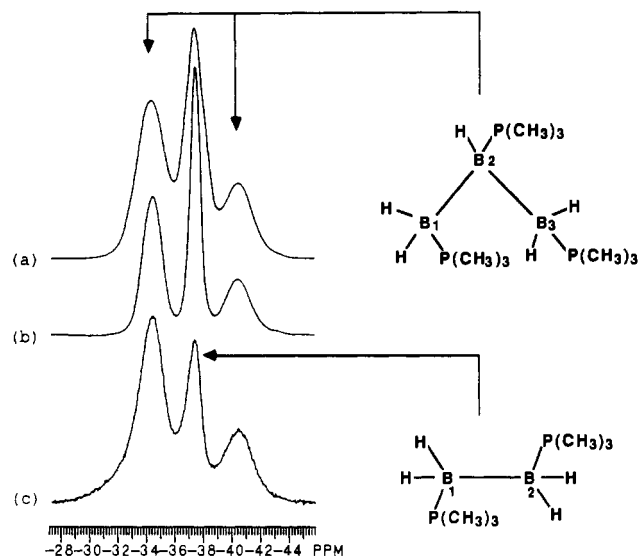


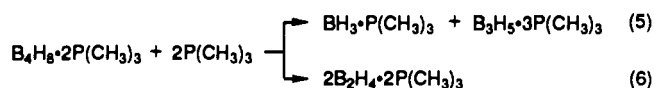
Figure 1. ^{11}B NMR spectra of a 1:1 mixture of $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$ and $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ in dichloromethane at +20 °C: (a) normal spectrum; (b) proton-spin-decoupled spectrum. (c) $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the products from the reaction of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ with excess $\text{P}(\text{CH}_3)_3$ in dichloromethane at -30 °C. $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$ had been removed from the product mixture.

instruments are available, the unequivocal identification of the reaction products is possible. Therefore, the reaction of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ with $\text{P}(\text{CH}_3)_3$ was reinvestigated, and the results of the study are reported in this note.

Results and Discussion

A. ^{11}B NMR Spectrum of $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$. The reaction of $\text{B}_5\text{H}_9\cdot 2\text{P}(\text{CH}_3)_3$ with a large excess of $\text{P}(\text{CH}_3)_3$ gives a 1:1 mixture of $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$.⁴ The 96.2-MHz ^{11}B NMR spectra of this mixture are shown in parts a and b of Figure 1. Unlike those in the 32.1-MHz spectra that were reported earlier,⁴ the signals of $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$ at -34.5 and -40.5 ppm in a 2:1 intensity ratio are seen to be clearly separated from the signal of $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ at -37.5 ppm. The two signals of $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$ are assigned to the $\text{B}_{1,3}$ and B_2 atoms, respectively.

B. Cleavage of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ with $\text{P}(\text{CH}_3)_3$. When B_5H_{11} was dissolved in $\text{P}(\text{CH}_3)_3$, a cleavage reaction of B_5H_{11} occurred immediately at -80 °C, thus producing $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$ and $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ as reported earlier.³ Then, the second reaction proceeded at room temperature, and the framework of the B_4H_8 moiety was cleaved by $\text{P}(\text{CH}_3)_3$ according to eqs 5 and 6. This



cleavage reaction was slow, requiring more than 24 h but less than 50 h for completion when ~ 0.5 -mmol samples of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ were used. No products other than those indicated in eqs 5 and 6 were produced. Shown in Figure 1c is the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of the products from the reaction of B_5H_{11} with $\text{P}(\text{CH}_3)_3$. Prior to the spectrum recording, $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$, one of the reaction products, was removed from the product mixture for spectrum clarity. The relative intensities of the signals indicated that the molar ratio of $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$: $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ in the product mixture was approximately 10:7, or the reactions shown in eqs 5 and 6 proceeded in a 10:3.5 ratio.

C. Conclusion. The trimethylphosphine adduct of tetraborane(8), $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$, was found to undergo clean cleavage reactions with trimethylphosphine to finally give the electron-precise borane adducts $\text{BH}_3\cdot\text{P}(\text{CH}_3)_3$, $\text{B}_2\text{H}_4\cdot 2\text{P}(\text{CH}_3)_3$ and $\text{B}_3\text{H}_5\cdot 3\text{P}(\text{CH}_3)_3$. Thus, the behavior of $\text{B}_4\text{H}_8\cdot 2\text{P}(\text{CH}_3)_3$ is reconciled with those of the $\text{P}(\text{CH}_3)_3$ adducts of other lower boranes.

Experimental Section

Chemicals and Equipment. Conventional high-vacuum line techniques were used throughout for the handling of air-sensitive volatile compounds.

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Pentaborane(11) and $P(CH_3)_3$ were from our laboratory stock and were described elsewhere.⁸ The ^{11}B NMR spectra were recorded on a Varian XL-300 spectrometer, the observe frequency being 96.2 MHz. Diethyl ether-boron trifluoride was used as the external standard for the ^{11}B chemical shifts.

Reaction of B_5H_{11} - $2P(CH_3)_3$ with $P(CH_3)_3$. A 0.129-mmol sample of B_5H_{11} was taken in a 10-mm-o.d. Pyrex tube equipped with a vertical-shaped Teflon valve, and a 26.8-mmol sample of $P(CH_3)_3$ was condensed into the tube at $-197^\circ C$. The tube was then placed in a $-80^\circ C$ bath, and the tube was shaken to mix the contents. A white solid was formed in the liquid $P(CH_3)_3$. As the tube was allowed to warm to $-23^\circ C$, a clear solution resulted. The $^{11}B\{^1H\}$ NMR spectrum of the solution at $-30^\circ C$ indicated that the original B_5H_{11} had been converted completely to $B_4H_8\cdot 2P(CH_3)_3$ and $BH_3\cdot P(CH_3)_3$. The tube was then kept at room temperature for 38 h, after which no noncondensable gas was found in the reaction tube. The $^{11}B\{^1H\}$ spectrum of this solution showed the signals of $B_3H_5\cdot 3P(CH_3)_3$ and $B_2H_4\cdot 2P(CH_3)_3$, which were overlapped by the signal of $BH_3\cdot P(CH_3)_3$. No other signals were present in the spectrum. The tube was placed in a $-45^\circ C$ bath to distill out the solvent $P(CH_3)_3$, and then $BH_3\cdot P(CH_3)_3$ was sublimed out from the tube by pumping at $-10^\circ C$ for 30 h. The resulting white solid residue in the tube was dissolved in CH_2Cl_2 , and the $^{11}B\{^1H\}$ spectrum shown in Figure 1c was recorded.

Several other experiments, in which varied amounts of B_5H_{11} (up to 0.5 mmol) and different reaction temperatures (0 – $45^\circ C$) were used, gave essentially the same $B_3H_5\cdot 3P(CH_3)_3$: $B_2H_4\cdot 2P(CH_3)_3$ product ratios (approximately 10:7). When a reaction solution was held at $0^\circ C$ for 50 h, the reaction was not completed. It was noted that, when the final product mixture was pumped at $0^\circ C$ to remove $BH_3\cdot P(CH_3)_3$, the other products, $B_2H_4\cdot 2P(CH_3)_3$ and $B_3H_5\cdot 3P(CH_3)_3$, remained unchanged; that is, $B_3H_5\cdot 3P(CH_3)_3$ was stable at $0^\circ C$ under vacuum, and its conversion into $B_6H_{10}\cdot 2P(CH_3)_3$ ⁷ did not occur at this temperature.

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- (8) See, for example: Dodds, A. R.; Kodama, G. *Inorg. Chem.* **1979**, *18*, 1465. Kameda, M.; Shimoi, M.; Kodama, G. *Inorg. Chem.* **1984**, *23*, 3705.

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Synthesis and Characterization of $Fe_2Ru(CO)_9(\mu_3-Te)_2$ and $Fe_2Ru_2(CO)_{11}(\mu_4-Te)_2$

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An important development in the area of transition-metal-non-metal cluster chemistry has been the successful use of single atom ligands (e.g. Ge, Sn, P, As, N, Bi, S, Se, and Te) for the purpose of bridging transition-metal moieties.³ The triply bridging configuration is the most commonly observed structure type for sulfur, selenium, and tellurium in clusters. The lone pairs of electrons on the μ_3-S ligands act as Lewis donors toward coordinatively unsaturated metal fragments in numerous cluster growth reactions.⁴ The trinuclear clusters $M_3(CO)_9(\mu_3-S)_2$ ($M = Fe$,

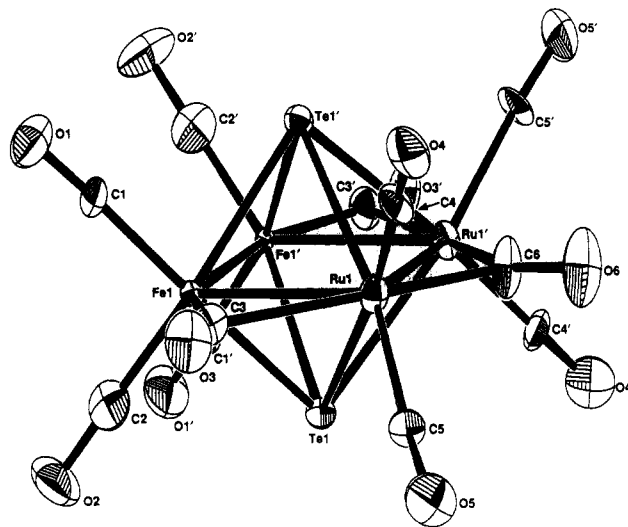


Figure 1. ORTEP drawing of $Fe_2Ru_2(CO)_{11}(\mu_4-Te)_2$, illustrating the atom-numbering scheme.

Ru , Os) have been among the most extensively used of all μ_3-S -containing clusters;⁵ the general strategy involved has been to allow the μ_3-S -containing cluster to interact with a complex containing one or more labile groups, such as $NCMe$,⁶ THF ,⁷ or C_2H_4 ,⁸ or, alternatively, to generate a coordinatively unsaturated species by photolysis⁵ in the presence of the μ_3-S -containing cluster. For instance, in the presence of UV irradiation, $Os_3(CO)_9(\mu_3-S)_2$ reacts with $W(CO)_5(PMe_2Ph)$ to give four mixed-metal clusters: $Os_3W(CO)_{12}(PMe_2Ph)(\mu_3-S)_2$, $Os_3W(CO)_{12}(PMe_2Ph)_2(\mu_3-S)_2$, $Os_3W(CO)_{11}(PMe_2Ph)_2(\mu_3-S)_2$, and $Os_3O_2(CO)_{14}(PMe_2Ph)_2(\mu_3-S)(\mu_3-S)$.⁹

In recent years, tellurium has also been noted for its ability to bridge between small metal aggregates to form larger clusters. Addition of mononuclear¹⁰ and polynuclear¹¹ metal carbonyl fragments occurs readily across the $Te-Te$ bond of $Fe_2(CO)_6(\mu-Te)_2$. Here, we report the synthesis and characterization of two new Te -containing mixed-metal clusters: $Fe_2Ru(CO)_9(\mu_3-Te)_2$ (**1**) and $Fe_2Ru_2(CO)_{11}(\mu_4-Te)_2$ (**2**).

Room-temperature stirring of a hexane solution containing $Fe_2(CO)_6(\mu-Te)_2$ and $Ru(CO)_4(C_2H_4)$ for 1 h formed the cluster $Fe_2Ru(CO)_9(\mu_3-Te)_2$ (**1**), as characterized by IR spectroscopy, mass spectrometry data, and elemental analysis. The infrared spectrum of **1** in hexane solvent shows carbonyl stretching frequencies at 2088 (w) 2084 (w), 2069 (sh), 2056 (s), 2048 (s), 2041 (m), 2027 (s), 2005 (m), and 1997 (m) cm^{-1} . The mass spectrum of **1** shows the molecular ion centered at m/z 722 and peaks at m/z 694, 666, 638, 610, 582, 554, 526, 498, and 470, corresponding to the successive loss of nine carbonyl groups. There is good agreement between the computer simulated and the experimentally obtained isotopic distribution pattern for the $[Fe_2RuTe_2]^+$ ion. Elemental analysis (Calcd for $C_9O_9Te_2Fe_2Ru$: C, 14.9. Found: C, 15.2) confirms the molecular formula of **1**.

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