**Table I.** Infrared Absorbances for Phenba Complexes

| complex | $\nu$,[a] cm$^{-1}$ $\nu$(C=O)[b] | $\nu$(C=O)[c] | $\nu$(C=C) | $\nu$(Os=O) | $\nu$(C≡O)[d] |
|---|---|---|---|---|---|
| (phenba)$Ru^{II}(PPh_3)_2$ | 1553 | 1585 | 1627 | | |
| (phenba)$Ru^{II}(CO)_2$ | 1555 | 1595 | 1630 | | 1910 |
| (phenba)$Os^{VI}(O)_2$ | 1570 | 1595 | 1660 | 848 | |
| (phenba)$Os^{II}_2(PPh_3)_2$ | 1573 | 1595 | 1619 | | |

[a] The medium used for all infrared spectra was Nujol mull. [b] Infrared absorbance for the coordinated acetyl group. [c] Infrared absorbance for the noncoordinated acetyl group. [d] Infrared absorbance for the coordinated carbon monoxide ligand.

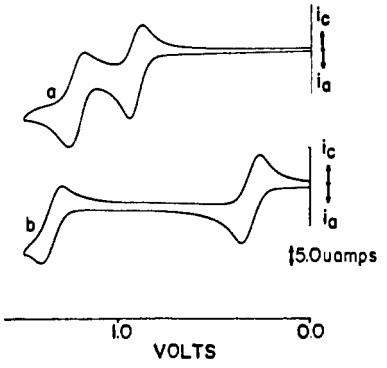


**Figure 6.** Cyclic voltammograms of (a) [(phenba)$Ru^{II}(CO)_2$] in acetonitrile and (b) [(phenba)$Ru^{II}(PPh_3)_2$ in methylene chloride. Scan rate = 100 mV/s.

the phosphine phenyl protons as a broad singlet ($\delta$ 7.19 (30 H)), the phenyl protons overlapped with the phosphine phenyl protons ($\delta$ 7.19 (4 H)), and the methylidene protons as a small singlet ($\delta$ 7.90 (2 H)) (Figure 3).

Starting with (phenba)$Ru^{II}(PPh_3)_2$, the ruthenium trans CO complexes is readily synthesized by utilizing a modification of the method for CO insertion used by Wilkinson.[33] The UV-vis spectrum of the (phenba)$Ru^{II}(CO)^2$ complex (Figure 2) shows one large absorption at 397 nm ($\epsilon$ = 17 700). The $^1$H NMR spectrum shows the resonances expected for the phenba ligand: $\delta$ 8.98 (methylidene, 2 H, s), 7.92, 7.26 (phenyl, 4 H, d), 2.55 (methyl, 6 H, s), 2.47 (methyl, 6 H, s).

Table I lists all assignable absorptions in the infrared region for the ruthenium and osmium complexes, and infrared spectra of selected complexes are shown in Figures 4 (supplemental material) and 5 (supplemental material). The assignment of the stretching frequencies in the $R_2C$=O region are based upon observed trends in other metal complexes with similar ligand environments.[34,35] The coordinated acetyl group is found at a lower frequency than that for the noncoordinated acetyl group and both of these absorptions are of lower energy than that for the olefin. The stretching frequencies for the aromatic rings are at slightly lower frequencies, and tend to be under other bands. The (phenba)$Ru^{II}(CO)_2$ complex shows a strong absorbance at 1910 cm$^{-1}$, which is in the range for a terminal carbon monoxide absorbance.[36]

All of the ruthenium complexes exhibit quasi-reversible waves for the M(III/II) couple (Figure 6). The electrochemical data for the cyclic voltammagrams of reported complexes are as follows: for the ruthenium trans triphenylphosphine complex in methylene chloride, $E_{1/2}$ = +0.29 V, $\Delta E_p$ = 85 mV, $I_{p,c}/I_{p,a}$ = 0.92, and scan rate = 100 mV/s; for the ruthenium trans carbon monoxide complex in acetonitrile, $E_{1/2}$ = +0.91 V; $\Delta E_p$ = 60 mV; $I_{p,c}/I_{p,a}$ = 0.84, and scan rate = 100 mV/s. The (phenba)$Os^{II}(PPh_3)_2$ complex also exhibits a quasi-reversible M(III/II) couple in methylene chloride, with $E_{1/2}$ = -0.03 V, $\Delta E_p$ = 60 mV, and $I_{p,c}/I_{p,a}$ = 0.88 at a scan of 100 mV/s.

**Reactivity.** From the electrochemical data, the $N_2O_2$ phenba ligand appears to be a suitable ligand for redox reagent design, in that the ligand is stable when coordinated to ruthenium(II), ruthenium(III), osmium(II), osmium(III), and osmium(VI). In fact, the osmium complex, (phenba)$Os^{VI}(O)_2$, can act as a stoichiometric oxidizer of benzyl alcohol, yielding exclusively benzaldehyde. Notably, (phenba)$Os^{VI}(O)_2$ is not the active oxidizer; it is necessary to first reduce the (phenba)$Os^{VI}(O)_2$ with 1 equiv of triphenylphosphine, generating the potent oxidizer, (phenba)$Os^{IV}(Ph_3P{=}O)(O)$. When benzyl alcohol and (phenba)$O^{VI}(O)_2$ are combined, the production of benzaldehyde is not observed, but when 1 molar equiv of triphenylphosphine is added, benzaldehyde is formed in stoichiometric amounts. The behavior of osmium(IV) as a more potent oxidizer than osmium(VI) is not unexpected, due to the stabilizing effect of *trans*-dioxo ligands with the osmium(VI) complex. In this regard, the potency of lower oxidation state compounds as oxidants can be observed with other elements, such as with the oxides of chlorine and phosphorus.[37] Notably, the suggested osmium(IV) complex is very reactive and presently cannot be isolated or characterized. Cyclic voltammetric and reactivity studies on the proposed intermediate (phenba)$Os^{IV}(Ph_3P{=}O)O$ are under current investigation.

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**Supplementary Material Available:** Infrared spectra of [(phenba)$Ru^{II}(PPh_3)_2$] (Figure 4) and [(phenba)$Os^{VI}(O)_2$] (Figure 5) (2 pages). Ordering information is given on any current masthead page.

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## $^1$H NMR Study of Iron-Bound Trimethylphosphine in Low-Spin Ferric Complexes of Various Hemoglobins and Myoglobins

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High-resolution nuclear magnetic resonance spectroscopy can be an important tool for characterization of the structure and function of hemoproteins in solution provided that signals corresponding to particular amino acids can be resolved and assigned.[1] These problems can often be eased by NMR investigations of isotopically enriched ligand molecules bound to the heme iron ($^{13}$CO, $^{13}$CNR, C$^{15}$N$^-$).[2-4] Surprisingly, the attractive properties

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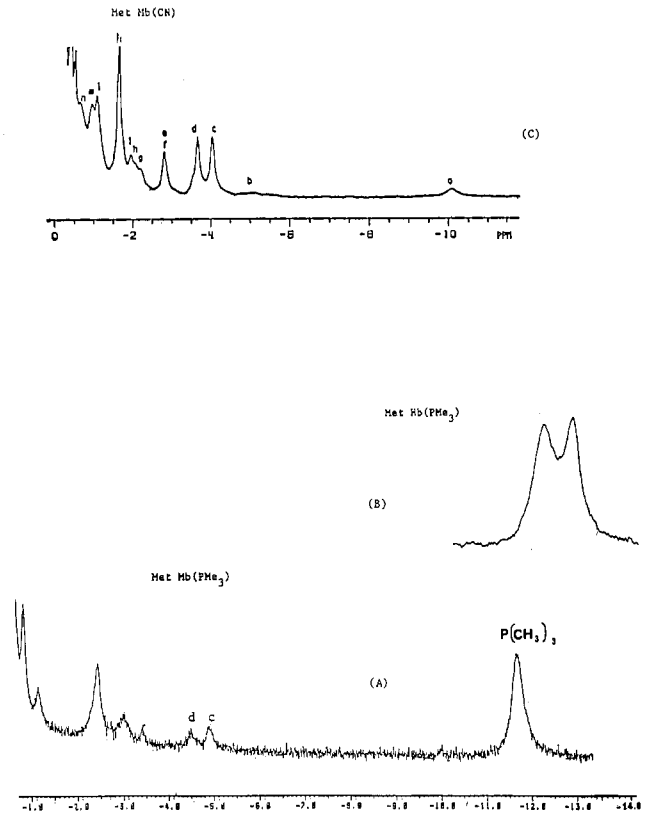


**Figure 1.** (A) Upfield hyperfine shifted portion of the 300-MHz $^1H$ NMR spectrum of sperm whale metMbPMe$_3$ (pH 7.4, 25 °C; 800–1000 transients were collected by using an approximately 10° pulse, 16K, a 15-kHz bandwith, and a pulse repetition time of 1.4 s). (B) $^1H$ NMR spectrum of metHbPMe$_3$ (bovine). (C) $^1H$ NMR spectrum of sperm whale metMbCN.[11]

of trimethylphosphine as a ligand in hemoproteins are only now being appreciated. There is no need of isotopic enrichment, and both $^{31}P$ and $^1H$ NMR spectral studies can be done.[5,6]

Phosphines are more versatile than CO in that they may serve as ligands to both the ferric and ferrous heme iron of hemoproteins. They have been used in an optical spectroscopy probe of the ferric hemoprotein structure in cytochrome P-450[7] and chloroperoxidase enzymes,[8] but neither of these phosphine adducts has been studied by NMR spectroscopy. Here, as an extension of our previous work on hemoglobins,[5,6] studies on $^1H$ paramagnetic shifts of the iron-bound PMe$_3$ in low-spin ferric phosphine complexes of various hemoglobins are reported. It is found that structural differences in the heme environment between PMe$_3$ bound to $\alpha$-type subunits and that bound to $\beta$-type subunits are quite sensitively manifested by the $^1H$ shifts of the heme-bound PMe$_3$.

Addition of PMe$_3$ (3–4 equiv) to sperm whale metmyoglobin immediately gave a phosphine myoglobin complex characterized by its electronic spectrum: 370 nm ($\epsilon$ 47 mM$^{-1}$ cm$^{-1}$), 424 (98), 536 (20). The highly resolved upfield portion of the 300-MHz $^1H$ spectrum of metMbPMe$_3$ is shown in part A of Figure 1. The methyl proton resonance of PMe$_3$ ($\delta$ = −11.65) is shifted upfield from the bulk of the protein resonances. A similar spectral feature was observed in horse heart metMbPMe$_3$ ($\delta$ = −11.7). When bound to various methemoglobins,[9] PMe$_3$ exhibits two distinct peaks in the region of −12 ppm upfield from DSS (Figure 1B). Identification of the two resonances exhibited by PMe$_3$ bound to subunits of human hemoglobin was accomplished by studies on the isolated subunits[10] although the resonances differ slightly from those observed for PMe$_3$ bound to these subunits in the intact tetramer. Table I summarizes the chemical shift data for PMe$_3$ bound to metmyoglobins and methemoglobins.

**Table I.** $^1H$ Chemical Shift Values for the PMe$_3$ Signals in Paramagnetic Hemoproteins from Various Sources[a]

| | source | $\delta$($\beta$ subunit) | $\delta$($\alpha$ subunit) |
|---|---|---|---|
| myoglobin | sperm whale | −11.65 | |
| | horse | −11.70 | |
| hemoglobin | human adult | −12.48 | −13.05 |
| | $\alpha$ SH | | −13.20 |
| | $\beta$ SH | −12.50 | |
| | bovine | −12.41 | −13.05 |
| | rabbit | −12.57 | −13.12 |

[a] Chemical shift in ppm from external DSS (4,4-dimethyl-4-silapentanesulfonate) ±0.04 ppm; 3 mM protein solution in 0.1 M pH 7.4 phosphate/$D_2O$ at 25 °C.

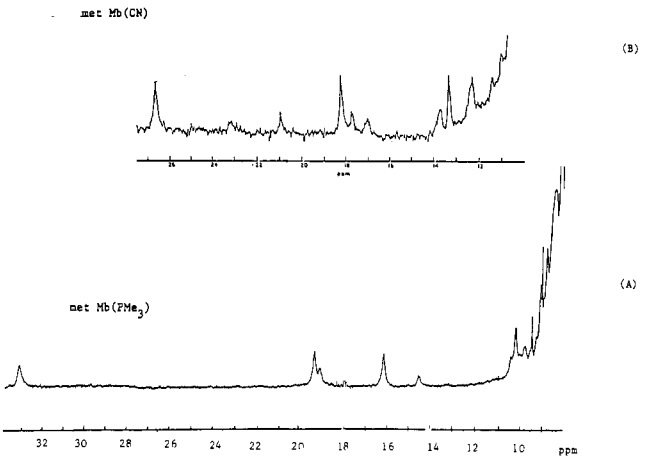


**Figure 2.** (A) 300-MHz downfield region of the $^1H$ NMR spectrum of horse metMbPMe$_3$ (pH 7.4, 25 °C). (B) $^1H$ NMR spectrum of horse metMbCN.[12]

The signals corresponding to PMe$_3$ bound to the $\alpha$ and $\beta$ subunits in human metHb, in bovine metHb, and in rabbit metHb are respectively separated by 0.57 ppm, 0.64 ppm, and 0.55 ppm. What are the origins for the difference between the environments experienced by trimethylphosphine bound to $\alpha$ and $\beta$ subunits in metHb PMe$_3$? We interpret the evidence presently at hand to suggest that these chemical shift differences principally reflect effects transmitted from the polypeptide helix through the proximal histidine $F_8$ to the heme iron and thence to the ligand.[3a] A major argument supports this conclusion: the minor difference in chemical shifts for PMe$_3$ bound to $\alpha$ (or to $\beta$) subunits having a variety of amino acid substitutions contrasts with the large difference between PMe$_3$ bound to $\alpha$-type subunits and that bound to $\beta$-type subunits. This suggests that the $^1H$ PMe$_3$ resonance can serve as a sensitive probe in delineating the binding nature between the heme iron atom and the fifth ligand (proximal histidine) in ferric hemoproteins.

The low-field portion $^1H$ NMR spectrum of metMbPMe$_3$ (horse heart) is illustrated in Figure 2A. The spectra for the metcyano complex of sperm whale[11] and horse heart[12] myoglobins are also

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given respectively in Figures 1C (high field) and 2B (low field) for the purpose of comparison. The striking similarities among the spectra are quite apparent, particularly in the upfield region where each displays a pair of methyl peaks, d and c near −3.5 ppm (Ileu FG5),[11] except for an obvious extra three methyl groups in the region of −12 ppm for the $PMe_3$ ligand. These similarities suggest that the $PMe_3$ complexes are low spin like the $CN^-$ complexes. The low-field regions are also similar, except for a methyl group that is in the region of 35 ppm for metMbPMe$_3$ and in the region of 27 ppm for metMbCN.[12,13] In all cases, the protein methyl peaks all exhibit intensities of 1:3 vs the methyl ligand peak. Since the resolved heme methyl assignments have been previously obtained for metMbCN,[12,13] we propose the same assignment for metMbPMe$_3$. However, the detailed interpretation leading to a description of the metMbPMe$_3$ structure must await definitive assignment of the heme methyl peaks and protein peaks based on nuclear Overhauser effects and 2D NMR methods. Such studies are in progress.

**Acknowledgment.** We thank S. Sinbandhit for 300-MHz NMR measurements (Centre de Mesures Physiques, Rennes, France) and for helpful discussions.

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## High-Yield Preparation of the Tetradecahydroundecaborate(1−) Anion, $[B_{11}H_{14}]^-$, from Pentaborane(9)

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An earlier report from this laboratory[3] described the use of pentaborane(9), $B_5H_9$, as a source for practical syntheses of several higher boron hydride species and the *nido*-carborane 5,6-R,R′-5,6-$C_2B_8H_{10}$ (R,R′ = $CH_3$,$CH_3$; H,H). In the course of this work it was observed that excess $B_5H_9$ employed in the preparation of $[B_9H_{14}]^-$ or reaction temperatures higher than room temperature led to the presence of significant amounts of a $[B_{11}H_{14}]^-$ impurity in the product. By exploitation of these observations, it was found that $B_5H_9$ and $[B_9H_{14}]^-$ react in a 0.4/1 molar ratio to form $[B_{11}H_{14}]^-$ essentially quantitatively. This result in turn led to a high-yield, "one-pot" preparation of $[B_{11}H_{14}]^-$ from the reaction of $B_5H_9$ with a metal hydride (NaH or KH) or a metal alkyl (*tert*-butyllithium, *t*-BuLi).

### Experimental Section

$B_5H_9$ was obtained from Callery Chemical Co., Callery, PA. It was purified by passing it through a U-trap maintained at −78 °C and collected in a second U-trap cooled to −111 °C. NaH and KH were obtained from the Aldrich Chemical Co. as mineral oil dispersions. The oil was washed away with dry pentane,and the compounds were stored in a controlled-atmosphere glovebox until use. Hydride activity was determined by reaction with methanol and measurement of the $H_2$ gas formed by using a calibrated Toepler system. *tert*-Butyllithium was obtained from the Aldrich Chemical Co. as a 2.17 M solution in pentane and refrigerated until use. $[(CH_3)_4N]Cl$, CsCl, and bis(triphenylphosphine)nitrogen(1+) chloride, (PPN)Cl, were obtained from the Aldrich Chemical Co. These salts were dried at 120–140 °C under high vacuum prior to use. Glyme (1,2-dimethoxyethane) was distilled from sodium benzophenone ketyl before use. Materials were handled by using standard vacuum-line and inert-atmosphere techniques.[4] Boron-11 and 2D $^{11}B$–$^{11}B$ NMR spectra were obtained at 96.3 MHz on a Bruker MSL-300 NMR spectrometer. Boron-11 decoupled proton NMR spectra were obtained on a Bruker WM-300 spectrometer. Fourier transform infrared (FT-IR) spectra were obtained on a Mattson Cygnus 25 spectrometer using KBr windows.

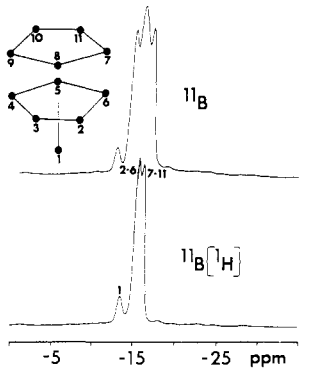


**Figure 1.** 96.3-MHz boron-11 NMR spectra of $K[B_{11}H_{14}]$ in glyme.

In a typical preparation, 373 mg of KH (97% active, 9.02 mmol) was reacted with 1.39 g of $B_5H_9$ (22.0 mmol) in 10 mL of dry glyme in a 500-mL reaction vessel. the KH was first loaded in the drybox, and the reaction vessel was then evacuated on the vacuum line. The volatile materials were condensed into the vessel at −196 °C. The vessel was allowed to warm to ambient temperature and heated to 85 °C for 20 h by using an oil-bath heater. During this time there was a gradual yellowing of the reaction solution. The reaction solution was then allowed to cool, and 32.3 mmol of $H_2$ gas was measured on a calibrated Toepler system and pumped away. Removal of the volatile materials under high vacuum ($<10^{-3}$ mmHg) left a yellow gum. Heating this yellow gum to 90 °C for 24 h, while the volatiles were being removed under dynamic vacuum, produced a yellow solid, $K[B_{11}H_{14}]$, in 85% yield. The IR spectrum in THF or glyme showed a single broad absorption in the B–H stretching region at 2527 $cm^{-1}$.

$Li[B_{11}H_{14}]$ was synthesized by syringing 1.00 mL (2.17M, 2.17 mmol) of *t*-BuLi in pentane into a nitrogen-filled flask through a septum. The flask was cooled to −196 °C, and the nitrogen was evacuated on the vacuum line. Glyme (5–6 mL) and $B_5H_9$ (5.91 mmol) were then condensed into the flask at −196 °C. The reaction was then completed by using the method given above. $[(CH_3)_4N]B_{11}H_{14}$ was obtained by the reaction of 359 mg of KH (99% active, 8.88 mmol), 1.00 g of $[(CH_3)_4N]Cl$ (9.17 mmol), and 1.31 g of $B_5H_9$ (20.9 mmol) in 15 mL of glyme by using a method similar to that given above. KCl produced in the metathesis reacton was separated by filtration of the glyme solution. Volatiles were pumped away, leaving behind 1.83 g (8.83 mmol, 99% based on $B_5H_9$) of yellow, free-flowing product. $CsB_{11}H_{14}$ was similarly prepared by the addition of CsCl to the $B_5H_9$, MH reaction mixture. Anal. Calcd for $CsB_{11}H_{14}$: Cs, 49.98; B, 44.71; H, 5.31. Found: Cs, 49.99; B, 45.16; H, 5.38. $PPN[B_{11}H_{14}]$ and $[(C_6H_5)_4P]B_{11}H_{14}$ were obtained by metathesis of $K[B_{11}H_{14}]$ or $Na[B_{11}H_{14}]$ with (PPN)Cl and $[(C_6H_5)_4P]Br$, respectively.

### Discussion

The reaction of $K[B_9H_{14}]$ with 0.4 equiv of $B_5H_9$ in glyme at 85 °C for 20 h produced $[B_{11}H_{14}]^-$ in essentially quantitative yield, according to eq 1. Boron hydride was not present in the volatiles.

$$K[B_9H_{14}] + 0.4B_5H_9 \xrightarrow[20\ h]{\text{glyme, 85 °C}} K[B_{11}H_{14}] + 1.8H_2 \quad (1)$$

The boron-11 NMR spectrum of the nonvolatile product (Figure 1) indicated the presence of $[B_{11}H_{14}]^-$ as the only boron-containing product. Since $[B_9H_{14}]^-$ is readily produced from the reaction of 1.8 equiv of $B_5H_9$ with KH or NaH in glyme at room temperature,[3,5,6] it was convenient to adapt this procedure to a

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