two resonances. The singlet is assigned to the bridging hydrides, while the quartet arises from the terminal hydride ligands, each of which is split by the three phosphorus nuclei on the corresponding rhenium atom. This assignment is supported by comparison with the spectrum of the structurally characterized complex $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$,[6] which is very similar to that of **3** except that the terminal hydride resonance is seen as a triplet since, in this case, there are only two phosphine ligands bound to each rhenium center. A close resemblance is also seen with the ^1H NMR spectrum of $[Re_2(\mu\text{-}H)_3H_2(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]BF_4$,[14] although the latter complex shows two resonances for the bridging hydride ligands in its low temperature limit (−60 °C) in accord with the presence of inequivalent bridging Re–H bonds. Although these results support structure I, they do not of course unequivocally establish the actual number of hydride ligands present.

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum displays a broad singlet at δ −31.3 in CD_2Cl_2 (δ −30.8 in CD_3OD) for the phosphorus atoms of the PMe_3 ligands and the expected septet near δ −143 for the $[PF_6]^-$ anion. Selective decoupling of the methyl protons of the PMe_3 ligands in the ^{31}P NMR spectrum gives a binomial sextet ($^2J_{PH}$ = 9.0 Hz), thereby confirming the presence of five hydride ligands. When a solution of **3** in CD_3OD is cooled to −40 °C the ^{31}P NMR spectrum splits into a doublet at δ −28.8 ($^2J_{PH}$ = 43.0 Hz). The splitting is comparable to that observed in the ^1H NMR spectrum for the terminal hydride resonance (vide supra). This doublet suggests that the phosphorus signal is split through coupling to only one adjacent hydride ligand. Therefore, I is further supported as being the correct structural formulation for this complex.

The reaction of **1** with PMe_3 that leads to the formation of $[Re_2H_5(PMe_3)_6]^+$ was also monitored by ^1H NMR spectroscopy. A sample of **1** was dissolved in CD_3OD, and an initial spectrum was recorded [δ −7.49 (pentet, Re–*H*), δ +1.66 (doublet, CH_3 of PMe_3)]. Four equivalents of PMe_3 was then injected into the NMR solution, and the progress of the reaction was monitored over time. Within 5 min the formation of the $[Re_2H_5(PMe_3)_6]^+$ cation had already begun, and within 4 h no octahydride remained; approximately 2 equiv of PMe_3 remained when the reaction was complete. An orange solid was isolated from the NMR solution following the addition of KPF_6 and H_2O, and the identity of this product as $[Re_2H_5(PMe_3)_6]PF_6$ (**3**) was confirmed by CV.

(c) Concluding Remarks. The reactions of the dirhenium octahydrides $Re_2H_8(PR_3)_4$ with additional phosphine can be anticipated to proceed as shown in eq 1. The first step has been

$$Re_2H_8(PR_3)_4 \xrightarrow[-H_2]{+PR_3} Re_2H_6(PR_3)_5 \xrightarrow[-H_2]{+PR_3} Re_2H_4(PR_3)_6 \qquad (1)$$

shown to occur in the case of $PR_3 = PMe_2Ph$,[15,16] and the resulting complex has been structurally characterized.[15] The second step has only been reported in the case of $Re_2H_8(PMe_2Ph)_4$ reacting with the phosphite ligand $P(OCH_2)_3CEt$, a reaction that affords $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$.[14] This complex is readily converted into its conjugate acid $[Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]^+$ upon treatment with $HBF_4{\cdot}Et_2O$.[14] One possibility is that in the reaction of $Re_2H_8(PMe_3)_4$ with PMe_3, the dirhenium tetrahydride $Re_2H_4(PMe_3)_6$ is formed but it is such a potent base (more so even than Caulton's complex)[14] that it is very rapidly protonated by the methanol solvent to form the weak acid $[Re_2H_5(PMe_3)_6]^+$, isolable as its $[PF_6]^-$ salt **3**. In the NMR experiment described in section b, we found no spectroscopic evidence for the presence of significant amounts of $Re_2H_4(PMe_3)_6$.[17] All attempts to deprotonate **3** and its one-electron-oxidized congener **4** failed (see Experimental Section). The dirhenium pentahydride complexes **3** and **4** constitute rare example of this class of complex; the complexes $[Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]BF_4$[14] and $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$[4,6] are the only examples to have been reported previously.

Acknowledgments. Support from the National Science Foundation (Grant No. CHE88-07444) is gratefully acknowledged. We also thank the National Institutes of Health (Grant No. RR-01077) and the National Science Foundation (Grant No. 8714258) for funds for the purchase of the NMR spectrometers. We are grateful to Professor K. G. Caulton (Indiana University) for helpful discussions relating to the possible mechanisms of the reactions described in this report. The variable-temperature NMR spectral measurements were carried out with the kind assistance of Perry Pellechia.

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(17) Note added in proof. We have now succeeded in isolating $Re_2H_6(PMe_3)_5$ from the reaction of $Re_2H_8(PMe_3)_4$ with an excess of PMe_3 in benzene; H_2 is the byproduct of this reaction. When $Re_2H_6(PMe_3)_5$ is reacted with PMe_3 in CH_3OH, then $[Re_2H_5(PMe_3)_6]^+$ is the final product (by ^1H NMR spectroscopy). This reaction proceeds through an intermediate [δ −6.47 (sextet, Re–*H*, $J_{PH} \simeq$ 7.6 Hz)], which could be the cation $[Re_2H_5(PMe_3)_5]^+$. This intermediate is captured by the excess PMe_3 present and converted into $[Re_2H_5(PMe_3)_6]^+$. Further mechanistic studies are under way.

Additions and Corrections

1989, Volume 28

Hyunkyu Kang, Shuncheng Liu, Shahid N. Shaikh, Terrence Nicholson, and Jon Zubieta*: Synthesis and Structural Investigation of Polyoxomolybdate Coordination Compounds Displaying a Tetranuclear Core. Crystal and Molecular Structures of $[n\text{-}Bu_4N]_2[Mo_4O_{10}(OMe)_4X_2]$ (X = –OMe, –Cl) and Their Relationship to the Catecholate Derivative $[n\text{-}Bu_4N]_2[Mo_4O_{10}(OMe)_2(OC_6H_4O)_2]$ and to the Diazenido Complexes of the *o*-Aminophenolate and the Naphthalene-2,3-diolate Derivatives $[n\text{-}Bu_4N]_2[Mo_4O_6(OMe)_2(HNC_6H_4O)_2(NNC_6H_5)_4]$ and $[n\text{-}Bu_4N]_2[Mo_4O_6(OMe)_2(C_{10}H_6O_2)_2(NNC_6H_5)_4]$. Comparison to the Structure of a Binuclear Complex with the $[Mo_2(OMe)_2(NNC_6H_5)_4]^{2+}$ Core, $[Mo_2(OMe)_2(H_2NC_6H_4O)_2(NNC_6H_5)_4]$.

Pages 920–933. The compound $[n\text{-}Bu_4N]_2$[III] and the previously reported compound $[n\text{-}Bu_4N]_2[Mo_4O_8(OEt)_4Cl_4]$ are incorrectly formulated as mixed-valence Mo(V)/Mo(VI) species. As previously indicated by Lincoln and Koch,[1] the latter complex is in fact the Mo(V) species $[n\text{-}Bu_4N]_2[Mo_4O_8(OEt)_2(HOEt)_2Cl_4]$, with coordinated alcohol, as well as alkoxy groups. Comparison of the Mo2–O6 distance for *III* to the corresponding Mo1–O3 distance for I (2.232 (5) Å vs 1.915 (2) Å) clearly establishes the former as an alcohol oxygen donor, rather than an alkoxy donor as previously suggested by us. The complexes of the type $[R_4N]_2[Mo_4O_8(OR)_2(HOR)_2Cl_4]$ exhibit the $[Mo_4O_8(OR)_2]^{2+}$ core with peripherally coordinated Cl^- and HOR ligands, not the $[Mo_4O_8(OR)_2]^{4+}$ core with Cl^- and OR^- ligands as originally formulated.

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—Jon Zubieta