Synthesis of Cyclopentadienyl Metal Compounds

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I

INTRODUCTION

A new field of organometallic chemistry was introduced in 1951 by the discovery of ferrocene. This independent discovery by Kealy and Pauson (*1*) and Miller *et al.* (*2*) stimulated intensive research in the field of cyclopentadienyl metal chemistry and led to the synthesis of several hundred compounds. Many more new compounds may be expected in the future.

Two general approaches have been applied to the synthesis of cyclopentadienyl metal compounds: direct formation of cyclopentadienyl–metal bonds; and transformation of cyclopentadienyl metal compounds to other related compounds. The first of these approaches encompasses methods of synthesis for most of the basic classes of cyclopentadienyl metal compounds and is the principal subject of this review. Methods for transforming one cyclopentadienyl metal compound into another are mentioned only in outline.

The final section is a tabular survey of cyclopentadienyl metal compounds and the methods by which they have been prepared. Yield, melting point, and color are also included. Compounds synthesized by substitution of various groups into the cyclopentadienyl rings of ferrocene are not included.

A special nomenclature for the cyclopentadienyl metal compounds has grown up because of the complexity of their chemical names. The dicyclopentadienyl metal compounds, $(C_5H_5)_2M$, are called ferrocene, cobaltocene, vanadocene, ruthenocene, etc., and these names will be used in this review. Furthermore, the abbreviation Cp will be used to represent C_5H_5, the cyclopentadienyl radical.

II

SYNTHESIS BY DIRECT FORMATION OF CYCLOPENTADIENYL—METAL BONDS

Cyclopentadienyl–metal bonds may be synthesized by direct reaction of cyclopentadiene with certain metals and their compounds or by reaction of ionic metal cyclopentadienides with compounds of metals wherein cyclopentadienide anion displaces a ligand bonded to the metal. These bonds may also be formed in a limited number of instances by reaction of alkenes or alkynes with metal compounds.

Synthesis of cyclopentadienyl compounds of metals from cyclopentadiene depends on the strongly acidic properties of cyclopentadiene. This acidity may be attributed to the ready formation of the highly resonance-stabilized cyclopentadienide anion, $C_5H_5^-$, in which there are six delocalized π electrons. This method is limited primarily to the active metals of Groups IA and IIA and to their strongly basic compounds. The compounds produced are principally the ionically bonded metal cyclopentadienides.

The reaction of the ionic cyclopentadienides with metal compounds is by far the most general method for synthesis of cyclopentadienyl metal compounds. This method is applicable both to transition metals, which form π-bonded cyclopentadienyl compounds principally, and to main group metals which form σ-bonded cyclopentadienyl compounds.

The classification of synthetic methods adopted here, based on whether cyclopentadiene or the cyclopentadienide anion is the reacting species, is somewhat arbitrary and may not be mechanistically correct in all cases. It is probable that in many of its reactions cyclopentadiene undergoes partial ionization and that the reacting species may actually be cyclopentadienide anion.

A. From Cyclopentadiene

The strong acidity of cyclopentadiene, estimated as approximately $pK_a = 17$ (*3*), was first recognized by Thiele, who took advantage of this property in the preparation of potassium cyclopentadienide from potassium metal and cyclopentadiene (*4*). While direct reaction with cyclopentadiene is limited in scope to the elements of Groups IA and IIA, to their strongly basic compounds, and to a few other elements, it is the only approach for the synthesis of the ionic cyclopentadienides of elements of Groups IA and IIA. Direct reaction of cyclopentadiene is also applicable to the preparation of certain compounds of the $(C_5H_5)_nM(CO)_x$ class from metal carbonyls and is often the preferred method.

Syntheses of cyclopentadienyl metal compounds from cyclopentadiene are carried out under widely varying conditions depending on the properties of the metallic reactants. These reactions may be carried out in the vapor phase at temperatures as high as 600° C or they may be carried out in the liquid phase in the presence of a solvent at 25° C. The cyclopentadienyl metal compounds produced are isolated either by sublimation, if the reaction has been run in the vapor phase, or by crystallization, if the compound has been formed in solution. If the compound is to be used as an intermediate in a subsequent synthesis, then it is not usually isolated in pure form, but is used in solution in a suitable solvent of high dielectric constant or as a slurry in a hydrocarbon solvent.

Nearly all synthetic methods for cyclopentadienyl metal compounds require first the preparation of cyclopentadiene from dicyclopentadiene. This is accomplished by thermal depolymerization of dicyclopentadiene at temperatures above 180° C. Because cyclopentadiene is unstable at room temperature it must be stored at low temperatures to prevent dimerization to dicyclopentadiene. The rate of dimerization is about 0.05% per hour at −20° C and 1% per hour at 10° C (*5*).

a. *Preparation of Cyclopentadiene from Dicyclopentadiene.* A convenient laboratory apparatus for the depolymerization of cyclopentadiene is shown in Fig. 1. Any solvent boiling between 180° and 350° C which does not react with cyclopentadiene is satisfactory as a heat transfer medium for the depolymerization process. Dicyclopentadiene is added to the refluxing solvent at a rate of 100–300 ml/hr. Depolymerization is nearly instantaneous and the vapors pass through the first condenser and are condensed in the second condenser. Cyclopentadiene is collected in a receiver cooled with ice. The first condenser prevents contamination of the cyclopentadiene with solvent by condensing the solvent and returning it to the flask. Yield is 95% of the theoretical value.

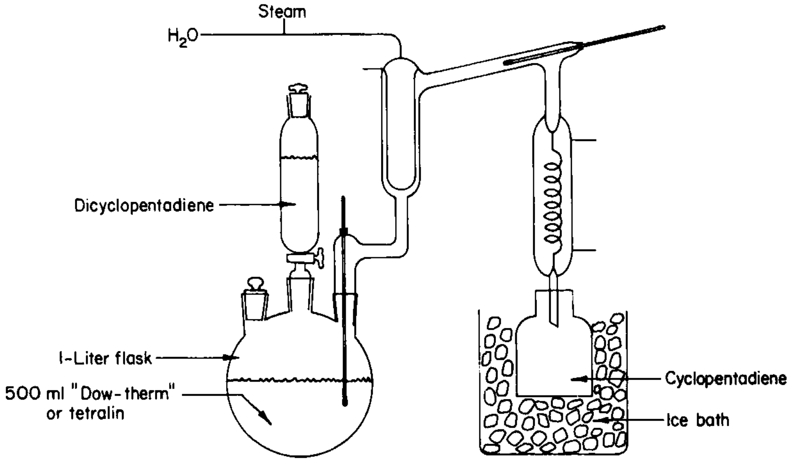


FIG. 1. Apparatus for depolymerization of cyclopentadiene.

1. *Reaction of Cyclopentadiene with Metals* (*Method 1*)

Direct reaction of metals with cyclopentadiene may be represented by the general equation:

$$M + nC_5H_6 = (C_5H_5)_nM + \tfrac{1}{2}nH_2 \qquad (1)$$

While this is the simplest method for preparing metal cyclopentadienyl compounds, it is one of the least general. It is limited to the elements Li, Na, K, Ca, and Sr and under rather vigorous conditions of temperature to Mg, In, Tl, and Fe. The reaction is usually carried out in the liquid phase at 25° to 100° C in the presence of a solvent for lithium, sodium, and potassium, or in the vapor phase at 400°–600°C for the less reactive elements. Usually the cyclopentadienides of lithium, sodium, and potassium are not isolated but are used in solution as intermediates for the preparation of other cyclopentadienyl metal compounds. Compounds produced by reaction of cyclopentadiene vapor with metal are usually sufficiently volatile to sublime away from the reaction zone and condense in the cooler portion of the apparatus.

Potassium is sufficiently active to react with cyclopentadiene when cyclopentadiene is added to a suspension of potassium shot in toluene (*4*). Sodium fails to react with cyclopentadiene under similar conditions. When, however, sodium is dispersed to particles 1–3 μ in diameter, reaction with cyclopentadiene proceeds in xylene at moderate rate at 25° C in 95% yield (*6*).

As might be expected, alkali metals react with cyclopentadiene much more readily in a solvent in which the alkali metal cyclopentadienide has some solubility. Fischer and Jira (*7–9*) first used liquid ammonia as a solvent for this reaction and obtained high yields of the ionic cyclopentadienides of Li, Na, and K. It is interesting that the reaction of sodium with cyclopentadiene in liquid ammonia does not produce hydrogen, but yields cyclopentene according to the stoichiometry of the following equation (*10*, *11*)

$$2Na + 3C_5H_6 \rightarrow 2NaC_5H_5 + C_5H_8 \qquad (2)$$

Wilkinson *et al.* (*12*, *13*) found tetrahydrofuran and 1,2-dimethoxyethane to be most convenient and versatile solvents for the reaction of alkali metals with cyclopentadienes. Sodium cyclopentadienide is generally formed in greater than 95% yields in tetrahydrofuran (THF) and only a few per cent of by-product cyclopentene is formed. Other solvents which have been used are diethyl ether (*14*), xylene, *tert*-butanol (*15*), and diethyl ether–xylene mixtures (*16*). A systematic study of the effect of solvent on yield in the reaction of Li, Na, and K with fluorene indicated that yield decreased in the order 1,2-dimethoxyethane > diethyl ether, $\approx$ THF > dioxane > diethyl ether (*17*). In general, however, sodium cyclopentadienide in tetrahydrofuran has been the most widely used reagent for the preparation of other cyclopentadienyl metal compounds. (See Section II,A,1*a*; representative experimental methods are collected at the end of each section.)

Reaction of cyclopentadiene vapor with metal at high temperature was the method used by Miller *et al.* (*2*) for one of the two original preparations of ferrocene. Iron for this reaction was prepared by reduction of Fe_2O_3 with hydrogen. Yields of ferrocene were low and the reaction continued at 300° C for only a few minutes before it stopped and it was necessary to reactivate the iron with hydrogen. Yields are improved slightly by adding molybdenum to the iron mixture. Others (*19*) have studied this method and have obtained yields of 20–40% by the passage of a mixture of cyclopentadiene and hydrogen over Fe_2O_3.

Magnesium reacts with cyclopentadiene vapor very readily at 500° C and gives magnesium dicyclopentadienide in excellent yield (*20*). This is the preferred method for the preparation of this compound. Other elements which react directly with cyclopentadiene are indium, at 460°–580° C and 3–4 atm pressure, and thallium, at 440°–470° C and 2–3 atm pressure (*21*).

Thallium cyclopentadienide is, however, more conveniently prepared by the reaction of thallium hydroxide with cyclopentadiene, a procedure which will be described under Method 2.

Substituted cyclopentadienes also form metallic derivatives by direct reaction in the liquid phase with elemental lithium, sodium, and potassium. Thus, indene reacts with sodium to form sodium indenide (*11*, *23*, *24*) and lithium, sodium, and potassium react with fluorene (*17*, *25*). Reaction of metals with substituted cyclopentadienes in the vapor phase has not been extended beyond methylcyclopentadiene.

a. *Preparation of Sodium Cyclopentadienide.* [Modification of *Organic Syntheses* procedure, (*18*)]. A 500-ml three-neck flask is fitted with a mechanical stirrer, a 125-ml addition funnel, and a reflux condenser topped with a nitrogen inlet tube which is connected through a T-joint to a nitrogen supply and a xylene-filled bubbler. In the flask are placed 125 ml of sodium-dried xylene, 11.5 gm (0.5 gram atom) of sodium, and 0.11 gm of aluminium monostearate. The mixture is heated above 105° C, and the sodium is finely dispersed by rapid stirring. Stirring is stopped and the mixture is cooled rapidly to 25° C under nitrogen. The cooled mixture is allowed to settle, the bulk of the xylene is decanted, and tetrahydrofuran (156 ml) is added to the finely divided sodium suspension. During a period of 1 hr a mixture of 44 ml (0.525 mole) of cyclopentadiene and 44 ml of tetrahydrofuran is added while the temperature is kept between 30° and 40° C by external cooling. Stirring is continued for 2 hr at 30°–40° C, after which only a trace of sodium remains unreacted. The yield is nearly quantitative based on sodium.

b. *Preparation of* $(C_5H_5)_2Mg$ (*22*). Nitrogen flowing at the rate of 275 to 300 ml/min is saturated with cyclopentadiene by passing the gas through a bubbler containing cyclopentadiene. This gaseous mixture is passed downward through a vertical Pyrex tube $1\frac{1}{4}$ inches O.D. which is heated electrically to 500°–600° C. Magnesium metal turnings are supported in the furnace tube by a circle of nichrome gauze held in place by a constriction in the tube. The product, which falls from the furnace as a white solid, is collected in a nitrogen-blanketed receiver at the bottom of the tube. Unreacted cyclopentadiene is collected in a dry ice–ethanol trap. Yields above 80%, based on the cyclopentadiene consumed, have been obtained.

2. *Reaction of Cyclopentadiene with Basic Metal Compounds* (*Method 2*)

The general equation for the reaction of basic metal compounds with cyclopentadiene is

$$MY + C_5H_6 = C_5H_5M + HY \qquad (3)$$

This method is applicable to the strongly basic compounds of alkalies and alkaline earths and of Tl, Fe, Co, Ni, Cu, and Pd. It is the preferred method for preparing CpTl and CpPdCl and is a novel method for CpK. Metal compounds which have been used are in the form of hydroxides, hydrides, acetylides, alkoxides, oxalates, oxides, and acetates. Organometallic derivatives of very weakly acidic hydrocarbons, such as Grignard reagent, butyllithium, and phenyllithium, are also included. This method has been used primarily for the preparation of cyclopentadiene derivatives, although derivatives of methyl cyclopentadiene, indene, and fluorene have also been prepared. The Grignard reagent, CpMgX, is generally prepared by reaction of cyclopentadiene with an alkyl Grignard reagent.

Although this reaction may be carried out either in the presence of an organic solvent of high dielectric constant or in the vapor phase at elevated temperature, substantially higher yields usually result when a solvent is used. Even water may be used as a solvent for preparation of thallium and potassium cyclopentadienides.

The synthesis of ionic cyclopentadienides of thallium and potassium in aqueous solution is somewhat surprising in view of the much greater acidity of water compared to cyclopentadiene. The presence, however, of a small concentration of cyclopentadienide anions in basic aqueous solution has been detected by UV spectrophotometry (*26*). The extreme insolubility of thallium cyclopentadienide presumably is sufficient to permit its nearly quantitative precipitation from 1 M potassium hydroxide solution (*27–29*). Greater solubility and ease of hydrolysis of potassium cyclopentadienide requires the use of saturated potassium hydroxide for its preparation (*30*). Potassium cyclopentadienide prepared in this manner is a white, air-sensitive precipitate with a curdy appearance.

Riemschneider and Helm (*31*) have investigated the reaction of ferrous oxalate with cyclopentadiene vapor at 300°–400° C. They found that ferrous oxalate does not react directly with cyclopentadiene but is reduced to metallic iron which then reacts with cyclopentadiene to form ferrocene. Thus, it is probably similar to the reaction described in Method 1 (*2*).

The only method for the preparation of a cyclopentadienyl derivative of copper is the reaction of cupric oxide with cyclopentadiene in the presence of triethylphosphine. The product of this reaction is $CpCu \cdot PEt_3$ (*32*). Attempts to prepare CpCu by reaction of cuprous halides with cyclopentadiene in the presence of base, or with CpNa or CpMgBr have failed (*32*).

By suitable modification, the direct reaction of cyclopentadiene may be applied even to acidic or neutral salts of those elements which do not readily form stable basic salts. This is accomplished by inclusion of a base in the reaction mixture. Thus, either a basic complex salt or a simple basic salt is formed.

$$MX_y + n\text{Base} \rightarrow MX_y \cdot n\text{Base} \tag{4}$$

$$MX_y \cdot n\text{Base} + C_5H_6 \rightarrow (C_5H_5)_nMX_{y-n} + n\text{Base} \cdot HX \tag{5}$$

Bases with a dissociation constant greater than 1×10^{-5}, such as diethylamine, triethylamine, piperidine, ammonia under pressure, and sodium alcoholate, have been used (*33–35*). Salts of Ni, Co, Fe, Ti, Zr, and Hg react in this manner. Although this reaction is limited in scope to a few elements, it does give high yields of those compounds which can be prepared.

In the usual experimental procedure, an acidic salt is first complexed with base and then treated with cyclopentadiene which reacts to form the cyclopentadienyl metal compound. The by-product salt is separated from the cyclopentadienyl metal compound by extraction with water.

Synthesis of cyclopentadienyl metal compounds from basic metal salts derived from a base and a neutral or acidic metal salt is limited primarily to cyclopentadiene and in a few instances methylcyclopentadiene (*37*). The use of other substituted cyclopentadienes has not been reported and it is probable that only the very strongest bases would be effective in promoting their reaction.

Solvents of high dielectric constant with good solvent properties for the reacting basic metal salt are most satisfactory media for the reaction of cyclopentadiene with metal salts in the presence of base. Most frequently used solvents are tetrahydrofuran and 1,2-dimethoxyethane; less frequently used solvents are dioxane, ethanol, ammonia, and diethylamine.

In the initial description of this method triethylamine, diethylamine, pyridine, and sodium ethylate were reported to be effective, but yields of ferrocene and titanocene dichloride were only 3–4% (*33*). These low yields probably resulted from the use of unreactive ferrous chloride prepared by high temperature dehydration.

Synthesis of ferrocene in high yield by this method has been reported by a number of investigators (*18*, *34–36*, *38*). Wilkinson *et al.* (*36*) have described the preparation of ferrocene, and dicyclopentadienyl compounds of cobalt and nickel in yields of 80–90%; anhydrous diethylamine served both as solvent and acceptor for hydrogen halide. This procedure for preparing ferrocene has been published in detail in *Organic Synthesis* (*18*).

A potentially low-cost synthesis of ferrocene based on this method has been devised by Pruett and Morehouse (*35*, *39*). If the by-product amine hydrochloride is recycled, a process which utilizes only iron and cyclopentadiene results. This sequence is:

$$Fe + 2HCl \cdot HN(C_2H_5)_2 = FeCl_2 \cdot 2HN(C_2H_5)_2 \qquad (6)$$

$$FeCl_2 \cdot 2HN(C_2H_5)_2 + C_5H_6 = Fe(C_5H_5)_2 + 2HCl \cdot HN(C_2H_5)_2 \qquad (7)$$

$$\text{Net reaction: } Fe + 2C_5H_6 = Fe(C_5H_5)_2 + H_2 \qquad (8)$$

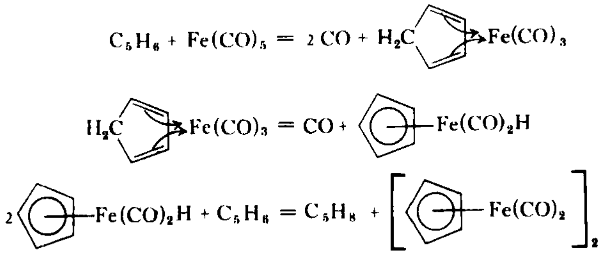
a. *Preparation of Thallium Cyclopentadienide* (*27*). To a solution of 25 gm of thallium sulfate and 10 gm of potassium hydroxide in 200 ml of water at 25°C is added 5 gm of cyclopentadiene. After stirring the mixture for a few minutes the precipitate of thallium cyclopentadienide is washed with ice water and cold methanol and then dried. Yield is 19.5 gm of CpTl (95% of theoretical yield based on cyclopentadiene).

b. *Preparation of Dicyclopentadienyltitanium Dichloride.* (Based on ref. *36*.) To 300 ml of tetrahydrofuran is added 60 gm (0.24 mole) of titanium tetrachloride with good mixing and cooling. To this mixture is added 100 ml (1 mole) of diethylamine followed by 120 ml (1.4 mole) of cyclopentadiene. The reaction mixture is refluxed (60°–65° C) for 8 hr, cooled to 5° C, and filtered. The precipitate which is a mixture of Cp_2TiCl_2 and diethylamine hydrochloride is washed with tetrahydrofuran, and petroleum ether (30°–60° C boiling range) and dried in air. The precipitate is added to 200 ml of 4 *N* hydrochloric acid, and the resulting slurry is stirred for 10 min and filtered. The red Cp_2TiCl_2 is washed with ice water and methanol and then dried. Yield is 45–48 gm (75–80% of theory), m.p. is 287°–289° C with slight decomposition.

3. *Reaction of Cyclopentadienes with Metal Carbonyls* (*Method 3*)

Cyclopentadiene reacts directly with metal carbonyls to form two classes of compounds, each with cyclopentadienyl–metal bonds. Under mild conditions cyclopentadienyl metal carbonyls, $C_5H_5M(CO)_x$, are formed, and this is the preferred method for preparing many of them. Under more vigorous conditions dicyclopentadienyl metal compounds, $(C_5H_5)_2M$, are formed. Because, however, yields of dicyclopentadienyl metals are low, this is not an important method for their preparation except possibly in the case of ferrocene (*40*). This reaction under mild conditions, is carried out in the liquid phase in refluxing dicyclopentadiene. Occasionally, a solvent of high dielectric constant is included if cyclopentadiene itself is used. The product may be isolated by simply filtering the crystals or by subliming the residue after removal of solvent. Under vigorous conditions the reaction is carried out in the vapor phase in a heated tube.

Attachment of one cyclopentadienyl group to iron by reaction of cyclopentadiene with iron pentacarbonyl has been formulated as proceeding through three steps (*41*).



The first step is a simple displacement of two molecules of carbon monoxide. In the second step the acidic hydrogen of π-bonded cyclopentadiene shifts to the iron atom to give π-cyclopentadienyliron dicarbonyl hydride, a known compound. Two molecules of this iron hydride then add hydrogen to cyclopentadiene to form cyclopentene and the dimer of π-cyclopentadienyliron dicarbonyl. This reaction proceeds at temperatures between 150° and 220° C. Above 220° C, the remaining carbon monoxide molecules are displaced by a second molecule of cyclopentadiene forming ferrocene (*42*).

The reaction of chromium carbonyl with cyclopentadiene at 280°–350° C to form Cp_2Cr (*43*) is reversible (*44, 45*).

$$2(C_5H_5)_2Cr + 3CO(10\ \text{atm}) \xrightleftharpoons{100°\text{–}110° C} [(C_5H_5)_2Cr][C_5H_5Cr(CO)_3] + C_5H_5\cdot \qquad (12)$$

$$[(C_5H_5)_2Cr][C_5H_5Cr(CO)_3] + 3CO(100\ \text{atm}) \xrightleftharpoons{150°\text{–}170° C} [C_5H_5Cr(CO)_3]_2 + C_5H_5\cdot \qquad (13)$$

$$[C_5H_5Cr(CO)_3]_2 + 6CO(100\ \text{atm}) \xrightleftharpoons{250° C} 2Cr(CO)_6 + 2C_5H_5\cdot \qquad (14)$$

Carbon monoxide under 100 atm pressure reacts with Cp_2Cr at 100°–110° C to form $[Cp_2Cr][CpCr(CO)_3]$ [reaction (12)] and at 150°–160° C to form $[CpCr(CO)_3]_2$, [reaction (13)]. At still higher temperatures the remaining ring is displaced and chromium hexacarbonyl is the final product [reaction (14)]. When Cp_2Cr is allowed to react with carbon monoxide (150 atm) in the presence of hydrogen (50 atm) at 65°–68° C for 15 hr, the major product is $CpCr(CO)_3H$ together with 15% of π-$C_5H_5Cr(\pi\text{-}C_5H_7)(CO)_2$ [reaction (15)] (*46*).

$$(C_5H_5)_2Cr \xrightarrow[65°\text{–}68°\,C,\ 15\ hr]{\substack{CO\ (150\ atm),\\ H_2\ (450\ atm),}} C_5H_5C(CO)_3H[85\%] + C_5H_5Cr(\pi\text{-}C_5H_7)(CO)[15\%] \quad (15)$$

At higher pressures and temperatures the product is predominantly $Cr(CO)_6$ derived from the decomposition of $CpCr(CO)_3H$.

Methylcyclopentadiene readily undergoes reaction with metal carbonyls (*47*) and even 1,3-diphenylcyclopentadiene reacts with iron carbonyl (*48*). A novel method for obtaining a ferrocene with one substituted ring, is the reaction of 1,3-diphenylcyclopentadiene with the dimer of cyclopentadienyliron dicarbonyl at 170° C to produce 1,3-diphenylferrocene in 15% yield. Other substituted cyclopentadienes which have been used are tetraphenylcyclopentadienone in the preparation of tetraphenyl(hydroxy)cyclopentadienylmanganese tricarbonyl (*49*) and indene in the preparation of the dimer of indenylmolybdenum tricarbonyl (*50*). A variety of substituted fulvenes have been used in the preparation of substituted cyclopentadienyl metal tricarbonyl compounds of Cr, Mo, and W (*51*, *52*). This latter reaction proceeds best in the presence of a solvent, such as 1,2-dimethoxyethane, to permit easy abstraction of hydrogen.

B. *Reaction of Ionic Cyclopentadienides with Metal Compounds*

The reaction of ionically bonded metal cyclopentadienides with metal compounds to form cyclopentadienyl metal compounds may be represented by the general equation

$$nC_5H_5M + M'X = Cp_nM'X_{y-n} + nMX \quad (16)$$

where the metal compound M'X is either a metal salt or a metal carbonyl. This is by far the most general method for synthesizing the cyclopentadienyl–metal bond. It is applicable to the preparation of cyclopentadienyl compounds of virtually all of the elements which form these compounds, whether the metals are of transition group or main group type. Ionic cyclopentadienides of Li, Na, and K, as well as the Grignard reagent, CpMgBr, are all suitable reagents for this reaction partially because they are ionized in solvents of high dielectric constant (*36*). The reactive species is undoubtedly the cyclopentadienide anion, which displaces a ligand from the less reactive metal compound and forms a cyclopentadienyl derivative of the less reactive metal. A salt of the more active metal M is the metathetical product.

The ionic cyclopentadienide is customarily prepared in advance in the same solvent to be used in the preparation of the cyclopentadienyl metal compound. Stock solutions of reactive cyclopentadienides may be prepared and used as needed. A solution of 2.5 M sodium cyclopentadienide in tetrahydrofuran may be conveniently prepared and stored for this purpose. Since ionic cyclopentadienides are air-sensitive, all reactions must be carried out in an inert atmosphere, usually nitrogen. It is important that the metal compound, usually a chloride or bromide, be anhydrous because the ionic cyclopentadienide reacts preferentially with water.

Reaction of ionic cyclopentadienides with metal compounds does not always proceed according to the stoichiometry of a metathetical reaction. The reason for this is that ionic cyclopentadienides provide a reducing medium and, if the metallic ion of the metal compound is in an easily reducible state, then a portion of ionic cyclopentadienide will be consumed in reducing the metal ion to a lower valence state. When trivalent metal salts are used for the preparation of dicyclopentadienyl metal compounds of the first transition series then at least 3 moles of ionic cyclopentadienide must be used to achieve good yields of the desired dicyclopentadienyl metal compound, the excess beyond 2 moles being necessary to effect reduction of the metal ion to the divalent state. An example of such a reduction is the reaction of ferric chloride with excess sodium cyclopentadienide to form ferrocene. When excess ionic cyclopentadienides are used as reducing agents, unidentified reduction products of cyclopentadiene are formed, usually polymeric in nature, and isolation of the product becomes difficult. Two elements which are not reduced with excess cyclopentadienide ions are Rh and Ir. They give the cation Cp_3M^+ when the metal ion in the $3+$ state reacts with excess cyclopentadienide.

Cyclopentadienyl compounds synthesized by the reaction of ionic cyclopentadienides with metal compounds are usually isolated by evaporating the solvent under vacuum and, if the product is unstable, extracting the dry residue with a hydrocarbon solvent, such as benzene or toluene. Air-sensitive products of sufficient volatility may be sublimed away from nonvolatile residues. When more than gram quantities are required the inconvenience of evaporating to dryness and transferring a pyrophoric residue renders these techniques rather impractical. It is then more convenient to add a hydrocarbon solvent which is less volatile than the reaction solvent and remove excess ionic cyclopentadienide by hydrolysis. The product may be crystallized from the hydrocarbon solvent. Hydrolytically sensitive products require a solvent in which the product is soluble but excess ionic cyclopentadienide is insoluble.

1. *Reaction of Alkali Metal Cyclopentadienides with Metal Salts* (*Method 4*)

Reaction of alkali metal cyclopentadienides with metal salts has been the most widely used method for the synthesis of cyclopentadienyl metal compounds. Alkali metal cyclopentadienides were first employed in the preparation of cyclopentadienyl metal compounds by Fischer *et al.* (*7–9*). They used lithium, sodium, and potassium cyclopentadienides in liquid ammonia and obtained complex ammine salts, $M[NH_3]_6(C_5H_5)_2$, which could be decomposed by heating under vacuum to give dicyclopentadienyl compounds of several elements in the first transition series. Wilkinson and Birmingham (*13*) improved the convenience of the method by using tetrahydrofuran and 1,2-dimethoxyethane as solvents for sodium cyclopentadienide. In these solvents most reactions are rapid and complete, and the reaction may be run conveniently at temperatures between 25° C and reflux. Even the ammine salts, $Ni(NH_3)_6Cl_2$ and $Co(NH_3)_6Cl_2$, react at 30°–40° C with CpNa in THF with complete displacement of ammonia (*53*). Other solvents which have been used are diethyl ether, *tert*-butanol, *N*,*N*-dimethylformamide, and a mixture of toluene and ether. Sodium cyclopentadienide is soluble to the extent of 1–2.5 moles/liter in most of these solvents, but is nearly insoluble in toluene and benzene. In those few cases where the solvent reacts with the product it is necessary to prepare the alkali metal cyclopentadienide in one solvent and displace it with another solvent which is compatible with the product. This procedure has been employed in the preparation of Cp_2Zn (*54*) and Cp_2Pb (*15*) where sodium cyclopentadienide was prepared in liquid ammonia or *tert*-butanol and these solvents were replaced with *N*,*N*-dimethylformamide. The influence of solvent is also illustrated in the preparation of tetracyclopentadienyls of Nb, Ta, Mo, W (*55*), U (*56*), and Th (*57*). When excess sodium cyclopentadienide in diethyl ether or benzene reacts with higher halides of the above metals, the tetracyclopentadienyls are produced in good yield. When tetrahydrofuran is substituted for ether or benzene in the above preparations, little if any tetracyclopentadienyl of Nb, W, U, or Th is produced, whereas salts of Mo and W form Cp_2MoH_2 and Cp_2WH_2 (*58*).

Choice of metal salt is generally governed by a number of factors such as solubility in the reaction medium, ease of preparation, and lack of reactivity with the product. The metal should preferably be in the same oxidation state as the final cyclopentadienyl metal compound to avoid excessive consumption of alkali metal cyclopentadienide and difficulties in work-up caused by the presence of oxidation products of cyclopentadiene. In liquid ammonia, thiocyanates of cobalt (*9*), nickel (*8*), cadmium, etc. have been preferred because of their good solubility, whereas in tetrahydrofuran chlorides and bromides have been most commonly employed. In any case, the selected salt should be anhydrous and may be added either in the dry state or in solution.

The preparation of cobaltocene presents a special problem because the product is partially destroyed through oxidation by cobaltous chloride.

$$2(C_5H_5)_2Co + Co^{2+} \rightarrow 2(C_5H_5)_2Co^{+} + Co \qquad (17)$$

Hexamminecobalt(II) chloride, on the other hand, is not readily reduced by cobaltocene. Hence, its use in place of cobaltous chloride leads to higher yields of cobaltocene (*53*).

In general, reactions between alkali metal cyclopentadienides and metal salts are carried out at the reflux temperature of the chosen solvent for a period of several hours. However, longer periods of reflux are required for the reaction of certain metal salts. Thus, the preparation of ruthenocene requires several days of refluxing in 1,2-dimethoxyethane to complete the reaction between $RuCl_3$ and NaCp (*59*).

Dicyclopentadienylrhenium has not been synthesized, although analogous compounds of the other elements in the manganese group, $(C_5H_5)_2Mn$ and $(C_5H_5)_4Tc_2$, have been prepared. When rhenium pentachloride reacts with excess sodium cyclopentadienide in tetrahydrofuran and the product is isolated by sublimation of the residue after removal of the solvent, the product is a yellow crystalline solid, $(C_5H_5)_2ReH$. This yellow sublimate is accompanied by a slightly more volatile brown oil which has previously been considered as a polymeric organic by-product. This oil is difficult to crystallize but can be made to form brown crystals which may very well be the missing $(C_5H_5)_2Re$. This possibility is strengthened by the observation that addition of sodium borohydride to the reaction mixture prevents the formation of oil (*60*).

The reaction of alkali metal cyclopentadienides with metal salts is generally applicable to the synthesis of substituted metalcyclopentadienyls. Thus, sodium methylcyclopentadienide readily reacts with metal halides to form methylcyclopentadienyl metal compounds (*47*). Similarly, fulvenes may be converted to substituted cyclopentadienide anions, $[C_5H_4CRR'H]$, by sodium (*61*), $LiAlH_4$, LiR′, or $NaNH_2$ (*62*, *63*). The cyclopentadienide anions thus produced will react with anhydrous ferrous chloride to give high yields of substituted ferrocenes. Azulene has been converted to its anion by lithium alkyls, and then into two stereoisomeric derivatives of ferrocene by reaction with anhydrous $FeCl_2$ (*63*). Also, azocyclopentadiene has been converted by phenyllithium into phenylazocyclopentadienide and subsequently into phenylazoferrocene (*64*). Although they have been used principally for ferrocene derivatives, these reactions with substituted cyclopentadienides should be applicable to other elements. Indeed, a derivative of cobaltocene, di(1-hydroxy-3-methyl-cyclopentadienyl)cobalt, has been synthesized from 3-methyl-2-cyclopentadienone, sodium amide, and cobaltous chloride in liquid ammonia (*65*).

a. *Preparation of Ferrocene* (*18*). In a 250-ml three-necked flask, fitted with a mechanical stirrer, a reflux condenser, and an inlet for admission of nitrogen, is placed 100 ml of tetrahydrofuran. With stirring, 27.1 gm (0.166 mole) of anhydrous ferric chloride is added in portions, followed by 4.7 gm (0.084 gram atom) of iron powder. The mixture is heated with stirring under nitrogen at the reflux temperature for 4.5 hr, giving a gray powder with a brown supernatant liquid.

The cooled contents of the 250-ml flask containing ferrous chloride are added to a solution of 0.5 moles of cold sodium cyclopentadienide in 200 ml of tetrahydrofuran (see Method 2 for the preparation of sodium cyclopentadienide) while passing a stream of nitrogen through both flasks. The combined mixture is stirred for 1.25 hr at a temperature just below the reflux temperature. Solvent is removed by distillation, and the ferrocene is extracted from the residue with several portions of refluxing petroleum ether (b.p. 40°–60° C). The product is obtained by evaporation of the petroleum ether solution. Ferrocene may be purified by recrystallization from pentane or cyclohexane (hexane, benzene, and methanol have also been used) or by sublimation. The yield is 31–34 gm (67–73%), m.p. 173°–174° C.

b. *Preparation of Cobaltocene* (*53*). *Hexamminecobalt(II) Chloride.* A solution of 476 gm of $CoCl_2 \cdot 6H_2O$ ($\sim$ 2 moles) is dissolved in 760 gm of water and is heated to 60° C, and during 6 hr about 400 gm of ammonia are added. The solution is cooled with an ice bath and large pinkish-colored crystals of $Co(NH_3)_6Cl_2$ are filtered, washed with ice water, ethanol, and ether. The product is slightly sensitive to oxidation by air and should be dried under nitrogen or in vacuum. The yield is 360–400 gm (78–86% of theoretical value).

Cobaltocene. To 0.5 mole of sodium cyclopentadienide in 400 ml of tetrahydrofuran (see Method 2 for the preparation of sodium cyclopentadienide) is added 75 gm of $Co(NH_3)_6Cl_2$ and the temperature is raised to 35°–40° C, whereupon ammonia evolution commences. When ammonia evolution is virtually complete, the mixture is refluxed at 65° C for 2 hr. The solvent is removed under vacuum and the dry residue transferred to a sublimation apparatus, where the cobaltocene is isolated in the form of dark violet crystals which are very rapidly oxidized by air. The yield is between 42 and 47 gm (86–96% of theoretical yield based on sodium cyclopentadienide).

An alternative method for isolating the product is to add toluene to the reaction mixture after the reflux period and remove most of the tetrahydrofuran by distillation through a packed column. The mixture is then washed with water to remove salts and residual tetrahydrofuran, and the resulting toluene solution of cobaltocene is dried with anhydrous sodium sulfate.

2. *Reaction of Cyclopentadienyl Grignard Reagent with Metal Salts (Method 5)*

The reaction of cyclopentadienylmagnesium halides with metal salts has been used in the synthesis of many cyclopentadienyl compounds from both transition group and main group elements. One of the two original methods for the synthesis of ferrocene was the reaction of cyclopentadienylmagnesium bromide with ferric chloride (*1*) and many compounds were prepared by this method during the early period of cyclopentadienyl metal chemistry. With the development of other methods the Grignard method became less favored until now it is seldom employed. One inconvenience of this method is that cyclopentadienylmagnesium halide is not prepared directly but must be prepared by a replacement reaction between cyclopentadiene and a more reactive alkylmagnesium halide. High yields in this replacement reaction are achieved only when diethyl ether is partially replaced by a higher boiling solvent, such as benzene or toluene. Another inconvenience is that it is often necessary to reflux the reaction mixture for 12–24 hr to achieve good yields of cyclopentadienyl metal compounds. When anhydrous halides are used in the preparation of cyclopentadienyl metal compounds from Grignard reagents, yields are often below 50%. Higher yields result with the use of metal complexes, such as acetylacetonates, which are soluble in organic solvents. The pyridine complex of ferrous chloride, $Fe(C_5H_5N)_2Cl_2$, gives an almost quantitative yield of ferrocene (*42*).

The reaction mixture may be worked up in one of two ways. If the product is not hydrolyzable, it may be isolated by hydrolyzing the reaction mixture in dilute mineral acid or ammonium chloride and extracting the product with an organic solvent. In the event that the product is water-sensitive, it may be isolated by sublimation of the dry reaction residue after removal of solvent. Contamination of the product with Cp_2Mg, a sublimable co-product, often occurs. This contaminant may be removed by dissolving the mixture in ether and passing CO_2 into the solution to decompose the Cp_2Mg.

The Grignard method is also applicable to the synthesis of substituted cyclopentadienyl metal compounds. Diindenyliron (*66*) has been prepared from indenylmagnesium bromide (*67*) and di(1,3-diphenylcyclopentadienyl)iron from 1,3-diphenylcyclopentadienylmagnesium bromide (*68*).

a. *Preparation of Vanadocene* (*69*). Ethylmagnesium bromide is prepared in the usual way from 8 gm (0.33 mole) of magnesium chips, 36.0 gm (0.33 mole) of C_2H_5Br, and 250 ml of absolute diethyl ether. The apparatus used is a 500-ml three-neck flask fitted with a stirrer, reflux condenser, addition funnel, and nitrogen inlet tube. To the Grignard solution is added 24.0 gm (0.36 mole) of cyclopentadiene and the mixture is refluxed for 3 hr or until the evolution of ethylene has stopped. (The rate and yield of this reaction may be improved by displacing part of the ether with benzene and refluxing at the higher temperature, which is attainable in this solvent system.)

To the cyclopentadienylmagnesium bromide solution is added 13.5 gm (0.07 mole) of VCl_4 with cooling. The mixture is refluxed for 8–10 hr, the solvent is removed under vacuum, and the residue sublimed in high vacuum to a temperature of 200° C to give a blue-violet sublimate which is a mixture of Cp_2V and Cp_2Mg. The separation of Cp_2Mg from Cp_2V is effected by dissolving the mixed crystals in 175 ml of nitrogen-saturated ether and passing a stream of CO_2 through the solution. The precipitate of the magnesium salt of cyclopentadienecarboxylic acid is removed by filtration and the precipitate washed with three 24-ml portions of ether. The violet filtrate is concentrated to 20% of its original volume and cooled to $-80°$ C to permit crystallization. The vanadocene is filtered, washed with a small portion of ether, and then resublimed in high vacuum at 80°–100° C to give 5 gm of violet vanadocene, melting at 167°–168° C. A further 1–2 gm of product may be isolated from the mother liquor. The yield is 47–55% of the theoretical value.

3. *Reaction of Alkali Metal Cyclopentadienides with Metal Carbonyls (Method 6)*

Displacement of carbon monoxide from metal carbonyls by alkali metal cyclopentadienides is a convenient method for preparing the alkali metal salts of the mixed cyclopentadienyl metal carbonyls. This reaction of carbonyls of Group VIB transition metals is represented by the equation

$$NaC_5H_5 + M(CO)_6 \rightarrow Na[C_5H_5M(CO)_3] + 3CO \qquad (18)$$

The salt which is formed may then be treated with acetic acid to yield cyclopentadienyl metal tricarbonyl hydride or with alkyl halides to form alkyl derivatives.

Reaction of sodium cyclopentadienide with the carbonyl halides of noble metals has been useful in the preparation of mixed cyclopentadienyl carbonyls which are usually sublimed directly from the reaction mixture after removal of solvent. In this manner monomeric $CpIr(CO)_2$ (*70*), $CpRh(CO)_2$ (*71*), $CpIr(CO)_2$, $[CpRu(CO)_2]_2$ (*72*), and $[CpPt(CO)]_2$ (*73*) have been synthesized. These reactions are usually carried out under reflux in the solvent which was used to prepare sodium cyclopentadienide.

Direct synthesis of mixed cyclopentadienyl carbonyls of certain other transition metals may be accomplished by reaction of metal halide, sodium cyclopentadienide, and carbon monoxide under high pressure (50–300 atm). This reaction probably proceeds via the formation of dicyclopentadienyl metal compound followed by displacement by CO, rather than via formation of metal carbonyl and subsequent displacement by cyclopentadienide anion. An excess of sodium cyclopentadienide is normally used to provide a reducing medium, which is especially important for metals initially in the 4+ or 5+ valence state. Some of the compounds which have been synthesized using this approach are $CpMn(CO)_3$ (*74*, *75*, *76*), $CpRe(CO)_3$ (*77*), $Cp_2Ti(CO)_2$ (*78*), $CpTc(CO)_3$ (*79*), and $CpNb(CO)_4$ (*80*).

C. From Alkenes and Alkynes

1. *Reaction of Alkenes and Alkynes with Metal Salts and Metal Carbonyls (Method 7)*

The direct formation of the cyclopentadienyl–metal bond by the reaction of alkenes and alkynes with metal compounds has been applied only to titanium and manganese. Röhl *et al.* (*81*) have prepared pentamethylcyclopentadienyltitanium trichloride in 20–30% yields by the reaction of certain olefins with titanium tetrachloride at 300° C and 30–60 atm.

$$1H_2C{=}C(CH_3)_2 + 2TiCl_4 \xrightarrow{300°C} C_5(CH_3)_5TiCl_3 + H_2,\ CH_4,\ C_2H_6,\ C_3H_8,\ n\text{-butane, isobutane, butenes, and HCl} \qquad (19)$$

Olefins which undergo this reaction are 1-butene, 2-butene, isobutylene, a mixture of pentene isomers, diisobutylene, and tetrapropylene. Coffield *et al.* (*82*, *83*) have shown that acetylene and manganese pentacarbonyl under 600 psi and at 150° C give 1,2-(propenylene)cyclopentadienylmanganese tricarbonyl. The conditions of this synthesis are similar to those described by Reppe (*84*) for the reaction of acetylene with other metal carbonyls to form π-bonded complexes.

III

SYNTHESIS BY REACTIONS OF π-BONDED CYCLOPENTADIENYL METAL COMPOUNDS

Syntheses of cyclopentadienyl metal compounds by reactions which do not involve the formation of cyclopentadienyl–metal bonds are not within the scope of this review. However, certain cyclopentadienyl metal compounds are difficult to make by the general methods outlined above, and are best made by converting easily prepared compounds without affecting the cyclopentadienyl–metal bonding. The most important reactions of this sort involve changes in the oxidation state of the central metal atom. Oxidation–reduction methods are therefore discussed in detail. In addition, several other general methods for transforming one cyclopentadienyl metal compound to another are listed with little discussion in order to complete the tabular survey of compounds and methods.

1. *Oxidation and Reduction* (*Method 8*)

Synthesis of cyclopentadienyl metal compounds by Methods 1–7 often leads to products in which the metal is in an oxidation state different from that required for a particular purpose. Oxidation or reduction of these compounds is frequently the most convenient method for producing compounds not readily synthesized by direct methods. The general equation for the oxidation of the dicyclopentadienyl compounds of the first transition series may be written as

$$C_5H_5M \underset{}{\overset{[0]}{\rightleftharpoons}} [C_5H_5M]^{1+,2+,3+} \tag{20}$$

This reaction is reversible for all elements of this series except cobalt. Oxidation and reduction may be accomplished by anodic or cathodic means or by chemical methods.

All neutral dicyclopentadienyl compounds of the first transition series except ferrocene are oxidized by air and hence must be carefully protected from air during storage. Ferrocene and nickelocene are oxidized to their unipositive cations by 3 N nitric acid, whereas vanadocene and cobaltocene are oxidized to their unipositive cations even by 3 N hydrochloric acid.

The stoichiometry of the oxidation of cobaltocene by hydrochloric acid is unusual in that, for every three moles of cobaltocene consumed, two moles of $(C_5H_5)_2Co^+$ and one mole of Co^{2+} are produced (*31*).

$$3Cp_2Co \xrightarrow{HCl} 2CpCo^+ + Co^{2+} \tag{21}$$

This formation of cobaltous ion may, however, be avoided by oxidizing cobaltocene with hydrogen peroxide to give nearly quantitative yields of cobalticinium hydroxide, Cp_2CoOH (*8*, *85*).

Ferricinium salts also are most conveniently prepared by oxidation of ferrocene. Ferric chloride or ceric sulfate will effect this oxidation, as will oxygen passing through acid containing a trace of ferric or cupric ion. In organic media, the oxidation of ferrocene to ferricinium cation may be accomplished by Br_2 in CCl_4 (*86*), by quinone in benzene (*87*), or by concentrated sulfuric acid (*88*).

Dicyclopentadienyl metal cations are soluble in aqueous acid and exhibit properties similar to those of the larger alkaline earth cations. In aqueous solution they are precipitated by large anions, such as picrate, reineckate, tetraphenylborate, hexafluorophosphate, and silicotungstate.

Lithium aluminum hydride in tetrahydrofuran reduced $(Cp)_2VCl_2$ to $(Cp)_2V$ (*89*), whereas the same reagent reduced $(Cp)_2Co^+$ to $CpCoC_5H_6$ (*90*). The ferricinium ion is easily reduced to ferrocene by sodium dithionite, titanous sulfate, or stannous chloride.

2. *Thermal Decomposition* (*Method 9*)

Although ferrocene and many other cyclopentadienyl metal compounds are thermally stable to very high temperatures, two examples of thermal decomposition are the disproportionation of cyclopentadienylmagnesium bromide (*36*, *91*) to give dicyclopentadienylmagnesium and magnesium bromide and the decomposition of ferricinium ion (*48*) to give ferrocene.

3. *Neutron Activation* (*Method 10*)

It is possible in certain cases to produce isotopic modification of cyclopentadienyl metal compounds by neutron activation. An example of this method is the synthesis of $(C_5H_5)_2Rh^{105}$ (*92*).

$$(C_5H_5)_2Ru^{104} \xrightarrow{n,\,\gamma} (C_5H_5)_2Ru^{105} \xrightarrow{\beta^-,\,\gamma} (C_5H_5)_2Rh^{105} \tag{22}$$

4. *Ligand Replacement* (*Method 11*)

Replacement of the cyclopentadienyl ring or of other ligands about the metal atom may be effected by many anionic and neutral species. An example of ligand replacement (*93*) is

$$(C_5H_5)_2TiCl_2 + 2LiC_6H_5 \rightarrow (C_5H_5)_2Ti(C_6H_5)_2 + 2LiCl_2 \tag{23}$$

5. *Addition Reactions* (*Method 12*)

Addition to the cyclopentadienyl ring or to the metal atom is a frequently used synthetic method, especially for the compounds of Group VIII elements. An example of an addition reaction (*94*) is

$$[(C_5H_5)_2Co]^+X + LiC_6H_5 \rightarrow C_5H_5Co(1\text{-}exo C_6H_5C_5H_5) + LiX \tag{24}$$

IV

TABULAR SURVEY

A survey of known cyclopentadienyl metal compounds is presented in Table I. This survey is complete through *Chemical Abstracts* index for Volume 58, June 1963, and includes several later references.

Compounds are arranged according to periodic groups starting with the lithium group. Within the compounds of each element the cyclopentadienyl metal compounds, Cp_nM, are listed according to increasing number of cyclopentadienyl groups. When other ligands are present, the compounds are arranged in order of decreasing number of cyclopentadienyl groups. Abbreviations used in addition to Cp are Ind for indenyl, Fluor for fluorenyl, ϕ for phenyl, Me for methyl, and Et for ethyl.

TABLE I

CYCLOPENTADIENYL-METAL COMPOUNDS

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references[a]
Lithium Group				
CpLi	dec without melting	Colorless	35	(1), *45*, *95*; (2), 96, *97*
IndLi	dec without melting	Colorless	—	(2), *24*
FluorLi	dec without melting	Colorless	31	(1), *17*, *95*; (2), *95*
9-PhenylfluorLi	dec without melting	Colorless	38–85	(2), *98*; (1), *95*
CpNa	dec 300	Colorless	97	(1), *6*, *7*, *8*, *11*, *13*, *18*, *45*, *85*, *99–103*; (2), *102*
IndNa	dec without melting	Colorless	—	(1), *11*, *24*
FluorNa	dec without melting	Colorless	70–90	(1), *11*, *17*, *100*
CpK	dec without melting	Colorless	87	(1), *4*, *7*, *9*, *45*; (2), *30*, *104*
FluorK	dec without melting	Colorless	70–90	(1), *17*, *25*
Beryllium Group				
$\mathrm{Cp_2Be}$	59–60	Colorless	74	(4), *105*
$\mathrm{MeCp_2Be}$	−29 to −30	Colorless	63	(4), *21*
$\mathrm{Cp_2Mg}$	176–178	Colorless	40	(1), *20*, *22*, *106*, *107*; (9), *36*, *108*
CpMgBr	—	Colorless	—	(2), *109*, *118*, *119*
$\mathrm{MeCp_2Mg}$	29–30	Colorless	45	(9), *107*, *111*
$\mathrm{Cp_2Ca}$	dec without melting	Colorless	17	(1), *112*; (2), *11*, *112*, *113*
$\mathrm{Cp_2Sr}$	dec without melting	Colorless	4.1	(1), *112*; (2), *112*
$\mathrm{Cp_2Ba}$	dec without melting	Colorless	0.2	(2), *112*

Scandium Group and the Rare Earths				
Cp_3Sc	240	Straw	75	(4), *114*
Cp_3Y	295	Pale yellow	85	(4), *114*
Cp_3La	395 (dec)	Colorless	25	(4), *114*
$MeCp_3La$	155–156	Colorless	27	(4), *111*
Cp_3Ce	435	Orange-yellow	72	(4), *114*
Cp_3Pr	415	Pale green	83	(4), *114*
Cp_3Nd	380	Reddish-blue	78	(4), *114*
$MeCp_3Nd$	165	Reddish-blue	70	(4), *47*
Cp_3Sm	365	Orange	75	(4), *114*
Cp_2SmCl	dec 200	Yellow	50–60	(4), *116*
$CpSmCl_2\cdot(C_4H_8O)_3$	dec 50–240	Beige	30–60	(4, 11), *115*
$CpEuCl_2$	dec 50–240	Purple	30–60	(4, 11), *116*
Cp_3Gd	350	Yellow	84	(4), *114*
Cp_2GdCl	dec 140	Colorless	50–60	(4, 11), *116*
$CpGdCl_2\cdot(C_4H_8O)_3$	82–86 (dec)	Lavender	30–60	(4, 11), *115*
$MeCp_3GdCl$	188–197	Colorless	50–60	(4, 11), *116*
$MeCp_3GdOOCCH_3$	207–209	Colorless	65	(11), *116*
Cp_3Dy	302	Yellow	85	(4), *114*
Cp_2DyCl	343–346 (dec)	Yellow	50–60	(4, 11), *116*
Cp_2DyOCH_3	dec > 235	Yellow	85	(4), *116*
$CpDyCl_2\cdot(C_4H_8O)_3$	85–90 (dec)	Colorless	30–60	(4, 11), *115*
Cp_2HoCl	340–343 (dec)	Yellow-orange	50–60	(4, 11), *116*
$CpHoCl_2\cdot(C_4H_8O)_3$	84–92	Yellow	30–60	(4, 11), *115*
Cp_3Er	285	Pink	88	(4), *114*
Cp_2ErCl	dec > 200	Pink	50–60	(4, 11), *116*
$Cp_2ErOOCCH_3$	331–335 (dec)	Pink	45	(11), *116*
$Cp_2ErOOCH_3$	dec > 270	Pink	27	(11), *116*
Cp_2ErOCH_3	236–240	Pink	52	(11), *116*
Cp_2ErNH_2	330–334	Pink	33	(11), *116*
$CpErCl_2\cdot(C_4H_8O)_3$	91–94	Pink	30–60	(4, 11), *115*

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references^a
$MeCp_2ErCl$	119–122	Pink	50–60	(4, 11), *116*
$MeCp_2ErOOCCH_3$	199–201	Pink	55	(11), *116*
Cp_3Yb	273	Dark green	82	(4), *114*
Cp_2YbCl	dec > 240	Orange-red	50–60	(4, 11), *116*
$Cp_2YbOOCCH_3$	325–329 (dec)	Orange	65	(11), *116*
$Cp_2YbOOC_6H_5$	350–375 (dec)	Orange	54	(11), *116*
Cp_2YbOCH_3	290–305	Orange	60	(11), *116*
$Cp_2YbOC_6H_5$	382–386	Red	64	(11), *116*
$CpYbCl_2 \cdot (C_4H_8O)_3$	78–81	Orange	30–60	(4, 11), *115*
Cp_2LuCl	318–320	Greenish-white	72	(4, 11), *116*
$CpLuCl_2 \cdot (C_4H_8O)_3$	76–78	Colorless	30–60	(4, 11), *115*
Thorium and the Actinides				
Cp_4Th	dec 170	Colorless	1–40.7	(4), *57*, *117*
Cp_4U	dec 270	Red	6	(4), *14*
Cp_3UCl	—	—	82–85	(4), *117*
Titanium Group				
Cp_2Ti	dec 130	Green	40	(4), *120*; (8), *121*
$Cp_2Ti \cdot OC_4H_8$	81	Brown and green forms	—	(4), *120*
Cp_3Ti	dec 130	Green	—	(4), *122*
Cp_4Ti	—	Brown	—	(4), *421*
Cp_2TiF_2	—	Yellow	—	(11), *13*
Cp_2TiCl_2	287–287.5 (dec)	Red	72–90	(4), *13*, *123–125*; (5), *126*; (2), *33*

Cp_2TiBr_2	309–310 (dec)	Red	70	(4, 5), *13, 126, 127*
Cp_2TiI_2	317–318	Purple	—	(11, 5), *13, 126*
$Cp_2Ti(OH)Br \cdot H_2O$	—	Orange	—	(11), *13*
$Cp_2Ti(Me)_2$	—	Orange	95	(11), *121, 186*
$Cp_2Ti(Me)Cl$	168–170 (dec)	Orange-red	95	(11), *121*
$Cp_2Ti(Et)Cl$	—	—	60	(11), *128*
$Cp_2Ti\phi_2$ and other substituted derivatives	146–148	Orange-yellow	81	(11), *97, 129*
$Cp_2Ti(OEt)Cl$	91–92	Greenish-yellow	61	(4), *130, 131*
$Cp_2Ti[OSi(Me)_3]Cl$	1	Orange	—	(11), *350*
$Cp_2Ti(OSi\phi_3)_2$	208–210	Yellew	—	(11), *350, 351*
$Cp_2Ti(S\phi)_2$	200–201	Red	—	(11), *352*
$Cp_2TiCl(NH_2) \cdot NH_3$	—	(Not fully identified)	—	(11), *132*
$CP_2Ti(CH_3COO)_2$	126–128	Orange	93	(11), *202, 282, 289, 349*
$Cp_2TiCl_2Al(Et)_2$ and related compounds	126–130	Blue	—	(8), *121, 128, 135–139, 158, 159, 273*
$[Cp_2TiBr]_2O$	—	—	—	(11), *140*
$Cp_2Ti(CO)_2$	90 (dec)	Red-brown	18	(11), *122, 133, 134*
Cp_2TiCl	—	Green	68	(8), *13, 89, 121, 127, 137, 140, 141, 142*
Cp_2TiBH_4	dec 150	Red-violet	83	(8), *154*
$CpTiCl_3$	208–211	Yellow	84	(11), *95, 144–146, 149, 151*; (5), *126*
$CpTiCl_2Br$	165–170 (dec)	Orange	66	(11), *145*
$CpTiBr_3$	174.5–175.5	Orange	25	(5), *126*
$CpTiI_3$	184–186	Red	97	(5), *126*
$(CpTiCl_2)_2O$	149–151	Yellow	91	(11), *144, 145, 148, 150, 152*
$(CpTiClO)_4$	285 (dec)	Yellow	—	(11), *150*
$(CpTiClO)_n$	—	—	78–92	(11), *145*
$CpTi(CH_3)_3$	dec >20	Yellow	77	(11), *121, 153*
$CpTi(OEt)_3$ and other alkoxy derivatives	(106–107/3)	Colorless	72	(4), *130, 131*

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references[a]
$CpTi(OC_4H_9)_2Cl$	(145–150/2–3)	Colorless	80	(2), *160–162*
$CpTi(OR)Cl_2$ (R = alkyl)	—	—	—	(11), *145*, *147*
$CpTi(OEt)$(8-hydroxyquinolinate)$_2$	158–159	Yellow	—	(11), *296*, *367*
$CpTiCl_2$	—	Blue	—	(8), *143*
$Cp(MeCp)TiCl_2$	—	—	—	(4), *145*; (12), *393*
$(MeCp)_2TiCl_2$	217–218 (dec)	Red	26	(4), *47*
$MeCpTi(OC_4H_9)_2Cl$	—	—	60	(2), *162*
$C_5(CH_3)_5TiCl_3$	—	Red-orange	20–30	(7), *81*
Cp_2ZrCl_2	244	Colorless	71–75	(4), *97*, *155*
Cp_2ZrBr_2	260	Colorless	30	(5), *13*, *127*
$Cp(C_5H_4)ZrCl$	~300	Colorless	—	(11), *156*
$Cp(C_5H_4SO_3H)ZrOSO_3H \cdot (CH_3CO)_2O$	—	—	—	(12), *97*
$CpZrCl_3$	—	—	—	(5), *157*
$CpZrCl$(acetylacetonate)$_2$	188–190	—	95	(11), *290*
$CpZr(CH_3COO)_3$	dec 170	—	65.7	(11), *367*
$CpZr(CH_3COO)$(acetylacetonate)$_2$	dec 128.5–131	—	70	(11), *367*
$(MeCp)_2ZrCl_2$	180–181	Colorless	38	(4), *47*
Cp_2HfCl_2	236	—	—	(4), *423*
Vanadium Group				
Cp_2V	167–168	Violet	47–80	(4), *36*, *164*; (5), *119*, *165*; (8), *89*; (2), *163*
Cp_2VCl_2 (also dibromide)	dec 250	Green	65	(4), *13*, *27*, *422*; (5) *13*, *127*

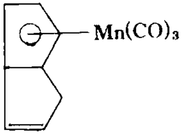
Cp_2VCl (also Br, I)	206–207	Blue	23.4	(4), *166*; (8), *167*
$Cp_2V\phi$	92	Black	50	(11), *168*
$Cp_2V(CH_2\phi)$ and related phenyl-substituted derivatives)	109	Green	—	(12), *167*
$CpVCl_3$ (also tribromide)	—	Dark green	42	(8), *166*
$CpVOCl_2$ (also dibromide)	—	—	73–75	(8, 11), *166*, *169*
$CpV(CO)_4$	138 (dec)	Orange	15–97	(11), *164*, *170*; (5), *119*
$K_2[CpV(CO)_3]$ (also Rb and Cs salts)	—	Yellow	68	(8), *164*
$CpV(CO)_2(C_4H_6)$	135–140 (dec)	Red	—	(11), *172*
$CpV(CO)_2(C_4H_{10})$	135–136 (dec)	Red	—	(11), *172*
$CpV(CO)_2(C_6H_8)$	98–100	Red	—	(11), *172*
$CpVC_7H_7$	dec 130	—	—	(11), *171*
$[CpV(CH_3S)_2]_2$	dec 200	Brown-black	59	(11), *353*
$[CpV(CF_3SC{=}CSCF_3)]_2$	Subl. 160/0.1	Green	50	(11), *354*
Cp_4Nb	—	Blue	9.3	(4), *55*
Cp_2NbCl_3	—	Brown	—	(4), *173*
Cp_2NbBr_3	dec 260	Brown	70	(4), *13*
$Cp_2Nb(OH)Cl_2$	—	Yellow	—	(11), *173*
$Cp_2Nb(OH)Br_2$	—	Orange-red	—	(11), *13*
$Cp_2Nb(Cl)BH_4$	—	Red-violet	—	(8), *80*
$CpNb(CO)_4$	Subl. 60/0.1	Orange	2–3	(4, 11), *80*
Cp_2TaCl_3	—	—	—	(4), *174*
Cp_2TaBr_3	280 (dec)	Rust	9.3–62	(4), *13*, *55*; (5), *13*
$CpTaH_2$	187–189 (dec)	Colorless	60	(4,8), *58*, *175*
Chromium Group				
Cp_2Cr	173	Scarlet	70–80	(4), *7*, *12*, *36*, *176*; (3), *43*; (5), *45*, *119*
Cp_2CrI	dec 150	Green	100	(8), *177*, *355*
$[Cp_2Cr][CpCr(CO)_3]$	190–193 (dec)	Brown	—	(11), *45*
$[Cp_2Cr][CpCrCl_3]$	—	—	—	(8), *358*

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references[a]
$CpCrX_2$ (X = Cl, Br, I)	—	Green or blue	—	(11), *358*
$CpCrC_6H_6$	227–229	Orange	—	(5), *178*
$CpCrC_7H_7$	230	Blue-green	—	(8, 3), *356*, *357*
$CpCrC_7H_6CH_3$	78	Black	—	(12), *179*
CpCrBr (acetylacetonate)	190 (dec)	Dark green	3	(5), *180*, *189*
$[CpCr(CO)_3]_2$	163–168 (dec)	Colorless	37	(4, 8), *170*; (11), *44*
$CpCr(CO)_3H$	dec 57–58	Yellow	45	(4), *45*, *190*
$[CpCr(CO)_3]_2Hg$	—	Yellow	40	(11), *44*, *170*
$[CpCr(CO)_4]BF_3$	—	—	—	(11), *181*
$CpCrC_5H_7(CO)_2$	74–75	Yellow	3.8	(11), *46*, *182*
$CpCr(CO)_2NO$	67–68	Orange-red	80	(11), *183*, *184*
$CpCr(NO)_2X$ (X = F, Cl, Br, I, SCN, CN)	—	—	—	(11), *185*
$CpCr(NO)_2R$ (R = CH_3, CH_2Cl, C_5H_5, C_2H_5, C_6H_5)	—	—	—	(11), *186*, *187*
$[CpCr(NO)_2CO]PF_6$	—	Olive	45	(11), *187*
$CpCr(CH_3S)_3CrCp$	(Subl. 180/0.2)	Purple	32	(11), *354*
$[CpCrO]_4$	74	Blue-violet	50	(8), *188*
Cp_4Mo	dec > 220	Red-violet	39	(4), *191*
Cp_2MoH_2	183–185	Yellow	50	(4, 8), *56*, *58*, *190*; (11), *192*
Cp_2MoCl_2	—	—	—	(4), *12*
$[Cp_2MoCl_2]_2PtCl_6$	—	—	—	(8), *12*
$[CpMo(CO)_3]_2$	(Subl. 150/0.1)	Red-violet	30	(3), *43*; (8), *193*; (4, 8), *170*
$CpMo(CO)_3H$	(Subl. 50/0.1)	Yellow	50–52	(4), *170*; (12), *44*, *58*
$CpMo(CO)_3X$ (X = Cl, Br, I)	—	—	—	(11), *186*

$CpMo(CO)_3R$ (R = Me, Et, *i*-Pr)	—	—	78–85	(11), *186, 193*
$CpMo(CO)_3CF_2CF_2H$	53–54	Orange-yellow	11	(11), *269, 362*
$CpMo(CO)_3(\sigma\text{-}CH_2CH{=}CH_2)$	dec 60	Yellow	40	(11), *361*
$[CpMo(CO)_3C_2H_4]PF_6$	dec 104	Yellow soln.	24	(11), *360, 361*
$[CpMo(CO)_4]PF_6$	—	—	—	(11), *363*
$CpMo(CO)_2C_7H_7$	230	Blue-green	—	(3), *356, 357*
$CpMo(CO)_2(\pi\text{-allyl})$	134 (dec)	Yellow	3	(UV light) *361*
$[CpMo(CO)C_6H_6]^+$	—	Red	19.1	(11), *364*
$[CpMo(CO)_2CH_3S]_2$	130 (dec)	Black	95	(11), *362*
$[CpMo(CH_3S)_2]_?$	(Subl. 170–85/0.1)	Brown	54	(11), *354*
$CpMoO_2Cl$	—	Yellow	3	(11), *361*
$[MeCpMo(CO)_3]_2$	146–147	—	4.2	(4, 7), *47*
$[RC_5H_4Mo(CO)_3]_2$ (R = alkyl)	—	Red or brown	20–70	(3), *51, 52*
$RC_5H_4Mo(CO)_3R'$ (R and R′ are alkyl radicals)	—	—	—	(11), *51*
$\phi_3P\text{-}C_5H_4Mo(CO)_3$	—	Yellow	60	(11), *359*
$[FluorMo(CO)_3]_2$	195–197 (dec)	—	10	(3), *50*
$Azulene[Mo(CO)_3]_2$	dec 150	Black	1	(3), *194*
$Cp(CO)_3Mo\text{-}W(CO)_3Cp$	—	—	—	(11) *51*
$[Cp_2W]_2PtCl_6$	—	—	—	(4), *12*
Cp_2WH_2	163–165	Yellow	—	(4, 7), *56, 58, 190*; (11), *192*
$Cp_2WH_2\cdot HCl$	—	—	—	(12), *56*
$[CpW(CO)_3]_2$	—	—	30	(3), *43*
$CpW(CO)_3H$	—	—	65.5–67	(11), *44, 45*
$CpW(CO)_3Me$	140 (dec)	Orange-red	80	(11), *45, 186*
$CpW(CO)_3Et$	—	Orange-red	75	(11), *186*
$CpW(CO)_3CF_2CF_2H$	65–65.5	—	8	(11), *362*
$[CpW(CO)_3C_2H_4]PF_6$	dec 120	Yellow soln.	20	(11), *360*
$CpW(CO)_2NO$	105–107	Orange-red	—	(11), *183, 186*
$[CpW(CO)_2CH_3S]_2$	dec 187	Dark red	63	(11), *362*
$[CpW(CO)(C_6H_6)]^+$	—	—	6.6	(11), *364*

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references[a]
Manganese Group				
Cp_2Mn	172–173	Brown	45–75	(4), *36*, *108*, *196–198*; (5), *203*, *204*
$CpMn(CO)_3$	76.8–77.1	Yellow	40–80	(6, 11), *74–76*, *108*, *157*, *241*, *404–408*, *410–419*
$CpMn(CO)_2C_2H_4$	116–118 (dec)	Orange-red	—	(11), *365*
$CpMn(CO)_2$(1,3-cyclohexadiene)	80–81	Brown-yellow	—	(11), *366*
$[CpMn(CO)_2]_2$(1,3-cyclohexadiene)	dec 120	Yellow	19	(11), *366*
$[CpMn(CO)_2NO]_2PtCl_6$	dec 165–175	—	30	(11), *74*
$CpMn(CO)_2NC_5H_5$	114	Yellow-brown	53	(11), *205*
$CpMn(CO)_2P\phi_3$	216–218	Yellow	25	(11), *368*
$CpMn(CO)_2(CF_3C{\equiv}CCF_3)$	68	Orange	50	(11), *367*
$CpMn(\pi\text{-diphenyl})$	73–75	—	—	(4), *195*
$Cp_3Mn_2(NO)_3$	dec > 100	Purple-black	30	(11), *185*
$[CpMn(NO)S_2]_x$	—	Brown-black	40	(11), *206*
$(MeCp)_2Mn$	61–63	Brown	66	(4), *37*, *47*
$MeCpMn(CO)_3$	70	Yellow	1.7–20	(6, 11), *47*, *199–201* ,*409*
$MeCpMn(CO)_2NC_5H_5$	75	Yellow-brown	60	(11), *205*
$MeCpMn(CO)_2$piperidine	—	Orange-red	—	(11), *369*
	—	—	40	(9), *82*, *83*, *208*

FluorMn$(CO)_3$	—	—	—	(11), *75*
(1-COOH)(2-CH_2COOH)$C_5H_3Mn(CO)_3$	—	—	—	(7) *82, 83*
$\phi_4(OH)C_5Mn(CO)_3$	180 (dec)	—	53	(3), *49*
$[Cp_2Tc]_2$	155	Golden-yellow	—	(4), *209*
$CpTc(CO)_3$	—	—	—	(8), *143*
Cp_2ReH	161–162	Yellow	20	(4), *60, 210*
$Cp_2ReH \cdot HCl$	—	Colorless	100	(12), *60, 210*
$CpRe(CO)_3$	111–114	Yellow	16	(3, 4, 11), *77, 211, 294*
$CpReC_5H_6(CO)_2$	111–112	Yellow	45–55	(11), *211, 212*
$CpReC_5H_8(CO)_2$	—	—	—	(12), *211*
Iron Group				
Cp_2Fe	173–174	Orange	85–90	(4), *36, 174, 200, 217–219*; (2), *18, 19, 33, 36, 38–40, 105, 125, 214–216, 224–229*; (3), *42, 74*; (1), *2, 213*; (5), *42, 220, 221*; (9) *48*
$[Cp_2Fe]^+$	—	Purple soln.	—	(8), *86–88, 222, 223*
$Cp_2Fe^{55,59}$	—	—	—	(10), *230*
$[Cp_2FeH]AlCl_3$	—	—	—	(12), *348*
CpFeFluor	74–76	Red-violet	0.5–8.8	(4, 5), *231, 232*
$CpFeC_6H_7$	—	—	—	(12), *233–235*
$CpFeC_5H_4C_6H_5$	109–110	Orange	—	(4), *68*
$CpFeC_5H_4CH_2C_6H_5$	76	—	—	(3), *48*
$CpFeC_5H_3(C_6H_5)_2$	107	Orange	—	(3), *48*
$CpFeC_5H_3(CH_3)_2$	—	Ivory	—	(11), *207*
$CpFeC_5H_4N{=}NR$ (R = Me, ϕ)	—	—	—	(4), *236*
$[CpFe(CO)_2]_2$	194	Red-violet	194	(3), *12, 48, 74, 170, 237–241*
$CpFe(CO)_2H$	−5	Yellow	—	(11), *192*
$CpFe(CO)_2Cl$	dec 87	Red	42–75	(8), *74, 242*
$CpFe(CO)_2Br$	98–102 (dec)	Red-brown	65	(8), *48*
$CpFe(CO)_2I$	119–120 (dec)	Black	65–72	(8), *170, 185*; (11), *48*

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references[a]
$CpFe(CO)_2CN$	dec 120	Yellow	46	(11), *74*
$[CpFe(CO)_2]_2Hg$	—	Gold-yellow	—	(11), *239*
$[CpFe(CO)_2C_2H_4]PF_6$	dec 165	Yellow	60	(11), *344*, *360*, *370*
$CpFe(CO)_2Et$	—	—	60	(11), *186*, *344*
$CpFe(CO)_2(\sigma\text{-}Cp)$	46	Red	15	(4), *243*; (11), *187*; (6), *48*
$CpFe(CO)_2\phi$	—	—	—	(11), *186*
$CpFe(CO)_2(C_5H_4C_6H_5)$	—	—	—	(6), *48*
$CpFe(CO)_2(CH_2CH{=}CH_2)$ and related compounds	—	—	—	(11), *377*, *379*, *380*
$CpFe(CO)_2Si(CH_3)_3$	70	Orange	42	(11), *345*
$CpFe(CO)_2(CF{=}CFCF_3)$	69.5–70.5	Orange	—	(11), *269*, *346*, *347*
$[CpFe(CO)_2]_2R$ [R = $(CH_2)_n$, $CH_2C{\equiv}CCH_2$, C_3N_3Cl]	—	Orange	—	(11), *383*
$CpFe(CO)_2RCO)$ (R = alkyl)	—	—	14–63	(11), *371*, *372*
$CpFe(CO)_2(C_6H_5COS)$	125–126	Orange	26	(11), *371*
$[CpFe(CO)CH_3S]_2$	104–105	Brown-black	—	(11), *373*
$CpFe(CO)(I)(CNC_6H_5)$	89	Black	—	(11), *244*
$Cp(CO)Fe(CO)_2NiCp$	132	Brown	—	(11), *245*
$Cp(CO)_2FeMo(CO)_3Cp$	209	Red-violet	—	(11), *246*
$CpFe(CO)_2Mn(CO)_5$	76	Red	—	(11), *246*
$Cp(CO)Fe(CO)_2Co(CO)_3$	52–53	Red	—	(11), *382*
$CpFe(CO)_2Sn\phi_3$	139–141	Orange	39	(11), *378*, *381*
$CpFe(CO)_2SnCl_3$	150 (dec)	Red-brown	85	(11), *381*
$CpFe(CO)_2P\phi_3Cl \cdot 3H_2O$	—	Yellow	—	(11), *374*
$[CpFe(CO)_3]^+$	3	Yellow soln.	37–100	(11), *360*, *374–376*

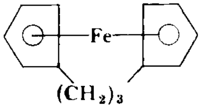
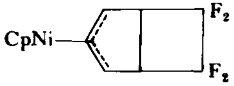
$(CpFeC_6H_6)B\phi_4$	dec 250–251	Yellow	60	(11), *297*
$(MeCp)_2Fe$	37–39	Orange	65	(4), *47*; (3), *47*
$(\phi Cp)_2Fe$	154	Orange	—	(4), *68*
$(1,3\text{-}\phi_2C_5H_3)_2Fe$	220–222	Orange	—	(5), *68*; (3), *48*
$(1,2,4\text{-}\phi_3C_5H_2)_2Fe$	227–228	Orange	—	(4), *68*
$(\phi_4C_5H)_2Fe$	322	Red	21 based on C_5H_6	(4), *88*
$(\phi CH_2C_5H_4)_2Fe$	102	—	—	(4), *48*
$(\phi_2CHC_5H_4)_2Fe$	162–163	Yellow	—	(4), *62*, *68*, *248*
$(\phi_3CC_5H_4)_2Fe$	174–175	Orange	—	(4), *62*
$(MeCHC_5H_4)_2Fe$	(91/0.025)	Orange-red	74	(4), *62*, *247*, *248*
$[(Me)_2(Et)CC_5H_4]_2Fe$	—	—	—	(5), *404*
$(Me_3CC_5H_4)_2Fe$	29–30	Orange	94	(4), *63*, *110*, *247*, *248*
$[(Me)_2\phi CC_5H_4]_2Fe$	133.5–135	—	90	(4), *62*, *63*, *247*, *248*
$(CH_2{=}CCH_3C_5H_4)_2Fe$	58–59	Orange-red	65	(4), *63*, *247*
$(RC_5H_4)_2Fe$ (R = carbocyclic radicals)	—	—	—	(4), *61*, *247*
 (and related compounds)	106–107	Orange	2.5	(4), *249*, *250*
$[(RC_6H_4CH_2)_2C_5H_3]_2Fe$ (R = H, *o*-Cl, *p*-Cl, *p*-CH_3, *p*-F, *m*-Br, *p*-Br)	—	—	10–30	(4), *251*
$(RN{=}NC_5H_4)_2Fe$ (R = $COOCH_3$, COOEt, $COOCH_2C_6H_5$)	—	—	—	(4), *236*
$[(CH_3C_5H_3O^{\ominus})_2Fe]Na_2$	—	—	—	(4), *65*
$(Ind)_2Fe$	184–185	Violet-black	11	(5), *66*, *280*, *424*
$(Tetrahydroind)_2Fe$	18.5–19	Orange	—	(12), *253*
$(RInd)_2Fe$ (R = Me, Et, allyl, butyl, ϕ, benzyl)	—	—	—	(4), *293*, *298*
Bis(3*a*,4-dihydroazulenyl)iron	68	Red	17	(4), *247*

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references[a]
[EtCpFe(CO)$_2$]$_2$	61–62	Purple	1.6	(3), *252*
ϕCpFe(CO)$_2$Br	82	Red	83	(8), *48*
ϕCpFe(CO)$_2$(σ-Cp)	—	Red oil	—	(6), *48*
[IndFe(CO)$_2$]$_2$	—	—	20	(3), *252*
[TetrahydroindFe(CO)$_2$]$_2$	—	—	39 on spiran	(3), *252*
(CH$_3$SiC$_5$H$_4$)$_2$Fe and related silyl and siloxyferrocenes)	—	—	50	(4), *254*, *255*, *425*
Cp$_2$Ru	199–200	Pale yellow	43–52	(4), *256*, *257*; (5), *118*
[CpRu(CO)$_2$]$_2$	dec 185	Orange-red	60	(6), *72*
CpRu(CO)$_2$H	—	Colorless liquid	—	(11), *258*
CpRu(CO)$_2$I	103–105	Orange	—	(11), *258*
CpRu(CO)$_2$Me also Et	39–40	Colorless	—	(11), *258*
(Ind)$_2$Ru	199	Orange	61	(5), *259*
Cp$_2$Os	229–230	Colorless	22–23	(4), *256*, *260*
[Cp$_2$OsOH]PF$_6$	185 (dec)	Red-brown	80	(8), *260*
[CpOs(CO)$_2$]$_2$	198	Yellow	1.8	(6), *261*
CpOs(CO)$_2$Br	120–121	Yellow	—	(8), *261*
(Ind)$_2$Os	214	Yellow	2.3	(5), *69*
Cobalt Group				
Cp$_2$Co	173–174	Purple	75–96	(4), *9*, *36*, *53*; (3), *42*; (2), *36*, *63*
[Cp$_2$Co]$^+$	—	Yellow soln.	75–100	(7), *9*, *85*, *228*, *262*, *263*
CpCoC$_5$H$_6$	98–99	Red	85	(12), *89*, *90*, *233*
CpCoC$_5$H$_5$CH$_3$	—	—	30	(12), *264*
CpCoC$_5$H$_5$C$_6$H$_5$	128–129	Red	80	(12), *349*

$CpCoC_5H_5COC_6H_5$	125.5–127	Red	80	(12), *349*
$CpCoC_5H_5CCl_3$	78–80	Orange-red	45	(12), *264*, *265*
$CpCoC_5H_5CHCl_2$	—	—	—	(11), *264*
$CpCoC_5H_5CF_3$	−10	Red	—	(12), *264*, *384*
$CpCoC_5H_5CF_2CF_2C_5H_5CoCp$	dec 140	Red-brown	—	(12), *384*, *385*
$CpCoC_5H_5C_5H_4C_5H_5CoCp$	dec 100	Red	90	(12), *266*
CpCo(1,3-cyclohexadiene) and related compounds	—	—	—	(11), *394*, *395*
CpCo[tetra(trifluoromethyl)cyclobutadiene]	264	Orange-yellow	—	(11), *396*, *397*
CpCo(tetraphenylcyclobutadiene)	—	—	—	(11), *396*, *397*
$CpCo(\pi\text{-}R)$ ($R = C_8H_8$, C_8H_{12}, $\phi C{\equiv}C\phi$)	—	—	—	(11), *390–392*
$(CpCoC_6H_6)(PF_6)_2$	—	Yellow	40	(11), *386*
$CpCo(CO)_2$	−22	Red	80	(3), *74*; (11), *170*, *267*, *268*
$CpCo(CO)CF_3I$	dec 145	Black	1	(11), *394*
$CpCo(CO)(C_2F_5)I$	138	Black	—	(11), *394*
$CpCo(CO)(C_3F_7)I$	120	Black	—	(11), *269*, *270*
$CpCo(CO)(CF_2CF_2CF_2CF_2)$	106–107	Pale yellow	—	(11), *388*
$[CpCoC_3H_4(CO)]PF_6$	dec 110	Green-yellow	36	(11), *389*
$[CpCo(CH_3S)]_2$	—	Black	—	(11), *373*
$CpCoCF_3SC{=}CSCF_3$	150	Violet	76	(11), *354*
CpCo(tetramethylcyclopentadienone)	—	—	—	(7), *387*
$MeCpCoC_5H_5Me$	—	—	—	(11), *264*
$MeCpCo(CO)_2$	—	Red	65	(11), *267*
$(Ind)_2Co$	178–181	Black	—	(4, 5), *271*
$[(Ind)_2Co]^+$	—	Yellow	—	(5), *271*, *272*
$[(C_5H_5COOH)_2CO]Br$	—	—	—	(8), *349*
$[(CH_3C_5H_3OH)_2Co]Cr(NH_3)_2(SCN)_4$	154–157	Orange-brown	—	(4), *65*
Cp_2Rh^{105}	—	—	—	(10), *273*
Cp_2RhX ($C = Cl^-$, OH^-, Br_3^-, $[Cr(CNS)_4NH_3]^-$)	—	—	—	(5), *274*
$CpRhC_5H_6$	118–120	Orange-yellow	26.8	(6), *275*, *276*

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references[a]
$CpRh(C_2H_4)_2$	72–73	Yellow	47	(4), *277*
$CpRh$(1,5-cyclooctadiene)	108–108.5	Yellow	—	(4), *278*, *279*
$CpRh$(cyclooctatetraene)	106	Yellow	11	(11), *280*
$[CpRh(CO)_2]_2$	−11	Orange	26.8	(6), *71*; (8), *398*
$(Cp_2Ir)Cr(CNS)_4NH_3$	—	—	—	(5), *274*
$CpIrC_5H_6$	130–132	Yellow	1	(4), *275*
$CpIr(CO)_2$	—	Yellow liquid	95	(6), *70*
Nickel Group				
Cp_2Ni	173–174 (dec)	Green	42–96	(4), *8*, *15*, *53*, *217*, *281*, *283*; (2), *34*, *36*, *125*, *163*; (3), *42*, *284*
$(Cp_2Ni)^+$	—	Yellow soln.	—	(8), *8*, *127*, *142*
$CpNiC_3H_7$	73–75	Red-violet	30	(4), *285*, *304*
$CpNiC_5H_7$	41–42	Red	18	(3), *286*, *302*, *305*, *306*
$CpNiNO$	(49/27)	Red	45–90	(3, 11), *74*, *183*, *299–301*
$(CpNiCO)_2$	146–147 (dec)	Green	50–74	(11), *287*, *288*, *307*, *309*
$Cp_3Ni_3(CO)_2$	dec 200	Dark green	40.5–82	(11), *288*, *307*, *309*, *311*
$CpNi(CO)I$	dec 20	Violet	28	(8), *309*
$(CpNi)_2C_2H_2$ and related compounds of substituted acetylenes	143–144	Green	48	(11), *303*, *307*, *310*, *396*, *399*
$CpNi$[2,3-bis(methoxycarbonyl)-2π,5-norbornadien-7-yl]	84	Red	—	(12), *400*
	93–94	Red	5.7	(12), *401*

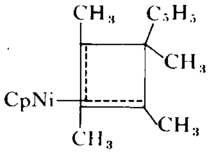
$CpNiC_5H_4N{=}NC_6H_5$	118–119	Purple	—	(11), *402*
$[CpNi(CNC_6H_5)]_2$	91	Red	—	(11), *244*
$CpNi(P\phi_3)Cl$	dec 140	Red	—	(11), *420*
	—	—	—	(4), *277*, *308*
$(MeCp)_2Ni$	39–40 (dec)	Green	36	(4), *47*
$MeCpNiC_5H_6CH_3$	(30–35/0.1)	Red oil	11	(3), *312*
$(Ind)_2Ni$	—	Red-brown	—	(4), *271*
$[CpPdCl]_2$	—	Red	100	(2), *313*
$CpPdC_3H_5$	63–64	Red	—	(4), *304*, *306*, *314*
$CpPdC_6H_9$	69	Red	60	(4), *306*, *315*
$CpPdC_7H_7$	dec 25	Red-violet	26	(4), *312*
$CpPdC_{10}H_{12}OCH_3$	(Subl. 80/1)	Orange	40	(4), *277*
$CpPd\text{-}\pi\text{-}[(CH_3)_2CCHCHC(CH_3)_2OCH_3]$	57–58	Red	—	(4), *403*
$RCpPdC_3H_5$ ($R = CH_3, C_2H_5,$ $n\text{-}C_3H_7, C_3H_5$)	—	—	—	(4), *314*
$MeCpPdC_6H_9$	1–3	Red	37	(4), *312*, *315*
$CpPt(CH_3)_3$	65	Colorless	—	(4), *316*
$(CpPtCO)_2$	103 (dec)	Red	58	(4), *73*
$CpPt(CO)I$	55 (dec)	Black	45	(11), *73*
Copper Group				
$CpCu \cdot P(Et)_3$	127–128	Colorless	60	(2), *32*, *317*
Zinc Group				
Cp_2Zn	dec 100–130	Colorless	14–60	(4), *54*, *318*, *319*
Cp_4Zn	—	—	41	(5), *320*
$CpZnEt$	69–70	Colorless	33–50	(5), *321*, *322*
$CpZn\phi$	74–76	Colorless	9–50	(5), *322*

TABLE I—*continued*

Compound	Melting point (boiling point/mm) (°C)	Color	Yield (%)	Methods of synthesis and references^a
CpZn(*t*-butyl)	—	Colorless	8	(5), *322*
CpZnCl	—	Colorless	—	(5), *323*
Cp$_2$Hg	83–85 (dec)	Yellow	20	(4), *32*; (2), *224*
CpHgCl	—	—	—	(2), *224*
IndHgBr	118	—	9	(4), *324*
Boron Group				
Cp$_3$B	138–139	Colorless	—	(4), *324*; (5), *290*
CpBF$_2$	38–41	Colorless	—	(5), *290*
Cp$_3$Al	50–60	Gray	95.6	(From Cp$_2$Hg), *325*, *326*
CpAl(Et)$_2$	(47.5/0.005)	—	61.5	(4), *327*
Na[CpAl(Et)$_3$]	—	—	—	(4), *328*
CpIn	dec 110	Pale yellow	55–65	(4), *329*, *330*; (1), *21*
Cp$_3$In	dec 130	Golden yellow	—	(4), *329*
MeCp$_3$In	60 (dec)	Yellow	—	(1), *21*
CpTl	dec 230	Colorless	61–95	(2), *27*, *29*, *331*, *332*
MeCpTl	88–89	Yellow	76	(2), *47*, *333*; (1), *21*
Silicon Group				
CpSi(Me)$_3$	(73/25)	Colorless	40–45	(5), *334*; (4), *32*, *291*
CpSiCl$_3$	(52–55/10)	Colorless	40	(4), *335*, *336*; (2), *292*
FluorSi(Me)$_2$	178–179	Colorless	—	(4), *337*
FluorSi(Me)$_3$	97.5	Colorless	—	(4), *337*
[FluorSi(Me)$_2$]$_2$O	216–217	Colorless	—	(4), *337*
C$_{13}$H$_8$[Si(Me)$_3$]$_2$	110	Colorless	—	(2), *337*
CpGeCl$_3$	(76/10)	Colorless	—	(2), *295*
CpGe(Me)$_3$	(32/9)	Colorless	62	(11), *295*
CpGe(Et)$_3$	(105/16)	Colorless	—	(5), *295*, *338*
Ce(CpC$_4$H$_9$)$_3$	(109/0.4)	Colorless	—	(5), *338*

$\mathrm{CpGe}\phi_3$	176–177	Colorless	—	(5), *338*
$\mathrm{Ind_4Ge}$	196–198	Colorless	—	(5), *338*
$\mathrm{Ind_2Ge}(\phi)_2$	144–145	Colorless	—	(5), *338*
$\mathrm{IndGe(Et)_3}$	(161/4)	Colorless	—	(5), *338*
$\mathrm{IndGe}(\phi)_3$	126	Colorless	—	(5), *338*
$\mathrm{FluorGe(Et)_3}$	(165/0.5)	Colorless	—	(5), *338*
$\mathrm{FluorGe}(\phi)_3$	214	Colorless	—	(5), *338*
$\mathrm{Cp_2Sn}$	104–105	Colorless	50–60	(4), *54*
$\mathrm{Cp_4Sn}$	71–73	Yellow	41.5	(5), *320*
$\mathrm{Cp_3Sn}\phi$	64–65	Yellow	40	(5), *320*
$\mathrm{Cp_2Sn}(\phi)_2$	105–106	Yellow	70	(5), *320*
$\mathrm{Ind_4Sn}$	215	Colorless	48.4	(4), *339*, *340*
$\mathrm{Ind_2Sn}(\phi)_2$	116–117	Colorless	40	(4), *339*, *340*; (5), *320*
$\mathrm{IndSn}(\phi)_3$	128	Colorless	68	(4), *339*, *340*; (5), *320*
$\mathrm{Fluor_4Sn}$	290 sinter dec 310	Colorless	41	(4), *339*, *340*
$\mathrm{Fluor_3Sn}\phi$	262 (dec)	Colorless	50	(4), *339*, *340*
$\mathrm{Fluor_2Sn}(\phi)_2$	179	Colorless	60	(4), *339*, *340*
$\mathrm{Fluor_2Sn}(\phi)\mathrm{Cl}$	143	Colorless	—	(11), *339*, *340*
$\mathrm{FluorSn}(\phi)_3$	129–130	Colorless	67.7	(4), *339*, *340*
$\mathrm{FluorSn}(\phi)\mathrm{Cl_2}$	140–141	Colorless	—	(11), *339*, *340*
$\text{2-(Me)}_2\text{N-C}_{13}\text{H}_8\text{Sn}(\phi)_3$	151	Colorless	60	(4), *339*, *340*
$\mathrm{Cp_2Pb}$	132–135	Yellow	25	(4), *15*, *281*, *341*
$\mathrm{IndPb}(\phi)_3$	122	—	75	(4), *324*
$\mathrm{FluorPb}(\phi)_3$	118–120	—	75	(4), *324*
Arsenic Group				
CpAs	—	Black	—	(4), *342*
CpSb	—	Red	50–60	(4), *342*, *343*
$\mathrm{Cp_4Sb_2}$	—	Red-violet	83	(4), *343*
$\mathrm{Cp_3Bi}$	dec 75	Red-orange (Black form, stable > 15°)	50–60	(4), *342*, *343*
$\mathrm{MeCp_3Bi}$	—	—	68	(4), *343*

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[a] Roman numbers in parentheses indicate Method; italic numbers indicate references.

Melting points are given for solids. For liquids the boiling point and pressure of measurement are enclosed in parentheses and are listed in the melting point column. When the compound melts with decomposition, (dec) is placed after the melting point. When the compound decomposes without melting, dec is placed before the decomposition point. The numbers enclosed in parentheses in the final column refer to methods of synthesis in the text.

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