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PENTAMETHYLCYCLOPENTADIENYL METAL COMPLEXES: AN ENTRY TO METAL CARBONYL DERIVATIVES WITH METAL—METAL MULTIPLE BONDING *

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Since the discovery of ferrocene [1,2] in 1952, the chemistry of cyclopentadienyl metal complexes has developed into one of the most important areas of transition metal organometallic chemistry [3]. The cyclopentadienyl ligand was found to be the unsaturated hydrocarbon ligand forming the most robust bonds with transition metals in most cases, thereby contributing to the considerable scope of this area of chemistry.

The extensive series of known cyclopentadienylmetal derivatives made of interest the corresponding chemistry of metal derivatives of cyclopentadienyl rings in which one or more of the C_5H_5 hydrogen atoms were substituted by other groups. The discovery of electrophilic substitution and other characteristic reactions of aromatic rings in cyclopentadienylmetal derivatives [4], such as ferrocene and $C_5H_5Mn(CO)_3$, provided one synthetic approach to substituted cyclopentadienylmetal derivatives. Alternatively, methylcyclopentadienylmetal derivatives could be prepared from the commercially available methylcyclopentadiene [5] by synthetic methods completely analogous to those used for preparing unsubstituted cyclopentadienylmetal derivatives from unsubstituted cyclopentadiene.

These approaches to the syntheses of metal derivatives of substituted cyclopentadienyl rings still left unexplored the synthesis of metal derivatives of cyclopentadienyl rings where all five hydrogens have been substituted with other groups. Such compounds were of particular interest since substitution of all five hydrogen atoms in a cyclopentadienyl ring would be expected to have the most profound effect on the properties of the resulting metal complexes. Known cyclopentadienes or cyclopentadienides of the general type R_5C_5 in which all five hydrogens are replaced by other groups included pentachlorocyclopentadiene [6], pentacyanocyclopentadienide [7], penta(methoxycarbonyl)cyclopentadienide [8], and pentamethylcyclopentadiene [9].

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A pentahapto [10] bond between the cyclopentadienyl ring and a transition metal contains several components [11]: (1) A σ-bond resulting in the donation of an electron pair from the filled cyclopentadienyl ring A orbitals with no nodes to an empty metal orbital. (2) Two orthogonal π-bonds resulting in the donation of electron pairs from the two filled orthogonal cyclopentadienyl ring E_1 orbitals into empty metal orbitals of appropriate symmetry. (3) Up to two orthogonal δ-bonds resulting in the back donation of electrons from metal orbitals of appropriate symmetry into the two orthogonal empty cyclopentadienyl ring E_2 orbitals. Complete substitution of cyclopentadienyl hydrogens with electronegative groups such as cyano and alkoxycarbonyl should lead to removal of electron density from the filled ring A and E_1 orbitals to the extent that stable pentahapto metal—ring bonds are no longer possible. In this connection the reaction between ferrous chloride and pentacyanocyclopentadienide was found [7] to give not decacyanoferrocene with pentahapto ring—metal bonds but instead a very air-sensitive ionic iron(II) pentacyanocyclopentadienide. Furthermore, attempted reactions [12] of lithium pentachlorocyclopentadienide [6] with anhydrous iron halides did not give decachloroferrocene. However, the recent syntheses of the very stable pentahapto pentachlorocyclopentadienyl derivatives $(C_5Cl_5)_2Fe$ [13] and $C_5Cl_5Mn(CO)_3$ [14] by other methods suggests that the failure to prepare $(C_5Cl_5)_2Fe$ from lithium pentachlorocyclopentadienide probably arose from inhibition of the reactivity of the pentachlorocyclopentadienide rather than instability of the pentachlorocyclopentadienyl—metal bond.

These considerations made pentamethylcyclopentadiene the most attractive pentasubstituted cyclopentadiene available in 1962 to use for the syntheses of transition metal complexes in order to evaluate the effects of complete substitution of the hydrogen atoms on the resulting chemistry. The electron-releasing effects of the five methyl groups should strengthen the metal—ring bond by increasing the electron density and hence the effective "basicity" of the filled ring A and E_1 orbitals. Furthermore, it appeared possible that the range of pentamethylcyclopentadienylmetal derivatives could even be more extensive than the already numerous unsubstituted cyclopentadienyl metal derivatives since the increase in stability of the metal derivatives of hexamethylbenzene relative to unsubstituted benzene had been shown to make possible the preparation of certain hexamethylbenzene derivatives [15] by methods which did not work for the corresponding unsubstituted benzene derivatives. Also of interest was the report in 1962 [16] of the first pentamethylcyclopentadienylmetal derivative, $(CH_3)_5C_5TiCl_3$, which, however, was not prepared by reactions between appropriate pentamethylcyclopentadiene and titanium chloride derivatives, but instead by rather unusual reactions between titanium tetrachloride and various simple hydrocarbons such as butene-1, butene-2, isobutene, pentene, diisobutene, or tetrapropylene. This unprecedented preparative method uses the transition metal to form the pentamethylcyclopentadienyl ring system

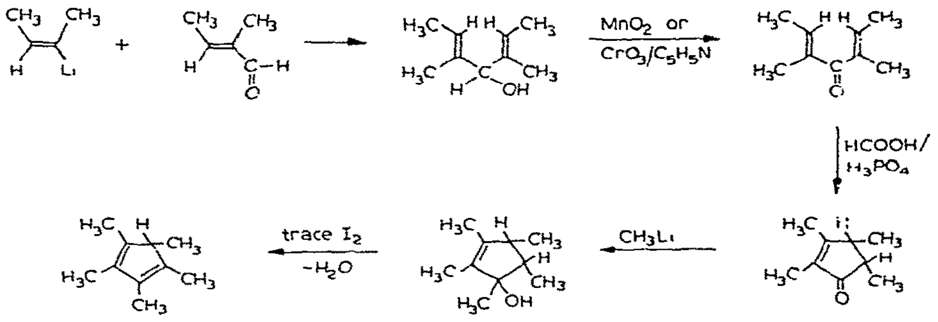


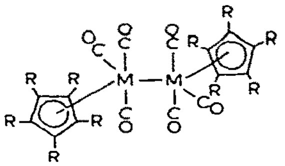
Fig. 1. Preparation of pentamethylcyclopentadiene (ref. 9).

from appropriate hydrocarbon raw materials.

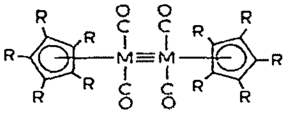
Our approach in 1962 at the Mellon Institute was to prepare a supply of pentamethylcyclopentadiene by the reported method (Fig. 1) [9] and to explore its reactions with various transition metal systems. In this original work we showed that the previously reported [16] $(CH_3)_5C_5TiCl_3$ could also be obtained from pentamethylcyclopentadiene by more rational and conventional methods. Furthermore, pentacarbonyliron was found to react with pentamethylcyclopentadiene to give $[(CH_3)_5C_5Fe(CO)_2]_2$, apparently completely analogous to $[C_5H_5Fe(CO)_2]_2$ [17,18], from unsubstituted cyclopentadiene. Octacarbonyldicobalt was found to react with pentamethylcyclopentadiene to give $(CH_3)_5C_5Co(CO)_2$ chemically completely analogous to the known $C_5H_5Co(CO)_2$ [17]. However, $(CH_3)_5C_5Co(CO)_2$ was a crystalline solid at room temperature in contrast to the liquid $C_5H_5Co(CO)_2$. The product from hexacarbonylmolybdenum and pentamethylcyclopentadiene did not appear to be analogous to $[C_5H_5Mo(CO)_3]_2$ [19]. Its analyses suggested $[(CH_3)_5C_5Mo(CO)_2]_2$, but in 1962 we did not really believe this formula and felt that there might be difficulties with the analyses or in obtaining a completely pure product. Such difficulties as well as the effort required to prepare sufficient pentamethylcyclopentadiene by the method shown in Fig. 1 to pursue this chemistry to the extent that we wished prevented us from publishing this work at that time.

After these initial but then unpublished studies, the area of pentamethylcyclopentadienyl metal chemistry lay essentially untouched until 1966, when we resurrected pentamethylcyclopentadienyl chemistry and prepared some more pentamethylcyclopentadiene by the method shown in Fig. 1 to continue these studies. At that time we prepared the additional metal carbonyl derivatives $(CH_3)_5C_5Re(CO)_3$ and $(CH_3)_5C_5Mo(CO)_3CH_3$ as well as the ferrocene $[(CH_3)_5]_2Fe$. More significantly, we confirmed the stoichiometry of the molybdenum carbonyl derivative as $[(CH_3)_5C_5Mo(CO)_2]_2$ rather than the expected $[(CH_3)_5C_5Mo(CO)_3]_2$. The seven pentamethylcyclopentadienylmetal derivatives which we had prepared by then were published [20].

The unusual stoichiometry of the pentamethylcyclopentadienylmolybdenum carbonyl $[(CH_3)_5C_5Mo(CO)_2]_2$ raised some interesting questions. At that time, the stoichiometry of the cyclopentadienylmetal carbonyls, except for the trimetallic $(C_5H_5)_3Ni_3(CO)_2$, appeared to be governed by the need for the metal atoms to attain the favored rare gas electronic configuration. A cyclopentadienylmolybdenum carbonyl derivative of the type $[R_5C_5Mo(CO)_3]_2$, and structure I (M = Mo) with a molybdenum—molybdenum bond, which is well known for the unsubstituted cyclopentadienyl group [21], would have the favored rare gas configuration for each molybdenum atom. However, a compound of stoichiometry $[R_5C_5Mo(CO)_2]_2$ with one less carbonyl group per metal atom requires structure II (M = Mo) with a molybdenum—molybdenum triple bond to give each molybdenum atom the favored rare gas configuration. Such metal—metal multiple bonding had not been demonstrated at that time for metal carbonyl derivatives. However, a related rhenium—rhenium quadruple bond had been indicated in $Re_2Cl_8^{2-}$ by X-ray crystallography [22]. Other metal—metal multiple bonds appeared to be present in related derivatives of other metals including chromium, molybdenum, and tungsten [23].



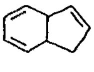
(I)



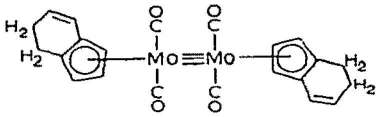
(II)

The chemistry of $[(CH_3)_5C_5Mo(CO)_2]_2$ (II: R = CH_3, M = Mo) was of considerable interest. The relative inertness of cyclopentadienyl and carbonyl groups towards many types of chemical reactions suggested that much of its chemistry might reflect reactions of the apparent molybdenum—molybdenum triple bond. However, the difficulty of preparing large quantities of pentamethylcyclopentadiene by the method shown in Fig. 1 discouraged our efforts to study the chemistry of $[(CH_3)_5C_5Mo(CO)_2]_2$ (II: R = CH_3, M = Mo) in more detail at that time.

In 1967 I made one other observation relevant to the chemistry of cyclopentadienylmetal carbonyl derivatives with apparent metal—metal triple bonds. Back in graduate school at Harvard around 1959 in the "dark ages" of olefin metal carbonyl chemistry, I had prepared some 8,9-dihydroindene (III). This hydrocarbon was found to react with molybdenum hexacarbonyl under relatively vigorous conditions to form a volatile dark red metal carbonyl derivative which was formulated in 1960 as a cyclononatetraenemolybdenum tricarbonyl, of stoichiometry $C_9H_{10}Mo(CO)_3$ [24]. In 1966 I began a detailed investigation of the mass spectra of transition metal organometallic derivatives [25]. During the course of this investigation the mass spectrum of this alleged $C_9H_{10}Mo(CO)_3$ was found to be inconsistent with this formulation. This prompted a thorough reinvestigation of this molybdenum complex, and eventually led to its reformulation as $[C_9H_9Mo(CO)_2]_2$, structure IV, with an apparent metal—metal triple bond similar to that in $[(CH_3)_5C_5Mo(CO)_2]_2$ (II: R = CH_3, M = Mo) [26]. This work indicated that even a disubstituted cyclopentadienyl ring could give a metal—metal triple bonded $[R_5C_5Mo(CO)_2]_2$ complex under appropriate conditions.



(III)



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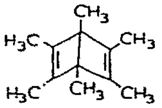


(V)

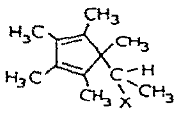
The next major breakthrough in pentamethylcyclopentadienylmetal chemistry came from the discovery by Maitlis and co-workers at McMaster University of simple methods for converting hexamethylbicyclo-[2,2,0]-hexadiene (V: colloquially known as "hexamethyl-Dewar benzene") to certain pentamethylcyclopentadienyl transition metal derivatives. A facile one-step good yield preparation of hexamethylbicyclo-[2,2,0]-hexadiene by the aluminium chloride catalyzed trimerization of dimethylacetylene had been discovered only a short time earlier [27].

In 1967, Booth et al. [28] first reported the reaction of hexamethylbicyclo-[2,2,0]-hexadiene (V) with hydrated rhodium trichloride in methanol to give a dark red product which they formulated as the hexamethylbenzene complex $[(CH_3)_6C_6RhCl_2]Cl_4$. Very shortly thereafter Kang and Maitlis [29] reported a much more extensive study of the same reaction which provided conclusive evidence that this dark red product was not a hexamethylbenzene complex but instead the pentamethylcyclopentadienyl rhodium derivative $[(CH_3)_5C_5RhCl_2]_2$. This discovery made pentamethylcyclopentadienylrhodium derivatives temporarily more readily accessible than any other type of pentamethylcyclopentadienylmetal derivative, even compounds containing abundant metals such as molybdenum, manganese, iron, and cobalt.

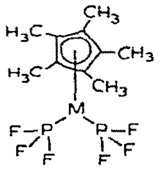
Maitlis and co-workers have subsequently exploited the ready availability of pentamethylcyclopentadienylrhodium derivatives to develop an extensive area of unusual and significant chemistry. Examples of new pentamethylcyclopentadienylrhodium derivatives prepared during the course of their work include the halides $[(CH_3)_5C_5RhX_2]_2$ (X = Cl and I) [29,30], the monometallic adducts $(CH_3)_5C_5RhX_2L$ (L = $(C_6H_5)_3P$, pyridine, toluidine, etc.) [29,30], the carboxylates $(CH_3)_5C_5Rh(OCOR)_2 \cdot H_2O$ (R = CH_3 and CF_3) [29,30], the diene complexes $(CH_3)_5C_5Rh(\text{diene})$ (diene = 1,5-cyclooctadiene, norbornadiene, dicyclopentadiene, and 1,3-cyclohexadiene [29—31], the arene complexes $[(CH_3)_5C_5Rh(\text{arene})]^{2+}$ (arene = benzene, *p*-xylene, pentamethylbenzene, and hexamethylbenzene) [32], and the cations $[(CH_3)_5C_5Rh]_2X_3^+$ (X = Cl, OH, etc.) with three bridging ligands [33].

Several catalytic properties of interest were observed for some of these pentamethylcyclopentadienylrhodium complexes. Thus, the 1,3-cyclohexadiene complex $(CH_3)_5C_5RhC_6H_8$ catalyzes the disproportionation of 1,3-cyclohexadiene to cyclohexane and benzene, especially in the presence of base and ethanol [34]. The complexes $[(CH_3)_5C_5RhX_2]_2$ (X = Cl, CO_2CH_3, and CO_2CF_3) catalyze the hydrogenation of olefins under ambient conditions [35]. The complex $[(CH_3)_5C_5Rh(OCOCH_3)_2]_2$ also catalyzes the aerial dehydrogenation of isopropanol to acetone [35]. The complex $[(CH_3)_5C_5Rh]_2(OH)_3Cl \cdot 4\,H_2O$ is of interest in completely exchanging its methyl protons with deuterium upon treatment with D_2O containing a small amount of OD^-, thereby providing a route to pentakis(trideuteromethyl)cyclopentadienylrhodium compounds [33].

The formation of pentamethylcyclopentadienylrhodium(III) derivatives from hydrated rhodium trichloride and hexamethylbicyclo-[2,2,0]-hexadiene-(V) is apparently related to some previously reported [27,36] additions accompanied by acid catalyzed rearrangements of V to pentamethylcyclopentadienyl derivatives of the type $(CH_3)_5C_5CHXCH_3$ (VI: X = Cl, Br and OCH_3). A similar reaction of hexamethylbicyclo-[2,2,0]-hexadiene with hydrated iridium trichloride gave only a low yield [30] of the pentamethylcyclopentadienyliridium derivative $[(CH_3)_5C_5IrCl_2]_2$. However, the yield of $[(CH_3)_5C_5IrCl_2]_2$ from iridium trichloride was considerably improved if the hexamethylbicyclo-[2,2,0]-hexadiene was rearranged to the pentamethylcyclopentadienyl derivative $(CH_3)_5C_5CHClCH_3$ (VI: X = Cl) before reaction with the hydrated iridium trichloride. Iridium analogues of most of the pentamethylcyclopentadienylrhodium complexes listed above could be readily prepared using $[(CH_3)_5C_5IrCl_2]_2$ as a starting material.



(VI)



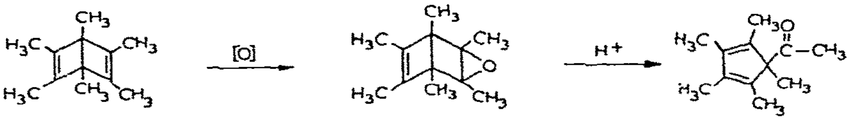
(VII)

Our original work with pentamethylcyclopentadienylmetal complexes indicated that $(CH_3)_5C_5Co(CO)_2$ was a crystalline solid at room temperature [20] in contrast to the liquid $C_5H_5Co(CO)_2$. Maitlis and co-workers found that reductive carbonylation of the rhodium and iridium complexes $[(CH_3)_5C_5MCl_2]_2$ (M = Rh and Ir) with iron carbonyls [30] (M = Ir) or with zinc [37] gave the corresponding rhodium and iridium carbonyls $[(CH_3)_5C_5MCl_2]_2$ (M = Rh and Ir) with iron carbonyls [30] (M = Ir) or temperature, in contrast to the liquid unsubstituted derivatives $C_5H_5M(CO)_2$ (M = Rh [38] and Ir [39]). The iridium derivative $(CH_3)_5C_5Ir(CO)_2$ is more readily prepared and handled than the unsubstituted $C_5H_5Ir(CO)_2$, which requires the difficultly prepared $Ir(CO)_3Cl$ as a starting material [39].

The ready availability of $(CH_3)_5C_5Ir(CO)_2$ relative to other cyclopentadienyliridium carbonyls has made it an attractive substrate for oxidative addition reactions [37,40]. In some cases, the products are cationic dicarbonyls of the type $[(CH_3)_5C_5Ir(CO)_2R]^+$, whereas in other cases one of the two carbonyl groups is lost to give products of the type $(CH_3)_5C_5Ir(CO)RX$. Reagents forming ionic dicarbonyls of the first type include methyl iodide ($R = CH_3$) [37], allyl iodide ($R = —CH_2CH{=}CH_2$) [40], and 1,2-diiodotetrafluoroethane ($R = ICF_2CF_2$) [40] whereas iodine ($R = I$) [37,40], perfluoroalkyl iodides ($R = CF_3$, C_2F_5, and n-C_3F_7) [40], and sulfonyl chlorides ($R = R'SO_2$) [37] give non-ionic monocarbonyls of the second type.

The high crystallinity of $(CH_3)_5C_5M(CO)_2$ ($M = Rh$ and Ir) made the pentamethylcyclopentadienyl systems also more attractive for the investigation of analogous trifluorophosphine complexes. Here the high cost of both the metal and the $Ni(PF_3)_4$ trifluorophosphinating agent made small scale experiments necessary which could be performed more readily with crystalline compounds [41]. Reaction of $[(CH_3)_5C_5RhCl_2]_2$ with $Ni(PF_3)_4$ gave a ~60% yield of orange crystalline $(CH_3)_5C_5Rh(PF_3)_2$ [41] (VII: M = Rh) which underwent oxidative addition reactions with iodine and perfluoroalkyl iodides [42] to give products of the type $(CH_3)_5C_5Rh(PF_3)RI$ ($R = I$, CF_3, C_2F_5, n-C_3F_7, and n-C_7F_{15}) completely analogous to the oxidative addition reactions of $(CH_3)_5C_5Ir(CO)_2$ mentioned above. These oxidative addition reactions of $(CH_3)_5C_5Rh(PF_3)_2$ are apparently the first reported oxidative addition reactions of a metal trifluorophosphine complex although Kruck and co-workers [43] have extensively investigated other reactions of metal trifluorophosphine complexes. The reaction of $[(CH_3)_5C_5IrCl_2]_2$ with $Ni(PF_3)_4$ was somewhat more complex than the corresponding reaction with the rhodium derivative [41]. In addition to the expected $(CH_3)_5C_5Ir(PF_3)_2$, a second isomeric $(CH_3)_5C_5IrP_2F_6$ was isolated. Spectroscopic studies on this second isomer suggested formulation as $(CH_3)_5C_5Ir(PF_3)(PF_2)F$ apparently formed by an internal oxidative addition reaction in which a phosphorus—fluorine bond in one of the trifluorophosphine ligands adds to the apparently very reactive $(CH_3)_5C_5Ir$ unit.

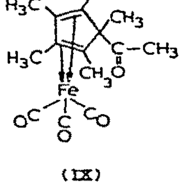
The facile synthesis of pentamethylcyclopentadienyl derivatives of rhodium and iridium from simple metal halides and the readily available hexamethylbicyclo-[2,2,0]-hexadiene (V) has led to extensive chemistry as outlined above. We were interested in developing methods for the preparation of pentamethylcyclopentadienyl derivatives of other metals using acid catalyzed rearrangement products of bicyclo-[2,2,0]-hexadiene as the source of the pentamethylcyclopentadienyl group. The most promising pentamethylcyclopentadienyl derivative was acetylpentamethylcyclopentadiene (VIII) which was readily obtained in one effective step by the treatment of hexamethylbicyclo-[2,2,0]-hexadiene with m-chloroperoxybenzoic acid according to the following sequence of reactions [44]:



(VIII)

Cleavage of the acetyl group from VIII by reaction with an appropriate transition metal derivative would provide a simple entry to pentamethylcyclopentadienyl chemistry. Such reactions were found to occur with certain metal carbonyls. Thus, simple thermal reactions of acetylpentamethylcyclopentadiene with the metal carbonyls $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe_2(CO)_9$, and $Co_2(CO)_8$ provided facile routes to the corresponding pentamethylcyclopentadienylmetal carbonyls $[(CH_3)_5C_5Cr(CO)_2]_2$, $(CH_3)_5C_5Mn(CO)_3$, $[(CH_3)_5C_5Fe(CO)_2]_2$, and $(CH_3)_5C_5Co(CO)_2$ with complete elimination of the acetyl group [45]. The chromium derivative $[(CH_3)_5C_5Cr(CO)_2]_2$ was of particular interest in being a direct analogue of the molybdenum complex $[(CH_3)_5C_5Mo(CO)_2]_2$, which had kindled our interest in pentamethylcyclopentadienylmetal chemistry nearly ten years previously because of the anticipated presence of a metal—metal triple bond. This chromium derivative $[(CH_3)_5C_5Cr(CO)_2]_2$ was a beautifully crystalline deep green volatile solid whose structure could be easily determined by X-ray crystallography [46]. This X-ray structural study indicated a chromium—chromium bond distance of 2.276 Å which is very short relative to the 2.50 Å chromium—chromium distance in metallic chromium. This provides excellent experimental evidence for our postulate of multiple metal—metal bonding in the pentamethylcyclopentadienylmetal carbonyls $[(CH_3)_5C_5M(CO)_2]_2$ (II: R = CH_3; M = Cr and Mo).

Other reactions of acetylpentamethylcyclopentadiene (VIII) with metal carbonyls gave metal carbonyl complexes retaining all, or a portion, of the acetyl group. Such reactions provided some clues as to the general pathway of the reactions leading to the eventual complete removal of the acetyl group from acetylpentamethylcyclopentadiene by means of metal carbonyls [45]. The reaction of acetylpentamethylcyclopentadiene (VIII) with $Fe_2(CO)_9$ under mild conditions gave not only $[(CH_3)_5C_5Fe(CO)_2]_2$ but also the diene complex $[(CH_3)_5C_5COCH_3]Fe(CO)_3$ (IX) containing an unchanged acetylpentamethylcyclopentadiene unit and the complex $CH_3COFe(CO)_2$-$C_5(CH_3)_5$ (X) containing an acetyl group directly bonded to iron. The reaction of acetylpentamethylcyclopentadiene (VIII) with $Mo(CO)_6$ unfortunately gave the very interesting $[(CH_3)_5C_5Mo(CO)_2]_2$ (II: R = CH_3, M = Mo) only as a minor product (~20% yield maximum); the major product from this reaction was the methylmolybdenum derivative $CH_3Mo(CO)_3C_5(CH_3)_5$ (XI: M = Mo), identical with that prepared in our earliest pentamethylcyclopentadienyl work [20] from $Mo(CO)_6$ and lithium pentamethylcyclopentadienide followed by addition of methyl iodide. The reaction of $(CH_3CN)_3W(CO)_3$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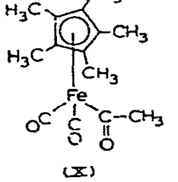
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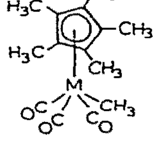
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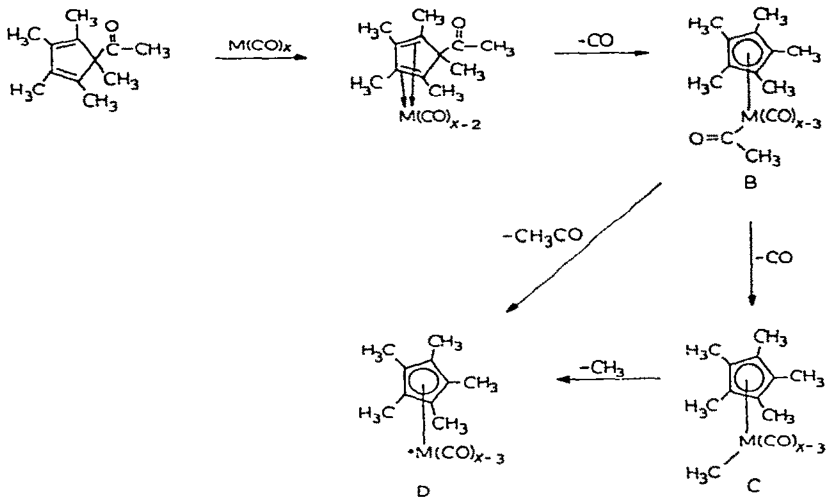
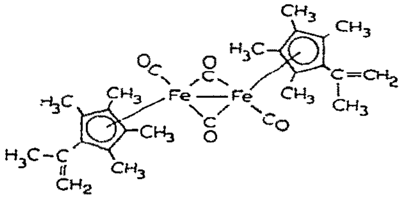


Fig. 2. Generalized scheme for the reactions of acetylpentamethylcyclopentadiene with metal carbonyls.

with acetylpentamethylcyclopentadiene (VIII) gave only the methyltungsten derivative $CH_3W(CO)_3C_5(CH_3)_5$ (XI: M = W) with no good evidence for the formation of $[(CH_3)_5C_5W(CO)_2]_2$ [45].

These observed products allowed us to suggest the scheme shown in Fig. 2 for the reactions of acetylpentamethylcyclopentadiene with metal carbonyls. In the first step, the acetylpentamethylcyclopentadiene coordinates to the transition metal as a diene to give a complex of type A exemplified by the iron carbonyl derivative $[(CH_3)_5C_5COCH_3]Fe(CO)_3$ (IX). This undergoes migration of an acetyl group from carbon to the transition metal to give a product of type B exemplified by $CH_3COFe(CO)_2C_5(CH_3)_5$ (X). Decarbonylation of this acetylmetal derivative can then take place by well-established processes [47] to give the corresponding methylmetal derivative of type C, exemplified by the derivatives $CH_3M(CO)_3C_5(CH_3)_5$ (XI): (M = Mo and W). Homolytic cleavage of a methyl group from a methylmetal derivative of type C or conceivably homolytic cleavage of an acetyl group from an acetylmetal derivative of type B can then give a pentamethylcyclopentadienylmetal unit of type D. In the case of transition metals of even atomic numbers a unit of type D will be a free radical which will dimerize to form a bimetallic derivative.

The reaction of acetylpentamethylcyclopentadiene (VIII) with $Fe(CO)_5$ at elevated temperatures appears to follow a different scheme, which was only recognized somewhat later [48]. In this case, the product is not the expected pentamethylcyclopentadienyliron carbonyl $[(CH_3)_5C_5Fe(CO)_2]_2$ but a mixture of the isopropenyltetramethylcyclopentadienyliron carbonyl $[(CH_2{=}CCH_3)(CH_3)_4C_5Fe(CO)_2]_2$ (XII) with lesser quantities of the isopropyltetramethylcyclopentadienyliron carbonyl $[(CH_3CHCH_3)(CH_3)_4C_5Fe(CO)_2]_2$ (XIII). The first clue to this anomaly in the reaction of acetylpentamethylcyclopentadiene(VIII) with $Fe(CO)_5$ was the observation that the $[R_5C_5Fe(CO)_2]_2$ product from this reaction upon reduction with sodium amalgam in tetrahydrofuran followed by treatment of the resulting sodium salt $Na[Fe(CO)_2C_5R_5]$ with acetyl chloride gave a liquid acetyl derivative $CH_3COFe(CO)_2C_5R_5$. However, $CH_3COFe(CO)_2C_5(CH_3)_5$ (X) was a known crystalline solid [45] obtained from VIII and $Fe_2(CO)_9$ as described above. The formulation of the product from VIII and $Fe(CO)_5$ as a mixture of XII and XIII was based on conversion of the $[R_5C_5Fe(CO)_2]_2$ product to the corresponding $CH_3COFe(CO)_2C_5R_5$ derivative as described above, and to the corresponding $CH_3Fe(CO)_2C_5R_5$ derivative by a similar method but using methyl iodide rather than acetyl chloride. These two derivatives gave the correct elemental analyses and exhibited NMR and mass spectra consistent with the proposed formulations.



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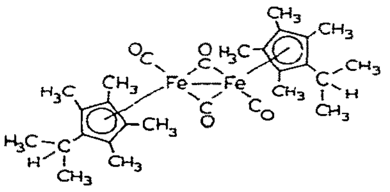
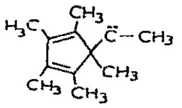
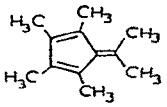


(XIII)

The reaction of acetylpentamethylcyclopentadiene (VIII) with $Fe(CO)_5$ to give a mixture of XII and XIII may first involve deoxygenation of VIII by the $Fe(CO)_5$ to give the carbene XIV, followed by methyl migration to give 1,2,3,4,6,6-hexamethylfulvene (XV). This fulvene XV can react with $Fe(CO)_5$ to give mixtures of XII and XIII by processes completely analogous to reported reactions [49] of fulvenes with metal carbonyls to give mixtures of isopropenylcyclopentadienyl and isopropylcyclopentadienyl derivatives.



(XIV)



(XV)

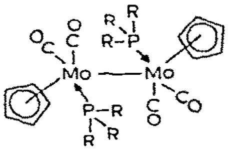
These reactions of acetylpentamethylcyclopentadiene (VIII) with metal carbonyls make a variety of pentamethylcyclopentadienyl metal carbonyl derivatives available for the first time for a detailed study of their reactions. Of particular interest was the chemistry of the metal—metal triple bonded derivatives $[(CH_3)_5C_5M(CO)_2]_2$ (II: R = CH_3, R = Cr and Mo) because of the possibility of uncovering unusual reactions of the metal—metal triple bond [50]. We used the chromium derivative $[(CH_3)_5C_5Cr(CO)_2]_2$ (II: R = CH_3, M = Cr) for most of these studies of compounds with metal—metal triple bonds since even the use of acetylpentamethylcyclopentadiene (VIII) did not provide a means for preparing large quantities of the molybdenum analogue $[(CH_3)_5C_5Mo(CO)_2]_2$ (II: R = CH_3, M = Mo) because of the poor yield in the reaction of VIII with $Mo(CO)_6$ to give II (R = CH_3, M = Mo).

The chemistry of $[(CH_3)_5C_5Cr(CO)_2]_2$ (II: R = CH_3, M = Cr) proved to be extremely disappointing, particularly after our wait of nearly ten years to be in a position to investigate the chemistry of cyclopentadienylmetal carbonyl derivatives with metal—metal triple bonds [50]. None of the observed reactions of $[(CH_3)_5C_5Cr(CO)_2]_2$ could be interpreted as additions to the chromium—chromium triple bond with retention of the bimetallic structure. Reaction of $[(CH_3)_5C_5Cr(CO)_2]_2$ with sodium amalgam in tetrahydrofuran resulted in an interesting color change from green through violet to yellow-brown. However, the final product was shown to be $Na[(CH_3)_5C_5Cr(CO)_3]$ by its reactions with $(C_6H_5)_3SnCl$, $HgCl_2$, and $Hg(CN)_2$ to give $(C_6H_5)_3SnCr(CO)_3C_5(CH_3)_5$, $ClHgCr(CO)_3C_5(CH_3)_5$, and $Hg[Cr(CO)_3C_5(CH_3)_5]_2$, respectively. The formation of $Na[(CH_3)_5C_5Cr(CO)_3]$ from $[(CH_3)_5C_5Cr(CO)_2]_2$ and sodium amalgam in the absence of added carbon monoxide necessarily must involve transfer of carbonyl groups from one chromium atom to another. The chromium—chromium bond in $[(CH_3)_5C_5Cr(CO)_2]_2$ was cleaved with iodine and with nitric oxide to give the unstable $(CH_3)_5C_5Cr(CO)_3I$ and the relatively stable $(CH_3)_5C_5Cr(CO)_2NO$, respectively. Numerous other reactions of $[(CH_3)_5C_5Cr(CO)_2]_2$ (II: R = CH_3, M = Cr) with an extensive variety of reagents of all types, including olefins, alkynes, phosphines, phosphites, and organosulfur compounds, failed to give any identifiable pentamethylcyclopentadienylchromium compounds except for unchanged $[(CH_3)_5C_5Cr(CO)_2]_2$ in cases where sufficiently mild reaction conditions were used. The molybdenum analogue $[(CH_3)_5C_5Mo(CO)_2]_2$ was too rare to try a similarly extensive series of reactions. Nevertheless, its reactions with sodium amalgam, iodine, and nitric oxide were shown to parallel completely those of its chromium analogue with cleavage of the metal—metal triple bond to give $Na[(CH_3)_5C_5Mo(CO)_3]$, $(CH_3)_5C_5Mo(CO)_3I$, and $(CH_3)_5C_5Mo(CO)_2NO$, respectively.

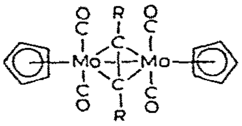
In retrospect it appears unfortunate that our supply of $[(CH_3)_5C_5Mo(CO)_2]_2$ in 1973 was still too limited for extensive exploration of its reactions since very recent work by Ginley and Wrighton [51] have led to the discovery of some interesting reactions of $[(CH_3)_5C_5Mo(CO)_2]_2$, which could be considered as additions to the molybdenum—molybdenum triple bond. Thus, $[(CH_3)_5C_5Mo(CO)_2]_2$ (II: R = CH_3, M = Mo) was shown to react reversibly with carbon monoxide at room temperature to form $[(CH_3)_5C_5Mo(CO)_3]_2$ (I: R = CH_3, M = Mo), the species that we had expected to obtain back in 1962 when we first studied the reaction of pentamethylcyclopentadiene with $Mo(CO)_6$. The instability of $[(CH_3)_5C_5Mo(CO)_3]_2$ (I: R = CH_3, M = Mo) towards loss of two equivalents of carbon monoxide to regenerate $[(CH_3)_5C_5Mo(CO)_2]_2$ (II: R = CH_3, M = Mo) upon heating in toluene or even visible light irradiation explains our failure to obtain $[(CH_3)_5C_5Mo(CO)_3]_2$ from a thermal reaction between pentamethylcyclopentadiene and $Mo(CO)_6$ under conditions where any $[(CH_3)_5C_5Mo(CO)_3]_2$ once formed would immediately lose carbon monoxide to give $[(CH_3)_5C_5Mo(CO)_2]_2$.

Recent work has shown that metal—metal triple bonded derivatives of the type $[C_5H_5M(CO)_2]_2$ (II: R = H, M = Cr and Mo) can even be obtained from unsubstituted cyclopentadiene. Thus, pyrolysis of $[C_5H_5Cr(CO)_3]_2$ (I: R = H, M = Cr) in boiling toluene results in the loss of one carbonyl group per chromium atom to give the metal—metal triply bonded derivative $[C_5H_5Cr(CO)_2]_2$ (II: R = H, M = Cr) [52]. No reactions of $[C_5H_5Cr(CO)_2]_2$ have been reported involving addition to the chromium—chromium triple bond.

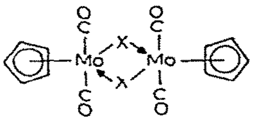
A similar pyrolysis of $[C_5H_5Mo(CO)_3]_2$ (I: R = H, M = Mo) in boiling toluene or 1-octene resulted in carbon monoxide loss to give $[C_5H_5Mo(CO)_2]_2$ (II: R = H, M = Mo) [53]. Determination of the structure of $[C_5H_5Mo(CO)_2]_2$ by X-ray diffraction gave a molybdenum—molybdenum bond distance of 2.45 Å which is 0.8 Å shorter than the molybdenum—molybdenum bond distance of 3.24 Å in $[C_5H_5Mo(CO)_3]_2$ [51] thereby providing direct experimental confirmation of the molybdenum—molybdenum triple bond in $[C_5H_5Mo(CO)_2]_2$ (II: R = H, M = Mo).



(XVI)



(XVII)



(XVIII)

Some of the observed reactions [53] of $[C_5H_5Mo(CO)_2]_2$ (II: R = H, M = Mo) correspond to addition to the molybdenum—molybdenum triple bond. Thus, $[C_5H_5Mo(CO)_2]_2$ reacts with tertiary phosphines and phosphites with addition to the molybdenum—molybdenum triple bond to give the adducts $[C_5H_5Mo(CO)_2PR_3]_2$ (XVI: R = C_6H_5 or OCH_3) identical with products obtained by carbonyl displacement from $[C_5H_5Mo(CO)_3]_2$ (I: R = H, M = Mo) [54,55]. Alkynes also add to the molybdenum—molybdenum triple bond to give adducts of the type $(RCCR')Mo_2(CO)_4(C_5H_5)_2$ (XVII: R = C_6H_5 or H, R′ = H). Iodine and dimethyldisulfide also add to the molybdenum—molybdenum triple bond in $[C_5H_5Mo(CO)_2]_2$ to give $[C_5H_5Mo(CO)_2I]_2$ (XVIII: X = I) and $[C_5H_5Mo(CO)_2SCH_3]_2$ (XVIII: X = SCH_3), respectively. The formation of $[C_5H_5Mo(CO)_2I]_2$ from $[C_5H_5Mo(CO)_2]_2$ and iodine contrasts with the previously observed [50] formation of $(CH_3)_5C_5Mo(CO)_3I$ from $[(CH_3)_5C_5Mo(CO)_2]_2$ and iodine. The unsubstituted derivative $[C_5H_5Mo(CO)_2]_2$ (II: R = H, M = Mo) may be more reactive towards additions to the molybdenum—molybdenum triple bond than its permethylated analogue $[(CH_3)_5C_5Mo(CO)_2]_2$ (II: R = CH_3, M = Mo) because the ten ring methyl groups in the latter compound may hinder access of attacking reagents to the metal—metal triple bond. This is similar to numerous examples of blocking the reactivity of carbon—carbon multiple bonds towards addition reactions by means of bulky substituents [56,57].

CONCLUSIONS

The work summarized in this account shows how a systematic comparison of the metal carbonyl chemistry of pentamethylcyclopentadiene with that of unsubstituted cyclopentadiene led to the discovery of a new and interesting class of compounds: cyclopentadienylmetal carbonyls with metal—metal triple bonds. Other interesting applications of pentamethylcyclopentadienylmetal complexes not discussed in detail in this account include their use in unravelling certain aspects of titanocene [58—61], zirconocene [62], and molybdenocene [63,64] chemistry, particularly certain aspects of nitrogen fixation by titanocene [60,61] and zirconocene [62]. The improved accessibility of pentamethylcyclopentadienylmetal derivatives from the commercially available hexamethylbicyclo-[2,2,0]-hexadiene (V) either through rhodium [29,30] or iridium [30] complexes or through acetylpentamethylcyclopentadiene (VIII) [45] now makes these metal derivatives readily enough available for consideration by chemists seeking unusual catalytic properties or chemical reactivity. Pentamethylcyclopentadienylmetal complexes are also likely to play a role in the further development of transition metal organometallic chemistry, an area of chemistry currently receiving much attention because of its importance in molecular catalysis and organic synthesis.

ACKNOWLEDGEMENTS

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