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Catalytic Carbon Monoxide Hydrogenation with $Os_3(CO)_{12}$ and Boron Tribromide

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The catalytic hydrogenation of carbon monoxide with $Os_3(CO)_{12}$ as a catalyst precursor and boron tribromide as a solvent, catalyst promoter, and ultimate reactant is described. Reaction conditions were relatively mild: 180 °C and ~2 atm. The hydrogenation products were unique and included methane, ethane, propane, isobutane, neopentane, methyl bromide, ethyl bromide, propyl bromides, and butyl bromides. The major products were methyl and ethyl bromides. During the course of the catalytic reaction $Os_3(CO)_{12}$ was converted to $Os_2(CO)_6Br_4$. The latter was shown to function as a catalyst precursor to produce a similar range of hydrocarbon and alkyl bromide products. Substitution of BCl_3 for BBr_3 gave an analogous reaction system. Conversion of $Os_3(CO)_{12}$ to $Os_3(CO)_{10}Cl_2$ and $Os_2(CO)_6Cl_4$ was established for the CO hydrogenation system. The BCl_3 reaction system was, however, sharply differentiated from the BBr_3 system in that only hydrocarbons were produced; no alkyl chloride products were detected.

Introduction

Reports on apparent homogeneous systems for the catalytic hydrogenation of carbon monoxide first appeared in the patent literature, in 1950[1] and 1974.[2] Since 1974, the scientific literature relating to this subject has substantially increased.[3-14] In our own studies we had found that the activity of coordination catalysts could be dramatically increased by the presence of a strong Lewis acid like $AlCl_3$.[3,4] The role of the Lewis acid has not been fully defined, but an important factor has been presumed[3,4] to be an M_x–CO–A interaction[15] with A as the Lewis acid. We describe here the characteristics of an apparently homogeneous catalytic system for carbon monoxide hydrogenation based on $Os_3(CO)_{12}$ as a catalyst precursor and a boron trihalide as the solvent, the Lewis acid, and a reactant.

Experimental Section

Materials. $Os_3(CO)_{12}$, prepared according to established literature[16] procedures or purchased from Strem Chemicals, Inc. was used without further purification. BBr_3 (Alfa Division, Ventron Corp.) was purified by treatment with mercury until all red hue had dissipated and was then vacuum transferred into a Teflon-valved flask as a clear colorless liquid which was stored under vacuum. Ethyl bromide, reagent grade, was purchased from Matheson, Coleman and Bell. Boron trichloride (99.9% min.), methyl chloride (99.5%), methyl bromide (99.5%), and the hydrogen–carbon monoxide mixture were purchased from Matheson Gas Products; the composition of the mixture was approximately 75% H_2 and 25% CO. Deuterium (99.5%) was purchased from Matheson Gas Products.

General Procedure for Catalytic Hydrogenation. A 40-mL Carius tube containing 20 mg of $Os_3(CO)_{12}$ was attached to a high-vacuum line, and 3 mL of BBr_3 or BCl_3 was condensed into the tube. After the H_2–CO gas mixture was introduced into the tube to 1 atm. at liquid-nitrogen temperature, the tube was sealed and was placed in an explosion-proof oven at 180 or 130 °C. After the reaction, the tube was attached to a high-vacuum line, and the seal was broken. The gaseous products were separated from the solvent by moving the gases through a −40 °C trap prior to collection by using a Toepler pump. Nonvolatile products were isolated from the reaction tube after all of the solvent had been removed.

Analytical Procedure. Hydrocarbon gases were analyzed on a gas chromatograph equipped with a flame ionization detector by using a 6 ft × $^1/_8$ in. Porapak Q column at 150 and 70 °C. H_2, CO, and CH_4 were analyzed on a gas chromatograph equipped with a thermal conduction detector by using a 6 ft × $^1/_8$ in. Molecular Sieve 5A column at ambient temperatures. A Finnigan mass spectrometer/gas chromatograph, using the aforementioned columns and conditions, was employed for the final verification of all of the products. Mass spectral characterization of $Os_2(CO)_6Br_4$, $Os_2(CO)_6Cl_4$ and $Os_3(CO)_{10}Cl_2$ were obtained with an AEI MS 12 (electron impact at 50 eV).

Reaction of Methyl Bromide with $Os_3(CO)_{12}$ and BBr_3. A 40-mL Carius tube was charged with 40 mg of $Os_3(CO)_{12}$, 3 mL of BBr_3, and ~1 mL of CH_3Br. The tube was sealed and was heated to 180 °C. Analytical procedures were those described for CO hydrogenation reactions.

Reaction of Ethyl Bromide with $Os_3(CO)_{12}$ and BBr_3. A procedure similar to the one described for the methyl bromide reaction was followed. In the reaction systems which included hydrogen, 700 torr at −196 °C of H_2 or D_2 was introduced prior to sealing the tube. Analytical procedures followed were those described for CO hydrogenation reactions.

Isolation and Characterization of $Os_2(CO)_6Br_4$. A 40-mL sealed tube which contained $Os_3(CO)_{12}$ (231 mg, 0.25 mmol), 4 mL of BBr_3, and 630 torr (at −196 °C) of a 3:1 H_2:CO gas mixture was heated at 150 °C for 1 h, at which time the reaction mixture became clear and colorless. Crystalline white solids (334 mg, 0.38 mmol, 99% on the basis of osmium) precipitated on cooling. $Os_2(CO)_6Br_4$ was purified by sublimation at 190 °C with approximately 20% loss. Alternatively, $Os_2(CO)_6Br_4$ was purified by treatment with 100 mL of a 1:1 mixture of H_2O and CH_2Cl_2 and was recrystallized from the CH_2Cl_2 portion. This preparation, when effected in the absence of CO and H_2, was much less clean and yields were generally lower. Anal. Calcd for $C_3Br_2O_3Os$: C, 8.3; Br, 36.8; Os, 43.8. Found: C, 8.5; Br, 36.4; Os, 41.1. Mass spectrometric data are as follows (electron impact at 50 eV). Calculated for $Os_2(CO)_6Br$: envelope of appropriate masses for the isotopes of osmium (^{188}Os, ^{189}Os, ^{190}Os, ^{192}Os) and bromine (^{79}Br, ^{81}Br) centered around 868. Found: envelope of appropriate masses centered around 868 for $Os_2(CO)_6Br_4$ and masses corresponding to successive losses of six carbon monoxide molecules and two bromine atoms. A detailed compilation of exact masses is

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Table I. Products[a] from Catalytic Hydrogenation of CO with $Os_3(CO)_{12}$ or $Os_2(CO)_6Br_4$ and Boron Tribromide at 180 °C

hydrocarbon products	$Os_3(CO)_{12}$			$Os_2(CO)_6Br_4$	
	2 h	100 h	100 h[b]	2 h	100 h
CH_4	29	75	45	20	68
C_2H_4	<1	0	0	<1	0
C_2H_6	4	10	29	2	0
C_3H_8	2	3	7	<1	2
i-C_4H_{10}	1	<1	0	1	0
neo-C_5H_{12}	0	<1	0	0	0
CH_3Br	51	10	13	69	13
C_2H_5Br	13	1	6	8	5

[a] Given in molar percentages. The values can be converted to moles of hydrocarbon per mole of catalyst precursor per unit time (h) by simply multiplying by the turnover rate. [b] This reaction was run with an H_2–CO mixture of 2:1 molar ratio (all others were with a 3:1 ratio).

Table II. Products[a] from Reaction of Various Substrates with $Os_3(CO)_{12}$ and Boron Tribromide at 180 °C

hydrocarbon products	CH_3Br[b]	C_2H_5Br[c]	C_2H_5Br + H_2[d]	H_2[e]
CH_4	84	2	19	33
C_2H_4	0	34	0	1
C_2H_6	3	44	63	4
C_3H_8	13	0	3	<1
C_4, C_5	0	0	0	1
CH_3Br	excess	20	15	50
C_2H_5Br	<1	excess	excess	8

[a] Given in molar percentages. The values can be converted to moles of hydrocarbon per mole of catalyst precursor per unit time (h) by simply multiplying by the turnover rate. [b] Reaction time of 50 h. Beyond these times decomposition was extensive. [c] Reaction time of 16 h. Beyond these times decomposition was extensive. [d] Reaction time of 100 h. [e] Reaction time of 1 h.

available as supplementary material. IR (CH_2Cl_2): ν(CO) 2125, 2052 cm^{-1}. White $Os_2(CO)_6Br_4$ melted reversibly at 315 °C, but on further heating to 345 °C, the dimer was converted quantitatively to yellow oligomeric $[Os(CO)_2Br_2]_x$.

Preparation of $Os(CO)_3Br_2(NCCH_3)$. $Os_2(CO)_6Br_4$ (120 mg, 0.14 mmol) was heated in acetonitrile to 80 °C for 15 min. Upon cooling, white crystals of the acetonitrile adduct (120 mg, 0.25 mmol, 91% on the basis of osmium) precipitated. Anal. Calcd for $C_5H_3Br_2NO_3Os$: C, 12.6; H, 0.6; Br, 33.6; N, 2.9; O, 10.1; Os, 40.0. Found: C, 12.8; H, 1.1; Br, 33.1; N, 2.9; O, 10.5; Os, 39.3 (mp 175 °C dec). ^1H NMR (C_6D_6): δ 2.47. IR (CH_2Cl_2): ν(CO) 2123, 2053, 2030 cm^{-1}.

Isolation and Characterization of $Os_3(CO)_{10}Cl_2$ and $Os_2(CO)_6Cl_4$. The reaction of $Os_3(CO)_{12}$ (606 mg, 0.68 mmol) and BCl_3 (5 mL) in the presence of H_2 and CO at 130 °C produced, after 20 h, a mixture of yellow and colorless crystals. After all readily volatile materials were removed by evacuation, the remaining solids were washed with water and then extracted with pentane. Vacuum removal of pentane from the extract yielded yellow microcrystals of $Os_3(CO)_{10}Cl_2$[17] (56 mg, 0.06 mmol, 9% yield on the basis of osmium), characterization by infrared spectroscopic and by mass spectrometric analysis (P^+ and ions resulting from successive losses of 10 carbon monoxides and two chlorines; see supplementary material). The colorless residue which remained after pentane extraction was washed with cold CH_2Cl_2. Isolated colorless crystals of $Os_2(CO)_6Cl_4$[18] (468 mg, 0.68 mmol, 68% on the basis of osmium) were characterized by infrared spectroscopy, mass spectral analysis (P^+ and ions resulting from successive losses of six carbon monoxide molecules and two chlorine atoms; see supplementary material), and elemental analysis. Anal. Calcd for $C_3Cl_2O_3Os$: C, 10.4; H, 0.0; Cl, 20.5. Found: C, 10.5; H, 0.1; Cl, 20.4.

Results and Discussion

The reaction of carbon monoxide with hydrogen under mild conditions (2 atm, 180 °C) in the presence of $Os_3(CO)_{12}$ and BBr_3 produced the low molecular weight hydrocarbons methane, ethane, propane, isobutane, and neopentane and the singly halogenated alkanes methyl bromide, ethyl bromide, propyl bromides, and butyl bromides. The major products were methane, ethane, propane, and methyl and ethyl bromide as shown in Table I. Completely deuterated alkanes and alkyl bromides were produced from a D_2–CO reaction mixture. Similarly, ^{13}C-containing alkanes and alkyl bromides were obtained from a H_2–^{13}CO reaction mixture.[19] The production of HBr (or DBr in the D_2–CO reaction system) was verified by GC mass spectrometric analysis.

Turnover rates for the carbon monoxide hydrogenation reaction was about 20/h on the basis of 1 g-atom of carbon in the hydrocarbon products/mol of $Os_3(CO)_{12}$ *for the first hour*. These rates dropped by 1 order of magnitude after the first hour of reaction wherein the trimeric osmium carbonyl was converted to a less active catalyst precursor, namely, $Os_2(CO)_6Br_4$. This dimeric bromide was recovered in nearly quantitative yield after reaction times of 1 h or several days. Clearly, these solution studies establish that the majority, if not all, of the $Os_3(CO)_{12}$ was rapidly converted to $Os_2(CO)_6Br_4$. Separate experiments with pure $Os_2(CO)_6Br_4$ as the catalyst precursor showed that the CO conversion to hydrocarbon proceeded at rates comparable to that for the $Os_3(CO)_{12}$ initiated reactions at reaction times beyond the first hour where high rates were observed and in the time period where rates stabilized at lower levels. On these bases, it would be reasonable to presume that $Os_2(CO)_6Br_4$ is the enduring catalyst precursor. A stricter test of this hypothesis would be in the comparison of the product distributions. In fact, as shown in Table I, the molar ratios of hydrocarbons and alkyl bromides were very similar for the bromide dimer and the carbonyl cluster initiated reactions.

Reaction time did substantially affect product distribution in the catalytic reaction.[20] At long reaction times, the concentrations of alkyl bromides decreased and those of methane and ethane increased markedly. Separate experiments established the reactivity of the alkyl bromides toward the reaction system. For example, as illustrated in Table II, substitution of ethyl bromide for carbon monoxide in the catalytic reaction system led to the conversion of the alkyl bromide to methane, ethane, propane, and methyl bromide with ethane as the major product. Thus the reactivity toward the reaction system of the initially produced alkyl bromides is *one* factor which may account for the product distribution dependence on reaction time.

When ethyl bromide was introduced into the BBr_3 solution of $Os_3(CO)_{12}$, a relatively rapid reaction ensued which resulted in the formation of significant amounts of ethylene and ethane, as well as methyl bromide (see Table II). With the addition of H_2 to this system, the concentration of ethylene fell to unobservable levels, and with the addition of D_2 to this system, a significant amount of deuterium was incorporated into the recovered ethyl bromide. These results suggest that the ethyl bromide (and other primary products) and the osmium carbonyl catalyst precursors may be in dynamic equilibrium with several organometallic intermediates such as alkyl and olefin complexes.

A noteworthy finding is that whereas predominantly methane was produced from metal carbonyl clusters in the absence of a Lewis acid,[5,21] there was a preponderance of

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(19) The catalyst precursor $Os_3(^{12}CO)_{12}$ was converted to $Os_2(CO)_6Br_4$ which comprised molecules with all possible combinations of ^{12}CO and ^{13}CO.

(20) There was another factor that affected product distribution, namely, the $CO{:}H_2$ ratio. With an increase in the CO concentration from 25 to 33%, there was a shift in the hydrocarbon products toward a higher molecular weight distribution as shown in Table I; methane concentration decreased substantially vis-à-vis those of ethane and propane.

Table III. Products[a] from the Catalytic Hydrogenation of CO with $Os_3(CO)_{12}$ and BX_3 at 130 °C

hydrocarbon products	BCl_3	BBr_3
CH_4	98	73
C_2H_6	2	7
C_3H_8	<1	0
CH_3X	0 (X = Cl)	16 (X = Br)
C_2H_5X	0 (X = Cl)	3 (X = Br)

[a] Given in molar percentages; reaction time for both systems was 20 h.

products which contained carbon–carbon bonds when the reduction was effected in the presence of Lewis acids, specifically, BBr_3, BCl_3, $AlCl_3$, or $AlBr_3$.[4,22]

Generation of alkyl halides from the catalytic hydrogenation of carbon monoxide is unique to this boron tribromide based system. The ostensibly analogous boron trichloride system discussed below produced only methane and ethane under the conditions that the boron tribromide system yielded both methyl and ethyl bromide as significant products (Table III).[22b] Also, no alkyl halides were detected as products in a similar reaction system based on metal carbonyls and aluminum chloride or bromide ($NaX–AlX_3$ melts[3,4]). In fact, experiments with the aluminum-based system unambiguously established that a methyl halide was not a primary product that was later converted by the reaction system to hydrocarbons. We suggest that the formation of alkyl halides in the boron tribromide system may result from alkyl halide reductive elimination from an $R(X)Os_x$ species; such a reductive elimination step is established for methyl derivatives of transition-metal halides.[23]

This catalytic reaction system could not be examined with boron trifluoride because of the low critical temperature of the fluoride but was examined with boron trichloride although to maintain a liquid phase at modest pressures (glass reaction vessels) with the chloride necessitated dropping the reaction temperature to 130 °C. Under these conditions, the BCl_3 system produced only methane and ethane with methane as the predominant (98%) product. The BBr_3 system under these same conditions yielded methane (73%) and ethane as well as substantial amounts of methyl (16%) and ethyl (3%) bromides (Table III). Despite the fact that boron tribromide is the better Lewis acid, the hydrogenation rate was about an order of magnitude higher with BCl_3 than with BBr_3. If the sole function of the boron halide were that of a Lewis acid to generate Os–C–O–B interactions, the reverse relation would be expected. One further curious feature of these lower temperature hydrogenation reactions was that, with both boron halides, methane became by far the major hydrogenation product.

The issue of the reactive intermediate(s) at reaction temperature was not resolved. Established initial transformation are as in eq 1. Not established was the fate of the carbonyl

$$Os_3(CO)_{12} \xrightarrow{BX_3} Os_3(CO)_{10}X_2 \xrightarrow{BX_3} Os_2(CO)_6X_4 \quad (1)$$

groups lost in these halogenations or the fate of the boron trihalide.[24] At 150 °C, the boron tribromide solutions of $Os_2(CO)_6Br_4$ were colorless but at 180 °C became very pale yet clear yellow,[25] suggesting that another species was present at the higher reaction temperatures. We still presume that $M_xCO–A$ interactions, with A as a Lewis acid, are critical intermediates in these catalytic CO hydrogenation reactions.[3,6] In addition, the Lewis acid may also interact with possible $M–CH_x$ intermediates, but no corroborative spectroscopic data were obtained.

All observations for this catalytic reaction system were consistent with a solution phase catalytic sequence. No particulate matter was ever detected even at reaction times up to 90 h; however, very small particles would not be detected in filtration or conventional light-scattering experiments. The osmium initially charged as $Os_3(CO)_{12}$ or $Os_2(CO)_6X_4$ was quantitatively recovered as $Os_2(CO)_6X_4$ at the end of the reaction. Osmium metal, generated by thermal decomposition of $Os_3(CO)_{12}$ under vacuum, catalyzed (180 °C) CO hydrogenation with a boron tribromide liquid phase present. However, the rate was low, and, most significantly, the distribution of specific hydrocarbon products was substantially different from that for the osmium carbonyl catalyzed reactions. The metal,[26] as a very fine powder dispersed in the liquid boron tribromide phase, gave a turnover rate that was 1 order of magnitude lower than for the $Os_2(CO)_6Br_4$-based reactions.[27] Methane, ethane, and propane in a 12:6:1 molar ratio were the major products whereas the molar ratio of these from the carbonyl-catalyzed reaction was ~25:3:1. The metal-catalyzed reaction produced a small amount of *n*-butane whereas the only C_4 hydrocarbon product detected in the osmium carbonyl catalyzed reactions was isobutane. Small amounts of methyl and ethyl bromide were produced in the metal-catalyzed reaction presumably by reaction of HBr with metal surface CH_3 and C_2H_5 intermediates. We conclude that the osmium carbonyl catalyzed CO hydrogenation reaction is primarily a solution-phase reaction.

Other metal carbonyls such as $Ir_4(CO)_{12}$ and $Ru_3(CO)_{12}$ showed catalytic activity in this reaction, but because solids formed as the reaction proceeded, it was not established whether the catalytic reaction was a solution-phase or surface-phase reaction. $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, and $Re_2(CO)_{10}$ all showed some activity in the boron tribromide system although the possibility of a noncatalytic pathway for the formation of hydrogenated products could not be precluded due to very low conversions and to decompositions of these zerovalent metal carbonyl complexes.

Acknowledgment. We thank Johnson Matthey, Inc., for the loan of precious metal halides for the synthesis of the metal

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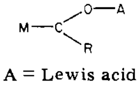
(21) Schunn, R. A.; Demitras, G. C.; Choi, H. W.; Muetterties, E. L., submitted for publication.

(22) (a) The mechanism of the CO hydrogenation reaction is undemonstrated. However, we note in the context of this finding that, if chain elongation were to proceed by CO insertion in an Os–R species, Lewis acids can promote this step through interactions of the type



A = Lewis acid

as shown by: Butts, S. B.; Holt, E. M.; Strauss, S. H.; Alcock, N. W.; Stimson, R. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 5864. (b) Methyl chloride cannot be a primary reaction product in the BCl_3 system. Experiments with H_2 + CH_3Cl reactants in the BCl_3–$Os_3(CO)_{12}$ reaction system demonstrated a conversion of CH_3Cl to hydrocarbons, but the rate was too low to account for the absence of CH_3Cl production in the BCl_3 based system *if* CH_3Cl (or RCl) were a primary reaction product.

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(24) The CO ligands are presumably displaced as free CO. This then requires a reduction of boron halide. A possible initial sequence is $BX_3 \rightarrow (BX_2) \xrightarrow{H_2} (HBX_2)$. However, since $Os_2(CO)_6X_4$ complexes are enduring catalyst precursors, the postulated sequence cannot be the source of an active hydride (for CO hydrogenation) in the $Os_2(CO)_6X_4$ initiated catalytic hydrogenations.

(25) This coloration was reversible; the reaction solution regained its clear, colorless cast below ~160 °C.

(26) The weight of metal charged was identical with the amount of osmium in the $Os_2(CO)_6Br_4$ based reaction.

(27) Were the catalytic reaction observed for the osmium carbonyl based reactions due to trace, nondetectable, very small particles of osmium metal, the reaction with a large quantity of metal powder should have been much more catalytically active than was observed.

carbonyls, the National Science Foundation for a grant in support of this research, and the University of California at Berkeley Mass Spectrometric Facility for mass spectrometric data. We also thank the Miller Institute for Basic Research in Science for a grant in the form of a Miller Professorship (to E.L.M.).

Registry No. H_2, 1333-74-0; CO, 630-08-0; $Os_3(CO)_{12}$, 15696-40-9; BBr_3, 10294-33-4; BCl_3, 10294-34-5; CH_3Br, 74-83-9; C_2H_5Br, 74-96-4; $Os_2(CO)_6Br_4$, 17731-88-3; $Os(CO)_3Br_2(NCCH_3)$, 77590-16-0; $Os_3(CO)_{10}Cl_2$, 28109-18-4; $Os_2(CO)_6Cl_4$, 17633-40-8; CH_4, 74-82-8; C_2H_4, 74-85-1; C_2H_6, 74-84-0; C_3H_8, 74-98-6; *i*-C_4H_{10}, 75-28-5; *neo*-C_5H_{12}, 463-82-1.

Supplementary Material Available: Figures 1–3, the mass spectra of $Os_2(CO)_6Br_4$, $Os_2(CO)_6Cl_4$, and $Os_3(CO)_{10}Cl_2$ (3 pages). Ordering information is given on any current masthead page.

Contribution from the Los Alamos National Laboratory,
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Synthesis, Characterization, and Reactions of Iron–Sulfur Clusters Containing the S_2 Ligand: $[Cp_2Fe_2(S_2)(SR)_2]^{0,1+}$, $[Cp_4Fe_4S_5]^{0,1+,2+}$, and $[Cp_4Fe_4S_6]$

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Syntheses of the following disulfide-containing dinuclear and tetranuclear organoiron compounds are described: $[Cp_2Fe_2(S_2)(SR)_2]^{0,1+}$, $[Cp_4Fe_4S_5]^{0,1+,2+}$, and $[Cp_4Fe_4S_6]$ (Cp = η^5-C_5H_5). The compounds have been characterized by spectroscopic, electrochemical, and chemical properties. Temperature-dependent ^{1}H NMR spectroscopy indicates fluxionality of the triply bridging disulfide ligand in $Cp_4Fe_4S_5{}^n$ (n = 0 and 2+). The cluster products resulting when these disulfide-containing complexes are chemically or electrochemically oxidized, including $[CpFe(SR)(NCMe)]_2{}^{2+}$, and adducts formed with other metals via the electron-rich disulfide ligands are discussed.

Introduction

The extreme versatility of sulfur as a ligand has been well established. A variety of complexes containing elemental sulfur (S, S_2, S_5, etc.) have been reported, and new modes of bonding have recently been characterized.[1] One reason for our interest in such systems is the potential for a rich and extensive redox chemistry and the differences in structure observable for pairs of a redox couple. Structural studies of the members of a reversible redox couple can lead to a better understanding of the bonding of these materials as well as their physical and chemical properties. Previous studies have shown that the structural features observed to vary upon changing the molecular oxidation state of transition-metal clusters usually involve metal–metal interactions.[2] This has been demonstrated, for example, in the case of $[Cp_2Fe_2(SEt)_2(S_2)]$,[3] which possesses an unprecendented planar FeSSFe geometry (Figure 1).[4] There are several features which we have found interesting in this and other disulfide-containing species. Among these are the following: (1) they undergo several electron oxidation state changes without complete structural change; (2) the disulfur ligands are electron rich and have the ability to form donor–acceptor complexes; (3) an understanding of the reactivity of these coordinated ligands could lead to an understanding of the mechanisms of some processes involving metal clusters, such as catalysis.

In part, a motivation behind these studies resides in the considerable interest in new modes of cluster configurations as potential models for the active sites in complex metalloenzymes, nature's catalysts. Obviously, a better understanding of the relationship between the structure of the metal centers in complex biochemical systems and their function could lead to new materials for energy storage, energy transfer, and catalysis . Although we feel it is premature to attempt a direct comparison of the configurations demonstrated by the compounds reported here and specific biochemical species, we feel that disulfur-containing clusters should not be ruled out as being involved in some active sites of metalloenzymes.

We have directed our efforts to the synthesis and characterization of dinuclear and tetranuclear organoiron-containing cluster compounds which feature bridging disulfur (S_2) ligands. Resulting compounds reported here include the dinuclear species $[Cp_2Fe_2(S_2)(SR)_2]^n$ [R = Me (**1a**), Et (**1b**), Bzl (**1c**); n = 0, 1+; Cp = η-C_5H_5] and the tetranuclear species $[Cp_4Fe_4S_5]^n$ (**5**; n = 0, 1+, 2+) and $[Cp_4Fe_4S_6]$ (**6**). Some chemical and electrochemical properties of these compounds are described as well. We also report variable-temperature ^{1}H NMR evidence for fluxionality in the bonding of the triply bridging disulfide ligand in **5** and its corresponding dication $[\mathbf{5}]^{2+}$.

Experimental Section

Materials and Methods. $[CpFe(CO)_2]_2$ was obtained from Strem Chemical Co. or Pressure Chemical Co. and was recrystallized from CH_2Cl_2–hexane under nitrogen before use. $[CpFe(CO)_2]_2$ is nearly black when purified in this manner, and its solutions are slightly air sensitive. Preparations of $[CpFe(CO)(SR)]_2$ were based on the literature methods.[5] Except as noted, all commercially purchased solvents and chemicals were used as received. PF_6^- and SbF_6^- salts were obtained from the Ozark-Mahoning Co.

The reactions described below have been carried out at an altitude of 7100 ft (atmospheric pressure ~590 mmHg) except for those involving Et_2S_x. The boiling points of solvents (hence reflux temperatures) are lower than the values at standard pressure. All reactions and manipulations of solutions were performed in a nitrogen atmosphere, except where noted.

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