Figure 3. View down C(7)–Re–C(5) axis. Angle is between plane of carbene ligand and plane defined by C(4), C(5), C(6), and C(7): 51.8° for I and 48.8° for V.

some π bonding between Re and the carbene ligand in I and V.

Within the carbene ligand, there is considerable π interaction between C(7) and its neighboring oxygens. In V, for example, the C(7)–oxygen distance is approximately 0.16 Å shorter than the C(1)–O(1) and C(2)–O(2) distances of 1.46 Å, which are typical of single carbon–oxygen bonds.[25] In both I and V the

dimensions of the dioxycarbene ligand are similar to those reported for $Mn(CO)_4Cl(\overline{COCH_2CH_2O})$.[26] The dioxycarbene ligands are very nearly planar; in both I and V all five atoms are within 0.018 Å of their least-squares plane. In I, the least-squares plane of the carbene ligand makes an angle of 51.8° with the least-squares plane defined by C(4), C(5), C(6), and C(7); the corresponding angle for V is 48.8°. A perspective view illustrating these angles is given in Figure 3. These values are similar to the angle of 49° reported between comparable planes of $Mn(CO)_4Cl(\overline{COCH_2}$-$\overline{CH_2O})$.[26] Frontier orbital arguments predict that the favored orientation of the plane of the carbene ligand should be perpendicular to the M–L bond for complexes of formula $M(CO)_4L$-(carbene) where L is a pure σ donor or weak π acceptor.[27] The deviation of I, V, and $Mn(CO)_4Cl(\overline{COCH_2CH_2O})$ from this predicted structure suggests that Re to carbene π bonding is relatively weak as also indicated by the Re–C(7) bond distance and that steric or possibly crystal-packing forces determine the orientation of the carbene ligand.

Supplementary Material Available: Listings of thermal parameters and hydrogen atom positions (4 pages); listings of calculated and observed structure factors (18 pages). Ordering information is given on any current masthead page.

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Synthesis, Reactivity, and Simultaneous Two-Electron Electrochemistry of Trinuclear Iron–Molybdenum and Cobalt–Molybdenum Carbonyl Thiolate Complexes†

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The new heterometallic trinuclear species $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$ (M = Fe, Co; R = Ph, Bz) have been prepared by three distinct methods: (a) reaction of $[Mo(CO)_4(SR)_2]^{2-}$ with MX_2 or $[MX_4]^{2-}$ (X = halide); (b) reaction of $[Mo(CO)_4(norbornadiene)]$ with $[M(SR)_4]^{2-}$; (c) reaction of $[Mo_2(CO)_8(SR)_2]^{2-}$ with MX_2 or $[MX_4]^{2-}$. All complexes have been characterized by IR and electronic spectroscopy, elemental analysis, and CO evolution studies. The Co complexes have been further characterized by EPR spectroscopy and shown to exhibit spectra consistent with the presence of three unpaired electrons from Co(II) in a tetrahedral environment. The trinuclear Fe– and Co–SPh species react with organic isocyanides to yield products that are postulated to be $[M(SR)_4(CyNC)_2\{Mo(CO)_4\}_2]^{2-}$ but whose IR spectra unexpectedly contain a carbonyl pattern significantly different from that of their precursors, leaving some doubt as to their structures. $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$ (M = Fe, Co; R = Ph) also react with 2,2'-bipyridine and o-phenanthroline (L) producing the dinuclear, neutral complexes $[(CO)_4Mo(SR)_2ML_2]$. Cyclic voltammetry studies of $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$ (M = Fe, Co; R = Ph, Bz) show that the complexes are oxidized at ca. 0 V by two electrons in a single step, a phenomenon attributed to the formation of two Mo–Fe(Co) metal–metal bonds in the product. Consistent with this hypothesis, chemical oxidation of $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$ (M = Fe, Co; R = Ph) with I_2 yields the neutral trinuclear complexes $[M(SR)_4\{Mo(CO)_4\}_2]$ (M = Fe, Co; R = Ph).

Introduction

As part of our efforts to better understand the chemistry of low-valent metal carbonyl thiolate species, we have recently reported the preparation of mononuclear[3] molybdenum complexes containing cis terminal thiolate groups and dinuclear[4–6] molyb-

denum and tungsten species with bridging thiolate moieties. One goal of this work was to generate starting materials for the syn-

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thesis of heterometallic *thiolate*-bridged compounds and thus complement the recent studies on low-valent Fe–Mo *sulfido*-bridged species. Some of these latter complexes, such as $[MoFe_3S_6(CO)_6]^{2-}$,[7] $[MoOFe_5S_6(CO)_{12}]^{2-}$,[8] $[Fe_6Mo_2S_6X_6-(CO)_6]^{3-/4-}$,[9] and several organometallic $[Mo_2Fe_2]$ species[10-12] have been designed as an approach to a synthetic analogue for the molybdenum site of nitrogenase.[13,14] In our preliminary work, we have described[3] preliminary data on the synthesis of $[Mo-(CO)_4(SR)_2]^{2-}$ (R = Ph, Bz) and have reported[4-6] the synthesis and spectroscopic and electrochemical characterization of a series of compounds of the form $[NEt_4]_2[M_2(CO)_8(SR)_2]$ (M = Mo, W; R = Ph, Bz, *t*-Bu). In addition we found[15] that the known[16] Mo(II) compounds $[Mo(RNC)_4(t\text{-BuS})_2]$ (R = Cy, *t*-Bu), structural analogues of the above mononuclear carbonyl starting material containing cis thiolate ligands, could chelate ferrous halides to form complexes with an Fe–$(t\text{-BuS})_2$–Mo unit. Herein we report the use of these mono- and dinuclear carbonyl species as reagents for the preparation of simple, trinuclear Fe–Mo–SR complexes and describe some aspects of the reactivity and electrochemistry of these heterometallic species, the latter indicating that the new complexes are characterized by a simultaneous two-electron oxidation. In addition, we have prepared and characterized some of the analogous Co–Mo–SR complexes, which can formally be viewed as equivalent to the one-electron-reduced form of the iron compounds.

Experimental Section

Materials and Methods. All reactions were carried out under argon in a Schlenk apparatus. Where required, temperatures of –23 °C were obtained by immersing the reaction vessel in a CCl$_4$/liquid nitrogen slush bath. Cyclohexyl and *tert*-butyl isocyanides (CyNC, *t*-BuNC) were purchased from Aldrich. The compounds $[C_7H_8Mo(CO)_4]$,[17] $[NEt_4]_2$-$[Fe(SPh)_4]$,[18] $[NEt_4]_2[Mo_2(CO)_8(SR)_2]$ (R = Ph, Bz),[4,5] and $[NEt_4]_2$-$[CoCl_4]$[19] were prepared by the literature methods cited. Sodium thiolate salts (NaSR) were prepared by reaction of NaOMe and thiol (in slight excess) in methanol, followed by evaporation of the reaction mixture to dryness and trituration of the residue with Et$_2$O. Acetonitrile was distilled over CaH$_2$; other solvents were used as obtained. Infrared spectra were run as KBr pellets prepared in a drybox, on a Beckman IR-20A instrument, and visible spectra were recorded on a Cary 118 or a Varian 2200 spectrophotometer. Voltammetric measurements[4-6] and carbon monoxide determinations[4,20] were carried out as previously described.

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Elemental analyses were performed in this laboratory on a Perkin-Elmer 240 instrument equipped with a Microjector from Control Equipment Corp. or by Galbraith Laboratories where noted.

Infrared (IR; values in cm^{-1}) and visible (vis; peak positions in nm with molar absorptivities given in parentheses) spectral data for all complexes is presented below along with their methods of synthesis.

[NEt$_4$][SPh]. This reagent, which we have previously[4-6,20] generated in situ, can also conveniently be isolated as a pure solid. NaSPh (5.0 g, 37.9 mmol) and anhydrous [NEt$_4$]Cl (6.30 g, 38.1 mmol) were suspended in MeCN (200 mL) and stirred for 2 days. The solution was filtered, the filtrate was evaporated to 60 mL, and Et$_2$O (100 mL) was added slowly. Oiling sometimes occurred, but on cooling, a white crystalline product (9.15 g; 90%) was always obtained. The infrared spectrum was consistent with the formulation, containing peaks characteristic of both [NEt$_4$]$^+$ and SPh moieties. Anal. Calcd for C$_{14}$H$_{25}$NS: C, 70.21; H, 10.54; N, 5.85. Found: C, 70.12; H, 11.22; N 5.79.

[NEt$_4$][SBz]. This compound can be isolated as a solid by a procedure similar to that used for [NEt$_4$][SPh] and used as such in the reactions below. However, because of the light, flaky form of the solid, it is difficult to contain during transfers. Since phenylmethanethiol has an unusually unpleasant and persistent odor and is a cancer suspect, it is preferable to generate [NEt$_4$][SBz] in situ by the following procedure without isolation. NaSBz (0.40 g, 2.74 mmol) and [NEt$_4$]Cl (0.45 g, 2.72 mmol) were stirred in MeCN (50 mL) for 21 h, and the solution was filtered. The white residue was washed with a small portion of MeCN and the combined filtrate reduced in volume to 15 mL. This procedure gives a virtually quantitative yield of [NEt$_4$][SBz] in MeCN.

[NEt$_4$]$_2$[Mo(CO)$_4$(SPh)$_2$]. A solution of [C$_7$H$_8$Mo(CO)$_4$] (0.50 g, 3.35 mmol) in MeCN (10 mL) was added over 15 min to a solution of [NEt$_4$][SPh] (0.80 g, 3.35 mmol) in MeCN (30 mL), which had been cooled to –23 °C. The reaction mixture was then stirred for 3 h at –23 °C, and Et$_2$O (20 mL) was added to precipitate the product (0.13 g; 27%) as a bright yellow solid, which was isolated by filtration, washed with Et$_2$O, and dried under vacuum. Anal. Calcd for C$_{32}$H$_{50}$N$_2$O$_4$S$_2$Mo: C, 55.94; H, 7.35; N, 4.07. Found (Galbraith): C, 55.08; H, 7.69; N, 4.09. Percent CO evolved on decomposition: 97%. IR: 1985 (m), 1885 (s), 1855 (s), 1790 (s) (ν_{CO}).

[NEt$_4$]$_2$[Mo(CO)$_4$(SBz)$_2$]. A solution of [C$_7$H$_8$Mo(CO)$_4$] (0.41 g, 2.7 mmol) in MeCN (15 mL) was added over 30 min to a solution of [NEt$_4$][SBz] (2.7 mmol) in MeCN (15 mL), which had been cooled to –23 °C, and the reaction mixture was stirred for an additional 15 min. Gradual addition (at –23 °C) of Et$_2$O (80 mL) produced an oil, which solidified upon stirring. The deep yellow solid (0.40 g; 41%) was filtered quickly, washed with ether, and dried in vacuo. Anal. Calcd for C$_{34}$H$_{54}$N$_2$O$_4$S$_2$Mo: C, 57.11; H, 7.62; N, 3.91. Found (Galbraith): C, 49.65; H, 8.24; N, 4.45. Percent CO on decomposition: 97%. IR: 1978 (m), 1875 (s), 1825 (s), 1765 (s) (ν_{CO}).

[NEt$_4$]$_2$[Fe(SPh)$_4${Mo(CO)$_4$}$_2$]. **Method 1. From [C$_7$H$_8$Mo(CO)$_4$].** Samples of [NEt$_4$]$_2$[Fe(SPh)$_4$] (1.26 g, 1.68 mmol) and [C$_7$H$_8$Mo(CO)$_4$] (1.0 g, 3.30 mmol) were dissolved in MeCN (50 mL) and stirred at room temperature for 2.5 h. The solution was then evaporated to 20 mL, and upon addition of Et$_2$O (50 mL) and cooling, the dark orange crystalline product (1.62 g; 83%) that precipitated was isolated by filtration, washed with Et$_2$O, and dried under vacuum. Anal. Calcd for C$_{48}$H$_{60}$N$_2$O$_8$S$_4$FeMo$_2$: C, 49.31; H, 5.18; N, 2.39. Found: C, 48.73; H, 5.46; N, 2.48. Percent CO on decomposition: 102%. IR: 1995 (m), 1908 (s), 1873 (s), 1828 (s), 1810 (s) (ν_{CO}). Vis (in MeCN at 20 °C): 425 (3490).

Method 2. From Mo(CO)$_6$. Samples of Mo(CO)$_6$ (1.0 g, 3.79 mmol), [NEt$_4$]$_2$[FeCl$_4$] (0.86 g, 1.88 mmol), and NaSPh (1.0 g, 7.58 mmol) were refluxed in MeCN (40 mL) under a static argon atmosphere for 1 h. After cooling, the solution was filtered and the filtrate evaporated to 20 mL. Addition of *i*-PrOH (30 mL) and cooling caused the orange product (1.57 g; 71%) to precipitate. Spectroscopic characterization and elemental analysis showed that this solid was identical with the product obtained by method 1. [NEt$_4$]$_2$[Fe(SPh)$_4$] can also be used in place of the [NEt$_4$]$_2$[FeCl$_4$] and NaSPh.

Method 3. From [NEt$_4$]$_2$[Mo(CO)$_4$(SPh)$_2$]. A freshly prepared sample of [NEt$_4$]$_2$[Mo(CO)$_4$(SPh)$_2$] (0.18, 0.26 mmol) was added to [NEt$_4$]$_2$-[FeCl$_4$] (0.06 g, 0.13 mmol) dissolved in MeCN (10 mL) at –23 °C, the mixture was stirred for 30 s, and *i*-PrOH (40 mL) was added. After a few minutes, the solution was filtered and the solid (0.08 g; 53%) was washed with *i*-PrOH and Et$_2$O. The IR spectrum of this solid was identical with that of the product prepared by method 1 above.

Method 4. From [NEt$_4$]$_2$[Mo$_2$(CO)$_8$(SPh)$_2$]. Samples of [NEt$_4$]$_2$-[Mo$_2$(CO)$_8$(SPh)$_2$] (0.50 g, 0.56 mmol) and FeBr$_2$ (0.06 g, 0.28 mmol) were stirred in MeCN (25 mL) for 0.5 h, during which time the FeBr$_2$ dissolved. Evaporation to 15 mL, addition of *i*-PrOH (25 mL), and cooling caused the orange solid product (0.48 g) to precipitate. Spectroscopic evidence showed this solid to be [NEt$_4$]$_2$[Fe(SPh)$_4${Mo(CO)$_4$}$_2$].

[NEt$_4$]$_2$[Fe(SBz)$_4${Mo(CO)$_4$}$_2$]. Method 1. From [NEt$_4$]$_2$[Mo(CO)$_4$-(SBz)$_2$]. A freshly prepared sample of [NEt$_4$]$_2$[Mo(CO)$_4$(SBz)$_2$] (0.40 g, 0.56 mmol) and FeBr$_2$ (0.16 g, 0.28 mmol) were added as solids to MeCN (25 mL) at −23 °C. The solution was stirred at this temperature for 1 h, during which time the FeBr$_2$ dissolved and a fine orange solid precipitated. The product (0.15 g; 43%) was isolated by filtration, washed with Et$_2$O, and dried under vacuum. This reaction was also performed with a 1:1 stoichiometry of reactants with a similar result. Other sources of iron such as Fe(S$_2$CNC$_5$H$_{10}$)$_2$ or [NEt$_4$]$_2$[FeCl$_4$] can also be used successfully. Anal. Calcd for C$_{52}$H$_{68}$N$_2$O$_8$S$_4$FeMo$_2$: C, 50.97; H, 5.60; N, 2.28. Found: C, 43.74; H, 5.81; N, 2.11. Percent CO on decomposition: 99%. IR: 1995 (m), 1880 (s), 1827 (s) (ν_{CO}). Vis (in MeCN at 20 °C): 444 (4150).

Method 2. From [NEt$_4$]$_2$[Mo$_2$(CO)$_8$(SBz)$_2$]. Samples of [NEt$_4$]$_2$-[Mo$_2$(CO)$_8$(SBz)$_2$] (1.0 g, 1.08 mmol) and FeBr$_2$ (0.12 g, 0.56 mmol) were stirred in MeCN (25 mL). After 0.5 h, the orange precipitated product (0.51 g; 80%) was isolated by filtration, washed with *i*-PrOH and Et$_2$O, and dried under vacuum. The infrared spectrum was identical with that of the product obtained from method 1. Anal. Calcd for C$_{52}$H$_{68}$N$_2$O$_8$S$_4$FeMo$_2$: C, 50.97; H, 5.60; N, 2.28; Fe, 4.55. Found: C, 44.83; H, 5.93; N, 2.11; Fe, 4.86.

[NEt$_4$]$_2$[Co(SPh)$_4$]. This compound, which has been reported[21] as the [PPh$_4$]$^+$ salt, was prepared by a modification of the method of Miller and Stiefel.[22] A solution of CoCl$_2$ (1.64 g, 12.6 mmol), NaOMe (4.0 g, 74 mmol), and PhSH (7.7 mL, 74 mmol) was stirred in EtOH (50 mL) for 1 h. Filtration into a solution of [NEt$_4$]Br (9.0 g, 42.9 mmol) in EtOH (30 mL) and cooling to 0 °C resulted in the precipitation of a bright green product (8.45 g; 89%), which was isolated by filtration, washed with EtOH and Et$_2$O, and dried under vacuum. Anal. Calcd for C$_{40}$H$_{60}$N$_2$CoS$_4$: C, 63.57; H, 7.94; N, 3.70. Found: C, 62.57; H, 8.05; N, 3.89.

[NEt$_4$]$_2$[Co(SPh)$_4${Mo(CO)$_4$}$_2$]. Method 1. From [C$_7$H$_8$Mo(CO)$_4$]. Samples of [C$_7$H$_8$Mo(CO)$_4$] (1.5 g, 5.0 mmol) and [NEt$_4$]$_2$[Co(SPh)$_4$] (1.89 g, 2.51 mmol) were stirred in MeCN (30 mL) for 40 min, during which time the color changed from green to deep purple. Gradual addition to Et$_2$O (50 mL) and cooling resulted in precipitation of a dark purple crystalline product (2.3 g; 78%), which was isolated by filtration, washed with Et$_2$O, and dried under vacuum. Anal. Calcd for C$_{48}$H$_{60}$N$_2$O$_8$S$_4$CoMo$_2$: C, 49.18; H, 5.16; N, 2.39. Found: C, 49.10; H, 5.41; N, 2.43. IR: 1992 (m), 1910 (s), 1875 (s), 1830 (s), 1810 (s) (ν_{CO}). Vis (in MeCN at 20 °C): 425 (4495), 535 (2155), 720 (450).

Method 2. From [NEt$_4$]$_2$[Mo(CO)$_4$(SPh)$_2$]. This procedure was identical with that for the iron system above, replacing [NEt$_4$]$_2$[FeCl$_4$] by CoCl$_2$. Yield: 80%.

Method 3. From [NEt$_4$]$_2$[Mo$_2$(CO)$_8$(SPh)$_2$]. This reaction was performed analogously to the iron reaction with CoCl$_2$ used in place of FeBr$_2$. The infrared spectrum showed it to be identical with the product obtained from method 1. Yield: 26%.

Method 4. From Mo(CO)$_6$. This reaction was also performed as described above for the analogous iron compound, using [NEt$_4$]$_2$[CoCl$_4$] and refluxing for only 0.5 h. The product from this method is not as pure as products obtained by the other methods, based on its infrared spectrum. Yield: 39%.

[NEt$_4$]$_2$[Co(SBz)$_4${Mo(CO)$_4$}$_2$]. Method 1. From [NEt$_4$]$_2$Mo(CO)$_4$-(SBz)$_2$]. The synthesis was analogous to the iron reaction above, but with CoCl$_2$ used. A 75% yield of essentially pure product was obtained. An analytical sample was obtained by dissolving 0.50 g of crude product in DMF (20 mL) at −23 °C and adding Et$_2$O (20 mL) to recover 0.32 g of solid. The CO bands in the infrared spectrum are somewhat sharper in this purified sample. Anal. Calcd for C$_{52}$H$_{68}$N$_2$O$_8$S$_4$CoMo$_2$: C, 50.84; H, 5.59; N, 2.28; Co, 4.79; Mo, 15.62. Found (Galbraith): C, 48.06; H, 5.57; N, 2.24; Co, 5.13; Mo, 15.57. Percent CO on decomposition: 102%. IR: 1990 (m), 1885 (s), 1833 (s) (ν_{CO}). Vis (in MeCN at 20 °C): 436 (4540), 610 (880).

Method 2. From [NEt$_4$]$_2$[Mo$_2$(CO)$_8$(SBz)$_2$]. This reaction was also performed analogously to the iron reaction above, but the solution was stirred for 2 h, as the reaction appeared slower (perhaps due to the lower solubility of CoCl$_2$ in MeCN). The dark red microcrystalline product (0.19 g; 29%) precipitated from the solution. The product was spectroscopically identical with that obtained from method 1.

[Fe(SPh)$_4${Mo(CO)$_2$}$_2$]. A sample of [NEt$_4$]$_2$[Fe(SPh)$_4${Mo(CO)$_4$}$_2$] (0.50 g, 0.43 mmol) was suspended in toluene (25 mL), and a solution of I$_2$ (0.130 g, 0.51 mmol) in toluene (25 mL) was added over a 5-min period. The starting material dissolved to give a dark red solution, which was filtered to remove [NEt$_4$]I and other insoluble dark byproducts of unknown nature. Evaporation of the filtrate to dryness yielded a dark residue, which was triturated with hexane to yield the product (0.10 g;

25%), which was isolated by filtration, washed with hexane, and dried under vacuum. Anal. Calcd for C$_{32}$H$_{20}$FeMo$_2$O$_8$S$_4$: C, 42.29; H, 2.20. Found: C, 42.66; H, 2.41. IR: 2050 (m), 2010 (w), 1980 (s) (ν_{CO}). Vis (in hexane at 20 °C): 365 sh (3010), 455 (3535), 640 sh (525).

[Co(SPh)$_4${Mo(CO)$_2$}$_2$]. This compound was prepared in 20% yield in the same way as its iron analogue above. Anal. Calcd for C$_{32}$H$_{20}$CoMo$_2$O$_8$S$_4$: C, 42.18; H, 2.19. Found: C, 42.05; H, 2.90. IR: 2040 (m), 1985 (m), 1965 (s) (ν_{CO}). Vis (in toluene at 20 °C): 392 (6180), 500 sh (3860), 650 sh (1045).

Reduction of [Fe(SPh)$_4${Mo(CO)$_4$}$_2$]. A solution of [Fe(SPh)$_4${Mo(CO)$_4$}$_2$] (0.15 g, 0.13 mmol) and [NEt$_4$]BH$_4$ (0.05 g, 0.35 mmol) in MeCN (20 mL) was stirred for 1 h and filtered. The product (0.06 g; 31%), which precipitated from the filtrate on addition of *i*-PrOH (50 mL), was isolated by filtration, washed with *i*-PrOH, and dried under vacuum. An infrared spectrum of this solid showed that it was [NEt$_4$]$_2$[Fe(SPh)$_4${Mo(CO)$_4$}$_2$] although its brown color seems to indicate that it is slightly impure.

[NEt$_4$]$_2$[Fe(SPh)$_4$(*t*-BuNC)$_2${Mo(CO)$_4$}$_2$]. A solution of [NEt$_4$]$_2$[Fe-(SPh)$_2${Mo(CO)$_4$}$_2$] (1.0 g; 0.855 mmol) and *t*-BuNC (0.19 mL, 1.7 mmol) were stirred in MeCN (25 mL) at −23 °C for 3 h and then the mixture kept at −20 °C for another 3 h. The orange solid (0.14 g; 12%) that precipitated from the solution was filtered, washed with Et$_2$O, and dried under vacuum. Anal. Calcd for C$_{58}$H$_{78}$N$_4$O$_8$S$_4$FeMo$_2$: C, 52.16; H, 5.89; N, 4.19. Found: C, 52.08; H, 6.04; N, 4.62. IR: 2160 (m), 2130 (m) (ν_{CN}); 1993 (m), 1910 (s), 1785 (s), 1743 (s) (ν_{CO}). Vis (at 20 °C in MeCN): 460 (4650).

[NEt$_4$]$_2$[Fe(SPh)$_4$(CyNC)$_2${Mo(CO)$_4$}$_2$]. This compound was prepared as above analogous *t*-BuNC species, but at 0 °C, by using 1.0 g (0.855 mmol) of the stirring material and 0.19 mL of CyNC (1.7 mmol). After the mixture was stirred for 1 h, 0.29 g (24%) of orange powder was obtained. Anal. Calcd for C$_{62}$H$_{82}$N$_4$O$_8$S$_4$FeMo$_2$: C, 53.66; H, 5.96; N, 4.03. Found: C, 53.75; H, 5.95; N, 4.04. IR: 2155 (m), 2125 (m) (ν_{CN}); 1990 (s), 1905 (s), 1780 (s), 1740 (s) (ν_{CO}). Vis (in MeCN at 20 °C): 463 (4120).

[NEt$_4$]$_2$[Co(SPh)$_4$(CyNC)$_2${Mo(CO)$_4$}$_2$]. This complex was prepared by the same method as that used for the analogous iron species. After the solution was stirred for 3 h at −23 °C, filtration yielded 0.09 g (8%) of dark powder. Anal. Calcd for C$_{62}$H$_{82}$N$_4$O$_8$S$_4$CoMo$_2$: C, 53.54; H, 5.95; N, 4.03. Found: C, 52.89; H, 5.50; N, 4.58. IR: 2155 (m) (ν_{CN}); 1906 (m), 1883 (s), 1835 (s) (ν_{CO}). Vis (in DMF at −48 °C): 378 (10 170), 424 (8310), 484 (7270), 584 (9110).

[Fe(bpy)$_2$(SPh)$_2$Mo(CO)$_4$]. A sample of [NEt$_4$]$_2$[Fe(SPh)$_4${Mo-(CO)$_4$}$_2$] (0.60 g, 0.52 mmol) was dissolved in MeCN 15 mL), cooled to −23 °C, and a solution of 2,2′-bipyridyl (0.16 g, 1.03 mmol) in MeCN (10 mL) was dropped into the flask over 45 min. After being stirred for an additional 15 min, the solution was filtered and the solid (0.17 g; 41%) was washed with Et$_2$O and dried under vacuum. Anal. Calcd for C$_{36}$H$_{26}$N$_4$O$_4$S$_2$FeMo: C, 54.41; H, 3.30; N, 7.05. Found: C, 53.10; H, 3.43; N, 6.52. IR: 1990 (m), 1895 (s), 1880 (s), 1835 (s) (ν_{CO}); 1610 (m), 1450 (m), (ν_{bpy}). Vis (in DMF at −56 °C): 416 sh (6250), 512 sh (2860), 534 sh (3720), 618 (4630).

[Fe(*o*-phen)$_2$(SPh)$_2$Mo(CO)$_4$]. This compound was prepared in a manner similar to that used for the bpy compounds in 67% yield. Anal. Calcd for C$_{40}$H$_{26}$N$_4$O$_4$S$_2$FeMo: C, 57.01; H, 3.11; N, 6.65. Found: C, 56.80; H, 3.24; N, 6.88. Percent CO on decomposition: 101%. IR: 1990 (m), 1895 (s), 1880 (s), 1830 (s) (ν_{CO}); 1590 (m), 1480 (m) (ν_{SPh}); 1528 (w), 1435 (m), 840 (m), 720 (m) ($\nu_{o\text{-phen}}$). Vis (in DMF at −56 °C): 386 (6230), 568 (6890), 616 (6920).

[Co(bpy)$_2$(SPh)$_2$Mo(CO)$_4$]·CH$_2$Cl$_2$. Cobalt compounds can be made by a procedure similar to that used for their iron analogues, but the following method is more convenient. Samples of [NEt$_4$]$_2$[Co(SPh)$_4$-{Mo(CO)$_4$}$_2$] (0.60 g, 0.51 mmol) and 2,2′-bipyridyl (0.16 g, 1.03 mmol) were stirred in CH$_2$Cl$_2$ (25 mL) for 2 h at room temperature. The solution was filtered and the solid washed with several portions of MeCN until the washes were no longer yellow. After the solid was washed with Et$_2$O and dried under vacuum, 0.22 g (49%) of purple-brown product was obtained. Anal. Calcd for C$_{37}$H$_{28}$N$_4$O$_4$S$_2$Cl$_2$CoMo: C, 50.34; H, 3.20; N, 6.34. Found: C, 49.11; H, 3.27; N, 6.27. Percent CO on decomposition: 105%. IR: 1990 (m), 1875 (s), 1820 (s), (ν_{CO}); 1580 (m), 1480 (m) (ν_{SPh}); 1610 (m), 1445 (m) (ν_{bpy}); 765 (w), 755 (w) (ν_{C-Cl}).

The combined MeCN washes were collected separately and evaporated to 10 mL. Addition of Et$_2$O (25 mL) caused the precipitation of a yellow solid (0.06 g; 26%), which was filtered, washed with MeOH and Et$_2$O, and dried under vacuum. The product was identified as [NEt$_4$]$_2$[Mo$_2$(CO)$_8$(SPh)$_2$] by its IR spectrum.

[Co(*o*-phen)$_2$(SPh)$_2$Mo(CO)$_4$]·0.5CH$_2$Cl$_2$. This reaction was carried out in a manner similar to that used for the cobalt–bpy compound above, with a yield of 48%. Anal. Calcd for C$_{40.5}$H$_{27}$N$_4$O$_4$S$_2$ClCoMo: C, 54.76; H, 3.07; N, 6.30. Found: C, 54.51; H, 3.04; N, 6.58. Percent CO on decomposition: 97%. IR: 1990 (m), 1900 (s), 1880 (s), 1825 (s) (ν_{CO});

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1590 (m), 1482 (m) (ν_{SPh}); 1525 (m), 1435 (m), 835 (m), 820 (m) ($\nu_{o\text{-phen}}$); 765 (w), 755 (w) (ν_{C-Cl}).

Reaction of $[NEt_4]_2[Fe(SPh)_4\{Mo(CO)_4\}_2]$ with CO. A sample of $[NEt_4]_2[Fe(SPh)_4\{Mo(CO)_4\}_2]$ (1.0 g, 0.86 mmol) was stirred in MeCN (50 mL) under an atmosphere of pure CO for 45 min, resulting in a change of color from orange to deep red. The solution was evaporated to an oil, which was extracted with $CHCl_3$ (30 mL), leaving an insoluble residue. Addition of hexane (20 mL) to the extract caused the formation of a oil which solidified after stirring for 1 h. This crude product (0.46 g) was then recrystallized twice from $CHCl_3$–hexane, with initial oiling each time. The IR spectrum of the final product contained CO peaks at 2040, 1995, 1985, 1970, 1900, and 1855 cm^{-1}. The first three are sharp peaks while the second three are broader, a pattern that suggests the presence of both iron carbonyl and molybdenum carbonyl moieties. The results of a typical analysis were consistent with the formulation $[NEt_4][Mo(CO)_4(SPh)_2Fe(CO)_3]$. Anal. Calcd for $C_{27}H_{30}N_2S_2FeMo$: C, 46.55; H, 4.35; N, 2.01. Found: C, 46.43; H, 4.72; N, 1.88. However, the CO released on oxidation (50–80% of theory) is variable and is not compatible with this compound nor is an EPR spectrum observed for its frozen solutions at 13 K as might be expected for a complex that formally contains Mo(O) and Fe(I). Thus, while the synthetic procedure is reproducible, the identity and purity of the compound are still questionable.

Results and Discussion

Sulfide moieties comprise the primary bridging atoms in most Fe–Mo heterometallic complexes, these species being of interest primarily because the proposed[23] catalytic site of the nitrogenase enzyme is an iron–molybdenum–sulfur cluster unit.[13] Less work has been carried out on heterometallic systems where sulfide is absent and where coordinated thiolate groups provide the capability of forming bridges in the clusters. The ability of metal complexes that contain at least two monodentate terminal thiolate ligands to bind another metal via SR^- bridges is documented in the literature, and, in fact, was exploited over 15 years ago to make a mixed-metal Fe–Mo complex when Dias and Green[24] prepared $[(C_5H_5)_2Mo(SR)_2FeCl_2]$ by reaction of the Mo(IV)–bis(thiolate) complex $[(C_5H_5)_2Mo(SR)_2]$ with $FeCl_2$. Other $(C_5H_5)_2M(SR)_2$ complexes,[25-28] as well as cobalt[27] and lutetium[29] cyclopentadienyl species, are also known to form thiolate bridges on reaction with other metal fragments. It appears that the only system without cyclopentadienyl ligands to exhibit this behavior is the aforementioned *cis*-$[Mo(R'NC)_4(SR)_2]$, which has been shown to react with FeX_2 (X = Cl, Br)[15] and $CuBr$.[30] Tetrahedral complexes of the form $[M(SR)_4]^{2-}$ are well-characterized for M = Fe,[18,19,21] Co,[19,21] Mn,[21,31] Ni,[21] and Zn,[21] but attempts to form simple adducts with other metal species have apparently not been reported. The well-studied[32] tetrahedral molybdenum(IV) thiolate species $[Mo(t\text{-BuS})_4]$ has been shown[33] to react with $[Fe_2(CO)_9]$ to yield $[(CO)_3Fe(t\text{-BuS})_2Mo(CO)_2(t\text{-BuS})_2Fe(CO)_3]$, indicating the utility of these thiolate species in heterometallic synthesis. No reactivity of the related, structurally hindered molybdenum(IV) thiolate species $[Mo\{S\text{-}2,4,6\text{-}C_6H_2(CHMe_2)_3\}_4]$ with other metal complexes has yet been reported.[34] Using Fe–SR, Co–SR, and

Mo–SR species as starting materials, we have now prepared a series of Mo–Fe(Co)–Mo trinuclear thiolate-bridged species by several routes.

Preparation of Complexes. $[NEt_4]_2[Mo(CO)_4(SR)_2]$ (R = Bz, Ph). These compounds[3] are synthesized by careful addition of (norbornadiene)$Mo(CO)_4$, a well-known precursor of disubstituted molybdenum carbonyl species, to a solution of $[NEt_4][SR]$ (R = Ph, Bz) in MeCN at –23 °C according to eq 1. The complexes,

$$[(C_7H_8)Mo(CO)_4] + 2[NEt_4][SR] \rightarrow [NEt_4]_2[Mo(CO)_4(SR)_2] + C_7H_8 \quad (1)$$
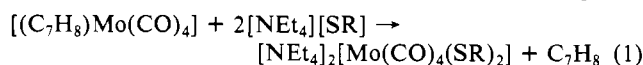
apparently the first examples of bis(monodentate thiolato)metal carbonyls, are generally unstable to both aerial oxidation and thermal decomposition and are best characterized and used immediately after preparation. They are stable for several hours at room temperature in the solid state but rapidly decompose in solution under these conditions to form the more stable dinuclear species $[Mo_2(CO)_8(SR)_2]^{2-}$ (eq 2). As noted in the Experimental

$$2[Mo(CO)_4(SR)_2]^{2-} \rightarrow [Mo_2(CO)_8(SR)_2]^{2-} + 2[SR]^- \quad (2)$$
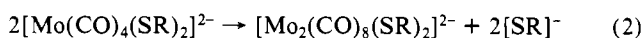
Section, we have been unable to obtain acceptable, reproducible elemental analytical data (particularly for carbon) for the phenylmethanethiolate derivative of this form, perhaps partially because of its thermal instability.[35] A structural comparison of these d^6 Mo(0) species with the d^4 Mo(II) complex $[Mo(t\text{-}BuNC)_4(S\text{-}t\text{-}Bu)_2]$ would be of interest. The latter compound has been structurally characterized[16,36] and found to have an unusually wide S–Mo–S angle, whereas it has been predicted[16] that the d^6 system will attain a geometry much closer to octahedral.

$[NEt_4]_2[M(SR)_4\{Mo(CO)_4\}_2]$ (M = Fe, Co; R = Ph, Bz). These trinuclear heterometallic carbonyl complexes were readily prepared by using three distinct methods: (a) reaction of $[Mo(CO)_4(SR)_2]^{2-}$ with MX_2 or $[MX_4]^{2-}$; (b) displacement of norbornadiene from $(C_7H_8)Mo(CO)_4$ with $[M(SR)_4]^{2-}$; (c) reaction of the dinuclear $[Mo_2(CO)_8(SR)_2]^{2-}$ with MX_2 or $[MX_4]^{2-}$. It is noteworthy that the thiolate bridges of the product can therefore be derived from either terminal Fe(Co)–SR, terminal Mo–SR, or bridging Mo–$(SR)_2$–Mo moieties in the different starting materials. However, not all methods are applicable to all compounds.

Method a involves the facile substitution of halide by two *cis*-$Mo(SR)_2$ moieties and proceeds in high yield in MeCN according to eq 3. The high affinity of the bis(thiolate) species

$$[MCl_4]^{2-} + 2[Mo(CO)_4(SR)_2]^{2-} \rightarrow [M(SR)_4\{Mo(CO)_4\}_2]^{2-} + 4Cl^- \quad (3)$$
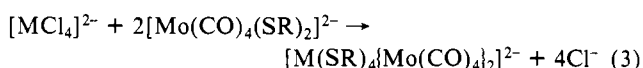
for other metals is indicated by the rapidity of the reaction, despite the reduced temperatures. FeX_2 (X = Cl, Br) or $CoCl_2$ can also be used instead of $[MX_4]^{2-}$. It is interesting to note that the above trinuclear species, not the dinuclear $[(CO)_4Mo(SR)_2FeX_2]^{2-}$, was obtained even under conditions of 1:1 stoichiometry. This result, along with the variety of synthetic methods from which they may be prepared, indicates that the trinuclear species represent a thermodynamically stable configuration for these components. The disadvantage of this procedure relates to the instability (vide supra) of the molybdenum starting materials, a characteristic that requires both that the reaction be carried out at low temperature and that freshly prepared $[Mo(CO)_4(SR)_2]^{2-}$ be used.

Method b, where norbornadiene is displaced from two $[(C_7H_8)Mo(CO)_4]$ molecules by the coordinated thiolates of tetrahedral $[M(SR)_4]^{2-}$, is also a rapid, high-yield reaction, which can

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(27) (a) Douglas, W. E.; Green, M. L. H.; Prout, K.; Rees, G. V. *J. Chem. Soc., Chem. Commun.* **1971**, 896. (b) Douglas, W. E.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1796. (c) Prout, K.; Critchley, S. R.; Rees, G. *Acta Crystallogr., Sect. B: Struct. Crystallog. Cryst. Chem.* **1974**, *30B*, 2305.
(28) (a) Harriss, M. G.; Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1969**, 1453. (b) O'Hare, D.; Green, M. L. H.; Cloke, F. G. N. *J. Organomet. Chem.* **1985**, *282*, 225.
(29) Schumann, H.; Albrecht, I.; Hahn, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 985.
(30) Payne, N. C.; Okura, N.; Otsuka, S. *J. Am. Chem. Soc.* **1983**, *105*, 245.
(31) Costa, T.; Dorfman, J. R.; Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 4091.
(32) Otsuka, S.; Kamata, M.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3014.
(33) Lu, S.; Okura, N.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1983**, *105*, 7470.

(34) Roland, E.; Walborsky, J. C.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5795.
(35) However, it should be noted that acceptable carbon data could also be obtained for the trinuclear species $[NEt_4]_2[M(SBz)_2\{Mo(CO)_4\}_2]$ (M = Fe, Co), which *are* thermally stable. Like $[NEt_4]_2[Mo(CO)_4(SBz)_2]$, these benzyl derivatives have IR spectra consistent with their formulation and evolve the predicted amount of CO on oxidation leading us to believe that they are pure. Nevertheless, it is also a definite possibility that the SBz complexes contain impurities that are responsible for the unacceptable carbon analyses.
(36) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3572.

be carried out at room temperature (eq 4). However, the synthesis

$$2[(C_7H_8)Mo(CO)_4] + [M(SR)_4]^{2-} \rightarrow$$
$$[M(SR)_4\{Mo(CO)_4\}_2]^{2-} + 2C_7H_8 \quad (4)$$
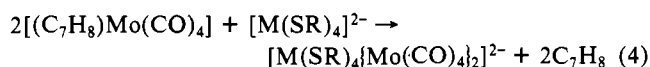
of the molybdenum starting material is rather time consuming, and more importantly, the method is inappropriate for the Bz system since $[M(Bz)_4]^{2-}$ (M = Fe, Co) complexes are unreported. An even simpler variation of this method, which can be used for the Fe– and Co–SPh species, involves refluxing $Mo(CO)_6$, $[NEt_4]_2[MCl_4]$, $[NEt_4]Cl$, and NaSPh in the appropriate stoichiometry in MeCN. The complexes $[M(SPh)_4]^{2-}$ are probable intermediates in this reaction since they are rapidly formed under these conditions in the absence of the other metal reagent.

Method c for preparation of the trinuclear species, the reaction of $[Mo_2(CO)_8(SR)_2]^{2-}$ with MX_2 or $[MX_4]^{2-}$, is the easiest to carry out and the most generally applicable route. The reaction stoichiometry is apparently as indicated in eq 5, although we have

$$2[Mo_2(CO)_8(SR)_2]^{2-} + MX_2 \xrightarrow{\text{MeCN}}$$
$$[M(SR)_4\{Mo(CO)_4\}_2]^{2-} + 2X^- + 2[Mo(CO)_4(MeCN)_2] \quad (5)$$
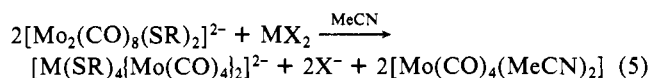
not confirmed the formation of $[Mo(CO)_4(MeCN)_2]$. The method is effective for both iron and cobalt and for both benzene- and phenylmethanethiolates and, although we have not yet explored this reactivity, might allow the synthesis of the tungsten analogues of the trinuclear species since the dinuclear $[W_2(CO)_8(SR)_2]^{2-}$ is available[6] for use as starting material. However, the reaction is not completely ubiquitous as no reaction occurs (perhaps for steric reasons) when $[Mo_2(CO)_8(S-t-Bu)_2]^{2-}$ is used.

Acceptable carbon, hydrogen, and nitrogen elemental analytical data were acquired without difficulty for the Fe–Mo–SPh and Co–Mo–SPh trinuclear species, and these compounds release the predicted amount of CO on oxidation, leaving little doubt as to their nature and purity. Unfortunately, as for $[Mo(CO)_4(SBz)_2]^{2-}$ (vide supra), we have been unable to obtain acceptable carbon analyses for either the cobalt or the iron trinuclear SBz derivatives, raising the possibility that they are somewhat impure. However, as described in the Experimental Section, these two compounds do evolve the proper amount of CO on oxidation and are characterized by good hydrogen, nitrogen, and, in some cases, metal analyses. These latter results, together with the variety of rational synthetic methods of these species and their spectroscopy and reactivity (vide infra), lead us to believe that they are, in fact, correctly formulated as $[M(SBz)_4\{Mo(CO)_4\}_2]^{2-}$ and contain only minimal impurities.[35]

Spectroscopy. As tabulated in the Experimental Section, consistent with the presence of coordinated CO, the infrared spectra of the trinuclear species contain strong bands in the 1800–2050-cm^{-1} region. However, the typical *four-band* pattern (one weak, three strong), which is characteristic[37] of complexes containing *cis*-M(CO)$_4$ fragments and which we observed in our previous[3-6] studies of $[Mo(CO)_4(SR)_2]^{2-}$ and $[M_2(CO)_8(SR)_2]^{2-}$ (M = Mo, W), was not present for $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$. Instead, while the spectra of the Fe and Co species for a particular thiolate are virtually identical, the complexes containing SPh bridges give rise to *five-band* patterns (one weak, four strong) while those with SBz bridges are characterized by *three bands* (one weak, two strong) as shown in Figure 1a,b for the Fe system. Although it is somewhat puzzling that the expected number of bands is not found for the trinuclear complexes, it is possible that relatively small distortions in the coordination environment of Mo could alter the number, positions, and/or relative intensities of the predicted A$_1$ bands in a general C_{2v} *cis*-Mo(CO)$_4$L$_2$ system.[37] Thus, in the absence of structural data, the infrared spectra unfortunately are not conclusive in defining the actual molecular arrangement of $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$ by confirming the presence of discrete Mo(CO)$_4$ units in the cluster. It should be noted, however, that these complexes do contain eight carbonyl ligands
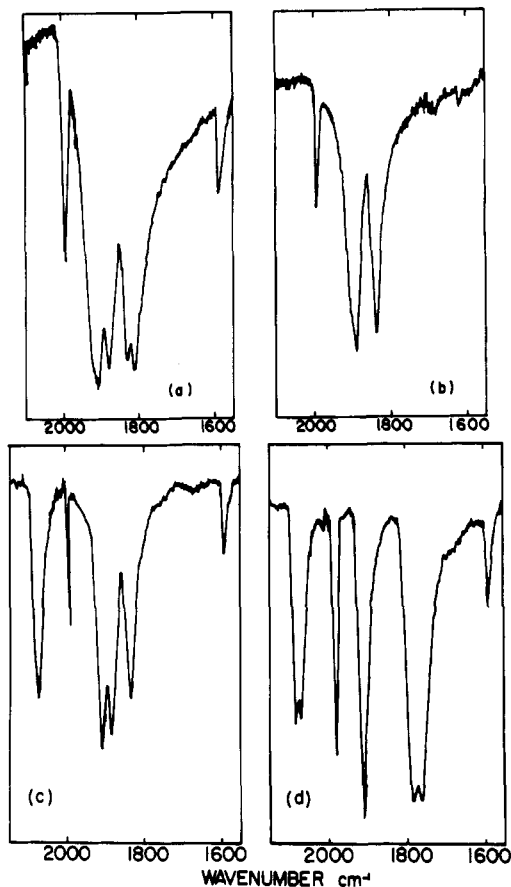
(37) Braterman, P. S. In *Metal Carbonyl Spectra*; Academic: London, 1975; p 255. We thank one of the reviewers for suggesting the use of this reference.

Figure 1. Infrared spectra as KBr pellets: (a) $[NEt_4]_2[Fe(SPh)_4\{Mo(CO)_4\}_2]$; (b) $[NEt_4]_2[Fe(SBz)_4\{Mo(CO)_4\}_2]$; (c) $[NEt_4]_2[Fe(SPh)_4(CyNC)_2\{Mo(CO)_4\}_2]$; (d) $[NEt_4]_2[Co(SPh)_4(CyNC)_2\{Mo(CO)_4\}_2]$.

(as evidenced by the amount of CO evolved on oxidative decomposition) and that their reactivity and redox behavior (vide infra) is consistent with a symmetrical disposition of the CO moieties. Precedent for the spectral difference between SPh and SBz species is found[3] in the $[Mo(CO)_4(SR)_2]^{2-}$ system, where it was conditionally attributed to the presence of different conformational isomers[30] for the two thiolates. A solid-state structural difference between the SBz and SPh compounds might also be indicated by the markedly lower solubility of the SBz derivative in MeCN.

The electronic spectra of the yellow iron trinuclear species are unremarkable, containing only a band at about 430 nm for both SPh and SBz species. The purplish brown cobalt complexes give rise to bands at higher wavelengths, and again the electronic spectra are similar for both thiolates, providing additional evidence that the Bz derivatives, in light of their less than acceptable carbon analyses and somewhat different IR spectra, are indeed correctly formulated.

The cobalt mononuclear starting materials, $[Co(SR)_4]^{2-}$, are EPR active at 10 K, exhibiting broad resonances in the $g = 4$ and $g = 2$ regions (Figure 2). These spectra are consistent with the presence of three unpaired electrons, the not unexpected $S = {}^3/_2$ state for d^7 Co(II) in a tetrahedral environment. The new trinuclear species $[Co(SR)_4\{Mo(CO)_4\}_2]^{2-}$, in which the thiolates are postulated to chelate two Mo(CO)$_4$ fragments, show similar (but not identical) $S = {}^3/_2$ type spectra as presented in Figure 2 for the SPh derivatives. (The spectra of the SBz species were not investigated.) The similarity of the spectra indicates that the overall magnetic properties of the central metal have been only slightly perturbed by formation of the trinuclear complex. Double integration of the signals gives a value of 1.0 ± 0.1 spin/CO in both the mono- and trinuclear systems, providing additional evidence that the benzyl derivative is pure.

Thus, the available analytical and spectroscopic data are consistent with the structure I for these trinuclear species, a formu-

I
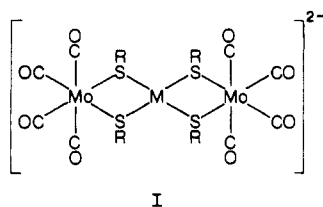
lation in which each octahedral Mo(0) is characterized by the expected 18 electrons with no metal–metal bonding to the tetrahedral central metal.

Reactivity of Trinuclear Compounds. The addition of a pair of two-electron-donating "organometallic" ligands such as PR_3, RNC, or CO to the central iron in $[Fe(SR)_4\{Mo(CO)_4\}_2]^{2-}$ would result in an 18-electron configuration for that metal, and therefore, we anticipated the possibility of this general type of reactivity. Indeed, the reaction of the Fe–SPh trinuclear species[38] with cyclohexyl and *tert*-butyl isocyanates at low temperature in MeCN results in the precipitation of solid products whose elemental analytical data are consistent with the addition of two RNC ligands to the cluster (eq 6). As shown in Figure 1c, the IR

$$[Fe(SPh)_4\{Mo(CO)_4\}_2]^{2-} + 2R'NC \rightarrow$$
$$[Fe(SPh)_4(R'NC)_2\{Mo(CO)_4\}_2]^{2-} \quad (6)$$
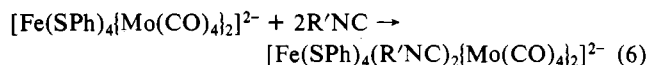
spectra of the products contain bands in the 2100–2200-cm^{-1} region characteristic[39] of coordinated isocyanides, and in the carbonyl region they show a four-band pattern which is significantly different from that exhibited by the starting material but is similar to that which is typical of *cis*-$Mo(CO)_4$ fragments as described above and thus consistent with the symmetric postulated structure II where the central Fe has undergone a change from tetrahedral to octahedral on addition of RNC.

II
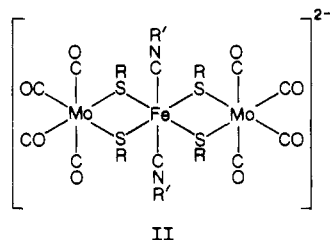
Reaction of the trinuclear Co–SPh species with isocyanides (which would result in a 19-electron cobalt center) gave a very low yield of a product whose analytical data was consistent with the formulation $[Co(SPh)_4(R'NC)_2\{Mo(CO_4\}_2]^{2-}$ but had a markedly different IR spectrum (Figure 1d) from the iron system (Figure 1c), the only instance in which a cobalt compound appeared to be structurally distinct from its iron counterpart. Possible explanations for this difference include rearrangement of the above postulated structure (II) to yield a species with Co–CO and Mo–CNR groups and/or formation of the isomer having cis isocyanides at Co. In any event, the reactivity of the Co complexes with RNC is somewhat more complicated than anticipated, and without an X-ray diffraction study, a completely definitive assignment of the nature of these species seems unlikely.

The reaction of $[Fe(SPh)_4\{Mo(CO)_4\}_2]^{2-}$ with CO in MeCN resulted in a color change from yellow to deep red. However, at least two products appeared to be formed in the reaction, as evidenced by the fact that extraction of the evaporated reaction mixture with $CHCl_3$ yielded a soluble fraction and a residue. The insoluble product was not further characterized, but the solid isolated from the extract had an infrared spectrum containing both $[NEt_4]^+$ and M–CO bands and analyzed consistently and closely for the formulation $[NEt_4][(CO)_4Mo(SPh)_2Fe(CO)_3]$. However, the CO released from this compound on oxidation was not in-
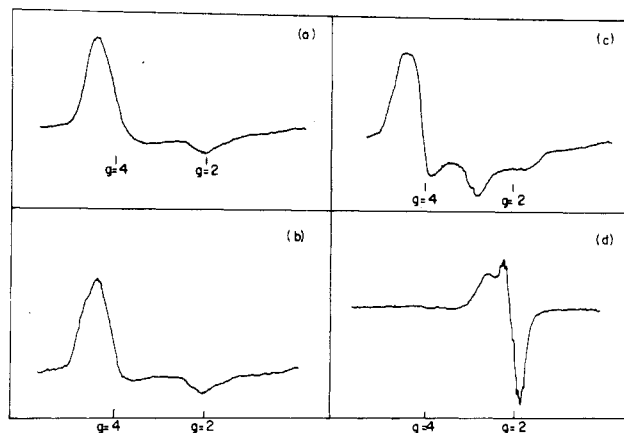
Figure 2. EPR spectra of cobalt complexes at 9 K and 9.24 gHz: (a) $[Co(SPh)_4]^{2-}$ (4.6 mM in MeCN); (b) $[Co(SPh)_4\{Mo(CO)_4\}_2]^{2-}$ (3.59 mM in MeCN); (c) $[(CO)_4Mo(SPh)_2Co(bpy)_2)]$ (3.34 mM in CH_2Cl_2); (d) $[Co(SPh)_4\{Mo(CO)_4\}_2]$ (4.41 mM in toluene). Microwave power was 0.83 mW for all spectra.

dicative of this formulation, and in addition, a MeCN solution did not exhibit an EPR spectrum at 13 K, a result seemingly inconsistent with a species that must formally contain either Fe(I) or Mo(I). Thus, some doubt exists as to the nature of the product in this system. Reaction of the trinuclear Co–SPh derivative with CO yielded no characterizable product nor did reaction of tertiary phosphines with any of the Fe or Co SPh trinuclear species.[38]

Under the proper conditions, the trinuclear SPh species[38] react cleanly with the bidentate N-donor ligands *o*-phenanthroline (phen) and 2,2′-bipyridyl (bpy) to yield the new dinuclear complexes $[(CO)_4Mo(SPh)_2ML_2]$ (M = Fe, Co; L = phen, bpy). The known[4,5] species $[Mo_2(CO)_8(SPh)_2]^{2-}$ was also identified as a product, suggesting that the reaction proceeds as shown in eq 7.

$$2[M(SPh)_4\{Mo(CO)_4\}_2]^{2-} + 4L \rightarrow$$
$$2[(CO)_4Mo(SPh)_2ML_2] + [Mo_2(CO)_8(SR)_2]^{2-} + 2[SR]^- \quad (7)$$
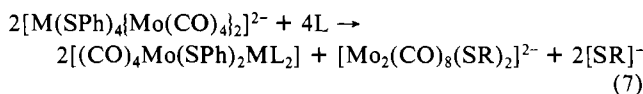
These bidentate ligands have a high affinity for Fe(II), making it necessary to carry out the reaction at low temperature with careful addition of ligand in order to prevent the complete abstraction of iron and the formation of $[FeL_3]^{2+}$. The isolated product $[(CO)_4Mo(SPh)_2ML_2]$ does, in fact, undergo this type of decomposition on dissolution at room temperature. The cobalt analogues are stable in solution at room temperature, allowing them to be more easily prepared by prolonged reaction in CH_2Cl_2 from which the product precipitates. Solids isolated in this way contain varying amounts of CH_2Cl_2 of crystallization as reflected in the analytical data and confirmed by the presence of C–Cl bands in their IR spectra. The products are highly colored, no doubt due to M–L charge transfer, and the cobalt species (which formally contain Co(II)) exhibit a strong $S = {}^3/_2$ EPR signal (Figure 2), which shows one spin/Co on double integration.

Electrochemistry and Redox Reactivity. The most interesting aspect (and perhaps the most predictable based on recent results (vide infra)) of the reactivity of the trinuclear species lies in their chemical oxidation. The ability of a number of low-valent dinuclear species, such as $[M_2(CO)_8(SR)_2]^{2-}$ (M = Mo, W),[4-6] $[Fe_2(CO)_6(PR_2)_2]^{2-}$,[40-42] and $[W_2(CO)_8(PR_2)_2]^{2-}$,[43] to undergo a net two-electron oxidation with concomitant metal–metal bond formation in the neutral dinuclear product has been well documented. The presence of the M–M bond in the oxidized species allows each metal to retain an 18-electron configuration and has a dramatic effect on the electrochemical oxidation as described below. It seemed likely to us that a similar redox pattern would

(38) The reactivity of $[M(SBz)_4\{Mo(CO)_4\}_2]^{2-}$ with RNC, bpy, phen, and CO was not investigated.

(39) Nakamoto, K. in *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley-Interscience: New York, 1970; p 186.

(40) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. *Inorg. Chem.* **1982**, *21*, 146.

(41) Shyu, S.-G.; Wojcicki, A. *Organometallics* **1984**, *3*, 809.

(42) Wojcicki, A. *Inorg. Chim. Acta* **1985**, *100*, 125.

(43) Keiter, R. L.; Madigan, M. J. *Organometallics* **1982**, *1*, 409.

be possible for the trinuclear species described above, but in this case each molybdenum would retain its 18-electron configuration not by metal–metal bonding with a like moiety but by metal–metal bonding with the central metal, as shown in eq 8. Under this
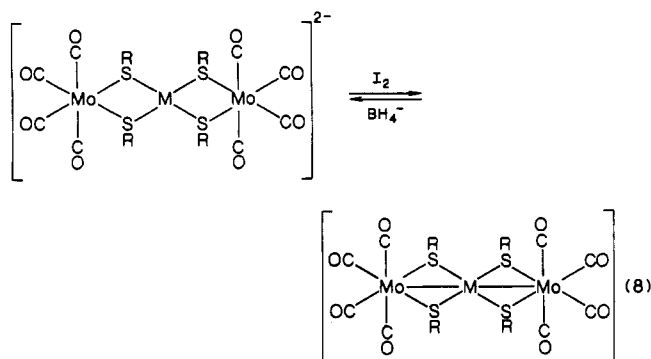
hypothesis, the central metal would be characterized by either 16 electrons (M = Fe) or 17 electrons (M = Co), but as pointed out above, noncompliance with the 18-electron rule is not unusual for systems that are not truly organometallic. Indeed, oxidation of $[M(SPh)_4\{Mo(CO)_4\}_2]^{2-}$ (M = Fe, Co) with iodine in toluene, conditions similar to those used in the $[M_2(CO)_8(SR)_2]^{2-}$ (M = Mo, W) system,[4–6] gave a solid product with elemental analytical and spectroscopic data consistent with the predicted formulation $[M(SPh)_4\{Mo(CO)_4\}_2]$ (M = Fe, Co), which may be viewed as comprising two Mo(I) moieties and a Fe(II) or Co(II) moiety. Particularly diagnostic in the characterization of the oxidation products are their IR spectra, which show a pattern very similar in appearance and energy to that exhibited[4–6,36] by the dinuclear complexes $[Mo_2(CO)_8(SR)_2]$, which also contain octahedral Mo(I) tetracarbonyl fragments. To further verify that the compound obtained from the iodine reaction was in fact simply the two-electron-oxidized form, the reverse process was carried out with the Fe species. With $[NEt_4][BH_4]$ in MeCN used as the reductant, the dianionic form was indeed obtained in fair yield.

The EPR spectrum of the oxidized trinuclear cobalt complex (Figure 2d) is characterized by a strong resonance at ca. g = 2.1, indicative of a net single unpaired electron in the postulated metal–metal-bonded system. The $S = \frac{1}{2}$ signal, which is also characterized by ^{59}Co hyperfine structure, can be assigned to low-spin Co(II), the change from high spin in $[Co(SPh)_4\{Mo(CO)_4\}_2]^{2-}$ being consistent with somewhat different geometry on metal–metal bond formation. We have only carried out chemical oxidations and isolated products for the SPh complexes, but the electrochemical data described below indicate that similar reactivity would also be observed for the SBz species of Fe and Co.

Precedent for this kind of metal–metal bonded structure is found in the previously reported[27] complexes $[Ni(SMe)_4\{(C_5H_5)_2M\}_2]^{2+}$ (M = Mo, Nb). For M = Nb, a short Nb–Ni distance of 2.78 Å was observed, while for M = Mo a longer, nonbonding intermetallic distance of 3.39 Å was present.[27c] For the former compound, the group V (group 5[47]) Nb moieties require the metal–metal bond to obtain 18 electrons, whereas replacing Nb with group VI (group 6[47]) Mo eliminates the need for this behavior. The two-electron oxidation reported in this paper is formally analogous to the replacement of Mo by Nb.

Cyclic voltammograms of $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$ (M = Fe, Co; R = Ph, Bz) in MeCN or DMF at ca. –45 °C are shown in Figure 3. In general, better resolved, significantly cleaner voltammograms were obtained at low temperature than under ambient conditions, possibly due to some decomposition of the complexes in the presence of the supporting electrolyte (0.1 M $[NBu_4][BF_4]$) at the higher temperature. The trinuclear species all undergo oxidation at ca. 0 V with oxidative current parameters (Table I) that are indicative of a *two-electron*-redox event at essentially the same potential. The Fe–SPh species has the lowest relative current parameter as compared with the standard one-electron-transfer values for $[Mo(S_2C_4N_2)_4]^{3-}$[44] (Table I), which
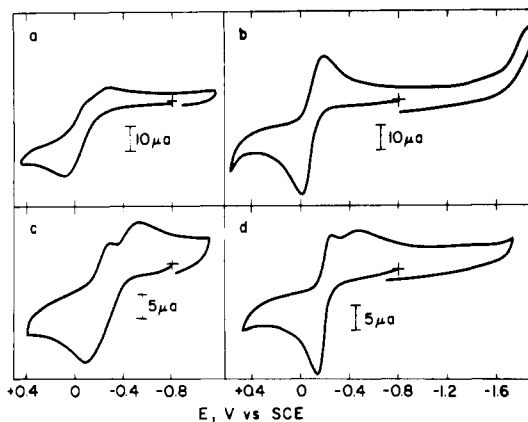

Figure 3. Cyclic voltammograms of $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$: (a) M = Fe and R = Ph in MeCN (1.62 mM) at –40 °C; (b) M = Co and R = Ph in DMF (1.87 mM) at –40 °C; (c) M = Fe and R = Bz in MeCN (1.77 mM) at –37 °C; (d) M = Co and R = Bz in DMF (1.87 mM) at –50 °C. Voltages are relative to SCE. Scan rate was 100 mV/s.

Table I. Cyclic Voltammetric Data for the Complexes $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$ (M = Fe, Co; R = Ph, Bz)

complex	T, °C	E_{pa}, V	E_{pc}, V	$i/v^{1/2}AC$,[c,d] A cm s$^{1/2}$ V$^{-1/2}$ mol^{-1}
M = Fe; R = Ph[a]	–40	0.10	–0.10, –0.27	708 (390)
M = Co; R = Ph[a]	–40	0.00	–0.20	939 (390)
M = Fe; R = Bz[b]	–37	–0.14	–0.27, –0.45	429 (247)
M = Co; R = Bz[b]	–50	–0.13	–0.25, –0.48	430 (210)

[a] In MeCN. [b] In DMF. [c] Current parameter where i = A, V = V/s, A = cm^2, and C = mM. Scan rate was 100 mV/s. [d] Values in parentheses represent $i/v^{1/2}AC$ for the one-electron reduction of $[Mo(i-mnt)_4]^{3-}$ at the indicated temperature.

were determined at each temperature in both MeCN and DMF. As seen in Figure 3, the oxidation wave for this compound is significantly broader than those for the other three species, and therefore the lower value is not unexpected. It is, however, much higher than would be expected for a single-electron oxidation.

The redox events for the four species show varying degrees of pseudoreversibility and/or complexity in the reverse reduction scan. Thus, the Co–SPh complex exhibits a single wave with an i_{pc}/i_{pa} value of 0.85, while the Fe–SPh species shows only a small reverse wave corresponding to its oxidation at +0.10 V but exhibits an additional reduction wave at –0.28 V. The voltammograms of the Fe–SBz and Co–SBz complexes are intermediate between these extremes, characterized both by reduction events corresponding to the primary oxidations at –0.14 V and by additional reduction waves at ca. –0.44 V. This behavior is very similar to that found[4–6] in the cyclic voltammetry of the dinuclear complexes $[M_2(CO)_8(SR)_2]^{2-}$ (M = Mo, W) where the additional reduction waves at more negative potentials were conclusively assigned to species characterized by varying degrees of carbonyl substitution by solvent, e.g., $[M_2(CO)_6(MeCN)_2(SR)_2]$. We therefore tentatively attribute the complex nature of the voltammetry of $[M(SR)_4\{Mo(CO)_4\}_2]^{2-}$ to a similar solvolysis reaction. As for the dinuclear system,[5] the oxidation of the SPh trinuclear complexes occurs at slightly more positive potential than that for their SBz analogues, probably reflecting the greater electron-donating ability of the latter thiolate. In any event, the most important feature of the cyclic voltammetric studies is that all four species undergo a *two-electron oxidation at the same potential*, a relatively rare phenomenon overall but behavior that, as described below, has become more widely recognized for polynuclear species where metal–metal bond formation is possible. It should also be noted that the electrochemical behavior of these compounds is entirely

(44) Smith, D. A.; McDonald, J. W.; Finklea, H. O.; Ott, V. R.; Schultz, F. A. *Inorg. Chem.* **1982**, *21*, 3825.

consistent with their chemical oxidation as described above.

Reversible transfer of two electrons at the same potential has been reported recently for a number of inorganic and organometallic species.[45] However, particularly relevant to the work described herein is the study by Collman and co-workers of the [Fe$_2$(CO)$_6$(PR$_2$)$_2$]$^{2-/0}$ system,[40] where this phenomenon was rationalized in terms of the formation/cleavage of the Fe–Fe bond in the oxidized species. They also pointed out that simultaneous two-electron-redox behavior requires that the addition or removal of the second electron be more thermodynamically favorable than that for the first and hypothesized that structural rearrangement, i.e. metal–metal bond formation, allowed this energetic reversal in their system. Subsequently, Wojcicki[42] has reviewed the reactivity of several other dinuclear phosphido-bridged species with metal–metal bonding that undergo net two-electron behavior, although the lack of electrochemical data in many of the systems leaves some doubt as to whether the oxidation/reduction is truly simultaneous. Geiger[46] has reviewed and summarized the effect of structural changes (including metal–metal bond formation) on electrode reactions. Our recent studies[4–6] of the electrochemistry

and chemistry of the Mo and W thiolate-bridged species [M$_2$-(CO)$_8$(SR)$_2$]$^{2-/0}$ have confirmed the generality of simultaneous two-electron transfer for *dinuclear* complexes where metal–metal bonding is present in one form of the couple. The electrochemical data presented herein for the symmetric complexes [M(SR)$_4$-{Mo(CO)$_4$}$_2$]$^{2-}$ are seemingly the first indication that this behavior can also occur in a *trinuclear* organometallic species, with the overall thermodynamics apparently governed by the formation of *two heterometallic* metal–metal bonds rather than one homometallic metal–metal bond. X-ray diffraction and/or EXAFS studies of these trinuclear complexes would substantiate this hypothesis.

Summary and Conclusions. The new trinuclear heterometallic carbonyl complexes [M(SR)$_4${Mo(CO)$_4$}$_2$]$^{2-}$ (M = Fe, Co; R = Ph, Bz) have been prepared by a variety of related methods, including simply refluxing a mixture of Mo(CO)$_6$, an Fe salt, and [NEt$_4$][SR] in MeCN. This formulation apparently has a high degree of thermodynamic stability and is likely to be produced in many systems involving synthesis of low-valent Fe–Mo–SR species. The complexes react with mono- and bidentate nucleophiles to form species resulting from attack at the central metal. The trinuclear species, formally containing a Mo(0)–Fe(II)–Mo(0) core, can be chemically oxidized by two electrons to the neutral [M(SR)$_4${Mo(CO)$_4$}$_2$], which in turn can be formally classified as Mo(I)–Fe(II)–Mo(I). Electrochemical studies of this oxidation show that these two electrons are *removed at the same potential*, a rare phenomenon in heterometallic complexes that we attribute to a structural change induced by the formation of a pair of Fe–Mo bonds in the product.

(45) (a) Fenton, D. W.; Schroeder, R. R.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 1931. (b) Fenton, D. E.; Lintvedt, R. L. *Ibid.* **1978**, *100*, 6367. (c) Lintvedt, R. L.; Kramer, L. S. *Inorg. Chem.* **1983**, *22*, 796. (d) Mandal, S. K.; Nag, K. *Ibid.* **1983**, *22*, 2567. (e) Louis, R.; Angus, Y.; Weiss, R.; Gisselbrecht, J. P.; Gross, M. *Nouv. J. Chim.* **1981**, *5*, 71. (f) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 6761. (g) Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2605. (h) Moraczewski, J.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7429. (i) Finke, R. G.; Voegeli, R. H.; Laganis, E. D.; Boekelheide, V. *Organometallics* **1983**, *2*, 347.
(46) Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275.
(47) 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 and 18. (Note that the former Raman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Electron Diffusion in Wet and Dry Prussian Blue Films on Interdigitated Array Electrodes

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The rate of electron transport has been measured in films of ferric ferrocyanide (Prussian blue, Fe(III/II)) coated on interdigitated array electrodes. By control of the electrode potentials, the films can be (1) partially reduced to the Fe(III/II)–Fe(II/II) mixed-valent state, (2) partially oxidized to the Fe(III/II)–Fe(III/III) mixed-valent state, and (3) disproportionated in the absence of solvent to contain both mixed-valent states, arranged spatially in series between the electrodes. Results show that the rate of electron transport, measured as the electron diffusion coefficient, D_e, in Fe(III/II)–Fe(II/II) mixed-valent films is surprisingly insensitive to which alkali-metal counterion is employed in the contacting electrolyte solution. The microscopic (local) lattice mobility of the counterion must exceed the electron mobility associated with self-exchange between Fe(III/II) and Fe(II/II) sites. In KNO$_3$ electrolyte, it is also shown that there are two electrochemically distinct Fe(III/II)–Fe(II/II) couples, which differ by about a factor of 10 in their electron-transport rates. The electron diffusion rate in Fe(III/II)–Fe(III/III) mixed-valent films yields an estimate for the electron self-exchange rate constant for ferricyanide and ferrocyanide lattice sites in Prussian blue, 1.3 × 10^6 M^{-1} s^{-1}, that is about 10 times larger than any known k_{ex} rate constant for the analogous homogeneous solution reaction. When exposed only to a bathing gas, Prussian blue films exhibit steady-state, solid-state voltammograms at potentials that can drive disproportionation of the Fe(III/II) material by oxidizing and reducing it at opposing electrode/film interfaces. The solid-state currents are critically dependent on the presence of water vapor in the bathing gas and vanish in dry N$_2$. Removal of the interstitial water in Prussian blue apparently lowers the local counterion mobility so severely as to become limiting upon the electron mobility.

The observation[1a] of electrochemical reactivity of thin-film coatings of the mixed-valent compound ferric ferrocyanide (Prussian blue) on electrodes has sparked a number of recent investigations.[1–4] Appealing features of these films include their