Coordination Compounds with Delocalized Ground States. α-Dithiodiketone-Substituted Group VI Metal Carbonyls and Related Compounds

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Abstract: New complexes of α-dithiodiketones of composition $MS_2C_2R_2(CO)_4$ ($M = W$, $R = CH_3$) and $MS_4C_4R_4(CO)_2$ ($M = Mo, W$; $R =$ alkyl, aryl) were obtained by the light-induced reaction of complexes $NiS_4C_4R_4$ with $Mo(CO)_6$ or $W(CO)_6$. In these complexes the coordinated CO may be substituted partly or completely by phosphines and other nucleophiles, producing complexes of the type $MS_4C_4R_4(CO)PR_3$, $MS_4C_4R_4(Ph_2CH_2CH_2PPh_2)$, and $MS_2C_2R_2(CO)_2(PPh_2CH_2CH_2PPh_2)$ of which several representative examples are described. The complexes $MS_4C_4R_4(Ph_2PCH_2CH_2PPh_2)$ may also be prepared directly from $MS_6C_6R_6$ and the chelating phosphine. With sulfide ion the bisdithiodiketone metal dicarbonyls afford binuclear sulfur-bridged complexes of composition $M_2S_2(S_4C_4R_4)_2$ for which a double-prismatic structure is proposed. The analogous reactions with the dithiolato dianions $R'_2C_2S_2^{-2}$ ($R' =$ H or CN) leads to the first asymmetrically substituted prismatic complexes $MS_6C_6R_4R'_2$. The nature of bonding in these complexes is discussed on the basis of their properties, spectra, and simple valence bond and MO considerations. It is shown that they are additional members of a class of unusual compounds with delocalized ground states. It is proposed that metal–dithiolate chelate rings receive significant stabilization by a resonance interaction similar to that in 1,3-dithiolium cations.

The extraordinary properties of many of the neutral transition metal complexes of α-dithiodiketones $M(S_2C_2R_2)_n$ ($n = 2$ or 3) and, in particular, the recently demonstrated aromatic character of $MoS_6C_6H_6$ and related prismatic compounds[2] have prompted us to attempt the preparation of new complexes derived from group VI metal hexacarbonyls in which two or four of the CO groups are substituted by one or two of the bidentate unsaturated sulfur ligands. These compounds would be members of the series $M(CO)_6$, $M(CO)_4S_2C_2R_2$, $M(CO)_2S_4C_4R_4$, $MS_6C_6R_6$ which could provide additional information regarding the nature of bonding in the metal–$S_2C_2R_2$ chelate systems in general. After several unsuccessful attempts we have succeeded in synthesizing various complexes of this type whose properties and reactions will be reported in the present paper.

Preparation, Properties, and Structure of Complexes $M(CO)_{6-2x}(S_2C_2R_2)_x$ ($x = 1, 2$)

The synthesis of the desired compounds was at first unsuccessfully attempted by reaction of $MS_6C_6R_6$ complexes of Cr, Mo, and W with carbon monoxide under various conditions of temperature and pressure. However, apart from ill-defined decomposition products only unreacted starting material could be recovered. Similarly unsuccessful was the reaction of the tris complexes with the respective metal hexacarbonyls. It was subsequently observed that the nickel complexes $NiS_4C_4R_4$ react with the hexacarbonyls of Cr, Mo, or W according to eq 1. When the reaction was conducted

$$M(CO)_6 + 3NiS_4C_4R_4 \xrightarrow[120^\circ]{} MS_6C_6R_6 + 1.5(Ni_2S_4C_4R_4)_x + 6CO \quad (1)$$

under milder conditions, particularly on irradiation with ultraviolet or visible light, the carbon monoxide containing intermediates of molybdenum and tungsten could be isolated (eq 2). In both reactions only

$$M(CO)_6 + nNiS_4C_4R_4 \xrightarrow[50^\circ,\ \text{ultraviolet irradiation}]{} M(CO)_{6-2n}(S_2C_2R_2)_n + (n/2)(Ni_2S_4C_4R_4)_x + 2nCO \quad (2)$$

one $S_2C_2R_2$ ligand was transferred to the group VI metal; the other ligand remained attached to the nickel, forming the insoluble and probably polymeric nickel dithiolate, $(Ni_2S_4C_4R_4)_x$. It was at first assumed that this partial transfer was caused by the insolubility of the latter compound. Therefore, the reactions were also carried out in the presence of the chelating diphosphine $Ph_2P–CH_2–CH_2–PPh_2$. Although no insoluble products were formed, again only one ligand was transferred; the nickel(II) dithiolate, on the other hand, was isolated out of the reaction solution as the 1:1 phosphine adduct, $NiS_2C_2R_2(Ph_2P–CH_2–PPh_2)$. With $Cr(CO)_6$, the formation of CO-containing intermediates could be detected by the color changes of the solutions. However, they were found to be too unstable to be isolated. With $Mo(CO)_6$ and $W(CO)_6$ the main products were the dicarbonyl–bisdithiodiketone complexes, $M(CO)_2S_4C_4R_4$. No tetracarbonyls of molybdenum could be isolated but the reaction of $W(CO)_6$ with $NiS_4C_4(CH_3)_4$ in addition to the dicarbonyl complex also afforded a $W(CO)_4S_2C_2(CH_3)_2$. This latter material proved to be light sensitive, and in solution even in the dark slowly decomposed into $W(CO)_2S_4C_4(CH_3)_4$. The dicarbonyl–bisdithiodiketone complexes are reasonably stable, crystalline solids which are soluble in various organic solvents, forming red solutions. On heating they decompose at the melting point into carbon monoxide, sulfur-containing organic products, metal sulfide, and the tris complexes $MS_6C_6R_6$. A similar decomposition also takes place on refluxing in toluene solution. It may be assumed that the initial

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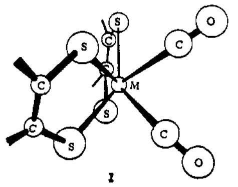
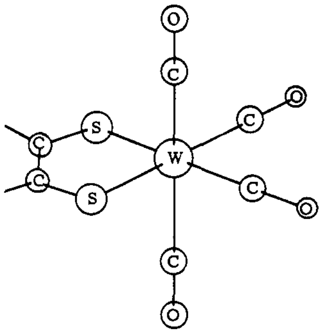
(1) (a) Paper XII of the series "The Chemistry of the Coordination Compounds"; (b) to whom correspondence should be addressed at the Department of Chemistry, University of California, La Jolla, Calif.

(2) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **88**, 3235 (1966).



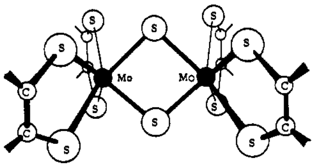
I

Figure 1. Proposed structure for complexes $MS_4C_4R_4(CO)_2$.



II

Figure 2. Proposed structure for complex $W(CO)_4S_2C_2(CH_3)_2$.



III

Figure 3. Proposed structures for complexes $Mo_2S_2(S_4C_4R_4)_2$.

decomposition products are the hypothetical bisdithiodiketone complexes $MS_4C_4R_4$ of these metals. If this is the case, they obviously must be extremely reactive; attempts to generate them at low temperature in a suitable matrix system have so far been unsuccessful.[2a] In the dicarbonyls, the two CO groups must be in *cis* position as evidenced by the two infrared-active CO-stretching vibrations observed (Table I). A structure (I) is therefore proposed in which one $S_2C_2R_2$ ligand in the prism of a tris complex $MS_6C_6R_6$ is replaced by two carbon monoxide groups (Figure 1). For the only tetracarbonyl complex isolated, structure II is proposed (Figure 2). Analogous complexes of tungsten with differently substituted dithiodiketones were found to be even less stable and could not be obtained in pure state. Evidently, the electron-donating methyl groups have a stabilizing effect. In both complexes of the type I or II, the CO groups can be substituted partly or completely by phosphines or other nucleophiles. Complexes of composition $MS_4C_4R_4(CO)PR_3$, $MS_4C_4R_4(Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2)$, and $W(CO)_2S_2C_2(CH_3)_2(Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2)$ were prepared. The bisdithiodiketone complexes containing the chelating diphosphine could also be obtained directly on heating the tris complexes with $Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2$. Also of interest is the reaction of the dicarbonyls with the dithiolato dianions $H_2C_2S_2^{-2}$ and $(CN)_2C_2S_2^{-2}$ (R' = H or CN) which produced the first asymmetrically substituted tris complexes $MS_6C_6R_4R'_2$. With cyanide ion or pyridine, on the other hand, the initially formed adducts $MS_4C_4R_4(CN)_2^{-2}$ or $MS_4C_4R_4(py)_2$ proved unstable. Polarographic reduction of the dicarbonyls and of $W(CO)_4S_2C_2(CH_3)_2$ did not produce reversible waves. However, the phosphine-substituted complexes $Mo(S_4C_4Ph_4)(CO)PPh_3$ and $Mo(S_4C_4Ph_4)(Ph_2P\text{-}CH_2\text{-}CH_2\text{-}P\text{-}Ph_2)$ gave three and two cathodic waves, respectively. In the monocarbonyl complex the first wave and in the complex with the chelating phosphine both waves proved to be reversible, indicating the existence of stable anionic species of these complexes. Perhaps the most interesting substitution product was obtained on reaction of the dicarbonyls with sulfide ion. The substances isolated were carbon monoxide free dimeric species of composition $M_2S_2(S_4C_4R_4)_2$ (M = Mo, W). In view of the prismatic metal coordination present in both the disulfides MS_2[3] and the tris complexes $MS_6C_6R_6$[4,5] of Mo and W, a doubly prismatic structure III is proposed (Figure 3). The complexes are crystalline, air-stable, and deeply colored solids. On polarographic reduction in acetonitrile the reversible formation of at least three anions $(Mo_2S_2(S_4C_4Ph_4)_2)^{-z}$ ($z = -1, -3, -4$) was detected. The molybdenum complexes could also be prepared by the benzoin-P_4S_{10} method[6] under somewhat modified conditions.[6a] It is conceivable that complexes of this type occur as intermediates in the reaction of MoS_2 (or $Mo(CO)_6$ + S) with diphenylacetylene.[7] In several runs, traces of $Mo_2S_2(S_4C_4Ph_4)_2$ have indeed been isolated in addition to $MoS_6C_6Ph_6$. These compounds cannot be obtained in better yields by this route as they decompose on prolonged heating in solution. The products of this decomposition (which also takes place at the melting point) are tetraphenylthiophene, 2-phenylthionaphthene, molybdenum sulfide, and $MoS_6C_6Ph_6$, respectively.

Discussion

The neutral dithiodiketone complexes $M(S_2C_2R_2)_n$ were shown to be novel delocalized systems. According to recent findings, some even possess aromatic character. On the basis of MO model calculations valence bond ("Kekulé") structures such as IV and V were proposed[2,8] which may be used to explain the

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[2a] Note Added in Proof. At the beginning of our work several of the tris complexes were formulated as "bis," due to analytical difficulties (see G. N. Schrauzer, V. Mayweg, H. W. Finck, U. Mueller-Westerhoff, and W. Heinrich, *Angew. Chem.*, **76**, 345 (1964)). This was soon corrected, first by us (see G. N. Schrauzer, H. W. Finck, and V. Mayweg, *ibid.*, **76**, 715 (1964)), and for $VS_6C_6Ph_6$ independently by A. Davison, *et al.*, *Inorg. Chem.*, **4**, 55 (1965). Prior to publication we have also informed Dr. H. B. Gray, Columbia University, of the correct composition, which resulted in a joint note (see J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964)). We have recently found, however, that Ru and Os form *both tris and bis* complexes which may be isolated (G. N. Schrauzer and V. P. Mayweg, unpublished results), which in part explains our previous findings.

(3) R. Dickinson and L. Pauling, *ibid.*, **45**, 1466 (1923).

(4) R. Eisenberg and J. A. Ibers, *ibid.*, **87**, 3776 (1965).

(5) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **87**, 5798 (1965).

(6) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *Inorg. Chem.*, **4**, 1615 (1965).

(6a) Note Added in Proof. In the meantime, sulfur-rich complexes showing a correct analysis for $(R_2C_2S_2MoS_{3.5})_x$ have been isolated as by-products of this reaction. *Anal* for R = C_6H_5 (violet crystals from benzene, mp 278° dec). Calcd for $C_{14}H_{10}S_{5.5}Mo$: C, 37.3; H, 2.3; S, 39.2; Mo, 21.3. Found: C, 36.0, 36.8; H, 2.2, 2.3; S, 39.6, 39.4; Mo, 21.1, 21.3 (analyses for two samples obtained from different experiments).

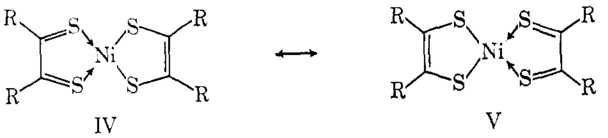
(7) G. M. Schrauzer, and V. P. Mayweg, *Z. Naturforsch.*, **19b**, 192 (1964); G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *ibid.*, **19b**, 1080 (1964).

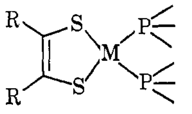
(8) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).

Table I. Infrared Spectra in KBr

Compound	ω_1, C=C	ω_2, C=S	ω_3, C=S	ω_4, M—S	ω_5, M—S	ω_6, CO	ω_7, CO	ω_8, CO	ω_9, CO
$MoS_6C_6Ph_6$	1400	1165	878	403	356				
$MoS_4C_4Ph_4(CO)_2$	1426	1168	875	404	358	2032	1992		
$MoS_6C_6(CH_3)_6$	1428	934	565	402	306				
$MoS_4C_4(CH_3)_4(CO)_2$	1449	934	565/555	400	295	2008	1960		
$WS_6C_6Ph_6$	1442	1165	872	403	359				
$WS_4C_4Ph_4(CO)_2$	1428	1156	824/874	407	374	2050	1990		
$WS_6C_6(CH_3)_6$	1470	930	562	398	300				
$WS_6C_6(CH_3)_4(CO)_2$	1470	934	562	401	300	2040	1960		
$WS_2C_2(CH_3)_2(CO)_4$	1515	943	546	392	300	2070	2024	1988	1969
$NiS_4C_4(CH_3)_4$	1333	914	558	435	333				
$Mo_2S_2(S_4C_4Ph_4)_2$	1406	1176	885/855						

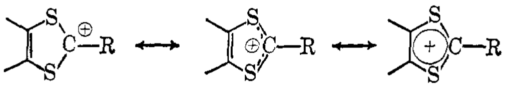
chemical properties. For instance, the observed mobility of only one $R_2C_2S_2$ ligand in the reaction of complexes $NiS_4C_4R_4$ with the group VI metal hexacarbonyls may be rationalized by assuming that only the $R_2C_2S_2$ unit formally present as the reactive α-dithiodiketone undergoes the ligand-exchange reaction.

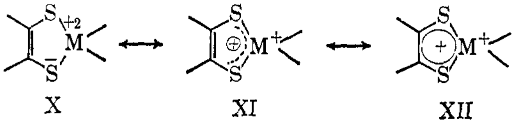

IV V


VI

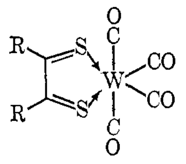
M = Ni, Pd, Pt

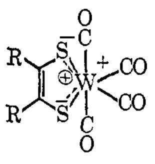
Similarly, the reaction of the nickel complexes with acetylenes at low temperature[9] may be interpreted as a Diels–Alder type addition of the alkyne to the S=C—C=S ligand. Another reaction to be mentioned in this context is the facile cleavage of the palladium and platinum compounds by phosphines which produces complexes of the type VI.[10,10a] These reactions indicate a remarkable stability of $MS_2C_2R_2$ chelate rings *in which the ligands are dithiols*, for reasons which are still insufficiently understood. An explanation is possible by relating them to the aromatic 1,3-dithiolium cations.[11] The type of resonance present in these compounds obviously also stabilizes the $MS_2C_2R_2$ chelate rings (formulas VII–XII). This proposal explains why the C=C stretching frequencies in all complexes of this type are observed at a relatively low value (range 1450–1550 cm^{-1}), whereas the M–S stretching bands occur at rather high frequencies.[2,8,9] Thus, the remarkable ability of the $R_2C_2S_2^{-2}$ and related dianions to stabilize planar situations in metal complex chemistry may be also partly due to dithiolium ion resonance. We shall now discuss the bonding in the complexes of this paper by making use of the concepts outlined above.


VII VIII IX


X XI XII

$W(CO)_4S_2C_2(CH_3)_2$. Two extreme structures (XIII, XIV) can be written which would lead to different chemical properties and spectra.


XIII


XIV

In XIII the metal is zerovalent and the ligand consists of a α-dithiodiketone, modified to some extent by back-bonding interactions. The molecule should possess a low-lying unoccupied π Mo and hence be deeply colored. In the infrared spectrum it is expected to show a C=C stretch at rather low energy; in $NiS_4C_4(CH_3)_4$, for instance, it is observed at 1333 cm^{-1}.[9] However, $W(CO)_4S_2C_2(CH_3)_2$ is yellow, which in itself eliminates structure XIII as a likely possibility. In addition, the C=C stretch is observed at 1515 cm^{-1}, still 45 cm^{-1} higher than, *e.g.*, in $WS_6C_6(CH_3)_6$;[2] the carbon–carbon bond thus must have a high double-bond character. The next band observed is found at 943 cm^{-1} and apparently consists of the C$\cdots$S stretch. It is somewhat higher than in $WS_6C_6(CH_3)_6$, but it is known that this band does not depend in a simple fashion on the bond order of the C–S bond.[2] A third band which is assigned to the second (*cis*) C–S stretch is observed at 546 cm^{-1}, again lower than in $NiS_4C_4(CH_3)_4$ or $WS_6C_6(CH_3)_6$ (Table I). The electronic spectrum (Figure 4) shows a similarity to those of $NiS_4C_4R_4^{-2}$ ions; in particular, it lacks intense low-energy absorptions. Hence, structure XIV must be the mainly contributing one.

Complexes $M(CO)_2S_4C_4R_4$ and Substituted Derivatives. The substitution of two CO groups by another $S_2C_2(CH_3)_2$ ligand in $W(CO)_4S_2C_2(CH_3)_2$ lowers the frequency of the C=C stretch and raises that of the second C=S band to the values observed in $WS_6C_6(CH_3)_6$. The suggests that the second dithion molecule does not raise the formal oxidation state of the metal

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(9) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).

(10) A. Davison and D. V. Howe, *Chem. Comun.*, 290 (1965). In a previous paper[9] we have erroneously reported the complexes of this type as $M(S_2C_2R_2)_2 \cdot 2PR_3$.

(10a) NOTE ADDED IN PROOF. Complexes of composition $M(S_2C_2R_2)_2 \cdot 2PR_3$ (M = Ni, Pt) are capable of existence and have recently been characterized: V. P. Mayweg and G. N. Schrauzer, *Chem. Commun.*, in press.

(11) See, for instance, E. Klingsberg, *J. Am. Chem. Soc.*, **84**, 3410 (1962); **86**, 5290 (1964).

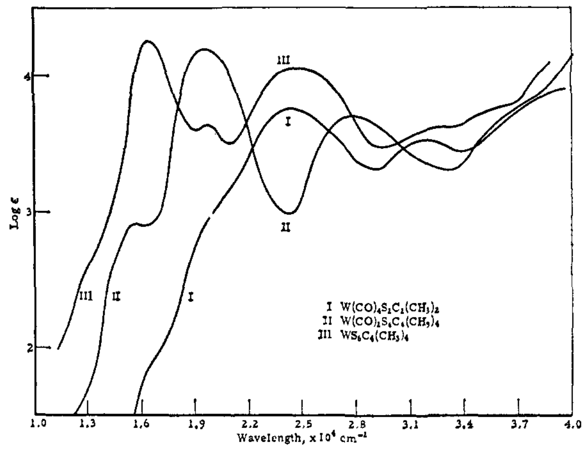
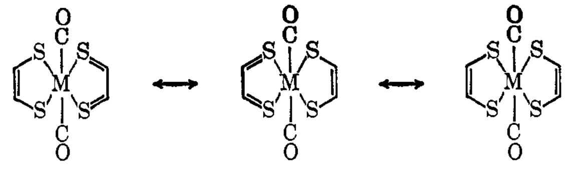
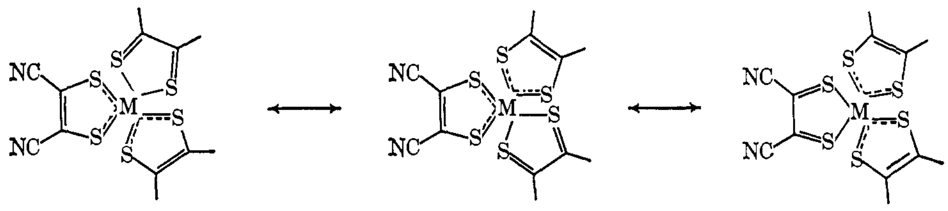


Figure 4. Electronic spectra of complexes $W(CO)_{6-2x}(S_2C_2(CH_3)_2)_x$ (x = 1, 2, 3), all in CH_2Cl_2.

from +II to +IV and that the ligands must be in a state between a dithiodiketone and a dithiolato dianion. Although similar limiting structures as for the planar bis complexes of nickel can be written to describe this bonding situation, it must be pointed out that orbital mixing in the nonplanar $MS_4C_4R_4$ is more extensive than in the planar $MS_4C_4R_4$ systems. A simple MO calculation using parameters similar to those used previously for the prismatic tris complexes[2] was carried out for a model complex $MS_4C_4R_4(X)_2$. The results indicate that the lowest unoccupied dithiodiketone ligand π MO's on interaction with the metal orbitals form the two orbitals $4a_1$ and $2b_2$ which become occupied in the complex. Since these orbitals have about 50 and 85% ligand π^* character it is concluded that the ligands have approximately one-third S=C—C=S and two-thirds S—C=C—S character. This situation requires the use of the additional limiting structure XVII. All properties are in accord with this formulation. The absorption spectra (Figures 5 and 6) show intense transitions in the visible and are sufficiently dissimilar from those of complexes such as $NiS_4C_4R_4^{-2}$ as well as $W(CO)_4S_2C_2(CH_3)_2$. In almost all complexes studied, the C=C stretch is at about the same or slightly higher frequency than in the analogous tris compounds, and the second C–S band at equal or somewhat lower values (Table I). It is expected that substitution of CO by phosphines will lead to a further stabilization of the dithiolium-type structure, as the



XV XVI XVII



XVIII XIX XX

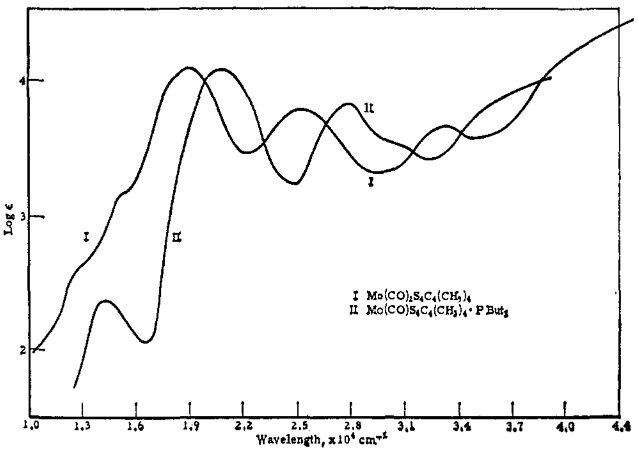


Figure 5. Electronic spectra of complexes $Mo(CO)_2S_4C_4(CH_3)_4$ and $Mo(CO)S_4C_4(CH_3)_4 \cdot P(t\text{-}Bu)_3$, in CH_2Cl_2.

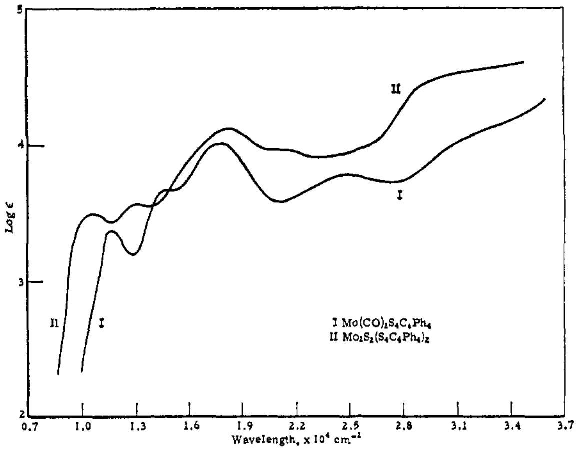
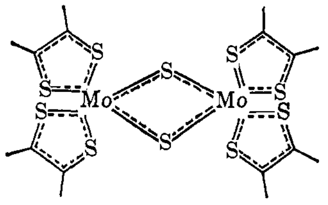


Figure 6. Electronic spectra of $Mo(CO)_2S_4C_4Ph_4$ and $Mo_2S_2(S_4C_4Ph_4)_2$, in CH_2Cl_2.

result of the donor action of these ligands. Indeed, in all cases studied introduction of phosphine causes a hypsochromic shift of the main bands (Figure 5), indicating that the dithion-resonance forms have a smaller contribution. In the complex $MoS_6C_6Ph_4(CN)_2$ the C=C stretch at 1376 cm^{-1} has a shoulder at 1400 cm^{-1} whereas the first C=S stretch at 1157 cm^{-1} has a side band at 1177 cm^{-1}. We attribute this to a greater contribution of structures XVIII and XIX, as the result of the strong electron affinity of the $S_2C_2(CN)_2$ system. In the complex $MoS_6C_6Ph_4H_2$, on the other hand, no splitting of these bands occurs, in keeping with the small differences between the Ph- and H-substituted ligands. The binuclear sulfur-bridge complexes of molybdenum, $Mo_2S_2(S_4C_4R_4)_2$, must contain delocalized $MoS_4C_4R_4$ units. In comparison with the mononuclear $Mo(X)_2S_4C_4R_4$ species, all electronic transitions are observed at longer wavelengths (Figure 6). This indicates that the

$MoS_4C_4Ph_4$ systems are coupled by resonance *via* the sulfur bridges, as shown in formula XXI.[12] A molecular orbital description of the bonding in the binuclear complexes will be presented at a later date. It is clear now, however, that the continuing study of metal-$S_2C_2R_2$ chelates will also strongly influence the development of the general theory of bonding in metal sulfides.



XXI

Experimental Section

Reaction of Complexes $NiS_4C_4R_4$ with Group VI Metal Hexacarbonyls. The nickel complexes $NiS_4C_4R_4$ were heated with an excess of the metal hexacarbonyls in toluene solution at 150°, using small laboratory autoclaves as reaction vessels. The main products isolated were the tris complexes $MS_6C_6R_6$ (identified by comparison with authentical samples obtained by other routes) and the polymeric $(Ni_2S_4C_4R_4)_x$. With R = phenyl the reactions were also conducted in the presence of tetraphenylethylenediphosphine. Under these conditions the green complex I, $NiS_2C_2Ph_2 \cdot Ph_2P\text{-}CH_2CH_2\text{-}PPh_2$, mp 253–255° dec, was isolated (instead of $(Ni_2S_4C_4Ph_4)_x$), and was recrystallized from CH_2Cl_2–CH_3OH.

Anal. Calcd for $C_{40}H_{34}S_2P_2Ni$: C, 68.7; H, 4.9; S, 9.2; Ni, 8.4. Found: C, 68.5; H, 5.1; S, 8.8; Ni, 8.4. Infrared spectrum (main bands, in KBr): 3413, 3050, 1587, 1527, 1479, 1429, 1406, 1302, 1186, 1157, 1110, 1074, 1029, 990, 877, 819, 760, 742, 714, 694, 677, 650, and 641 cm^{-1}.

Preparation of $MoS_4C_4Ph_4(CO)_2$ and $WS_4C_4Ph_4(CO)_2$. A stirred solution containing 1 g of $NiS_4C_4Ph_4$ and 0.5 g of $Mo(CO)_6$ in 125 ml of benzene was irradiated for 15 hr using two 125-w Hg vapor lamps as the light source. The solutions were kept at 25° with external cooling. During the reaction the originally deep green solution became dark violet. After filtration the solvent was removed under reduced pressure and the excess of $Mo(CO)_6$ was sublimed off under vacuum. Subsequent chromatography of the residue over a silica gel column (mesh 0.05–0.2 mm used throughout in this work) with a 1:4 benzene–pentane mixture as eluent afforded a violet zone which was isolated. After removal of the solvent the product was recrystallized from a CH_2Cl_2–light petroleum mixture, yielding 250 mg of product, dec pt 150°.

Anal. Calcd for $C_{30}H_{20}O_2S_4Mo$: C, 56.6; H, 3.2; S, 20.1; Mo, 15.1, mol wt, 636.7. Found: C, 57.0; H, 3.4; S, 20.5; Mo, 14.9, mol wt, 615.

Polarographic reduction produced ill-defined waves indicating that decomposition occurred during the measurements.

Under essentially identical conditions 330 mg of $WS_4C_4Ph_4(CO)_2$ (mp 165° dec) were isolated. The compound forms red-brown crystals.

Anal. Calcd for $C_{30}H_{20}O_2S_4W$: C, 49.8; H, 2.8; S, 17.7; mol wt, 724.6. Found: C, 50.4; H, 2.9; S, 20.2; mol wt, 680.

Polarographic reduction of $WS_4C_4Ph_4(CO)_2$ gave two main waves at −0.3 and −0.7 v, respectively (in CH_3CN solution *vs.* the Ag AgCl electrode at 25°), plus some smaller waves indicating that some decomposition occurred during the measurement. Both complexes were allowed to react with warm pyridine affording the tris complex $M(S_6C_6Ph_6)$ as the main products (identified by comparison with authentic samples). In the concentrated filtrates small amounts of tetraphenylthiophene and 2-phenylthionaphthene were detected by glpc analysis.

Reaction of Complexes $MS_4C_4Ph_4(CO)_2$ (M = Mo, W) with Triphenyl- and Tributylphosphine. To solutions of the complexes containing about 0.4 mmole in 50 ml of benzene 1 mole of triphenylphosphine was added. Carbon monoxide started to evolve after the addition of the phosphine and the solutions turned red. Chromatographic work-up using a 1:4 benzene–Skellysolve mixture afforded a red zone in each case from which the complexes were recovered and recrystallized from mixtures of CH_2Cl_2 and light petroleum.

Anal. Calcd for $C_{47}H_{35}OPS_4Mo$ (mp 155° dec): C, 64.8; H, 4.05; S, 14.7; P, 3.5; mol wt, 871.0. Found: C, 64.6; H, 4.50; S, 14.2; P, 2.9; mol wt, 950. Calcd for $C_{47}H_{35}OPS_4W$ (mp 161° dec): C, 58.9; H, 3.7; S, 13.4; P, 3.2; mol wt, 958.9. Found: C, 59.4; H, 4.0; S, 14.5; P, 3.0; mol wt, 943.

With tributylphosphine, $MoS_4C_4Ph_4(CO)_2$ gave a red, crystalline monosubstitution product, mp 191° dec, twice recrystallized from CH_2Cl_2–CH_3OH.

Anal. Calcd for $C_{41}H_{47}OPS_4Mo$: C, 60.7; H, 5.8; S, 15.8; P, 3.8; Mo, 11.8. Found: C, 60.2; H, 5.8; S, 15.1; P, 3.5; Mo, 11.8. Infrared spectra (intense absorptions only, in KBr) of $Mo(S_4C_4Ph_4)PPh_3(CO)$: 3048, 1980 ($\nu_{C\equiv O}$), 1600, 1488, 1468, 1443 (ω_1), 1182, 1173 (ω_2), 1092, 1088, 1030, 1002, 912, 868 (ω_1), 762, 746, 693, 613, 521, 505, 496, 450 sh, 433 (M–C), 403 (M–S), and 359 (M–S) cm^{-1}.

Polarographic measurements on the monotriphenylphosphine substitution product indicate three one-electron reduction steps at −0.706, −1.396, and −2.376 v, of which only the first is reversible. ($E_{1/2}$ values of $MoS_6C_6Ph_6$ for comparison: first, 0.0; second, −0.62 v.) Measurements were performed in DMF *vs.* the Ag|AgCl electrode in 0.10 *N* aqueous LiCl.

Reaction of Complexes $MS_4Ph_4(CO)_2$ (M = Mo, W) with Tetraphenylethylenediphosphine. Reaction of the dicarbonyls under conditions similar to those described above with $Ph_2P\text{-}CH_2CH_2\text{-}PPh_2$ afforded red crystals of the complexes $MS_4C_4Ph_4(Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2)$.

Anal. Calcd for $C_{54}H_{44}S_4P_2Mo$ (mp 243° dec): C, 66.1; H, 4.5; S, 13.1; P, 6.3; Mo, 9.8. Found: C, 65.9; H, 4.5; S, 12.4; P, 6.1; Mo, 9.2. Calcd for $C_{54}H_{44}S_4P_2W$ (mp 281° dec): C, 60.8; H, 4.2; S, 12.0; P, 5.8; W, 17.2. Found: C, 60.5; H, 4.1; S, 11.4; P, 5.6; W, 18.0. Infrared spectrum (cm^{-1}, in KBr) of $MoS_4C_4Ph_4(Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2)$: 3039, 1592, 1488, 1468, 1436 (ω_1), 1190 sh, 1179 (ω_2), 1162 sh, 1101, 1090, 1075, 1028, 1000, 909, 877, 826, 762, 744, 694, 610, 526, 515 sh, 486, 415 (M–S, M–P?), 383, 367 sh, 358 (M–S, M–P), 346 sh.

Preparation of $WS_4C_4Ph_4(Ph_2P\text{-}CH_2CH_2\text{-}PPh_2)$ from $WS_6C_6Ph_6$. A solution of 1 g of $WS_6C_6Ph_6$ was refluxed with 3 g of $Ph_2P\text{-}CH_2CH_2\text{-}PPh_2$ in 50 ml of benzene for 3 days. To the brown reaction product methanol was added after the removal of the benzene, which yielded a brown crystalline material which was recrystallized three times from CH_2Cl_2–methanol. The product was identical in every respect with $WS_4C_4Ph_4(Ph_2P\text{-}CH_2CH_2\text{-}PPh_2)$ obtained by the above method. Under similar conditions $MoS_6C_6Ph_6$ afforded $MoS_4C_4Ph_4(Ph_2P\text{-}CH_2CH_2\text{-}PPh_2)$. In the concentrated filtrates of the preparation of the tungsten compound, diphenylacetylene, stilbene, and 2-phenylthionaphthene were detected by glpc, in a ratio of approximately 3:2:1. Polarographic measurements on $MoS_4C_4Ph_4(Ph_2P\text{-}CH_2CH_2\text{-}PPh_2)$ (in DMF, Ag|AgCl electrode in 0.1 *N* aqueous LiCl) gave $E_{1/2}$ at −1.152 and −1.96 v; both are one electron-transfer reactions, and reversible.

Preparation of Complexes $MS_4C_4R_4(CO)_2$ (R = Aryl and Methyl, M = Mo and W). Under conditions essentially identical with those described above, several analogous complexes $MS_4C_4R_4(CO)_2$ were prepared. Properties and analytical data are summarized in Table II.

Reaction of Complexes $MoS_4C_4Ph_4(CO)_2$ with Sulfide Ion. The complex $MoS_4C_4Ph_4(CO)_2$ (1 g) was suspended in 10 ml of CH_3OH and a concentrated solution of NaSH in 1:1 water–methanol was added dropwise until the original red color of the solution disappeared. The solution was then acidified with concentrated HCl and extracted with benzene. The benzene layer was chromatographed on silica gel using a 1:1 mixture of *n*-pentane and benzene as the eluent. Besides a green zone which was found to be due to $MoS_6C_6Ph_6$ a red zone separated which afforded red crystals from CH_2Cl_2–light petroleum. The reaction with the tungsten complex was carried out analogously; the substance was found to be less stable and partly decomposed on recrystallization.

Anal. Calcd for $C_{56}H_{40}S_{10}Mo_2$ (mp 275° dec): C, 54.9; H, 3.3; S, 26.2; Mo, 15.7. Found: C, 53.5; H, 3.3; S, 26.7; Mo, 16.2. Calcd for $C_{56}H_{40}S_{10}W_2$ (mp 229° dec): C, 48.0; H, 2.9; S, 22.9; W, 26.3. Found: C, 47.8; H, 2.8; S, 22.4; W, 26.0.

Polarographic measurement on the molybdenum compound in DMF: three waves at $E_{1/2}$ −0.38, −0.80, and −0.9 v. The

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(12) The less stable tungsten complex, $W_2S_2(S_4C_4Ph_4)_2$, though expected to have a similar structure has a somewhat different infrared spectrum which either suggests partial decomposition or an unsymmetrical structure. Further work is in progress to decide on this issue.

Table II. Properties and Analytical Data of Complexes $MoS_4C_4R_4(CO)_2$

M	R	Mp, °C (dec)	Color (solid)	Composition	Calcd, % C	H	S	Found, % C	H	S
Mo	CH_3	151	Brown-black	$C_{10}H_{12}S_4O_2Mo$	30.9	3.1	33.0	30.6	3.1	33.3
Mo	p-$C_6H_4OCH_3$	135	Violet-black	$C_{34}H_{28}O_6S_4Mo$	54.0	3.7	16.9	53.6	3.8	16.3
W	CH_3	162	Dark green	$C_{10}H_{12}S_4O_2W$	25.4	2.5		25.4	2.5	
W	p-$C_6H_4OCH_3$	140	Dark blue	$C_{34}H_{28}O_6S_4W$	48.4	3.3		49.0	3.9	

Table III

R	Mp, °C	Formula	Calcd, % C	H	S	Mo	Found, % C	H	S	Mo
C_6H_5	275 dec	$C_{56}H_{40}S_{10}Mo_2$	54.9	3.3	26.2	15.7	53.5	3.4	26.4	14.8
p-$C_6H_4CH_3$	187 dec	$C_{64}H_{56}S_{10}Mo_2$	57.5	4.2	24.0	14.3	57.1	4.2	24.2	14.0

Table IV. Electronic Spectra in $CHCl_3$[a]

$W(CO)_4S_2C_2(CH_3)_2$	606 sh (1.95)	494 sh (3.05)	411 (3.77)	317 (3.54)	250 (3.90)	
$W(CO)_2S_2C_2(CH_3)_2 \cdot Ph_2PCH_2CH_2PPh_2$	581 sh (2.65)	478 sh (3.1)	392 (3.7)	294 (3.95)		
$W(CO)_2S_4C_4(CH_3)_4$	641 (2.92)	507 (4.21)	347 (3.71)	270 sh (3.80)		
$WS_4C_4(CH_3)_4 \cdot Ph_2PCH_2CH_2PPh_2$	526 (3.54)	464 (3.68)	390 (3.72)	340 (3.68)	276 (4.11)	
$Mo(CO)_2S_4C_4(CH_3)_4$	724 (2.70)	629 (3.20)	526 (4.06)	394 (3.79)	300 (3.64)	
$Mo(CO)_2S_4C_4Ph_4$	861 (3.14)	666 (3.44)	571 (3.79)	406 (3.56)	323 sh (3.80)	286 sh (4.00)
$Mo(CO)S_4C_4Ph_4 \cdot PPh_3$	689 (3.53)	536 (3.80)	417 (3.70)	312 (4.17)		
$MoS_4C_4Ph_4 \cdot Ph_2PCH_2CH_2PPh_2$	571 (3.60)	513 (3.83)	442 (3.93)	376 (3.90)	333 sh (3.80)	285 sh (4.00)
$Mo_2S_2(S_4C_4Ph_4)_2$	952 (3.49)	769 (3.56)	553 (4.11)	477 (3.94)	393 (3.96)	313 sh (4.54)

[a] Wavelengths in mμ; log ε in parentheses.

ratio of the number of electrons is 1:2:1, as judged from the heights of the waves, but the absolute numbers are unknown.

Preparation of Complexes $Mo_2S_2(S_4C_4R_4)_2$ *via* the Benzoin–P_4S_{10} Method. A "thioester solution[6]" obtained from the reaction of 100 g of benzoin and 100 g of P_4S_{10} in 500 ml of xylene was treated with a solution of 15 g of $MoCl_5$ containing a 1:1 equiv of tetraethylammonium bromide in 100 ml of acetonitrile. The mixture was heated on a steam bath for 5 min after which 800 ml of alcohol was added. The solution turned yellow. Heating on the steam bath was continued for 90 min, and the solution was acidified with concentrated HCl. Two layers formed. The lower, deep red, layer was separated and concentrated under reduced pressure. Acetone was added to the residue which caused the precipitation of a large amount of crystalline product which was purified by Soxhlet extraction with acetone. The method was so far successfully applied for the preparation of $Mo_2S_2(S_4C_4R_4)_2$ with R = C_6H_5 and p-$C_6H_4CH_3$, but could not be extended to tungsten. Under similar conditions the only products formed were the tris species, $WS_6C_6R_6$ (see Table III for analysis).

Isolation of $WS_2C_2(CH_3)_2(CO)_4$. A partly dissolved suspension of 2 g of $NiS_4C_4(CH_3)_4$ and 2 g of $W(CO)_6$ in 60 ml of CH_2Cl_2 was irradiated with a 125-w G.E. mercury vapor light source maintaining the temperature at 20°. After 3 hr of irradiation the reaction solution was filtered and evaporated *in vacuo*. The residue was treated with 200 ml of n-pentane. After filtration, the brown-red pentane solution was filtered and concentrated under reduced pressure to about 20 ml. Subsequent chromatography on silica gel with pentane as the eluent gave a yellow zone which was separated. After evaporation of the pentane, yellow crystals contaminated with $W(CO)_6$ were obtained. The hexacarbonyl was removed by vacuum sublimation. The complex decomposed at 92° and was not recrystallized owing to its lability in solution. The main decomposition product both on melting and on prolonged standing in solution is $WS_4C_4(CH_3)_4(CO)_2$.

Anal. Calcd for $C_8H_6O_4S_2W$: C, 23.2; H, 1.5; S, 15.4; W, 44.5. Found: C, 23.4; H, 1.5; S, 15.8; W, 45.0. Infrared spectrum (in KBr): 2915, 2849, 2070 (ν_{CO}), 2024 (ν_{CO}), 1988 (ν_{CO}), 1969 (ν_{CO}), 1934, 1893, 1515 ($\nu_{C=C}$), 1438, 1373, 1097, 943, 546, 505, 446, 415, 407, 393, and 347 cm^{-1}.

Reaction of $WS_2C_2(CH_3)_2(CO)_4$ with Ph_2P–CH_2CH_2–PPh_2. A solution containing $WS_2C_2(CH_3)_2(CO)_4$ in pentane was treated with an approximate twofold stoichiometric excess of tetraphenylethylenediphosphine at room temperature. Orange-yellow crystals precipitated and carbon monoxide evolved out of the reaction solution. The complex was recrystallized twice from dichloromethane, mp 229° dec.

Anal. Calcd for $C_{32}H_{30}O_2P_2S_2W$: C, 50.8; H, 4.0; S, 8.5; P, 8.2; W, 24.4. Found: C, 50.8; H, 4.2; S, 8.6; P, 7.8; W, 24.9. Infrared spectrum (cm)$^{-1}$: 3039, 2915, 2840, 1919 (ν_{CO}), 1845 (ν_{CO}), 1615, 1488, 1432, 1190, 1162, 1097, 1075 sh, 1030, 1002, 934, 884, 826, 746, 694, 617, 592, 555, 532, 518, 485, 424, 420, 411 sh, 385, 345.

Reaction of $MoS_4C_4Ph_4(CO)_2$ with Anions $R'_2C_2S_2^{-2}$ (R' = H, CN). To a solution of 1 g of $MoS_4C_4Ph_4(CO)_2$ in 10 ml of a CH_2Cl_2–CH_3OH mixture (1:1), 2 ml of a concentrated solution of $Na_2S_2C_2(CN)_2$ or $Na_2S_2C_2H_2$ in methanol was added. The solution turned green immediately. After acidification with concentrated HCl, green crystals precipitated which were recrystallized from a mixture of CH_2Cl_2 and methanol and finally from CH_2Cl_2–light petroleum (bp 60–80°). (See Table IV for electronic spectra of compounds.)

Anal. Calcd for $MoS_6C_6Ph_4H_2$ (mp 85° dec), $C_{30}H_{22}S_6Mo$: C, 53.7; H, 3.3; S, 28.7; Mo, 14.3. Found: C, 53.8; H, 3.7; S, 28.4; Mo, 13.6. Calcd for $MoS_6C_6Ph_6(CN)_2$ (mp 183° dec), $C_{32}H_{20}N_2S_6Mo$: C, 53.3; H, 2.8; S, 26.7; N, 3.9; Mo, 13.3. Found: C, 53.2; H, 2.8; S, 26.2; N, 4.0; Mo, 13.1.