1971

Relative Chalcogen Donor Properties in Transition Metal Complexes.

Eugene D. Schermer
Louisiana State University and Agricultural & Mechanical College

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RELATIVE CHALCOGEN DONOR

PROPERTIES IN TRANSITION METAL COMPLEXES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

by

Eugene D. Schermer
M.S., Oregon State University, 1962

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### TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>v</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vi</td>
</tr>
<tr>
<td>ABBREVIATIONS USED FOR HYDROCARBON GROUPS</td>
<td>vii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>viii</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. EXPERIMENTAL - GENERAL</td>
<td>14</td>
</tr>
<tr>
<td>1. Materials</td>
<td>14</td>
</tr>
<tr>
<td>2. Instrumentation</td>
<td>16</td>
</tr>
<tr>
<td>3. General Preparative Technique</td>
<td>17</td>
</tr>
<tr>
<td>4. Analysis</td>
<td>19</td>
</tr>
<tr>
<td>III. EXPERIMENTAL - SYNTHETIC</td>
<td>20</td>
</tr>
<tr>
<td>1. Reactions of ( \Pi )-Cyclopentadienyliron Dicarbonyl with Diphenyl Dichalconides</td>
<td>20</td>
</tr>
<tr>
<td>A. Preparation of ( \Pi )-CpFe(CO)(_3)TePh</td>
<td>20</td>
</tr>
<tr>
<td>B. Preparation of a Pair of Dinuclear Isomers, ( [\Pi \text{-CpFe(CO)TePh}]_2 )</td>
<td>21</td>
</tr>
<tr>
<td>C. Preparation of ( \Pi )-CpFe(CO)(_3)SePh</td>
<td>22</td>
</tr>
<tr>
<td>D. Preparation of a Pair of Dinuclear Isomers, ( [\Pi \text{-CpFe(CO)SePh}]_2 )</td>
<td>23</td>
</tr>
<tr>
<td>E. Reactions of ( [\Pi \text{-CpFe(CO)(_3)}]_2 ) with Diphenyl Disulfide</td>
<td>24</td>
</tr>
<tr>
<td>2. Reactions of Triirondodecacarbonyl with Diphenyl Dichalconides</td>
<td>25</td>
</tr>
<tr>
<td>A. Formation of ( [\text{Fe(CO)}_3\text{TePh}]_2 )</td>
<td>25</td>
</tr>
<tr>
<td>B. Formation of ( [\text{Fe(CO)}_3\text{SePh}]_2 )</td>
<td>26</td>
</tr>
<tr>
<td>3. Reactions of Dodecacarbonyl Triruthenium with Diphenyl Dichalconides</td>
<td>27</td>
</tr>
<tr>
<td>A. Preparation of Dinuclear ( [\text{Ru(CO)}_3\text{TePh}]_2 ) and Polymeric Derivatives of Formula ( [\text{Ru(CO)}_3\text{TePh}]_n )</td>
<td>27</td>
</tr>
<tr>
<td>B. Preparation of Dinuclear ( [\text{Ru(CO)}_3\text{TePh}]_2 ) and Polymeric Derivatives of Formula ( [\text{Ru(CO)}_3\text{SePh}]_n )</td>
<td>29</td>
</tr>
<tr>
<td>4. Reactions of ( \Pi )-Cyclopentadienylmolybdenum Tricarbonyl Dimer with Diphenyl Dichalconides</td>
<td>32</td>
</tr>
<tr>
<td>A. Preparation of ( \Pi )-CpMo(CO)(_3)SePh</td>
<td>32</td>
</tr>
<tr>
<td>B. Evidence of Additional Carbonylated Products in the Reaction of Diphenyl Diselenide with ( [\Pi \text{-CpMo(CO)(_3)}]_2 )</td>
<td>33</td>
</tr>
</tbody>
</table>
C. Extended Reaction of Diphenyl Ditelluride with \([\Pi-CpMo(CO)_3]_2\)............................ 34
D. Extended Reactions of Diphenyl Disulfide with \([\Pi-CpMo(CO)_3]_2\)....................... 35

5. Reactions of \(\Pi\)-Cyclopentadienyltungsten Hydride with Diphenyl Dichalconides.......................... 36
   A. Preparation of Dinuclear \([\Pi-CpW(CO)_3SPh]_2\) and Other Carbonylated Products.............. 36
   B. Reactions of Diphenyl Diselenide with \(\Pi-CpW(CO)_3H\)....................................... 37
   C. Formation of \(\Pi-CpW(CO)_3SPh\) and Other Carbonylated Products............................ 39

IV. RESULTS AND DISCUSSION........................................ 42
   1. Formulations.............................................. 42
      A. Monomeric \(\Pi\)-Cyclopentadienyliron Dicarbonyl Phenylchalconides............................ 42
      B. Isomeric Dimers \([\Pi-CpFe(CO)EPh]_2\)....................................... 47
      C. Chalcogen Bridged Iron Carbonyl Dimers........................................ 50
      D. Dinuclear Chalcogen Bridged Ruthenium Carbonyls.................................... 60
      E. Polymeric Chalcogen Derivatives of Triruthenium Dodecacarbonyl.......................... 63
      F. Monomeric Chalconides of Tungsten and Molybdenum........................................ 67
      G. Dinuclear Tungsten-Tellurium Complex.................................................. 69
      H. Additional Carbonylated Products Containing Chalcogen Bonds with Tungsten or Molybdenum............. 70
   2. Relative Chalcogen Donor Properties........................................ 80

V. SELECTED BIBLIOGRAPHY........................................ 85

VI. VITA.............................................................. 89
## LIST OF TABLES

<table>
<thead>
<tr>
<th>I. Spectral Data on Π-Cyclopentadienyliron Carbonyl Dimers</th>
<th>43</th>
</tr>
</thead>
<tbody>
<tr>
<td>II. Infrared Spectra of Some Π-Cyclopentadienyliron Dicarbonyl Derivatives, Π-CpFe(CO)$_2$X</td>
<td>45</td>
</tr>
<tr>
<td>III. Comparative Analytical Data</td>
<td>51</td>
</tr>
<tr>
<td>IV. Carbonyl Stretching Frequencies for Compounds of Formula [Fe(CO)$_3$X]$_2$</td>
<td>54</td>
</tr>
<tr>
<td>V. Analytical and Other Data on Compounds of Formula [M(CO)$_3$EPH]$_2$</td>
<td>55</td>
</tr>
<tr>
<td>VI. Mass Spectra Relative Abundance of Fe$_2$(CO)$_6$EP$_2$R$_2$</td>
<td>57</td>
</tr>
<tr>
<td>VII. Infrared Spectra of Some Ruthenium Carbonyl Derivatives</td>
<td>61</td>
</tr>
<tr>
<td>VIII. Spectral Data on Mo and W Monomers and Dimers</td>
<td>68</td>
</tr>
<tr>
<td>IX. Infrared Spectra of Three Series of Carbonylated Products from Reactions of Diphenyl Dichalconides with Cyclopentadienyl Metal Carbonyls</td>
<td>76</td>
</tr>
<tr>
<td>X. New Compounds Prepared in This Work</td>
<td>81</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Selected Reactions of Triiron Dodecarbonyl</td>
<td>6</td>
</tr>
<tr>
<td>2.</td>
<td>Selected Reactions of Π-Cyclopentadienyl Dicarbonyl Dimer</td>
<td>7</td>
</tr>
<tr>
<td>3.</td>
<td>Selected Reactions of Π-Cyclopentadienyltungsten Tricarbonyl Hydride</td>
<td>8</td>
</tr>
<tr>
<td>4.</td>
<td>Infrared Spectra of Π-CpFe(CO)$_2$EPh</td>
<td>46</td>
</tr>
<tr>
<td>5.</td>
<td>Planar Configurations for [Π-CpFe(CO)EPh]$_2$</td>
<td>48</td>
</tr>
<tr>
<td>6.</td>
<td>Infrared Spectra of [Π-CpFe(CO)SEPh]$_2$</td>
<td>52</td>
</tr>
<tr>
<td>7.</td>
<td>Infrared Spectrum of [Π-CpFe(CO)TePh]$_2$</td>
<td>53</td>
</tr>
<tr>
<td>8.</td>
<td>Mass Spectrum of [Fe(CO)$_3$TePh]$_2$</td>
<td>58</td>
</tr>
<tr>
<td>10.</td>
<td>Infrared Spectra of [Ru(CO)$_3$EPh]$_2$</td>
<td>64</td>
</tr>
<tr>
<td>11.</td>
<td>Infrared Spectra of [Ru(CO)$_2$(EPh)$_2$]$_n$</td>
<td>65</td>
</tr>
<tr>
<td>12.</td>
<td>Infrared Spectrum of [Π-CpW(CO)$_3$TePh]$_2$</td>
<td>71</td>
</tr>
<tr>
<td>13.</td>
<td>Some Possible Configurations of Complexes of Formula [Π-CpM(CO)$_2$EPh]$_2$</td>
<td>75</td>
</tr>
<tr>
<td>14.</td>
<td>Two Possible Structures of Trinuclear [Π-CpM(CO)EPh]$_3$</td>
<td>77</td>
</tr>
<tr>
<td>15.</td>
<td>Infrared Spectrum of Unknown Complex (Series III) from Extended Reactions of Π-CpW(CO)H and Ph$_2$Se$_2$</td>
<td>79</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>Methyl</td>
<td></td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
<td></td>
</tr>
<tr>
<td>i-Pr</td>
<td>iso-Propyl</td>
<td></td>
</tr>
<tr>
<td>n-Bu</td>
<td>normal-Butyl</td>
<td></td>
</tr>
<tr>
<td>s-Bu</td>
<td>secondary-Butyl</td>
<td></td>
</tr>
<tr>
<td>t-Bu</td>
<td>tertiary-Butyl</td>
<td></td>
</tr>
<tr>
<td>η-Cp</td>
<td>η-Cyclopentadienyl</td>
<td></td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
<td></td>
</tr>
<tr>
<td>Bz</td>
<td>Benzyl</td>
<td></td>
</tr>
</tbody>
</table>
Reactions of diphenyl dichalconides with several π-cyclopentadienylmetal and metal carbonyls were investigated. Several new organometallic compounds were prepared and their properties studied in an effort to compare the donor properties of sulfur, selenium, and tellurium in transition metal complexes.

The reaction of [(π-CpFe(CO)₂)₂ (Cp = cyclopentadienyl) with Ph₂E₂ (Ph = phenyl; E = Se, Te) yields monomeric products π-CpFe(CO)₂EPh which may be thermally decomposed to two isomers each of the dinuclear complexes [π-CpFe(CO)EPh]₂. The relative ease of dimerization of monomers and tendency toward isomerization from the less stable to the more stable dinuclear isomer were studied and compared for donor atoms S, Se, and Te.

Reactions of metal carbonyls, M₃(CO)₁₂ (M = Fe, Ru) with diphenyl dichalconides yield chalcogen bridged dinuclear complexes [M(CO)₃EPh]₂ (M = Ru, Fe; E = Se, Te). Comparisons are made with these compounds and their previously reported sulfur analogues. Major products from the reactions of Ru₃(CO)₁₂ with E₂Ph₂ were two types of polymers with the general formula [Ru(CO)₂(EPh)₂]ₙ (E = Se, Te). The types were distinguished by molecular weight measurements, one having 6-7 units per molecule and the other about 14 units per molecule.

Monomeric compounds of formula π-CpM(CO)₃EPh (M = Mo; E = Se and M = W, E = S) were characterized. These complexes complete a series of molybdenum and tungsten compounds that have been prepared in this laboratory. The dinuclear complex [π-CpW(CO)₂TePh]₂ was prepared and its chemistry compared with the previously reported molybdenum analogue.
addition to these monomers and dimer, three series of carbonylated products have been isolated from reactions of \( \Pi\text-P\text{cp}W(\text{CO})_3\text{H} \) and \([\Pi\text-P\text{cp}\text{Mo}(\text{CO})_3]\_2\) with diphenyl dichalconides. Tentative formulations for two of the series are \([\Pi\text-P\text{cp}M(\text{CO})_2\text{EPh}]_2\) (\(M = \text{Mo}, \text{E} = \text{Se} \) and \(M = \text{W}; \text{E} = \text{S}, \text{Se}, \text{Te}\)) and \([\Pi\text-P\text{cp}M(\text{CO})\text{EPh}]_3\) (\(M = \text{Mo}, \text{W}; \text{E} = \text{S}, \text{Se}\)).
INTRODUCTION

Considerable attention has been devoted in the past decade to various sulfide complexes with carbonylcyclopentadienyl metal and carbonyl metal skeletons.¹ The rapidly expanding literature on the subject of sulfur-containing metal carbonyls includes preparative work as well as structural and mechanistic studies. The situation is much different, however, for heavier members of the chalcogen family. Only limited investigations have been carried out involving selenium as a donor atom toward transition metals, and there are very few known complexes containing tellurium-transition metal bonds.

Among the elements generally considered as donors in transition metal complexes it is only these heavier members of group VIA that have suffered this apparent neglect. Recent surveys² mention significant numbers of papers reporting preparative and structural studies dealing with donor properties of groups IVA, VA, VIIA, and sulfur in group VIA. Possibly the offensive nature of potential ligands containing selenium and tellurium has deterred coordination chemists from considering these elements in their experimental work. The diphenyl dichalconides are, however, reasonably stable, non-volatile, crystalline compounds that do not possess the objectionable odor characteristic of seleno and telluro mercaptans and dialkyl or diaryl selenides and tellurides. Furthermore, the considerable body of information that has accumulated relative to reactions of diphenyl disulfide with transition metal substrates can serve as a source for comparison of relative donor properties of similar selenium and tellurium ligands.

¹
²

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Until the work begun in this laboratory by Tillay, the known complexes containing a tellurium-transition metal bond were primarily due to work by Chatt and to Hieber. Chatt's group prepared chloro-bridged complexes of the following type:

\[
\begin{array}{c}
\text{L} \\
\text{M} \\
\text{Cl} \\
\text{M} \\
\text{Cl} \\
\text{L}
\end{array}
\]

\[M = \text{Pd, Pt; } L = R_2S, R_2Se, R_2Te\]
\[R_3P, R_3As, R_3Sb\]
\[R = \text{Et, n-Pr, N-Bu, Ph}\]

Relative stabilities of the platinum complexes were determined to be in the order of donor atoms, \(\text{P} > \text{As} > \text{S} > \text{Se} > \text{Te} > \text{Sb}\). A reversal of the order of stability of \(R_2Se\) and \(R_2Te\) ligands with palladium complexes was suggested by Chatt to be due to the relative size of the orbitals involved in sigma bonding, Se comparing with Pd, and Te with Pt.

Tellurium containing complexes reported by Hieber are of two general types. The first includes the binuclear complexes \([\text{Fe(CO)}_3\text{Te(p-C}_6\text{H}_4\text{OCH}_3)]_2\) and \([\text{Mn(CO)}_4\text{TePh}]_2\). The second type were trinuclear complexes of the form \(\text{Fe}_3(\text{CO})_9\text{X}_2\) \((X = \text{S, Se, Te})\). A study of substitution reactions of this second type has recently been reported. A substantial difference was noted in the reactions of the tellurium adduct compared with the other chalcogen derivatives. With sulfur or selenium-bridged complexes, a substitution reaction occurred,

\[
\text{Fe}_3(\text{CO})_9\text{X}_2(X = \text{S, Se}) + \text{PR}_3 \rightarrow \text{Fe}_3(\text{CO})_9\text{X}_2\text{PR}_3 + \text{CO}
\] (1)
However, with tellurium as the bridging atom, an addition complex was the first isolated product.

\[
\text{Fe}_3(\text{CO})_9\text{Te}_2 + \text{PR}_3 \rightarrow \text{Fe}_3(\text{CO})_9\text{Te}_2\text{PR}_3
\] (2)

It is argued that a larger and more electropositive tellurium atom can act as a weak Lewis acid in coordinating with the basic ligand, but with the sulfur and selenium complexes, a ligand preferentially substitutes a carbonyl group.

In his Ph.D. Dissertation, Tillay\(^3\) reported the preparation of several diphenyl dichalconide derivatives of \([\Pi-\text{CpMo(CO)}_3]_2\), \([\Pi-\text{CpW(CO)}_3\text{H}]_2\), and \([\Pi-\text{CpV(CO)}_4]_2\). Compounds either well characterized or identified in solution by their infrared spectra include monomers of the form \([\Pi-\text{CpM(CO)}_3\text{EPh}]_2\) (M = Mo, W; E = S, Se, Te), dinuclear complexes of the form \([\Pi-\text{CpM(CO)}_2\text{EPh}]_2\) (M = Mo, W; E = Se, Te) and totally decarbonylated species of general formula \([\Pi-\text{CpM(EPh)}_2]_x\) (M = Mo, W, V; E = S, Se, Te). The stabilities of complexes in this study were reported to be in the order of donor atoms: Te > Se > S.

The existence of several of the complexes mentioned in the above paragraph was inferred from spectral evidence without the compounds being isolated. Also, evidence existed for other carbonylated products in reactions of \([\Pi-\text{CpMo(CO)}_3]_2\) and \([\Pi-\text{CpW(CO)}_3\text{H}]_2\) with diphenyl dichalconides. The initial efforts of the research reported in this Dissertation were directed toward the isolation and characterization of these compounds with a view toward gaining a better understanding of the relative donor properties of chalcogens in transition metal complexes. To expand the comparisons, reactions of other transition metal carbonyl substrates

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including triiron dodecarcarbonyl, triruthenium dodecacarbonyl and cyclopentadienyliiron dicarbonyl dimer with diphenyl dichalconides were studied under conditions that allow for monitoring the appearance of products.

Complexes of soft "class b" metals in low oxidation states were chosen to correspond with the soft nature\textsuperscript{11} of the phenylchalconide ligands. The stabilization of low oxidation states of metal complexes by cyclopentadienyl and carbonyl ligands is well known;\textsuperscript{12} the cyclopentadienyl ring acts as a non-labile stabilizing ligand and the carbonyl groups are able to accept "extra" electron density through back bonding.

An illustration of the softening of a transition metal by cyclopentadienyl ligands is offered in the reports\textsuperscript{13,14} of compounds of formula \((\Pi\text{-Cp})_2M(SR)_2\) \((M = \text{Ti or Zr})\). If one considers the Ti(IV) and Zr(IV) central atoms in the above compounds to be formally void of "d" electrons, they would be classified as type "A" metals using the Chatt\textsuperscript{15} designation or as hard acids according to Pearson.\textsuperscript{16} Accordingly, bonding to a "hard" second period donor atom would be expected to be favored over bonding to a third row atom. However, the dimercaptide complexes were easily formed and attempts to synthesize the corresponding diphenoxide product were unsuccessful. Evidently, the \(\Pi\)-bonding cyclopentadienyl ligands sufficiently soften the central metal atom such that bonding with sulfur is preferred to the "harder" oxygen-containing ligands.

In addition to their "soft" nature the metal carbonyls offer a particular advantage toward comparisons of donor properties of ligands in that the carbonyl stretching frequencies are especially sensitive to
electronic factors on the central metal atom.\textsuperscript{17} This feature makes infrared spectroscopy a useful method for monitoring the progress of reactions and identifying products.

A number of reported reactions of metal substrates used in this work are illustrated in Figures 1-3. Examples chosen are for compounds whose structural formulas are reasonably well established.

The reactions of triiron dodecacarbonyl with sulfur-containing ligands have been extensively investigated.\textsuperscript{18-23} The tendency for formation of dinuclear rather than monomeric products is accounted for by the existence of a rather strong metal-metal bond.\textsuperscript{24}

Hieber and Beck\textsuperscript{19} inferred the structure of \([\text{Fe(CO)}_3X]_2\) (\(X = \text{S, Se, SET, SEt}\)) from infrared and nmr spectra and dipole moment measurements, to involve a non-planar four-membered ring of metal and bridging atoms. This structure, which has a bent metal-metal bond, was confirmed by an x-ray diffraction study for the complex with \(X = \text{SET}\).\textsuperscript{24} Isomers of the dimer with methyl sulfide bridges have been isolated and characterized as either syn or anti with respect to the alkyl groups attached to the bridging atoms.\textsuperscript{24,25} Mass spectra have been reported for several sulfur bridged iron carbonyls \([\text{Fe(CO)}_3SR]_2\) (\(R = \text{Me, Et, Ph, n-Bu}\)).\textsuperscript{26} The strength of the metal-metal and metal-sulfur bonds are reflected in the fact that the base peaks on these spectra represent the \(\text{Fe}_2\text{S}_2\text{R}_2^+\) ion.

An interesting trinuclear iron carbonyl chalconide structure has been recently proposed\textsuperscript{27} for the product obtained by irradiating \(\text{Fe(CO)}_5\) and \(\text{Ph}_2\text{E}_2\) (\(E = \text{S, Se}\)) in pentane. Far infrared spectra suggest retention of chalcogen-chalcogen bonds in the complex and two chemical shifts for phenyl protons are observed in the nmr spectra.
Figure 1. Selected Reactions of Triiron Dodeca carbonyl.
\[
\text{Fe}_3(\text{CO})_{12} \xrightarrow{RSCN \quad R = \text{Me}, \text{Bz}} \quad \text{R}_2\text{S} \xrightarrow{R = \text{Me}, \text{Et}} \quad \text{RSNH} \xrightarrow{R = \text{Me}, \text{Et}, \text{t-Bu}, \text{Ph}} \quad \text{R}_2\text{S}_2 \xrightarrow{R = \text{Et}, \text{i-Pr}, \text{Ph}} \quad [\text{Fe(CO)}_3\text{SR}]_2
\]
Figure 2. Selected Reactions of η-Cyclopentadienyliiron Dicarbonyl Dimer.
Figure 3. Selected Reactions of η-Cyclopentadienyltungsten Tricarbonyl Hydride.
These data have prompted Hieber, et. al. to suggest the following structure.\textsuperscript{27}

Other trimeric sulfur bridged iron carbonyls have recently been reported by DeBeer and Haines.\textsuperscript{28} Reacting Fe\textsubscript{3}(CO)\textsubscript{12} with alkylthiols yields one of two trinuclear structures.

\textbf{R} = t-Bu

\textbf{R} = i-Pr, s-Bu

Although these rather novel structures have not been unequivocally established, the possibility of their existence extends considerably the scope of metal carbonyl compounds with chalcogen bridges.

Cyclopentadienylironcarbonyl complexes with sulfur ligands are well known.\textsuperscript{34} Monomeric compounds of the form $\pi$-CpFe(CO)\textsubscript{2}SR\textsuperscript{22,23,29-32} were first isolated by King\textsuperscript{23} and shown to lose CO and form dinuclear complexes of the form $[\pi$-Cp(CO)SR]$\textsubscript{2}$. When the \textbf{R} group in the above monomers is a perfluorocarbon (i.e., C\textsubscript{6}F\textsubscript{5}\textsuperscript{30} or CF\textsubscript{3}\textsuperscript{32}) dimerization...
does not occur, even at pyrolysis temperatures. The failure to dimerize was suggested to be due to the reduced nucleophilicity of the potential bridging atoms with strong electron withdrawing groups attached. Thus, the sulfur in $\text{C}_6\text{F}_5\text{S}$ is a weaker base and poorer nucleophile toward substitution of a carbonyl than is the sulfur in $\text{C}_6\text{H}_5\text{S}$.

Preparation of monomeric species as well as the subsequent dimerizations are illustrated in Figure 2. Irradiation or heating of the monomer gave a mixture of isomeric dimers for the reaction:

$$2\text{H-CpFe(CO)}_2\text{SMe} \rightarrow [\text{H-CpFe(CO)SMe}]_2 + 2\text{CO}. \quad (3)$$

One isomer, distinguished by its nmr spectrum, is less stable thermodynamically than the other into which it can be converted by refluxing in benzene. A kinetic study of this isomerization has been carried out and has shown the process to be largely intramolecular. Only 16% cross-product occurred when an equimolar mixture of unstable isomers containing phenylsulfide and p-tolylsulfide ligands were heated.

An x-ray diffraction study of the more stable isomer of $[\text{H-CpFe(CO)SPh}]_2$ establishes the cis-configuration with a slightly puckered Fe-S-Fe-S ring. The diamagnetism of this compound as well as an Fe-Fe distance of 3.29 Å indicates absence of a bent metal-metal bond of the type observed in $[\text{Fe(CO)}_3\text{SeEt}]_2$.

Dodecacarbonyltriruthenium is a trimeric tetracarbonyl $[\text{Ru(CO)}_4]_3$ with a molecular structure involving a triangle of metal atoms and terminal carbonyl groups. The discovery of an easy synthesis of this compound has prompted an active investigation of its chemistry. The report by Johnson et al. of the reaction with thiols to yield
[Ru(CO)₃SR]₂ and a polymer [Ru(CO)₂(SR)₂]ₙ (R = Me, Et, n-Br, or Ph), and the report by Cetini et al. of reactions with R₂S₂ (R = Et or Ph) to yield a dimer and four different polymeric products suggests that analogous compounds of selenium and tellurium might be prepared. The interest in preparing these analogous compounds is generated not only from the potential comparisons of chalcogen donor properties, but also there is appeal in comparing a third period transition metal complex with a similar complex of a fourth period metal. Of particular significance is the number of Ru complexes that have been reported with retention of metal-metal bonds. The increasing tendency toward polymerization of ruthenium-sulfur complexes as compared to iron-sulfur complexes has been observed.

Monomeric complexes of the type Ru(CO)₄X₂ (X = H, halogen, or R₃Sn) have been reported. The monomer Ru(CO)₄PPh₃ was formed only under CO pressure and additional carbonyl could be replaced to yield Ru(CO)₃(PPh₃)₂. No monomer was identified, however, in reactions of sulfur-containing ligands with Ru₃(CO)₁₂. On the other hand, polymeric complexes have been formed with halogens, thiols, diphenyl disulfide, and moist nitric oxide. The variety of possible products of reactions between Ru₃(CO)₁₂ and diphenyl diselenide or diphenyl ditelluride increase the incentive for inclusion of these reactions in this study.

There are numerous reports of monomeric compounds of the type Τ-CpM(CO)₃X (M = Mo or W) [X = halogen, hydrogen or Me; SnCl(Me₃)₂, Ge(Ph)₃ or Sn(Ph)₃, CH₃SCH₂; SC₆H₁₃; SPh, SePh or TePh. It is of interest in comparing the donor properties of chalcogen ligands to appraise the relative stability of monomeric products. Tillay has...
done this for a portion of the above series where $X = EPh$ ($E = S, Se, Te$). However, the monomers $M = W, E = S$ and $M = Mo, E = Se$ have not previously been isolated and characterized, and therefore these preparations were included in the present work.

Dinuclear complexes of the type $[\Pi-CpM(CO)_2X]_2$ include the compounds with $M = Mo, X = SMe$ \textsuperscript{50} or $TePh$ \textsuperscript{3} and infrared evidence suggested the existence of $M = Mo, X = SePh$, and $M = W, X = TePh$.\textsuperscript{3} Attempts to prepare the remaining members of the series of dimers with phenylchalconide bridges will be discussed in later sections.

Of greater concern to the present work is the possible existence of trinuclear or even higher order complexes that might be formed in reactions of diphenyl dichalconides with $[\Pi-CpMo(CO)_3]_2$ and $\Pi-CpW(CO)_3H$. Infrared spectra of samples, taken from this type of reaction mixture, revealed the presence of carbonylated species other than the previously mentioned monomers and dimers.\textsuperscript{3} There is precedence for the existence of cluster type complexes in the reports of a trinuclear product in reactions of $[\Pi-CpMo(CO)_3]_2$ with $P_2R_4$ \textsuperscript{51} and poly-nuclear complexes of the type $[M(CO)_3ER]_n$ ($M = Mn, Re; E = S, Se; R = Me, Ph$)\textsuperscript{52,53} reported originally to be trimers but shown later to be tetramers by mass spectroscopy\textsuperscript{54} and analysis of combinations of fundamental infrared absorptions.\textsuperscript{55}

Several types of reactions that have led to an alkyl or aryl chalconide bond with a transition metal are illustrated in Figures 1-3. Other methods that have been successful include replacement of halide in reactions with thiols such as.\textsuperscript{56}
Metal carbonyl hydrides react with alkyl or aryl thiols to yield complexes of types already mentioned.\textsuperscript{58,59}

Of the possible ligand starting materials that could be used in the present work, the diphenyl dichalconides were selected because of their availability and stability and, as already mentioned, they are less offensive in the laboratory than other potential sulfur, selenium, and tellurium ligands.
EXPERIMENTAL - GENERAL

1. Materials

Known compounds that required preparation included \( \Pi \)-cyclopentadienylmolybdenum tricarbonyl dimer, \( \Pi \)-cyclopentadienyltungsten tricarbonyl hydride, and \( \Pi \)-cyclopentadienylmolybdenum tricarbonyl iodide. The preparation of \( [\Pi \text{-CpMo(CO)}_3]_2 \) is described by King\textsuperscript{60} and proceeds smoothly if certain precautions are observed. Into a 250 ml round-bottom flask fitted with welded stopcock for nitrogen inlet and a straight reflux condenser, was placed 150 ml dicyclopentadiene and 25 g molybdenum hexacarbonyl. The system was purged of air and a gentle stream of nitrogen allowed to flow through the flask and out the condenser. An oil bath on a magnetic stirrer-hot plate was used to maintain a reaction temperature of about 130\textdegree{} C for approximately 24 hours. Completeness of the reaction was evidenced by the disappearance of white crystalline \( \text{Mo(CO)}_6 \) which sublimes onto the lower portion of the condenser and must be periodically scraped back into the reaction flask. Too high reaction temperature causes dicyclopentadiene to polymerize. Too long reaction time also leads to this brown intractable polymer, whereas insufficient reaction time will result in a very poor yield. Unfortunately, all of these above hazards were experienced before a successful reaction was completed.

After cooling, the crude product was collected on a filter, washed several times with hexane and placed in a sublimer at 50\textdegree{} C and 0.1 mm Hg for several hours. The sublimation removes residual molybdenum hexacarbonyl. A yield of about 50\% was somewhat less than the maximum suggested.
\( \Pi \)-Cyclopentadienyltungsten tricarbonyl hydride, \( \Pi \text{-Cp(CO)}_3\text{H} \), was prepared by the method of King.\(^{61}\) Sodium cyclopentadienide was prepared by adding freshly cracked cyclopentadiene drop-wise to a sodium sand in very dry tetrahydrofuran. The sodium sand was made in a 500 ml reaction flask with baffles to increase agitation when a refluxing toluene-sodium suspension was stirred with a motor-driven stirrer with Teflon blades. Vigorous stirring until the toluene cooled usually resulted in a fine sand. Toluene was siphoned off through a septum in the sidearm of the flask and the sodium washed with 50 ml tetrahydrofuran before addition of reaction solvent. Even with dry clean sand, several hours are required for complete reaction of sodium with cyclopentadiene. Addition of too much of the latter results in polymer formation and complicates subsequent separation of product.

To the sodium cyclopentadienide solution was added tungsten hexacarbonyl and the reaction refluxed for at least 72 hours. Less time resulted in poor yield while a greater reaction time did not significantly increase the yield. After cooling, a slight molar excess of acetic acid was added drop-wise to the yellow \( \text{Na}[\Pi \text{-CpW(CO)}_3] \) and the mixture stirred for two hours. Solvent was removed under reduced pressure and the resulting tarry mass placed in a large sublimer. Several hours were required for complete sublimation.

\( \Pi \)-Cyclopentadienylmolybdenum tricarbonyl iodide was prepared using the method of Abel et. al.\(^{62}\) in reasonably good yield with no special difficulty.

Molybdenum hexacarbonyl, tungsten hexacarbonyl, triirondodecacarbonyl, triruthenium dodecacarbonyl and \( \Pi \)-cyclopentadienyliron
dicarbonyl dimer were obtained from Alfa Inorganics, Beverly, Massachusetts. Diphenyl diselenide and diphenyl ditelluride were from Metallomer Laboratories, Fitchburg, Massachusetts. All of the above reagents were used without further purification.

Solvents were commercially available, of reagent grade and were degassed prior to use by bubbling dry nitrogen through them for a few minutes. Tetrahydrofuran and 1,2-dimethoxyethane were refluxed for several hours over sodium, distilled onto lithium aluminum hydride and then redistilled onto molecular sieves for storage. Hydrocarbon solvents were dried over sodium.

2. Instrumentation

A. Molecular weights were determined with a Hewlett-Packard Model 302 Vapor Pressure Osmometer. Measurements were made in benzene solution when solubility in this solvent permitted. For less soluble materials, chloroform solutions were employed. Standardization plots were made using triply-recrystallized benzil.

B. Infrared spectra were obtained with a Beckman IR-7 instrument. Samples were dissolved in carbon disulfide, cyclohexane, methylene chloride or chloroform and measured versus neat solvent in either 0.9 mm or 0.4 mm matched sodium chloride cells.

C. Proton magnetic resonance spectra were obtained with a Varian Model A-60A instrument in carbon disulfide or deuterated chloroform solutions. The low solubility of new compounds reported in this work required a high gain in order to observe a signal. Baselines were therefore wide and integration of peaks made difficult. In some cases,
a Varian HA-100 instrument with computer averaged transients was used to observe weak signals.

D. Mass spectra were taken by Mrs. Cheryl White of the Louisiana State University Chemistry Department on a Varian M-66 instrument. Although attempts were made to obtain mass spectra of each of the reported new compounds, only a few gave significant results. These spectra were observed at an energy of 70 electron volts.

E. Melting points were observed in open capillary tubes on a Hoover Melting Point Instrument.

3. General Preparative Techniques

A. Reactions were carried out in dried hydrocarbon solvents under a nitrogen atmosphere. Glassware which was acid washed, rinsed with water and acetone, and oven dried, included reaction flasks fitted with stopcock for nitrogen inlet, outer ST(24/40) joint for condenser and inner ST(24/40) joint which facilitated filtering under nitrogen.

B. Monitoring the progress of reactions was accomplished by either or both of two methods. The strong infrared absorbance of the carbonyl group in transition metal complexes and its sensitivity to electronic factors on the metal makes the monitoring of the 1800 to 2050 cm$^{-1}$ region of a reaction mixture's infrared spectrum a useful method for following the course of a reaction. The disappearance of starting material absorptions were used as evidence for completeness of the reactions and after the infrared spectra of initial products had been identified, formation of subsequent products was observed by the growth of new absorption maxima.
A measured sample of the reaction solution, usually 0.2 ml, was transferred under a constant flow of nitrogen to a small round-bottom flask filled with nitrogen. The solvent was removed at reduced pressure and a dry degassed solvent added, also under nitrogen. The solution was then transferred to a sodium chloride cell. Even with careful and rapid technique, partial decomposition was sometimes evident. Careful regulation of sample and solution volumes allowed quantitative estimation of product formation and reactant disappearance.

Thin layer chromatography on microscope slides coated with silica was also used as a monitoring technique. The slides were prepared by dipping a microscope slide into a chloroform-silica slurry and allowing to air dry. Samples of the reaction mixture along with solutions of starting materials or other reference compounds are then spotted on the slide with a fine capillary. Development is accomplished in small jars to which 5-10 ml of eluent has been added. This technique has the advantage of indicating relative \( R_f \) values that may be employed in subsequent separation procedures. There is no guarantee that two materials will not have identical \( R_f \) values, but use of several solutions of differing elution power minimizes this possibility. Also, the use of 5 x 20 cm thin layer plates provides a greater separation when spots appear close on a micro-slide plate.

C. Most of the reactions carried out in this work afforded a mixture of products. Chromatography, both column and preparative layer, was extensively used for the separation of these reaction mixtures. A 70 cm glass column fitted with ST(24/40) joints, a stopcock for introduction of nitrogen and a pressure equilibration tube was slurry packed.
with either alumina or silica for column chromatography. Washing the column with several hundred milliliters of dry degassed solvent tends to remove adsorbed oxygen and proves particularly important for air sensitive materials.

Separation was often accomplished by gradually changing to more polar eluents. This procedure allows for the separation of materials with a considerable range of $R_f$ values, on the same column. Caution must be used against too severe a change for solvent interactions are sometimes large enough to cause heat and bubbling of the column. Fortunately, all new compounds reported herein are colored and visual means were usually sufficient to detect separation. Thin layer chromatography and infrared spectroscopy were used as criteria of the purity of fractions.

Preparative layer chromatography was often able to effect separation when a column did not. Since reaction products were generally formed in less than one gram amounts, this was a useful technique for the more stable products. However, for materials that are air sensitive, decomposition seems to occur rapidly on the silica surface.

4. Analysis

Analysis for carbon and hydrogen were by Mr. Ralph Seab of the Louisiana State University Chemistry Department. Analysis of metals and chalcogens were by Schwarzkopf Microanalytical Laboratories, Woodside, New York.
EXPERIMENTAL – SYNTHETIC

The preparation of new compounds is described in this Section. Infrared, proton magnetic resonance, and mass spectral data are included in the Results and Discussion Section.

1. Reactions of \( \pi \)-Cyclopentadienyliron Dicarbonyl Dimer and Diphenyl Dichalconides

A. Preparation of \( \pi \)-CpFe(CO)\(_2\)TePh

Diphenylditelluride (2.87 g, 7 mmoles) and \([\pi\text{-CpFe(CO)}\text{]}_2\) (2.00 g, 5 mmoles) were mixed in a 250 ml reaction flask with 150 ml benzene. The reaction mixture was heated to reflux temperature and monitored periodically by observing the infrared spectrum of extracted samples. After 1 hr. there was significant decrease in the starting material's bridging carbonyl absorbtion at 1781 cm\(^{-1}\), and new peaks appeared at 1916, 1971, and 2014 cm\(^{-1}\). A sample taken after 3 hr. reflux showed no evidence of starting material.

The reaction mixture was cooled and then taken to dryness on a rotary evaporator and the resulting green solid redissolved in diethyl ether. This solution was chromatographed in 5 ml portions on an alumina column. Elution with (9/1) hexane-ethyl ether caused a yellow band to precede a green band down the column affording yellow and green solutions respectively. The yellow material had no significant absorptions in the carbonyl region of its infrared spectrum and further characterization was not attempted.

Evaporation of solvent from the green solution yielded a green tar. Crystallization of this tar from methylene chloride-hexane at -70\(^{\circ}\) C gave a green crystalline material, m.p. 66\(^{\circ}\) C.
**A.** Calcd for C_{13}H_{10}O_{2}TeFe: C, 40.89; H, 2.62; mol wt, 382.

**B.** Preparation of a Pair of Dinuclear Isomers Formulated as

\[ \text{[\text{II-CpFe(CO)TePh}]_2}. \]

Diphenylditelluride (2.87 g, 7 mmoles) and \[ \text{[\text{II-CpFe(CO)2}] \] (2.00 g, 5 mmoles) were refluxed in 150 ml benzene in a 250 ml reaction flask. Within a few minutes the green coloration, observed in reactions described in 1-A, appeared. A sample taken after 5 hr reflux had an infrared spectrum with strong peaks at 2014 and 1971 cm^{-1} and a significant new peak at 1917 cm^{-1}.

Infrared spectra of samples taken at 8, 10, and 23 hr reflux indicated only slight increases in the 1971 cm^{-1} absorption. However, in the course of examining the last sample, it was noticed that successive scans through the 1800–2050 cm^{-1} region of the infrared spectrum caused a growth of the 1917 cm^{-1} peak with corresponding decrease of absorption due to the monomeric product. A visible-infrared heat lamp was used to irradiate the reaction mixture and within 3 hr the 2014 cm^{-1} absorption due to monomer was no longer observable.

After taking the reaction mixture to dryness on a rotary evaporator, the resulting solid was dissolved in methylene chloride and developed in two portions on an alumina column. Elution with cyclohexane separated a brown band from excess diphenylditelluride. Upon removal of solvent, a brown solid was formed. This material was recrystallized from methylene chloride-ethanol to yield fine dark crystals.

Evidence which will be presented in the Results and Discussion Section indicates this material to be a mixture of two isomers of formula...
Several attempts were made, unsuccessfully, to separate the mixture into its components. Techniques employed included crystallization from various solvent systems, column chromatography with both silica and alumina and preparative layer chromatography on silica plates. The latter method proved to give slight enrichment of one isomer over the other, but a pure isomer was not isolated.

**Anal. Calcd for C\textsubscript{24}H\textsubscript{20}O\textsubscript{2}Te\textsubscript{2}Fe\textsubscript{2}:** C, 40.73; H, 2.85; mol wt, 707. **Found:** C, 40.45; H, 3.16; mol wt, 680.

**C. Preparation of Monomeric [\benzene]-CpFe(CO)\textsubscript{2}SePh.**

Diphenyl diselenide (2.19 g, 7 mmoles) and [\benzene]-CpFe(CO)\textsubscript{2}\textsubscript{2} (2.00 g, 5 mmoles) were mixed in 150 ml benzene and the reaction maintained at room temperature. The infrared spectrum of a sample taken after 2 hr showed a product peak developing at 2025 cm\textsuperscript{-1}. This peak continued to grow slowly but after 20 hr a substantial amount of carbonyl starting material remained unreacted. The reaction was taken to benzene reflux temperature (\sim 80\degree C) for 2 hr at which time the dark green solution gave no evidence for the bridging carbonyl absorptions of starting material.

Solvent was removed under reduced pressure and the resulting solid dissolved in methylene chloride. Hexane was added and after the lower boiling methylene chloride was partially removed under reduced pressure, the mixture was cooled to -10\degree C. A fine brown precipitate was collected on a filter leaving a green filtrate. Upon further evaporation of the filtrate and cooling in a dry ice-acetone slush, some small dark crystals were formed. Several recrystallizations of the above-mentioned brown solid yielded additional dark crystals as well as a buff-colored material that was not identified.
Yield of dark crystalline \( \Pi\text{-CpFe(CO)}_2\text{SePh} \); 53\%, m.p. 50-52° C.

Anal. Calcd. for \( \text{C}_{13}\text{H}_{10}\text{O}_2\text{SeFe} \): C, 46.89; H, 3.03; mol wt, 333.

Found: C, 46.45; H, 3.20; mol wt, 372 (osmometry), 333 (mass spectrometry).

D. Preparation of a Pair of Dinuclear Isomers Formulated as \( [\Pi\text{-CpFe(CO)}_2\text{SePh}]_2 \).

Diphenyl diselenide (2.19 g, 7 mmoles) and \( [\Pi\text{-CpFe(CO)}_2]_2 \) (2.00 g, 5 mmoles) were added to 150 ml benzene. To encourage dimer formation, the heat lamp used successfully in reaction 1-B, was employed. The reaction was maintained at a gentle reflux while being irradiated.

An infrared spectrum of a sample taken after 3 hr indicated the starting carbonyl compound to be nearly absent and the monomer, \( \Pi\text{-CpFe(CO)}_2\text{SePh} \) to be the principal carbonyl containing constituent. At 6 hr, a broad band had developed at 1928 cm\(^{-1}\) while the monomer peak at 2026 cm\(^{-1}\) was reduced to half its former size. An additional 4 hr, 10 hr total, were required to completely remove this monomer peak from the spectrum of a monitored sample.

Solvent was removed under reduced pressure and resulting solid material dissolved in methylene chloride. Addition of hexane and cooling caused precipitation of a brown solid which was collected on a filter. This material has a single absorption at 1975 cm\(^{-1}\) in the carbonyl region of its infrared spectrum. The filtrate yielded, after partial evaporation and cooling, a dark crystalline material which has strong carbonyl absorptions at 1931 and 1947 cm\(^{-1}\) with only a very weak peak at 1975 cm\(^{-1}\).
Each of the materials was chromatographed on an alumina column using (1/1) benzene-hexane as eluent and the solids remaining after removal of solvent were recrystallized from methylene chloride-hexane. The dark material, m.p. 172-175° resembles the product of reaction 1-B, but the carbonyl region of its infrared spectrum has only two absorptions, at 1931 and 1947 cm⁻¹. Estimated yield; 10%.

**Anal.** Calcd. for C_{24}H_{20}O_{2}Se_{2}Fe_{2}: C, 47.23; H, 3.33; mol wt, 610. Found: C, 46.85; H, 3.38; mol wt, 589.

Recrystallization of the brown solid afforded fine brass-colored crystals, m.p. 170-172° in estimated yield of 30%.

**Anal.** Calcd for C_{24}H_{20}O_{2}Se_{2}Fe_{2}: C, 47.23; H, 3.33; mol wt, 610. Found: C, 46.94; H, 3.43; mol wt, 601.

E. Reaction of \[\text{[II-CpFe(CO)_{2}]}\] with Diphenyl Disulfide.

Because of the previous experience of light catalyzing the dimerization of iron-chalcogen monomers and because Ahmad had reported no monomer formed in the reaction of these two materials, light was excluded from the reaction mixture by wrapping the reaction flask with aluminum foil. Diphenyldisulfide (1.53 g, 7 mmoles) and \[\text{[II-CpFe(CO)_{2}]}\] (2.00 g, 5 mmoles) were dissolved in 150 ml benzene and heated to a gentle reflux.

A sample withdrawn after 2 hr had a infrared absorption characteristic of monomeric product at 2029 cm⁻¹ and relatively weak absorptions due to the bridging carbonyl of starting material. A shoulder at 1926 cm⁻¹ was indicative of the reported dimer \[\text{[II-CpFe(CO)SPh]_{2}}\]. After 3 hr reflux there was only a very weak peak at 1782 cm⁻¹ due to starting material. The reaction was refluxed an additional 15 min and then cooled to room temperature.
After filtering, the reaction mixture was reduced to about 25 ml, under water aspirator vacuum, and one-fifth of this solution placed on an alumina column. Elution with (3/2) hexane-benzene solution caused a small yellow band to move down the column with slight separation at the bottom from a band which spread nearly the length of the column. Neat benzene separated the second band from a third band which appeared violet on the column. Each of the fractions were collected and the process repeated until all the reaction mixture was separated.

The first fraction yielded a small amount (about 2% of all products) of yellow-brown material while the second fraction was estimated at 50% of reaction products. The infrared spectra of these materials correspond to the less stable and more stable isomers of \([\Pi\text{-CpFe(CO)}\text{SPh}]_2\) respectively. The third compound which is dark red, has strong sharp carbonyl absorptions at 2033 and 1985 cm\(^{-1}\). This agrees with reported values for \([\Pi\text{-CpFe(CO)}\text{SPh}]_2\).

2. Reactions of Triirondodecacarbonyl with Diphenyl Dichalconides

A. Formation of \([Fe(CO)_3TePh]_2\)

Triirondodecacarbonyl (2.52 g, 5 mmoles) and diphenyl ditelluride (3.28 g, 8 mmoles) were taken to reflux temperature in 100 ml benzene. Within a few minutes a color change from green to deep red occurred while a gas was being evolved. An infrared spectrum of a monitored sample taken after 1 hr reflux had no absorptions in the carbonyl region, characteristic of \(Fe_3(CO)_{12}\).

The reaction mixture was filtered, solvent removed and the resulting solid recrystallized twice from methylene chloride-hexane. Dark red crystals of \([Fe(CO)_3TePh]_2\), melting at 104-106\(^0\) C, were obtained.
Anal. Calcd for C_{18}H_{10}O_{6}TeFe_{2}: C, 31.27; H, 1.58; mol wt, 689. Found: C, 31.59; H, 1.79; mol wt, 675 (osmometer), 689\(^{(a)}\) (parent peak in mass spectrum).

Mass and infrared spectral data are presented in the Results and Discussion Section.

B. Formation of \([Fe(CO)_{3}SePh]_{2}\)

Diphenyl diselenide (2.50 g, 8.0 mmoles) and triirondodeca-carbonyl (2.52 g, 5 mmoles) were added to 80 ml benzene. The reaction was gently refluxed for 1 hr producing a color change similar to that observed in reaction 2-A.

Removal of solvent yielded a yellow-red solid which was re-crystallized from methylene chloride-hexane. The melting range of the recrystallized product was quite broad indicating the need for further purification.

A benzene solution of the product was chromatographed in two portions on an alumina column. Elution was accomplished with (7/4) hexane-benzene. An orange-red band moved down the column while a second red-brown band would not move with benzene, benzene-acetone or acetone and only slowly, with apparent decomposition, with 95% ethyl alcohol. A small amount of yellow material recovered from this band had no infrared absorptions in the metal carbonyl region.

From the first band was obtained red crystalline \([Fe(CO)_{3}SePh]_{2}\), melting point 94-96\(^{0}\) C, whose infrared spectrum in the carbonyl region

\((a)\) Due to the existence of several isotopes of tellurium, the parent peak is a multiplet. An estimated average value is given.
is similar to that of \([\text{Fe(CO)}_3\text{TePh}]_2\) and to that reported by Kettle and Orgel\(^20\) for \([\text{Fe(CO)}_3\text{SPh}]_2\).

\[\text{Anal. Calcd for } \text{C}_{18}\text{H}_{10}\text{Se}_2\text{Fe}_2: \text{ C, 36.52; H, 1.70; mol wt, 592. Found: C, 37.02; H, 2.12; mol wt, 572 (osmometer), 592}\(^{(a)}\) parent peak in mass spectrum.\]

3. **Reactions of Dodecacarbonyl Triruthenium with Diphenyl Dichalconides**

A. **Preparation of Dinuclear \([\text{Ru(CO)}_3\text{TePh}]_2\) and polymeric derivatives of Formula \([\text{Re(CO)}_2(\text{TePh})_2]_n\)**

Diphenyl ditelluride (1.04 g, 2.55 mmoles) in 20 ml benzene was added drop-wise with stirring to dodecacarbonyl triruthenium (1.07 g, 1.66 mmoles) dissolved in 150 ml benzene. The reaction was maintained at about 60\(^\circ\) for 4 hr with periodic IR and TLC monitoring. A thin layer slide of a sample taken after 1 hr had a yellow spot that moved with slightly smaller \(R_f\) than that of carbonyl starting material and an orange spot that remained at the origin when petroleum ether was used as eluent. Infrared spectra of withdrawn samples revealed new peaks in the carbonyl stretching region first at 2002, 2034, and 2073 cm\(^{-1}\) and later additional absorptions at 2030, 2080, and 2095 cm\(^{-1}\).

After 4 hr there was no evidence on a thin layer slide for diphenyl ditelluride, but a significant amount of dodecacarbonyl triruthenium was still present in the reaction mixture. The volume of the reaction mixture was reduced to about 30 ml and chromatographed in three portions on a silica column. Elution with petroleum ether moved a wide

\(\text{(a) Due to the existence of several isotopes of selenium, the parent peak is a multiplet. An estimated average is given.}\)
yellow band which was indicated by its infrared spectrum to be a mixture of Ru$_3$(CO)$_{12}$ and some new material. A second light orange band was eluted with (4/1) benzene-chloroform while a third dark orange band moved very slowly and was finally extracted from the silica with chloroform.

Further separation of the first column fraction was accomplished with preparative layer chromatography. Several elutions with petroleum ether separated slightly two yellow bands; extraction of the upper band yielded Ru$_3$(CO)$_{12}$, while the second band afforded (from several plates) about 100 mg of a light yellow solid, m.p., 104°C.

Anal. Calcd for [Ru(CO)$_3$TePh]$_2$, C$_{18}$H$_{10}$O$_6$Te$_2$Ru$_2$: C, 27.81; H, 1.29; mol wt, 778. Found: C, 28.16; H, 1.80; mol wt, 735.

The infrared spectrum (CHCl$_3$ Soln) of the yellow material has absorptions in the carbonyl stretching region at 2073(s), 2044(vs), and 2002 cm$^{-1}$ (s,br).

The second band from the chromatographic separation of the reaction mixture was collected in three fractions. Infrared spectra (1900-2100 cm$^{-1}$ region) of these fractions each had absorptions at 1974(m), 2030(vs), and 2080 cm$^{-1}$ (s), differing only in the relative intensity of the 2080 cm$^{-1}$ absorption. The third of those fractions was the only one collected in sufficient amount for characterization studies. The dark orange plates decompose slowly above 200°C. The material is quite soluble in chloroform and gives osmometric molecular weight measurements in the order of 3700.

Anal. Calcd for [Ru(CO)$_2$(TePh)$_2$]$_n$, (C$_{14}$H$_{10}$O$_6$Te$_2$Ru)$_n$: C, 29.68; H, 1.91. Found: C, 30.27; H, 2.10
The final material separated from the reaction composed about 90% of isolated products. It is an orange-brown powder that can be re-crystallized from chloroform or methylene chloride by addition of a hydrocarbon solvent, acetone or methanol. Its infrared spectrum (CHCl₃ soln) had absorptions in the carbonyl region at 1974 (m, br), 2027 (s), and 2095 cm⁻¹ (w). Molecular weight measurements give values of 7800-8200 but are subject to considerable error because of the low molal concentrations (~0.001 m).

Anal. Calcd for [Ru(CO)₂(TePh)₂]ₙ, (C₁₄H₁₀O₂Te₂Ru)ₙ: C, 29.68; H, 1.91. Found: C, 29.42; H, 1.89.

When the reaction was repeated with a ligand material to metal carbonyl molar ratio greater than three to two in an attempt to completely react the Ru₃(CO)₁₂, and thereby eliminate a portion of the rather tedious separation, the only isolated products were the two polymeric materials. It appears that diphenyl ditelluride reacts with the dinuclear product to form a polymer at least nearly as rapidly as with dodecarbonyl triruthenium to form [Ru(CO)₃TePh]₂.

B. Preparation of Dinuclear [Ru(CO)₃SePh]₂ and Polymeric Derivatives of Formula [Ru(CO)₂(SePh)₂]ₙ.

Diphenyl diselenide (0.94 g, 3 mmoles) in 20 ml benzene was added drop-wise to a 200 ml solution of dodecarbonyl triruthenium (1.28 g, 2 mmoles) in benzene. The reaction proceeded analogously to the previous one with diphenyl ditelluride. After heating to 60° for 3 hr, a thin layer slide had spots corresponding to Ru₃(CO)₁₂, dinuclear product and an orange-yellow spot at the origin. No spot corresponding to ligand material was evident.
The solvent was removed under reduced pressure and the resulting orange residue redissolved in about 20 ml methylene chloride. This solution was placed on five 20x20 cm preparative layer silica plates and eluted with petroleum ether. Two yellow bands moved slowly with partial separation but drying the plates and elution with petroleum ether several times moved the upper band of Ru\(_3\)(CO)\(_{12}\) to the top of the plate well separated from the second yellow band I which was followed by a faint yellow band II with another band moving only slightly from the orange band at the origin. Fractions I and II were scraped from the plates and extracted with methylene chloride. Removal of solvent yielded about 100 and 2 mg of light yellow solids respectively. The carbonyl region of the infrared spectra of I and II both had absorptions at 2006(vs, br), 2052(vs), and 2091 cm\(^{-1}\) (s), with the only possible difference being in the relative intensities of these absorptions. Yellow solid I melts at 97° C, and in a thermogravimetric analysis was shown to lose mass (presumably CO) very slowly above 150° C and at a considerably greater rate above about 250° C.

**Anal.** Calcd for I, [Ru(CO)\(_3\)SePh]\(_2\), C\(_{16}\)H\(_{10}\)O\(_6\)Se\(_2\)Ru\(_2\): C, 31.69; H, 1.47; mol wt, 682. Found: C, 32.16; H, 2.10; mol wt, 644.

The somewhat high values for carbon and hydrogen are possibly caused by occluded hydrocarbon solvents. Although the material was dried under vacuum for several hours, heating was avoided to prevent decomposition to polymer.

After removal of fractions I and II, the preparative plates were returned to a developing chamber. With (2/1) benzene-petroleum ether a yellow III and a yellow-orange IV band separated from each other.
and from an orange band V remaining at the origin. Each of these were removed and extracted with methylene chloride. Addition of hexane and removal under reduced pressure of the methylene chloride produced yellow-orange precipitates of IV and V. Sample III was somewhat soluble in hexane and removal of the solvent yielded only about 2 mg of a light yellow solid whose infrared spectrum included absorptions at 1963(w), 2007(m), 2024(s), 2054(m), 2081(m), and 2105 cm\(^{-1}\) (w). No further characterization of III was attempted.

From fraction IV was obtained about 100 mg of orange plate-like material that gave osmometric molecular weight values of 3200. 

**Anal.** Calcd for \([\text{Ru(CO)}_2(\text{SePh})_2]_n\), (C\(_{14}\)H\(_{10}\)O\(_2\)Se\(_2\)Ru\(_n\)) \(\text{C, 35.84; H, 2.31. Found: C, 36.17; H, 3.03.}\)

The infrared spectrum of IV has three absorptions in the carbonyl stretching region at 1974(m), 2037(s) and 2096 cm\(^{-1}\)(m). Comparison of this spectrum with that of similar compounds is made in the Results and Discussion Section.

Fraction V was the major product of the reaction. It is a dark yellow powder that slowly darkens when heated above 200\(^0\) C. The infrared spectrum of V is similar to that of IV, but with different relative intensities of the three absorptions at 1974(m, br), 2037(s), and 2205 cm\(^{-1}\)(w). Molecular weight of V is about 6700.

**Anal.** Calcd for \([\text{Ru(CO)}_2(\text{SePh})_2]_n\), (C\(_{14}\)H\(_{10}\)O\(_2\)Se\(_2\)Ru\(_n\)) \(\text{C, 35.84; H, 2.30. Found: C, 35.05; H, 2.41.}\)
4. Reactions of Π-Cyclopentadienylmolybdenum Tricarbonyl Dimer with Diphenyl Dichalconides

A. Preparation of Π-CpMo(CO)₃SePh

Diphenyl diselenide (0.50 g, 1.6 mmoles) and [Π-CpMo(CO)₃]₂ (0.79 g, 1.6 mmoles) were added to 100 ml benzene and the reaction maintained at 10° C in a water bath. The infrared spectrum of a monitored sample included, in addition to the characteristic absorptions of starting material, new strong peaks at 2026 and 1948 cm⁻¹. These two absorptions were indicated to be due to the principal carbonyl-containing species after 2 hr stirring and were quite analogous to the carbonyl absorptions of the monomer Π-CpMo(CO)₃TePh.⁴⁹

The reaction mixture was filtered and solvent removed from the filtrate at reduced pressure. Recrystallization of the resulting solid from methylene chloride-hexane yielded a red solid which had an infrared spectrum indicative of a mixture of Π-CpMo(CO)₃SePh and [Π-CpMo(CO)₂SePh]₂. The material was dissolved in toluene and chromatographed on an alumina column using (2/1) hexane-benzene as eluent. A band developed whose upper portion was red and lower portion brown. The infrared spectrum of the brown portion of the band indicated again, a mixture of monomer and dimer products but with a considerably greater concentration of dimer. The red portion of the band was collected and rechromatographed yielding, after removal of solvent and recrystallization from toluene-hexane, a red solid, m.p., 92-94°

Anal. Calcd for C₁₄H₁₀O₂SeMo: C, 41.92; H, 2.61; mol wt, 401.
Found: C, 41.59; H, 2.91; mol wt, 465.
B. Evidence for Additional Carbonylated Species in the Reaction of Diphenyl Diselenide and [\textit{T}-\textit{CpMo(CO)}_3]_2.

Diphenyl diselenide (0.94 g, 3 mmoles) and [\textit{T}-\textit{CpMo(CO)}_3]_2 (1.0 g, 2 mmoles) were added to 100 ml of toluene in a reaction flask placed in a 60° C bath. After 8 hr, the infrared spectrum of a monitored sample included absorptions at 1853, 1975, 1948, 1958, and 2026 cm\(^{-1}\), corresponding to a mixture of monomeric \textit{T}-\textit{CpMo(CO)}_3SePh and the dimer [\textit{T}-\textit{CpMo(CO)}_2SePh]_2. Further reaction resulted in gradual disappearances of these absorptions. At no time did the infrared spectrum of a sample indicate the dimeric product to be the predominant specie in solution as was the case in corresponding reactions with tellurium ligand.\(^3\) After the mixture was allowed to sit overnight at room temperature, it was maintained an additional 8 hr at 60° C (16 hr total). The only infrared absorptions in the carbonyl region at this time were at 1851, 1907, and 1967 cm\(^{-1}\).

The reaction mixture was filtered and the volume of the filtrate halved under reduced pressure. Addition of hexane and cooling to -78° C for several hours caused a precipitate to form. Filtration yielded 0.4 g of a fine green powder whose infrared spectrum was similar to the last one observed from the reaction mixture. A molecular weight determination on the green solid gave a value of 780. This material was shown to be a mixture of compounds which could be separated by column chromatography.

A benzene solution of the green solid was placed on a 50 cm alumina column and eluted with benzene. Three bands developed; a green-brown and a violet band were removed with benzene, but a dark green band
required chloroform to be eluted. Solutions obtained from the three bands were evaporated and yielded solids whose colors were green-brown, violet, and yellow. The yellow solid had a single infrared absorption in the carbonyl region at 1968 cm\(^{-1}\) and a molecular weight measurement in chloroform gave a value of 790. Calculated molecular weight for dinuclear \(\text{[Tf-CpMo(CO)\textsubscript{2}SePh]}\textsubscript{2}\) is 746. The yellow solid decomposed into an insoluble brown material within two days.

The violet material, which was observed as a product only in reactions that had been allowed to remain at room temperature for several hours, had a single, strong carbonyl band at 1825 cm\(^{-1}\) in its infrared spectrum. The green-brown material exhibited bands at 1951 and 1907 cm\(^{-1}\) and was obtained as approximately 90% of the three carbonylated products of "extended" reactions. Several attempts to characterize these materials resulted in excessive decomposition.

C. Extended Reaction of Diphenyl Ditelluride with \(\text{[Tf-CpMo(CO)\textsubscript{3}]}\textsubscript{2}\)

Diphenyl ditelluride (1.0 g, 2.45 mmoles) and \(\text{[Tf-CpMo(CO)\textsubscript{3}]}\textsubscript{2}\) (0.98 g, 2.0 mmoles) were refluxed in toluene for 75 hr with periodic monitoring by both infrared spectroscopy and thin layer chromatography. No evidence was obtained, after disappearance of \(\text{Tf-CpMo(CO)\textsubscript{3}TePh}\), of any soluble carbonylated product other than \(\text{[Tf-CpMo(CO)\textsubscript{2}TePh]}\textsubscript{2}\). This dimer was separated from an amorphous sludge by filtration and then crystallized from hexane-benzene. The melting point and infrared spectrum agree with reported data for this compound.\(^3\)

To attempt further substitution, \(\text{[Tf-Cp(CO)\textsubscript{2}TePh]}\textsubscript{2}\) (0.78 g, 1.8 mmoles) and diphenyl ditelluride (0.82 g, 2 mmoles) were added to 100 ml xylene and taken to reflux temperature (about 137° C). Again,
monitoring gave no evidence of new products, but a gradual decrease in concentration of starting materials was observed. After 18 hr reflux and removal of solvent, the reaction residue soluble in methylene chloride was placed on an alumina column and eluted with (19/1) benzene-ethyl acetate. An orange band of diphenyl ditelluride was followed by unreacted \([\text{Ir-CpMo(CO)}_2\text{TePh}]_2\). More polar eluents caused small amounts of four additional colored materials to be removed. None of these materials had infrared spectra characteristic of compounds observed in the extended reactions of diphenyl diselenide or diphenyl disulfide. The absence of significant absorptions in the 1800-2050 cm\(^{-1}\) region indicate these materials to be completely decarbonylated species. No further characterization of these materials was attempted.

D. Extended Reactions of Diphenyl Disulfide with \([\text{Ir-CpMo(CO)}_3]\)_2

Diphenyl disulfide (0.2 g, 1 mmole) and \([\text{Ir-CpMo(CO)}_3]\)_2 (0.5 g, 1 mmole) were dissolved in 80 ml benzene and refluxed for 15 hr. During this time infrared spectra of the 1800-2050 cm\(^{-1}\) region indicated growth of peaks first at 2033 cm\(^{-1}\) and then at 1864 cm\(^{-1}\). The first band is characteristic of a monomer, \(\text{Ir-CpMo(CO)}_3\text{SPh}\).

The reaction mixture was filtered and the filtrate chromatographed on an alumina column. A single green band was eluted, and yielded, after removal of solvent, a brown solid that had an infrared spectrum comparable to a similar appearing material from the extended reaction of diphenyl diselenide with \([\text{Ir-CpMo(CO)}_3]\)_2 with carbonyl bands at 1864 and 1913 cm\(^{-1}\). Attempts to purify the material for analysis led to excessive decomposition.
7. **Reactions of Π-Cyclopentadienyltungsten Tricarbonyl Hydride with Diphenyl Dichalconides**

A. Preparation of Dinuclear [Π-CpW(CO)₃TePh]₂ and Other Carbonylated Products

Diphenyl ditelluride (1.30 g, 3.2 mmoles) was mixed in 70 ml toluene with Π-CpW(CO)₃H (1.00 g, 3 mmoles) and maintained at reflux temperature. Periodic monitoring with IR and TLC indicated a slow change from monomeric Π-CpW(CO)₃TePh to other products. After 18 hr, a 10 ml portion of the reaction mixture was chromatographed on a silica column. Petroleum ether eluted the excess ligand material while (9/1) petroleum ether-ethyl acetate moved a light green band in front of a brown band. The green band afforded a green-yellow solution which, upon evaporation, yielded about 5 mg of a green-yellow solid. This material was dried under vacuum and stored under nitrogen, but within one-half hour it had darkened to a yellow-brown. The infrared spectrum of this material has a single absorption in the carbonyl region at 1942 cm⁻¹ which is characteristic of compounds isolated from similar reactions.

The brown band from the column yielded 0.2 g of a light brown solid with an infrared spectrum similar to that of [Π-CpMo(CO)₂TePh]₂, but with additional weak absorptions at 1822, 1882, 1905, and 2022 cm⁻¹. Rechromatographing the brown solid gave a material whose only absorptions in the carbonyl region are the four bands characteristic of a dimeric product, m.p., 200° C.

**Anal.** Calcd for C₂₆H₂₀O₄W₂Te₂: C, 30.68; H, 1.98; mol wt, 1018. Found: C, 31.24; H, 2.83; mol wt, 990.
The proton magnetic spectrum has a phenyl multiplet centered at 7.2 ppm which integrates one to one with a sharp cyclopentadienyl proton signal at 5.30 ppm.

Continued elution of the chromatogram of the reaction mixture on silica with (2/1) ethyl acetate-petroleum ether removed a dark green band which yielded 0.05 g of a green solid (m.p. ~ 200° C dec). The infrared spectrum of this material includes carbonyl absorptions at 1872, 1926, 1951, 1960, and 1982 cm⁻¹.

Anal. Calcd for [\(\Pi\)-CpW(CO)TePh]\(_n\), (C\(_{12}\)H\(_{10}\)OTeW)\(_n\): C, 29.90; H, 2.09. Found: C, 29.92; H, 2.36.

The proton magnetic spectrum does not agree with the above formulation. A broad phenyl proton multiplet centered at 7.09 ppm and a pair of cyclopentadienyl proton singlets at 5.70 and 5.72 ppm have relative size 1:5:3:2, respectively.

B. Reactions of Diphenyl Diselenide with \(\Pi\)-CpW(CO)\(_3\)H.

To a toluene extract of unsublimed residue from the preparation of \(\Pi\)-CpW(CO)\(_3\)H was added diphenyl diselenide (1.26 g, 4 mmoles). The infrared spectrum of the toluene extract corresponded to the reported spectrum of the tungsten hydride. Following 4 hr of reflux, there remained a strong infrared absorption due to the hydride and no indication of ligand material on a thin-layer slide. An additional 4 mmoles of diphenyl diselenide was added and reflux of the reaction continued for a total of 8 hr.

The mixture was cooled and filtered, yielding about 2 g of an amorphous solid and a reddish-brown filtrate. The filtrate was chromatographed in three portions using (2/1) benzene-cyclohexane as eluent. A
light yellow band of excess ligand was followed by a green-brown band which yielded a very small amount of light green solid. There was an insufficient amount of this green solid for characterization studies, but its infrared spectrum is compared with those of other light green chalcogen derivatives in the Results and Discussion Section.

A second yellow band was eluted with (4/1) benzene-ethyl acetate and afforded, after removal of solvent and recrystallization from methylene chloride-hexane, 0.2 g of a light brown powdery solid, m.p., 235° dec.

Anal. Calcd for \([\text{CpMo}(\text{CO})_2\text{SePh}]_2\), \(C_{13}H_{10}O_2\text{SeW}\): C, 33.87; H, 2.18; Se, 17.12; W, 39.88; mol wt, 922. Found: C, 32.10; H, 2.54; Se, 17.88; W, 36.88; mol wt, 1025.

The tungsten and selenium analysis as well as the molecular weight measurements were done on a sample that was shown by nmr to contain molecular benzene although the sample had been dried for several hours at 1.0 mm and 80° C. A thermogravimetric analysis of this benzene containing sample indicates no mass loss under nitrogen at one atmosphere until at 190° C there was a rapid loss of 2.9% Continued heating resulted in negligible mass loss until between 235 and 270° C a loss of 13% occurred. The calculated percent mass loss of four carbonyl groups from \([\text{CpW}(\text{CO})_2\text{SePh}]_2\) is 12.2%. There was no additional mass loss to 500° C.

The carbonyl region of the yellow compound's infrared spectrum has a single absorption at 1952 cm\(^{-1}\). The nmr spectrum of a sample which had been dried at 110° C and 1 mm for 20 hrs. had a sharp cyclopenta-dienyl proton peak at 5.59 ppm which integrates one to one with a phenyl proton multiplet at 7.3 ppm.
The above reaction was also examined using benzene as a solvent. Monitoring by both IR and TLC indicated rapid formation of monomeric product \( \Pi\text{-CpW(CO)}_3\text{SePh} \), but no evidence for a dimer of the type isolated in analogous tellurium reactions. Neither was there indication of a dark green product, with strong carbonyl absorption in the 1850-1900 cm\(^{-1}\) region, of the type formed in similar sulfur reactions.

After 20 hr reflux, a somewhat greater yield of the light green product was obtained but still in only milligram amounts. The more extended reflux period decreased considerably the yield of the yellow product.

C. Formation of \( \Pi\text{-CpW(CO)}_3\text{SPh} \) and Other Carbonylated Products

Diphenyl disulfide (0.72 g, 3.3 mmole) and freshly sublimed \( \Pi\text{-CpW(CO)}_3\text{H} \) (1.00 g, 3 mmole) were dissolved in 100 ml benzene and maintained at about 50° C in a water bath. After 3 hr, a thin layer slide indicated a single red product, identified by its infrared spectrum as \( \Pi\text{-CpW(CO)}_3\text{SPh} \). A sample withdrawn from the reaction mixture after 2 hr still had strong infrared absorptions at 2029 and 1945 cm\(^{-1}\) due to the monomeric product. An additional strong peak at 1857 cm\(^{-1}\) with a 1898 cm\(^{-1}\) companion is similar to that of a green material isolated from analogous molybdenum reactions.

A 5 ml portion of the reaction mixture was chromatographed on a silica column. Elution with (4/1) benzene-cyclohexane removed a dark green-brown band I followed by an orange-red band II while a dark green band remained at the top of the column. This upper band was resolved into three fractions with (4/1/1) benzene-cyclohexane-ethyl acetate. A very small amount of light green III and 2-3 mg each of dark brown IV and light brown V were collected.
Fraction II yielded about 15 mg of red solid, m.p., 100-102° formulated as \( \text{II-CpW(CO)}_3\text{SPh} \) by analogy of its infrared spectrum with known monomeric compounds. An infrared spectrum of V revealed a single absorption in the carbonyl region at 1966 cm\(^{-1}\). There was an insufficient amount of this yellow solid for further characterization, but comparison with other isolated materials is made in the Results and Discussion Section.

The reaction mixture was heated an additional 10 hr (3½ hr total), filtered, reduced to one-third volume and chromatographed. Samples corresponding to I, III, and IV above, were collected, but only trace amounts of II and V were detected. Sample I was a dark non-crystalline solid (0.5 g) with no sharp melting or decomposition point. The material decomposed in solution and was insufficiently soluble for molecular weight measurements or taking nmr spectra. Attempted purification by sublimation or crystallization resulted in decomposition to an amorphous material with no observable carbonyl absorptions in its infrared spectrum.

Anal. Calcd for I, \((\text{C}_{12}\text{H}_{20}\text{OSW})_x\): C, 37.30; H, 2.59; S, 8.30; W, 47.41. Found: C, 34.84; H, 2.80; S, 7.95; W, 47.71.

The infrared spectrum of I is compared with spectra of similar compounds in the Results and Discussion Section.

The light green material III has an infrared spectrum with four absorptions in the carbonyl region similar to those observed for green compounds of selenium and tellurium. There was insufficient material for an elemental analysis. The infrared spectrum of III is presented in the Results and Discussion Section.
Sample IV is a dark brown powder which melts with decomposition at 128° C. The carbon and hydrogen analysis were unexpectedly high at carbon, 40.73%, and hydrogen, 4.78%. The nmr spectrum of V has a sharp cyclopentadienyl proton signal at 5.31 ppm, and a broad phenyl proton multiplet centered at 7.1 ppm with an integration of signals of about 2.5 to 1, respectively.
1. Formulations

A. Monomeric \( \Pi \)-Cyclopentadienyliron Dicarbonyl Phenylchalconides

A comparison of spectral data on the products formulated as \( \Pi \)-CpFe(CO)\(_2\)EPh (E = Se, Te) with the reported sulfur analogue is given in Table I. Both compounds formed easily when the reactions were maintained at about 80° C for 2-3 hr, but were slow to form at room temperature. Evidence for the assigned structures include data from infrared and nuclear magnetic resonance spectra, molecular weight measurements, mass spectra, and elemental analysis.

In contrast to the sulfur compound \( \Pi \)-CpFe(CO)\(_2\)SPh, which is reported to be bright vermillion,\(^{29}\) the analogous selenium and tellurium products are deep green to black. The low melting points are consistent with a monomeric formulation, but it is surprising that the selenium and tellurium compounds melt at a lower temperature than the 80.5° C of the sulfur monomer. With \( \Pi \)-CpFe(CO)\(_2\)TePh, loss of CO and dimer formation occurred in a sublimation apparatus heated slightly above its 66° C melting point, while \( \Pi \)-CpFe(CO)\(_2\)SePh melts at 50-52° C and sublimes onto the cap of a storage bottle. The rather drastic difference in color between the sulfur compound and other chalcogen derivatives as well as considerable difference of melting points suggests that a notable difference in bonding exists.

Infrared spectra (carbonyl region) of both the Se and Te compounds include shoulders or separate peaks that are identified in Part IB of this Section with dinuclear complexes. The tendency to lose carbon monoxide and form a dinuclear complex in solution resulted in molecular
**TABLE I**

SPECTRAL DATA ON \(\pi\)-CYCLOPENTADIENYLIRON CARBONYL DERIVATIVES

<table>
<thead>
<tr>
<th></th>
<th>A. Monomers, (\pi)-CpFe(CO)(_2)EPh</th>
<th>B. Dimeric ([\pi\text{-CpFe(CO)EPh}]_2)</th>
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<tbody>
<tr>
<td><strong>E</strong></td>
<td>Infrared(^{(a)}) Proton Magnetic(^{(b)})</td>
<td>Infrared(^{(a)}) Proton Magnetic(^{(b)})</td>
</tr>
<tr>
<td>S</td>
<td>2033 1990 4.83</td>
<td>S(_I) 1953 1937 4.03(^{(d)})</td>
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<tr>
<td>Se</td>
<td>2026 1984 4.79</td>
<td>S(_{II}) 1982 4.43(^{(e)})</td>
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<td>Te</td>
<td>2018 1976 4.77</td>
<td>Se(_I) 1947 1931 4.02</td>
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<td>Se(_{II}) 1975 4.46</td>
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<tr>
<td></td>
<td></td>
<td>Te(_{(I+II)}) 1965 1937 1921 4.48 4.11</td>
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</tbody>
</table>

(a) Carbonyl stretching region, cyclohexane solution, cm\(^{-1}\).
(b) Cyclopentadienyl proton singlets, CS\(_2\) solution, in ppm from T.M.S.
(c) Subscript I represents isomer I, subscript II represents isomer II (Figure 5).
(d) Value by Ahmad.
(e) Ahmad reports 4.49 ppm.
weight measurements too high for the formulations given. The dimeric products may be separated from the monomers by column chromatography, but in the process of collecting and crystallizing the sample, partial dimerization occurs.

A comparison of infrared spectra for several known \( \eta^2\text{-CpFe(CO)\textsubscript{2}X} \) compounds is given in Table II. The trend toward lower energy carbonyl absorptions as ligand changes from PhS to PhSe to PhTe parallels the trend for ligands Cl to I and CF\textsubscript{3}S to CH\textsubscript{3}S. The nmr spectra for cyclopentadienyl protons presented in Table I are sharp singlets which have equivalent area to the phenyl proton multiplets.

Convincing evidence for the formulations of the new complexes comes from the mass spectrum of the selenium compound. A very weak parent peak was observed for \( \eta^2\text{-CpFe(CO)\textsubscript{2}SePh}^+ \). No peak was observed corresponding to loss of one carbonyl group, but there was a medium peak for the ion \( \text{CpFeSePh}^+ \), while the only other peaks representing ions containing iron were \( \text{Fe(Cp)}^+_2 \) (very strong), \( \text{FeCp}^+ \) (strong) and \( \text{Fe}^+ \) (strong).

The reaction of diphenyl disulfide with \( \eta^2\text{-CpFe(CO)\textsubscript{2}} \) was carried out for a comparison of the reaction conditions necessary to produce the various chalcogen compounds. Products obtained were in agreement with those reported by Ahmad, Bruce, and Knox\textsuperscript{29} except that these workers had not isolated the monomeric product from this reaction. The greater tendency for the sulfur monomer to dimerize is illustrated by the fact that 3 hr reflux in benzene, of \( \eta^2\text{-CpFe(CO)\textsubscript{2}} \) with Ph\textsubscript{2}S\textsubscript{2}, yielded mostly dimeric products whereas in comparable reactions with selenium and tellurium ligands, only a trace of dimer was observed.
<table>
<thead>
<tr>
<th>X</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>Solvent</th>
<th>Ref.</th>
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<tr>
<td>PhTe</td>
<td>2018</td>
<td>1976</td>
<td>Cyclohexane</td>
<td>(b)</td>
</tr>
</tbody>
</table>

(a) Carbonyl stretching frequencies, cm$^{-1}$.
(b) This work.
Figure 4. Infrared Spectra of η-CpFe(CO)$_2$EPh.
B. Isomeric Dimers $[\Pi\text{-CpFe(CO)EPh}]_2$ ($E = \text{Se, Te}$).

Comparison of the infrared and proton magnetic spectra of the new selenium and tellurium bridged dimers with the known sulfur isomers can be made from data in Table II. The similarities in shape and relative intensities of the carbonyl absorptions as well as comparable chemical shifts for cyclopentadienyl protons suggests that the isomeric pairs of the three chalcogen derivatives have similar structures. Irreversible isomerization of the less stable to more stable isomer of $[\Pi\text{-CpFe(CO)SPh}]_2$ has been observed.29

Figure 5 illustrates five possible planar configurations of $[\Pi\text{-CpFe(CO)EPh}]_2$, of which could exist two conformations each, due to folding of the four member ring. Structures in which the cyclopentadienyl rings are not in similar environments can be ruled out because of the absence of multiplicity in the proton resonances of these groups. Furthermore, the nmr spectra of the two isomers of $[\Pi\text{-CpFe(CO)SR}]_2$ ($R = \text{Me or p-methoxyphenyl}$)29 have singlets for the methyl protons in each case. Also, when $R$ in the above formula is $p\text{-C}_6\text{H}_4\text{F}_3$,33 $^{19}\text{F}$ singlets appear in the nmr spectrum of each isomer.

An X-ray diffraction study34 has shown a folded conformer of I (Figure 5) to be the most stable isomer when $E = \text{S}$. Applying the above spectral considerations then requires that structure II (Figure 5), or a folded conformation of it, be the less stable isomer.

A considerably different distribution of isomers was isolated from the reactions of the three diphenyl dichalcogenides. Thus, the sulfur reaction yielded about 25% isomer II, the selenium about 10% of this isomer and with tellurium, the relative sizes of the cyclopentadienyl proton signals in a nmr spectrum of the isolated mixture revealed
Figure 5. Planar Configurations for [η-CpFe(CO)EPhe]₂.
that isomer II was the major product. It is unlikely that these observed distributions represented equilibrium mixtures in the three cases, but rather formation of the isomeric dimers is a kinetically controlled process and the isomer distribution represents some combination of rate of formation with rate of isomerization. In a recent paper, which supports this premise, Dekker, Knox, and Robertson report that in irradiation of \((p\text{-thiol})\text{dicarboxyl-}\pi\text{-cyclopentadienyliiron}\) with ultraviolet light a dimer corresponding to structure I was obtained in 35% yield while the yield of the less stable isomer was 50%. Synthesis of the isomer pair from di-\(p\text{-tolyl disulfide}\) and \([\pi\text{-CpFe(CO)}_2]_2\) by thermal means, yielded I in 88% yield and II in about 1% yield.

A sample of II \((E = \text{Se})\) dissolved in cyclohexane and placed in a sodium chloride cell was scanned several times through the 1900-2000 cm\(^{-1}\) region. A slowly decreasing intensity of 1931 and 1947 cm\(^{-1}\) absorptions with corresponding increases in the 1975 cm\(^{-1}\) absorption indicated isomerization was taking place. In similar experiments with isomer I \((E = \text{Se})\) or a mixture of I and II \((E = \text{Te})\), no evidence was observed for isomerization over a 30-minute period. This decreased tendency to isomerize for the tellurium products can be rationalized if one assumes the metal-chalcogen bond strength to be in the order: \(\text{Te} > \text{Se} > \text{S}\). The increasing energy of the carbonyl stretching frequencies as the ligands change from S to Se to Te is also suggestive of the above order of bond strength. Thus, a stronger iron-tellurium bond would give more stability to both of the dimeric isomers and render isomerization via a dissociative mechanism less likely than with the sulfur and selenium analogues. This stronger bond from the "softer" chalcogen atom
though primarily due to better $\sigma$-bonding, may also include an increasing amount of double bond character due to $\pi$-bonding. An intramolecular isomerization involving the inversion of tetrahedral chalcogen atoms would become less likely as the metal-chalcogen bond increased in double bond character. Also, if steric factors are a driving force in the isomerization of II to I ($E = S$, $Se$), they would be expected to be of less importance when $E = Te$ because of the greater size of the bridging atom.

Mass spectra of I ($E = S$, $Se$), II ($E = Se$), and of the mixture of isomers with phenyl telluride bridges were taken. In no case was a peak for a parent molecular ion or for any other iron carbonyl species observed. The base peak in each spectrum was at $m/e = 186$, assigned to $Fe(Cp)_2^+$, with other intense peaks assigned to $PhE^+ (E = S$, $Se$, $Te)$, and $Fe^+$.

Samples of the selenium and tellurium compounds have been stored in ordinary capped bottles for two years without noticeable decomposition, and this fact illustrates the high stability of these materials. A sample of isomer I ($E = S$) was, however, partially decomposed to an insoluble material after several months' storage.

C. Chalcogen Bridged Iron Carbonyl Dimers

Evidence for the compounds with proposed formula $[Fe(CO)_{3}EPh]_{2}$ ($E = Se$, $Te$), includes elemental analysis, molecular weight measurements, and comparison of infrared spectra with those of previously reported sulfur compounds. Tables IV and V summarize infrared data for several bridged iron carbonyl dimers and analytical data on the new compounds.
### TABLE III

COMPARATIVE ANALYTICAL DATA

#### A. Monomers \( \text{III-CpFe(CO)EPh} \)

<table>
<thead>
<tr>
<th>E</th>
<th>C</th>
<th>H</th>
<th>Wt</th>
<th>C</th>
<th>H</th>
<th>Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>46.45</td>
<td>3.20</td>
<td>372</td>
<td>46.89</td>
<td>3.03</td>
<td>333</td>
</tr>
<tr>
<td>Te</td>
<td>40.36</td>
<td>3.01</td>
<td>434</td>
<td>40.89</td>
<td>2.62</td>
<td>381</td>
</tr>
</tbody>
</table>

#### B. Dimers \( \text{[III-CpFe(CO)EPh]_2} \)

<table>
<thead>
<tr>
<th>E</th>
<th>C</th>
<th>H</th>
<th>Wt</th>
<th>C</th>
<th>H</th>
<th>Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se(b)</td>
<td>46.85</td>
<td>3.38</td>
<td>589</td>
<td>47.23</td>
<td>3.33</td>
<td>610</td>
</tr>
<tr>
<td>Se(c)</td>
<td>46.94</td>
<td>3.43</td>
<td>601</td>
<td>47.23</td>
<td>3.33</td>
<td>610</td>
</tr>
<tr>
<td>Te(d)</td>
<td>40.45</td>
<td>3.13</td>
<td>680</td>
<td>40.73</td>
<td>2.85</td>
<td>707</td>
</tr>
</tbody>
</table>

(a) Vapor pressure osmometer, CHCl₃ solution.
(b) Isomer I (Figure 5).
(c) Isomer II (Figure 5).
(d) Mixture of isomers I and II.
Figure 6. Infrared Spectra of [η-CpFe(CO)SePh]₂ Isomer I (above) and Isomer II (below).
Figure 7. Infrared Spectrum of \([\text{II-CpFe(CO)TePh}]_2\) Mixture of Isomers I and II.
TABLE IV
CARBONYL STRETCHING FREQUENCIES\(^{(a)}\) FOR
COMPOUNDS OF FORMULA \([\text{Fe(CO)}_3X]_2\)

<table>
<thead>
<tr>
<th>X</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(\nu_4)</th>
<th>Solvent</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>2081</td>
<td>2042</td>
<td>----</td>
<td>2005</td>
<td>CCl(_4)</td>
<td>19</td>
</tr>
<tr>
<td>SPh</td>
<td>2078</td>
<td>2041</td>
<td>2009</td>
<td>2001</td>
<td>CCl(_4)</td>
<td>20</td>
</tr>
<tr>
<td>SeEt</td>
<td>2073</td>
<td>2037</td>
<td>2000</td>
<td>1991</td>
<td>CCl(_4)</td>
<td>20</td>
</tr>
<tr>
<td>SeEt</td>
<td>2066</td>
<td>2033</td>
<td>----</td>
<td>1984</td>
<td>CCl(_4)</td>
<td>19</td>
</tr>
<tr>
<td>P(CH(_3))(_2)</td>
<td>2050</td>
<td>2010</td>
<td>1977</td>
<td>1962</td>
<td>CS(_2)</td>
<td>74</td>
</tr>
<tr>
<td>PEt(_2)</td>
<td>2045</td>
<td>2007</td>
<td>1972</td>
<td>1962</td>
<td>CHCl(_3)</td>
<td>75</td>
</tr>
<tr>
<td>As(CH(_3))(_2)</td>
<td>2037</td>
<td>2024</td>
<td>1998</td>
<td>1965(_)</td>
<td>1958 (_)</td>
<td>CHCl(_3)</td>
</tr>
<tr>
<td>SePh</td>
<td>2061</td>
<td>2031</td>
<td>1998</td>
<td>1991(_)</td>
<td>1980(_)</td>
<td>(_)</td>
</tr>
<tr>
<td>TePh</td>
<td>2058</td>
<td>2021</td>
<td>1990</td>
<td>1983(_)</td>
<td>1972(_)</td>
<td>(_)</td>
</tr>
</tbody>
</table>

\(^{(a)}\) In cm\(^{-1}\).

\(^{(b)}\) This work.
### TABLE V

**ANALYTICAL AND OTHER DATA ON COMPOUNDS OF FORMULA: \([M(CO)_3EPh]_2\)**

<table>
<thead>
<tr>
<th></th>
<th>(M = \text{Fe})</th>
<th>(M = \text{Ru})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>E = Se</td>
<td>E = Te</td>
</tr>
<tr>
<td>Found</td>
<td>37.02</td>
<td>31.59</td>
</tr>
<tr>
<td>Calculated(^a)</td>
<td>(36.52)</td>
<td>(31.37)</td>
</tr>
<tr>
<td>H</td>
<td>E = Se</td>
<td>E = Te</td>
</tr>
<tr>
<td>Found</td>
<td>2.12</td>
<td>1.79</td>
</tr>
<tr>
<td>Calculated(^a)</td>
<td>(1.70)</td>
<td>(1.58)</td>
</tr>
<tr>
<td><strong>Mol Wt</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Found(^b)</td>
<td>573</td>
<td>675</td>
</tr>
<tr>
<td>Calculated(^a)</td>
<td>(591)</td>
<td>(689)</td>
</tr>
<tr>
<td>Color</td>
<td>Orange-red</td>
<td>Red</td>
</tr>
<tr>
<td>Melting Point</td>
<td>94-96°</td>
<td>104-106°</td>
</tr>
</tbody>
</table>

\(^a\) Calculated for \(C_{18}H_{30}O_6E_2M_2\).

\(^b\) Vapor pressure osmometer, benzene solution.
Isolation of a pair of isomers of \([\text{Fe(CO)}_3\text{SR}]_2\) (\(R = \text{Me}^{25}\), \(\text{Et}\), or \(\text{Bu}^{66}\)) has been accomplished. No isomers were reported for \(R = \text{Ph}^{18}\) or \(\text{t-Bu}^{66}\) nor have any been isolated with the SePh or TePh bridging groups reported here. Repeated elution with pentane on a silica thin-layer plate moved only a single red spot of \([\text{Fe(CO)}_3\text{TePh}]_2\). An x-ray study\(^{24}\) of the dimeric \([\text{Fe(CO)}_3\text{SR}]_2\) (\(R = \text{Et}\)) coupled with nmr evidence when \(R = \text{Me}^{25}\) indicated the two isomers existed in cis and trans configurations with respect to the \(R\) groups with other similar groups cis to each other. It seems reasonable to assume that for the larger \(R\) groups (e.g., \(\text{Ph}\) or \(\text{t-Bu}\)) attached to the bridging atom an anti or trans isomer would be favored to the extent that it is the only specie isolated. However, in the absence of isomers for comparison of dipole moment or other criteria that may distinguish possible configurations, a structure assignment is only conjecture.

Mass spectral data on the new compounds is given in Table VI. Relative sizes of ion peaks are given for the species containing two iron and two chalcogen atoms, but only approximate comparisons are made for other ions. The several natural occurring isotopes of both selenium and tellurium mixed into a dinuclear complex causes a rather complex multiplet of peaks to appear for a given type ion. For those ions containing the same isotope distribution (e.g., \(\text{Fe}_2\text{E}_2^+\) containing species) relative intensities were obtained from the most prominent peaks.

The appearance of a molecular ion and of ions representing loss of successive carbonyl groups is the expected phenomenon for dinuclear metal carbonyl complexes that possess a metal-metal bond.\(^{67}\) The only deviation from this behavior for compounds reported here is the
TABLE VI
MASS SPECTRA RELATIVE ABUNDANCE OF Fe$_2$(CO)$_6$E$_2$R$_2$ (a)

<table>
<thead>
<tr>
<th>Ion</th>
<th>E=Se$^a$</th>
<th>E=Se(b,c)</th>
<th>E=Te(b,c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$(CO)$_6$E$_2$R$_2$+</td>
<td>8.2</td>
<td>4.4</td>
<td>6.2</td>
</tr>
<tr>
<td>Fe$_2$(CO)$_5$E$_2$R$_2$+</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_2$(CO)$_4$E$_2$R$_2$+</td>
<td>16.3</td>
<td>9.7</td>
<td>3.0</td>
</tr>
<tr>
<td>Fe$_2$(CO)$_3$E$_2$R$_2$+</td>
<td>8.2</td>
<td>3.8</td>
<td>4.9</td>
</tr>
<tr>
<td>Fe$_2$(CO)$_2$E$_2$R$_2$+</td>
<td>5.7</td>
<td>3.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Fe$_2$(CO)E$_2$R$_2$+</td>
<td>13.2</td>
<td>7.9</td>
<td>3.6</td>
</tr>
<tr>
<td>Fe$_2$E$_2$R$_2$+</td>
<td>100</td>
<td>61.6</td>
<td>43.8</td>
</tr>
<tr>
<td>Fe$_2$E$_2$R$_2$+</td>
<td>51</td>
<td>19.5</td>
<td>(vw)</td>
</tr>
<tr>
<td>FeE$_2$+</td>
<td>41.7</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>FeE$_2$+</td>
<td>-</td>
<td>(w)</td>
<td>(w)</td>
</tr>
<tr>
<td>Fe$_2$E</td>
<td>16.3</td>
<td>(w)</td>
<td>(m)</td>
</tr>
<tr>
<td>Fe$_2$+</td>
<td>2.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$^+$</td>
<td>4.8</td>
<td>(w)</td>
<td>(m)</td>
</tr>
</tbody>
</table>

(a) Taken at 70 ev, R = C$_6$H$_5$.
(b) This work.
(c) (m) = Medium, (w) = weak, (vw) = very weak.
Figure 8. Mass Spectrum of $[\text{Fe(CO)}_3\text{TePh}]_2$. 

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Figure 9. Infrared Spectra of \([\text{Fe(CO)}_3\text{EPh}]_2\).
absence (or at least insufficient intensity to measure) of ions with one CO group less than the parent molecular ion.

The mass spectrum of \([\text{Fe(CO)}_3\text{SPh}]_2\) has been reported\(^{26}\) and is included in Table VI for comparison. It is particularly interesting that the most significant difference in the three spectra is in the abundance of \(\text{Fe}_2\text{E}_2^+\) relative to \(\text{Fe}_2\text{E}_2\text{Ph}_2^+\) which increases in the order \(\text{S} < \text{Se} < \text{Te}\). Also of significance is the appearance of the \(\text{FeE}_2^+\) ion when \(\text{E} = \text{Se}\) or \(\text{Te}\) and not when \(\text{E} = \text{S}\). A metal chalcogen bond strength increasing in the order \(\text{S} < \text{Se} < \text{Te}\) would give increasing stability to \(\text{Fe}_2\text{E}_2^+\) and \(\text{FeE}_2^+\) species and thereby increase their abundance in a mass spectrum.

D. Dinuclear Chalcogen Bridged Ruthenium Carbonyls.

Evidence for the formulation \([\text{Ru(CO)}_3\text{EPh}]_2\) (\(\text{E} = \text{Se}, \text{Te}\)) includes analytical data, molecular weight measurements and comparison of infrared spectra with similar iron compounds and with previously reported ruthenium-sulfur dimers. Table VII lists the carbonyl stretching frequencies for reported ruthenium-sulfur dimers as well as the selenium and tellurium compounds reported here. Excellent agreement is noted between the latter compounds and \([\text{Ru(CO)}_3\text{SPh}]_2\) reported by Centini.\(^{39}\) The "usual" shift in energy of \(\nu_{\text{CO}}\) as the chalcogen ligand changes is observed. Highest energy absorptions listed for compounds reported by Johnson, \textit{et al.}\(^{38}\) in which the reported dimers were products of reaction of thiols with \(\text{Ru}_3(\text{CO})_{12}\), may arise from polymeric impurities in the samples or may possibly be due to metal hydrogen bonds.

As with the previously discussed iron carbonyl dimers, the possibility of syn or anti isomers exists with the complexes \([\text{Ru(CO)}_3\text{EPh}]_2\). Although isomers were not isolated in sufficient amount for characterization,
### Table VII

**Infrared Spectra\(^{(a)}\) of Some Ruthenium Carbonyl Derivatives**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ref</th>
</tr>
</thead>
</table>

#### A. Dimers

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(\nu_4)</th>
<th>Solvent</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru(CO)}_3\text{SPh}]_2)</td>
<td>2105(w)</td>
<td>2080(m,sh)</td>
<td>2060(br)</td>
<td>2018(m,br)</td>
<td>(\text{CCl}_4)</td>
<td>38</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_3\text{Sbu}]_2)</td>
<td>2110(w)</td>
<td>2080(m,sh)</td>
<td>2056(s)</td>
<td>2010(s,br)</td>
<td>(\text{CCl}_4)</td>
<td>38</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_3\text{SEt}]_2)</td>
<td>2110(w)</td>
<td>2080(m)</td>
<td>2058(s)</td>
<td>2010(s,br)</td>
<td>(\text{CCl}_4)</td>
<td>38</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_3\text{SPh}]_2)</td>
<td>2086(m)</td>
<td>2058(vs)</td>
<td>2010(s)</td>
<td>2000(s)</td>
<td>(\text{CCl}_4)</td>
<td>39</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_3\text{SePh}]_2)</td>
<td>2081(s)</td>
<td>2052(vs)</td>
<td>2006(s,br)</td>
<td>(\text{CHCl}_3)</td>
<td>(\text{b})</td>
<td></td>
</tr>
<tr>
<td>([\text{Ru(CO)}_3\text{TePh}]_2)</td>
<td>2073(s)</td>
<td>2044(vs)</td>
<td>2002(s,br)</td>
<td>(\text{CHCl}_3)</td>
<td>(\text{b})</td>
<td></td>
</tr>
</tbody>
</table>

#### B. Polymers

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(\nu_4)</th>
<th>Solvent</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ru(CO)}_2\text{Cl}_2]_n)</td>
<td>2066(m)</td>
<td>1988(m)</td>
<td></td>
<td></td>
<td>(\text{CHCl}_3)</td>
<td>38</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_2\text{Br}_2]_n)</td>
<td>2059(s)</td>
<td>1990(m)</td>
<td></td>
<td></td>
<td>(\text{CHCl}_3)</td>
<td>38</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_2\text{I}_2]_n)</td>
<td>2053(s)</td>
<td>1995(s)</td>
<td></td>
<td></td>
<td>(\text{CHCl}_3)</td>
<td>38</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_2(\text{SPh})_2]_n)</td>
<td>2105(w)</td>
<td>2042(s)</td>
<td>1985(s)</td>
<td>1945(sh)</td>
<td>(\text{Nujol})</td>
<td>38</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_2(\text{SPh})_2]_n)</td>
<td>2112(vs)</td>
<td>2052(vs)</td>
<td>1996(s)</td>
<td></td>
<td>(\text{CCl}_4)</td>
<td>39</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_2(\text{SPh})_2]_n)</td>
<td>2106(m)</td>
<td>2046(s)</td>
<td>1991(m)</td>
<td>1945(sh)</td>
<td>(\text{CCl}_4)</td>
<td>39</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_2(\text{SePh})_2]_n)</td>
<td>2096(m)</td>
<td>2037(s)</td>
<td>1974(m)</td>
<td>1942(sh)</td>
<td>(\text{CHCl}_3)</td>
<td>(\text{b})</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_2(\text{SePh})_2]_n)</td>
<td>2105(w)</td>
<td>2037(s)</td>
<td>1974(m,br)</td>
<td></td>
<td>(\text{CHCl}_3)</td>
<td>(\text{b})</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_2(\text{TePh})_2]_n)</td>
<td>2080(m)</td>
<td>2030(s)</td>
<td>1974(m,br)</td>
<td></td>
<td>(\text{CHCl}_3)</td>
<td>(\text{b})</td>
</tr>
<tr>
<td>([\text{Ru(CO)}_2(\text{TePh})_2]_n)</td>
<td>2095(w)</td>
<td>2027(s)</td>
<td>1974(m,br)</td>
<td></td>
<td>(\text{CHCl}_3)</td>
<td>(\text{b})</td>
</tr>
</tbody>
</table>

\(\text{(a)}\) Carbonyl stretching frequencies in cm\(^{-1}\).

\(\text{(b)}\) This work.
there was some evidence for their existence. In the TLC separation of the reaction of Ru₃(CO)₁₂ with Ph₂Se₂ there was a faint yellow band following the band characterized as [Ru(CO)₃SePh]₂. The infrared spectra of these two bands were similar and it is possible that the two materials are isomers. Carbonyl stretching frequencies of reported isomer pairs of [Fe(CO)₃SR]₆₆ are quite similar, as is expected, because the local symmetry about the metal atom should change very little with a change in the position of groups attached to bridging atoms. Of the possible configurations suggested for [M(CO)₃ER]₂,²⁴ the two that appear most reasonable are (a) and (b) below

Steric repulsions that may preclude structure (a) when M = Fe, E = S, and R is a bulky group, should be less significant when M is the larger ruthenium atom and E is one of the larger chalcogen atoms.

Corresponding iron complexes discussed in the previous part of this Section yielded significant information from their mass spectra. Attempts to obtain mass spectra of the ruthenium complexes were unsuccessful in that no ions containing metal-chalcogen or metal-metal bonds were observed. This is at first surprising in consideration of the expected
strong metal-metal bond in \([\text{Ru(CO)}_3\text{EPh}]_2\) (E = Se, Te). Thermogravimetric plots of these compounds revealed no mass loss until between 150 and 160° C gradual loss occurred. Residue removed from the thermogravimetric balance after heating to about 200° C had an infrared spectrum with two peaks in the carbonyl stretching region, neither of which corresponded to spectra previously observed. Apparently, loss of carbon monoxide is accompanied by aggregation of the dinuclear units. This process must occur at temperatures too low to volatilize the sample in the mass spectrometer.

The ruthenium-chalcogen dimers are separated from the reaction mixtures by preparative layer chromatography and obtained in less than ten percent yield. Principle products of these reactions were polymeric derivatives discussed in part E of this Section. In similar reactions, with \(\text{Fe}_3(\text{CO})_{12}\) as metal substrate, the chalcogen bridged dimers were the only carbonylated products observed. This considerable difference in the chemistry of ruthenium carbonyl and iron carbonyl derivatives may be caused by the greater size of the ruthenium atom which would make it more susceptible to nucleophilic substitution. Also, a stronger metal-metal bond in the case of ruthenium may decrease the "back bonding" to carbonyl groups and thus decrease the metal-carbon bond strength. It is noteworthy that the highest energy carbonyl stretching frequencies are about 15 cm\(^{-1}\) lower for the iron dimers than for corresponding ruthenium complexes.

E. Polymeric Chalcogen Derivatives of Triruthenium Dodecacarbonyl.

Compounds of general formula \([\text{Ru(CO)}_2(\text{EPh})_2]_n\) (E = Se, Te) have been prepared. There are two different aggregations of basic units with each of the donor ligands. Molecular weight measurements, which because
Figure 10. Infrared Spectra of [Ru(CO)$_3$EPh]$_2$. 

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Figure 11. Infrared Spectra of $[\text{Ru(CO)}_2(\text{EPh})_2]_n$. (Lower Molecular Weight Telomers.)
of low molal concentrations are subject to considerable deviation, indicate a lower weight polymer (n in above formula = 6-7) and a higher molecular weight polymer (n = ~14). The lower weight polymers containing selenium and tellurium correspond well both in number of structural units and carbonyl stretching frequencies with a similarly formulated polymer (E = S) reported by Cetini.\textsuperscript{39}

A kinked chain polymer structure similar to that proposed for the halide bridged compounds, [Ru(CO)\textsubscript{2}X\textsubscript{2}]\textsubscript{n} (X = Cl, Br, I)\textsuperscript{38} has been suggested by Johnson, et al.\textsuperscript{38} as the structure for the phenylsulfido-bridged polymer.

![Diagram of polymer structure](image)

This structure was invoked to explain the existence of two carbonyl stretching absorptions in the ir spectrum of [Ru(CO)\textsubscript{2}X] (X = Cl, Br, I). If the CO groups were \textit{trans} in a symmetrical octahedral environment, only one \textit{\textmu}CO band should appear. However, the chalcogen bridged polymers have three and possibly four (considering the broadness of the lowest energy band) absorptions in the carbonyl stretching region and the symmetry arguments no longer hold. Also, the above structure does not require metal-metal bonding in order to conform to the 18-electron rule. Considering the much greater tendency for polymerization of ruthenium dimers than corresponding iron dimers, it would be surprising if a polymer without metal-metal bonding would be formed at the
expense of a probably strong metal-metal bond in the dimer. Furthermore, it would seem that a chain structure would be of quite variable length and not yield the fairly consistent molecular weight values found here.

Whatever the structure, each of the four polymers are quite stable. Attempts to obtain melting points on a hot stage or in capillaries led to slow decomposition at temperatures above about 220°. They are quite soluble in methylene chloride or chloroform, but not in hydrocarbons, methanol, or acetone. Repeated recrystallization from mixed solvents causes no apparent decomposition.

Comparison of infrared spectra of these compounds with the corresponding absorptions for halogen bridged polymers (Table VII) offers a significant clue to chalcogen donor character. The decrease in energy of a given peak as bridging atoms change from Cl to Br to I is in the same order of magnitude as when bridging atoms change from S to Se to Te.

F. Monomeric Chalconides of Tungsten and Molybdenum.

Monomers of formula \( \pi\text{-CpMo(CO)}_3\text{SePh} \) and \( \pi\text{-CpW(CO)}_3\text{SPh} \) were prepared. The former compound was a product of a reaction carried out at low temperature with the expressed purpose of obtaining a monomeric product, while the latter was obtained as a minor product in a higher temperature reaction. Table VIII compares the carbonyl region infrared spectra for several tungsten and molybdenum cyclopentadienyl carbonyl monomeric derivatives.

Molecular weight measurements of \( \pi\text{-CpMo(CO)}_3\text{SePh} \) give values consistently too high which is indicative of the tendency toward loss of CO and formation of a dinuclear complex. The infrared spectrum of a
@TABLE VIII
SPECTRAL DATA ON Mo AND W MONOMERS AND DIMERS

A. MONOMERIC MOLYBDENUM AND TUNGSTEN COMPLEXES, $\Pi\text{-CpM(CO)}_3\text{EPh}$

<table>
<thead>
<tr>
<th>M</th>
<th>E</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_{\text{cp}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Te</td>
<td>2016</td>
<td>1948(sh)</td>
<td>1937</td>
<td>5.28</td>
<td>3</td>
</tr>
<tr>
<td>Mo</td>
<td>Se</td>
<td>2026</td>
<td>-</td>
<td>1948(br)</td>
<td>(c)</td>
<td>(d)</td>
</tr>
<tr>
<td>Mo</td>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(e)</td>
</tr>
<tr>
<td>W</td>
<td>Te</td>
<td>2012</td>
<td>1937</td>
<td>1926</td>
<td>5.41</td>
<td>3</td>
</tr>
<tr>
<td>W</td>
<td>Se</td>
<td>2022</td>
<td>-</td>
<td>1936(br)</td>
<td>5.5</td>
<td>3</td>
</tr>
<tr>
<td>W</td>
<td>S</td>
<td>2030</td>
<td>-</td>
<td>1946(br)</td>
<td>(c)</td>
<td>(d)</td>
</tr>
</tbody>
</table>

B. DIMERIC MOLYBDENUM AND TUNGSTEN COMPLEXES, [$\Pi\text{-CpM(CO)}_2\text{EPh}$]$_2$

<table>
<thead>
<tr>
<th>M</th>
<th>E</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_4$</th>
<th>$v_{\text{cp}}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Te</td>
<td>1950</td>
<td>1935</td>
<td>1875</td>
<td>1860</td>
<td>5.12</td>
<td>3</td>
</tr>
<tr>
<td>Mo</td>
<td>Se</td>
<td>1660</td>
<td>1945</td>
<td>1875</td>
<td>1865</td>
<td>5.2</td>
<td>3</td>
</tr>
<tr>
<td>Mo</td>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(e)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Te</td>
<td>1942</td>
<td>1927</td>
<td>1861</td>
<td>1848</td>
<td>5.30</td>
<td>(d)</td>
</tr>
<tr>
<td>W</td>
<td>Se</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(f)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(f)</td>
<td></td>
</tr>
</tbody>
</table>

(a) Carbonyl stretching frequencies, CS$_2$ solution, in cm$^{-1}$.

(b) Cyclopentadienyl proton resonance, CS$_2$ solution, in ppm from T.M.S.

(c) Not measured.

(d) This work.

(e) Preparation of compound reported in a note$^{48}$, but spectral data not given.

(f) Preparation attempted, but compound not found.

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sample of monomer removed from a vapor pressure osmometer had considerably increased absorptions at energies corresponding to $[\Pi\text{-CpMo(CO)}_2\text{SePh}]_2$.

Other compounds of the series $\Pi\text{-CpM(CO)}_3\text{EPh}$ ($M = \text{Mo}; \ E = \text{Te}$ and $M = \text{W}; \ E = \text{Se}, \text{Te}$) were prepared by Tillay$^3$ and the member ($M = \text{Mo}, \ E = \text{S}$) has been mentioned in a note.$^{48}$ Attempts to prepare the sulfur-molybdenum monomer by irradiation of $[\Pi\text{-CpMo(CO)}_3\text{H}]_2$ and diphenyl disulfide at low temperature and by a metathetical route with sodium phenylsulfide and $\Pi\text{-CpMo(CO)}_3\text{I}$ were not successful. Monitoring of these reactions revealed that the desired monomer was never the major component of the reaction mixture.

The considerably greater stability of tungsten derivatives as compared to analogous molybdenum compounds is evidenced by the observation that after heating a reaction mixture of $\Pi\text{-CpW(CO)}_3\text{H}$ and $\text{Ph}_2\text{S}_2$ at 50-60° for 34 hr a trace of $\Pi\text{-CpW(CO)}_3\text{SPh}$ was present, whereas 16 hr at the same temperature completely decomposed $\Pi\text{-CpMo(CO)}_3\text{SePh}$. Agreement was found with the order of stability of chalcogen monomers Te > Se > S as reported by Tillay.$^3$ However, information is insufficient to make a cross comparison between the molybdenum and tungsten series other than that mentioned above.

G. Dinuclear Tungsten-Tellurium Complex.

The dinuclear complex $[\Pi\text{-CpW(CO)}_2\text{TePh}]_2$ was prepared. Initial samples of this compound were mixed with other carbonylated materials, possibly isomers, as evidenced by infrared absorptions at 1822, 1882, and 1905 cm$^{-1}$ in addition to the four-banded pattern at 1848, 1861, 1927, and 1942 cm$^{-1}$ which is similar to the spectrum of $[\Pi\text{-CpMo(CO)}_2\text{EPh}]_2$ ($E = \text{Se}, \text{Te}$). Two weak signals in the cyclopentadienyl proton region of the nmr spectrum indicated the impurities contained the $\Pi\text{-Cp}$ group.
Rechromatographing the impure sample yielded an apparently pure compound, but insufficient amounts of the impurities were obtained for their characterization.

In contrast to the relative stability of the Mo and W monomeric compounds, the tungsten-tellurium dimer is more prone toward decomposition to other materials than is its molybdenum analogue. After 18 hr reflux in toluene, three metal carbonyl products in addition to \([\Pi\text{-CpW(CO)}_2\text{TePh}]_2\) were obtained whereas in a similar reaction the molybdenum-tellurium dimer was the only carbonyl-containing product observed (after disappearance of monomer) through 75 hr of toluene reflux. It is likely that this difference is a reflection of relative ease of substitution of carbonyl groups and not necessarily dependent on relative thermodynamic stability.

No evidence was observed for corresponding dinuclear products from the reaction of diphenyldisulfide or diphenyldiselenide with \(\Pi\text{-CpW(CO)}_3\)H. Monitoring of these reactions indicated formation of \(\Pi\text{-CpW(CO)}_3\text{EPh} (E = \text{S, Se})\) followed by decomposition of this monomer and appearance of materials discussed below.

H. Additional Carbonylated Products Containing Chalcogen Bonds with Tungsten or Molybdenum.

In addition to the well-characterized monomers and dimers, there were three series of compounds isolated from the molybdenum and tungsten cyclopentadienylcarbonyl reactions with diphenyl dichalcogenides. Series I compounds are yellow with a single infrared absorption in the carbonyl region. They have lower \(R_f\) values on either silica or alumina columns than other compounds of these reactions and, with the exception
Figure 12. Infrared Spectrum of $[\eta^2$-CpW(CO)$_2$TePh]$_2$. 

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of the diphenyl diselenide reactions, were observed as only trace products. Series II compounds have two broad absorptions in the 1950-1925 cm\(^{-1}\) region of their infrared spectra. They are dark green to black amorphous powders. The tendency of these compounds to decompose in solution has prevented their purification and characterization. The compounds in series III are minor products of extended reactions. They are light green solids with a characteristic four-banded infrared spectrum in the carbonyl stretching region.

Compounds labeled as series I are tentatively formulated as isomers of the previously characterized dimers. The only samples isolated in sufficient amounts for characterization studies were the tungsten and molybdenum complexes with phenyl selenide bridges. In these cases, molecular weight measurements were in reasonable agreement with the dimeric formulation \([\Pi\text{-CpM(CO)}_2\text{EPh}]_2\). When \(M = \text{Mo}\) and \(E = \text{Se}\), the calculated molecular weight is 746, and experimental 790. When \(M = \text{W}\) and \(E = \text{Se}\), the calculated molecular weight is 922, and experimental 1025. The nmr spectrum of I (\(M = \text{W}, E = \text{Se}\)) has a sharp cyclopentadienyl proton singlet at 5.59 ppm which integrates 1:1 with a phenyl proton multiplet centered at 7.3 ppm. This is in agreement with a diamagnetic complex as formulated.

Only after heating to 110\(^\circ\)C for several hours at a pressure of about 0.1 mm Hg was benzene, identified by a spire in the nmr spectrum, removed from the latter sample. A thermogravimetric plot of this compound revealed loss of the occluded benzene at about 160\(^\circ\)C followed by a loss between 235 and 270\(^\circ\)C of 13\% of the sample mass. This corresponds quite well with a loss of four CO groups from \([\Pi\text{-CpW(CO)}_2\text{SePh}]_2\).
in which the total mass of CO is 12.2% of the molecular weight. The decomposition temperature (235°) of this compound is high compared to melting or decomposition points of other reported dimeric compounds. However, \([\Pi-CpW(CO)_{2}TePh]_{2}\) melts at 200° C and it is conceivable that a change in configuration could be accompanied by a sizable change in melting point.

Table 9 lists the infrared spectra of the carbonyl region for series I compounds. The trend that has been consistently observed of a 7-10 wave number decrease in a given carbonyl stretching frequency as the donor atom changes from S to Se to Te is again evident.

Several possible configurations for compounds of formula \([\Pi-CpMo(CO)_{2}EPh]_{2}\) are illustrated in Figure 13. Structures in which the cyclopentadienyl groups are not in a similar environment are not included because proton resonances of these groups were always observed as sharp singlets in nmr spectra. An idealized square pyramidal orientation about the metal atoms is shown in Figure 13 and would lead to the prediction of two carbonyl stretching frequencies in the infrared spectra of these compounds. However, the dinuclear complexes previously characterized have four absorptions in the carbonyl stretching region (Figure 12) and series I compounds have a single \(\nu CO\). A trigonal bipyramidal structure with trans carbonyl groups could be expected to have a single carbonyl stretching frequency in its infrared spectrum. In the absence of x-ray
<table>
<thead>
<tr>
<th>Metal</th>
<th>Chalcogen</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Se</td>
<td>1968</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>S</td>
<td>1966</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Se</td>
<td>1952</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Te</td>
<td>1942</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>S</td>
<td>1914</td>
<td>1864</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td></td>
<td>1908</td>
<td>1851</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>S</td>
<td>1896</td>
<td>1855</td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>S</td>
<td>2002</td>
<td>1976</td>
<td>1940</td>
<td>1866</td>
</tr>
<tr>
<td>Se</td>
<td></td>
<td>1994</td>
<td>1968</td>
<td>1932</td>
<td>1866</td>
</tr>
<tr>
<td>Te</td>
<td></td>
<td>1982</td>
<td>1960,1936 (b)</td>
<td>1926</td>
<td>1868</td>
</tr>
</tbody>
</table>

(a) Carbonyl stretching frequencies, CS$_2$ solution, in cm$^{-1}$.
(b) Shoulder.
Figure 13. Some Possible Configurations of Complexes of Formula

\[ \text{[\textit{II-CpM(CO)}_2\text{EPh}]}_2. \]
data on dinuclear bridged-complexes of this type, the structures remain in doubt.

The existence of isomeric dimers can account for some previously unexplained results of preparative reactions. Thus, in reactions producing phenyl telluride bridged dimers of tungsten and molybdenum, the isomer with a four-banded IR spectrum was the major product. Although it was not isolated there was evidence for this type dimer in the Se-Mo reactions while in reactions in which M = Mo, E = S, or M = W; E = S, Se, there was no evidence for this type product. Series I compounds were produced in reactions in which the other type dimers were either not observed or existed as nonisolated intermediates. Analytical data was obtained on only one of the series I compounds and agreement for metal was poor. The formulation is therefore speculative and cannot be rigorously defended.

Series II compounds were formed in a reaction in which stable dimeric compounds were not formed in significant yield. Three reactions; (M = Mo, E = S, or Se) and (M = W, E = S) yielded small amounts of these dark green unstable products after extended periods of reaction (1-4 days) at high temperature (80-110°C). The deep green solutions as well as the strong broad band in the 1850-1900 cm⁻¹ region are characteristic of the reported trimeric compound, [η⁶-CpMo(CO)₂P₆]₃. Possible structures for these compounds are indicated in Figure 114. A bridging carbonyl structure (b) is the more plausible in consideration of the rather low energy of the carbonyl stretching frequencies although an equilibrium between terminal and bridged carbonyl groups is a likely possibility.
Figure 14. Two Possible Structures of Trinuclear [η-CpM(CO)EPh]₃.
Analytical and molecular weight data on these compounds are not reliable because of the extensive decomposition occurring in solution or when the dry compounds are exposed to air. The analytical data presented in the Experimental Section indicates reasonable agreement of tungsten and sulfur with carbon about 2% low for \([\text{CpW(CO)SPh}]_x\). In the absence of more convincing data, the proposed formulation is at best tentative. It does seem significant, however, that isolable amounts of this compound were obtained only in reactions in which a dimer was not found. Apparently the selenium, and especially the sulfur containing ligands, are better nucleophiles than the tellurium ligands and tend toward greater substitution of carbonyl and hence higher order aggregates.

Reactions of diphenyl dichalconides with \(\text{CpW(CO)H}_2\) led to small amounts of series III compounds. These are light green complexes. The analysis is in approximate agreement with a formula, \([\text{CpW(CO)Ph}]_n\). However, the nmr spectrum \((E = \text{Te})\) has a broad phenyl proton multiplet at 7.09 ppm and two sharp cyclopentadienyl proton signals at 5.70 and 5.62 ppm with an integration of 15:3:2, respectively. This data would imply three phenyl groups per cyclopentadienyl ring and it is not consistent with the approximate \((1/1)\) tungsten-tellurium ratio.

The \((3/2)\) cyclopentadienyl proton ratio implies a minimum of five of these groups but molecular weight measurements are more in line with a dinuclear product. That series III "compounds" are mixtures seems an obvious explanation, but then it is difficult to explain the consistent infrared spectra for the three materials. Certainly, the presently available information is insufficient to propose a formulation for these materials.
Figure 15. Infrared Spectrum of Unknown Complex (Series III) from Extended Reaction of \( \text{H-Cp}^\text{W(CO)}_3H \) and \( \text{Ph}_2\text{Se}_2 \).
2. **Relative Chalcogen Donor Properties.**

Experiments described herein were designed and carried out in an effort to gain a better understanding of the comparative donor chemistry of sulfur, selenium and tellurium. The experimental work was concentrated mostly on tellurium and selenium compounds because in many cases the sulfur chemistry had already been investigated. Table X summarizes the new products that have been isolated and characterized.

Stability of monomer species of cyclopentadienyl metal carbonyl derivatives were found to increase with chalcogen donor atom in the order: S < Se < Te. The stability referred to is probably a kinetic one dependent on relative ease of loss of CO from the complex. As the "softness" of the donor atom increases (i.e., decreasing electronegativity and increasing polarizability) the electron density at the metal atom should increase. This in turn will increase "back bonding" to the carbonyl group and give more double bond character (i.e., $M = C = O$) to the metal carbon bond. A lowering of the carbonyl stretching frequencies as the donor atom changes from sulfur to selenium to tellurium is also accounted for by increased metal-carbon bonding with a corresponding decrease in the order of the carbon-oxygen bond. Additional evidence of this effect has been reported recently by Stanghellini, et al. These workers investigated $^{14}$CO exchange with Fe$_3$(CO)$_5$E$_2$ ($E = S, Se, Te$) and report that "positivity" on the metal atoms decreases in the order: $S > Se > Te$.

A comparison of relative stabilities of dinuclear chalcogen bridged complexes is complicated by the variety of products obtained. Well characterized dimeric complexes of molybdenum and tungsten were

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<table>
<thead>
<tr>
<th>Metal Substrate</th>
<th>Product</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Tt-CpFe(CO)}_2])_2</td>
<td>([\text{Tt-CpFe(CO)}_2\text{SePh}])_2</td>
<td>Dimerizes in solution.</td>
</tr>
<tr>
<td>([\text{Tt-CpFe(CO)}_2])_2</td>
<td>([\text{Tt-CpFe(CO)}_2\text{TePh}])_2</td>
<td>Dimerizes in solution.</td>
</tr>
<tr>
<td>([\text{Tt-CpFe(CO)}_2])_2</td>
<td>([\text{Tt-CpFe(CO)}\text{SePh}]_2</td>
<td>Two isomers.</td>
</tr>
<tr>
<td>([\text{Tt-CpFe(CO)}_2])_2</td>
<td>([\text{Tt-CpFe(CO)}\text{TePh}]_2</td>
<td>Two isomers.</td>
</tr>
<tr>
<td>([\text{Fe}<em>3\text{(CO)}</em>{12}]</td>
<td>([\text{Fe(CO)}_3\text{SePh}]_2</td>
<td>Only isolated carbonylated product.</td>
</tr>
<tr>
<td>([\text{Fe}<em>3\text{(CO)}</em>{12}]</td>
<td>([\text{Fe(CO)}_3\text{TePh}]_2</td>
<td>Only isolated carbonylated product.</td>
</tr>
<tr>
<td>([\text{Ru}<em>3\text{(CO)}</em>{12}]</td>
<td>([\text{Ru(CO)}_3\text{SePh}]_2</td>
<td>Minor product.</td>
</tr>
<tr>
<td>([\text{Ru}<em>3\text{(CO)}</em>{12}]</td>
<td>([\text{Ru(CO)}_3\text{TePh}]_2</td>
<td>Minor product.</td>
</tr>
<tr>
<td>([\text{Ru}<em>3\text{(CO)}</em>{12}]</td>
<td>([\text{Ru(CO)}_2\text{(SePh)}_2]_n</td>
<td>Two forms characterized.</td>
</tr>
<tr>
<td>([\text{Ru}<em>3\text{(CO)}</em>{12}]</td>
<td>([\text{Ru(CO)}_2\text{(TePh)}_2]_n</td>
<td>Two forms characterized.</td>
</tr>
<tr>
<td>([\text{Tt-CpW(CO)}_3\text{H}]</td>
<td>([\text{Tt-CpW(CO)}_3\text{SePh}]</td>
<td>Isolated as minor product.</td>
</tr>
<tr>
<td>([\text{Tt-CpW(CO)}_3\text{H}]</td>
<td>([\text{Tt-CpW(CO)}_2\text{TePh}]_2</td>
<td>Similar to reported Mo dimer.</td>
</tr>
<tr>
<td>([\text{Tt-CpW(CO)}_3\text{H}]</td>
<td>([\text{Tt-CpW(CO)}_2\text{SePh}]_3</td>
<td>E = S, Se. Formulation in doubt.</td>
</tr>
<tr>
<td>([\text{Tt-CpW(CO)}_3\text{H}]</td>
<td>([\text{Tt-CpW(CO)}_2\text{TePh}]_2</td>
<td>E = S, Se. Formulation in doubt.</td>
</tr>
<tr>
<td>([\text{Tt-CpMo(CO)}_3])_2</td>
<td>([\text{Tt-CpMo(CO)}_3\text{SePh}]</td>
<td>Formed at 10°C under irradiation.</td>
</tr>
<tr>
<td>([\text{Tt-CpMo(CO)}_3])_2</td>
<td>([\text{Tt-CpMo(CO)}_3\text{EPh}]_3</td>
<td>E = S, Se. Formulation in doubt.</td>
</tr>
<tr>
<td>([\text{Tt-CpMo(CO)}_3])_2</td>
<td>([\text{Tt-CpMo(CO)}_2\text{SePh}]_2</td>
<td>Formulation in doubt.</td>
</tr>
</tbody>
</table>
isolated, in this work, only when the bridging atom was tellurium. Both cyclopentadienylcarbonyliron and carbonyl iron derivatives form stable dinuclear complexes with phenyl chalconide bridges. Relative chalcogen donor properties in the \([\text{I}-\text{CpFe(CO)EPh}]_2\) compounds are illustrated by the relative tendency to isomerize from the less stable to the more stable isomer in the three cases. When \((E = \text{Te})\) in the above formula, isomerization was not observed under conditions in which it takes place readily for \(E = \text{S}\) or \(\text{Se}\). Tellurium acting as a better donor atom in the above example would increase electron density on the metal atom, thereby increasing "back bonding" to the carbonyl groups and making them less likely to dissociate.

Mass spectra of the iron carbonyl dimers \([\text{Fe(CO)}_3\text{EPh}]_2\) \((E = \text{S, Se, Te})\) add further evidence that the strength of an iron-phenylchalconide bond increases in the order: \(\text{S} < \text{Se} < \text{Te}\). Relative abundance of ions containing these bonds increases in the order given.

Comparisons of chalcogen derivatives of molybdenum and iron carbonyls with similar compounds of tungsten and ruthenium were made. The general trend of increasing stability with the heavier metal of a family can be rationalized in terms of "better" metal-chalcogen bonding. As the softness of the metal atom increases (i.e., increased size and polarizability) a stronger bond will be formed with the soft chalcogen ligands.

Products were isolated from reactions of diphenyl dichalconides with molybdenum and tungsten cyclopentadienyl carbonyls for which formulations are in doubt. These are usually minor products of extended reactions and are described in the previous part of this Section as.
series I, II, and III compounds. Successful characterization of these compounds will probably require synthesis of larger samples than obtained in this study. This task is made difficult by the rather tedious separation procedures required. The principal product of these extended reactions are insoluble amorphous solids previously identified as totally decarbonylated compounds of formula \([\text{II-CpM(EPh)}_2]_x\).³

Although molecular weight measurements are in reasonable agreement with a dinuclear complex for series I compounds, it is possible that a higher order complex undergoes sufficient dissociation in chloroform solution to give molecular weight measurements that are too low. A behavior of this kind has been observed⁵ with alkylthio bridged manganese carbonyls.

Further study of chalcogen bonding with transition metals could take any one of several courses. Reactions of the type described here might be investigated with noble metal substrates. Many perfluoroalkyl or aryl sulfide complexes have been prepared and comparisons of the corresponding selenide and telluride complexes would be of interest.

Another area that has been extensively explored with sulfur donors and should offer a corresponding chemistry with selenium and tellurium is in the reaction of chalcogen dioxides with transition metal substrates. Two possibilities are insertion reactions of the type:⁷¹

\[
\text{II-CpFe(CO)}_2\text{R} + \text{SO}_2 \rightarrow \text{II-CpFe(CO)}_2\text{SO}_2\text{R} \quad (6)
\]

and reactions with metal carbonyls.⁷²

\[
\text{Fe}_2(\text{CO})_9 + \text{SO}_2 \rightarrow (\text{OC})_4\text{Fe}\left\langle \begin{array}{c} \text{Fe(CO)}_4 + \text{CO} \end{array} \right\rangle
\]

(7)
A vast potential chemistry of selenium and tellurium with transition metals would be available for investigation if ligands capable of delocalized bonding through a ring system were prepared. The great number of dithiol and 1,2-dithioketone complexes prepared in recent years should offer several potential systems.
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VITA

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EXAMINATION AND THESIS REPORT

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Major Field: Chemistry

Title of Thesis: Relative Chalcogen Donor Properties and Transition Metal Complexes

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

August 6, 1970