Russian Chemical Reviews **62** (11)1025 – 1045 (1993)
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UDC 547.1'13

The chemistry of cymantrene

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Abstract. The advances in the synthesis and study of derivatives of cyclopentadienyltricarbonylmanganese (cymantrene) are considered. The bibliography includes 356 references.

I. Introduction

The cyclopentadienyl complexes of metals constitute one of the classes of organic transition metal complexes which have been studied in greatest detail. In terms of the number of experimental studies, cyclopentadienyltricarbonylmanganese (cymantrene, CTM) occupies the second place after ferrocene. Two stages may be distinguished in the studies on cymantrene. The synthetic aspect, based on the analogy with the electrophilic substitution reactions in benzene and ferrocene, was characteristic of the first stage in the chemistry of cymantrene. Other reactions involving the substitution of hydrogen in the Cp ring are known for cymantrene although their number is somewhat smaller than in the case of ferrocene. These are the acylation, alkylation, and phosphorylation reactions under Friedel – Crafts conditions, sulfonation, chloromethylation, metallation with butyllithium, mercuration with mercury(II) salts, and hydrogen isotope exchange with acids and bases. A multiplicity of cymantrene derivatives with a wide variety of substituents in the Cp ring have been obtained by means of the reactions listed above (for the literature data up to 1972, see the references in a review[1]).

On the other hand, reactions involving the substitution of CO by other ligands as well as processes occurring with a change in the ligand environment of the metal are extremely characteristic of cymantrene, as for all metal carbonyl complexes.

The second stage in the development of studies on cymantrene was associated with the synthesis of its derivatives both with 'classical' ligands, coordinated to manganese via the electron-donating atoms of Group IV – VI elements, and with ligands of a new type such as complexes with molecular hydrogen, free – radical complexes, complexes with 'indene' ligands, etc.

The combination of the reactions involving substitution of hydrogen in the Cp ligand and CO substitution reactions made it possible to obtain a large number of a wide variety of derivatives with C_5H_5Mn, C_5H_4RMn, C_5R_5Mn (R = alkyl, halogen, etc.) fragments. A unique feature of cymantrene is a combination of a varied reactivity with thermal and oxidative stabilities, which are unusually high for π-complexes.

On average, 30 – 40 studies devoted to the chemistry of cymantrene are published each year. However, despite very extensive experimental data, review information on the recent chemistry of cymantrene is virtually lacking. The reviews[1 – 3] and monographs[4] published previously are to a greater or lesser extent obsolete. A review[5] dealing with the structural aspects of manganese carbonyl complexes was published comparatively recently. The present review presents a compilation in one article of extremely extensive and comprehensive data for the last 10 – 12 years on the chemistry of compounds containing one or several cymantrene residues [the cymantrenyl radical $(CO)_3MnC_5H_4$ is designated below in the text by (**Mn**)]. The limited space available in the review precluded the consideration of data concerning the synthesis and properties of numerous complexes of the type $CpMn(CO)(LL')$, where L and L' are two-electron ligands. Studies in which the key role was assumed by various physicochemical and computational studies (optical and microwave spectroscopy, kinetic and electrochemical methods, gas-phase chemistry of cymantrene, mass-spectrometric studies, and quantum-chemical calculations) are also not considered.

Cymantrene, the isoelectronic cation $CpMn(NO)(CO)_2^+$, and their derivatives are diamagnetic 18-electron complexes which contain an Mn atom with the d^6 configuration and a formal +1 oxidation state. Cymantrene and its derivatives can be regarded as pseudooctahedral complexes in which the Cp ligand occupies three coordination sites. This follows from X-ray diffraction (XRD) data, according to which the OC – Mn – CO bond angles are 87° – 93° in virtually all structurally characterised cymantrene derivatives. However, in stereochemical studies it has become unusual to consider cymantrene and analogous molecules with the geometry of the 'piano stool with three legs' type as pseudotetrahedral assuming that the Cp ligand occupies one coordination site.

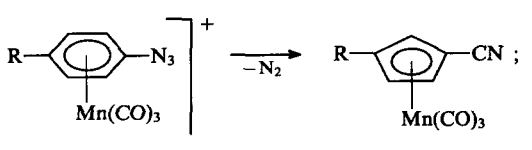
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Received 4 June 1993
Uspekhi Khimii **62** (11) 1098 – 1118 (1993); translated by A K Grzybowski

II. The formation and cleavage of the cymantrene system

Detailed X-ray diffraction data for cymantrene have been obtained by Fitzpatrick et al.[6] and Cowie et al.[7] A difference between the C–C bond lengths in the Cp ring was observed in the above investigations. They vary in the ranges 1.400–1.439 Å [6] and 1.399–1.426 Å.[7] The study of cymantrene by vibrational spectroscopic methods also indicated slight deviations from the C_{5v} symmetry for the Cp ligand, which may be induced by crystal packing effects.[6] The heat capacities of cymantrene and of its π-pyrrole analogue[8] as well as the heat of formation of cymantrene[9] have been measured.

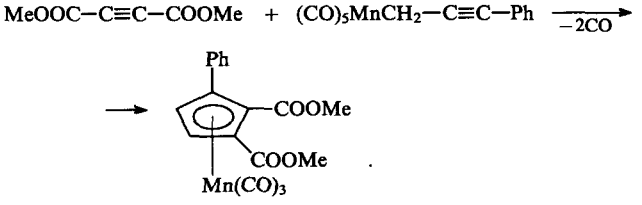
In addition to the procedures known earlier (see the relevant review[1]), a number of new methods of synthesis of cymantrene have been proposed. On reduction[10,11] of a mixture of anhydrous $MnCl_2$ and cyclopentadiene by metallic magnesium or manganese in the presence of $TiCl_4$ or $Ti(OBu)_3$ followed by carbonylation with CO (180 °C, 80 atm), the yield of cymantrene reaches 70%–75%. The interaction of anhydrous $MnCl_2$ and $Me_3SiC_5H_4^-Na^+$ and subsequent carbonylation afford Me_3Si(**Mn**).[12] Cymantrene exhibits a high thermodynamic stability and its derivatives are formed as a result of thermal or photochemical reactions of manganese carbonyl complexes with olefins and dienes. Thus, in the thermal decomposition of solid cationic complexes of azidobenzene and azidotoluene with $Mn(CO)_3$, nitrogen is evolved even at 130 °C and an intermediate complex of phenylnitrene with $Mn(CO)_3$ is apparently formed. The ring contraction reaction takes place readily in the intermediate and leads to cyano- or 1-methyl-3-cyano-cymantrene.[13]



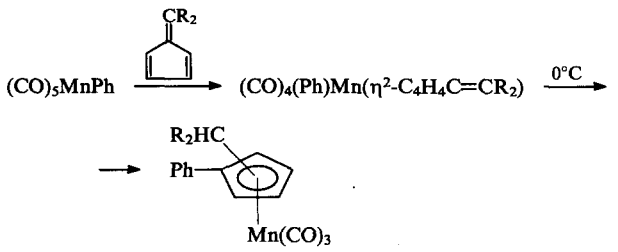
R = H, Me.

After the thermal decomposition of non-coordinated phenyl azide in solution, azobenzene (resulting from the dimerisation of phenylnitrene) and aniline (produced by the abstraction of hydrogen from the solvent) were detected among the reaction products. Thus coordination to $Mn(CO)_3$ alters sharply the mode of thermal decomposition of the coordinated azides.

The [3 + 2]-cycloaddition reaction takes place on interaction of $(CO)_5MnCH_2C{\equiv}CPh$ with dimethylacetylenedicarboxylate and affords a trisubstituted cymantrene derivative.[14]



One of the most general methods of synthesis of cymantrene derivatives is based on the reaction of the carbonyl halides $Mn(CO)_5X$ or $Mn(CO)_3L_2X$ (X = Cl, Br; L = a ligand, for example, amine, pyridine, etc., linked by labile bonds), $Mn(CO)_5Ph$, and $Mn_2(CO)_{10}$ with substituted cyclopentadienes or cyclopentadienylthallium derivatives. The reaction of $H_3Mn_3(CO)_{12}$ with 6-dimethylaminofulvene leads to the formation of dimethylaminomethylcymantrene (**Mn**)CH_2NMe_2.[15] Under the conditions of photchemical activation on irradiation with UV light of 6,6-dimethyl- or 6,6-diphenyl-fulvene in the presence of $Mn(CO)_5Ph$ in hexane at –20 °C, the displacement of CO and coordination of fulvene to one of the double bonds result in the formation of the intermediates $Mn(CO)_4LPh$ (L = η^2-fulvene), which rearrange on heating to 0 °C to disubstituted cymantrenes with insertion of the fulvene double bonds in the Mn–Ph bond.[16]



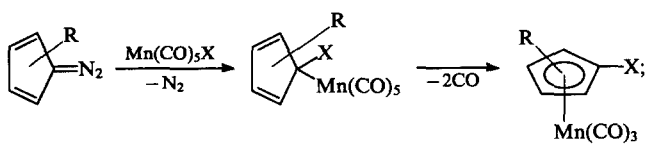
The phosphine oxide $Ph_2P(O)CH_2C_2H_5$ reacts with $Mn_2(CO)_{10}$ to form the complex (**Mn**)$CH_2P(O)Ph_2$.[17] Reaction of the bromide $Mn(CO)_5Br$ with the cyclopentadiene derivatives $Me_3SnC_5H_4CH_2CH_2PPh_2$ is accompanied by elimination of two CO molecules and Me_3SnBr and leads to the formation of the complex (**Mn**)$CH_2CH_2PPh_2$.[18] Phenylcymantrene is formed similarly from phenylcyclopentadiene and $Mn(CO)_5Br$.[19]

The reaction of $Mn(CO)_5Br$ with cyclopentadienylthallium derivatives containing functional group substituents constitutes a thoroughly developed method of synthesis of substituted cymantrenes.

$$RC_5H_4Tl + Mn(CO)_5Br \longrightarrow (\eta^5\text{-}RC_5H_4)Mn(CO)_3 + 2CO + TlBr\ .$$

Compounds with R = $-C(CN)=C(CN)_2$,[20,21] CF_3,[22] Ph, CH_2Ph,[23] Cl, Br,[24], *m*-, *p*-FC_6H_4,[25,26] CHO, C(O)Me, C(O)OMe, C(O)OEt [27] have been synthesised in this way. This reaction can be extended also to dinuclear complexes. Thus the corresponding biscymantrenyl derivative has been obtained from 1,4-bis(cyclopentadienylthallium)buta-1,4-dione by reaction with $Mn(CO)_5Br$.[28] The reaction of tricyano(ferrocenyl)ethylene $Fc-C(CN)=C(CN)_2$ with 1 equivalent of $Mn(CO)_5Br$ and C_5H_5Tl affords the dinuclear complex $Fc-C[=C(CN)_2]$(**Mn**).[21]

The simultaneous elimination of nitrogen and two CO molecules results in the ready formation of mono- and polyhalocymantrenes in the reactions of $Mn(CO)_5X$ with diazacyclopentadienes.[29]



X = Cl, Br, I.

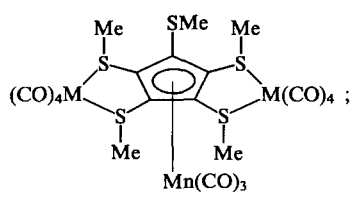
Chloro-, bromo-, and iodo-cymantrenes have been obtained in 60%–80% yields from unsubstituted diazacyclopentadiene $C_5H_4=N_2$ in one stage, while the reaction of $C_5Ph_4=N_2$ with $ClMn(CO)_5$ afforded chlorotetraphenylcymantrene.[30] The single-stage syntheses of halocymantrenes via CpTl or diazacyclopentadienes as well as the syntheses via the interaction of mercurio-derivatives of cymantrene with copper(II) salts[31] are much simpler than the previously proposed multistage method of synthesis via aminocymantrene (see the relevant review[1]). Halo-derivatives of indenylmanganese tricarbonyl have been obtained from diazaindene.[32]

The synthesis via diazacyclopentadienes constitutes a convenient path to polyhalocymantrenes. The reaction of tetrachlorodiazacyclopentadiene with $XMn(CO)_5$ leads to a mixture of the monohapto-complexes η^1-$C_5Cl_4XMn(CO)_5$ and to pentahalocymantrenes formed from them as a result of a σ → π

rearrangement and the elimination of CO. The proportions of the above products depend greatly on the reaction conditions. On heating to fusion, the η^1-complexes readily split off CO and are converted into the thermodynamically more stable pentahalocymantrenes in a quantitative yield.[33] The conversion of η^1-$C_5Cl_5Mn(CO)_5$ into η^5-$C_5Cl_5Mn(CO)_3$ can also take place photochemically via the intermediate η^3-$C_5Cl_5Mn(CO)_4$.[34] Pentabromo- and tetrabromoiodo-cymantrenes have been obtained from tetrabromodiazacyclopentadiene and $XMn(CO)_5$ (X = Br or I), while tri-iodocymantrene has been obtained from di-iododiazacyclopentadiene and $IMn(CO)_5$.[35] A preparative synthesis of mono- and poly-halocymantrenes by this procedure has been described.[36] When an attempt was made to obtain dibromocymantrene by the reaction of bis(bromomercurio)-cymantrene with $CuBr_2$ in acetone (by analogy with the synthesis of bromocymantrene[31]), a mixture containing cymantrene, bromocymantrene and all possible di-, tri-, tetra-, and penta-bromocymantrenes, which was separated into its components with the aid of preparative gas–liquid chromatography (GLC), was obtained instead of the expected dibromides.[37]

The chemistry of polychlorocymantrenes and their derivatives has developed vigorously in recent times. In the metallation of bromotetrachlorocymantrene with butyllithium (hexane, −60 °C), a key synthon—the lithio-derivative (η^5-C_5Cl_4Li)$Mn(CO)_3$—is formed as a result of the substitution of bromine by lithium. The reactions of the synthon with various electrophiles yielded a series of tetrachlorocymantrenes [(η^5-C_5Cl_4R)$Mn(CO)_3$, R = H, Me, $SiMe_3$, $SiPh_3$, COOH, COOMe, SMe, and SPh,[38] as well as $SnMe_3$, PPh_2, SePh, and CHO [39]]. The dicymantrenyl sulfide $S[(C_5Cl_4)Mn(CO)_3]_2$ has been obtained by the reaction of the lithio-derivative with SCl_2.[39] The corresponding acid chloride, azide, isocyanate, and amine have been synthesised from tetrachlorocymantrenecarboxylic acid. Haloferrocenes are known to form nitriles on reaction with CuCN. However, the reaction of $(C_5Cl_4Br)Mn(CO)_3$ and CuCN does not afford stable products in pyridine, and the usual procedure was therefore used to obtain the nitrile. The reaction of the acid chloride with ammonia afforded the amide [R = $C(O)NH_2$], while dehydration of the latter by $POCl_3$ afforded the nitrile (R = CN).[39]

A whole series of compounds having the general formula [η^5-$C_5Cl_{5-n}(SMe)_n$]$Mn(CO)_3$, where $n = 1-5$, have been obtained from (η^5-C_5Cl_4SMe)$Mn(CO)_3$ by successive metallation with BuLi and treatment with Me_2S_2.[40] The corresponding compounds containing two or three SPh groups and mixed complexes containing simultaneously the SPh and SBu groups have been obtained similarly from (η^5-C_5Cl_4SPh)$Mn(CO)_3$ by metallation and treatment with Ph_2S_2 or Bu_2S_2.[41] More than three SPh groups cannot be introduced in this way. The complexes $C_5(SMe)_5Mn(CO)_3$,[40] $C_5Cl_2(SPh)_3Mn(CO)_3$, etc.[41] have been characterised by XRD. Compounds containing two or four SMe or SPh groups in the Cp ring readily form a wide variety of dinuclear complexes as a result of the coordination of the metal-containing fragments to the sulfur atoms.[41,42] Trinuclear complexes with two chelate rings, whose structure has been established by the XRD method, are formed in the case of $C_5(SMe)_5Mn(CO)_3$.[42]



M = Cr, Mo, W.

The reaction of $(C_5Cl_4Li)Mn(CO)_3$ with sulfur leads to the monothiolate derivative $(C_5Cl_4SLi)Mn(CO)_3$, which does not afford the expected thiol on protonation, the disulfide $[(CO)_3MnC_5Cl_4S-]_2$ being formed instead. On the other hand, on repeated metallation of the monothiolate and treatment with sulfur, the dithiolate $C_5Cl_3(SLi)_2Mn(CO)_3$ was obtained. On protonation, the latter was smoothly converted into the dithiol $C_5Cl_3(SB)_2Mn(CO)_3$, which was characterised by XRD.[43]

Apart from the tetra- and penta-halocymantrenes, pentaalkylcymantrenes have also been obtained. Pentaethyl-cymantrene was synthesised as early as 1964 by the successive acylation of cymantrene with $MeC(O)Cl/AlCl_3$ and the reduction of the keto-group to CH_2 on treatment with $LiAlH_4/AlCl_3$ (ten stages altogether).[44] Pentamethylcymantrene is formed as a result of the reaction of pentamethylcyclopentadiene with $MeMn(CO)_5$ or $Mn_2(CO)_{10}$.[45,46] An improved version of this method, involving the interaction of C_5Me_5H with $Mn_2(CO)_{10}$ without a solvent at 180 °C, has been proposed,[47] but it was shown later that a mixture of pentamethyl- and tetramethyl-cymantrenes is formed under these conditions.[48] Pentabenzylcymantrene, the structure of which was confirmed by XRD, has been obtained by the reaction of pentabenzylcyclopentadiene with $Mn_2(CO)_{10}$.[49] A series of pentamethylderivatives of cymantrene have been investigated[50,51] by ^1H, ^{13}C, and ^{17}O NMR spectroscopic methods. The pentasubstituted complex $C_5(SiMe_2H)_5Mn(CO)_3$, characterised by XRD, as well as all the intermediates, each containing from one to four $SiMe_2H$ groups, have been synthesised from $C_5Br_5Mn(CO)_3$ by multistage metallation (2 equiv. of BuLi) and alkylation (2 equiv. of Me_2SiHCl).[52]

Penta(methoxycarbonyl)cymantrene $[C_5(COOMe)_5]Mn(CO)_3$ has been synthesised by the reaction of the anion $C_5(COOMe)_5^-$ with $BrMn(CO)_5$. It reacts with NH_3, affording a mixture of compounds containing simultaneously C(O)OMe and $C(O)NH_2$ groups in the ring. The reaction with butylamine leads to the monoamide derivative, while exhaustive reduction with $LiAlH_4$ results in the formation of $C_5Me_5Mn(CO)_3$.[53]

Apart from the reactions described above, in which the thermodynamically stable cymantrene system is formed, examples of reverse processes occurring with dissociation of the Mn–Cp bond are known. The reduction of cymantrene with sodium in hexamethylphosphoramide leads initially to $NaMn(CO)_5$ and then to $Na_3Mn(CO)_4$.[54]

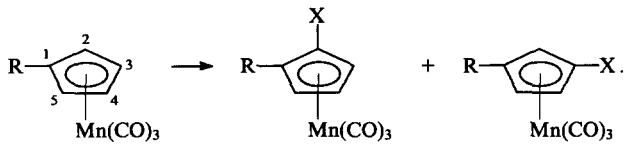
The thermal decomposition of cymantrene at 380–420 °C and a pressure of 10^{-2} Torr gives rise to the cyclopentadiene dimer, metallic manganese, and CO.[55,56] On catalytic hydrogenation in acetic acid in the presence of Pd/C, cymantrene and many of its derivatives are completely cleaved to cyclopentane and cyclopentene.[57] The reaction of ferrocene and cymantrene, adsorbed in the large cavities of zeolites, with phthalonitrile vapour at 100–150 °C *in vacuo* leads to cleavage, induced by the zeolite matrix, and to the formation of iron- and manganese-phthalocyanines. The latter are retained within the zeolite cavity, not as a consequence of chemical bonding with the skeleton, but as a result of the difference between their diameters and the dimensions of the inlet windows of the zeolite.[58]

The interaction of methylcymantrene with bis(1,3-diphenyl-propane-1,3-dionato)tin proceeds with complete cleavage of the molecule and the transfer of propanedionate ligands from tin to manganese. The complex bis(1,3-diphenylpropane-1,3-dionato)manganese$(THF)_2$, in which the manganese atom is surrounded octahedrally by six oxygen atoms, has been isolated from the reaction mixture and characterised by XRD.[59] Treatment of methylcymantrene with the potassium derivative of 18-crown-6 in THF resuts in two-electron reduction accompanied by a profound rearrangement of the molecule with dissociation of the Mn–Cp bond. In the presence of 1 equiv. of naphthalene, the reaction product is the anionic complex (η^4-$C_{10}H_8$)$Mn(CO)_3^-$, in which the naphthalene molecule is involved in η^4-type of coordination.[60] The Mn–Cp bond dissociates also when an attempt is made to achieve the photochemical substitution of CO by PPh_3 in the complex $Ph_2PC_5H_4Mn(CO)_3$.[61,62]

III. Reactions involving the substitution of hydrogen in the Cp ligand and the syntheses of compounds with the cymantrenyl substituent

Numerous cymantrene derivatives, examined in detail in a review,[1] have been synthesised by a set of substitution reactions. Yet another reaction involving the substitution of hydrogen atoms in the Cp ring was discovered subsequently: direct boryl-ation of the Cp ligand. It was shown that cymantrene, methyl-cymantrene, and ferrocene react with BI_3, BBr_3, $PhBI_2$, and $MeBI_2$ in carbon disulfide in cyclohexane or without a solvent at 80 to 100 °C with substitution of a hydrogen atom in the Cp ring by the BI_2, BBr_2, PhBI, or MeBI group. The resulting compounds enter into reactions with $SnMe_4$, Et_2O, Me_2S_2 and $NHMe_2$ involving the substitution of the halogen by the alkyl, OEt, SMe, and NMe_2 groups respectively.[63,64]

On passing from unsubstituted cymantrene to its mono-substituted derivative $RC_5H_4Mn(CO)_3$, the problem of the site of substitution arises, as in the case of the benzene derivatives RC_6H_5. The newly introduced substituent can replace hydrogen in the 2- and 3-positions. Substitution reactions in cymantrene as a rule proceed nonselectively and mixtures of 1,2- and 1,3-isomers are formed, the proportions of which depend significantly on the nature of the substituent and the type of reaction.

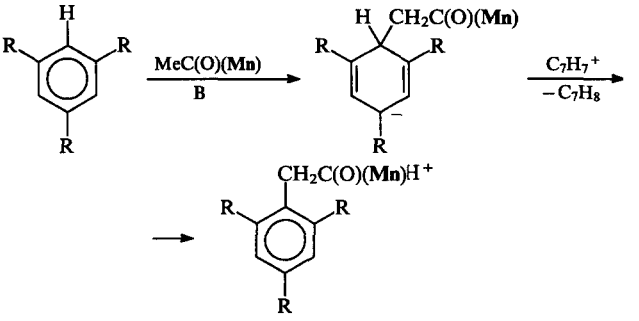


If the substituent R contains a chiral centre, then the CH groups in the 2,3- and 4,5-positions become nonequivalent (diastereotopic). In this case the substitution reaction may be stereoselective if the substitution proceeds exclusively or predominantly in one of the two nonequivalent positions. The instances of regio- and stereo-selectivity on substitution in cymantrene will be noted below.

A large group of ketones of the cymantrene series have been synthesised by the acylation and benzoylation of cymantrene, alkylcymantrenes, and other cymantrene derivatives (see the relevant review[1]). A series of substituted benzoylcymantrenes having the general formula $[\eta^5\text{-}C_5H_3(Y)C(O)C_6H_4X]Mn(CO)_3$ (X = *o*-, *m*-, and *p*-Me, MeO, Cl, Br, F, etc.; Y = H, 1- and 2-Me) have been obtained by benzoylating cymantrene and methylcymantrene with the acid chlorides $XC_6H_4C(O)Cl/AlCl_3$ in CH_2Cl_2.[19] β-Phenylethyl- and styryl-cymantrenes as well as the carbinol $PhCH_2CH(OH)(\mathbf{Mn})$ have been obtained from benzyl cymantrenyl ketone $PhCH_2C(O)(\mathbf{Mn})$.[19] Refluxing of substituted benzoylcymantrenes with $Cr(CO)_6$ in dibutyl ether leads to a series of benchrotrenyl cymantrenyl ketones having the general formula $(CO)_3Cr[\eta^6\text{-}XC_6H_4C(O)C_5H_3Y\text{-}\eta^5]Mn(CO)_3$ as a result of the coordination of the benzene ring to chromium.[65] On reduction with sodium, these ketones afford the corresponding Na ketyls, in which the radical centre is stabilised simultaneously by the cymantrenyl and benchrotrenyl substituents.[66]

The ω-chloroketones $Cl(CH_2)_nC(O)(\mathbf{Mn})$ have been synthesised by acylating cymantrene with the chlorides of ω-chlorocarboxylic acids. Clemmensen reduction of the ketones affords the ω-cymantrenyl chlorides $Cl(CH_2)_{n+1}(\mathbf{Mn})$, where n = 2 and 3.[67] The interaction of the chlorides with trimethyl-amine leads to the ammonium salts $Me_3N^+(CH_2)_n(\mathbf{Mn})Cl^-$,[68] while their reaction with $(EtO)_2PONa$ leads to the alkylphosphonic acid esters $(EtO)_2P(O)(CH_2)_n(\mathbf{Mn})$.[69] The ketoacid chlorides $PhC(O)(CH_2)_nC(O)Cl$, where n = 4 and 6, afford on acylation of cymantrene the asymmetric diketones $PhC(O)(CH_2)_nC(O)(\mathbf{Mn})$ in a high yield, but the acid chlorides with n = 2 and 3 do not interact with cymantrene under these conditions.[70]

Ketones of the cymantrene series form the corresponding derivatives with functional group substituents (oximes, hydrazones, etc.) and enter into reactions characteristic of ketones. Acetylcymantrene reacts with trinitrobenzene in the presence of bases (triethylamine) with abstraction of a proton and the formation of anionic cyclohexadienyl complexes, which react with the tropylium cation with transfer of a hydride ion, forming cymantrenyl trinitrobenzyl ketone and cycloheptatriene.[71]



R = NO_2.

Cymantrenecarbaldehyde and acetylcymantrene enter readily into the Wittig reaction with the ylide $Ph_3P=CH_2$ and its analogues with formation of the corresponding olefines — vinyl- and alk-2-enyl-cymantrenes.[72,73] Acetylcymantrene also enters into the Reformatskii reaction with ethyl bromoacetate in the presence of zinc dust.[73]

The acylation and benzoylation reactions constitute virtually the only method of synthesis of cymantrenyl ketones. The acyl-ation of cymantrene derivatives is a nonselective reaction. As early as 1970, it was shown that the acylation of alkyl-, halo-, acylamino-, and methoxy-cymantrenes always results in the formation of a mixture of two isomeric ketones.[74–76] The results of the study of the acetylation of methyl(methylthio)cymantrene agree with this finding. The acetylation of both the 1,2- and 1,3-isomers leads to the formation of a mixture of three isomeric ketones containing the Me, MeS, and C(O)Me substituents in different positions in the Cp ring.[77]

The alkylation of cymantrene with $Bu^tCl/AlCl_3$ results in the formation of a complex mixture of alkylation products containing one or two Bu^t and/or C(O)Bu groups in the Cp ring. Reactions involving the succinoylation of *tert*-butylcymantrene, leading to the synthesis of a series of compounds in which the substituted Cp ring has been condensed with the tetramethylene ring, were investigated in the same studies.[78,79]

The mononuclear ketones $(\mathbf{Mn})C(O)CH_2X$, the dinuclear ketones $(\mathbf{Mn})C(O)CH_2XCH_2C(O)(\mathbf{Mn})$, and their ferrocene analogues (X = residues with thiolan and thiolene 1,1-dioxide groups) have been obtained by acylating cymantrene and ferrocene with the acid chlorides $XCH_2C(O)Cl$ and the acid dichlorides $ClC(O)CH_2XCH_2C(O)Cl$.[80]

The reaction involving metallation with butyllithium,[81,82] which proceeds via two pathways depending on the conditions (temperature, solvent), is undoubtedly of greatest importance for the synthetic chemistry of cymantrene. In tetrahydrofuran (THF) or in THF–hexane mixtures at temperatures between −50 °C and −70 °C, the Cp ring is metallated with formation of only the monolithio-derivative.

$$C_5H_5Mn(CO)_3 + BuLi \longrightarrow LiC_5H_4Mn(CO)_3 + BuH.$$

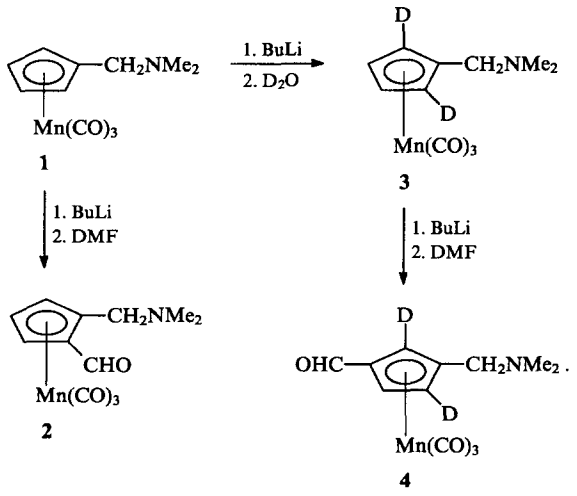
It has been established that, like phenyllithium, cymantrenyl-lithium is unstable in THF: the highest yield of the acid $(\mathbf{Mn})COOH$ (up to 70%–75%) is obtained only when the reaction with CO_2 is carried out 5–15 min after adding butyllithium. On the other hand, if the reaction mass is kept at −60 °C for 1–1.5 h and CO_2 is then added, the yield falls

appreciably.[83] A wide variety of complexes, which are difficult to obtain or are altogether unobtainable by other methods, including compounds with the (Mn)—M, (Mn)—B, etc. bonds, have been obtained via cymantrenyllithium.[1,83]

Under other conditions (ether, 20 °C), cymantrene reacts with various RLi (R = alkyl, Ph), in which the carbon atom of the carbonyl group is subjected to nucleophilic attack by R^- with formation of oxo-derivatives, the alkylation of which with trialkyloxonium salts leads to carbene complexes (classical Fischer synthesis of carbene complexes).[84]

$$C_5H_5Mn(CO)_3 \xrightarrow{RLi} C_5H_5Mn(CO)_2C(R)O^-Li^+ \xrightarrow{Me_3O^+BF_4^-} C_5H_5Mn(CO)_2{=}C(R)OMe.$$

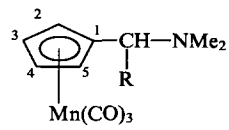
The reaction of cymantrenyllithium (Mn)Li with dimethylformamide leads to the formation of cymantrenecarbaldehyde (Mn)CHO.[85–87] The oxime (Mn)CH=N(OH) has been synthesised from the aldehyde and hydroxylamine in HCOOH. Its dehydration affords the nitrile (Mn)CN, which had been obtained previously by other methods.[1] The interaction of the aldehyde (Mn)CHO with dimethylformamide (DMF) on refluxing in HCOOH (the Leuckart—Wallach reaction) leads to the formation of dimethylaminomethylcymantrene **1**, the metallation of which with butyllithium takes place stereoselectively, the α-positions being metallated to the extent of 97%.[87]



After the decomposition of the lithio-derivative of the amine **1** with DMF, the 2-aldehyde **2** was obtained and after treatment with D_2O the product was 2,5-dideuteriodimethylaminomethylcymantrene **3**. However, if the amine **3**, where both α-positions contain C—D bonds, is metallated, then a mixture of aldehydes containing 30% of the 2-aldehyde and 70% of the 3-aldehyde **4** is obtained after treatment with DMF. Thus, when hydrogen is replaced by deuterium in the α-position in the amine **1**, the site of attack by butyllithium and the mode of substitution in the Cp ring are altered, i.e. the kinetic isotope effect in the metallation reaction (the ratio of the rates of reaction involving the C—H and C—D bonds) should be very large.[87] The fact that, when an attempt is made to metallate the 2,5-dideuterioamine **3** (with subsequent decomposition of the lithio-derivative with H_2O), deuterium is hardly removed from the α-position in the Cp ring agrees with the above finding.

The regioselectivity of the metallation of the amine **1** (the α-position is metallated exclusively) is apparently associated with the presence of the lone electron pair at the nitrogen atom to which lithium may coordinate. If this electron pair is blocked, as in the complex (Mn)$CH_2NMe_2W(CO)_5$, then metallation with butyllithium proceeds nonselectively and virtually to equal extents in the α- and β-positions.[88]

In the metallation of the chiral alkylamines **5** followed by decomposition with D_2O, the insertion of deuterium is also regioselective, and 2- and 5-positions being 75%—80% methylated.



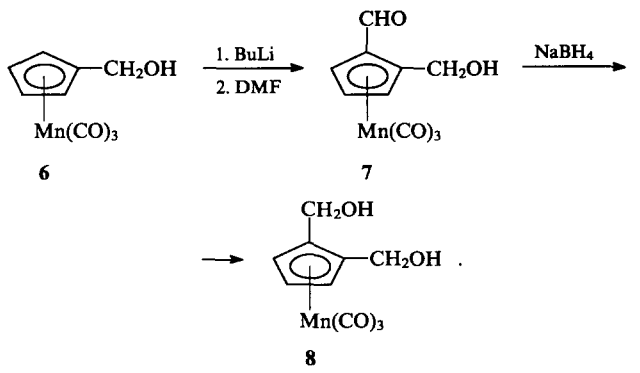
5

R = Me, Et.

Stereochemical induction takes place in the metallation of the amines **5**: substitution in the 2- and 5-positions is unequal, the ratio of the substitution products amounting to 65 : 35 (R = Me) and 95 : 5 (R = Et).[89] The protons and the carbon nuclei in the 2- and 5- (and also 3- and 4-) positions in the amines **5** are diastereotopic and give rise to four different signals in the ^1H and ^{13}C NMR spectra, as in those of the cymantrene derivatives containing a chiral centre in the side chain, which were investigated previously.[90,91]

The mode of substitution in the metallation of cymantrene derivatives has been investigated also for several substituents. In the case of R = Me, metallation takes place nonselectively—simultaneously in the α- and β-positions (the product ratio is 1 : 1.5).[92] However, the metallation of the carbinol (Mn)CH_2OH, obtained by reducing cymantrenecarbaldehyde with $NaBH_4$,[93] and also of the sulfonamide derivative (Mn)SO_2NMe_2 [94] proceeds regioselectively and only in the α-position. On the other hand, the metallation of diphenylphosphinocymantrene (Mn)PPh_2 as well as diphenylphosphinomethylcymantrene (Mn)CH_2PPh_2 also takes place stereoselectively but only in the β-position.[93,95] Apparently, in the metallation of the carbinol (Mn)CH_2OH **6**, the hydrogen atom in the OH group is initially replaced by lithium, and the lithium cation may remain bound to the oligomeric structure of butyllithium, which facilitates the abstraction of a proton, on treatment with a second molecule of butyllithium, and subsequent substitution in the nearest α-position. The directing influence of the amino-groups in the metallation of amines is most probably induced by the coordination of lithium via the nitrogen atom. The direction of the methylation reaction to the α-position in the case of the SO_2NMe_2 substituent may be associated both with the coordination of lithium to the nitrogen of the sulfonamide group and with the pronounced electron-accepting properties of this group, which are manifested more effectively precisely in the α-position adjoining the substituent. The direction of the substitution reaction to the more remote β-position in the case of the bulky substituents PPh_2 and CH_2PPh_2 is most probably associated with steric effects. Thus the metallation of monosubstituted derivatives constitutes a general method of synthesis of 1,2- and 1,3-disubstituted cymantrene derivatives, while methylation of diphenylphosphinocymantrenes represents the only method in the selective synthesis of 1,3-disubstituted compounds among metallocenes.[92–95]

The capacity of the carbinol **6** for selective metallation in the α-position made it possible to achieve the syntheses of a series of 1,2-disubstituted cymantrene derivatives. Carboxylation of the lithio-derivative of the carbinol **6** afforded 2-hydroxymethylcymantrenecarboxylic acid and reduction of the latter by the ionic hydrogenation method gave rise to 2-methylcymantrenecarboxylic acid.[92] Metallation of the carbinol **6** followed by decomposition with DMF affords the aldehydoalcohol **7**, the reduction of which with $NaBH_4$ leads to 1,2-dihydroxymethylcymantrene **8**.



Substitution of the hydroxy-groups in the diol **8** by Cl or Br on treatment with gaseous hydrogen halides leads to the corresponding 1,2-di(chloromethyl)- or 1,2-di(bromomethyl)-cymantrene. Oxidation of the diol **8** with manganese dioxide affords 1,2-diformylcymantrene, which is also obtained on oxidation of compound **7**.[96]

The interaction of (**Mn**)Li with benzopyridines and their *N*-acyl derivatives has been investigated.[97]

Other substitution reactions, apart from acylation and metallation with butyllithium, have been investigated in lesser detail. After the pioneering work by Cais on the sulfonation of cymantrene,[98] only two studies were published in which it was shown that the sulfonation of methylcymantrene proceeds nonselectively and leads to a mixture of 1,2- and 1,3-isomers.[77,99] Cymantrenesulfonic acids can be conveniently isolated in the form of readily crystallising salts with *p*-toluidine or *p*-chloroaniline. These salts serve as the starting materials for the synthesis of compounds with C_5H_4-S bonds. The sulfonyl chloride (**Mn**)SO_2Cl, obtained on treatment with PCl_5, is reduced with zinc dust to the thiol (**Mn**)SH, which can be extremely readily oxidised to the disulfide (**Mn**)SS(**Mn**).[76,100] Methylcymantrenesulfonic acids react similarly.[77,99] 1,2- and 1,3-Di(methylthiomethyl)cymantrenes were synthesised from 1,2- and 1,3-di(mercaptomethyl)derivatives by methylation with diazomethane.[99] The synthesis of the disulfide $[(CO)_3MnC_5Cl_4S]_2$ has been described.[43]

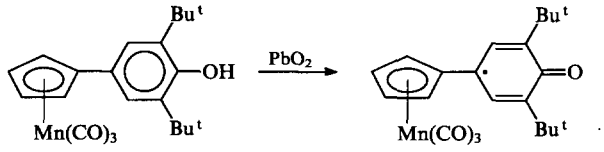
The mercuration of cymantrene with mercury acetate leads to the substitution of one and to a slight extent also two hydrogen atoms of the Cp ring. Early studies on the synthesis and properties of the mercurio-derivatives of cymantrenes were described in a review.[1] The interaction of cymantrene with mercury trifluoroacetate, a powerful mercurating agent, entails exhaustive mercuration with substitution of all five hydrogen atoms and the formation of $C_5(HgOCOCF_3)_5Mn(CO)_3$.[101] We may note that the reaction involving the cyclopalladation of amines, which has been thoroughly developed for ferrocene, has not been investigated in the cymantrene series.

A large series of studies on the hydrogen isotope exchange (HIE) reactions involving metallocenes (ferrocene, ruthenocene, cymantrene and its rhenium analogue, and benchrotrene) were carried out in the 1960s – 1970s. All these complexes enter into the HIE reactions with both acids and bases. Extensive experimental data on the HIE reactions involving cymantrene and its derivatives have been published in reviews.[102–104] A mechanism involving the protonation of the transition metal atom (Fe, Mn, Re, Cr) and subsequent migration of the proton to the π-linked ligand has been proposed for HIE reactions in the presence of acids.

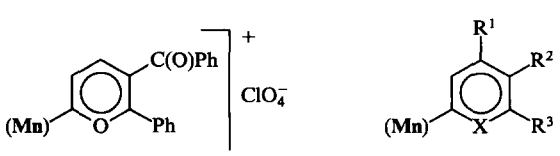
Isotope exchange in the presence of bases, for example in the alcohol – sodium alkoxide and cyclohexylamine – lithium, sodium, potassium, etc. cyclohexylamide systems, as well as metallation with butyllithium are protophilic substitution reactions in which the rate-determining stage is the abstraction of a proton from the Cp ring by the base. For example, measurements of the kinetic isotope effects in the HIE reactions in basic media agree with this postulate. On the other hand, the mechanism of the isotope exchange with acids cannot be regarded as reliably established. For reactions with electrophiles, a special case of which is the hydrogen isotope exchange with acids, two mechanisms are possible. The first involves the attack by the reagent on the Cp ring, while the second involves the attack on the metal with subsequent migration of the electrophile to the Cp ring (the so called 'ricochet' substitution mechanism proposed at an early stage by A N Nesmeyanov). The hydrogen isotope exchange in the reactions of cymantrenylferrocene with acids has been investigated[105] and the acidity of the C – H bonds in the Cp ring of cymantrene and its derivatives in the HIE in alkaline media has been determined by a kinetic method.[106,107]

In addition to the early studies[1] concerned with the preparation of a wide variety of cymantrene derivatives, mention may be made of syntheses the majority of which have been carried out through cymantrenyllithium. In this connection, we may mention that, in contrast to benzene derivatives, for the syntheses of which both organolithium and organomagnesium compounds are equally widely employed, in the cymantrene chemistry the corresponding Grignard reagent, namely (**Mn**)MgI formed in a moderate yield from (**Mn**)I and magnesium,[76] is used extremely rarely.

The attack on the keto-group in the 4-position in the interaction of (**Mn**)Li with 2,5-di(*tert*-butyl)-1,4-quinone results in the formation of a carbinol, the Clemmensen reduction of which leads to the cymantrenylphenol **9**. The oxidation of the latter with PbO_2 affords the free-radical complex **10**, which has been characterised by EPR spectroscopy.[108]



A series of studies[109–113] have been devoted to the synthesis of pyryllium salts containing cymantrenyl substituents. The reaction of β-chloro-β-cymantrenylacrolein and dibenzoylmethane in $MeCOOH/HClO_4$ with acetic anhydride led to the formation of the cation **11**, the reactions of which with copper and cobalt acetates afford the bimetallic copper and cobalt β-keto-pyranolates.[109] The cyclisation of acetylcymantrene with α,β-unsaturated ketones $R^1CH=CR^2C(O)R^3$ in a mixture of acetic and perchloric acids gives rise to the tetrasubstituted pyryllium salts **12** with R^1-R^3 = Ph, $MeOC_6H_4$, etc. On treatment with ammonia and aniline, they are converted into the corresponding pyridines.[110]



Cymantrenyllithium (**Mn**)Li and 2,5-disubstituted pyryllium salts afford 4*H*-pyrans, the abstraction of a hydride ion from which on treatment with $Ph_3C^+ClO_4^-$ leads to the formation of pyryllium salts with the cymantrenyl substituent in the 4-position.[111] The reaction of acetylcymantrene with orthoformic ester in the presence of 70% $HClO_4$ affords 2,6-dicymantrenyl-pyryllium perchlorate, which, on refluxing in ethanol, reacts with $PdCl_2$ in the presence of Na_2CO_3 with cleavage of the pyryllium ring and the formation of the bis-η^3-allyl complex of palladium with perchlorate bridges. The reaction of the latter with CpTl in

acetonitrile leads to the rupture of the dimeric structure and the formation of the allyl complex (η^3-RCH···CH···CHR)PdCp, where R = $(CO)_3MnC_5H_4C(O)$.[112] The electrochemical properties of pyryllium salts with cymantrenyl substituents have been described.[113].

A series of studies have been devoted to the chemistry of thioketones of the cymantrene series. Benzoylcymantrene reacts with P_4S_{10} in CS_2 in the presence of the base $NaHCO_3$ to form the thioketone (**Mn**)C(S)Ph.[114] The latter is readily coordinated by the 16-electron fragments ML_n [ML_n = $W(CO)_5$, $Mn(CO)_2Cp$, etc.], forming dinuclear complexes of the type (**Mn**)(Ph)C=S →ML_n, in which the cymantrenyl thioketone is a two-electron ligand.[115] The structure of the dinuclear complex where ML_n = $Mn(CO)_2Cp$, was established by X-ray diffraction.[116] Reversible temperature variations have been noted in the ^1H and ^{13}C NMR spectra. It follows from them that in solution the complex exists as a mixture of (*E*)- and (*Z*)-isomers with different dispositions of the manganese-containing fragments relative to the C=S bond. The barriers to rotation about his bond, determined from the NMR data, amount to 12.4–13.0 kcal mol^{-1}.[116,117] The thioketone (**Mn**)(Ph)C=S reacts with the anions Cp^- or $CpFe(CO)_2^-$ to form initially phenyl(cymantrenyl)fulvene, which rapidly dimerises under the reaction conditions via a diene synthesis type of reaction or enters into a cycloaddition reaction via the C=S bond.[118] The formation of the dimer is reversible: on interaction of the dimer with $Cr(CO)_6$, it dissociates to the monomer, which affords the complex [η^6-C_4H_4C=C(Ph)(**Mn**)]$Cr(CO)_3$ in which the Cr atom is coordinated to the three C=C bonds of cymantrenylfulvene.[119]

Cymantrenylthioketones are reactive compounds. Thus, on being kept in air (at 25 °C, 20 days), the thioketone (**Mn**)C(S)Me is converted into a complex mixture of products, from which biscymantrenyl derivatives with trithiolan and dithietan rings, characterised by X-ray diffraction, were isolated.[120]

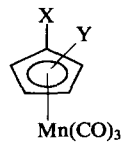
Among the numerous studies on the synthesis of various organic and heterocyclic compounds with a cymantrenyl substituent, one may distinguish the syntheses of cymantrenyl analogues of mandelic acid[121] and alanine[122] as well as cymantrenylthioglycolic acid.[100] Carbinols containing the $SiMe_3$ group have been obtained by the reactions of acetylcymantrene and benzoylcymantrene with the Grignard reagents Me_3SiCH_2MgCl and $Me_3SiC_6H_4MgBr$.[123] The syntheses and reactions of dihydric alcohols in the acetylene series of the type (**Mn**)C(OH)(R)C≡CC(OH)R^1R^2 have been studied.[124–126]

A series of cymantrenyl vinyl ketones (cymantrenyl analogues of chalcones) having the general formula (**Mn**)CH=CHC(O)R, where R = phenyl, cymantrenyl, ferrocenyl, and vinylcymantrene or vinylferrocene residues, have been obtained by condensing formylcymantrene with the ketones MeC(O)R.[127] These compounds readily enter into cyclisation reactions with hydrazine, forming relatively unstable pyrazolines, the acylation of which affords the more stable *N*-acetyl derivatives.[128] Condensation of the pyrazolines with benzaldehydes gives rise to 4-benzylidenepyrazolines.[129,130] Catalytic pyrolysis of cymantrenylpyrazolines results in the formation of cymantrenylcyclopropanes, including dicymantrenylcyclopropanes.[129–132] This reaction is nonselective and gives rise to mixtures of the *cis*- and *trans*-isomers of the substituted cyclopropanes.

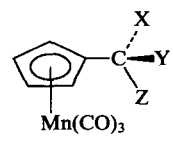
In reactions with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, cymantrenyl vinyl ketones form mixtures of heterodiene complexes of iron tricarbonyl and olefin derivatives of iron tetracarbonyl in which the diene or olefin ligand contains the cymantrenyl substituent.[133,134] The reaction of ferrocenylideneacetylcymantrene with MeMgI affords a mixture of the substituted allyl alcohol FcCH=C(OH)Me(**Mn**) and the ketone FcCHMeCH$_2$C(O)(**Mn**).[135] Cymantrenyl vinyl ketones and their complexes with $Fe(CO)_3$ are protonated on treatment with CF_3COOH at the oxygen atom of the carbonyl group with formation of cations of the allyl type.[136,137] A reaction involving the addition of dimethyl malonate to cymantrenyl vinyl ketones has been described.[138]

IV. Chiral derivatives of cymantrene

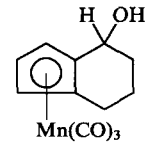
Two types of chiral derivatives of cymantrene are known. The structural characteristics of metallocenes as well as compounds containing one planar cyclic ligand (C_5H_5, C_6H_6, etc.), linked to a $M(CO)_3$ fragment, are such that, when the ring contains two different substituents, these molecules become chiral. Accordingly, disubstituted cymantrene derivatives are planarly chiral (type **A**) regardless of whether the two different substituents occupy the 1,2- or 1,3-positions. The second type of chiral derivatives consists of compounds containing a chiral centre in the α- or more remote position in the side chain (type **B**). Compounds containing simultaneously both elements of chirality, in particular the carbinol **13** and its analogues, have been obtained.



A



B

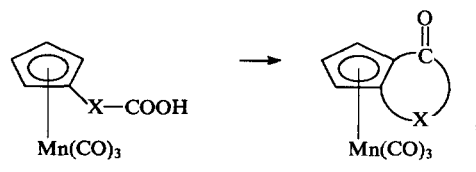


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The first studies on the stereochemistry of cymantrene derivatives were carried out on compounds with planar chirality, mainly on a series of different derivatives of methylcymantrene. As early as 1961, 2- and 3-methylcymantrenecarboxylic acids, obtained by acylating methylcymantrene and then oxidising with iodine the mixture of ketones (2- and 3-methylacetylcymantrenes), were resolved into the enantiomers.[139] Systematic study of the stereochemistry of the cymantrene derivatives was begun in the middle of the 1960s. Schlögl and his group[140–143] synthesised, resolved into enantiomers, investigated the chirooptical properties, and established the absolute configurations of a series of derivatives of methylcymantrene [C_5H_3(R)Me]$Mn(CO)_3$, where R = COOH, C(O)Cl, $C(O)N_3$, Na_2, Cl, Br, I, NCO, etc.] and also cymantrenylbutyric acids and methylcymantrenylcyclohexa-1,2-dienes, obtained by succinoylating methylcymantrene with succinic anhydride and subsequent cyclisation (see also Schlögl[144,145]).

Studies on the synthesis, resolution into enantiomers, and the determination of the absolute configurations of 1-methyl-2-cymantrenyl- and 1-methyl-3-cymantrenylpropionic and 1-methyl-2-cymantrenyl- and 1-methyl-3-cymantrenyldimethylpropionic acids were carried out at the beginning of the 1970s.[146–149]

All the known planarly chiral derivatives of cymantrene have been obtained in one way — by introducing the second substituent into monosubstituted cymantrenes. Since the acylation reaction is nonselective, mixtures of the 1,2- and 1,3-isomers of different ketones of the cymantrene series are always formed (see the table in the relevant review[1]) with the sterically less hindered 1,3-isomers predominating. In order to separate the mixtures, laborious chromatographic separation procedures have to be resorted to.



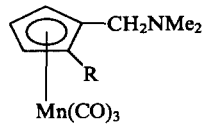
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X = SCH_2,[76] CH_2CH_2,[150] $CH_2CH_2CH_2$ [151].

One of the methods of selective introduction of the second substituent in the 2-position involves the intramolecular acylation of monosubstituted acids and their chlorides, which leads to the 1,2-isomers of cymantrenyl ketones with a condensed polymethylene ring.[76,150,151]

When the keto-group is reduced to the CH(OH) fragment by $NaBH_4$ or $LiAlH_4$, a chiral centre arises in the α-position and diastereoisomers containing two elements of chirality — the plane and the centre — are formed.[152]

Metallation of monosubstituted derivatives of cymantrene has been used widely in recent times for the synthesis of planarly chiral cymantrene derivatives with substituents in the 1- and 2-positions. This reaction is based on the fact that, for certain substituents containing a heteroatom with a lone electron pair, such as CH_2NMe_2 and CH_2OH, metallation is regioselective and proceeds almost exclusively only in the position adjoining the substituent. Metallation of dimethylaminomethylcymantrene followed by treatment with electrophiles afforded the 1,2-disubstituted cymantrenes **14a–c**.[87,93]

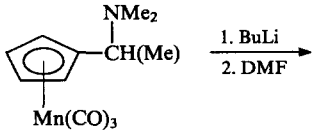


14a–c

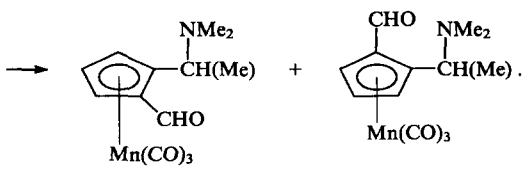
R = D (**a**), CHO (**b**), PPh_2 (**c**).

Stable Cu^{2+} complexes with Schiff bases, obtained from the aminoaldehyde **14b** and chiral dipeptides, have been proposed for the resolution of the racemic aminoaldehyde **14b** into enantiomers. The copper complexes are mixtures of diastereoisomers, which were resolved by extraction and liquid chromatographic methods. Acid hydrolysis of the diastereoisomers affords the optically pure enantiomers of the aldehyde **14b**.[153–156] The absolution configuration of one of them as well as the structure of the copper complex of the dipeptide Ala–Ala have been established by X-ray diffraction.[155,157]

Metallation of α-(*N*,*N*-dimethylamino)ethylcymantrene **15**, containing a chiral centre in the α-position, followed by treatment with dimethylformamide produced a mixture of two diastereoisomers of the aminoaldehyde **16** in proportions of 7:2 (asymmetric induction). The Cu^{2+} complexes obtained from the Schiff bases formed from these aldehydes and a different dipeptide were resolved by liquid chromatography. The enantiomers of the aldehyde **16**, the absolute configuration of one of which was established by X-ray diffraction,[159] were obtained from them by acid hydrolysis.[158]

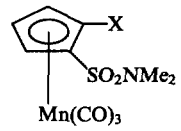


15



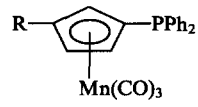
16

The regioselective metallation only in the α-position in cymantrene derivatives with the substituents R = CH_2OH [93] and SO_2NMe_2 [94] was noted above. A series of racemic 1,2-disubstituted complexes **17** [X = COOH, COOMe, CMe_2OH, CPh_2OH, CH(Ph)OH, etc.] have been obtained by the reactions of the lithio-derivative containing the sulfonamide group with electrophiles.[94]



17

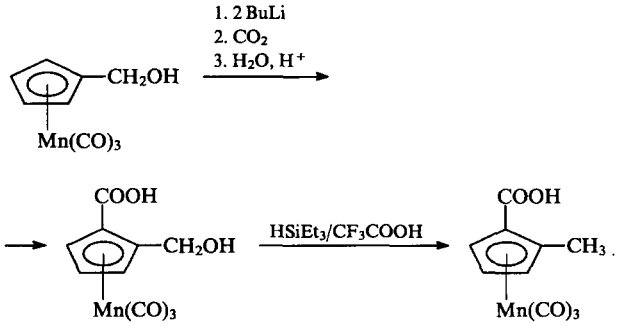
On the other hand, the metallation of the diphenylphosphino-derivative **(Mn)**PPh_2 also proceeds regioselectively but only in the β-position, which is evidently associated with steric factors. The reaction of the lithio-derivative of this phosphine with DMF and Ph_2PCl leads to the phosphinoaldehyde **18a** and 1,3-bis(diphenylphosphino)cymantrene **18b**. The dimethylaminomethyl derivative **18c** was obtained from the aldehyde in the reaction with DMF and HCOOH.[93]



18a–c

R = CHO (**a**), PPh_2 (**b**), CH_2NMe_2 (**c**).

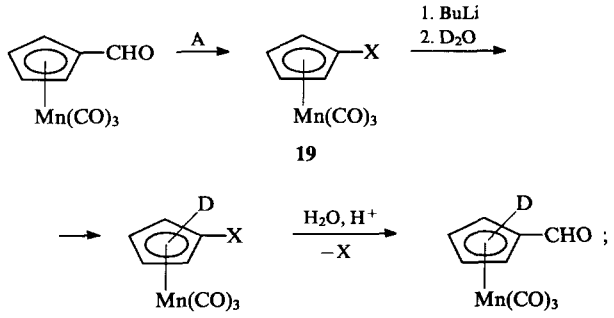
A method, based on the acylation of methylcymantrene with subsequent oxidation of the mixture of the resulting methylacetyl derivatives by iodine in pyridine and the separation by fractional recrystallisation and chromatography of the mixture of acids or their esters produced, was proposed previously for 2-methylcymantrene-1-carboxylic and 3-methylcymantrene-1-carboxylic acids.[141] As a result of the numerous stages in the synthesis, the yield of 2-methylcymantrene-1-carboxylic acid does not exceed 10%. An improved method of synthesis of 2-methylcymantrenecarboxylic acid, based on the stereoselective metallation of hydroxymethylcymantrene, obtained readily from cymantrenecarbaldehyde by reduction with $NaBH_4$ and EtOH,[93] has been developed recently.[92] The hydroxymethyl group was reduced to the methyl group by ionic hydrogenation in the Bu_2SiH_2/CF_3COOH system. The absolute configuration of 2-methylcymantrenecarboxylic acid was determined by chemical correlation with the aldehyde **14b**, the absolute configuration of which had been obtained earlier by X-ray diffraction.[155]

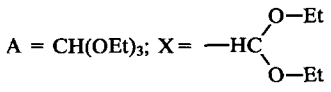


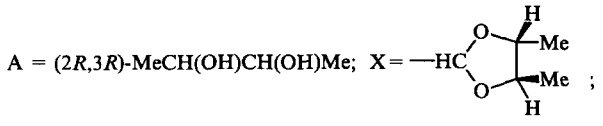
There are at present two methods of synthesis of optically active compounds of the cymantrene series with a planar chirality. The first of these is the classical resolution of racemates via the intermediate formation and separation of diastereoisomers.[141–143,155] The second method is based on the kinetically controlled enzymic reduction of disubstituted chiral and achiral compounds, one example of which has been described.[160] In each specific case, it is essential to select carefully the optimum reactants and resolution conditions.

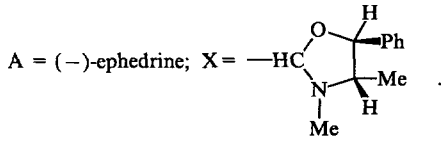
A new approach to the synthesis of optically active 1,2-disubstituted cymantrene derivatives with a planar chirality, based on the regioselective metallation of a series of new monosubstituted derivatives with butyllithium, has been

developed recently.[161-164] In this method, the initial achiral compound with a functional group substituent—cymantrenecarboxylic acid or cymantrenecarbaldehyde—is converted in a preliminary step into a chiral derivative with the aid of the optically active molecule of the inductor **A**. This is followed by the stage in which the second substituent is introduced—usually metallation with butyllithium and treatment with the appropriate reagents (D_2O, CO_2, etc.). In the third stage, the inductor molecule is removed from the diastereoisomeric product by acid hydrolysis.



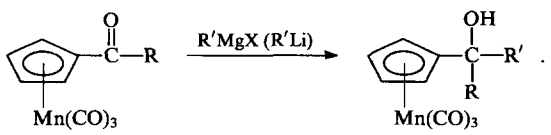






Metallation of compounds **19** by treatment with BuLi proceeded exclusively at the CH positions of the Cp ring, whereupon the regioselectivity of the process depends on the nature of the reagent **A**.[161,162] (−)-Norephedrine, (−)-2-aminobutanol, (*R*)-phenylethanediol, and (*S*)-prolinol may be used as the inductor molecules **A**.[162,163] This approach has been used to synthesise the enantiomers of 2-methylcymantrene-1-carboxylic and 3-methylcymantrene-1-carboxylic acids.[161] By virtue of the extensive possibilities of the metallation reaction, this method makes it possible to obtain directly the enantiomers of planarly chiral compounds with a wide set of substituents. Compounds containing two elements of chirality—the chiral centre at the metal atom and the chiral plane—have been obtained by substituting two CO groups in 3-methylcymantrenecarboxylic acid and its esters by various phosphine ligands.[165,166]

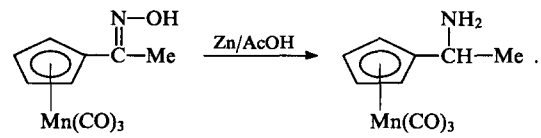
Cymantrene derivatives with a chiral centre in the side chain are usually obtained by forming this centre from a prochiral fragment already available. A typical example is provided by the synthesis of secondary and tertiary carbinols from ketones.[167,168]



In the case of cymantrenyl methyl ketones, it has been shown that the reduction of the 1,2-isomers proceeds with a high degree of stereoselectivity, whereas the selectivity for the 1,3-isomers is much lower.[169] The stereoselectivity in organomagnesium synthesis is fairly high, the proportions of the enantiomers depending significantly on the nature of the groups R and R'. Similar reactions for a ketone with a condensed polymethylene ring have been investigated.[152] Chiral carbinols of the cymantrene series can be converted into other chiral derivatives (esters, azides, nitriles, amines, etc.) by esterification and nucleophilic substitution reactions.

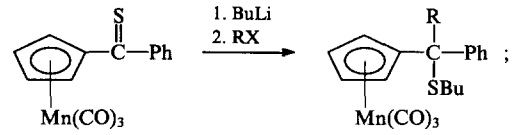
In certain cases, asymmetric synthesis has been used to obtain optically active cymantrene derivatives with a chiral centre. In the reduction of acetyl- and benzoyl-cymantrenes by a complex of lithium tetrahydroaluminate and quinine, the corresponding carbinols are formed, but their optical yield does not exceed 10%–15%.[169]

Yet another example of the formation of a chiral centre involves the reduction of ketone oximes to primary amines.[170]



The racemic α-aminoethylcymantrene synthesised in this way was resolved into enantiomers by crystallising the salts with (+)-*d*-tartaric acid. α-Dimethylaminoethylcymantrene (**Mn**)CH(Me)NMe_2, its methiodide (**Mn**)CH(Me)$^+NMe_3I^-$, and the acetamido-derivative (**Mn**)CH(Me)NHC(O)Me have been obtained from this amine. The absolute configuration of the acetamido-derivative was established by X-ray diffraction.[170] Subsequently 14 optically active derivatives of aminocymantrenes having the general formula (**Mn**)CH(Me)X [X = NH_2, NHCHO, NHMe, $NHCH_2Ph$, $NHCH_2$(**Mn**), N_3] as well as the Schiff bases (**Mn**)CH(Me)N=CHPh, (**Mn**)CH(Me)N=CH(**Mn**), etc. were synthesised and their chirooptical properties were investigated.[171] The reactions of the optically active (+)-α-phenylethylamine with (**Mn**)CH_2Cl, (**Mn**)C(O)Cl, and (**Mn**)CHO, which resulted in the synthesis of the corresponding compounds with a chiral centre in the β-position in the side chain, have been described.[172] As for compounds with the chiral centre in the α-position, the protons and carbon nuclei in the 2,5- and 3,4-positions are diastereotopic and give rise to different signals in the ^1H and ^{13}C NMR spectra.

The reaction of the thioketone (**Mn**)(Ph)C=S with butyllithium follows the so called 'thiophilic' path with metallation of the sulfur atom. Treatment of the reaction product with electrophiles afforded the previously unknown metallocenyl sulfides with the chiral centre in the α-position.[173]

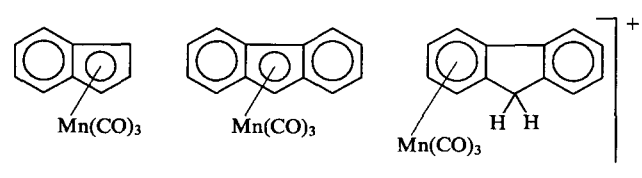


R = H, D, Me .

V. Complexes with polycyclic ligands and polynuclear derivatives of cymantrene

The synthesis and properties of the complexes of $Mn(CO)_3$ with indene, fluorene, and related compounds, in which the Cp ligand is part of a more complex cyclic system, are considered below.

If the ligand contains simultaneously five- and six-membered rings, there is a possibility of two types of coordination of the



20 **21** **22**

$Mn(CO)_3$ fragment. The η^5-type of coordination affords the neutral compounds **20** and **21**, containing the indenyl or fluorenyl ligands. The cationic complex **22**, in which the $Mn(CO)_3$ residue is η^6-linked to the cyclic ligand, is also known.

Metallotropic rearrangements, in which the $Mn(CO)_3$ fragment migrates from the five- to the six-membered ring and conversely, are characteristic of the indenyl and fluorenyl complexes.

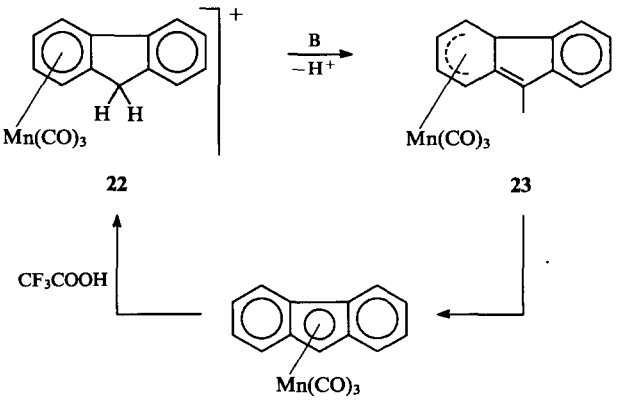
Complexes **20** and **21** were first obtained by the reaction of $Mn(CO)_5Br$ with indenyl- and fluorenyl-sodium (in 56% and 11% yields)[174] or with the $SnMe_3$ derivatives of indene and fluorene (in 62% and 20% yields).[175] An improved method of their synthesis by the reactions of $Mn(CO)_3(MeCN)_2$ with indenyl- or fluorenyl-potassium was developed subsequently.[176] The indenyl complexes of manganese and rhenium can also be obtained by direct synthesis in yields up to 90% on refluxing the decacarbonyls $M_2(CO)_{10}$ in an excess of indene as the solvent.[177]

The CO groups in complexes **20** and **21** undergo photochemical substitution by PPh_3, $AsPh_3$, and $SbPh_3$,[174] but, in contrast to cymantrene, in these compounds there is a possibility of not only photochemical but also of thermal substitution of CO by phosphines and phosphites. In the study of the kinetics of the thermal substitution of CO (decalin, 200 °C), an appreciable increase in the rate of reaction in the sequence $C_5H_5 < C_9H_7 < C_{13}H_9$ was noted.[178,179] These reactions are second order overall and first order with respect to the complex and the ligand; an associative mechanism has been proposed for them with the formation of an η^3-intermediate. In the photochemical substitution of CO by PPh_3, such an effect was not observed, which indicates a dissociative process mechanism.[180] A CO group in complex **20** can be substituted by NO with formation of the cation $(\eta^5\text{-}C_9H_7)Mn(CO)_2(NO)^+$.[176] The cationic complex $(\eta^5\text{-}C_9H_7)Mn(CO)(NO)(PPh_3)^+$, chiral with respect to the Mn atom, has also been obtained.[181] Its interaction with the anions $X^- = Br^-$, I^-, or CN^- involves the ready cleavage of the Mn–C(Cp) bond with the removal of the indenyl ligand and the formation of the complexes $Mn(NO)_2(PPh_3)_2X$.[181]

A series of studies on the hydrogen substitution reactions in the indenyl and fluorenyl ligands were carried out in the 1980s. In the reaction of $(\eta^5\text{-}C_9H_7)Mn(CO)_3$ with an excess of $MeC(O)Cl/AlCl_3$, acetylation takes place simultaneously both in the five- and six-membered rings, the ratio of the isomers depending significantly on the reaction conditions.[182] It has been shown by the competitive acylation method that the reactivity of the indenyl ligand is higher than that of the cyclopentadienyl ligand. In the case of $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$, acylation takes place only in the six-membered ring and is accompanied by the cleavage of the Mn–η^5-ligand bond.[183] Apart from the 2-acetyl derivative, 2-acetylfluorene and fluorenone were also isolated. The appreciably lower strength of the bond between the η^5-ligand and $Mn(CO)_3$ in $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ compared with $(\eta^5\text{-}C_9H_7)Mn(CO)_3$ agrees with the mass-spectrometric data on the strength of the corresponding bonds in the gas phase.[184] The acylation of $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ led to the isolation and characterisation by X-ray diffraction also of the products of the partial hydrogenation of one of the six-membered rings.[185]

In the isotope exchange of hydrogen in the $CF_3COOD/D_2SO_4/CH_2Cl_2$ system, H is substituted by D in both rings of the $\eta^5\text{-}C_9H_7$ ligand, although the substitution in the five-membered ring predominates.[183] The complex $(\eta^5\text{-}C_9H_7)Mn(CO)_3$ can be metallated by butyllithium in THF at −40 °C, but the reaction proceeds nonselectively and a mixture of the 1- and 2-isomers containing lithium in the five-membered ring is formed.[186] Competitive metallation of a mixture of $(C_9H_7)Mn(CO)_3$ and $(C_{13}H_9)Mn(CO)_3$ has shown that the indenyl ligand is more reactive.[187]

Metallotropic rearrangements are very characteristic of the indenyl and fluorenyl derivatives of manganese and rhenium. The reaction of fluorene with $Mn(CO)_5Br$ (refluxing in hexane) afforded the cationic complex **22**. Its deprotonation by bases (Bu^tOK, MeONa, NEt_3, etc.) gives rise to the neutral complex **23**, which on heating or storage in the solid state is converted into the thermodynamically more stable complex **21** as a result of the $\eta^6 \rightarrow \eta^5$ rearrangement.[188]



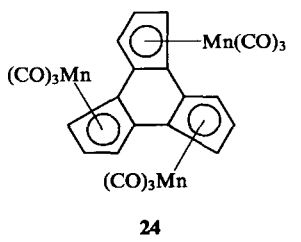
22 **23** **21**

It has been established by X-ray diffraction that complex **23** has a structure typical for cyclohexadineyl derivatives.[189] Quantum-chemical calculations for the $\eta^6 \rightarrow \eta^5$ rearrangement of fluorenyl complexes have shown[190] that the η^6-isomer is less stable (by ~7 kcal mol^{-1})† than the η^5-isomer, while the activation energy for the rearrangement via the η^3-intermediate is 25 kcal mol^{-1}. Kinetic studies on $\eta^6 \rightarrow \eta^5$ rearrangements for the fluorenyl complexes $(\eta^6\text{-}C_{13}H_9)Mn(CO)_2L$ (L = CO or PBu_3) confirmed the results of the calculations.[191]

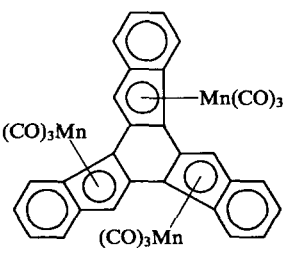
The reverse $\eta^5 \rightarrow \eta^6$ rearrangement has been observed in the study of the protonation of complex **21** in the presence of CF_3COOH.[192] It has been suggested that the acid proton adds directly to the fluorenyl ligand. In the η^5-indenyl complexes of manganese and rhenium, the analogous $\eta^5 \rightarrow \eta^6$ rearrangements take place (according to Ezernitskaya et al.[193]) only in the presence of stronger acids HSO_3F and $AlCl_3$ + HCl. In the complexes with phosphine ligands $(\eta^5\text{-}C_9H_7)Mn(CO)_2PPh_3$ and $(\eta^5\text{-}C_{13}H_9)Mn(CO)_2PPh_3$, the basicity of the central metal atom is greater than the basicity in the tricarbonyl complexes and in the presence of CF_3COOH only protonation at the Mn atom takes place and there is no metallotropic rearrangement..

The $\eta^5 \rightarrow \eta^1$ rearrangement of the fluorenyl ligand has been observed in the reaction of $(\eta^5\text{-}C_{13}H_9)Mn(CO)_3$ with an excess of PBu_3.[179] In a later study,[194] the complex $(\eta^1\text{-}C_{13}H_9)Mn(CO)_3(PEt_3)_2$ was isolated and characterised by a set of spectroscopic methods.

The properties of the indenyl and fluorenyl complexes of manganese and other transition metals have been examined in detail in a review.[195] Communications concerning the study of the metallotropic rearrangements of the manganese tricarbonyl complexes with other polycyclic hydrocarbons, such as fluoradene[196] and 9,10-dihydro-9-methylindeno[1,2-*a*]indene and its analogues,[197,198] have appeared recently. The structure of the dinuclear complex $(\eta^5,\eta^5\text{-}L)Mn_2(CO)_6$, where L = 3,5-dimethylazulene, has been established by X-ray diffraction.[199]



24



25

† 1 kcal = 4.18 kJ.

Bismanganese tricarbonyl complexes of *sym*- and *asym*- indacenes have been obtained[200,201] by the reaction of the corresponding biscyclopentadienyl anions with $Mn(CO)_5Br$ or $Mn(CO)_3Py_2Br$. The trismanganese tricarbonyl complex **24** has also been obtained recently[202] and complexes containing one and two $Mn(CO)_3$ residues as well as the triscomplex **25** have been synthesised from the hydrocarbon truxene.[203,204]

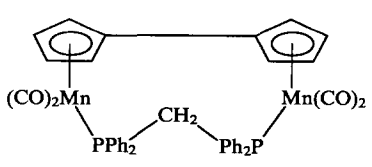
The simplest compound in which the two parts of the ligand are linked by a single C–C bond is the complex bicymantrenyl **(Mn)–(Mn)**. It was synthesised in 1969 by three groups of investigators simultaneously.[76,205,206] A compilation of different methods of its synthesis is given in Table 1. These methods for the reactions involve the oxidative coupling of two $(CO)_3MnC_5H_4$ fragments, formed when the Grignard reagent **(Mn)**MgI or **(Mn)**Li is acted upon by metal salts, and radical dimerisation reactions in the course of the pyrolysis of cymantrene metallo-derivatives [**(Mn)**Cu, **(Mn)**Ag, $(Mn)_2Hg$]. The optimised yield of bicymantrenyl in the reaction of **(Mn)**Li with carefully dehydrated $CuCl_2$ reaches up to 90%.[212]

Table 1. Syntheses of bicymantrenyl.

Initial compounds	Yield of cymantrenyl, (%)	Other reaction products	Ref.
$(Mn)AuPPh_3 + Cl_2$	72	(Mn)Cl	205
$(Mn)AuPPh_3 + Br_2$	33	(Mn)Br	205
(Mn)MgI + $CoCl_2$	30	–	76
	15	–	206
(Mn)Li + $CoCl_2$	13	–	206
(Mn)I + Cu[a]	21	–	206
$(Mn)_2Hg$ + Ag[a]	67	–	206, 207
(Mn)Cu + I_2	10	(Mn)I	208
$(Mn)B(OH)_2 + Cu(OAc)_2$	10	cymantrene	209
(Mn)Li + $CuBr_2$	52	–	210
(Mn)Li + $CuCl_2$	69	–	211
(Mn)Li + $CuCl_2$	90	–	212
(Mn)Cu + Br_2	50	–	211
(Mn)Ag + Br_2	23	–	211
$Mn(CO)_5Br$ + fulvalenedithallium	86	–	213

[a] Pyrolysis in the presence of metal powders.

Although bicymantrenyl has been known for more than 20 years, only one substitution reaction in the Cp ring has been described for this compound: acetylation with the MeC(O)Cl + $AlCl_3$ mixture, which proceeds in the 3-position.[207] Other substitution reactions, including metallation with BuLi, have not been investigated. As in cymantrene, the CO groups in one or simultaneously in two $Mn(CO)_3$ fragments can be substituted by n- and π-donor ligands (triphenylphosphine, ethylene, cyclooctene, dimethylacetylene, and pyridine) with formation of both mono- and di-substituted compounds. After the reaction of bicymantrenyl with the diphosphine $Ph_2PCH_2PPh_2$, complex **26** was isolated and characterised by X-ray diffraction. Because of the presence of the rigid chelate skeleton of the diphosphine, the coplanarity of the two Cp rings in complex **26** is significantly disturbed. Their planes form with one another a dihedral angle of 65°.[212]



26

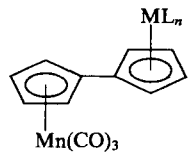
In the absence of steric hindrance, the similar bifulvalenyl system is known to be planar.

Cymantrenylferrocene[214] and a series of its derivatives[215–217] have been obtained by the thermal reaction of haloferrocenes with **(Mn)**Cu, **(Mn)**Ag, or $(Mn)_2CuAg$.

The properties of cymantrenylferrocene have been investigated in greater detail than those of bicymantrenyl.[217] Depending on the type of reagent, substitution takes place either in the ferrocene or in the cymantrenyl ring. Thus, on acetylation with acetic and anhydride in the presence of H_3PO_4, i.e. under mild conditions, the acetyl substituent enters the unsubstituted ferrocene ring. On the other hand, on treatment with BuLi the Cp ring in the cymantrene nucleus is metallated. The reaction of the lithio-derivative of cymantrenylferrocene with $B(OBu)_3$ affords after hydrolysis (3-ferrocenyl)cymantreneboronic acid, from which complexes with the Br or HgCl substituents in the cymantrenyl fragment were obtained after treatment with $CuBr_2$ or $HgCl_2$. The study of the hydrogen isotope exchange with acid showed that the introduction of the electron-accepting cymentrenyl substituent lowers the rate of exchange in the ferrocenyl nucleus approximately by an order of magnitude compared with the unsubstituted ferrocene.[105]

As a result of the coupling of the two metallocenyl fragments, the thermolysis of a mixture of the Ag derivative of dimethylaminomethylferrocene together with **(Mn)**Cu or **(Mn)**Ag at 120 °C afforded 2-(dimethylaminomethyl)-1-cymantrenylferrocene and a series of its derivatives.[218,219] The same complex is formed also by the oxidative coupling of a mixture of lithio-derivatives of dimethylaminomethylferrocene and cymantrene.[219]

A cymantrenylbenchrotrene complex has been obtained by the reaction of phenylcymantrene with $Cr(CO)_3(MeCN)_3$.[220] The interaction of $H_3Mn_3(CO)_{12}$ with azulene led to the isolation of a complex[221] in which two azulene nuclei are linked by a C–C bond in the 4–4′ positions; its structure was established by X-ray diffraction.[222] The heterodinuclear complexes **27** have been synthesised from the monometallic derivatives of difulvalene.[223]



27

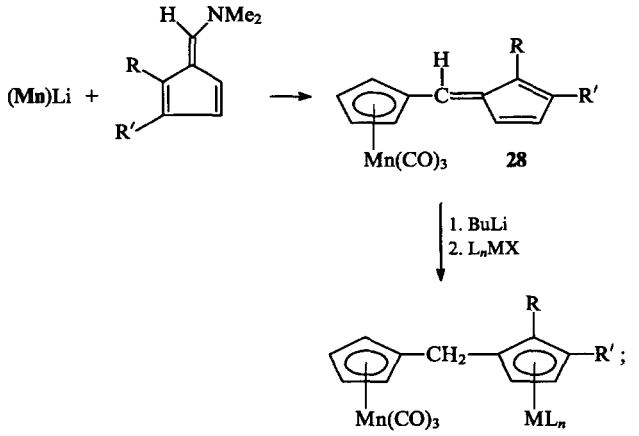
ML_n = $W(CO)_3$, $Mo(CO)(PMe_3)_2Me$.

In the compounds examined above, two identical or different metal-containing fragments are joined by a C–C bond. Together with these, a large number of compounds having the general formula **(Mn)**–X–ML_n, where the cymantrene residue is linked to another organometallic group ML_n via a carbon-containing fragment X [X = CO, CH_2, $C(O)CH_2$, etc.], have also been synthesised. The interaction of benzoylcymantrenes **(Mn)**$C(O)C_6H_4R$ or the ketone **(Mn)**$C(O)CH_2Ph$ and a series of its derivatives with $Cr(CO)_6$ on refluxing in diglyme led to the formation of the dinuclear complexes **(Mn)**–X–$C_6H_4RCr(CO)_3$, where X = CO, CH_2, CH_2CO, CHCH(OH), CH=CH, etc.[224] The dithallio-derivative of dicyclopentadienylmethane is a convenient precursor in the synthesis of various homo- and hetero-dinuclear complexes, including also dicymantrenyl-methane $(Mn)_2CH_2$.[225]

It has been suggested that 6-dimethylaminofulvene be used for the synthesis of heterodinuclear derivatives of cymantrene (Scheme 1).[226]

The comparatively ready availability of the intermediate **28**, the structure of which has been characterised by X-ray diffraction, opens a pathway to the synthesis of various dinuclear complexes

Scheme 1



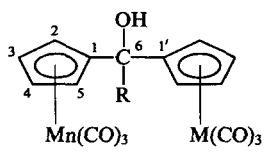
ML_n = $Co(CO)_2$, $Mo(CO)_3Br$.

with the $(Mn)CH_2$ fragment. The interaction of dimethylaminofulvene with indenyllithium and further with $(CO)_3Py_2Mn(Br)$ (Py = pyridine) led to the formation of cymantrenylbenzofulvene—an analogue of compound **28**, where RR′ = condensed benzene rings.[227] The auration of acetylcymantrene by treatment with the oxonium salt $(Ph_3PAu)_3O^+BF_4^-$ in the presence of NaH led to the formation[228] of the complex $(Mn)C(O)CH_2AuPPh_3$, in which the C—Au bond is readily cleaved on treatment with HCl. A series of dinuclear complexes having the general formula (Mn)—X—ML_n, where X = CH_2,[229] $C(O)CH_2$,[230] or C(O),[231–235] while ML_n = $Fe(CO)_2Cp$, $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Mn(CO)_5$, or $Re(CO)_5$, have been obtained by the reactions of the chlorides $(Mn)CH_2Cl$ and $(Mn)C(O)CH_2Cl$ or the acid chloride (Mn)C(O)Cl with the carbonylate anions Na^+ML_n in THF. The compounds containing the $Fe(CO)_2Cp$ and $W(CO)_3Cp$ fragments were characterised by X-ray diffraction.[236, 237] The reactions involving the photochemical substitution of the CO ligands by PPh_3 at the Fe, Mo, and W atoms were carried out for some of the complexes of this type. A characteristic property of these compounds is the capacity for ready decarbonylation with formation of the corresponding compounds having the C_5H_4—M bonds (see below).

Tungsten hexacarbonyl $W(CO)_6$ reacts in the usual way with (Mn)Li, affording after alkylation with $Et_3O^+BF_4^-$, the carbene complex $(CO)_5W=C(OEt)(Mn)$ with the cymantrenyl substituent at the carbene carbon atom. On treatment with $AlBr_3$, it is readily converted[238] into the carbyne complex $[(CO)_4W\equiv C(Mn)]^+$. Dinuclear complexes of the type $(C_6H_6)Cr(CO)_2(Mn)L$, where L = PPh_2 or CH_2PPh_2, have been obtained by the reactions of $(C_6H_6)Cr(CO)_3$ with cymantrenylphosphines.[239]

Compounds containing two or three cymantrenyl fragments in one molecule have been synthesised in a series of studies. The vast majority of these syntheses were carried out via cymantrenyllithium. The reaction of (Mn)Li with cyanoferrocene in the presence of MeOH gives rise to the ketimine (Mn)—C(NH)—Fc (Fc = ferrocenyl).[240] Hydrolysis of the ketimine leads to the ketone (Mn)C(O)Fc, which is identical with the one obtained previously[241] by acylating ferrocene with the acid chloride (Mn)C(O)Cl/$AlCl_3$. Metallation of methylcymantrene and subsequent treatment with DMF result in the formation of a mixture of isomers of 2- and 3-methylformylcymantrenes,the reduction of which with $NaBH_3(CN)$ in the presence of NH_4OAc in MeOH leads to secondary amines of the type $[(CO)_3MnC_5H_3(Me)CH_2]_2NH$. Layered materials based on acid zirconium phosphate were obtained from the latter compounds.[242] The reaction of the Grignard reagent (Mn)MgI (obtained from iodocymantrene and magnesium in THF) with $N(CH_2Cl)_3$ leads to the tertiary amine $[(Mn)CH_2]_3N$.[243]

A series of studies have been devoted to the synthesis and the properties of polynuclear carbinols of the cymantrene series. The dinuclear carbinols $(Mn)_2C(R)OH$, where R = Me or Ph, have been synthesised by the reactions of (Mn)Li with acetyl- and benzoyl-cymantrenes,[83] while the carbinol $(Mn)_3C(OH)$ has been obtained in the reaction with dicymantrenyl ketones.[244] On treatment with acids, these carbinols are converted into the corresponding stable carbenium ions (see below). The dinuclear carbinols $(Mn)_2C(R)OH$ can be obtained also in one stage as a result of the interaction of 2 equiv. of (Mn)Li with the acid chloride RC(O)Cl. With M = Mn, the plane passing through the O(hydroxy-groups) and C(6) atoms and the neighbouring atom H or C of the group R in the carbinols **29** cannot be a plane of symmetry, because, as shown below, both $(CO)_3MnC_5H_4$ residues occupy different positions relative to it. Therefore, in each C_5H_4 fragment the CH groups in the 2,5- and 3,4-positions are diastereotopic (symmetry elements are absent). This is clearly manifested in the ^1H NMR spectra, where the four protons of the C_5H_4 ligand form the *ABCD* spin system and give rise to four individual signals,[245] and also in the ^{13}C NMR spectra. The study of the reactivities of the carbinols with R = H or Me showed that metallation with BuLi proceeds with a high regio- and stereoselectivity, while in the case where R = CF_3 or Ph the carbinols decompose. When the lithio-derivatives are quenched[245] with D_2O, deuterium is ~90% incorporated in only one of the two α-positions in each C_5H_4 ring. The study of the structures of these carbinols in the crystal by X-ray diffraction and by the method of molecular mechanics (calculation of conformations) showed that the molecules have a chiral conformation with different orientations of the two cymantrenyl residues and that the structure of the carbinols with R = Me differs from that of the carbinols with R = CF_3 or Ph, which makes it possible to explain the observed differences between their reactivities.[246] The structures of the carbinol with R = Me and related compounds have been established by X-ray diffraction.[247, 248]



29

M = Mn, Re; R = H, Me, CF_3, Ph.

A series of communications[249–252] have been devoted to the application of the palladium-catalysed cross-coupling of the organometallic fragments (Mn) in order to synthesise dinuclear complexes. The interaction of iodocymantrene [obtained from (Mn)Li and 1,2-diiodoethane or I_2] with $Bu_3SnC\equiv CSnBu_3$ in the presence of $(MeCN)_2PdCl_2$ in DMF results in the formation of the disubstituted acetylene $(Mn)C\equiv C(Mn)$, the reaction of which with $Co_2(CO)_8$ leads[249] to the tetrahedral cluster $(Mn)C\equiv C(Mn)Co_2(CO)_6$ with the Co_2C_2 skeleton. The initially monosubstituted acetylene $(Mn)C\equiv CH$ was obtained similarly from (Mn)I and $Bu_3SnC\equiv CH$ and its interaction with Et_2NSnR_3 afforded the complex $(Mn)C\equiv CSnR_3$ (R = Me or Bu). The cross-coupling of this acetylene with the iodo-derivatives $IC_5H_4ML_n$ led to the synthesis of the heterodinuclear complexes $(Mn)C\equiv CC_5H_4ML_n$, where ML_n = $Fe(CO)_2Me$, $W(CO)_3Me$, or $Re(CO)_3$.[250] The dinuclear complex $(Mn)C\equiv CC_5H_4Fe(CO)_2CH_2Ph$ was obtained from $(Mn)C\equiv CSnMe_3$ and $IC_5H_4Fe(CO)_2CH_2Ph$, while the reaction with $Co_2(CO)_8$ afforded a cobalt-containing cluster [as a result of the coordination of $Co_2(CO)_6$ to the triple bond]. The structure of the latter complex was demonstrated by X-ray diffraction.[251] Treatment of the acetylene complex $(Mn)C\equiv CH$ with the base KOH in MeOH at 0 °C in the presence of a source of iodine (*N*-iodosuccinimide or 1,2-diiodoethane) afforded the iodo-substituted acetylene $(Mn)C\equiv CI$, which is converted into the

β-vinyl iodide (**Mn**)CH = CHI by the reaction with an excess of the diimide NH = NH as a result of the reduction of the triple bond to a double bond. The cross-coupling of this vinyl iodide with $Me_3SnC{\equiv}CC_5H_4ML_n$ led to the formation of complexes of the type (**Mn**)CH = CH − C = $CC_5H_4ML_n$, where ML_n = $Re(CO)_3$, $W(CO)_3Me$, or $Fe(CO)_2Me$.[252]

The formation of the intermediate $CpMn(CO)_2$ and small amounts of a new dinuclear complex $Cp_2Mn_2(CO)_5$ was noted in a study of the photochemistry of cymantrene in liquid paraffin at 77 K. The new dinuclear compound is formed as a result of the addition of $CpMn(CO)_2$ to cymantrene.[253] The photochemical reactions of dinuclear complexes of manganese and chromium, including (**Mn**) – (**Mn**) and (**Mn**)CH_2(**Mn**), have been investigated in argon matrices at 12 K.[254].

A new organometallic porphyrin — *meso*-tetracymantrenylporphyrin — has been obtained by the reaction of cymantrenecarbaldehyde with pyrrole on refluxing in MeCOOH in the presence of a stream of air.

VI. Compounds with organoelement substituents

A multiplicity of compounds with the $(CO)_3MnC_5H_4$ − E bonds, where E = Group I − VIII elements (Li, Cu, Ag, Au, Mg, Cd, Hg, B, Tl, La, Y, Sm, Sr, Ge, Sn, Pb, P, Sb, Bi,Ti, Mo, W, Mn, Re, Fe, Ni, and Pt) have now been obtained. Their syntheses and properties are considered below.

1. Compounds with Group I − V elements

Syntheses of cymantrene derivatives via (**Mn**)Li have been described in a review[1] and in Sections III − V of the present review. Much attention has been devoted also to the synthesis of cymantrene derivatives containing copper, silver, and gold. The compounds (**Mn**)Cu and (**Mn**)Ag have been obtained by the reaction of cymantreneboronic acid (**Mn**)$B(OH)_2$ or its anhydride with $Cu(OAc)_2$ [208] and $AgNO_3$ [256] respectively. Two types of reactions are characteristic of these compounds: cleavage of the C − Cu and C − Ag σ-bonds on treatment with electrophiles and their use in syntheses as sources of the (**Mn**) fragment. The compounds (**Mn**)Cu and (**Mn**)Ag successfully supplement (**Mn**)Li, the coupling of the cymantrenyl radicals with formation of bicymantrenyl being characteristic of the reactions involving them.[208, 211]

Treatment of (**Mn**)Li with copper(I) halides (in proportions of 1 : 2) in THF at −50 °C leads to the dissolution of CuHal with formation of solutions of cymantrenyl cuprates, $(Mn)_2CuLi$, etc. In contrast to (**Mn**)Li, these solutions are stable both at room and elevated temperatures, which makes it possible to use the compounds for the introduction of the cymantrenyl residue over a wide range of temperatures.[257]

The polymeric or oligomeric derivative $(Mn)_2AgCu$ has been obtained by treating CuI with (**Mn**)Ag.[216] Its structure has not been established, whilst its properties are similar to those of the monometallic derivatives. In particular, the reactions with iodobenzene and bromoferrocene lead to the formation of phenylcymantrene and cymantrenylferrocene respectively.[216]

The complex (**Mn**)$AuPPh_3$, in which one carbonyl group can be replaced photochemically by PPh_3 without dissociation of the C − Au bond, has been obtained by the reaction of (**Mn**)Li with $ClAuPPh_3$.[205] The reaction of (**Mn**)$AuPPh_3$ and its phosphine derivative with HBF_4 or $Ph_3PAu^+BF_4^-$ affords the complex salts $[(CO)_2LMnC_5H_4(AuPPh_3)_2]^+BF_4^-$.[258] Later the same salts were obtained by the reaction of $(Mn)_2Hg$ with $MeAuPPh_3$ in the presence of HBF_4.[259] The C − Au bond in the cymantrenyl derivatives of gold is readily cleaved by electrophiles.[205, 256]

The properties of the mercury derivatives of cymantrene — (**Mn**)HgX (X = Cl, Br, I) and $(Mn)_2Hg$ — were investigated in detail in the 1960s (see the relevant review[1]). The use of $(Mn)_2Hg$ in the synthesis of bicymantrenyl was examined above.[207] Treatment of CdI_2 with (**Mn**)Li gave rise to a mixture of (**Mn**)CdI and $(Mn)_2Cd$.[260] The 1,2-disubstituted cymantrenes $(CO)_3MnC_5H_3(HgR)CH_2NMe_2$ were obtained by metallating the amine (**Mn**)CH_2NMe_2 and treating its lithio-derivative with the mercury compounds RHgX, where R = $Mn(CO)_5$, $Re(CO)_5$, or phenylcarbaboranyl. Depending on the reactant ratio, treatment of $(CO)_3MnC_5H_3(Li)CH_2NMe_2$ with mercury halides HgX_2 (X = Cl, Br, I) led to the isolation of the mercurio-derivatives $(CO)_3MnC_5H_3(HgX)CH_2NMe_2$ (1 : 1) and $[(CO)_3MnC_5H_3CH_2NMe_2]_2Hg$ (2 : 1); the latter was characterised by X-ray diffraction.[261] A weak intramolecular coordination of mercury to the two nitrogen atoms of the dimethylamino-groups was observed in this complex.

The synthesis of cymantreneboronic acid and of its anhydride was first described as early as 1969.[262] The acid (**Mn**)$B(OH)_2$ was used to obtain the copper and silver derivatives of cymantrene.[208, 256] Its reactions with the copper salts $CuCl_2$ and $CuBr_2$ constitute a convenient method of synthesis of chloro- and bromo-cymantrenes (in yields greater than 85%).[209] The synthesis and reactions of ferrocenylcymantrenelboronic acid have been described.[217]

Cymantrenyl derivatives of the lanthanides (Yb, Sm, Eu) have been obtained by treating the iodides $LnI_2.nTHF$ or metallic lanthanide powders with (**Mn**)Li or $(Mn)_2Hg$.[263−266]

$$(Mn)_2Hg + YbI_2 \cdot nTHF \longrightarrow (Mn)YbI_2 \cdot nTHF + Hg,$$

$$(Mn)Li + YbI_2 \cdot nTHF \longrightarrow (Mn)_2Yb \cdot nTHF + LiI,$$

$$(Mn)I + Ln \longrightarrow (Mn)LnI \cdot nTHF,$$

$$(Mn)_2Hg + Ln \longrightarrow (Mn)_2Ln \cdot nTHF.$$

Like (**Mn**)Li, the complex (**Mn**)YbI reacts readily with Me_3SiCl and Ph_3SnCl, forming compounds with the (**Mn**) − Si and (**Mn**) − Sn bonds.[266] Dicymantrenylthallium chloride $(Mn)_2TlCl$ was obtained by the reaction of (**Mn**)Li with $TlCl_3$ (THF, −50 °C). The same compound has been synthesised from $(Mn)_2Hg$ and $TlCl_3$ in ether or in $CHCl_3$ at 25 °C.[267]

The reactions of (**Mn**)Li with the corresponding halides have been used to synthesise compounds with the (**Mn**) − E bonds, where E is a Group IV element (Si, Ge, Sn, Pb). Cymantrenylsilanes (**Mn**)SiR_3, where SiR_3 = $SiPh_3$ [268] or SiRR′R″,[269, 270] have been obtained from chlorosilanes R_3SiCl. The reaction of (**Mn**)SiMePhCl with $LiC{\equiv}CFc$ afforded cymantrenylsilylacetylene (**Mn**)SiMePh − C ≡ CFc.[271] Reactions involving the hydrosilylation of the acetylenes RC ≡ CH (where R = $SiEt_3$, $SiPh_3$, Ph, Fc) with the silane (**Mn**)SiMePhH in the presence of the Speier catalyst based on H_2PtCl_6 proceed nonselectively and give rise to mixtures of products of two types,[272−275] which have been characterised by X-ray diffraction.[276, 277] Tricymantrenylsilane $(Mn)_3SiMe$ has been synthesised by the reaction of (**Mn**)Li with $MeSiCl_3$.[278] The addition of a solution of (**Mn**)Li to the silane Me_2SiHCl (THF, −80 °C) affords (**Mn**)$SiMe_2H$, but when the reactants were introduced in the reverse order, the disubstituted complex $(Mn)_2SiMe_2$ was obtained. The reactions of (**Mn**)$SiMe_2H$ with $Co_2(CO)_8$ or $Ir(CO)(PPh_3)_3H$ are accompanied by the cleavage of the Si − H bond and lead to the synthesis of complexes of the type (**Mn**)$SiMe_2-ML_n$, where ML_n = $Co(CO)_4$ or $Ir(CO)(PPh_3)_2H_2$.[279]

The reactions of (**Mn**)Li with the chlorides Ph_3ECl led to the formation of the corresponding compounds (**Mn**)EPh_3, where E = Ge, Sn, or Pb.[268] For E = Sn, treatment with HCl results in the simultaneous cleavage of the C − Sn σ-bond (yield of cymantrene approximately 10%) and the substitution of Ph by Cl with formation of (**Mn**)$SnPhCl_2$, which reacts with $NaMn(CO)_5$ to form the trinuclear complex (**Mn**)$SnPh[Mn(CO)_5]_2$.[268] The syntheses of cymantrenylstannanes $(Mn)_2SnR_2$, where R = Cl, Ph, or Fc,[280] and also of $(Mn)_4Sn$ [280] as well as a series of their derivatives[281] have been described. The structures of the chlorostannanes $(Mn)_2SnCl_2$ and $(Mn)_3SnCl$ have been characterised by X-ray diffraction.[282, 283]

The cymantrenylphosphonic acids (Mn)P(O)(OH)H [cymantrenylphosphonous acid? (translator)] and $(Mn)_2P(O)OH$ [cymantrenylphosphinic acid? (translator)] have been obtained by direct phosphorylation under the conditions of the Friedel–Crafts reaction between cymantrene and PCl_3,[100] while the reaction of cymantrene with $Et_2NPCl_2/AlCl_3$ gave rise to the phosphine $(Mn)_3P$.[284] The phosphine $(Mn)PPh_2$ has been synthesised by treating Ph_2PCl with the Grignard reagent (Mn)MgI (obtained from iodocymantrene and magnesium in the presence of 1,2-dibromoethane) and its quaternisation by reaction with $PhCH_2Br$ afforded the quaternary phosphonium salt $(Mn)P^+Ph_2CH_2Ph\ Br^-$. Its decomposition with alkali gives rise to cymantrene (92.3%) and toluene (6.3%), which indicates the high stability of the anion $(Mn)^-$.[285] The phosphines $(Mn)PPh_2$ and $(Mn)CH_2PPh_2$ have also been obtained with the aid of (Mn)Li.[95] The phosphine $(Mn)PPh_2$ is formed in the reaction of the phosphine sulfide $C_5H_5P(S)Ph_2$ with $Mn_2(CO)_{10}$.[286] Dichlorophosphine $(Mn)PCl_2$ and $(Mn)PR_2$, where R = OEt or NEt_2, have been synthesised by the reactions of (Mn)Li with PCl_3 or chlorophosphines.[287] The interaction of $(Mn)P(OEt)_2$ with 1,3-dichloroacetone leads[288] to the cymantrenylphosphonate $(Mn)P(O)(OEt)OC(CH_2Cl)=CH_2$. Treatment of (Mn)Li with $PhPCl_2$ afforded dicymantrenylphenylphosphine $(Mn)_2PPh$.[289] It has been shown that cymantrenylphosphines exhibit all the usual properties of tertiary phosphines, in particular, they are oxidised to phosphine oxides, combine with sulfur, and enter into the Staudinger, Perkow, and other reactions.[284–287] Metallation of $(Mn)PPh_2$ followed by the reaction with Ph_2PCl led to the formation of 1,3-bis(diphenylphosphino)cymantrene — the only compound containing two phosphine substituents in the Cp ligand.[93]

Compounds with (Mn)–As bonds have not been described. The reaction of $BiCl_3$ with (Mn)Ag affords $(Mn)_3Bi$,[256] which has, according to X-ray diffraction data, a trigonal-pyramidal structure.[290] $(Mn)_3Sb$ and $(Mn)_3Bi$ have been obtained by the reaction of (Mn)Li with $SbCl_3$ and $BiCl_3$. Their thermolysis at 330 °C leads to the formation of the following products: cymantrene, CO, a cyclopentadiene polymer, and metallic manganese and antimony for the antimony compound and metallic bismuth and bicymantrenyl for the bismuth compound.[291] The lithio-derivative (Mn)Li reacts with $PhBiCl_2$, whereupon the product is $(Mn)_2BiPh$, which reacts with $CuCl_2$ to form chlorocymantrene, chlorobenzene, bicymantrenyl, and biphenyl.[292]

The sulfonation reaction has been used to obtain compounds with (Mn)–S bonds. Sulfonation of methylcymantrene results in the formation of a mixture of the 1,2- and 1,3-isomers of methylcymantrenesulfonic acid. Sulfonyl chlorides and other derivatives have been synthesised from them by reaction with PCl_5 in accordance with the following scheme:[76,77,99]

$$(Mn)SO_3 \xrightarrow{PCl_5} (Mn)SO_2Cl \xrightarrow{Zn} (Mn)SH \xrightarrow{CH_2N_2} (Mn)SMe.$$

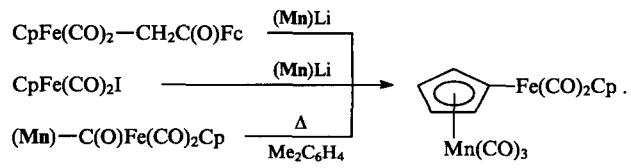
Acylation of the MeS derivatives gives rise to mixtures of ketones.[77,99] The synthesis of cymantrenes with MeS and PhS substituents has been described by Sunkel and coworkers,[39–42] while the preparation of the disulfides has been described in other communications.[43,76,100] Physiologically active derivatives of barbituric acid containing the $(Mn)SO_2CH_2$ fragments have been described.[293] The synthesis of the 1,2-disubstituted derivatives $(CO)_3MnC_5H_3(R)SO_2NMe_2$ was already mentioned above.[94]

The interaction of $Mn(CO)_3(MeCN)_3^+$ with the ylides $C_5H_5ER_3$ leads to the formation of new cationic complexes $(CO)_3MnC_5H_4-ER_n^+\ X^-$, where ER_n = PPh_3 or SMe_2.[294] The complex with the SMe_2 group was characterised by X-ray diffraction.[295] The interaction of (Mn)Li and also of its Re analogue with free chalcogens affords the relatively unstable intermediates (Mn)ELi as a result of the insertion of the chalcogen in the C–Li bond. On oxidation with atmospheric oxygen, the intermediates are converted into dimetallo-dichalcogenides with the general formula (M)–E–E–(M) [here (M) = $(CO)_3MnC_5H_4$ or $(CO)_3ReC_5H_4$ with E = S, Se, or Te]. The reactions of 2 equiv. of (M)Li with SCl_2, $SeCl_4$, or $TeCl_4$ led to the formation of complexes having the general formula (M)–E–(M).[289]

2. Compounds with transition metals

The reaction of (Mn)Li with Cp_2TiCl_2 affords the complex $Cp_2Ti(Mn)_2$ in which the titanium atom has a tetrahedral environment according to X-ray diffraction data.[296]

A series of studies by Nesmeyanov and coworkers[297–331] on the synthesis and the chemistry of complexes of the type (Mn)–ML_n, where M = Mo, W, Mn, Re, Fe, or Ni, were published in 1974–1984. The properties of the complex (Mn)–$Fe(CO)_2Cp$ **30** were investigated most fully. It is formed either on treatment of $CpFe(CO)_2I$ or $CpFe(CO)_2-CH_2C(O)Fc$ with (Mn)Li [297] or on thermal decarbonylation of $(Mn)C(O)Fe(CO)_2Cp$.[231]



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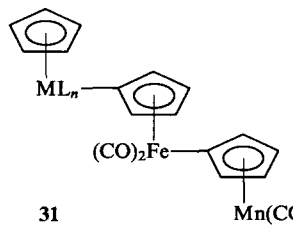
The analogous complexes (Mn)–ML_n, where ML_n = $Mo(CO)_3Cp$, $W(CO)_3Cp$,[232–234] $Mn(CO)_5$, or $Re(CO)_5$,[235] are also formed on thermal decarbonylation in accordance with the mechanism

$$(Mn)-C(O)ML_n \longrightarrow (Mn)-ML_n + CO.$$

The complex (Mn)–$Ni(PPh_3)Cp$ with the (Mn)–Ni bond is formed in the reaction of (Mn)Li with $CpNi(PPh_3)Cl$ or with nickelocene.[298] The ready cleavage of the C_5H_4-M bonds by electrophiles [acids, mercury salts, iodine, MeC(O)Cl, etc.] with formation of cymantrene, mercury halides, (Mn)HgX, and iodocymantrene respectively, is characteristic of all compounds of the type (Mn)–ML_n.[235,298] Under the conditions of the thermal or photochemical reaction, there is a possibility of the substitution of CO by PPh_3 at the Fe, Mo, and W atoms[231–234] or of CO at the Mn atom by PPh_3 and tolane in the complex (Mn)–$Ni(PPh_3)Cp$.[299] Thermal decarbonylation has also been used to synthesise the complex $(CO)_2PPh_3MnC_5H_4-Fe(CO)_2Cp$,[300] in which the CO group at the Fe atom is substituted by PPh_3 on UV irradiation.[301] The structure of the complexes (Mn)–Fe(CO)(L)Cp, where L = CO or PPh_3, has been established by X-ray diffraction.[302]

The chemistry of complex **30** and its derivatives has been studied in greater detail. The C–Fe bond is readily cleaved on treatment with I_2 in CH_3Cl or with $MeCO^+BF_4^-$, but it proved resistant to the action of $HgCl_2$ in benzene.[303] Under the conditions of the mercuration of cymantrene, complex **30** reacts with mercury acetate and mercuration takes place in the C_5H_4 ring at the Mn atom. After treatment with $CaCl_2$, the chloromercurio-derivative was obtained, forming readily a symmetrical compound.[304] It was found that the C–H bonds in the Cp ring attached to the Fe atom exhibit a high CH acidity and are capable of participating in the protophilic substitution reaction. Complex **30** enters into hydrogen isotope exchange with EtOD–EtONa (benzene, 100 °C) and is metallated on treatment with BuLi.[305] Carboxylation of the Li derivative of complex **30** affords the acid (Mn)–$Fe(CO)_2C_5H_4COOH$ (pK_a = 5.09 in 50% EtOH), which is three–four times stronger than benzoic acid (pK_a = 5.7 under the same conditions).[305] The capacity of complex **30** to be metallated made it possible to obtain a series of polynuclear complexes based on it. The trinuclear complexes **31**, where ML_n = $Fe(CO)_2$,[306] $Mo(CO)_3$, and $W(CO)_3$,[307] have been synthesised by the reaction of the lithio-derivative with the

organometallic halides $CpFe(CO)_2I$, $CpMo(CO)_3Cl$, or $CpW(CO)_3Cl$.



31

Compounds containing a sequence of metals, Fe–Fe–Mn and Mo–Fe–Mn, have been characterised by X-ray diffraction.[306, 307] Treatment of complex **30** with BuLi and then with C_3F_7I led to the formation of the iodo-derivative **(Mn)**–$Fe(CO)_2C_5H_4I$, which on reaction with the lithio-derivative **(Mn)**–$Fe(CO)_2C_5H_4Li$ affords the analogous tetranuclear complex of the 'ladder' type with the Mn–Fe–Fe–Mn metal sequence.[308] The synthesis of the tetranuclear complex with the sequence Fe–Fe–Fe–Mn, characterised by X-ray diffraction, has been described.[309]

The thermolysis of the complexes **(Mn)**–$M(CO)_3Cp$, where M = Mo [234] or W,[310] results in the formation of complex mixtures of dinuclear and trinuclear complexes containing the products of the migration of the **(Mn)** fragments to the Cp rings attached to Mo and of the $(CO)_3WC_5H_4$ fragment to the Cp ring at Mn. The interaction of **(Mn)**–$Ni(PPh_3)Cp$ with *p*-isocyanotoluene leads to the dissociation of the Ni–C bond.[311]

In the reaction of **(Mn)**Li with *cis*-L_2PtCl_2 at −50 °C, one Cl atom is readily substituted with formation of the complex **(Mn)**–PtL_2Cl (L = PPh_3).[312] The mercury halides **(Mn)**HgX readily react with the zerovalent platinum complex PtL_3 with insertion of the carbenoid fragment PtL_2 in the Hg–Cl or Hg–Br bonds.[313, 314] The structure of the reaction products depends on the conditions: at −20 °C in toluene, compounds with a Pt–Hg bond of the type **(Mn)**–Hg–PtL_2Cl are formed, readily splitting off mercury on heating to 20 °C and forming the complexes **(Mn)**–PtL_2Cl. The two PPh_3 ligands at the mercury atom are readily substituted by the chelating diphosphine $Ph_2PCH_2CH_2PPh_2$. Photolysis of platinum–mercury complexes involves protodemercuration with liberation of mercury and the formation of cymantrene.[314] Dicymantrenylmercury $(Mn)_2Hg$ readily reacts with PtL_3 at −20 °C, forming the compound **(Mn)**–Hg–PtL_2–**(Mn)**, which on heating to 20 °C is converted, as a result of the elimination of mercury, into the complex $(Mn)_2PtL_2$, where the Pt atom is linked simultaneously to two cymantrene residues.[315]

VII. Cymantrene as an organometallic Lewis base

Low-valence transition metal complexes constitute a new class of organometallic Lewis bases. Their basicity is associated with the presence in the metal of fully or partially occupied *d* orbitals,[316–318] which is characteristic mainly of complexes of Group V–VIII metals with the configuration d^6–d^9. Organometallic bases have several potential basicity centres. Depending on the structure of the complex, the ligand environment of the metal, and the nature of the electrophile and the solvent, the attack by the electrophile can be directed to one or several centres. Cymantrene and its phosphine derivatives exhibit all the properties of Lewis bases: they are capable of combining with a proton, aprotic acids, the halogens, etc.

1. Reactions with protic acids

It has been shown by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopic methods that cymantrene, pentaethylcymantrene, and mono- and di-phosphine derivatives of cymantrene are protonated at the manganese atom on treatment with protic acids.[319–324] Unsubstituted cymantrene is a very weak base: protonation of the metal takes place only in the presence of the strong acid HSO_3F in CH_2Cl_2 at low temperatures. Even at −100 °C, the exchange between the proton in Mn–H and the medium is rapid on the NMR time scale. Pentaethylcymantrene, in which the basicity of the metal is appreciably higher owing to the electron-donating effect of the five ethyl substituents, is wholly protonated under the same conditions with formation of the Mn–H bond. At −105 °C, there is a slow exchange of the proton in Mn–H with the medium.[324] On substitution of one and especially two CO groups by phosphine ligands, the basicity of the metal increases greatly: the mono- and di-phosphine complexes are capable of being protonated at the Mn atom even in the presence of CF_3COOH.[321–325] The proton affinity of $MeC_5H_4Mn(CO)_3$ was determined as 203 kcal mol^{-1} in a study of the gas-phase protonation.[326]

A new type of hydrogen bond in the η-complexes of transition metals has been discovered in cymantrene and benchrotrene derivatives. In a study of the interaction of cymantrene and its phosphine derivatives with weaker proton donors such as $(CF_3)_3COH$ and anhydrous HCl (in solution in liquid xenon at 160–240 K and also in CCl_4 at 293 K), it was possible to detect the formation of hydrogen bonds with the oxygen of the CO ligand. The formation of such bonds is accompanied by a shift of the ν(CO) frequencies and also of the ν(OH) frequency of the proton donor. The frequency shifts $\Delta\nu$(OH) depend greatly on the basicity of the metal and on the number of phosphine ligands, ranging from ~75 cm^{-1} for cymantrene to 240 cm^{-1} and more for the diphosphine complexes. There is a possibility of hydrogen bond formation with both one and two CO groups simultaneously.[327–330]

The formation of intramolecular and intermolecular hydrogen bonds as well as the preferred conformations in carbinols containing one **(Mn)** fragment, having the general formula **(Mn)**C(OH)RR', and also in their rhenium analogues have been investigated by IR spectroscopic and molecular mechanics methods.[331]

2. Reactions with aprotic acids

Cymantrene and its phosphine derivatives react as bases not only with a proton but also with aprotic acids — their Hg, Al, Ga, and Sn salts. Unsubstituted cymantrene does not react with $HgCl_2$, while in the case of mercury acetate or trifluoroacetate the final result of the reaction is mercuration with substitution of one or all five hydrogen atoms.[101] It may be that the initial attack by Hg is directed to the metal atom with subsequent migration to the Cp ring. Cymantrene does not react with $SnCl_4$, but pentaethylcymantrene affords an adduct via the Mn atom even on reaction with $SnCl_4$.

Coordination to the oxygen atoms of the CO groups occurs only on interaction of unsubstituted cymantrene with $AlCl_3$ or $AlBr_3$ in benzene.[332, 333] The site of attack by AlX_3 (the centre in the cymantrene molecule with the highest basicity) depends on the nature of the solvent. On passing from the nonpolar C_6H_6 to the polar CH_2Cl_2 or $ClCH_2CH_2Cl$, the site of attack changes: in benzene, AlX_3 affords adducts via the oxygen atoms of the CO groups, while in polar solvents the adducts are formed via the metal atom.[333] The site of attack and of the addition of AlX_3 follows unambiguously from the direction and magnitude of the ν(CO) frequency shifts in the IR spectra. The mono- and di-phosphine complexes react with AlX_3 and $GaCl_3$ only via the Mn atom.

The energetics of the interaction of cymantrene and pentaethylcymantrene with $AlBr_3$ has been studied by calorimetric titration:[334, 335] the enthalpy of formation of the adduct ($-\Delta H$) via oxygen, i.e. $Cp(CO)_2MnCO \cdots AlBr_3$, is 18.9 kcal mol^{-1}, while that of the adduct $(Et_5C_5)(CO)_3Mn \cdots AlBr_3$, formed as a result of coordination to the metal atom, is 22.0 kcal mol^{-1}.

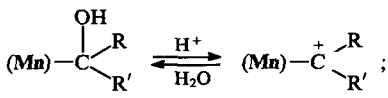
The halogens Cl_2 and Br_2 cleave cymantrene at 20 °C with dissociation of the Mn–ring bond.[1] However, on treatment of cymantrene in solution in CH_2Cl_2 at −50 °C with 1 equiv. of the

halogen in CCl_4, the latter adds to the metal with formation of the ionic complex $[CpMn(CO)_3Cl]^+Cl^-$ or $[CpMn(CO)_3Br]^+Br_3^-$.[336]

Thus the centre with the highest basicity in the cymantrene molecule may be either the Mn atom (H^+, halogens) or the oxygen atom of the CO group (only $AlCl_3$ and $AlBr_3$ in benzene) depending on the type of reagent. On passing to azacymantrene $(\eta^5\text{-}C_4H_4N)Mn(CO)_3$, the situation changes sharply: in this case, the attack by aprotic acids is directed to the nitrogen atom.[337]

VIII. Stabilisation by the cymantrenyl group of the neighbouring cationic and radical centres

Treatment of carbinols of the cymantrene series with acids (for example, with CF_3COOH) leads to the formation, as a result of the elimination of water, of very stable carbonium ions, which are stabilised by 1–3 (**Mn**) residues.[338–343]



R, R′ = H, Me, Et, Ph, Fc.

Treatment of the carbinol $(\mathbf{Mn})_3COH$ with acid afforded the tricymantrenyl carbenium cation $(\mathbf{Mn})_3C^+$, while the corresponding phosphine-containing carbonium ions, the stability of which is appreciably increased by the electron-donating phosphine ligands, were obtained from carbinols containing one or two phosphine ligands.[244] The conversion of the cymantrene carbinols into carbonium ions is accompanied by an increase in the frequency ν(CO) and a displacement of all the signals in the ^1H and ^{13}C NMR spectra, which is associated with the marked delocalisation of the positive charge with participation of the Cp ring and the metal carbonyl fragment. The kinetic stability of the carbonium ions with cymantrene residues has been characterised by measuring the rates of solvolysis of the acetates.[344] Treatment of the carbonium ions with HBF_4 led to the isolation of solid cymantrenylcarbenium tetrafluoroborate salts.[345] The ease of the reactions involving the ionic hydrogenation of cymantrenyl ketones is associated with the high stability of the cymantrenylcarbenium ions and the ability of the cymantrenyl group to stabilise greatly the neighbouring cationic centre.[346] The electrochemical properties of cymantrenylcarbenium salts have been investigated.[347]

In connection with the ability of the cymantrenyl group to stabilise effectively the neigbouring cationic centre mentioned above, it is of interest to estimate the electronic effects of the cymantrenyl group as a substituent. The inductive (σ_I) and resonance (σ_R) components of the overall electronic influence, amounting to 0.172 and −0.02 according to Gubin et al.[348] and 0.141 and −0.024 according to Bitterwolf,[26] have been estimated by the ^{19}F NMR method for the *meta*- and *para*-substituted fluorophenylcymantrenes. The cymantrenyl group is a weak acceptor in terms of its inductive influence and a weak donor in terms of the conjugation mechanism. On substitution of CO by phosphines, its electron-accepting properties are weakened, while its electron-donating properties are enhanced.[26]

The cymantrenyl group can also stabilise the neighbouring radical centre. The reduction with sodium of benzoylcymantrene[349] or dinuclear ketones[66] of the type $(CO)_3MnC_5H_3R-C(O)-C_6H_5RCr(CO)_3$ results in the formation of the corresponding radical-anions (ketyls), in which the radical centre is stabilised by a cymantrenyl, phenyl, or benchrotrenyl substituent. Their structure and th delocalisation of the unpaired electron have been investigated by the EPR method.

In describing the properties of compounds with the (**Mn**)–P bond above (see Section VI), it was noted that the alkaline decomposition of the phosphonium salt $(\mathbf{Mn})P^+Ph_2CH_2PhBr^-$ results in the formation of mainly cymantrene and of an insignificant amount of toluene. This led to the conclusion that the cymantrenyl group is capable of stabilising effectively the neighbouring anionic centre.[285]

* * *

In conclusion, we shall consider several studies which were published during the preparation of the manuscript for printing. The complex $(\eta^5\text{-}PhN{=}NC_5H_4)Mn(CO)_3$ has been obtained in 45% yield from the lithium salt of the phenylazocyclopentadienyl anion by reaction with $Mn(CO)_3(CH_3CN)_2Br$.[350] The preparation of new substituted cyclopentadienylthallium derivatives and the syntheses based on them have been described. The anion of $MeC_5H_4^-Na^+$ reacts with ethyl acetate to form a mixture of 1-acetyl-2-methyl- and 1-acetyl-3-methyl-cyclopentadienyl anions (in proportions of 1 : 1), which on treatment with EtOTl are converted into a mixture of the corresponding thallium derivatives. The latter were separated by recrystallisation from ethanol. The planarly chiral complex 1-acetyl-2-methylcymantrene has been obtained by the reaction of the 1,2-derivative with $Mn(CO)_5Br$.[351] Benzoylcyclopentadienylsodium has been obtained from the anion in Cp^-Na^+ by reaction with ethyl benzoate. On treatment with EtOTl, it gives rise to $TlC_5H_4C(O)Ph$. On reaction with $Mn(CO)_5Br$, the latter affords benzoylcymantrene.[352] Dinuclear complexes having the general formula (**Mn**)–X–(**Mn**), where X = S or $SiPh_2$, have been obtained by the reactions of cymantrenyllithium with SCl_2 and Ph_2SiCl_2. The reduction of 1-acetyl-2-methylcymantrene by $LiAlH_4/TiCl_3$ leads to mixtures of diastereoisomeric complexes of the type $(CO)_3MnC_5H_3Me-C_5H_3MeMn(CO)_3$. Under mild conditions, the products are the pinacols [X = C(OH)Me–C(OH)Me], which are converted into the olefins [X = C(Me)=C(Me)] under more severe conditions as a result of dehydration. The reduction of acetylcymantrene by the $KC_8/TiCl_3$ system results in the formation of a mixture of the analogous dinuclear olefins.[353] Further development of the study by Herberhold and Biersack[289] demonstrated that the lithio-derivatives of cymantrene and $C_5H_5Re(CO)_3$ readily react with the chalcogens, affording (**Mn**)ELi (E = S, Se, Te) and their rhenium analogues. These lithio-derivatives are protonated with formation of the chalcogenols (**Mn**)EH, which are readily oxidised to the disulfides; the reactions of (**Mn**)ELi with CH_2I_2, PhC(O)Cl, and other acid chlorides have been investigated.[354] The interaction of cymantrenyllithium with *C*-carbaboranyl derivatives of mercury or *B*-carbaboranyl derivatives of thallium leads to the synthesis of new dinuclear complexes with (**Mn**)–Hg and (**Mn**)–Tl bonds.[355] The reaction of $(CO)_3MnC_5Cl_4Li$ with the halide $Mn(CO)_5Br$ or $Au(PPh_3)Cl$ affords the complexes $(CO)_3MnC_5Cl_4X$, where X = $Mn(CO)_5$ or $AuPPh_3$.[356]

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