

imation mentioned above is valid only if the orbitals e_1 and g_2 are orthogonal, which is highly unlikely for bridged dimers. This orthogonality may be struck as the result of the molecular symmetry, or it may be accidental. Both cases are discussed by Kahn and co-workers.^{22,23}

An analytical expression analogous to the one of Moriya may be derived by second-order instead of third-order perturbation theory.^{4,10} This is a consequence of the fact that we are no longer dealing with an infinite lattice but instead with two spins each with $S = 1/2$. Therefore, it is possible to start from ground and excited singlet ($|\psi_S^n\rangle$) and triplet ($|\psi_T^n\rangle$) states in which the exchange interactions have been included to the highest accuracy possible. The resulting singlet-triplet splitting in the state n is defined as $2J_n$, where J_n is the effective exchange constant in the spin Hamiltonian $-2J_n\vec{S}_1\cdot\vec{S}_2$. The spin-orbit perturbation is $\mathcal{H}_{SO} = \zeta_1\vec{l}_1\cdot\vec{s}_1 + \zeta_2\vec{l}_2\cdot\vec{s}_2$ where ζ_i is the one-electron spin-orbit coupling constant. The second-order energy correction to the three triplet ground-state functions may be calculated by diagonalizing the matrix with elements

$$E_{ij}^{(2)} = \sum_n \sum_\sigma \frac{\langle \psi_T^0 | \mathcal{H}_{SO} | \psi_\sigma^n \rangle \langle \psi_\sigma^n | \mathcal{H}_{SO} | \psi_T^0 \rangle}{E_T^0 - E_\sigma^n} \quad (2)$$

where the summation σ runs over all (four) spin states of the excited states n . After some algebra this may be written as

$$E_{ij}^{(2)} = 2 \sum_n \sum_{\alpha, \beta = x, y, z} \langle \psi_T^0 | \zeta_1 l_{1\alpha} | \psi_T^n \rangle \langle \psi_T^n | \zeta_2 l_{2\beta} | \psi_T^0 \rangle \times \\ (T_i | S_{1\alpha} S_{2\beta} + \delta_{\alpha\beta} T_j) [1/(E_n + 2J_n) - 1/E_n] \quad (3)$$

By comparison with the matrix elements within the ground state triplet manifold of the spin-Hamiltonian $\vec{S}_1\cdot\vec{D}_{SO}\cdot\vec{S}_2$ and after omitting an isotropic contribution, one obtains for the tensor elements

$$D_{SO, \alpha\beta} = \\ 2 \sum_n \langle \psi_T^0 | \zeta_1 l_{1\alpha} | \psi_T^n \rangle \langle \psi_T^n | \zeta_2 l_{2\beta} | \psi_T^0 \rangle [1/(E_n + 2J_n) - 1/E_n] \quad (4)$$

In case $|J_n| \ll E_n$, this can also be written as

$$D_{SO, \alpha\beta} = -4 \sum_n \langle \psi_T^0 | \zeta_1 l_{1\alpha} | \psi_T^n \rangle \langle \psi_T^n | \zeta_2 l_{2\beta} | \psi_T^0 \rangle J_n / E_n^2 \quad (5)$$

This expression is equivalent to the one derived by Moriya, and it shows that the spin-orbit coupling contributes to the ZFS provided that the singlet-triplet splitting in the excited states is not zero. Moreover, this alternative derivation clearly shows that J_n in formula 5 is not a simple two-electron exchange integral but instead is the singlet-triplet separation in the excited state. Therefore, we think it dangerous that in recent articles the effective exchange has been treated as a simple exchange integral.

In this context we think it worthwhile to mention another aspect of the analytical expression for J_0 mentioned above: the model upon which this expression is based is a two-electron description. The effects of the doubly occupied orbitals in the dimer are neglected. They play a role only insofar as they influence the energies and delocalization of the unpaired electron functions. Wormer and Van der Avoird²⁴ tested this approximation on the O_2 - O_2 dimer (two spins $S = 1$). They compared the results of an extensive all-electron calculation with a four-electron model and found that the orientational dependencies of J_0 are qualitatively the same but are quantitatively not so! The much more economic four-electron model turns out to be quite inaccurate. This was also found by Charlot et al.²⁵ on a model system for azido-bridged copper dimers. A full CI calculation including all core levels was needed in order to understand the behavior of the singlet-triplet separation in these systems.

In conclusion, we think it is now clear that the spin-orbit term will contribute to the ZFS if an effective exchange interaction

is present in the excited states and that this effective exchange interaction represents a singlet-triplet splitting and is not equal to a simple two-electron exchange integral. Furthermore, extensive all-electron calculations are needed in order to obtain quantitatively correct results for the single-triplet splittings.

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Synthesis and Characterization of the $[(CO)_4MoS_2MS_2]^{2-}$ and $[(CO)_4MoS_2MS_2Mo(CO)_4]^{2-}$ Ions ($M = Mo, W$): Species Containing Group VI (6^+) Metals in Widely Separated Formal Oxidation States

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Although the group VI tetrathiometalates $[(MS_4)]^{2-}$; $M = Mo, W$) were initially prepared over 100 years ago,² their ability to function as bidentate ligands to other metals has only been explored extensively in the past 10-15 years.³

Much of the interest in this behavior has arisen because of the importance of molybdenum-sulfur moieties in biological systems. For example, an Fe-Mo-S cluster unit is thought to comprise the active site of the nitrogenase enzyme,⁴ Mo=S linkages have been implicated in other molybdenum enzymes that contain the "Mo cofactor",⁵ and thiomolybdates are thought to be an important factor in the copper-molybdenum antagonism in ruminants.⁶ In addition, there is considerable interest in molybdenum-sulfur species as industrial catalysts for hydrodesulfurization.⁷ Activity in this area has focused on reactions involving the chelation of relatively *high-valent* metals such as Fe(II/III),⁸ Co(II),⁹ Ni(II),¹⁰ and Zn(II)¹¹ by $[MS_4]^{2-}$ ions to form simple $M'S_2MS_2$ units. By contrast, reactions of thiometalates with *low-valent* metals containing π -accepting ligands, such as CO and PR_3 , are rare. However, the feasibility of this type of reactivity recently has been demonstrated¹² by studies that showed that $[MS_4]^{2-}$ ($M = Mo, W$) will readily chelate Rh(I) and Ru(II) fragments to form heterometallic, sulfido-bridged complexes, such as $[(COD)-RhS_2MS_2Rh(COD)]$ (COD = cyclooctadiene), where the tetrathiometalate functions as a ligand to an organometallic moiety.

We have recently begun to investigate the chemistry of low-valent Mo and W carbonyl-sulfur species,¹³⁻¹⁷ some of which^{16,17} were prepared by utilizing the labile $Mo(CO)_4$ (norbornadiene) complex as a source of reactive $Mo(CO)_4$ fragments. Herein we report that this type of reactivity can also be exploited with $[MS_4]^{2-}$ ($M = Mo, W$), resulting in simple dinuclear and trinuclear sulfido-bridged complexes that are unusual in that they contain group VI metals in the same cluster that differ in formal oxidation state by 6 units.

Experimental Section

Materials and Methods. The compounds $Mo(CO)_4(C_7H_8)$ ($C_7H_8 =$ norbornadiene)¹⁸ and $[Et_4N]_2[MS_4]$ ($M = Mo, W$)¹⁹ were prepared by the literature methods cited. All operations were carried out under an argon atmosphere by using Schlenk tube or glovebox techniques. Reagent grade solvents were used as obtained, except for MeCN, which

(22) Kahn, O. In ref 3, pp 57-85.

(23) Charlot, M. F.; Journaux, Y.; Khan, O.; Bencini, A.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* 1986, 25, 1060.

(24) Wormer, P. E. S.; Van der Avoird, A. *J. Chem. Phys.* 1984, 81, 1929.

(25) Charlot, M. F.; Kahn, O.; Chaillet, M.; Larrieu, C. *J. Am. Chem. Soc.* 1986, 108, 2574.

[†] The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

was distilled from CaH_2 . Elemental analyses were performed in this laboratory on a Perkin-Elmer 240 instrument equipped with a Microjector from Control Equipment Corp. Cyclic voltammetry experiments¹² and carbon monoxide analyses²⁰ were performed as previously described. Electrochemical potential values are vs. SCE. Infrared spectra were obtained as KBr pellets prepared in a drybox, by using a Beckman IR-20 instrument, and visible spectra were obtained with a Cary 118C spectrophotometer.

Preparation of $[\text{Et}_4\text{N}]_2(\text{CO})_4\text{MoS}_2\text{MS}_2$ (1; M = Mo, W). A sample of $[\text{Et}_4\text{N}]_2[\text{MS}_4]$ (0.99 mmol) was dissolved in warm MeOH (25 mL), $\text{Mo}(\text{CO})_4(\text{C}_7\text{H}_8)$ (0.30 g; 1.00 mmol) in MeOH (30 mL) was added over 30 min at ambient temperature, and the mixture was then stirred for an additional 15 min. The resulting dark green solution was filtered, yielding the crude product (ca. 0.45 g; 65%), which was washed with MeOH and Et_2O and dried under vacuum. This material was shown spectroscopically to contain a significant amount of compound 2 (vide infra) and therefore was recrystallized from MeCN- Et_2O to obtain ca. 0.20 g (30%) of purified product in crystalline form. An analytical sample was obtained by further recrystallization of this solid from dilute MeOH solution.

Anal. Calcd for $\text{C}_{20}\text{H}_{40}\text{N}_2\text{Mo}_2\text{O}_8\text{S}_4$ (1; M = Mo): C, 34.67; H, 5.83; N, 4.04. Found: C, 34.34; H, 5.75; N, 4.00. Amount of CO on decomposition: 104%. IR (cm^{-1}): 1860 (s), 1885 (sh, s), 1905 (s), 2000 (m) (ν_{CO}); 485 (m) ($\nu_{\text{Mo-S}}$); 440 (w) ($\nu_{\text{MoS}_2\text{Mo}}$). Anal. Calcd for $\text{C}_{20}\text{H}_{40}\text{N}_2\text{MoO}_4\text{S}_4\text{W}$ (1; M = W): C, 30.76; H, 5.17; N, 3.58. Found: C, 30.16; H, 5.23; N, 3.19. Amount of CO on decomposition: 94%. IR (cm^{-1}): 1845 (sh, m), 1860 (s), 1895 (s), 1915 (s), 2000 (m) (ν_{CO}); 480 (m) ($\nu_{\text{W-S}}$); 440 ($\nu_{\text{MoS}_2\text{W}}$).

Preparation of $[\text{Et}_4\text{N}]_2(\text{CO})_4\text{MoS}_2\text{MS}_2\text{Mo}(\text{CO})_4$ (2; M = Mo, W). Samples of $[\text{Et}_4\text{N}]_2[\text{MS}_4]$ (0.99 mmol) and $\text{Mo}(\text{CO})_4(\text{C}_7\text{H}_8)$ (0.60 g; 2.0 mmol) were stirred for 2 h at ambient temperature in MeOH (30 mL). The dark mixture was filtered, yielding the products as crystalline solids (for M = Mo, 0.69 g, 78%; for M = W, 0.28 g, 29%), which were washed with MeOH and Et_2O and dried under vacuum. For 2 (M = Mo), the best analysis from this procedure was unsatisfactory in carbon, but hydrogen and nitrogen analytical data were consistently correct. Recrys-

Table I. Electronic Spectral and Cyclic Voltammetric Data for Complexes 1 and 2 in MeCN

complex	electronic data ^a	electrochemical data ^b
1 (M = Mo)	360 (10 000), 460 (8800), 565 (3160)	-1.94 ^c +0.31 ^d
1 (M = W)	405 (8860), 460 (3740)	-2.33 ^c +0.19 ^d
2 (M = Mo)	375 sh, 455 (19 000), 675 (5380)	-1.68 ^c +0.21 ^d
2 (M = W)	426 (16 500), 545 (5220)	-1.99 ^c +0.18 ^d

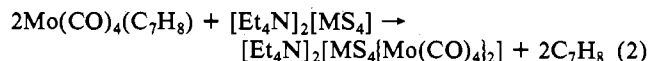
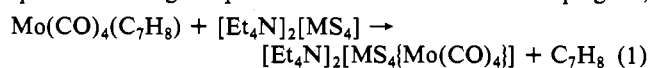
^a Peak positions in nanometers with molar absorptivities in parentheses. ^b Values in volts vs. SCE. Data obtained from cyclic voltammograms taken at -40 °C. ^c Pseudoreversible reduction. ^d Irreversible oxidation.

tallization of this product from MeOH did not significantly improve these data.

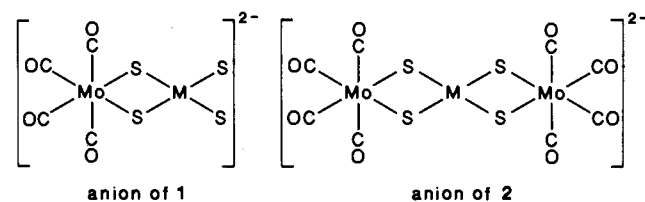
Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{Mo}_3\text{O}_8\text{S}_4$ (2; M = Mo): C, 32.00; H, 4.48; N, 3.11. Found: C, 29.66; H, 4.58; N, 3.19. Amount of CO on decomposition: 103%. IR (cm^{-1}): 1855 (s), 1900 (s), 1930 (s), 1990 (m) (ν_{CO}); 450 (w) ($\nu_{\text{MoS}_2\text{Mo}}$). Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{Mo}_2\text{O}_8\text{S}_4\text{W}$ (2; M = W): C, 29.15; H, 4.08; N, 2.83. Found: C, 28.83; H, 3.97; N, 2.52. Amount of CO on decomposition: 102%. IR (cm^{-1}): 1875 (s), 1925 (s), 1955 (s), 2000 (m) (ν_{CO}); 460 (w), 425 (w) ($\nu_{\text{MoS}_2\text{W}}$).

Results and Discussion

Reaction of 1 or 2 equiv of $\text{Mo}(\text{CO})_4(\text{C}_7\text{H}_8)$ (C_7H_8 = norbornadiene) with $[\text{Et}_4\text{N}]_2[\text{MS}_4]$ (M = Mo, W) in MeOH results in the rapid formation of dark solutions which deposit dinuclear (1; M = Mo, W) or trinuclear (2; M = Mo, W) sulfido-bridged species according to eq 1 and 2. While this work was in progress,



we learned that Ruffing,²¹ as part of a program²² on mixed-metal/mixed-valence compounds, had also carried out the preparation of the dinuclear species using CH_2Cl_2 as solvent. Elemental analytical data (CHN and CO evolution on oxidative decomposition) for these highly air-sensitive products are consistent with these proposed formulations, but IR spectral studies provide the best insight into their structures. The spectra of all four compounds contain strong bands in the carbonyl region that have general patterns and positions similar to those of $[\text{Mo}(\text{CO})_4(\text{SR})_2]^{2-16}$ and $[\text{M}_2(\text{CO})_8(\text{SR})_2]^{2-}$ (M = Mo, W)¹³⁻¹⁵ and that are thus characteristic of *cis*- $\text{Mo}(\text{CO})_4$ fragments containing Mo(0). In addition, the IR spectra contain low-energy bands (400–500 cm^{-1}) characteristic of terminal and bridging M–S vibrations in linear, polynuclear, sulfido-bridged species. Thus, we formulate the structures of the products as indicated by 1 and 2, the geometry presumed to be effectively octahedral around Mo and tetrahedral for the coordinated MS_4 (M = Mo, W) moiety.



From the point of view of formal oxidation states, these di and trinuclear species could contain both M(VI) (M = Mo, W) and Mo(0) in the same complex. Electrochemical experiments, for which data are compiled in Table I, support this hypothesis. The cyclic voltammograms of 1 (M = Mo) and 2 (M = Mo) contain two redox events, a pseudoreversible one-electron reduction at negative potentials and an irreversible one-electron oxidation at ca. +0.2 V. The average current parameter for these redox events at ca. -40 °C was 425 $\text{A s}^{-1} \text{V}^{1/2} \text{mol}^{-1}$ compared to 390 A s^{-1}

- (1) (a) Present address: Department of Chemistry, Indiana State University, Terre Haute, IN 47809. (b) Present address: Battelle Columbus Laboratories, Columbus, OH 43201.
- (2) (a) Kruss, G. *Justus Liebig's Ann. Chem.* **1884**, 225, 1. (b) Corleis, E. *Justus Liebig's Ann. Chem.* **1886**, 232, 244.
- (3) (a) Diemann, E.; Muller, A. *Coord. Chem. Rev.* **1973**, 10, 79. (b) Muller, A.; Diemann, E.; Jostes, R.; Bogge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 934.
- (4) Orme-Johnson, W. H. *Annu. Rev. Biophys. Biophys. Chem.* **1985**, 14, 419.
- (5) Cramer, S. P.; Wahl, R.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, 103, 7721.
- (6) Clarke, N. J.; Laurie, S. H. *Inorg. Chim. Acta*, **1982**, 66, L35 and references therein.
- (7) Massoth, F. E.; Muralidhar, G. in *Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum*; Climax Molybdenum Co.: Ann Arbor, MI, 1982; p 343.
- (8) (a) Holm, R. H. *Chem. Soc. Rev.* **1981**, 10, 455. (b) Coucouvanis, D. *Acc. Chem. Res.* **1981**, 14, 201. (c) Averill, B. A. *Struct. Bonding (Berlin)* **1983**, 53, 59.
- (9) Muller, A.; Jostes, R.; Hellmann, W.; Romer, C.; Bogge, H.; Schimanski, U.; Zhuang, B.; Rosenhein, L. D.; McDonald, J. W.; Newton, W. E. *Z. Anorg. Allg. Chem.* **1986**, 533, 125.
- (10) (a) Muller, A.; Chakravorty, M. C.; Dornfeld, H. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, 30B. (b) Callahan, K. P.; Piliero, P. A. *J. Chem. Soc., Chem. Commun.* **1979**, 13.
- (11) Muller, A.; Ahlborn, E.; Heinsen, H. H. Z. *Anorg. Allg. Chem.* **1971**, 386, 102.
- (12) Howard, K. E.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, 108, 297.
- (13) Zhuang, B.; McDonald, J. W.; Schultz, F. A.; Newton, W. E. *Organometallics* **1984**, 3, 943.
- (14) Smith, D. A.; Zhuang, B.; Newton, W. E.; McDonald, J. W.; Schultz, F. A. *Inorg. Chem.*, in press.
- (15) Zhuang, B.; McDonald, J. W.; Schultz, F. A.; Newton, W. E. *Inorg. Chim. Acta* **1985**, 99, L29.
- (16) Rosenhein, L. D.; Newton, W. E.; McDonald, J. W. *J. Organomet. Chem.* **1985**, 288, C17.
- (17) Rosenhein, L. D.; Newton, W. E.; McDonald, J. W. *Inorg. Chem.* **1987**, 26, 2524.
- (18) King, R. B. In *Organometallic Synthesis*; Academic: New York, 1965; Vol. 1, p 124.
- (19) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, 72, 205.
- (20) Templeton, J. L.; Herrick, R. S.; Rusik, C. A.; McKenna, C. E.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1985**, 24, 1383.

- (21) Ruffing, C. J. Ph.D. Thesis, University of Illinois, Urbana, IL, 1984, p 60.
- (22) Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, 3, 524.

Table II. Electronic Spectral Data for **1** and **2** as a Function of Solvent

complex	solvent	electronic spectral data ^a
1 (M = Mo)	MeOH	467, 613
	EtOH	467, 595
	MeCN	460, 565
	DMF	450, 555
	CH ₂ Cl ₂	465, 555
1 (M = W)	MeOH	418, 490
	MeCN	405, 460
	CH ₂ Cl ₂	412, 470
2 (M = Mo)	MeOH	457, 687
	MeCN	455, 675
	CH ₂ Cl ₂	457, 669
2 (M = W)	MeOH	426, 549
	MeCN	426, 545
	CH ₂ Cl ₂	424, 535

^a Values in nanometers.

V^{-1/2} mol⁻¹ for the known one-electron transfer in [Mo-(S₂C₄N₂)₄]³⁻ at the same temperature. Assignment of the reduction waves to relatively localized electron transfer to the coordinated M(VI) MS₄ moiety is consistent with previous electrochemical data on Fe-Mo-S species. Thus, [(*o*-xyl-S₂)-FeS₂MS₂]²⁻ complexes (*o*-xyl-S₂ = C₆H₄(CH₂S)₂; M = Mo, W), which contain formally M(VI) tetrathiometalates bound to an Fe(II)-thiolate moiety, undergo reversible reduction at -1.6 V (M = Mo) and -1.8 V (M = W), events postulated²⁴ on the basis of EPR spectroscopic evidence to involve formation of M(V). The similarity of the potentials for the reductions in this system and those in **1** and **2** indicate that assignment of the reversible reductions to M(VI)/M(V) couples is reasonable. It is also worthwhile to note (a) that the shift to more negative reduction potentials on substitution of tungsten for molybdenum is consistent with the electrochemistry of both the above (*o*-xyl-S₂)Fe system²⁴ and the [Fe(MS₄)₂]³⁻ ions²⁵ and (b) that the addition of a second Mo(CO)₄ unit to **1** results in a shift of the reduction wave to more positive potential, an effect presumably due to a lowering of the electron density at the MS₄ center via donation to the extra Mo(0) moiety. The irreversible wave at ca. +0.2 V for these complexes is likely to be due to a Mo(CO)₄-centered oxidation of Mo(0) to Mo(I) and is about 0.4 V more positive than the net two-electron Mo(0)/Mo(I) couple in [M₂(CO)₈(SR)₂]²⁻ (M = Mo, W)¹³⁻¹⁵ and the one-electron oxidation of [Mo(CO)₄(SR)₂]²⁻.¹⁶ It is interesting that the oxidation wave of trinuclear **2** is a one-electron Mo(0)/Mo(I) redox event, while the similar couple in the trinuclear, thiolate-bridged complex [(CO)₄Mo(SR)₂M'(SR)₂Mo(CO)₄]²⁻ accounted for the simultaneous transfer of two electrons,¹⁷ this latter phenomenon postulated¹⁷ to be due to the formation of two M'-Mo bonds. The lack of ability of the central Mo(VI) in **2** to participate in metal-metal bonding is consistent with the observed one-electron behavior. Thus, as noted above, the electrochemical data are consistent with the presence of both high-valent Mo or W and low-valent Mo in the same polynuclear complex.

Complexes that contain metals in such widely differing oxidation states should be candidates for internal charge-transfer (CT) behavior. Indeed, the visible spectra of both dinuclear and trinuclear species are characterized by several intense bands (Table I), with the low-energy transitions particularly good candidates for charge transfer since they are characterized by solvatochromic behavior (Table II). Solvent-dependent CT bands are well-documented for a number of structurally related, but neutral, M(0) complexes of the forms Mo(CO)₄(N'-N) (N'-N = 2,2'-bipyridyl, 1,10-phenanthroline, 1,4-diazabutadiene, 2,3-bis(2-pyridyl)-pyrazine, etc.),²⁶⁻²⁹ W(CO)₅L, and W(CO)₄L₂ (L = substituted

pyridine).³⁰ However, for these neutral compounds, the CT bands shift to higher energy with increasing solvent polarity, "negative" solvatochromism as described by Tom Dieck and Renk,²⁸ while compounds **1** and **2** in general show the opposite shift on solvent variation (Table II). The "positive" solvatochromic effect²⁸ in **1** and **2** could indicate that the CT transitions for these species are MS₄ → Mo(0) in character (rather than Mo(0) → L in the Mo(CO)₄L₂ systems²⁸), but this hypothesis is seemingly inconsistent with the above electrochemical data, which would predict that Mo(0) → MS₄ charge-transfer behavior is more likely for **1** and **2**. In addition, it is possible that specific hydrogen-bonding interactions between the alcohols (where the largest solvatochromic effects are observed) and the MS₄ sulfurs could be at least partially responsible for this different trend.

Previous studies by Coucouvanis and co-workers³¹ have shown the utility of a substitution-labile Mo(0) starting material as a source of reactive Mo(CO)₃ fragments. Their reaction of Mo(CO)₃(MeCN)₃ with the hexairon prismane species [Fe₆S₆X₆]³⁻ (X = Cl, OR) yielded novel complexes with a [Fe₆Mo₂S₆]^{3+/2+} core, which are exciting in that they may be susceptible to oxidative decarbonylation³² to produce species that mimic certain aspects of the iron molybdenum cofactor of nitrogenase.^{4,33} Our results on the utilization of Mo(CO)₄(norbornadiene), as described both herein and elsewhere,^{15,16} complement this synthetic concept and suggest that the reactivity of Mo(0) species with Fe-S complexes (or vice versa) may result in the synthesis of a variety of new heterometallic clusters.

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Registry No. **1** (M = Mo), 110015-34-4; **1** (M = W), 110015-36-6; **2** (M = Mo), 110026-45-4; **2** (M = W), 110015-38-8; Mo(CO)₄(C₄H₈), 12146-37-1; [Et₄N]₂[MoS₄], 14348-09-5; [Et₄N]₂[WS₄], 14348-05-1.

Supplementary Material Available: Figures showing cyclic voltammograms of **1** (M = Mo) and **2** (M = Mo) and the electronic spectra of **1** (M = Mo) in MeOH and CH₂Cl₂ (2 pages). Ordering information is given on any current masthead page.

- (26) (a) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3306. (b) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1987**, *26*, 68 and references therein.
 (27) Burgess, J.; Chambers, J. G.; Haines *Transition Met. Chem. (N.Y.)* **1981**, *6*, 145 and references therein.
 (28) (a) Tom Dieck, H.; Renk, I. W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 793. (b) Tom Dieck, H.; Renk, I. W. *Chem. Ber.* **1971**, *104*, 110.
 (29) Ruminski, R. R.; Johnson, J. O. *Inorg. Chem.* **1987**, *26*, 210.
 (30) (a) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1977**, *99*, 4105. (b) Abrahamson, H. B.; Wrighton, M. S. *Inorg. Chem.* **1978**, *17*, 3385.
 (31) (a) Coucouvanis, D.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 5005. (b) Kanatzidis, M. G.; Coucouvanis, D. *J. Am. Chem. Soc.* **1986**, *108*, 337.
 (32) Kovacs, J. A.; Baskin, J. K.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 1784.
 (33) Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3249.

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Preparation and Characterization of Bis(aryldiazenido) Complexes of Iron

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In a previous paper¹ we described the reaction of the dihydride FeH₂[P(OEt)₃]₄ toward aryldiazonium cations, which gave the

- (23) Smith, D. A.; McDonald, J. W.; Finklea, H. O.; Ott, V. R.; Schultz, F. A. *Inorg. Chem.* **1982**, *21*, 3825.
 (24) Friesen, G. D.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1982**, *67*, L1.
 (25) Friesen, G. D.; McDonald, J. W.; Newton, W. E.; Euler, W. B.; Hoffman, B. M. *Inorg. Chem.* **1983**, *22*, 2202.