

then "rivet" with carbon, providing a remarkably simple new route to complex carbon structures.

### Conclusion

It is difficult to realize that less than 2 years has passed (at the time of this writing) since the initial experiments with carbon monoxide. However, progress can be very rapid with the assistance of competent, interested coworkers. It is important to have the right men at the right place at the right time. The development of hydroboration was greatly facilitated by the major contributions of Dr. B. C. Subba Rao and Dr. George Zweifel. The development of carbonylation was especially facilitated by the major contributions of Michael W. Rathke (now Dr.) and Dr. Eiichi Negishi. Developments in newer areas are being facilitated by the major contributions of George W. Kabalka, Dr. Milorad M. Rogić, and Dr. Akira Suzuki.

*It is a pleasure to acknowledge the assistance of Grant GM 10937 from the National Institutes of Health.*

## Coordination Compounds with Delocalized Ground States. The Transition Metal Derivatives of Dithiodiketones and Ethylene(1,2)dithiolates (Metal Dithienes)

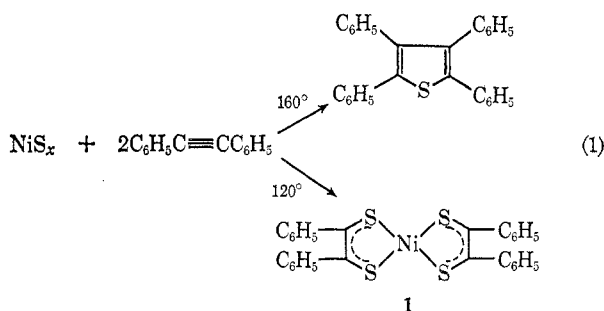
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### Early Developments

In 1961 the reaction of nickel sulfides with diphenylacetylene was studied<sup>1</sup> as a modification of Steinkopf's historical thiophene synthesis<sup>2</sup> from acetylene and pyrite. With technical grade nickel sulfide containing excess sulfur the formation of tetraphenylthiophene was observed to occur at higher reaction temperatures. Under milder conditions a complex was isolated for which structure **1** was proposed<sup>1</sup> on the basis of degradation experiments (eq 1). The structure of **1** was con-



firmed by X-ray analysis.<sup>3</sup> Complex **1** was also obtained from the combined reaction of sulfur with diphenylacetylene and metallic nickel (or Ni(CO)<sub>4</sub>).<sup>1</sup>

In substantiation of the initial working hypothesis, **1** was found to react with alkynes to yield thiophene derivatives. The reaction involves a 1,4 addition of the alkyne to a C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>S<sub>2</sub> ligand in the complex, producing a dithiadene intermediate which cleaves off sulfur to yield the thiophene. Due to the low yield of **1** obtained, the new thiophene synthesis at this stage was of course devoid of practical utility. Therefore, a more convenient synthesis of **1** was sought.

In the reaction of benzoin with P<sub>2</sub>S<sub>10</sub>,<sup>4</sup> thiophosphates of stilbenedithiol are formed which on treatment with metal salts afford the desired complexes. The reaction could be extended to acyloins and has become the most widely applicable method of synthesis.

Shortly after the appearance of the first report on "dithiobenzilnickel," several complex salts derived from maleonitriledithiol (MNT) were described.<sup>5</sup>

(1) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **84**, 3221 (1962).

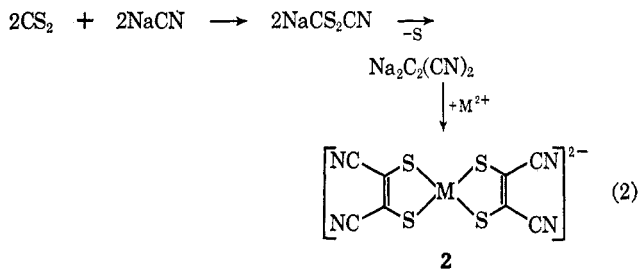
(2) W. Steinkopf and G. Kirchoff, *Ann.* **403**, 1 (1914); **403**, 11 (1914).

(3) D. Sartain and M. R. Truter, *J. Chem. Soc., A*, 1264 (1967).

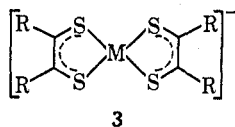
(4) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *Inorg. Chem.*, **4**, 1615 (1965).

(5) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, **84**, 4756 (1962).

The MNT ligand was discovered in 1957 (eq 2).<sup>6</sup> Although the first complexes of type 2 were prepared<sup>6</sup> in 1957, these received little attention until 1962.



Subsequently it was demonstrated that the neutral and anionic species  $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2^0$  and  $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2^{2-}$  are related by reversible electron-transfer reactions,<sup>7</sup> and synthesis of the first paramagnetic monoradical anion salts (3) of the compounds, with  $\text{R} = \text{CN}$ ,  $\text{CF}_3$ , or  $\text{C}_6\text{H}_5$ , was reported.<sup>7</sup> The existence of the mono-



radical anions and of the neutral species gave rise to an interesting controversy concerning the true nature of the complexes. Whereas we regarded, *e.g.*, both the neutral and anionic species as  $\pi$ -delocalized, covalent derivatives of the metals in the 2+ state, others considered the central metal to be more highly oxidized, *e.g.*, 3+ in the monoanions and 4+ in the neutral compounds, with ligands essentially consisting of ethylene-dithiolato dianions. This controversy initiated a very thorough study of these complexes.

In the present Account only a part of the considerable literature on this subject can be covered. For more detailed information the review literature should be consulted.<sup>8</sup>

### "Even" and "Odd" Ligands

The apparent failure of the traditional assignment of oxidation numbers to the metal atoms in the complexes  $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2^{0,1-,2-}$  at first seemed to be alarming. However, analogous ambiguities are encountered in all complexes of ligands containing an even number of vertical  $\pi$  orbitals. That similar difficulties were essentially unknown previously is merely because most of the ligands studied contained "odd"  $\pi$ -orbital systems. Every "odd" unsaturated ligand system will tend to exist as a monoanion owing to the presence of the non-bonding, singly occupied  $\pi$  MO in its energy level scheme (Figure 1). Since no other low-lying  $\pi$  molecular orbitals are present, the "odd" ligands usually

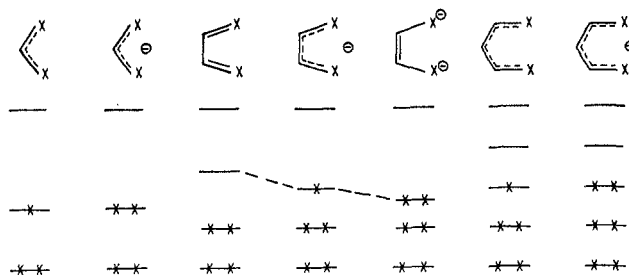
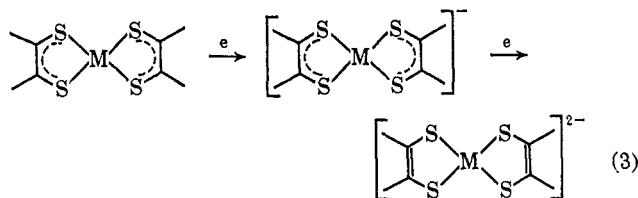


Figure 1. Schematic molecular orbital energy level diagrams for "even" and "odd" unsaturated ligand systems ( $\text{X} = =\text{O}$ ,  $=\text{NR}$ , or  $=\text{S}$ ). "Odd" or "even" are ligands containing an odd or even number of vertical  $\pi$  orbitals.

do not accept additional electrons and hence behave "normally." In the four-atom "even" ligands the lowest unoccupied  $\pi$  MO is only weakly antibonding if the two atoms at positions 1 and 4 of the butadiene framework are sulfur.<sup>9</sup> Hence, this system may exist as the neutral ligand, the monoanion, or the dianion, as is shown in Figure 1. In metal complexes of such ligands a decision between the three possibilities cannot be reached without additional experimental evidence.

All neutral, planar complexes  $\text{M}(\text{S}_2\text{C}_2\text{R})_2$  of Ni, Pd, and Pt, as well as the neutral tris complexes  $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_3$  of Cr, V, Mo, W, and Re, show three intense bands in the infrared spectrum which were assigned to perturbed  $\text{C}=\text{C}$  and  $\text{C}=\text{S}$  stretching vibrations. The complexes consequently could not have neutral dithiodiketones or dithiolato dianions as ligands. Rather, the ligands appear to be in a state intermediate between the two extremes. On reduction of the neutral complexes to the mono- and dianions the frequency of the  $\text{C}=\text{C}$  and  $\text{C}=\text{S}$  bands increases and decreases, respectively.<sup>10</sup> In the most highly reduced species the infrared spectrum corresponds to that of substituted ethylene-dithiolates. Hence, the reduction is formulated according to eq 3.<sup>10</sup>



From the  $\text{C}=\text{C}$  stretching frequencies of the neutral and reduced species it is possible to determine the approximate number of electrons in predominantly ligand-based  $\pi$ -MO's. For complexes with the same substituents the relationships are shown in Figure 2. Since all lines in Figure 2 are nearly parallel, the electrons on reduction are evidently placed into orbitals of appreciable  $\pi$ -ligand character.

(6) G. Bähr and G. Schleitner, *Ber.*, **90**, 438 (1957).

(7) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, **85**, 2029 (1963).

(8) (a) G. N. Schrauzer, *Transition Metal Chem.*, **4**, 299 (1968); (b) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(9) H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Amer. Chem. Soc.*, **84**, 4782 (1962).

(10) The partial  $\pi$ -double bond character of the  $\text{M}-\text{S}$  bonds, which undoubtedly is present in most complexes of this type, has usually not been explicitly indicated in the structural formulas.

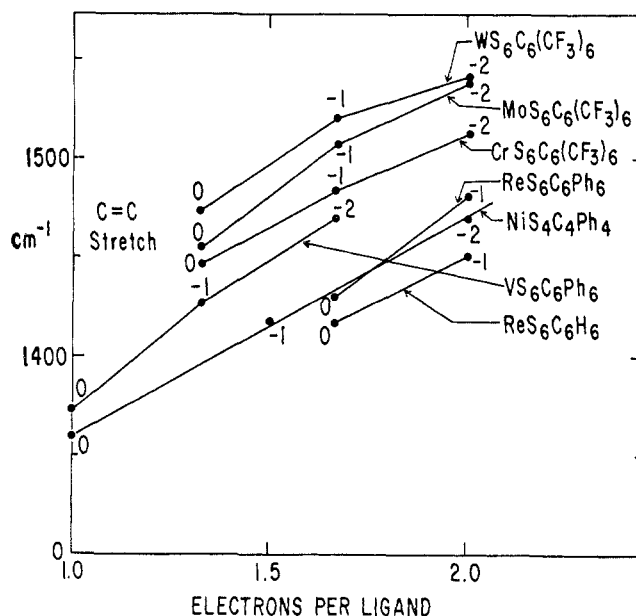


Figure 2. Changes of the C=C stretching frequency in metal dithiolenes on reduction. Note that the  $\nu_{\text{C}=\text{C}}$  changes to approximately the same extent on the reduction of all neutral dithiene complexes.

Strong absorptions in the visible region of the spectra are another characteristic of the neutral complexes. In the most highly reduced species similar bands are usually absent, since the ligands in this case are dithiolato dianions which do not have chromophoric properties. It must be stressed at this point that the traditional description of complexes as composed of a "central metal ion" and of "ligands" is no longer advantageous for these sulfur ligand complex systems. These are evidently highly delocalized and in many ways resemble unsaturated, heterocyclic organic compounds. This is largely due to the unsaturated nature of the ligands and the covalent metal-ligand bonding.

The sulfur ligands are by no means the only ones which lead to ambiguities in the assignment of metal atom valence states. The well-known  $\pi$  complexes of transition metals with quinones provide another example. Thus, bis(duroquinone)nickel(0)<sup>11</sup> can also be written as a nickel(II)-bis(semiquinone radical) complex, or even as a derivative of Ni(IV) with hydroquinone dianions as ligands. Although the latter formulation is the least likely as it violates the electroneutrality principle, an *a priori* decision between the first two is not possible. The chemical and physical properties of the compound leave little doubt that the correct metal valence state is Ni(0).

### Nomenclature

In view of the foregoing discussion it is clear that **1** is neither "bis(dithiobenzil)nickel" nor "bis-(1,2-stilbene-dithiolato)nickel," but rather "bis(dithiosembenzil)-nickel." Since this nomenclature cannot be generalized it is perhaps most convenient to designate all species with intermediate ligands as "metal dithiolenes" or the whole group of compounds as "metal dithiolenes."<sup>8</sup>

(11) G. N. Schrauzer, *Advan. Organometal. Chem.*, **2**, 17 (1964).

### The Electronic Structure of the Planar Complexes, $M(\text{S}_2\text{C}_2\text{R}_2)_2$

The problems associated with the assignment of the metal oxidation state and the correct nature of the ligands in the neutral complexes  $M(\text{S}_2\text{C}_2\text{R}_2)_2$  may be resolved through the application of group theoretical principles and simple molecular orbital theory.<sup>12</sup> The two isolated neutral dithiodiketone ligand  $\pi$  orbitals are butadienelike and transform as  $B_{1u}$ ,  $B_{2g}$ ,  $A_u$ , and  $B_{3g}$ , respectively. The most important orbital combinations are the lowest unoccupied MO's of symmetry  $B_{1u}$  and  $B_{2g}$  (axes as given in Figure 3). Of these,  $B_{1u}$  interacts significantly with  $4p_z$  of the central metal. Since  $4p_z$  is at lower energy, the  $B_{1u}$  orbital set becomes stabilized and occupied in the complex.  $B_{2g}$ , on the other hand, interacts only weakly with  $3d_{zz}$ . Since  $E_{3d_{zz}} > E_{B_{2g}}$ ,  $B_{2g}$  becomes somewhat antibonding (Figure 3) and remains the lowest unoccupied orbital of the system.<sup>12</sup> All electron-transfer reactions, including the solid-state conductivity mentioned later, depend on the energy of this orbital.

A schematic molecular orbital diagram of  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2$  is shown in Figure 3. The nodal properties of the important MO's  $2b_{1u}$  and  $3b_{2g}$  are illustrated in Figure 4. Since the  $2b_{1u}$  ligand MO is filled in the complex, the intermediacy of the ligands between dithiodiketones and dithiolato dianions is fully accounted for (C-C and C-S distances observed, 1.37 and 1.70 Å, respectively). In the electronic spectra of all neutral dithiolenes of Ni, Pd, and Pt as well as in the monoanions, a very intense band is observed in the near-infrared region. Since it is substituent dependent it must be a  $\pi-\pi^*$  transition and was assigned<sup>12</sup> to the allowed transition  $2b_{1u}-3b_{2g}$ , in excellent agreement with the calculated one-electron excitation energies. There is also good quantitative correlation between the observed and calculated transition energies for the other bands in the optical spectrum (Figure 5). The occupation of the  $3b_{2g}$  OM by one of two electrons on reduction causes the expected increase in the C-C and C-S  $\pi$  bond orders. In the species  $M(\text{S}_2\text{C}_2\text{R}_2)_2^{2-}$  the ligands thus are essentially ethylenedithiolate dianions.

The symmetry assignment of the MO containing the unpaired electron is in agreement with epr analysis.<sup>12-14</sup> The electronic structure of the Pd and Pt complexes furthermore is qualitatively and quantitatively very similar to that of the nickel compounds. Complexes containing selenium instead of sulfur, e.g.,  $\text{Ni}(\text{Se}_2\text{C}_2(\text{CF}_3)_2)_2$ , have recently been reported.<sup>15</sup>

### Dithiene Resonance

The remarkable ligand intermediacy in the metal dithiolenes can also be expressed in terms of the formal-

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

(13) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

(14) R. Schmitt and A. H. Maki, *J. Amer. Chem. Soc.*, **90**, 2288 (1968).

(15) A. Davison and E. T. Shawl, *Chem. Commun.*, 670 (1967).

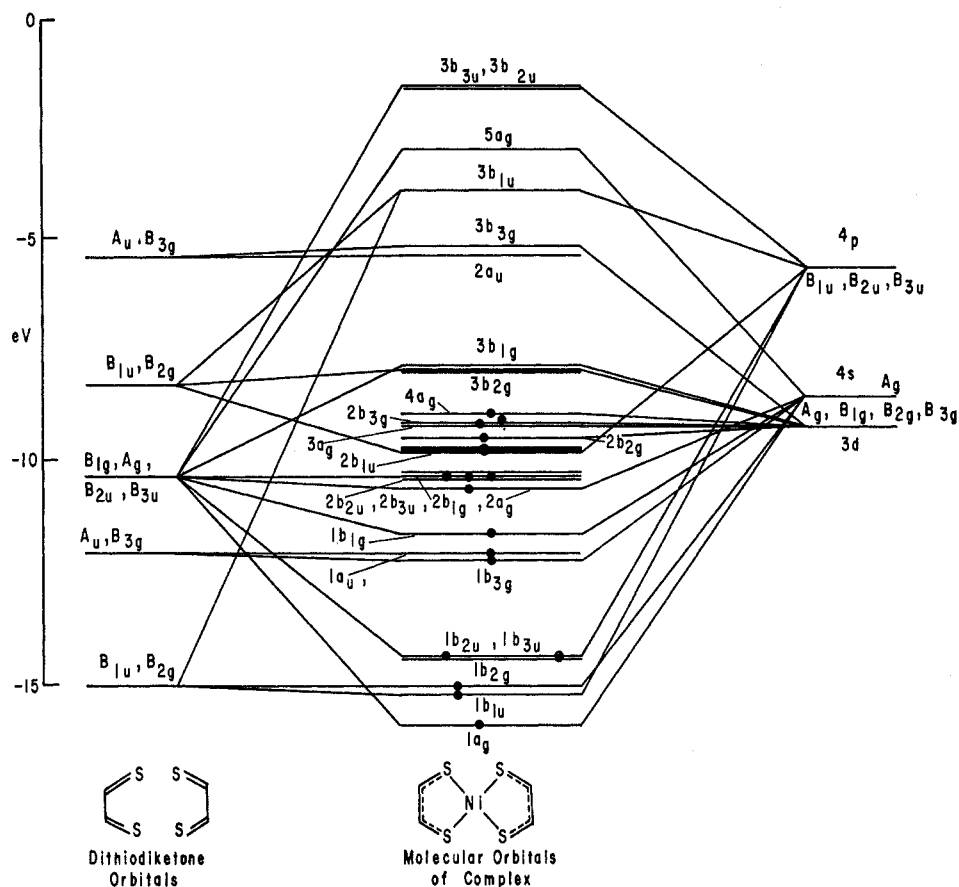


Figure 3. Schematic one-electron molecular orbital energy level scheme of the complex  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2$ . The important orbitals are  $2b_{1u}$  and  $3b_{2g}$ . Electron pairs designated by ●.

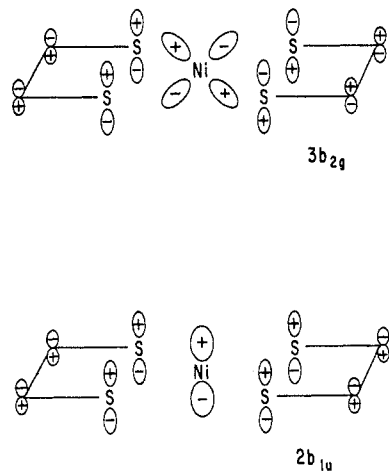


Figure 4. Nodal properties of the "dithiene MO's"  $2b_{1u}$  and  $3b_{2g}$ . Orbital  $2b_{1u}$  is occupied, and  $3b_{2g}$  is empty in the neutral dithienes  $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_2$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ).

isms of resonance theory.<sup>8,12</sup> The ground-state of the planar nickel complexes, for example, is represented by the two mainly contributing equivalent "dithiene resonance" structures, 4 and 5.<sup>8</sup>

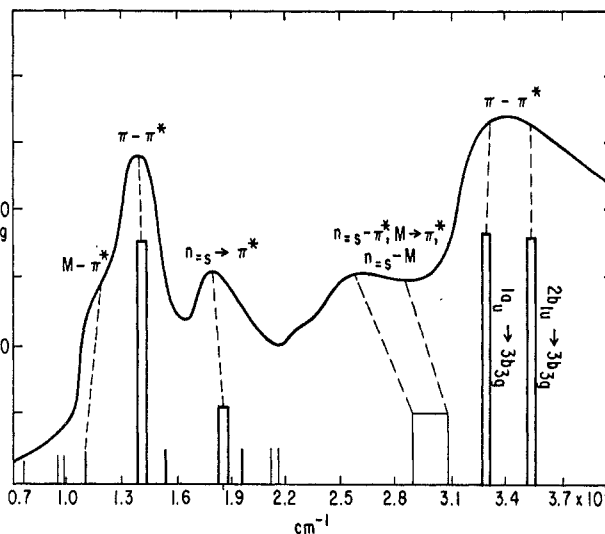
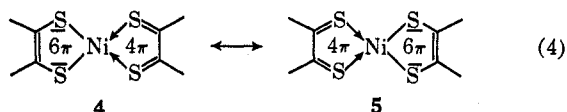
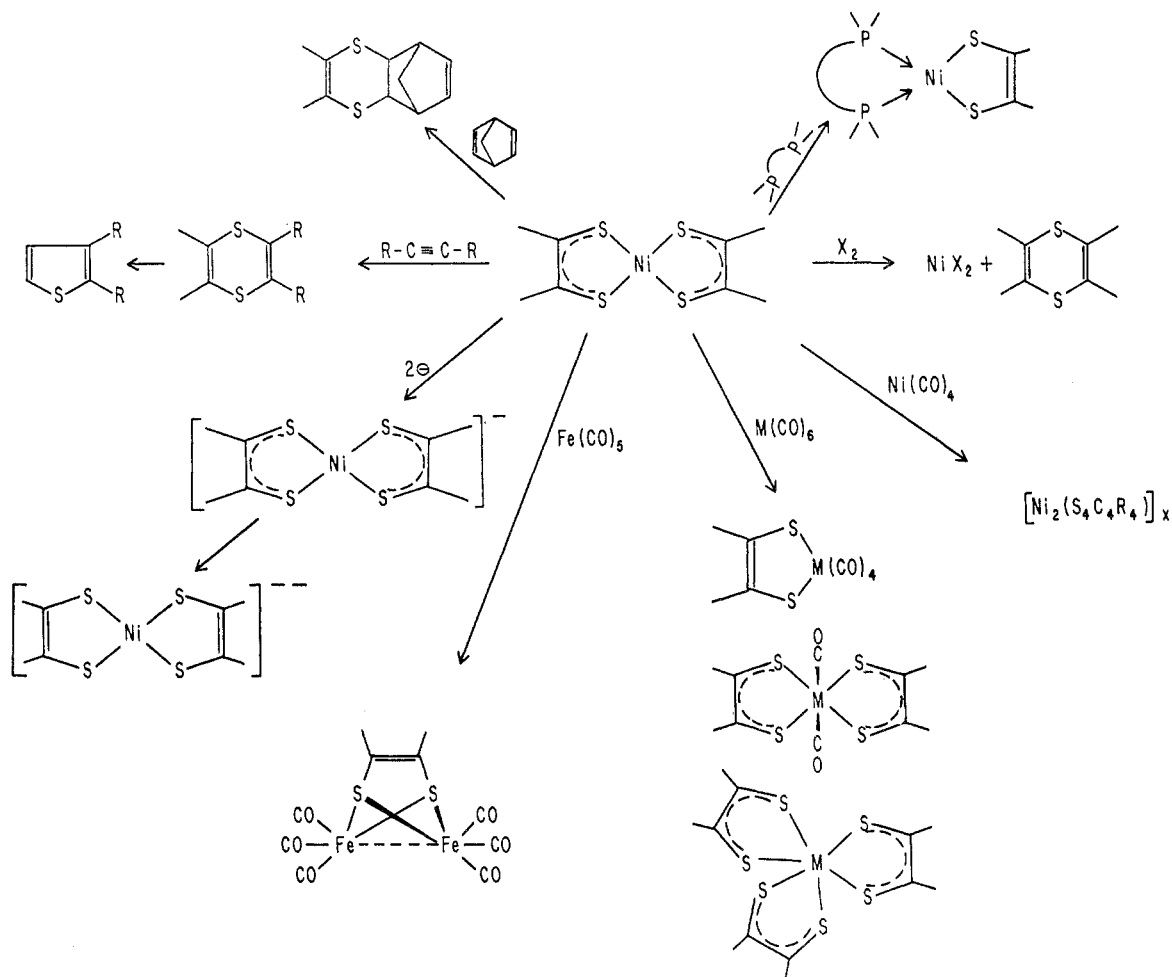


Figure 5. Solution of absorption spectrum of  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2$  (in  $\text{CH}_3\text{OH}$ ), calculated one-electron transition energies, and suggested assignments.

The formulation indicates that the ligands possess "residual dithiodiketone character." The reported Diels-Alder reactions of complex I with norbornadiene and with alkynes as dienophiles<sup>16,17</sup> can be well understood on this basis.

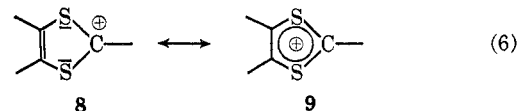
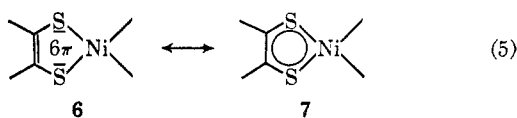
(16) G. N. Schrauzer and H. N. Rabinowitz, *J. Amer. Chem. Soc.*, in press.  
 (17) G. N. Schrauzer, and V. P. Mayweg, *ibid.*, **87**, 1483 (1965).

Scheme I: Some Important Reactions of Nickel Dithienes



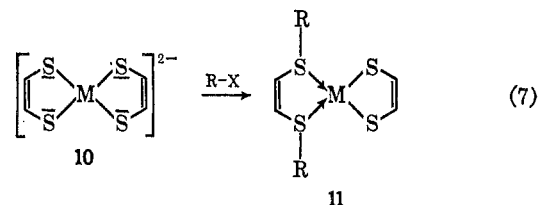
The considerable stability of the five-membered (ethylenedithiolato)metal chelate suggests that it is strongly covalent. In addition, some stabilization may result from a  $\pi$ -electron delocalization analogous<sup>17</sup> to that present in the 1,3-dithiolium cations.<sup>18,19</sup> A number of pertinent reactions of nickel dithienes are summarized in Scheme I.

or the monoanions. The sulfur atoms in the dianions were subsequently shown to be sufficiently nucleophilic to undergo reaction with alkylating agents, yielding the 1,4-bis-alkyl derivatives, a new class of remarkably stable compounds<sup>16</sup> (eq 7 and Scheme II).



### Charge Distribution and Nucleophilic Reactivity

Model calculations<sup>16</sup> of the charge distribution in species  $\text{Ni}(\text{S}_2\text{C}_2\text{H}_2)_2^{0,1-,2-}$  suggested a considerable accumulation of the negative charge on the sulfur atoms in the dianions, but not in the neutral complex



### Dithienes of Iron and Cobalt

Interpretation of the metal dithienes of the nickel group transition elements as delocalized  $\pi$ -electron systems provides the basis for our description of the more complicated derivatives of other metals. Most, if not all, neutral dithienes of iron and cobalt are probably dimeric.<sup>20-22</sup> The basic structure is **12** and was

(20) G. N. Schrauzer, V. P. Mayweg, H. W. Finck, and W. Heinrich, *ibid.*, **88**, 4604 (1966).

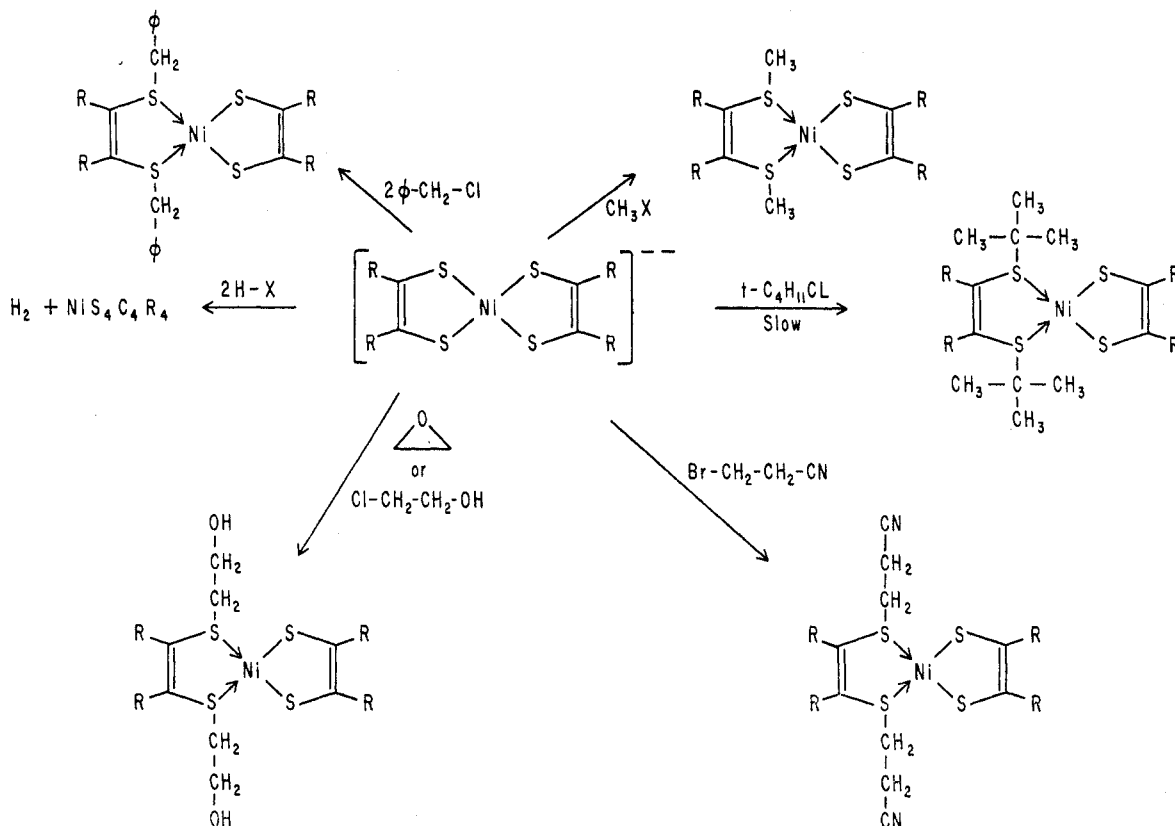
(21) A. L. Balch and R. H. Holm, *Chem. Commun.*, 552 (1966).

(22) A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968).

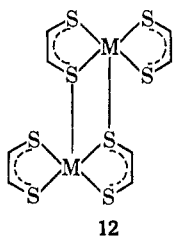
(18) E. Klingsberg, *J. Amer. Chem. Soc.*, **84**, 3410 (1962).

(19) E. Klingsberg, *ibid.*, **86**, 5290 (1964).

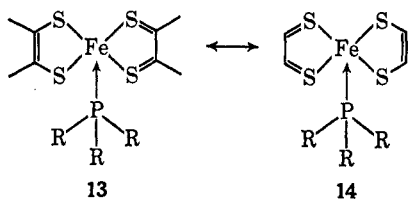
Scheme II: Alkylation of the Nickel(bisethylenedithiolato) Dianions



first observed for  $\text{Co}_2(\text{S}_2\text{C}_2(\text{CF}_3)_2)_2$ .<sup>23</sup> The monomeric dithienes in this case have not been isolated, but remarkable 1:1 adducts with phosphines exist<sup>20</sup> in which the monomeric form is stabilized. The adducts



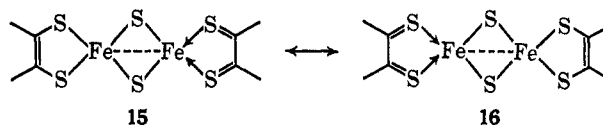
$\text{Fe}(\text{S}_2\text{C}_2\text{R}_2)_2 \cdot \text{PR}_3$  spectroscopically resemble the nickel-dithienes.<sup>20</sup> The ground state can therefore be represented by formulas **13** and **14**. Corresponding five-



coordinate 1:1 phosphine adducts of cobalt dithienes have also been synthesized.

In view of the similar metal orbital energies and ligand-metal overlap integrals, the hypothetical cobalt and iron dithiene monomers are calculated to have electronic structures similar to the neutral nickel com-

plexes. Their tendency to dimerize is presumably caused by the vacancies in the highest metal orbitals which enhance axial interactions with donor molecules. If two of the monomeric species are allowed to approach to each other so as to produce the dimers, extensive mixing of the ligand  $\pi$  and the metal orbitals between the two molecules occurs. A spin-paired ground state results, but there is evidence that a low triplet state is thermally accessible in several complexes.<sup>22</sup> Some typical reactions of the phenyl-substituted dithienes of iron are summarized in Scheme III. Of particular interest is the thermal decomposition leading to the binuclear dithiene  $\text{Fe}_2\text{S}_2(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2$ .<sup>20</sup> The same complex is also formed directly from metallic iron, sulfur, and diphenylacetylene. In this complex the ligand  $\pi$ -electron systems are delocalized across the sulfur bridges.<sup>20</sup>



### The Tris(dithienes)

The neutral tris(dithienes)  $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_3$  ( $\text{M} = \text{V}, \text{Cr}, \text{Mo}, \text{W}, \text{Re}$ ) are trigonal prismatic<sup>24-26</sup> (Figure 6)

(24) R. Eisenberg, and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 3776 (1965).

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

(26) R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2874 (1966).

(23) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

Scheme III: Some Reactions of the Phenylthiethene Complex of Iron

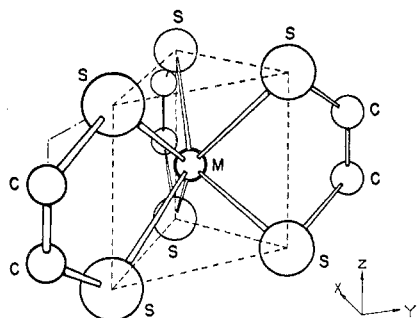
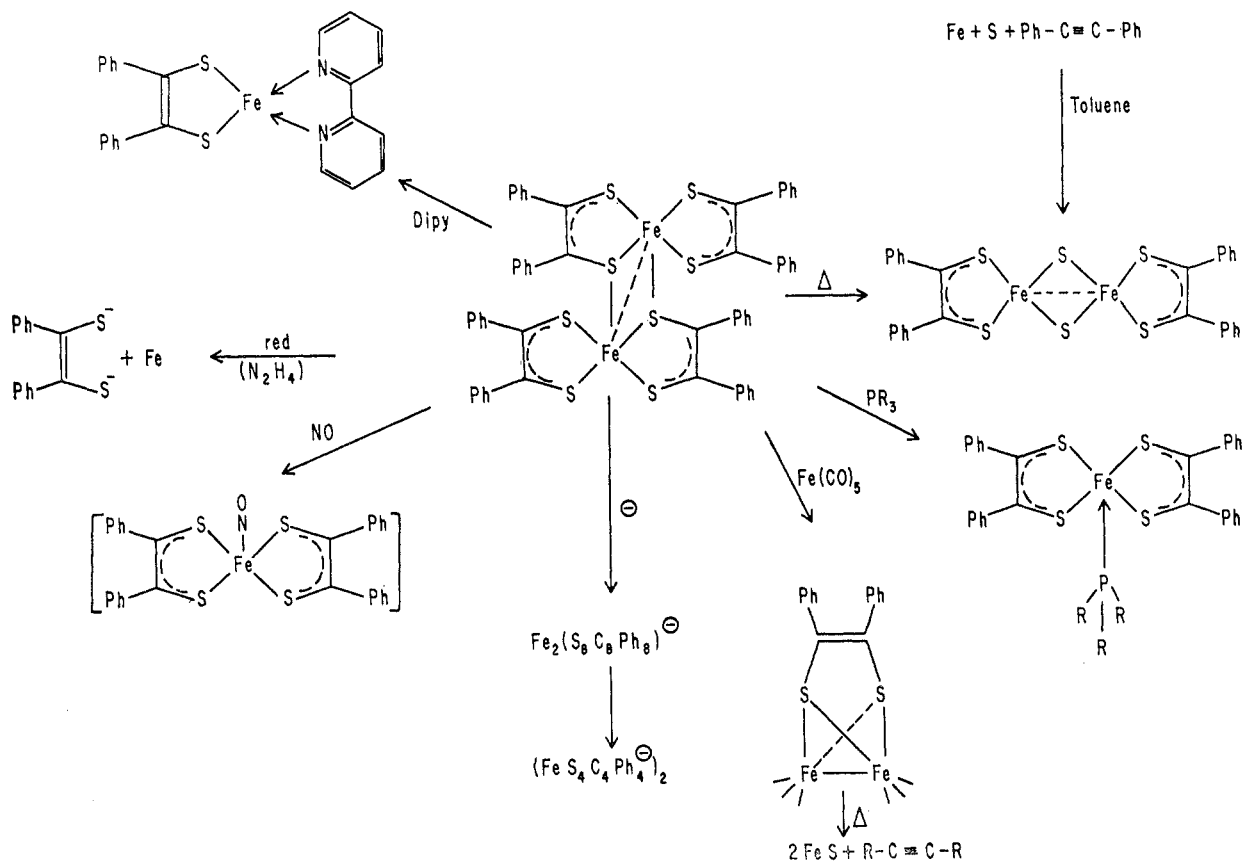
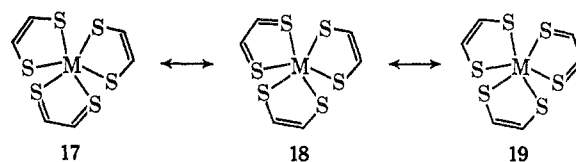


Figure 6. Idealized structure of a trigonal-prismatic dithiene complex.

and have delocalized electronic structures with features not unrelated to the planar bis(dithienes) of nickel, palladium, and platinum. The bonding situation is more complicated than in the latter, however, since  $\sigma$  and  $\pi$  interactions are no longer strictly separable. Since the C-C stretching frequencies in the complexes of Cr, Mo, and W are observed at consistently higher energy than in the planar nickel species,<sup>27</sup> a greater participation of "dithiolato" structures to the ground state is implicated. This argument is supported by group-theoretical considerations. Neglecting, for simplicity, the  $\sigma$ -bonding metal-ligand interactions, the lowest unoccupied  $\pi$  MO's of the three dithiodiketones in the prismatic arrangement transform as  $A'_2$  and  $E'$ . The  $E'$  set can be shown to interact significantly

with the metal  $p_x$  and  $p_y$  orbitals and is stabilized to about the same extent as the  $B_{1u}$  MO in the planar nickel complex. The  $A'_2$  MO, on the other hand, does not interact with any metal orbital for symmetry reasons. Its energy is therefore not appreciably altered on complex formation (Figure 7). Accordingly, four valence electrons of the metal occupy the metal-ligand-delocalized  $E'$  orbitals, a situation consistent<sup>27</sup> with the valence bond formulation



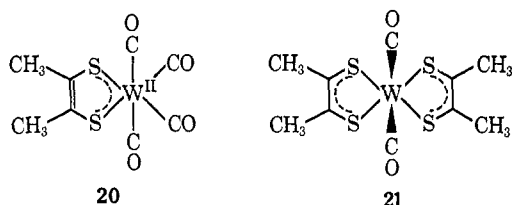
Structures in which two or three of the  $S_2C_2R_2$  groups are dithiodiketones should lead to much lower C=C stretching frequencies and could not be accommodated in any group theoretical scheme. It is therefore concluded that they contribute little, if at all. The same also applies for the structure in which all three ligands are dithiolato dianions, which would lead to improbably high formal oxidation states of the metals.

Identical conclusions were derived from the study of CO-substituted dithienes, namely  $W(S_2C_2(CH_3)_2)(CO)_4$  and  $W(S_2C_2(CH_3)_2)_2(CO)_2$ .<sup>28</sup> The tetracarbonyl derivative must be formulated essentially as the di-

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

(28) G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **88**, 5174 (1966).

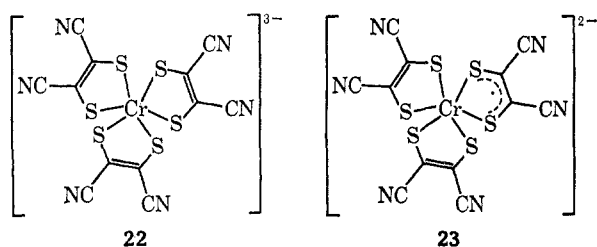
thiolate **20**, but the dicarbonyl **21** is clearly a dithiene, as follows from spectroscopic evidence.



In the neutral vanadium complexes the  $E'$  MO is believed to be occupied by three electrons rather than four. This would be in accord with infrared evidence which indicates a lower C=C stretching frequency as compared to the complexes of the group VI elements. This ground-state configuration should give rise to a Jahn-Teller distortion. The ions  $V(S_2C_2R_2)_3^-$  are predicted to have a closed-shell electronic configuration isoelectronic with the neutral group VI metal dithienes. Evidence for the highly delocalized electronic structure of the trisdithienes was also obtained through nmr measurements and a successful Friedel-Crafts-type substitution experiment.<sup>27</sup>

Several explanations for the remarkable stability of the trigonal-prismatic geometry have been advanced.<sup>27,29,30</sup> All authors agree that interligand interactions of some sort are important stabilizing factors. The trigonal-prismatic structure containing four electrons in the  $E'$  orbitals is clearly favored over  $C_3$  symmetry as it allows the placement of all electrons into two equivalent MO's. The  $E'$ -orbital stabilization is furthermore enhanced by ligand-ligand  $\pi$ - $\pi$  interactions such as shown in Figure 8. The trigonal-prismatic coordination geometry thus would seem to be closely associated with the tendency of the system to achieve a maximum amount of  $\pi$  delocalization or dithiene resonance, respectively. Recent work has shown that anionic tris(MNT) complexes have distorted octahedral structures.<sup>31</sup>

Although a detailed discussion of these anionic species must be deferred, it should be mentioned that  $Cr(MNT)_3^{3-}$  is best considered a dithiolate (**22**) rather than a dithiene. An adequate limiting formulation of its oxidation product,  $Cr(MNT)_3^{2-}$ , is **23**. The prismatic geometry is evidently not favored in the more highly reduced compounds. This is certainly in part due to the electrostatic repulsion between the ligands. In addition,



(29) E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 2956 (1966).

(30) I. Bernal and A. Sequeira, Abstracts, Association of American Crystallographers, Washington D. C., Aug 1967, cited in ref 22.

(31) E. I. Stiefel, Z. Dori, and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3353 (1967).

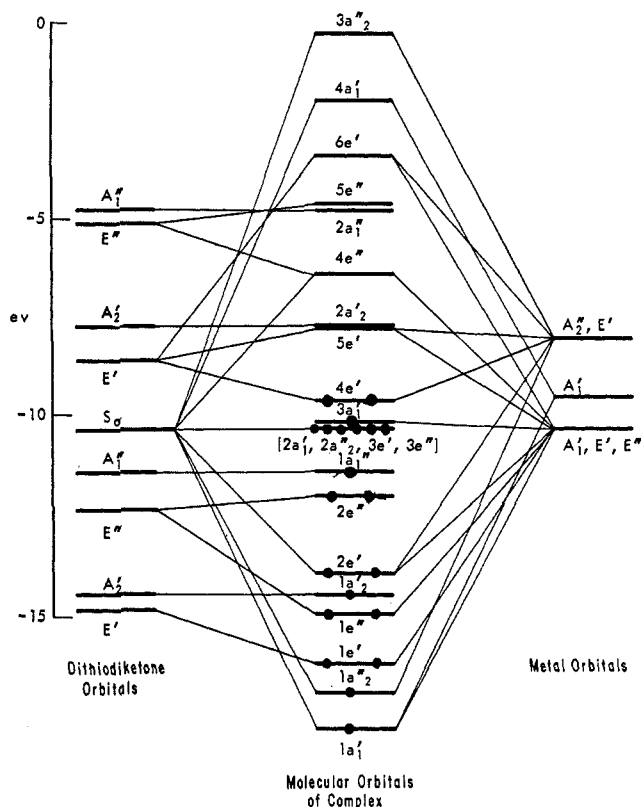


Figure 7. Schematic molecular orbital diagram of a neutral, group VI metal tris-dithiene complex,  $M(S_2C_2R_2)_3$  ( $R = H$ , alkyl, aryl); axes are given in Figure 6. Electron pairs denoted by  $\bullet$ . The MO equivalent to the  $2b_{1u}$  orbital in the planar bis-dithienes is  $4e'$ .

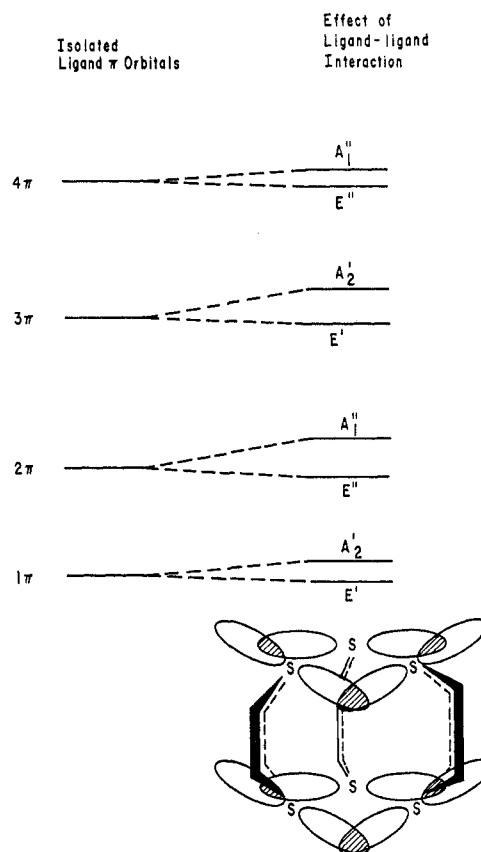


Figure 8. Effect of interligand  $\pi$  overlap onto the  $\pi$  MO's of the tris(dithiodiketone) system.



interligand  $\pi$ - $\pi$  overlap is significantly diminished in the octahedral species. Hence, the type of interaction suggested to produce "dithiene resonance" may well be the most important stabilizing factor of the prismatic geometry.

### Semiconducting Properties of Metal Dithienes

The semiconducting properties of the metal dithienes provide another striking example for the far-reaching analogy of the complexes with  $\pi$ -delocalized organic heterocyclic systems. The conductivity of organic compounds is well known to correlate with the energy difference between the highest occupied and the lowest unoccupied  $\pi$  molecular orbitals.<sup>32</sup> Since this energy difference is small in the dithienes, their conductivity is indeed much higher than that of large aromatic compounds, and in some cases even equal to that of charge-transfer complexes.<sup>33</sup>

The present Account on metal dithienes shows that while progress has been made toward the qualitative

(32) For general references see: "Organic Semiconductors," T. T. Brophy and T. W. Buttrey, Ed., The Macmillan Co., New York, N. Y., 1962.

(33) E. J. Rosa and G. N. Schrauzer, *J. Amer. Chem. Soc.*, in press.

understanding of the bonding situation, considerable efforts are still necessary to explain finer details of the electronic structures in numerous individual compounds of this type. Will other unsaturated sulfur ligands form transition metal derivatives with dithiene-type properties? On the basis of group theoretical considerations and the distinction of the ligands into "even" and "odd" systems, this author predicted that the chelates of the latter will not possess the unusual chemical properties, stabilities, and structures of the dithienes.<sup>34</sup> In the meantime sufficient data have become available on transition metal chelates of dithiocarboxylic acids (*e.g.*, dithiobenzoic acid),<sup>34</sup> of 2,4-pentanedithione,<sup>35</sup> and of 1,2-dithiotropolone<sup>36</sup> which indicate that this prediction is probably correct. The metal dithienes thus form a group of compounds whose properties are strongly determined by the topology of the ligands.

(34) (a) J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *ibid.*, **90**, 2734 (1968); (b) C. Furlani and M. L. Luciani, *Inorg. Chem.*, **7**, 1586 (1968); (c) M. Bonamico and G. Dessy, *Chem. Commun.*, 483 (1968).

(35) (a) R. L. Martin and I. M. Stewart, *Nature*, **210**, 522 (1966); (b) R. Beckett and B. F. Hoskins, *Chem. Commun.*, 909 (1967).

(36) C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 6884 (1968).

## Chemiluminescence from Concerted Peroxide Decomposition Reactions<sup>1</sup>

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Chemiluminescence, the emission of light from chemical reactions at ordinary temperatures in the absence of flame, has attracted interest since man first became aware of the fireflies and other luminescent organisms in his environment. A variety of reactions, inorganic and organic as well as biochemical, are known to emit light, and although most chemiluminescent reactions are dim and inefficient, chemiluminescence has been the subject of considerable investigation.<sup>2</sup>

(1) Research in the author's laboratory has been supported in part by the Advanced Research Projects Agency under contract to the Office of Naval Research, by the Naval Ordnance Laboratory, and by the U. S. Army, Picatinny Arsenal.

(2) T. Goto and Y. Kishi, *Angew. Chem. Intern. Ed. Engl.*, **7**, 407 (1968); F. McCapra, *Quart. Rev. (London)*, **20**, 485 (1966); K. D. Gundermann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 566 (1965); V. I. Papisova, V. Y. Shlyapintokh, and R. F. Vasl'ev, *Russ. Chem. Rev.*, **34**, 599 (1965); *Photochem. Photobiol.*, **4**, 957 (1965); H. H. Seliger and W. D. McElroy, "Light: Physical and Biological Action," Academic Press, New York, N. Y., 1965; E. J. Bowen, *Pure Appl. Chem.*, **9**, 473 (1964); "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins Press, Baltimore, Md., 1961; E. N. Harvey, "A History of Luminescence," The American Philosophical Society, Philadelphia, Pa., 1957; H. Eyring, F. P. Johnson, and M. J. Polissar, "The Kinetic Basis for Molecular Biology," John Wiley & Sons, Inc., New York, N. Y., 1954, p 162; A. Zweig, *Advan. Photochem.*, in press.

In addition to the scientific interest customary for unusual phenomena, chemiluminescence has potential importance as a practical light source. In principle, one molecule of reactant can generate one quantum of light, and in a perfectly efficient process 1 mol of reactant would generate 1 mol of quanta or 1 einstein. It is easily calculated on that basis that 1 lb of perfectly efficient chemiluminescent material might provide 67,000 lumen hr of light, equivalent to the output of a 40-W incandescent bulb operating for 6 days.

This practical potential has stimulated fundamental chemiluminescence research in this laboratory since 1961. Aside from the enzymatic firefly process (approximately 0.88 einstein mol<sup>-1</sup> or 88%),<sup>3</sup> chemiluminescent reactions known at that time were poorly efficient, providing quantum yields on the order of 1% at best. It was clear that practical chemiluminescence would require a new reaction deliberately designed to accommodate the specific factors inherent to efficiency. This Account surveys certain aspects of an effort to establish efficiency criteria for chemiluminescence.

(3) H. H. Seliger and W. D. McElroy, *Arch. Biochem. Biophys.*, **88**, 136 (1960).