

# RECENT STUDIES IN METAL-CYCLOPENTADIENYL AND METAL-ARENE CHEMISTRY

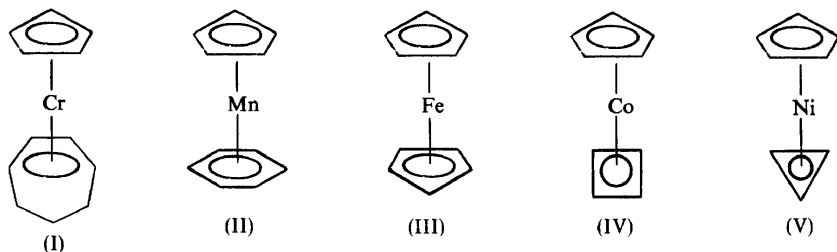
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## ABSTRACT

The formation, chemical reactivity, and spectral properties of a variety of new  $\pi$ -bonded and  $\sigma$ -bonded organic derivatives of the transition metals are described.

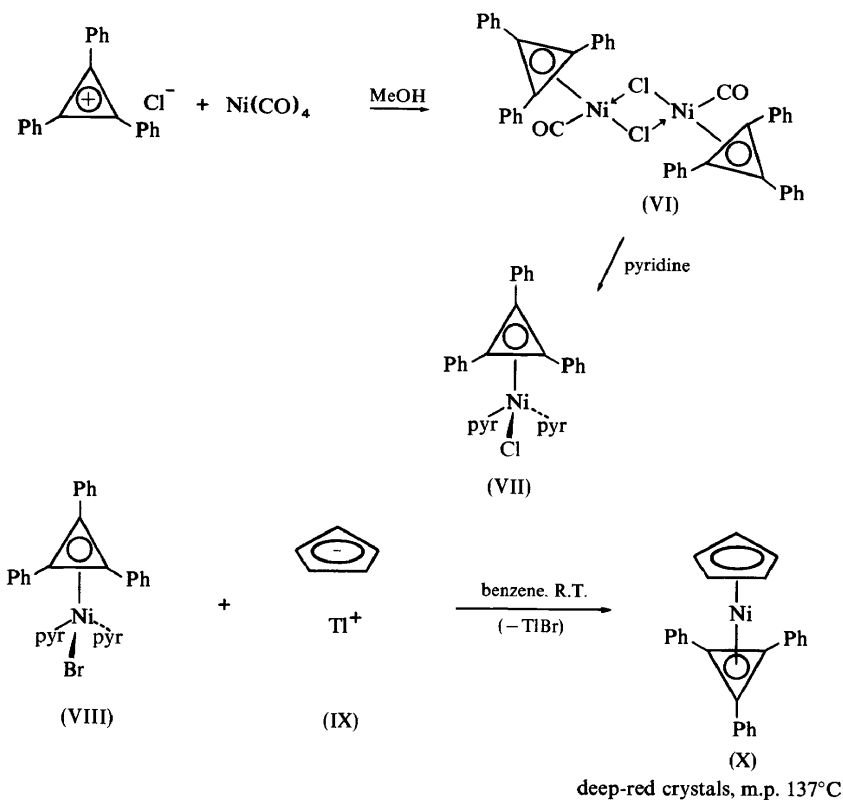
The Effective Atomic Number (E.A.N.) Rule predicts the existence of an isoelectronic series of mixed 'sandwich' complexes which contain a cyclopentadienyl ring and carbocyclic rings of varying sizes. Bis( $\pi$ -cyclopentadienyl)iron or ferrocene (III) was the first member of this series to be discovered, and ( $\pi$ -cyclopentadienyl)( $\pi$ -cycloheptatrienyl)chromium (I)<sup>1,2</sup>



( $\pi$ -cyclopentadienyl)( $\pi$ -benzene)manganese (II)<sup>3,4</sup>, and  $\pi$ -cyclopentadienyl)-( $\pi$ -cyclobutadiene)cobalt (IV)<sup>5-8</sup> have also been recently described in the literature.

Gowling and Kettle<sup>9</sup> reported the first example of a  $\pi$ -cyclopropenyl complex (VI), and the structure of its pyridine adduct (VII) has recently been determined by x-ray methods<sup>10</sup>. We have now found that a reaction of (VIII), which is the bromo analogue of (VII), with cyclopentadienylthallium (IX), proceeds readily to give the new mixed sandwich complex ( $\pi$ -cyclopentadienyl)( $\pi$ -triphenylcyclopropenyl)nickel (X) in 70 per cent yield.

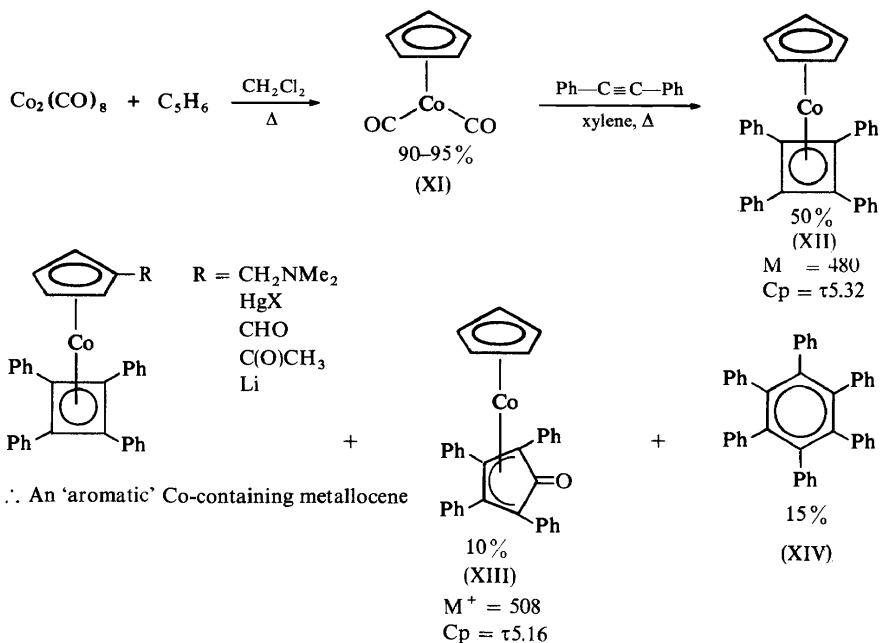
An x-ray study<sup>10</sup> of (VII) showed that the geometry around the Ni atom was a distorted tetrahedron; the Ni atom is bonded symmetrically to all the carbon atoms of the three-membered ring. Mass spectral and n.m.r. data are consistent with the proposed formulation of (X), and a subsequent



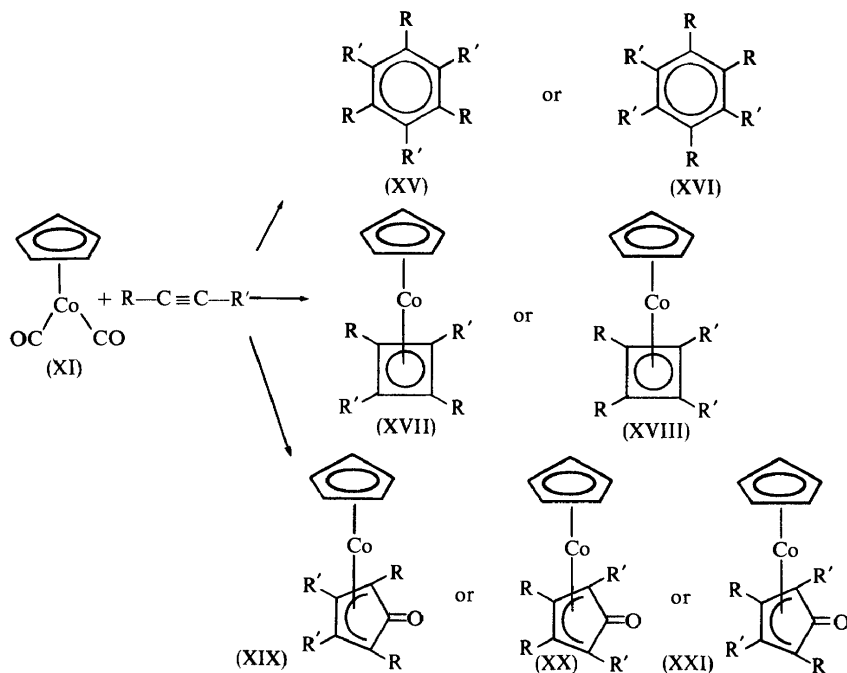
x-ray crystallographic investigation has confirmed the structure<sup>11</sup>. Like other members of this isoelectronic series of mixed sandwich complexes, the nickel complex (X) might be expected to undergo aromatic-type substitution reactions, and such studies are currently in progress in our laboratory.

We have recently shown that a reaction between  $\pi$ -cyclopentadienyl-dicarbonylcobalt (XI) and diphenylacetylene affords a good yield of ( $\pi$ -cyclopentadienyl)(tetraphenylcyclobutadiene)cobalt (XII), together with lower yields of ( $\pi$ -cyclopentadienyl)(tetraphenylcyclopentadienone)cobalt (XIII) and the cyclotrimerization product hexaphenylbenzene (XIV)<sup>6</sup>. The mixed sandwich complex (XII) exhibits unusual stability for a cyclobutadiene complex, and undergoes a variety of electrophilic substitution reactions, such as aminomethylation, mercuration, Vilsmeier formylation, etc., as well as metallation with *n*-butyllithium<sup>6, 12</sup>. Complex (XII) can thus be considered to behave as an 'aromatic' metal  $\pi$ -complex, in a manner analogous to ferrocene (III), and an extensive chemistry of this new organometallic system seems possible.

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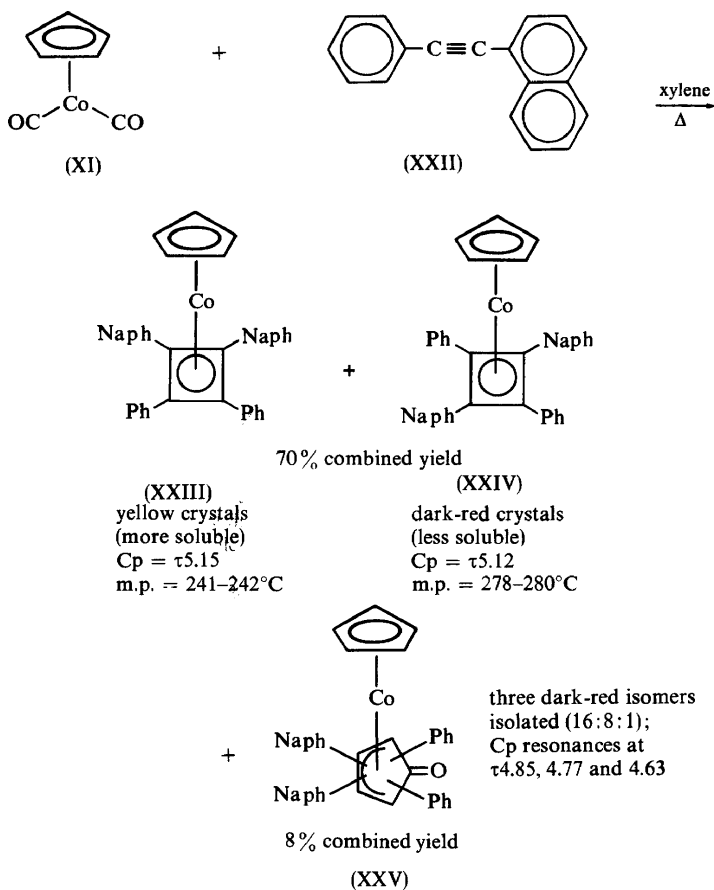


On the other hand reactions between (XI) and unsymmetrical disubstituted acetylenes could theoretically lead to two types of trimerization products, both symmetrical (XV) and unsymmetrical (XVI). Furthermore, both *cis*



(XVII) and *trans* (XVIII) tetra-substituted cyclobutadiene cobalt complexes should be possible reaction products, as well as three types of tetra-substituted cyclopentadienone cobalt complexes (XIX–XXI).

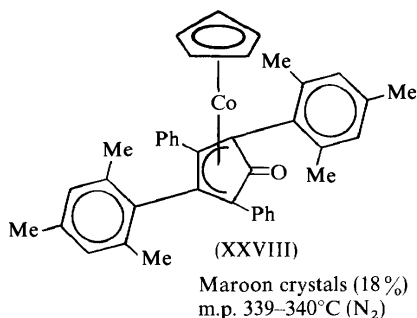
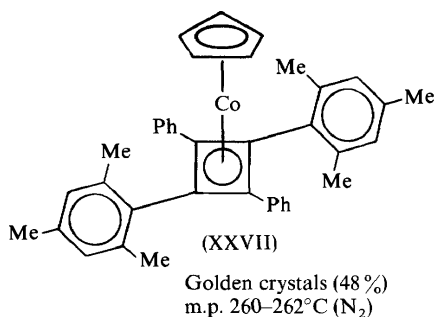
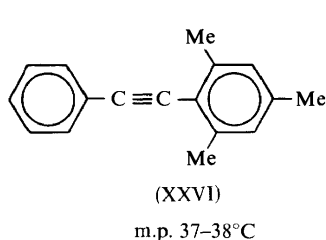
We have carried out a series of reactions of this type which are well illustrated by the reaction between (XI) and phenyl-1-naphthylacetylene (XXII). In this instance, two cyclobutadiene complexes (XXIII) and (XXIV) as well as all three possible cyclopentadienone complexes (XXV) have been isolated. The cyclobutadiene complexes (XXIII) and (XXIV) can best be



separated by fractional crystallization, and exhibit distinctly different melting points as well as slightly different resonances for the respective cyclopentadienyl protons. The cyclopentadienone isomers (XXV) also exhibit slight but distinct cyclopentadienyl proton resonances, and can be separated by preparative thin layer chromatography.

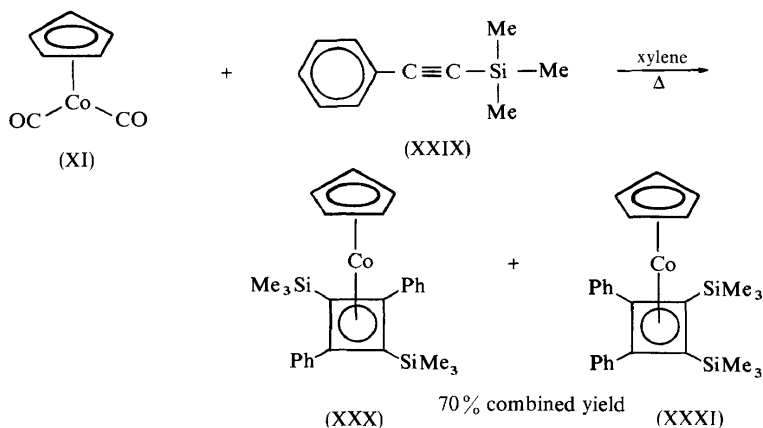
A reaction between phenyl mesitylacetylene (XXVI) and (XI), on the other hand, produces only a single cyclobutadiene complex and a single cyclopentadienone complex. Molecular models indicate that the cyclobutadiene

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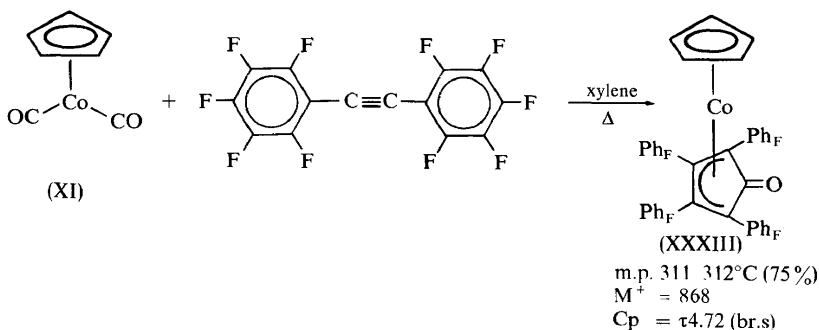
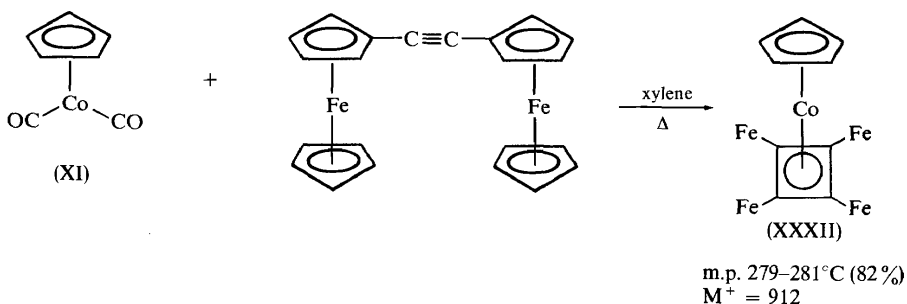
complex is probably the *trans* isomer (XXVII), since the corresponding *cis* isomer would be extremely hindered. Even so, the 12 *ortho*-methyl protons in (XXVII) appear as a broad resonance, suggesting that there is restricted rotation of the mesityl groups even in (XXVII). The single cyclopentadienone complex formed is assigned the unsymmetrical structure (XXVIII), since only this geometry would explain the *six* non-equivalent methyl resonances which are observed in the n.m.r. spectrum of the product. Again, severe steric hindrance to rotation of the mesityl groups is indicated.

A reaction between (XI) and phenylethynyltrimethylsilane (XXIX) produces two isomeric cyclobutadiene complexes (XXX) and (XXXI) in 70 per

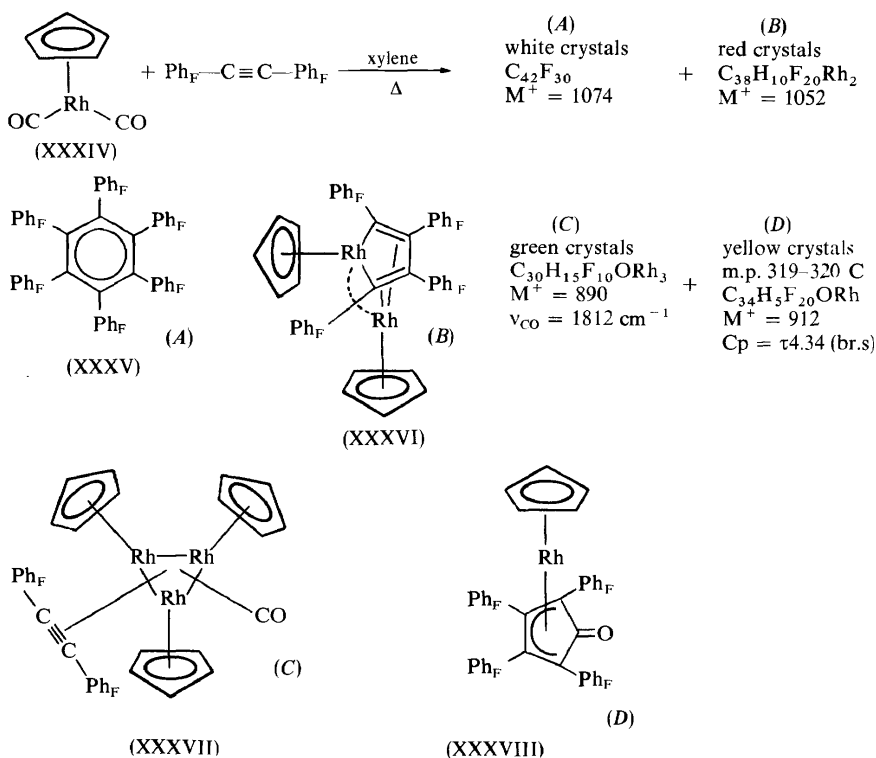


cent combined yield. These isomers show slightly different trimethylsilyl proton resonances and slightly different cyclopentadienyl proton resonances. The isomers can be separated by preparative thin layer chromatography. The isomer with the lowest  $R_f$  value has tentatively been assigned as the *cis* isomer (XXXI) on the basis of additional mass spectral and chemical studies<sup>13</sup>.

Symmetrical acetylenes other than diphenylacetylene also undergo reactions with (XI) to give various organocobalt complexes. Thus, a reaction with differrocenylacetylene produces the cyclobutadiene complex (XXXII) as virtually the only product (82 per cent yield), while a reaction with bis-pentafluorophenylacetylene affords the tetra-substituted cyclopentadienone complex (XXXIII) as the sole product in 75 per cent yield, no cyclobutadiene complex being detected in this instance.



We have also extended this phase of our research programme to include reactions between ( $\pi$ -cyclopentadienyl)dicarbonylrhodium and -iridium. Remarkably, in no instance thus far have we been able to detect cyclobutadiene complexes of either of these metals. However, a large variety of other polynuclear products are formed and can be separated. These types of products are illustrated by the reactions between ( $\pi$ -cyclopentadienyl)dicarbonylrhodium (XXXIV) and bis(pentafluorophenyl)acetylene. Four different products (A–D) are obtained from this reaction. Product (A) is the cyclotrimerization product, perfluorohexaphenylbenzene (XXXV). This

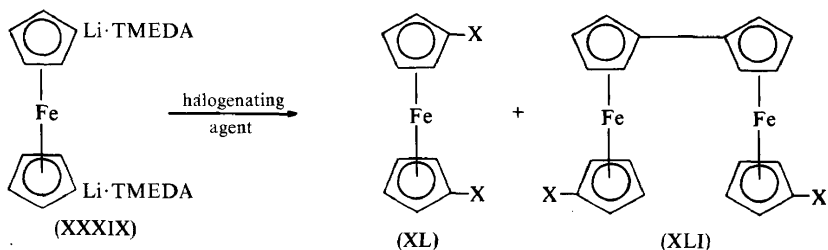


novel perfluorinated aromatic hydrocarbon exhibits a strong parent molecular ion at  $m/e = 1074$ , and has proved to be a very useful marking agent in the high mass region.

Product (B) is formed in the smallest amount, and on the basis of total elemental analyses and mass spectrometry, appears to be dimeric in nature. A possible structure for product (B) is (XXXVI), in analogy with previously isolated iron tricarbonyl complexes<sup>13</sup>. Product (C), on the basis of analytical data and mass spectrometry, is a trinuclear ( $\pi$ -cyclopentadienyl)rhodium complex which also contains a bis(pentafluorophenyl)acetylene ligand and a carbonyl group (XXXVII). The latter exhibits a carbonyl stretching frequency at 1812 cm<sup>-1</sup>, indicating that it is bridging. More definitive structural assignments for products (B) and (C) must await the results of x-ray diffraction studies currently being conducted by Professor Dahl and his associates at the University of Wisconsin. The fourth reaction product (D) is the expected cyclopentadienone complex (XXXVIII).

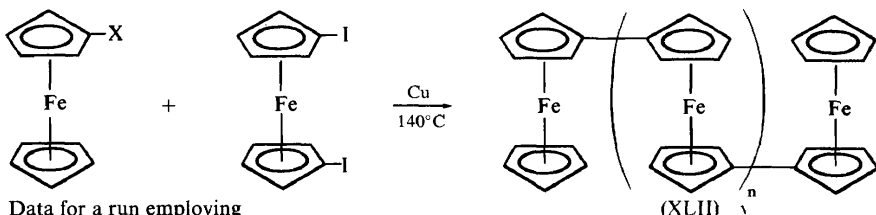
Several years ago, we reported<sup>15</sup> a facile route to dimetallated ferrocenes starting with ferrocene and *n*-butyllithium-(TMEDA)\*. Reaction of this intermediate (XXXIX) with halogens, *p*-toluenesulphonyl halides, or halo-carbons has provided a useful new route to 1,1'-dihalogenated ferrocenes (XL), as well as 1',6'-dihalobiferrocenes (XLI)<sup>16</sup>.

\* TMEDA = *N,N,N',N'*-tetramethylethylenediamine.



| Halogenating agent   | % Yield | % Yield |
|--|---------|---------|
| I <sub>2</sub>   | 50      | 6       |
| Br <sub>2</sub>  | 23      | 2       |
| CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Br | 70      | 6       |
| CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl | 75      | 6       |
| CF <sub>2</sub> BrCF <sub>2</sub> Br                             | 78      |         |
| CF <sub>2</sub> ClCF <sub>2</sub> Cl                             | 68      |         |

We have now been able to extend our earlier studies to include the formation of 1,1'-polyferrocenes (XLII) via mixed Ullmann reactions between 1,1'-diiodoferrocene (XL, X = I) and monohaloferrocenes<sup>17</sup>. These ferrocene oligomers can be separated by column chromatography on alumina and by solubility differences. Their mass spectra are particularly interesting, and each oligomer exhibits the expected parent molecular ion.



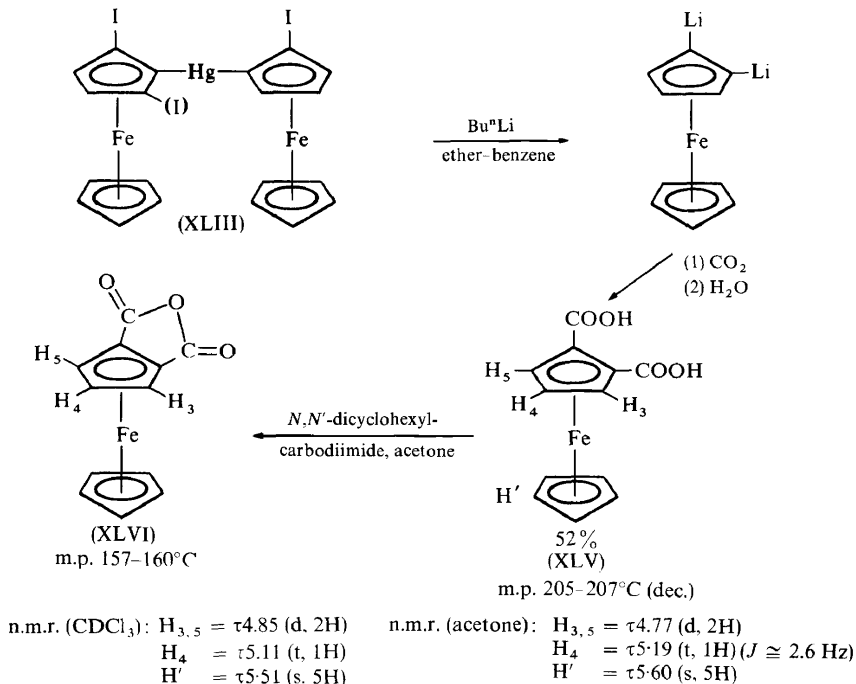
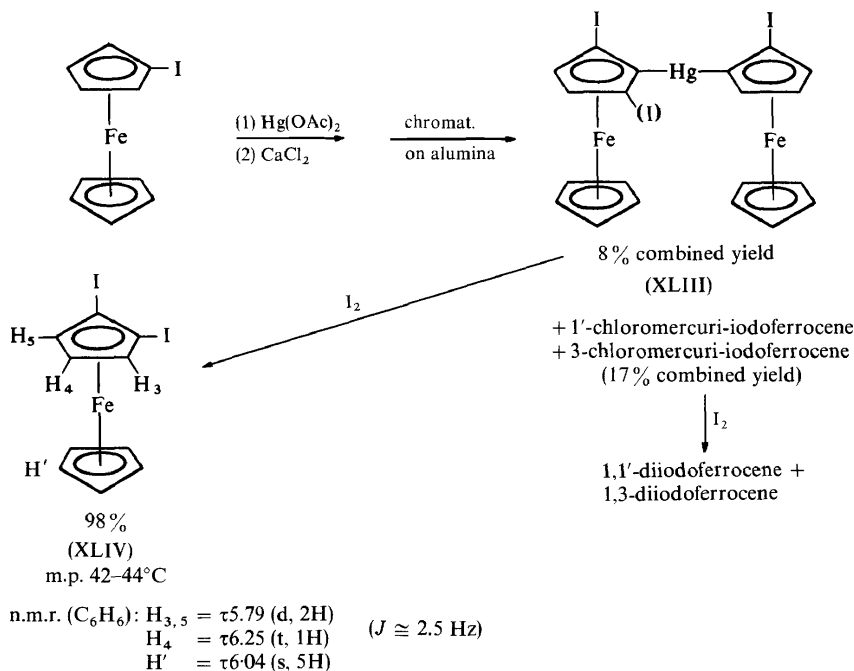
Data for a run employing 3.2 mmol of iodoferrocene, and 6.4 mmol of 1,1'-diiodoferrocene; 23 h.

| n | name                  | % Yield | M <sup>+</sup> |
|---|-----------------------|---------|----------------|
| 0 | 1,1'-biferrocene      | 54      | 370            |
| 1 | 1,1'-terferrocene     | 24      | 554            |
| 2 | 1,1'-quaterferrocene  | 11      | 738            |
| 3 | 1,1'-quinqueferrocene | 6       | 922            |
| 4 | 1,1'-sexiferrocene    | 1       | 1106           |

We have recently reinvestigated the acetoxymercuration of iodoferrocene, a reaction originally studied by Nefedov<sup>18</sup>. Following treatment of the mercuration mixture with calcium chloride and chromatography on alumina, the 2-chloromercuri-iodoferrocene originally formed undergoes symmetrization on the alumina column, and is eluted as a mixture of *meso*- and *dl*-isomers of bis(2-iodoferrocenyl)mercury (XLIII). Continued elution produces a mixture of isomeric 1'-chloromercuri- and 3-chloromercuriferrocenes.

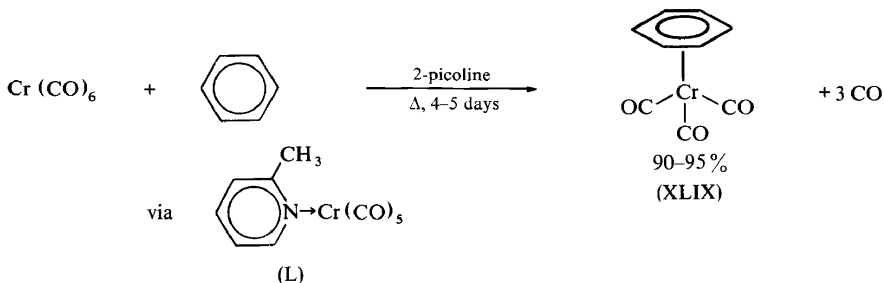
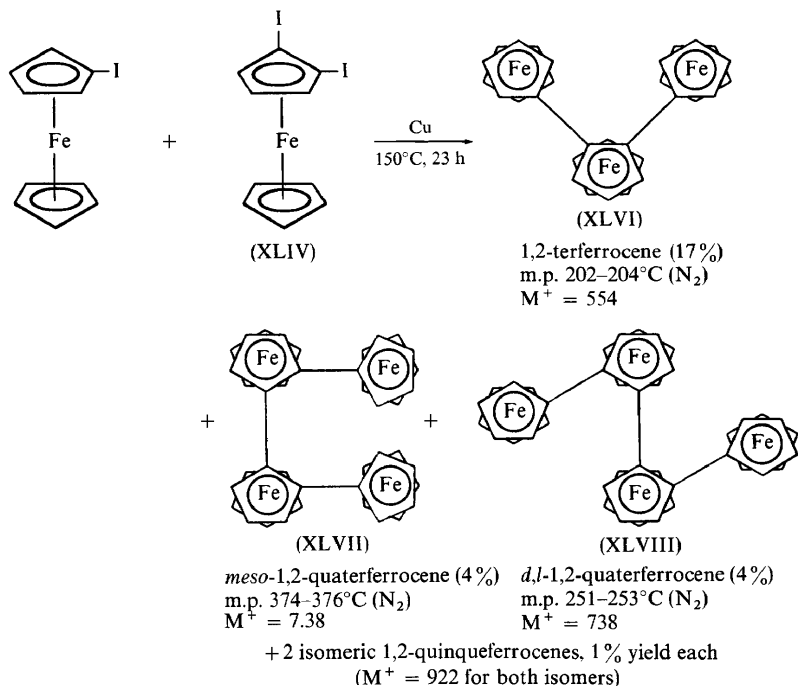


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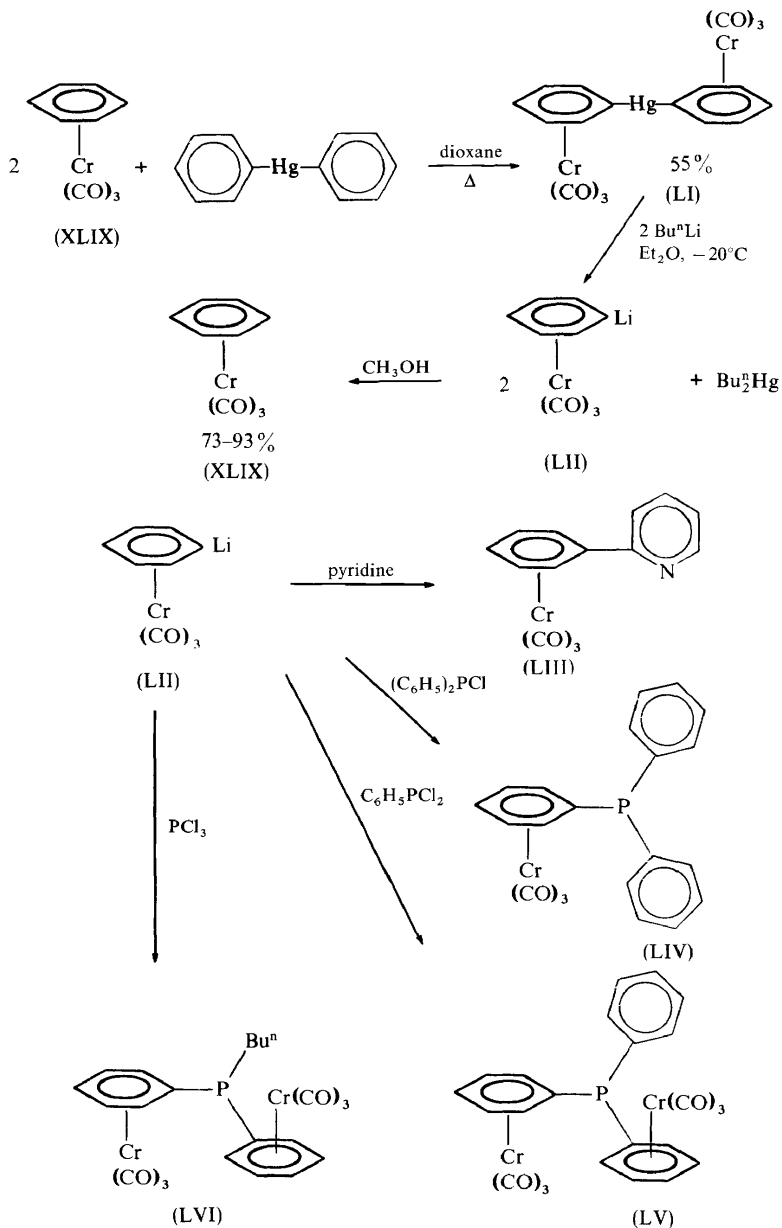


Iodination of the mercurial (XLIII) produces 1,2-diiodoferrocene (XLIV) in high yield. The n.m.r. spectrum of (XLIV) indicates that it is the 1,2-isomer, compared to the original assignment of 1,3-diiodoferrocene by Nefedov<sup>18</sup>. The structure of (XLIII) was confirmed by treating it with n-butyllithium followed by carbonation and hydrolysis, a process which produced ferrocene-1,2-dicarboxylic acid (XLV) in 52% yield. A 1,2-disposition of substituents was further proved by conversion of (XLV) to 1,2-ferrocene dicarboxylic anhydride (XLVI) of known structure.

The availability of 1,2-diiodoferrocene (XLIV) afforded us the opportunity to undertake mixed Ullmann reactions of this substance with iodoferrocene, leading to 1,2-terferrocene (XLVI), *meso*-1,2-quaterferrocene (XLVII), and *dl*-1,2-quaterferrocene (XLVIII), as well as several 1,2-quinqueferrocenes.



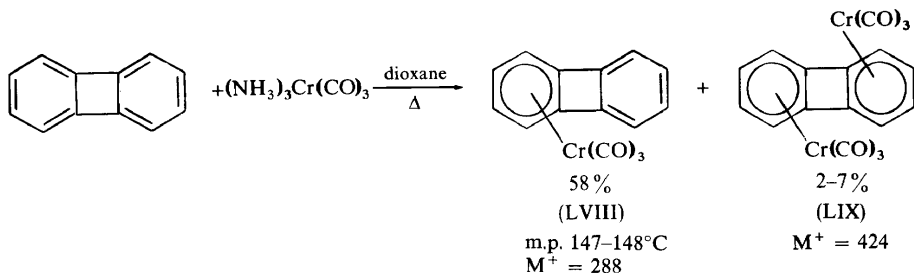
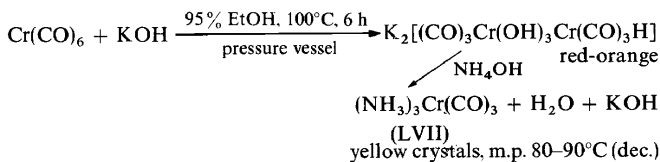
The n.m.r. spectrum of 1,2-terferrocene in particular is quite different than that of 1,3-terferrocene<sup>19</sup>. Molecular models indicate that in the former case, the three ferrocene nuclei cannot assume a co-planar configuration, as has been already found to occur in biferrocene. An x-ray crystallographic structural study of (XLVI) is currently in progress of Professor Palenik at the University of Florida.



Although the chemistry of arene tricarbonylchromium complexes has been developed extensively in recent years, the parent complex of this series, benzene tricarbonylchromium (XLIX) is still relatively difficult to prepare. We have found that (XLIX) can now be obtained in 90–95 per cent yield from a reaction between chromium hexacarbonyl, benzene, and 2-picoline at reflux temperature. We presume that the reaction proceeds initially via a dative complex such as (2-picoline)pentacarbonylchromium (L), which is subsequently converted to the more thermodynamically stable product (XLIX).

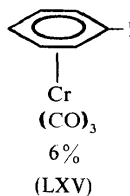
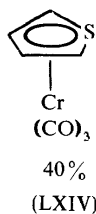
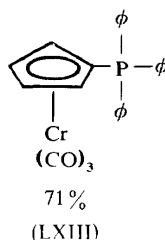
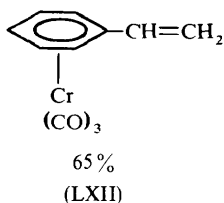
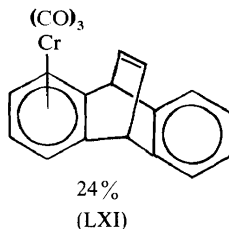
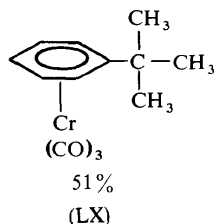
The availability of the parent complex (XLIX) has prompted us to initiate a study concerning its reactions. For example, (XLIX) undergoes facile ligand exchange with diphenylmercury to provide the mixed metal complex (LI) in 55 per cent yield. The latter serves as a useful intermediate to (phenyllithium)tricarbonylchromium (LII). Hydrolysis studies indicate this novel intermediate is formed in the metal-metal interchange reaction in 73–93 per cent yield. Reactions of (LII) with pyridine and various chlorophosphines have produced a variety of new organochromium complexes (LIII–LVI) which would be impossible to obtain by direct complexation methods. We are currently studying the coordination chemistry of these organometallic ligands.

We have recently developed a convenient new synthesis of the reagent triammine tricarbonylchromium (LVII), and shown it to be a valuable intermediate for the synthesis of a wide variety of arene tricarbonylchromium complexes<sup>20</sup>. For example, a reaction between (LVII) and biphenylene in



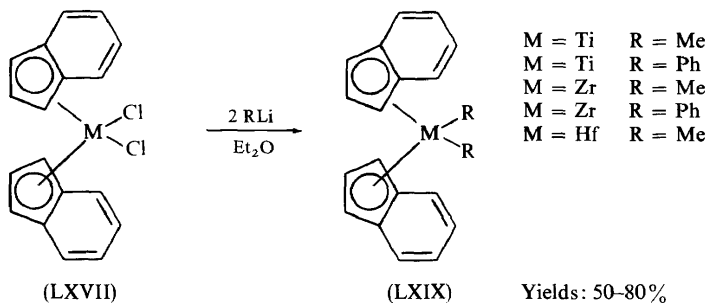
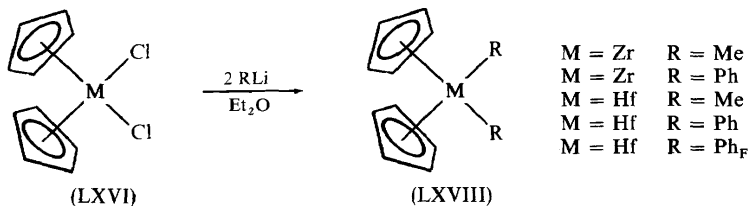
refluxing dioxane produces biphenylene tricarbonylchromium (LVIII) and biphenylene hexacarbonyldichromium (LIX) in yields of 58 per cent and 2–7 per cent, respectively. We are currently studying the chemical reactivity of (LVIII) in an effort to determine the effects of the coordinated Cr(CO)<sub>3</sub> group. An x-ray structural determination of this complex is also in progress by Professor Dahl in order to ascertain how complexation affects various bond lengths in the molecule.

Similar reactions between (LVII) and various arenes have afforded a variety of organometallic complexes such as (LX-LXV). The styrene complex (LXII) does not undergo homo-polymerization, but can be copolymerized with a variety of monomers. Iodobenzene tricarbonylchromium (LXV) reacts with magnesium in tetrahydrofuran to form a Grignard reagent, and a

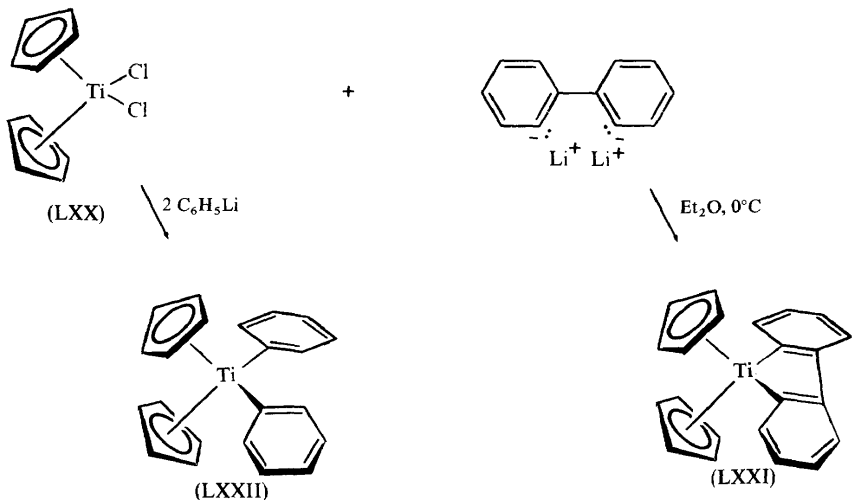


solution of this intermediate with trimethylchlorosilane affords trimethylsilylbenzene tricarbonylchromium.

In the area of  $\sigma$ -bonded organotransition metal chemistry, we have recently studied reactions between bis( $\pi$ -cyclopentadienyl)metal dihalides (LXVI) and bis( $\pi$ -indenyl)metal dihalides (LXVII) with organolithium reagents, and have been able to isolate an interesting new series of metallocene dialkyls and diaryls (LXVIII-LXIX). The zirconium and hafnium analogues are especially sensitive to moisture and air, although they appear reasonably stable thermally. All compounds have been characterized by total elemental analyses and by n.m.r. spectra. A study of trends in the n.m.r. spectra of these new organometallic compounds has been conducted, and we are also currently examining their chemical reactivities.

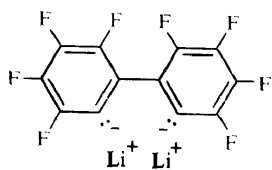


We have recently shown that a reaction between titanocene dichloride (LXX) and 2,2'-dilithiobiphenyl results in formation of the novel titanium heterocycle (LXXI)<sup>21</sup>. In contrast to the non-metallo-cyclic analogue diphenyltitanocene (LXXII) (Summers *et al.*, 1955), (LXXI) is completely stable in the air. In a similar manner, reactions of the perfluorinated aryl-dilithium reagent (LXXIII) with zirconocene or hafnocene dichloride



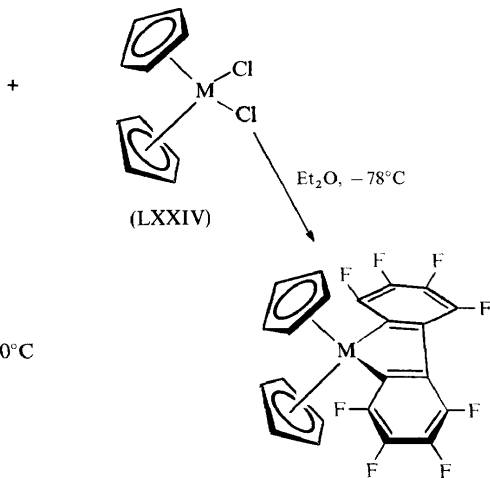
orange crystals which must be stored  
in a refrigerator to prevent decomposition

bright-red crystals (16%)  
 $\tau$ 3.76 ( $\pi$ -C<sub>5</sub>H<sub>5</sub>); M<sup>+</sup> 330  
air-stable



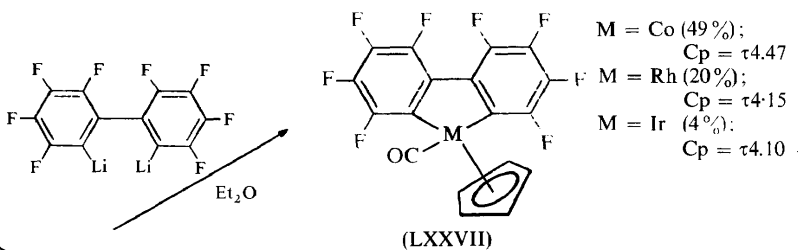
(LXXIII)

M = Zr and Hf;  
 pale-yellow crystals, dec. > 300°C  
 Yields = 8-23%  
 Zr:  $\tau$ 3.48 ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)  
 Hf:  $\tau$ 3.62 ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)  
 (hydrolytically unstable)



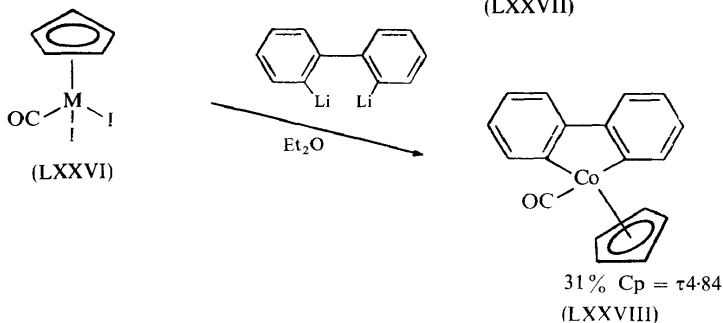
(LXXV)

(LXXIV), produces the corresponding metalcycles (LXXV) which are also very stable thermally. In the cobalt series, reactions between ( $\pi$ -cyclopentadienyl)carbonylmetal diiodides (LXXVI) with various dilithium reagents have provided unique series of new metalcycles such as (LXXVII) and (LXXVIII). These metalcycles are again remarkably stable compared to normal  $\sigma$ -bonded analogues. Dr. Bernal at Brookhaven National Laboratory is presently undertaking x-ray diffraction studies of several of these metalcycles, in order to ascertain the extent of electron delocalization in such systems, while we are presently examining in detail their spectral properties and chemical reactivities.



(LXXVII)

M = Co (49%);  
 Cp =  $\tau$ 4.47  
 M = Rh (20%);  
 Cp =  $\tau$ 4.15  
 M = Ir (4%);  
 Cp =  $\tau$ 4.10



31% Cp =  $\tau$ 4.84  
 (LXXVIII)

## ACKNOWLEDGEMENTS

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