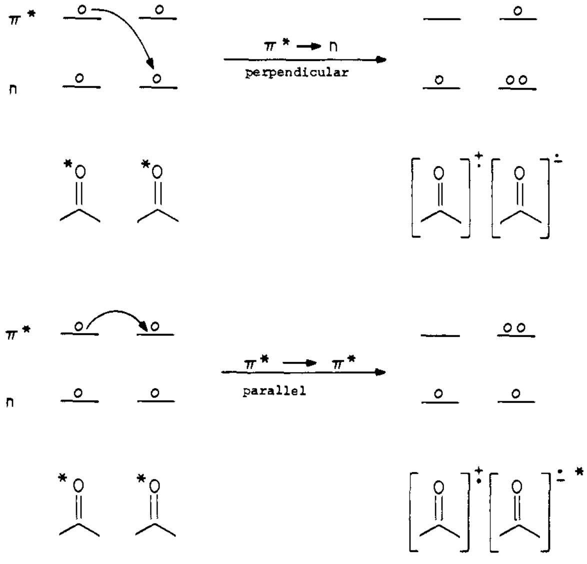

Figure 3. Molecular orbital diagram for the interaction of two n,π* excited states. For simplicity, an extreme CT situation is depicted. The emission of X* could be due either to a local transition perturbed by the companion ketone of the complex or to a transition involving both partners.

thermore, for the n,π* state in either pathway, the n orbital is a potential one-electron acceptor and the π* orbital is a potential one-electron donor. Which of these acceptor–donor properties is manifest depends on the species interacting with the n,π* state. If we postulate[8] that the interactions of *two* n,π* triplets are analogous to those of an n,π* triplet and a ground state, then the simple MO diagram given in Figure 3 suggests that a perpendicular approach should favor a π* → n CT interaction, whereas a parallel approach should favor a π* → π* interaction (in the latter case, the system need not be symmetrical in order to take advantage of CT interactions). For the π* → π* interaction, the model indicates that an electronically excited complex X* is favored. The solvent effects on the emission of X* are expected if it possesses considerable substantial CT character, since radiationless relaxation pathways of such species are known to be strongly favored by increasing solvent polarity.[7b] The absence of emission may be due to several factors including short triplet lifetimes which allow first-order decay to dominate even at high laser powers and to differences in quenching mechanisms, e.g., π* → n interactions (Figure 3) in the triplet–triplet annihilation step.

Although the above proposal is consistent with our observations, several rather ad hoc postulates are required. We, therefore, mention that two other possibilities could be considered to explain the unusual emission, namely, that triplet–triplet interactions produce a structure that is difficult or impossible to achieve via triplet–ground state interactions. For example, two triplets can interact cooperatively to stimulate an emission analogous to the "dimole" emission of excited pairs of oxygen molecules.[9] However, the energy of this emission would be expected to be observed at much higher, not lower, energies than that of a single triplet. A second possibility is that X* is an emissive excimer and that its formation does not occur via triplet–ground state interactions.[10]

In conclusion, at high laser intensities excitation of benzophenone and certain substituted benzophenones in nonpolar, inert solvents results in the observation of a novel emission that is attributed to an electronically excited complex produced by triplet–triplet interactions.

Acknowledgment. We thank the Air Force Office of Scientific Research and the National Science Foundation for their generous support of this research. Professor Larry Singer is also thanked for his kind gift of several of the ketones employed in this study.

Registry No. Benzophenone, 119-61-9; 4-methoxybenzophenone, 611-94-9; 4-methylbenzophenone, 134-84-9; 4-chlorobenzophenone, 134-85-0; 4-(carbomethoxy)benzophenone, 6158-54-9; 4,4′-bis(trifluoromethyl)benzophenone, 21221-91-0; 4,4′-difluorobenzophenone, 345-92-6; 4,4′-dimethoxybenzophenone, 90-96-0.

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(7) (a) Knibbe, H.; Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 839. (b) Weller, A. *Pure Appl. Chem.* **1968**, *16*, 115.

(8) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

(9) Kasha, M.; Brabham, D. E. *Org. Chem. (N.Y.)* **1979**, *40*, 1. We thank a referee for this clever suggestion.

(10) Dr. T. Evans of Kodak Co. has suggested that the annihilation of two triplets could lead to the geometry that is required for excimer formation.

(11) Thus, it is conceivable that excimer formation via the "usual" excited-state–ground-state interactions is unfavorable, whereas excimer formation via excited-state–excited-state interaction is favorable.

Metal-Metal Bonded Complexes of the Early Transition Metals. 3. Synthesis, Structure, and Reactivity of $Ta_2Cl_4(PMe_3)_4H_2$ (Ta=Ta)[1]

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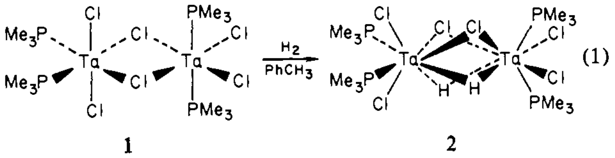
Metal-metal bonded binuclear complexes of the group 5 transition elements are quite rare,[2] especially when compared to the plethora of such compounds in group 6 chemistry.[3] We are currently exploring the binuclear chemistry of the group 5 elements in search of new structural and reactivity patterns. Our initial investigations[2f] led to the synthesis of the tantalum(III) dimer, $Ta_2Cl_6(PMe_3)_4$ (**1**), whose edge-sharing bioctahedral geometry contrasts with the confacial bioctahedral stereochemistry found earlier in the tetrahydrothiophene (THT) complexes of Templeton and McCarley,[2b] e.g., $Ta_2Br_6(THT)_3$. Compound **1** is the only known metal-metal multiply bonded (Ta=Ta) complex which reacts directly (reaction 1) with molecular hydrogen, and it does so under very mild conditions (25 °C, 1 atm of H_2) to form the quadruply bridged tantalum(IV) dimer, $Ta_2Cl_6(PMe_3)_4H_2$ (**2**).[2f] We have now found that **2** offers a convenient entry into tantalum(III) dimer chemistry.



1 **2** (1)

Reduction of **2** in ethylene glycol dimethyl ether (glyme) with 2 equiv of sodium amalgam (reaction 2) provides air-sensitive, deep green, crystalline **3** in essentially quantitative yield.[4]

$$\underset{\mathbf{2}}{Ta_2Cl_6(PMe_3)_4H_2} + 2Na/Hg \xrightarrow{(CH_3OCH_2)_2} \underset{\mathbf{3}}{Ta_2Cl_4(PMe_3)_4H_2} + 2\,NaCl \quad (2)$$

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(1) Part 2: Sattelberger, A. P.; McLaughlin, K. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2880–2882.

(2) (a) Broil, A.; Schnering, H. G.; Schäfer, H. *J. Less-Common Met.* **1970**, *22*, 243–245. (b) Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263–1267. (c) Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886–7891. (d) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354–2356. (e) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* **1981**, *20*, 2716–2719. (f) Sattelberger, A. P.; Wilson, R. B., Jr.; Huffman, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7111–7113.

(3) (a) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 26. (b) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225–232. (c) Chisholm, M. H.; Cotton, F. A. *Ibid.* **1978**, *11*, 356–362. (d) Templeton, J. L. *Prog. Inorg. Chem.* **1979**, *26*, 211–300.

(4) Elemental analyses and molecular weight measurements were performed by Galbraith Laboratories, Knoxville, TN. Anal. Calcd for $Ta_2Cl_4(PMe_3)_4H_2$ ($Ta_2Cl_4P_4C_{12}H_{38}$): C, 17.78; H, 4.69; Cl, 17.51; M_r, 810. Found: C, 17.82; H, 4.65; Cl, 17.84; M_r, 813.

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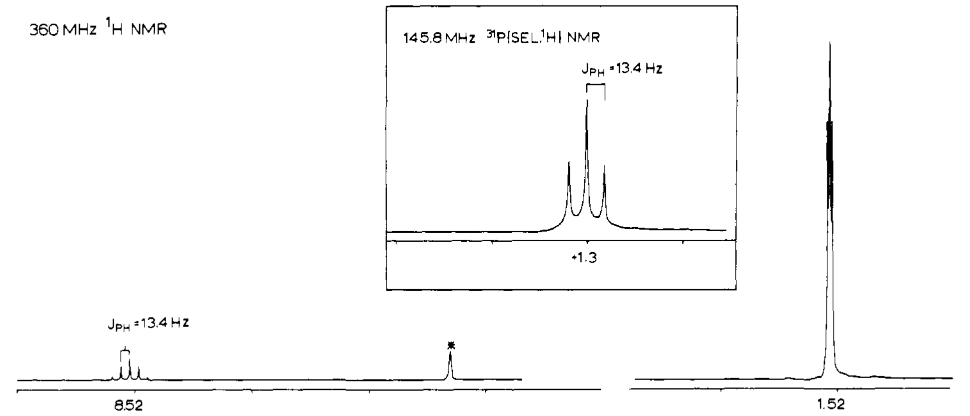


Figure 1. 360-MHz ^1H NMR spectrum of **3** at 25 °C, C_6D_6 solvent (*). Chemical shifts (δ) are in ppm downfield from Me_4Si. The insert shows the 145.8-MHz ^{31}P NMR spectrum of **3** with selective ^1H decoupling at δ 1.52. ^{31}P chemical shifts are in ppm from external H_3PO_4.[5]

Compound **3** is dimeric in benzene, and its ^1H and ^{31}P [selectively decoupled from $P(CH_3)_3$] NMR spectra[5,6] are shown in Figure 1. The ^1H resonance at δ 8.52 (area 2) is assigned to two bridging hydride ligands[7] and the resonance at δ 1.52 (area 36) to the methyl hydrogens of virtually coupled, pseudotrans PMe_3 ligands (vide infra). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ +1.3 which splits into a 1:2:1 triplet upon selective decoupling of the methyl protons. Because the NMR data indicate chemical and magnetic equivalence of the hydride and phosphine ligands, and by analogy with the structure of **1**, we assumed that **3** was an edge-sharing bioctahedron with bridging hydride ligands and four axial phosphines. Space-filling molecular models, however, render such a ligand arrangement sterically untenable. Structural characterization of **3** was therefore desirable to ascertain the correct geometry.

Crystals of **3** were grown from concentrated glyme solutions at −35 °C and its structure determined from X-ray diffraction data collected at −160 °C.[8] The molecular geometry is shown in Figure 2. Neglecting, momentarily, the bridging hydride ligands, we note that the $Ta_2Cl_4(PMe_3)_4$ substructure closely resembles that of the quadruply bonded dimers $Mo_2Cl_4(PMe_3)_4$[10] and $W_2Cl_4(PMe_3)_4$.[10,11] The pseudo square planes of chloro and phosphine ligands are in the eclipsed conformation and the four PMe_3 ligands are staggered among themselves. The Ta═Ta separation of 2.545 (1) Å is comparable to the W═W bond length of 2.530 (2) Å found in $W_2S_2(S_2CNEt_2)_4$.[12] The Ta–Ta–Cl and Ta–Ta–P angles are 116.0 (1) and 102.0 (1)°, respectively. A twofold axis passing through Ta(1) and Ta(2) is required by the space group.

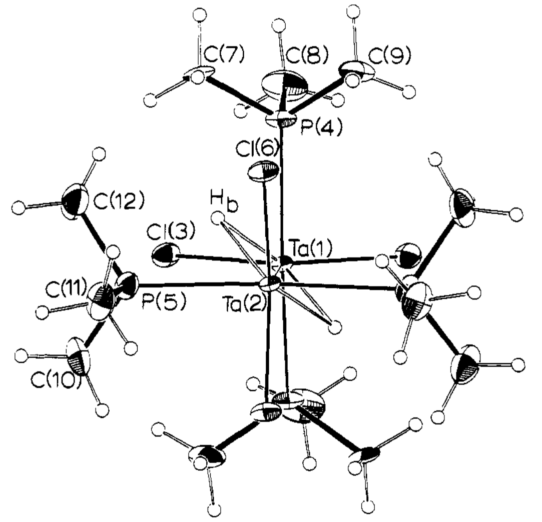
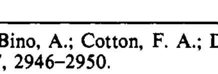
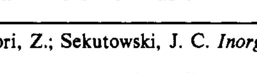


Figure 2. ORTEP drawing of $Ta_2Cl_4(PMe_3)_4H_2$ (**3**). Selected data not presented in the text: Ta(1)–Cl(3), 2.418 (3) Å; Ta(2)–P(5), 2.600 (3) Å; Cl(3)–Ta(1)–Cl(3′), 128.1 (1)°; P(5)–Ta(1)–P(5′), 156.1 (1)°.

There are two conceivable locations for the bridging hydrides in **3**. They are either on the mirror planes of C_{2v} structure A or on the diagonal planes of C_2 structure B. Neither of these static



A



B

structures can account for the NMR data in Figure 1, and regardless of which is the correct solid-state structure, there must be rapid rotation of the end groups and/or bridging ligands in solution to account for the apparent magnetic equivalences.[13] We favor structure B on the basis of the following considerations: (1) A peak[14] was located in the final difference Fourier 1.97 Å from

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[5] Proton and ^{31}P NMR spectra were recorded at 360.1 and 145.8 MHz, respectively, on a Brucker 360 spectrometer. Proton chemical shifts (δ) are in ppm downfield from Me_4Si. ^{31}P chemical shifts are in ppm from external H_3PO_4. Shifts are negative for lines upfield of H_3PO_4. Free PMe_3 in benzene-d_6 appears at δ −63.3. Benzene-d_6 was used in all experiments except as noted.

[6] NMR data on **3**: ^1H NMR (ppm, C_6D_6) 8.52 (quintet, 2, J_{PH} = 13.4 Hz, H_b), 1.52 [virtual triplet, 36, J_{PH} (apparent) = 3.8 Hz, $P(CH_3)_3$]; ^{31}P NMR (ppm, C_6D_6, $\{^1H\}$) +1.3 (s); ^{31}P NMR (ppm, C_6D_6, selective $\{^1H\}$ of $P(CH_3)_3$) +1.3 (t, J_{PH} = 13.4 Hz).

[7] The IR spectrum of **3** (KBr disk) at ambient temperature shows a band of moderate intensity at 1232 cm^{-1} which we have assigned as a Ta–H–Ta vibration. The corresponding band in $Ta_2Cl_4(PMe_3)_4D_2$ (prepared from $Ta_2Cl_6(PMe_3)_4D_2$ + 2Na/Hg) appears at 860 cm^{-1}.

[8] $Ta_2Cl_4(PMe_3)_4H_2$ (**3**) crystallizes in the monoclinic space group $C2/c$ with a = 18.371 (5) Å, b = 9.520 (3) Å, c = 18.942 (6) Å; β = 125.36 (2)°, V = 2701.8 Å^3, and ρ(calcd) = 1.991 g cm^{-3} for M_r 810.04 and Z = 4. X-ray diffraction data were collected at −160 °C by a θ–2θ scan technique described in detail elsewhere.[9] Date were corrected for absorption (μ = 86.3 cm^{-1}) and the structure solved by a combination of Patterson, difference Fourier, and full-matrix least-squares refinement techniques. All atoms, including the bridging hydride (see text), were located. The positional and thermal parameters (anisotropic for Ta, Cl, P, and C; isotropic for H) of all *nonbridging* atoms were refined. The resulting discrepancy indexes are R_F = 0.046 and R_{wF} = 0.047 for those 2155 reflections with $F_0 \geq 2.33\sigma(F_0)$. The limits of data collection were $6 \leq 2\theta \leq 45°$ (Mo Kα radiation).

[9] Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755–2762.

[10] Cotton, F. A.; Extine, M. W.; Felthouse, T. R.; Kolthammer, B. W. S.; Lay, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4040–4049.

[11] Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430–1431.

[12] Bino, A.; Cotton, F. A.; Dori, Z.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 2946–2950.

[13] No significant changes were observed in the ^1H or ^{31}P NMR spectra of **3** from −80 to +30 °C (toluene-d_8 solution).

[14] We have made a careful search of the final difference Fourier map, and this is the only peak which can be assigned to a bridging hydride ligand. Several other peaks of comparable or greater density were also observed, but these were close to chlorine, phosphorus, or tantalum atoms. No attempt has been made to refine the positional and thermal parameters of the bridging hydride. We note that the calculated Ta–H distances and the Ta–H–Ta angle are comparable to those found in the bridging region of $H_8Re_2(PEt_2Ph)_4$[15] (Re–H, 1.878 (7) Å; Re–H–Re, 85.0 (3)°; Re–Re, 2.538 (4) Å) by neutron diffraction. Attempts are being made to grow crystals of **3** which are suitable for neutron diffraction.

Ta(1) and 1.86 Å from Ta(2). Its density (~0.8 eÅ^{-3}) is appropriate for a bridging hydrogen, and it lies on the diagonal plane. The Ta–H$_b$–Ta angle is 83.1° and the shortest intramolecular contact is H$_b$–P(5) at 2.54 Å. (2) Rotation of the hydrogen position by 45° into the all eclipsed conformation of structure A shortens the aforementioned contact to 2.02 Å. (3) The stereochemistry of the oxidative–addition products of **3** (vide infra) follows logically from structure B. (4) Molecular orbital arguments, advanced by Hoffmann and co-workers,[16] suggest that the staggered hydride arrangement is favored in dimers with eclipsed pyramidal end groups.

Ether solutions of **3** react readily with hydrogen, hydrogen chloride or chlorine to give the binuclear products indicated in

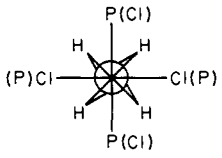
$$3 + H_2 \xrightarrow{Et_2O} \underset{\mathbf{4}}{Ta_2Cl_4(PMe_3)_4H_4} \qquad (3)$$

$$3 + HCl \xrightarrow{Et_2O} \underset{\mathbf{5}}{Ta_2Cl_5(PMe_3)_4H_3} \qquad (4)$$

$$3 + Cl_2 \xrightarrow{Et_2O} \underset{\mathbf{2}}{Ta_2Cl_6(PMe_3)_4H_2} \qquad (5)$$

reactions 3–5.[17] These products have been characterized by elemental analyses and molecular weight measurements[18,19] or, in the case of $Ta_2Cl_6(PMe_3)_4H_2$ (**2**), by comparison with a sample prepared by the original route (vide supra). In the absence of definitive crystallographic proof, we suggest that $Ta_2Cl_4(PMe_3)_4H_4$ (**4**)[20] and $Ta_2Cl_5(PMe_3)_4H_3$ (**5**) have structures intimately related to **2**, i.e., all have similar $Ta_2Cl_4(PMe_3)_4$ substructures, Ta–Ta single bonds, and four bridging ligands (4 H in **4**; 3 H, 1 Cl in **5**; 2 H, 2 Cl in **2**).

The NMR data on **4**[18] and **5**[19] are consistent with the end-on projections shown below. (Atoms in parenthesis are associated with the second tantalum.) Further work on the reactivity of **3** is in progress and will be reported in the future.



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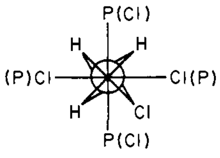

5

In summary, we make the following observations: (1) The structure of $Ta_2Cl_4(PMe_3)_4H_2$ (**3**) represents a distinct new stereochemisty in binuclear tantalum chemistry and suggests that triply bonded eclipsed $Ta_2Cl_4(PMe_3)_4$ is a realistic synthetic objective. (2) X–Y substrates can add across the metal–metal bond of **3**, decreasing the bond order from 2 to 1, and there are none of the gross structural rearrangements which usually accompany oxidative–addition reactions of metal–metal bonded complexes.[21] (3) The oxidative–addition of H_2, HCl, and Cl_2 to a single metal–metal multiply bonded complex has no precedent in binuclear chemistry.[22]

Acknowledgment. The financial support of the U.S. Department of Energy under Grant DE-FG02-80ER10125 is gratefully acknowledged. We also thank the Marshall H. Wrubel Computing Center, Indiana University, for a generous gift of computing time. The Brucker 360 NMR spectrometer used in our research was purchased, in part, by funds provided by the National Science Foundation.

Supplementary Material Available: Tables of final fractional coordinates and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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(15) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1977**, *99*, 3872–3874.

(16) Dedieu, A.; Allbright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141–3151.

(17) Reaction 3 was run at 25 °C under 4 atm of hydrogen in a Fisher–Porter pressure vessel. In reactions 4 and 5, the reagent (HCl or Cl_2) was dissolved in ether and added dropwise to a precooled (−20 °C) solution of **3**.

(18) Anal. Calcd for $Ta_2Cl_4(PMe_3)_4H_4$ (**4**) ($Ta_2Cl_4P_4C_{12}H_{40}$): C, 17.75; H, 4.96; Cl, 17.46; M_r, 812. Found: C, 17.61; H, 5.01; Cl, 17.39; M_r 799. NMR data: ^{1}H NMR (ppm, C_6D_6) 8.79 (m, 4, H$_b$), 1.47 (m, 36, J_{HP} ~4 Hz, $P(CH_3)_3$); ^{31}P NMR (ppm, C_6D_6, {^{1}H}) −1.8(s); IR (cm^{-1}, KBr disk) 1225 (m, $\nu_{Ta-H-Ta}$).

(19) Anal. Calcd for $Ta_2Cl_5(PMe_3)_4H_3$ (**5**) ($Ta_2Cl_5P_4C_{12}H_{39}$): C, 17.03; H, 4.64; Cl, 20.94; M_r, 846.5. Found: C, 16.89; H, 4.60; Cl, 20.95; M_r, 853. NMR data: ^{1}H NMR (ppm, C_6D_6) 9.68 (complex m, 1, H$_b$), 7.69 (complex m, 2, H$_b'$), 1.60 (d, 18, J_{PH} = 9.3 Hz, $P(CH_3)_3$), 1.29 (d, 18, J_{PH} = 8.8 Hz, $P'(CH_3)_3$); ^{31}P NMR (ppm, C_6D_6, {^{1}H}) +8.45 (AA′XX′, m, 1, $P(CH_3)_3$), $J_{AX} + J_{AX'}$ = 28.7 Hz), −13.34 (AA′XX′, m, 1, $P'(CH_3)_3$, $J_{AX} + J_{AX'}$ = 28.7 Hz). IR (cm^{-1}, KBr disk): 1335, 1260 (m, $\nu_{Ta-H-Ta}$).

(20) (a) $Ta_2Cl_4(PMe_3)_4H_4$ (**4**) has been prepared previously by Fellmann[20b] and Schrock from monomeric $Ta(CHCMe_3)(H)Cl_2(PMe_3)_3$ and molecular hydrogen. Schrock, R. R.; Fellmann, J. D., private communication. (b) Fellman, J. D. Ph.D. Thesis, Massachusetts Institute of Technology, 1980.

(21) (a) Chisholm, M. H. *Transition Met. Chem.* **1978**, *3*, 321–333 and references therein. (b) Chisholm, M. H.; Kirkpatrick, C. C.; Huffman, J. C. *Inorg. Chem.* **1981**, *20*, 871–876.

(22) (a) The Mo≡Mo triple bond of $[CpMo(CO)_2]_2$ will add HI and I_2 but not H_2.[22b] (b) Curtis, M. D.; Messerle, L.; Fotinos, N. A.; Gerlach, R. F. In "Reactivity of Metal–Metal Bonds"; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, Chapter 12.

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^{95}Mo and ^{1}H ENDOR Spectroscopy of the Nitrogenase MoFe Protein

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The resting state of the nitrogenase molybdenum-iron (MoFe)[1] protein exhibits an EPR spectrum unique among biological systems.[2] It is associated with the molybdenum-iron cofactor (FeMo-co; 6–8 Fe, 4–6 S* per molybdenum) and is characteristic of a metal center with total electron spin of $S = {}^{3}/_{2}$.[3] Enrichment with ^{57}Fe broadens the signal, proving that the unpaired spins are associated with iron,[4] but lack of resolution precludes detailed analysis. Analysis of the Mössbauer effect of MoFe proteins shows that six Fe atoms are present in the $S = {}^{3}/_{2}$ center.[4] The EPR signal was not detectably broadened by enrichment with ^{95}Mo.[4] This shows that the signal is not associated with a simple $S = {}^{3}/_{2}$ Mo(II) but gives no further information about the characteristics of the molybdenum in the cofactor, although EXAFS measurements suggest that S and Fe atoms are nearby.[5] The modulation of electron-spin echo decay curves is affected by ^{95}Mo, but these data have been refractory to detailed analysis.[6] In short, present data associate the Fe with the $S = {}^{3}/_{2}$ center and the Mo with

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(1) Abbreviations: MoFe, molybdenum–iron; FeMo-co, molybdenum–iron cofactor; EPR, electron paramagnetic resonance; ENDOR, electron nuclear double resonance.

(2) Orme-Johnson, W. H.; Hamilton, W. D.; Jones, T. L.; Tso, M.-Y. W.; Burris, R. H.; Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 3142–3145.

(3) Rawlings, J.; Shah, V. K.; Chisnell, J. R.; Brill, W. J.; Zimmerman, R.; Munck, E.; Orme-Johnson, W. H. *J. Biol. Chem.* **1978**, *253*, 1001–1004.

(4) Munck, E.; Rhodes, H.; Orme-Johnson, W. H.; Davis, L. C.; Brill, W. J.; Shah, V. K. *Biochim. Biophys. Acta* **1975**, *400*, 32–53.

(5) Tullius, T. D.; Conradson, S. D.; Berg, J. M.; Hodgson, K. O. In "Molybdenum Chemistry of Biological Significance"; Newton, W. E., Otsuka, S., Eds.; Plenum Press: New York, 1980.

(6) Orme-Johnson, W. H.; Peisach, J.; Mims, W. B., in progress.

0002-7863/82/1504-0860$01.25/0