spectrum exhibits three peaks. That close to 285 eV is due to the usual adventitious carbon "contaminant", while the primary photoline at 286.4 eV can be assigned[8,9,15] to an overlap in the C 1s energies of the cyano and methyl carbons. Since the fwhm value of this peak was not large (1.8 eV), we chose not to deconvolute it. At ~3 eV above the 286.4-eV peak is a satellite whose intensity relative to that of the primary photoline (arising from the two different types of carbon) is ~0.14. Its intensity relative to that of the cyano C 1s peak will be approximately twice this value, thereby making I_s/I_p comparable with the value observed for the N 1s satellite (vide supra). The difference in the positions of the N 1s and C 1s satellites relative to the primary photolines (ΔE ~3.5 eV for N 1s and 3.0 eV for C 1s) may reflect differences in relaxation energy contributions to the chemical shifts.

The C 1s spectra of the *tert*-butyl and cyclohexyl complexes are very similar to that shown in Figure 1 for $[Mo(CNMe)_7](PF_6)_2$, with the exception that there is a marked increase in the intensity of the peak at ~285 eV due to the overlap between the C 1s energies of the aliphatic carbons of the *tert*-butyl and cyclohexyl groups and that due to the adventitious carbon.

The Mo $3d_{3/2,5/2}$ binding energy spectra of the solid complexes ($3d_{3/2}$ at 232.2 ± 0.1 eV and $3d_{5/2}$ at 229.1 ± 0.1 eV) are of a quality comparable with that reported[5] for gas-phase $Mo(CO)_6$, with fwhm values of 1.2–1.4 eV (Figure 1). When the Mo 3d spectrum of $[Mo(CNCH_3)_7](PF_6)_2$ was recorded to high statistics, a very weak feature ($I_s/I_p \approx 0.05$) at ~3.5 eV to the high binding energy side of the primary Mo $3d_{3/2}$ photoline was observed (Figure 1). Three possibilities arise. (1) This is a genuine shake-up satellite associated with the same charge-transfer transition as that giving rise to the N 1s and C 1s satellites. Its position supports this interpretation.[16] (2) It arises from a trace amount of high oxidation state molybdenum oxide contaminant. (3) It is due to a characteristic "plasmon" energy loss. While the two latter possibilities are difficult to eliminate entirely, the dramatic intensity difference between the "satellite" associated with the Mo 3d and N 1s (and C 1s) lines, together with the differences in the satellite position (relative to the primary photoline) in the Mo 3d, N 1s, and C 1s spectra, does not support possibility 3 as the likely explanation.

The similarity of the N 1s and C 1s I_s/I_p ratios for $Mo(CNR)_7^{2+}$ to the O 1s and C 1s I_s/I_p ratios for $Mo(CO)_6$ argues for a similarity in bonding since, as described in detail by Plummer et al.[6] for $M(CO)_6$ species, a decrease in the M–C bond length (i.e., stronger M–CO bonding) will influence both the satellite position relative to the primary peak and the I_s/I_p intensity ratio. The latter becomes smaller the stronger the M–CO (and presumably M–CNR) interaction.

In the case of $Mo(CO)_6$, the lowest energy satellite on the C 1s, O 1s, and metal levels has been assigned[5] to a transition which is predominantly $Mo(d) \rightarrow CO(\pi^*)$. Intense charge-transfer bands in the electronic absorption spectra of $[Mo(CNR)_7]^{2+}$ occur between 4 and 5 eV and may be assignable[17] to the corresponding $Mo(d) \rightarrow RNC(\pi^*)$ transitions. Since the formation of a positive hole upon photoionization lowers the orbital energy of most valence and virtual orbitals, the shake-up energy is usually smaller than that expected on the basis of electronic absorption spectral data. Thus satellites in the 3.0–3.5-eV region for $[Mo(CNR)_7](PF_6)_2$ conform to this expectation. Furthermore, since a $Mo(d) \rightarrow RNC(\pi^*)$ transition involves a virtual orbital which is principally ligand in character, only the C 1s and N 1s satellites should have appreciable intensity since it is the C≡N moiety which is the acceptor species in the shake-up process.[2] The weakness of the Mo 3d satellite supports this assignment, agreeing well with the experimentally observed[5] intensity differences in the XPES of $Mo(CO)_6$. Further analysis must await the results of molecular orbital calculations on such seven-coordinate species. Additional efforts to identify satellite structure in complexes of the heavier transition elements with π-acceptor ligands are currently in progress in our laboratory.

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(14) Different XPES sample preparations using different synthetic batches of these complexes gave perfectly reproducible spectra.
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Patrick Brant, William S. Mialki, Richard A. Walton*
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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Self-Assembly of Molybdenum–Iron–Sulfur Clusters as a Synthetic Approach to the Molybdenum Site in Nitrogenase. Identification of the Major Products Formed by the System $FeCl_3/MS_4^{2-}/C_2H_5SH$ (M = Mo, W)

Sir:

We are currently pursuing a synthetic approach to the Mo site in the FeMo proteins of nitrogenase, more recent preparations of which contain, per 220 000–250 000 daltons, ~2 g-atoms of Mo, 24–33 g-atoms of Fe, and an apparently somewhat smaller quantity of inorganic sulfur than Fe.[1,2] This approach is based on the conclusion from EXAFS analysis that Mo occurs as part of one or two as yet unidentified Mo–Fe–S clusters[3,4] and on the premise that, as with the $[Fe_4S_4(SR)_4]^{2-}$ analogues of ferredoxin sites,[5,6] such clusters, or appropriate precursors thereto, may assemble spontaneously from elementary reagents. We have examined the reaction system $FeCl_3/(R_4N)_2MS_4$/EtSH (M = Mo, W) in alcohol solvents in some detail. Here we document that the principal Mo-containing products formed by this system are the "double-cubane" complexes I ($[Mo_2Fe_6S_9(SEt)_8]^{3-}$), II ($[Mo_2Fe_6S_8$-

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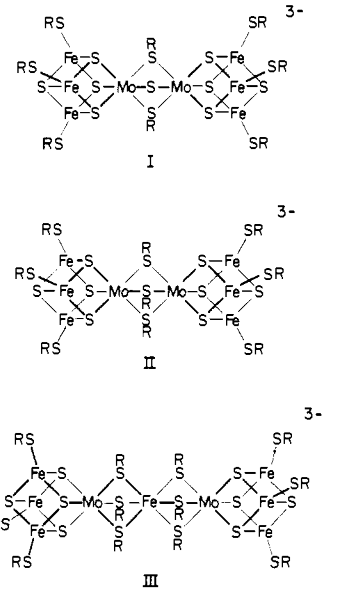

Figure 1. Structures of principal reaction products I, II, and III (R = Et) from the system $FeCl_3/MoS_4^{2-}/EtSH$. Detailed structures of I and II are given elsewhere.[8,11]

$(SEt)_9]^{3-})$, and III ($[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$), each of which contains a different type of bridging unit. Structures are illustrated in Figure 1.

Complexes I–III were obtained under anaerobic conditions from reaction mixtures containing 1 equiv of $(R_4N)_2MoS_4$, 3 equiv of $FeCl_3$ and 10 equiv of EtSH/NaOMe in 600 mL of methanol. Preferential isolation and purification of product was primarily controlled by choice of R_4N^+. Thus pure $(Et_3NCH_2Ph)_3$ (II) (λ_{max} 277 nm (ϵ_M 58 200), 391 (36 300)) was obtained in 20% yield[7] by reduction of solution volume to 250 mL after 15-h reaction time followed by cooling and recrystallization (MeCN/THF) of the separated product. Complete removal of solvent from the reaction mixture and recrystallization from ethanol of the acetonitrile extract of the residue afforded 28% previously reported I[8] as its $(Et_3NCH_2Ph)^+$ salt (λ_{max} 268 nm (ϵ_M 51 100), 396 (31 300)). Use of a slurry of $(Me_3NCH_2Ph)_2MoS_4$ caused, over a 15-h period, separation of a solid, which after recrystallization from acetonitrile gave 25% $(Me_3NCH_2Ph)_3$ (III) (λ_{max} 281 nm (ϵ_M 77 000), 392 (58 900)). Salts of the tungsten analogues of I and III, $(Et_4N)_3[W_2Fe_6S_9(SEt)_8]$ (I-W, λ_{max} 257 nm (sh, ϵ_M 51 900), 390 (32 900)) and $(Et_4N)_3[W_2Fe_7S_8(SEt)_{12}]$ (III-W, λ_{max} 262 nm (ϵ_M 64 600), 388 (47 600)), were prepared by closely related procedures.[9]

The structures of salts of I–III have been determined by X-ray diffraction[10] and consist of bridged "double-cubane" arrangements of individual $MoFe_3S_4(SEt)_3$ clusters. Those of $(Et_4N)_3$ (I) and $(Et_3NCH_2Ph)_3$ (II) (Figure 1) are detailed elsewhere[11] and differ principally in the Mo···Mo distances of 3.306 (3) and 3.668 (4) Å respectively. The structure of II is nearly isodimensional with those of $[Mo_2Fe_6S_8(SR)_9]^{3-}$ (R = Ph,[12] CH_2CH_2OH[13]) prepared by apparently similar means; consequently, Mo···Mo distances are diagnostic of $(\mu_2\text{-SR})_3$ and $(\mu_2\text{-S})(\mu_2\text{-SR})_2$ bridging groups. $(Me_3NCH_2Ph)_3$ (III) crystallizes in space group *Pbcn* with $a = 37.868$ (6), $b = 12.922$ (2), $c = 19.844$ (5) Å; $V = 8428$ (5) Å^3; and $Z = 4$.[14] From 2127 unique data ($F_o^2 > 3\sigma(F_o^2)$) with $2\theta \leq 45°$, the structure (Figure 2) was refined to $R = 6.2\%$ by standard procedures. The clusters in centrosymmetric anion III, which closely approaches S_6 overall symmetry, are supported by a third type of bridge. Here each cluster functions as tridentate ligand to the central Fe atom, resulting in trigonally distorted octahedral coordination and D_{3d} cluster symmetry. The $Mo(\mu_2\text{-SEt})_3Fe(\mu_2\text{-SEt})_3Mo$ bridge unit has no established precedent but is similar to that proposed for $\{Fe[Co(SCH_2CH_2NH_2)_3]_2\}^{3+}$.[15] Mössbauer parameters[16] (δ, ΔE_Q in mm/s) for III (0.31, 2.13) and III-W (0.31, 2.16) identify the bridge Fe atom as low-spin Fe(III).

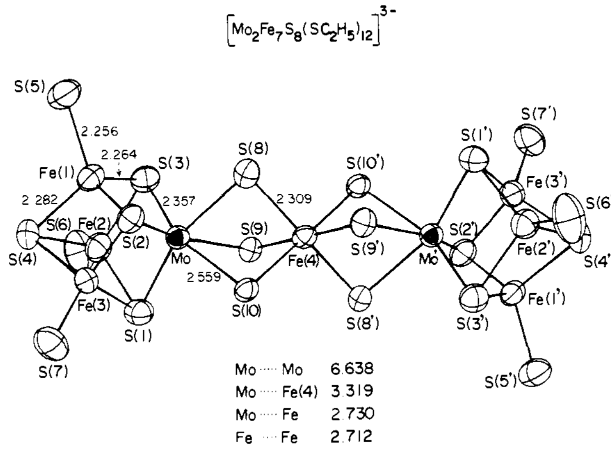

Figure 2. Structure of $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ as its $Me_3NCH_2Ph^+$ salt, showing 50% probability ellipsoids and principal interatomic distances; ethyl groups are omitted.

^{1}H NMR and Mössbauer spectral data for I, I-W, II, III, and III-W indicate virtual electronic equivalence of cluster Fe atoms. Values of $Fe\text{-}SCH_2$ chemical shifts (−52 to −55 ppm downfield of Me_4Si, CD_3CN, ~30 °C), ΔE_Q (0.74–1.33 mm/s), and δ (0.27–0.32 mm/s) fall into narrow ranges. Interpolation of the latter values with the linear dependence of isomer shifts of tetrahedral FeS_4 units on Fe formal oxidation state[1] affords a mean $Fe^{+2.67}$ oxidation state, leading to the formal M (Mo, W) oxidation state assignments M (+3, +4) in I and M (+3, +3) in II and III. However, successive one-electron reduction potentials[17] of I (−1.29, −1.49), I-W (−1.41, −1.60), and II (−1.28, −1.47 V) are not strongly dependent on M and are essentially independent of its formal oxidation state, indicating that the Fe_3 portions are the sites of reduction or, more likely, that the clusters in I–III are appreciably electronically delocalized.

Voltammetry of III and III-W reveals one-electron reductions at potentials ($E_{p,c} \simeq -1.11$ and −0.82 V, respectively) well separated from those ($\lesssim 1.3$ V) associated with cluster reduction, suggesting the existence of a fourth type of bridged complex. Exploration of the reaction system $FeCl_3/(n\text{-}Bu_4N)_2MS_4/PhCH_2SH$ in methanol has resulted in the isolation of $(n\text{-}Bu_4N)_4[M_2Fe_7S_8(SCH_2Ph)_{12}]$ (M = Mo, W). Mössbauer data for the Mo compound (δ (ΔE_Q) = 0.31 (0.96), 0.90 (1.76) mm/s) indicate the presence of $MoFe_3S_4$-type clusters bridged by Fe(II), a matter confirmed by X-ray diffraction for both compounds. Using 4061 unique data ($F_o^2 > 3\sigma(F_o^2)$, to 2θ of 40°) the structure of the Mo compound has been refined to $R = 4.9\%$. $(n\text{-}Bu_4N)_4$ (IV) crystallizes in space group $P2_1/c$ with $a = 15.883$ (4), $b = 35.035$ (7), $c = 15.836$ (4) Å; $\beta = 109.90$ (2)°; and $Z = 2$. Centrosymmetric anion IV differs importantly from III (Figure 2) only in the bridging region and in a manner consistent with the larger size of Fe(II): e.g., Mo···Mo', 6.924 (1); Mo···Fe, 3.462 (1); and mean Fe—S, 2.53 (4) Å. $(n\text{-}Bu_4N)_4$ (IV-W) is isomorphous with $(n\text{-}Bu_4N)_4$ (IV) and the structure of $[W_2Fe_7S_8(SCH_2Ph)_{12}]^{4-}$ is nearly isometric with that of IV.

These results serve to demonstrate the diversity of products (I–IV) obtainable from the indicated reaction systems. The persistent assembly of clusters containing the MFe_3S_4 core from simple reagents attests to the stability of this unit and may be a matter of further significance in view of the similarity of Mo environments in the bridged clusters[8,11] and nitrogenase.[3,4] The essential components of the former, individual [Mo-

$Fe_3S_4(SR)_6]^{2-,3-}$ clusters, have not yet been detected among the principal products of the reaction systems above but may be accessible by removal of the bridging Fe atom in III or IV. Further studies are in progress.

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(18) Alfred P. Sloan Foundation Fellow, 1976–1978.

Thomas E. Wolff, Jeremy M. Berg, Philip P. Power,
Keith O. Hodgson,[18] R. H. Holm*
Department of Chemistry, Stanford University,
Stanford, California 94305

Richard B. Frankel
Francis Bitter National Magnet Laboratory
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received April 5, 1979

Additions and Corrections

Synthesis Using Transition Metal Diatomic Molecules. Dirhodium Octacarbonyl, $Rh_2(CO)_8$, and Diiridium Octacarbonyl, $Ir_2(CO)_8$ [*J. Am. Chem. Soc.*, **96**, 6324 (1974)]. By L. A. HANLAN and G. A. OZIN,* Lash Miller Chemistry Department and Erindale College, University of Toronto, Toronto, Ontario, Canada.

A recently unveiled supplier's error in our original publication of purported $Ir_2(CO)_8$ (rhodium metal confused for iridium) necessitated a complete reinvestigation and reappraisal of the products of Ir/CO matrix cocondensations at 10–12 K. The reactions (*J. Organomet. Chem.*, in press) of Ir/CO have been shown to yield authentic samples of $Ir(CO)_4$ which can be induced to dimerize to $Ir_2(CO)_8$. Unlike $Rh_2(CO)_8$, $Ir_2(CO)_8$ is found to exist as the metal-metal bonded, nonbridged isomer (analogous to nonbridged $Co_2(CO)_8$) which around 200 K undergoes what appears to be decomposition to quite large iridium clusters onto which CO is chemisorbed, rather than to a well-defined disproportionation product such as $Ir_4(CO)_{12}$ or $Ir_6(CO)_{12}$.

The Structure of 1,3,6,8-Tetra-*tert*-butylnaphthalene [*J. Am. Chem. Soc.*, **99**, 3345 (1977)]. By JADY HANDAL, JOHN G. WHITE,* RICHARD W. FRANCK,* Y. H. YUH, and NORMAN L. ALLINGER,* Departments of Chemistry, Fordham University, Bronx, New York, 10458, and the University of Georgia, Athens, Georgia 30602.

In the numbering diagram **3**, the *tert*-butyl group 15–18 should be bonded to 3 via 15, and the *tert*-butyl group 11–14 should be bonded to 6 via 11.

In Figure 3 the labels C20 and C21 should be reversed, as should labels C24 and C26; the interhydrogen distance labeled 1.998A should be 1.855A, and that labeled 1.885A should be 1.998A.

Catalytic Homogeneous Hydrogenation of Arenes. 6. Reaction Scope for the η^3-$C_3H_5Co[P(OCH_3)_3]_3$ Catalyst [*J. Am. Chem. Soc.*, **100**, 2405 (1978)]. By L. S. STUHL, M. RAKOWSKI DUBOIS, F. J. HIRSEKORN, J. R. BLEEKE, A. E. STEVENS, and E. L. MUETTERTIES,* Department of Chemistry and Cornell Materials Science Center, Cornell University, Ithaca, New York 14853.

In Table II, p 2408, under the column entitled Reactant, the 7th to the last entry "allylbenzene" should read "propenylbenzene (*cis* and *trans*)".

"Increased Valence" When the Octet Rule Is Obeyed. A Reply to a Challenge [*J. Am. Chem. Soc.*, **100**, 8060 (1978)]. By RICHARD D. HARCOURT, Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.

In References and Notes (8), nine lines down, replace "they need to overlap . . ." with "there must be an antiferromagnetic (and partial) interaction between them and another pair of atomic spin orbitals". In the next sentence, replace "$\bar{y}$ or y" with "$\bar{y}$ and y".

Intramolecular Dibromo Ketone–Iron Carbonyl Reaction in Terpene Synthesis [*J. Am. Chem. Soc.*, **101**, 220 (1979)]. By R. NOYORI,* M. NISHIZAWA, F. SHIMIZU, Y. HAYAKAWA, Department of Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan, and KEIJI MARUOKA, SHINSAKU HASHIMOTO, HISASHI YAMAMOTO,* and HITOSI NOZAKI, Department of Industrial Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan.

The name of one of the authors is incorrect; Shinsaku Hashimoto should be Shinsuke Hashimoto.

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