Russian Chemical Reviews **78** (3) 195 – 210 (2009) © 2009 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2009v078n03ABEH003902

The chemistry of cymantrene

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Contents

I.	Introduction	195
II.	Synthesis and properties of new cymantrene derivatives	196
III.	Bicymantrenyl and its derivatives	201
IV.	'Ladder'-type complexes	203
V.	Phosphacymantrenes	204

Abstract. Recent data on the synthesis and properties of cyclopentadienyltricarbonylmanganese (cymantrene) derivatives are considered. The bibliography includes 154 references.

I. Introduction

Cyclopentadienyltricarbonylmanganese (cymantrene, CymH) is unique among organometallic complexes, due to a whole set of properties. First of all, it is very high oxidative and thermal stabilities and versatile reactivity. As for ferrocene, hydrogen substitution reactions in the Cp ligand (Cp = η^5-C_5H_5) are also typical of CymH. Using these reactions and general methods of synthetic organic chemistry, numerous CymH derivatives with a broad range of substituents in the Cp ring have been synthesised. In addition to the substitution reactions in the Cp ring, other transformations leading to changes in the ligand environment of the metal atom are known. Ligand substitution for CO groups has in most details been studied. The coordinatively unsaturated 16e fragment $Cp(CO)_2Mn$ formed upon abstraction of one CO group adds readily various two-electron ligands with different donor atoms (H_2, isonitriles, carbenes, thiocarbonyl and vinylidene groups, amines, nitriles, NO, N_2, hydrazines, imines, phosphines, phosphites, their arsenic and antimony analogues, *etc.*). The oxidative addition reactions of substituted silanes (R_3SiH) to form complexes $Cp(CO)_2Mn(H)(SiR_3)$ are well-known for CymH and its derivatives. Cymantrene mono- and diphosphine derivatives where the basicity of the metal atom is markedly enhanced are protonated under the action of acids to form the Mn – H bonds. They also add aprotic acids and halogens to the manganese atom to form cationic or neutral seven-coordinate manganese species, the chemistry of which is virtually unexplored.

A wide variety of cymantrene derivatives have been synthesised by the combination of both type reactions (substitution in the Cp ring and substitution of CO groups or other reactions changing the ligand environment of the Mn atom). Judging from the number of derivatives obtained, CymH ranks next to ferrocene among organometallic complexes. Two stages can be distinguished in the development of cymantrene chemistry. It the first stage (starting from the discovery of CymH and to mid-1980s), the synthesis of different derivatives with substituents in the ring, studies on their reactivities, stereochemistry and chiroptical properties by traditional methods of organic chemistry dominated. The second stage is characterised by the synthesis of novel complexes including anionic cymantrene complexes, complexes with dihydrogen, with free-radical ligands, 'inidene complexes', *etc.* Currently chemistry of carbene, carbyne, vinylidene, cumulenylidene complexes, complexes with borylene and more complicated ligands is being actively developed; cymantrene-based photochromic materials have been prepared, and possibilities for the application of manganese tricarbonyl complexes in organic synthesis are being studied. At the same time, the number of publications concerning cymantrene derivatives markedly decreased, according to an approximate estimation, to 10 – 15 papers per year, whereas during 1980 – 1990, 30 – 35 papers per year were published. This number includes, in addition to synthetic communications, studies on kinetics of ligand exchange, calculations, *etc.*

It is impossible to cover all information on the chemistry of cymantrene derivatives within the frame of one review, that is why only the main results concerning the synthesis and investigations of the cymantrene derivatives obtained over recent 10 – 12 years are discussed below. Earlier papers are cited, only in special cases.

Earlier, a review [1] (with references up to 1971), a monograph [2] (with references up to 1990) and a review [3] (with references up to 1993) have been published, but they have become out of date. The data on the chemistry of cymantrene and its derivatives is also presented in two issues [4, 5] of the multivolume edition '*Comprehensive Orga-*

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Received 22 October 2008
Uspekhi Khimii **78** (3) 211 – 226 (2009); translated by M G Ezernitskaya

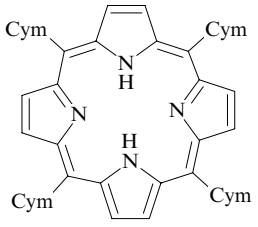
nometallic Chemistry' (publications up to 1994 and 2005, respectively, are covered). The results of X-ray diffraction studies on manganese carbonyl complexes are considered in a review.[6]

II. Synthesis and properties of new cymantrene derivatives

In this Section, the synthesis of novel cymantrene derivatives and the known compounds by improved or modified methods are considered. The reaction conditions have been comprehensively studied and optimised for the reactions of easily accessible lithium derivatives of cymantrene and its rhenium analogue $CpRe(CO)_3$, *vis*., CymLi and $(CO)_3Re(\eta^5\text{-}C_5H_4Li)$, respectively, with different organic compounds including benzoyl chloride, terephthaloyl, phthaloyl and fumaroyl dichlorides, diethyl fumarate, maleic anhydride, *etc*. These reactions with an excess of a lithium derivative result in alcohols and lactones that have mostly been described earlier. The reaction of these lithium reagents with methyl chloroformate (THF, −78 °C) results in the tertiary alcohol $(Cym)_3COH$ or its rhenium analogue. The reactions with paraformaldehyde and subsequent hydrolysis give primary alcohols $(CO)_3MC_5H_4CH_2OH$ (M = Mn, Re), which upon further *ortho*-metallation and reaction with paraformaldehyde form diols $(CO)_3M\{\eta^5\text{-}C_5H_3(CH_2OH)_2\text{-}1,2\}$.[7] The reactions of CymLi with non-metal halides (Ph_2SiCl_2, $PhPCl_2$, SCl_2 and $SOCl_2$) result in compounds $(Cym)_2Z$ (Z = $SiPh_2$, PPh, S or SO, respectively).[7] More than 30 cymantrene derivatives were thus synthesised and characterised.

The synthesis of *m*-carboranyl derivatives of cymantrene and ferrocene was reported.[8] A novel convenient one-pot method for the synthesis of chloro- and bromocymantrenes in high yields by the reactions of CymLi with CCl_4 and 1,2-dibromotetrafluoroethane, respectively, was developed.[9]

Tetracymantrenylporphyrin (**1**) and tricymantrenylcorrol were obtained by the reaction of cymantrenecarbaldehyde (Cym)CHO with pyrrole.[10]

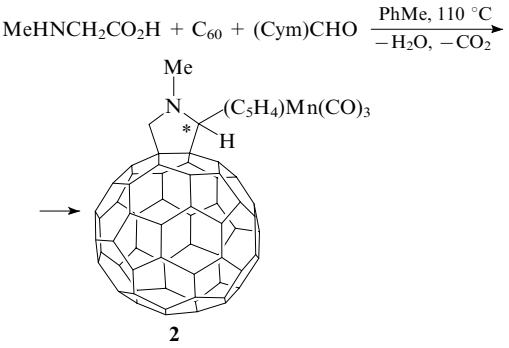


1

Cym = $(\eta^5\text{-}C_5H_4)Mn(CO)_3$.

The first chiral organometallic porphyrin, *vis*., *meso*-tetrakis[(1*S*)-2-methylcymantrenyl]porphyrin was synthesised by the coupling of pyrrole with the optically active planar chiral (+)-(1*S*)-2-methylcymantrenecarbaldehyde and characterised by the CD spectrum.[11] This complex is an analogue of substututed porphyrin **1** and contains four fragments $(\eta^5\text{-}MeC_5H_3)Mn(CO)_3$ with planar chirality. The reaction of an equimolar mixture of aldehyde (Cym)CHO and benzaldehyde with pyrrole in the presence of $BF_3 \cdot Et_2O$ as a catalyst gave a mixture of phenyltricymantrenyl-, diphenyldicymantrenyl- (two isomers) and triphenylcymantrenylporphyrins (^{1}H NMR data) together with tetraphenylporphyrin and complex **1** isolated in the pure form.[12]

Cymantrene- and ferrocenecarbaldehydes react as typical aldehydes not only in solutions, but also in the solid phase. Both aldehydes regio- and stereoselectively react with secondary β-hydroxy amines (for example, ephedrine and pseudoephedrine) in the solid state at room temperature to form the corresponding oxazolidines.[13, 14] A novel preparative method for the synthesis of Schiff bases by the solid-phase reaction of organic and organometallic aldehydes with amines was suggested.[15] The solid-phase reaction of these aldehydes with 1,8-naphthylenediamine yields organometallic derivatives of 2,3-dihydroperimidine.[16] Cymantrenecarbaldehyde reacts with *N*-methylglycine (sarcosine) and fullerene C_{60} under conditions of the Prato reaction[17] to form the cymantrenyl derivative of *N*-methyl[60]fullereno[*c*]pyrrolidine **2**.[18]



2

The reaction of 3-(*O*-*tert*-butyldimethylsilyl)-1,2-*O*-isopropylidene-5-*O*-(*p*-tolylsulfonyl)-α-D-xylofuranose with cyclopentadienylsodium in DMF gave the corresponding carbohydrate-substituted cyclopentadiene C_5H_5R. Its subsequent treatment with thallium ethoxide in hexane gave the thallium salt $(C_5H_4R)Tl$, which reacted with $Mn(CO)_5Br$ in THF to form cymantrene with a carbohydrate substituent R in the Cp ring $[(\eta^5\text{-}RC_5H_4)Mn(CO)_3]$.[19]

A method for the synthesis of cyclopentadienes with perfluoroaryl substituents has been developed. Perfluorobenzene reacts with C_5H_5Na or C_5H_5Li and NaH to give, depending on the reactant ratio, solvent and temperature, (perfluorophenyl)cyclopentadienes containing from one to four C_6F_5 substituents in the ring after hydrolysis.[20–22] In the absence of NaH, only monosubstituted (perfluorophenyl)cyclopentadiene is formed (Table 1). Treatment of the thus obtained cyclopentadienes with NaH in THF gives readily the corresponding anions, which react with $Mn(CO)_5Br$ or $Mn(CO)_3Py_2Br$ to form perfluorophenylcymantrenes $(\eta^5\text{-}RC_5H_4)Mn(CO)_3$, $(\eta^5\text{-}1,3\text{-}R_2C_5H_3)Mn(CO)_3$,

Table 1. The synthesis of pentafluorophenyl-substituted cyclopentadienes.[20–22]

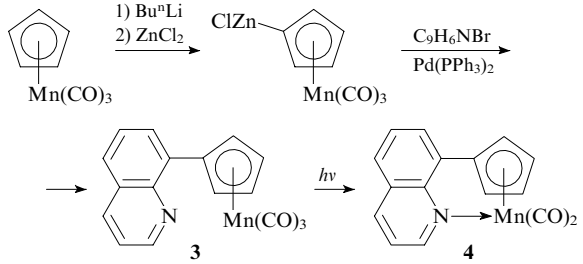
Cyclopentadiene[a]	Ratio $C_5H_5Na : C_6F_6 : NaH$	Reaction conditions
RC_5H_5	1 : 1 (see[b])	THF, 25 °C, 15 h
$1,3\text{-}R_2C_5H_4$	1 : 2.5 : 3	THF, 65 °C, 72 h
$1,2,3\text{-}R_3C_5H_3$	1 : 4.8 : 5.2	diglyme, 110 °C, 15 h
$1,2,4\text{-}R_3C_5H_3$	1 : 4.8 : 5.2	diglyme, 110 °C, 15 h
$R_4C_5H_2$	1 : 6 : 6	diglyme, refluxing, 48 h

[a] R = C_6F_5; [b] in the absence of NaH.

(η^5-1,2,3-$R_3C_5H_2$)$Mn(CO)_3$, (η^5-1,2,4-$R_3C_5H_2$)$Mn(CO)_3$ and (η^5-1,2,3,4-R_4C_5H)$Mn(CO)_3$ (the two latter compounds were studied by X-ray diffraction analysis).[21,22]

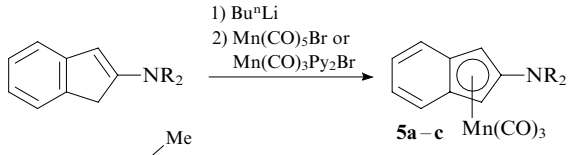
Similarly, the reaction of perfluorotoluene $CF_3C_6F_5$ with C_5H_5Na in the presence of excess NaH in THF or diglyme followed by acid hydrolysis results in a mixture of products. Depending on the reactant ratio and conditions (temperature, reaction time), mono-, bis-, tris- and tetrakis(perfluoro-4-tolyl)cyclopentadienes could be obtained and isolated by chromatography. Complexes (η^5-RC_5H_4)$Mn(CO)_3$ and (η^5-1,2,4-$R_3C_5H_2$)$Mn(CO)_3$ characterised by X-ray diffraction analysis were obtained by the reactions of the monosubstituted derivative RC_5H_5 ($R = CF_3C_6F_4$) with NaH in THF and of trisubstituted derivative 1,2,4-$R_3C_5H_2$ with NaH in dimethoxyethane, respectively, followed by the interaction with $Mn(CO)_5Br$.[23]

In the reaction of CymLi with 1 equiv. $ZnCl_2$ in THF (−78 °C, 1 h), the lithium atom is replaced by ZnCl to form (η^5-C_5H_4ZnCl)$Mn(CO)_3$. Cross-coupling of this zinc derivative with 8-bromoquinoline [in the presence of $Pd(PPh_3)_2$] gives complex **3** with a quinolyl substituent, which was studied by X-ray diffraction. Under UV irradiation of complex **3** in a hexane–toluene mixture, one CO group is abstracted to form the chelate complex **4** due to coordination of the Mn atom to the nitrogen atom of the quinoline fragment. Complex **4** was studied by X-ray diffraction.[24]

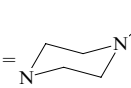


3 **4**

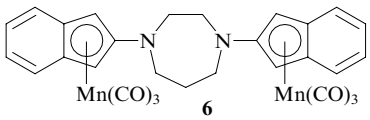
A series of publications is devoted to indenyl and fluorenyl analogues of cymantrene. The reactions of indan-2-one with secondary amines in boiling methanol provided the corresponding 2-aminoindenes; these were deprotonated by the treatment with Bu^nLi (THF, −50 °C) and reacted with $Mn(CO)_3Py_2Br$ to give 2-aminoindenyl derivatives **5a–c**, **6**. Complexes **5a**,**b** were characterised by X-ray diffraction.[25]



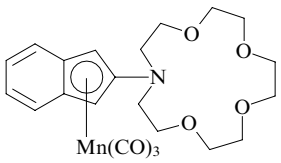
5a–c

NR_2 =  (**a**), $NMe(CH_2)_2NMe_2$ (**b**), $NMe(CH_2)_2NHMe$ (**c**).

Similarly, the reaction of indan-2-one with aza-15-crown-5 afforded 2-aminoindene derivative where the nitrogen atom at position 2 of the indenyl fragment is incorporated into the aza-crown moiety. Treatment of these product with Bu^nLi and subsequent reaction with $Mn(CO)_3Py_2Br$ yielded the 2-aminoindenyl analogue of cymantrene **7**, the structure of which was confirmed by X-ray diffraction.[26]



6



7

The reaction of 1,3-bis(diphenylphosphino)indene with sulfur led to the bissulfide derivative 1,3-$(Ph_2P{=}S)_2C_9H_6$. This was metallated with Bu^nLi and the resulting cyclopentadienyl anion was made to react with $Mn(CO)_5Br$ to give the indenyl complex {η^5-$C_9H_5(Ph_2P{=}S)_2$-1,3}$Mn(CO)_3$ (C_9H_7 is indenyl), which was examined by X-ray diffraction.[27]

Stradiotto and co-workers reported the synthesis and investigation of a series of complexes (η^5-indenyl)$Mn(CO)_3$ based on 2-dimethylaminoindene and a bifunctional N,P-ligand, 1-diisopropylphosphino-2-dimethylaminoindene or its (P=S) derivative.[28–30]

A novel method for the synthesis of heterobimetallic complexes by the reaction of $(CO)_3Cr(\eta^6$-$PhC_5H_4)$ or its sodium salt with the corresponding metal derivatives was suggested.[31] Thus the reaction of this salt with 0.5 equiv $[Mn(CO)_4Br]_2$ resulted in the complex $(CO)_3Cr(\eta^6,\eta^5$-$PhC_5H_4)Mn(CO)_3$ where the Cr atom is coordinated to the benzene ring, while the Mn atom is coordinated to the cyclopentadienyl fragment. Similarly, the reaction of the salt $[(CO)_3Cr(\eta^6$-$PhC_9H_6)]Na$ with $[Mn(CO)_4Br]_2$ affords the indenyl complex $(CO)_3Cr(\eta^6,\eta^5$-$PhC_9H_6)Mn(CO)_3$.[31] A method for the synthesis of chromium–manganese bimetallic complexes starting from the substituted 2-cycloheptatrienylindenyl complex ($CO)_3Mn(\eta^5$-2-$C_7H_7C_9H_6$) (**8**, C_7H_7 is cyclohepta-1,3,5-trienyl) was developed.[32] The reaction of complex **8** with $Ph_3C^+BF_4^-$ results in the abstraction of the hydride ion from the cycloheptatriene moiety to form the cationic indenyl complex $[(CO)_3Mn(\eta^5$-2-$C_7H_6C_9H_6)]^+BF_4^-$ where the positively charged substituent C_7H_6 is the tropylium cation. In the reaction of complex **8** with $(MeCN)_3Cr(CO)_3$, the Cr atom coordinates to the cycloheptatrienyl moiety to give the neutral complex $(CO)_3Mn(\eta^5$-C_9H_6-2-C_7H_7-$\eta^6)Cr(CO)_3$ as a mixture of two isomers (cyclohepta-1,3,5-trien-1-yl- and cyclohepta-1,3,5-trien-2-ylindenes). The reaction of $Ph_3C^+BF_4^-$ with the latter compound results also in the abstraction of the hydride ion to give the cationic complex with the tropylium moiety.[32]

9-R-Substituted fluorenyltricarbonylmanganese complexes (η^5-9-$RC_{13}H_8$)$Mn(CO)_3$ (R = Ph, Bu^t) were synthesised; their haptotropic rearrangements, electrochemical properties and the mechanism of redox-induced change in the binding mode were studied.[33–35] The dependence of the type of the reaction product of fluorenyllithium with $Mn(CO)_5Br$ on temperature was studied. The reaction in THF at 20 °C afforded the known complex (η^5-$C_{13}H_9$)$Mn(CO)_3$ (**9**, $C_{13}H_9$ is fluorenyl), as well as

fluorene, 9,9′-bifluorenyl and $Mn_2(CO)_{10}$. If the reaction was conducted at −78 °C, a new complex (η^1-$C_{13}H_9$).$Mn(CO)_5$ (**10**) was isolated and characterised by X-ray diffraction; the $Mn(CO)_5$ group is σ-bonded to the C(9) atom of the fluorenyl fragment. Complex **10** is moderately stable at −23 °C; in boiling THF, it loses two CO groups after 30 min and transforms into the thermodynamically stable η^5-complex **9** due to σ → π-rearrangement.[36] In the reaction with bases, the cation (η^6-cpp)$Mn(CO)_3^+$ undergoes deprotonation and haptotropic rearrangement to give the neutral complex (η^5-cpp)$Mn(CO)_3$ (cppH is a tetracyclic ligand, 4*H*-cyclopenta[*def*]phenanthrene).[37]

The search for new catalytic systems gave an impetus for the development of methods for the synthesis of polyfluoroalkyl derivatives of cymantrene containing one or several substituents $(CH_2)_2(CF_2)_nCF_3$ (n = 5, 7, 9). Two approaches have been used. According to the first approach, deprotonation of the substituted cyclopentadiene C_5H_5R with Bu^nLi afforded the corresponding cyclopentadienyl anion, its reaction with $Mn(CO)_5Br$ resulted in the complex $(CO)_3Mn(\eta^5$-$C_5H_4R)$ [R = $(CH_2)_2(CF_2)_9CF_3$].[38]

The second approach included cross-coupling of mono- or polybromocymantrene with the fluorous organozinc iodide IZnR [R = $(CH_2)_2(CF_2)_7CF_3$] in boiling THF in the presence of the catalyst L_2PdCl_2 [L = PPh_3 or L_2 = 1,1-bis(diphenylphosphino)ferrocene]. The monosubstituted complex CymR was obtained in high yield starting from bromocymantrene. In the reaction of (η^5-C_5Br_5)$Mn(CO)_3$ with the above zinc reagent, from 2 to 5 bromine atoms were involved and a mixture of compounds $(CO)_3Mn.(\eta^5$-$C_5H_{5-n}R_n)$ with 2 to 5 substituents R was obtained.[39] UV irradiation of this mixture for 20 min resulted in the detachment of the corresponding substituted cyclopentadienes from the manganese complexes, which could be isolated by chromatography.

The synthesis and studies of compounds formed upon substitution of different atoms or groups for one or several Cl or Br atoms in pentachloro- (PCC) or pentabromocymantrenes (PBC) were reported by Sünkel and co-workers. The reactions proceed in two steps: (1) metallation of (η^5-C_5Br_5)$Mn(CO)_3$ with butyllithium leading to the replacement of one Br atom by Li; (2) the reaction of lithium derivatives with electrophiles (E).

(η^5-C_5Br_5)$Mn(CO)_3$ $\xrightarrow[\text{THF, } -78\ ^\circ\text{C}]{Bu^nLi}$ (η^5-C_5Br_4Li)$Mn(CO)_3$ $\xrightarrow{E}$ $\longrightarrow$ (η^5-C_5Br_4E)$Mn(CO)_3$.

The iteration of this reaction sequence affords di-, tri-, tetra- and pentasubstituted cymantrenes. The reaction of PBC first with 1 or 2 equiv. of Bu^nLi and then with 1 or 2 equiv. of $SiMe_3Cl$ or $SiMe_3OTf$ resulted in (η^5-$C_5Br_4SiMe_3$)$Mn(CO)_3$ and {η^5-1,3-$(SiMe_3)_2C_5Br_3$}.$Mn(CO)_3$ (its structure was established by X-ray diffraction analysis). The repeated consecutive treatment of the latter with Bu^nLi and $SiMe_3Cl$ gave the tris-substituted derivative {η^5-$C_5Br_2(SiMe_3)_3$}$Mn(CO)_3$, which reacted with 1 or 2 equiv. of Bu^nLi and 1 or 2 equiv. of $SiMe_2HCl$ to form tetra- and pentasubstituted complexes {η^5-$C_5H(SiMe_3)_3$.$(SiMe_2H)$}$Mn(CO)_3$ and {η^5-$C_5(SiMe_3)_3(SiMe_2H)_2$}$Mn.(CO)_3$.[40]

Trithiocomplexes {η^5-$C_5Cl_2(SR)_3$}$Mn(CO)_3$, where $(SR)_3$ = $(SMe)_2SPh$, $(SMe)(SPh)_2$, were synthesised by the metallation of the complexes with alkyl- or arylthio groups (η^5-C_5Cl_4SR)$Mn(CO)_3$ and {η^5-$C_5Cl_3(SR)_2$}$Mn(CO)_3$ (R = Me, Ph) with Bu^nLi followed by the reaction with disulfides MeSSMe or PhSSPh. Similarly, selenides of the general formula {η^5-$C_5Cl_{5-n}(SeR)_n$}$Mn(CO)_3$, where R = Me (n = 1–3), Ph (n = 2) were also prepared from bromotetrachlorocymantrene (η^5-C_5Cl_4Br)$Mn(CO)_3$ and diselenides RSeSeR.[41]

The influence of the reactant ratio, temperature, solvent and reaction time on the composition of the PBC metallation products with Bu^nLi and subsequent hydrolysis has been comprehensively studied. It was found that prolonged reaction with a considerable excess of Bu^nLi resulted in the formation, in addition to monolithium derivative, of a dilithium derivative.[42] The reactions of {η^5-$C_5X_4(SiMe_2H)$}$Mn(CO)_3$ (X = Br, Cl, H) and {η^5-$C_5Br_3(SiMe_2H)_2$}$Mn(CO)_3$ with $PdCl_2$ as the chlorinating agent under mild conditions (dry benzene, 15–24 h, 20 °C) result in the substitution of Cl for the H atom of the Si–H bond to form chlorosilyl derivatives with the $SiMe_2Cl$ groups. The latter undergo alcoholysis with saturated alcohols (ROH) to the corresponding alkoxy derivatives with the $SiMe_2OR$ groups.[43] Mono- and bis-derivatives {η^5-$C_5X_{5-n}(AuPPh_3)_n$}$Mn(CO)_3$ (X = Cl, Br; n = 1, 2) are formed in the metallation of PCC or PBC with butyllithium followed by the reaction of the lithium derivatives with the electrophilic agent $Au(PPh_3)Cl$. Similarly, complexes (η^5-C_5Cl_4Q)$Mn(CO)_3$ (Q = $AgPPh_3$, $AuNCBu^n$) were obtained. The addition of $NiL_2(C_2H_4)$ (L = PBu^n_3) to the complex (η^5-C_5Cl_4AuL)$Mn(CO)_3$ prepared *in situ* results in the oxidative addition of one C–Cl bond to Ni^0 to form the complex {η^5-$C_5Cl_3(AuL).(NiL_2Cl)$}$Mn(CO)_3$ containing three different metal atoms.[44]

The treatment of a solution of PCC in THF with a 10-fold excess of Bu^nLi (solution in hexane at −78 °C) yielded the dilithium derivative (η^5-$C_5Cl_3Li_2$)$Mn(CO)_3$. The reaction of this complex with PPh_2Cl and PEt_2Cl in Et_2O gave the complexes with two phosphine substituents {η^5-$C_5Cl_3(PR_2)_2$}$Mn(CO)_3$ (R = Ph, Et). At most two chlorine atoms can be exchanged for lithium by the treatment of PCC with Bu^nLi. The bromine atoms in PBC are more mobile; for this reason, metallation can give products with higher degree of substitution. Triple metallation of PBC with an excess of Bu^nLi at −78 °C followed by the reaction with excess PMe_2Cl provided a mixture of {η^5-$C_5H(PMe_2)_4$}$Mn(CO)_3$ and {η^5-$C_5(PMe_2)_5$}$Mn(CO)_3$ (in a 4 : 1 ratio), from which the pentasubstituted complex was isolated by chromatography. According to the X-ray diffraction data, it contains a planar C_5 ring, five PMe_2 substituents adopting a 'paddle wheel' conformation.[45] Complex {η^5-$C_5(SiMe_2H)_5$}$Mn(CO)_3$ was obtained earlier and characterised by X-ray diffraction.[46]

The reaction of chlorocymantrene with a large excess of Bu^nLi and $SiMe_3Cl$ gives the {η^5-$C_5H_2(SiMe_3)_2Cl$}.$Mn(CO)_3$ complex as a mixture of 1-Cl-2,5-$(SiMe_3)_2$- and 1-Cl-2,4-$(SiMe_3)_2$ isomers. Treatment of this mixture with Bu^tLi and an excess of $SiMe_3Cl$ yielded a complicated product mixture, from which the complex {η^5-1,2,3-$C_5H_2(SiMe_3)_3$}$Mn(CO)_3$ was isolated and characterised by X-ray diffraction.[47] The reaction of (η^5-C_5Cl_4Li)$Mn(CO)_3$ with tetrachlorodiazocyclopentadiene and subsequent hydrolysis resulted in the organometallic hydrazone (η^5-$C_5Cl_4NHN{=}C_5Cl_4$)$Mn(CO)_3$, which was also studied by the X-ray diffraction method. Tosyl azide (4-$MeC_6H_4SO_2N_3$) reacts with the monolithium derivatives (η^5-C_5X_4Li)$Mn(CO)_3$ (X = Cl, Br, H) to form

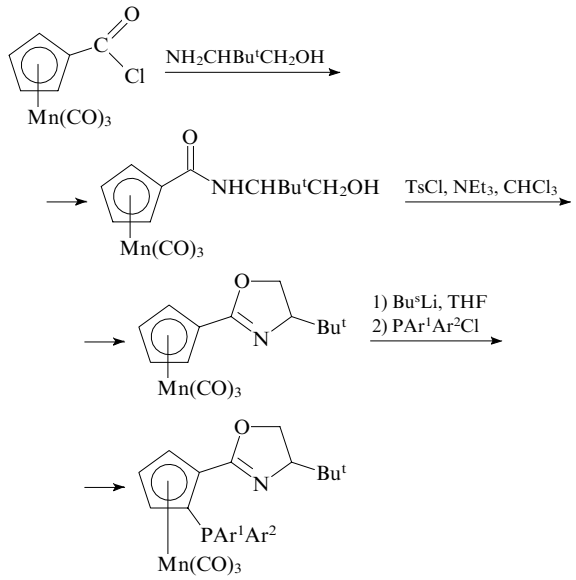
cymantrenyl azides $(\eta^5\text{-}C_5X_4N_3)Mn(CO)_3$, which can be reduced with $NaBH_4$ to the corresponding aminocymantrenes $(\eta^5\text{-}C_5X_4NH_2)Mn(CO)_3$.[48,49] 2,5-Di- and 2,3,5-tribromodiazocyclopentadienes were prepared by the reaction of diazocyclopentadiene with 1.5 and 2.5 equiv. of *N*-bromosuccinimide, respectively, in MeCN or Me_2CO at -40 °C, which react with $Mn(CO)_5Br$ in CF_3Ph at 80 °C to form 1,2,3-tribromocymantrene (studied by X-ray diffraction method) and tetrabromocymantrene.[50]

Almost simultaneously, two research groups discovered that the reaction of cymantrene with 5 equiv. of mercury(II) acetate in boiling ethanol for 48 h[51] or in dichloroethane for 4 h[52] resulted in complete mercuration of the Cp ring to form the pentasubstituted derivative $\{\eta^5\text{-}C_5(HgOAc)_5\}.Mn(CO)_3$ (**11**). It was found earlier[53] that the reaction of cymantrene with such a strong electrophilic agent as mercury trifluoroacetate leads to full mercuration of the Cp ring (CH_2Cl_2, 20 °C, 3 h) with the formation of $\{\eta^5\text{-}C_5(HgOCOCF_3)_5\}Mn(CO)_3$. Complex **11** readily undergoes the reactions common to organomercury compounds, for example, substitution of halide atoms for the $HgOCOCH_3$ groups: pentachloro- or pentabromocymantrenes were obtained by the reaction with 25 equiv. of $CuCl_2$ or $CuBr_2$ in boiling acetone;[52] the reaction with an excess of KI_3 in aqueous MeOH[51] or in water[52] provided pentaiodocymantrene (PIC) characterised by the X-ray diffraction.[52] Cross-coupling of the latter compound with alkynes $Me_3SnC{\equiv}CR$ (R = Pr^i, Me) in the presence of the catalyst $PdCl_2(MeCN)_2$ (DMF, 40 h) yielded pentasubstituted derivatives $\{\eta^5\text{-}C_5(C{\equiv}CR)_5\}Mn(CO)_3$ (the complex with R = Me is characterised by the X-ray diffraction method).[51] The pentasubstituted derivatives $\{\eta^5\text{-}C_5.(C{\equiv}C{-}C{\equiv}CR)_5\}Mn(CO)_3$ (R = Pr^i, Bu^t) were synthesised by the cross-coupling of PIC with diacetylenes $Me_3SnC{\equiv}CC{\equiv}CR$.[54] The cross-coupling of $(CO)_3Fe(\eta^4\text{-}C_4I_4)$ with the monosubstituted cymantrene derivatives $(Cym)(C{\equiv}C)_nSnMe_3$ (n = 1, 2) afforded the corresponding complexes $(CO)_3Fe[\eta^4\text{-}C_4\{(C{\equiv}C)_nCym\}]_4$ (Ref. 54). Metallation of the compound $(Cym)C{\equiv}CSiMe_3$ with Bu^sLi followed by the treatment with ICH_2CH_2I and cross-coupling with $Me_3SnC{\equiv}CSiMe_3$ resulted in 1,2- and 1,3-$\{\eta^5\text{-}C_5H_3(C{\equiv}CSiMe_3)_2\}Mn(CO)_3$, which were desilylated to bisethynyl complexes $\{\eta^5\text{-}C_5H_3(C{\equiv}CH)_2\}.Mn(CO)_3$. Treatment of these compounds with CuCl and tetramethylenediamine gives a mixture of oligomers.[55] The synthesis of organometallic copolymers with phenyl and cymantrenyl fragments by the Suzuki reaction is described.[56]

The crystal structure of the pentasubstituted complex $(\eta^5\text{-}C_5R_5)Mn(CO)_3$ (R = cyclo-C_5H_5) was established by X-ray diffraction; a mass spectroscopic study revealed that the laser-induced desorption/ionisation results in the formation of fullerene C_{60} and, probably, other carbon clusters.[57] Estradiol derivatives with the $Mn(CO)_3$ fragment were synthesised (see Refs 58–60 and references cited therein). The synthesis of cymantrene-based chiral complexes, *viz*., (*R*)-2-iodocymantrenecarbaldehyde, (2*R*,4*R*)-2-cymantrenyl-4-(hydroxymethyl)-1,3-dioxane, *etc*., was reported.[59]

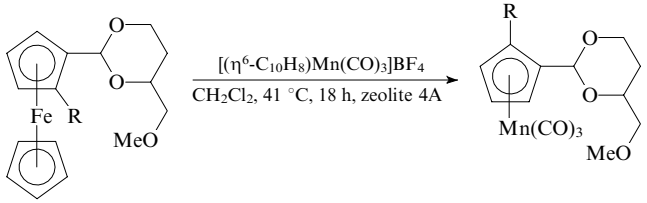
A series of new chiral cymantrene derivatives was synthesised, in particular, planar chiral phosphites and iminodiaminophosphites, as well as their palladium complexes. These compounds can be used as catalysts for asymmetric hydrogenation and allylic alkylation of 1,3-diphenylallyl acetate with dimethyl malonate (optical yield up to 73%).[61–64]

Two novel approaches to the synthesis of cymantrene-based chiral bidentate ligands were suggested.[65–67] According to the first approach, planar chiral ligands with 2-oxazolin-2-yl and PAr_2 substituents in positions 1,2 of the Cp ring were synthesised in three steps. It the first step, the acid chloride (Cym)C(O)Cl reacted with commercially available and enantiopure amino alcohols NH_2CHRCH_2OH (R = Pr^i, Bu^t); it the second step, the oxazoline substituent is formed due to cyclisation. The third step is metallation at position 2 with Bu^sLi followed by the reaction with diarylchlorophosphines PAr^1Ar^2Cl.[65–67]



Ar^1, Ar^2 = Ph, 3,5-$Me_2C_6H_3$, 3,5-$(CF_3)_2C_6H_3$, biphenyl-2-yl.

The other approach consists of the ligand exchange that occurs on refluxing equimolar amounts of a planar chiral ferrocene derivative and the cationic arene complex $[(\eta^6\text{-}C_{10}H_8)Mn(CO)_3]BF_4$ ($C_{10}H_8$ is naphthalene) in CH_2Cl_2 in the presence of zeolite 4A; as a result, the planar chiral Mn complex is formed.[68,69]



R = Me, $SiMe_3$, $SiMe_2(CH{=}CH_2)$.

These complexes demonstrated high activity in palladium-catalysed asymmetric allylic substitution. The methods for the preparation of chiral bidentate ligands based on ferrocene, cymantrene, $CpRe(CO)_3$ and other transition metal complexes and their application in enantioselective catalysis have briefly been considered in a review.[70]

With the aim of search for new organometallic photochromic systems, bifunctional complexes with a 2-pyridyl fragment (R = 2-C_5H_4N) have been synthesised, *viz*., ketone $(Cym)CH_2C(=O)R$, thioamide $(Cym)CH_2.CH(R)C(=S)NH_2$ and more than 20 their derivatives. Their properties and the reactions leading to the formation of chelate rings with Mn–N or Mn←O=C bonds due to

the abstraction of one CO group under UV irradiation have been studied.[71] The structure of the binuclear complex $(Cym)_2C(CN)R$ was established by the X-ray diffraction study.[72] Hydrolysis of nitrile (Cym)CN under mild conditions (K_2CO_3 in MeOH) gave imidate (Cym)C(=NH).OMe, which was suggested as a new protein redox label for the studies of bovine serum albumin.[73] Electrochemical reduction of cymantrene and its imidate was also studied.[74] Thermolysis of cyclometallated arenes or heterocycles with the general formula *cis*-(LC)$Mn(CO)_4$ (LC is a carbanionic chelating ligand) in the pesence of diazocyclopentadiene, 7-diazoindene or 9-diazofluorene [in boiling hexane (or heptane)–toluene mixtures] resulted in the abstraction of one CO group to form different polycyclic complexes having the $Mn(CO)_3$ group and a substituted pentadienyl, indenyl or fluorenyl fragment.[75] The reaction of dicymantrenyl disulfide (Cym)SS(Cym) with $Pt(PPh_3)_4$ resulted in the cleavage of the S–S bond and incorporation of the $Pt(PPh_3)_2$ fragment to form the binuclear complex *cis*-$(PPh_3)_2Pt(SCym)_2$ studied by the X-ray diffraction method.[76] Cyclopentadienyl silyl ethers $C_5H_3X_2OR$ (X = H, Me; R = $SiMe_2Bu^t$) were prepared by the reaction of cyclopentenone or 3,4-dimethylcyclopentenone with silyl triflate ROTf in the presence of triethylamine. Their deprotonation with Bu^nLi followed by the reaction of the cyclopentadienyl anion formed with $Mn(CO)_3Py_2Br$ in THF resulted in cymantrenyl silyl ethers $(CO)_3Mn(\eta^5\text{-}C_5H_2X_2OR)$. Hydrolysis of the latter with a small excess of $NBu^n_4F\cdot 3H_2O$ in THF under mild conditions resulted in hitherto unknown alcohols $(CO)_3Mn(\eta^5\text{-}C_5H_2X_2OH)$.[77]

Direct borylation of the Cp ring by the reaction of cymantrene or ferrocene (FcH) with halides BBr_3 or BI_3 with the formation of monosubstituted derivatives $CymBBr_2$ or $FcBBr_2$ was discovered more than 30 years ago (see the review[3] and citations in Refs 78 and 79), however the structures of these compounds have not been investigated for a long time. Refluxing methylcymantrene with BBr_3 gave the complex $(CO)_3Mn.\{\eta^5\text{-}C_5H_3(Me)BBr_2\}$ characterised by the X-ray diffraction method.[78] The most interesting structural feature of this complex is that the boron atom is not coplanar with the Cp ligand, it deviates toward the Mn atom by 12.5°. The reactions of $CymBBr_2$ with the salts $M[(\eta^5\text{-}C_5R_5)Fe(CO)_2]$ (M = K, Na) afforded compounds $CymBBrFe(CO)_2.(\eta^5\text{-}C_5R_5)$ (R = H, Me).[78] Some time later, another research group managed to grow a single crystal and perform an X-ray diffraction study for the parent complex $(CO)_3Mn(\eta^5\text{-}C_5H_4BBr_2)$.[79] According to the X-ray data, in this case, too, the boron atom is deviated toward the metal atom by 11.4°.

The exchange and substitution reactions at the boron atom were also studied.[79] Thus the reaction of $CymBMe_2$ with potassium pyrazolide (KPz, HPz is pyrazole) resulted in the anionic complex $[CymBMe_2Pz]K$; that of $CymBBr_2$ with $CymB(NMe_2)_2$ yielded $CymB(NMe_2)Br$ upon disproportionation. The reaction of the latter with MeMgCl afforded $CymB(NMe_2)Me$. This complex reacted with HPz or KPz to give the disubstituted derivative $[CymB(Pz)_2Me]K$. The reaction of $[CymB(Pz)_3]H$ with Bu^tOK leads to $[CymB(Pz)_3]K$. The anionic complex $[CymBPh_3]Li$ was synthesised by the reaction of $CymBBr_2$ with 3 equiv. of PhLi;[79] disubstituted complex $\{\eta^5\text{-}1,3\text{-}(BBr_2)_2C_5H_3\}Mn(CO)_3$ was obtained by refluxing cymantrene with excess BBr_3.[80] According to X-ray diffraction data, in this case too, both boron atoms deviate toward the metal atom by 7.6 and 3.7°.

For all cymantrene derivatives studied so far by the X-ray diffraction method, the atom (C, O, N, P, *etc.*) bound to the Cp ring lies in the plane of the ring. In the case of mangenese complexes, the only exclusion was the diphenyl(cymantrenyl)carbenium cation ($CymC^+Ph_2$, **12**) obtained by the reaction of diphenyl(cymantrenyl)methanol ($CymCPh_2OH$, **13**) with an acid. In alcohol **13**, the $C(Cp)-C^\alpha Ph_2OH$ bond lies in the plane of the Cp ring; the antibonding $Mn-C^\alpha$ distance is equal to 3.340 Å. In cation **12**, the $C(Cp)-C^\alpha$ bond is displaced toward Mn by 6.6°, while the $Mn-C^\alpha$ distance decreased to 3.045 Å.[81] Quantum chemical calculations by the DFT method performed for cation **12** agree satisfactorily with X-ray diffraction data. A similar bending of the $C(Cp)-C^\alpha$ bond toward the Fe atom was found for boron-containing ferrocene derivatives.[79–81] The bending of the $C(Cp)-C^\alpha$ bonds toward the metal atom (in the case of carbocation **12**) and of the C(Cp)–B bonds (in the case of BBr_2-derivatives of cymantrene and ferrocene) can be explained by the fact that the carbenium centre at the α-carbon and the boron atoms with vacant p-orbitals are electron-deficient and seem to be able to interact with the occupied d-orbitals of the metal atom. The possibility of this interaction for $FcBBr_2$ was for the first time considered[82] on the basis of the X-ray data (the dip angle 17.7°) and DFT calculations. The state of the art of the problem was considered using a wide range of ferrocenylboranes with different substituents as examples.[83] Note that for metallocenylcarbenium ions with different metals (Fe, Ru, Os, Mn, Co), the bending of the $C(Cp)-C^\alpha$ bond to the metal atom is a special feature, though the dip angle varies within a wide range depending on the metal nature and its ligand environment.[81]

The complexes $(CO)_3Mn\{\eta^5\text{-}C_5H_3(R)BBr_2\}$ (R = H, Me) obtained from cymantrene and CymMe react with 3 equiv. of pyrazole or its 4-substituted derivatives in the presence of triethylamine with elimination of HBr; treatment with EtOTl resulted in stable complexes $[(CO)_3Mn\{\eta^5\text{-}C_5H_3(R)B(Pz)_3\}]Tl$ [**14a**,**b**; R = H (**a**), Me (**b**)]. According to X-ray diffraction data, in the crystal compound **14a** forms polymeric chains, whereas complex **14b** forms cyclic tetramers. In both complexes, the thallium atoms are bound to three nitrogen atoms of the pyrazole fragments.[84] Complex **14a** reacts with $Mn(CO)_5Br$ in an inert atmosphere with the elimination of TlBr to form the binuclear complex $CymB(\mu\text{-}Pz)_3Mn(CO)_3$. If this reaction is not conducted in an inert atmosphere, compound $CymB(\mu\text{-}Pz)_2(\mu\text{-}OH)Mn(CO)_3$ is obtained due to partial hydrolysis. The reaction of complex **14a** with 0.5 equiv. of $ZnBr_2$ afforded the complex $\{CymB(\mu\text{-}Pz)_3\}_2Zn$ where one nitrogen atom of the Pz group was bound to the boron atom and the other, to the Zn atom, the latter having the octahedral environment of six nitrogen atoms.[85]

3,5-Bis(chloromethyl)-*N*-R-pyrazole (the protecting group R is tetrahydropyran-2-yl) does not react with CymLi, but the reaction occurs under the conditions of Pd-catalysed cross-coupling. The zinc derivative ClZn(Cym) formed from CymLi and $ZnCl_2$ in the presence of $Pd(PPh_3)_2$ as a catalyst [prepared *in situ* by reduction of $(PPh_3)_2PdCl_2$ with diisobytylaluminium hydride] reacts with a pyrazole derivative to give the complex $(Cym)CH_2(cyclo\text{-}C_3HN_2R)CH_2Cl$ (**15**), which was studied by the X-ray diffraction method. The attempts to introduce the second cymantrenyl substituent in this way failed.[86]

Compound **15** reacted with di(α-picolyl)amine with involvement of the second CH_2Cl group in the presence of Na_2CO_3 with elimination of HCl; after acid hydrolysis and removal of the protecting group R, the complex (Cym)CH_2(cyclo-$C_3H_2N_2$)$CH_2N(Pic)_2$ (**16**, Pic is α-picolyl) was obtained. If the starting compound was a more reactive 3,5-bis(bromomethyl)-*N*-R-pyrazole, the dicymantrenyl derivative 3,5-bis(cymantrenylmethyl)pyrazole (**17**) could be obtained in high yield by this method.[87,88] Complexes **15**–**17** were used as the starting compounds for the synthesis of a wide variety of heterobinuclear organometallic complexes with a bridging pyrazole ligand: the C(3) atom of its ring is bound to the Cp ring of the cymantrenyl fragment through the methylene group, the N(2) atom is coordinated to the Mn atom, the N(1) atom is bound to the fragment ML_n [M = Mn, Ni, Co, Zn, *etc.*; L are O- and N-donor ligands that are usually considered in the classical theory of coordination compounds (for example, acetate, nitrate, *etc.*].[86–92] The properties of pyrazolylborate complexes based on ferrocene and cymantrene are briefly considered in the review.[93]

It was found that UV or sunlight irradiation of cymantrene and its derivatives in the presence of potential proton sources (diethyl ether–MeOH, diethyl ether–water mixtures) results in photolytic abstraction of the $Mn(CO)_3$ fragment to give free cyclopentadienes, which can be used in organic synthesis. This method can be employed for the preparation of polyfunctional molecules such as ethynylestradiol.[94,95]

The thallium salt of the phosphaferrocenyl-substituted cyclopentadienyl anion (2-$RCH_2C_5H_4$)Tl (R is 3,4-dimethylphosphaferrocenyl) reacts with $Mn(CO)_5Br$ to form complex (η^5-$RCH_2C_5H_4$)$Mn(CO)_3$ where the phosphorus atom is not bound to the Mn atom; UV irradiation in THF results in the easy loss of one CO group and formation of the chelate complex (η^5-$RCH_2C_5H_4$)$Mn(CO)_2$ with the P–Mn bond. Its structure was confirmed by the X-ray diffraction analysis. Since the 2-substituted phosphaferrocenyl fragment is planar-chiral, (see Section V), photochemical substitution of the PPh_3 ligand for one CO group gives a mixture of two diastereomers of the monocarbonyl complex (η^5-$RCH_2C_5H_4$)$Mn(CO)(PPh_3)$.[96] The synthesis and reactivity of cymantrene analogues, complexes with the general formula (η^5-Q)$Mn(CO)_3$ (Q is the 1,2-oxaborolide ligand C_3H_3OBPh with the five-membered ring C_3OB or the carborane ligand η^5-*nido*-$C_2B_9H_{11}$), are considered;[97,98] both complexes are characterised by X-ray diffraction.

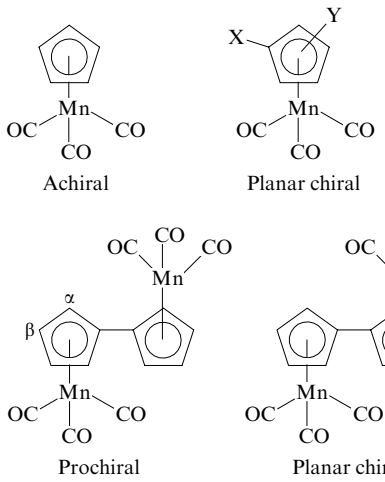
The quantum chemical calculations by the DFT method have been performed for the unsaturated binuclear complexes $Cp_2Mn_2(CO)_n$ ($n = 2–5$)[99] and the role of haptotropic shifts in the addition reaction of phosphine (PH_3) to tricarbonyl manganese complexes was assesed.[100] Complexes $CpML_3$ where the central atom is in the high and low oxidation states (M = Mn, Re; L = O, CO) were repeatedly studied by IR and Raman spectroscopic methods at the modern level.[101] Rate constants were measured for the oxidative addition of $Pd(PPh_3)_4$ to iodides CymI, (η^5-IC_5H_4)$Re(CO)_3$ and FcI in DMF; it was found[102] that the reaction rate is substantially higher for complexes with electron-withdrawing groups $Mn(CO)_3$ and $Re(CO)_3$ as compared to that for ferrocenyl iodide and decreases in a series Mn > Re ≫ Fe. Disubstituted cymantrenes {η^5-$C_5H_3(CO_2R)_2$}$Mn(CO)_3$ (R = Et, Ph) were synthesised by the reactions of the corresponding 1,2-disubstituted cyclopentadienyl anions Na{$C_5H_3(CO_2R)_2$} (prepared in two steps from C_5H_5Na) with $Mn(CO)_5Br$.[103] It was found that in the system EtOH–$SiCl_4$, acetylcymantrene and acetylferrocene are readily trimerised to tris-substituted benzenes 1,3,5-$C_6H_3R_3$ (R is cymantrenyl or ferrocenyl); the structures of trimers were established by X-ray analysis.[104]

It was mentioned above[68,69] that in the reaction of planar-chiral ferrocenes with the cationic complex [(η^6-$C_{10}H_8$)$Mn(CO)_3$]$^+$ under relatively mild conditions (reflux in CH_2Cl_2), the ligand exchange occurs to form a planar chiral complex with the fragment $Mn(CO)_3$ and a cationic iron complex [η^6-($C_{10}H_8$)FeCp]$^+$. In the reaction of 'electron-rich' metallocenes Cp^*_2M ($Cp^* = \eta^5$-C_5Me_5; M = Fe, Ru, Os) with complexes [(η^6-Ar)$Mn(CO)_3$]$^+$, where Ar is 1-methylnaphthalene or acenaphthene, in boiling CH_2Cl_2, a transfer of the fragment $Mn(CO)_3$ to one of the Cp* rings of metallocene occurs to form 'capped' cationic complexes with the general formula [Cp*MCp*$Mn(CO)_3$]$^+$; the compound with M = Ru was studied by the X-ray diffraction.[105]

III. Bicymantrenyl and its derivatives

Bicymantrenyl [η^5,η^5-$(CO)_3Mn(C_5H_4–C_5H_4)Mn(CO)_3$, bcymH], was synthesised in 1969, but its properties have not practically been studied till the mid-1990s. It was found earlier that bcymH can be involved into acetylation reaction to form 3-acetylbicymantrenyl;[106] the substitution reactions of of PPh_3 for a CO group for and other ligands were also performed.[107]

Cymantrene is an achiral molecule. A characteristic feature of the geometry of cymantrene and its analogues, complexes with one cyclic ligand like [η^n-C_nH_n)$M(CO)_3$ (for instance, $CpRe(CO)_3$, $C_6H_6Cr(CO)_3$, *etc.*] is the fact that their molecules become planar-chiral when two different substituents are introduced into the cyclic ligand. The molecule of bcymH is prochiral. All bcymH derivatives with one substituent X in any of the two non-equivalent positions (α and β) are planar-chiral and theoretically can be separated into enantiomers. Any derivative of bcymH with a substituent X can be considered as cymantrene with two different substituents, Cym and X.



In 1994–1999, we performed studies on the reactivity of bcymH. A detailed study of the Friedel–Crafts acetylation and benzoylation showed that these reactions were non-selective. Both non-equivalent positions (α and β) were substituted; a mixture of two isomeric ketones always

formed, which could easily be separated by chromatography on a column with Al_2O_3. The substitution at the sterically more accessible β-position dominated; the β:α ratio for acylation was equal to ~5:1.[108] With an excess of the acetylating agent, a mixture of products containing, in addition to monoketones, several isomeric diketones was obtained. Ethyl and benzyl derivatives were prepared by reduction of acetyl- and benzoylcymantrenes.[108]

Acylation of bcymH occurs less readily as compared to that of cymantrene. In the competitive acylation of an equimolar mixture CymH + bcymH with 1 equiv. of the acetylating mixture $AcCl-AlCl_3$ in CH_2Cl_2, cymantrene reacted virtually completely, while more than 85% – 90% of bcymH was recovered unchanged.[108] The less efficient acylation of bcymH as compared to that of cymantrene seems to be associated with a marked electron-withdrawing effect of the fragment $(CO)_3MnC_5H_4$ on the neighbouring ring. For bcymH, the possibilities for isomerisation are significantly wider than for cymantrene. In the case of one subsituent, only two isomers (α and β) can exist, but the number of possible isomers significantly grows with an increase in the number of substituents. Thus for two equal substituents, four isomers can exist with two substituents in the same ring and eight more isomers with substituents in different rings.

Like cymantrene, bcymH undergoes metallation with Bu^nLi (THF, −60 °C).[109] Monolithium derivative or a mixture of mono- and polylithium derivatives are formed depending on the amount of Bu^nLi. If ~1.2 – 1.3 equiv. of Bu^nLi is used, some starting bcymH is recovered and it is virtually only β-lithium derivative that is formed. At four- to fivefold excess of Bu^nLi, the metallation resulted in a mixture of compounds containing from 1 to 4 Li atoms; subsequent treatment with D_2O afforded a mixture of isotopomers containing, according to the data from mass spectrometry, from 1 to 4 deuterium atoms. Like acylation, metallation of bcymH is non-selective: the lithium atom enters both positions, though β-substitution predominates. Treatment with D_2O revealed the ratio to be β:α ~ (3 – 4):1. Complex 3-Et(bcym) prepared by the reduction of 3-Ac(bcym) was metallated non-selectively involving all seven positions of the fragment $C_5H_4-C_5H_3$.

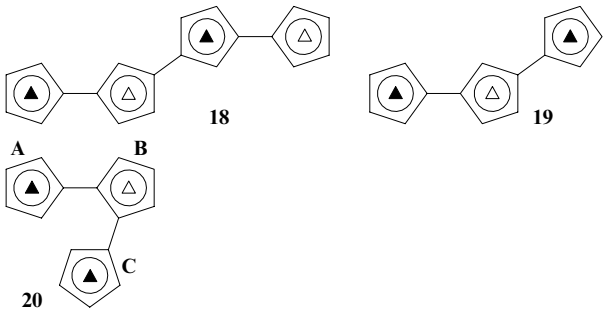
When β-Li(bcym) was quenched with CO_2, the carboxylic acid, 3-HO_2C(bcym), was obtained; it was transformed to the acid chloride: with more than 2 equiv. of Bu^nLi used for metallation, a mixture of dicarboxylic acids was obtained. The reaction of lithiated bcymH with iodine resulted in a mixture of mono- and diiodobicymantrenyls;[109] the reaction of β-Li(bcym) with PPh_2Cl afforded β-diphenylphosphino derivative.[110] Two isomeric aldehydes, α- and β-(bcym)CHO, ~1:10, were obtained by the treatment of lithiated bcymH with DMF followed by hydrolysis and chromatographic separation.[109, 110]

Both isomeric aldehydes are planar chiral, they were resolved into enantiomers through the formation of the Schiff base with (*S*)-(−)-phenylethylamine; a mixture of diastereomers was separated by crystallisation, then optically active enantiomers of the aldehydes were isolated by acid hydrolysis.

A diastereomer from the β-aldehyde less soluble in benzene was characterised by X-ray diffraction; it has the (S_c, R_p) absolute configuration, the subscripts refer to the chiral centre (c) and the chiral plane (p), respectively. Starting from the optically active β-aldehyde, its derivatives β-(bcym)CH_2OH and β-Me(bcym) were obtained and their CD spectra were examined.[111]

Like cymantrene, bicymantrenyl undergoes mercuration. With a strong aprotic acid $SnCl_4$, its phosphine derivative forms an adduct with tin coordinated to the Mn atom.[112] The reaction of bcymH with 8 equiv. of $Hg(OCOCF_3)_2$ in CH_2Cl_2 resulted in easy exhaustive mercuration to form octakis(trifluoroacetatomercurio)-bicymantrenyl. According to the IR spectroscopic data, this reaction proceeds in two steps. In the first step, rapid addition of the strong aprotic acid $Hg(OCOCF_3)_2$ occurs to the most basic site of the molecule, *i.e.*, the metal atom, to form an unstable intermediate with a $Mn-Hg(OCOCF_3)_2$ bond, which can be identified by the characteristic bands in the IR spectrum. It the second step, the fragment $Hg(OCOCF_3)_2$ migrates to the Cp ring with substitution of $HgOCOCF_3$ for the hydrogen atom for and liberation of CF_3CO_2H, (IR spectroscopic data). Octamercuriobicymantrenyl undergoes common reactions of organomercurials, *viz.*, regeneration of the parent bcymH under the action of strong acids, exchange reaction with I_2 to form octaiodobicymantrenyl. The reaction with $CuCl_2$ in boiling acetone resulted in the substitution of chlorine for the $HgOCOCF_3$ groups. However, in contrast to cymantrene, which gives only pentahalo-derivatives in good yields,[51 – 53] bcymH affords a mixture of hexa- and heptachlorobicymantrenyl.[112]

A preparative method for the synthesis of bicymantrenyl is the oxidative coupling of cymantrenyllithium upon the action of anhydrous $CuCl_2$ (reaction [1 + 1]).[107] Application of this reaction to a lithium derivative of bcymH was expected to afford polycymantrenyls. The oxidative coupling of β-Li(bcym) in the presence of anhydrous $CuCl_2$ occurred as a [2 + 2]-reaction resulting in a first representative of a new homologous series of polycymantrenyls, quatercymantrenyl (**18**). The oxidative coupling of lithium derivatives of cymantrene and bcymH under the action of $CuCl_2$ followed by hydrolysis afforded, in addition to recovered cymantrene and bcymH, complex **18** and two isomers of tercymantrenyl (**19**, **20**) (products of the [2 + 1] reaction) isolated by chromatography.[110, 113] The structures of complexes **18** – **20** were established by the X-ray diffraction analysis.[110]



▲ and △ are $Mn(CO)_3$ fragments above and under the plane of the Cp ring, respectively.

Polycymantrenyls with more than three cymantrenyl fragments can have isomers differing only in the mode of coupling of the parts of the molecule, *viz.*, β – β-, α – β- and α – α-isomers. According to X-ray diffraction data, in complex **18**, two bicymantrenyl fragments are bound in the β – β mode, *i.e.* the central C – C bond arises between the β-positions of each of the fragments $H_3C_5-C_5H_4$. This type of

binding is also observed in compound **19**. In complexes **18** and **19**, four and three Cp rings, respectively, are approximately coplanar (deviations are 8–12°). In complex **20** where two substituents in the central ring **B** are in the α-position, the rings **A** and **B** are almost coplanar, while the ring **C** deviates from the plane of the rings **A**–**B** due to significant steric hindrances and is virtually orthogonal to the central ring **B** (the corresponding dihedral angle is equal to 88.3°).[110] Complex **18** undergoes the reactions typical of cymantrene, in particular, acetylation and metallation with Bu^nLi, which, as in the case of bcymH, are non-selective. A mixture of several isomeric monoacetyl derivatives and a diacetyl derivative was obtained upon acetylation of compound **18**.[113]

Earlier the monophosphine complex η^5,η^5-$(CO)_3Mn(C_5H_4-C_5H_4)Mn(CO)_2PPh_3$ (**21**) was synthesised by the substitution of the PPh_3 ligand for one CO group in bcymH,[107] but its properties have not been studied. It was found that the introduction of a phosphine ligand causes a strong difference in reactivities of two C_5H_4 fragments of complex **21**. Reactions with electrophilic agents are strictly regioselective proceeding at only two positions of the $(\eta^5\text{-}C_5H_4)Mn(CO)_2PPh_3$ ring. Thus upon the H/D-exchange with CF_3CO_2D, deuterium enters only the α- and β-positions of this ring, but the ring $(\eta^5\text{-}C_5H_4)Mn(CO)_3$ is not involved. Acetylation gives a mixture of two isomeric α- and β-ketones, no acetylation of the $(\eta^5\text{-}C_5H_4)Mn(CO)_3$ ring occurs (Scheme 1). This orientation in the reactions with electrophilic reagents is obviously associated with the donor effect of the phosphine ligand.[114] On the contrary, metallation with Bu^nLi (the protophilic substitution reaction where the proton abstraction from the C–H bond by a base takes place) also proceeds regioselectively, but only at the $(\eta^5\text{-}C_5H_4)Mn(CO)_3$ ring, because the electron-withdrawing group $Mn(CO)_3$ increases proton lability for only this ring, while the electron-donating ligand PPh_3 inhibits the proton abstraction from the second Cp ring. Metallation of complex **21** with subsequent treatment with DMF resulted in a mixture of two isomeric α- and β-aldehydes (Scheme 1).

Selective metallation of the only ring $(\eta^5\text{-}C_5H_4)Mn(CO)_3$ opens wide possibilities for the synthesis of derivatives with different substituents in this ring. Metallation of complex **21** followed by oxidative coupling under the action of $CuCl_2$ resulted in a mixture from which four quatercymantrenyls **22**–**25** were isolated and characterised by the ^1H and ^{31}P NMR spectra. These compounds contained the $Mn(CO)_2PPh_3$ groups in two terminal Cp rings and differ only in the binding mode of two fragments $C_5H_3-C_5H_4$. The signals in the ^1H NMR spectra of complexes **22** and **23** can be easily assigned using the one-dimensional spectrum, because Cp rings are equivalent in pairs. On the contrary, for compounds **24** and **25** where all four Cp rings are non-equialent the signals were unambigously assigned only using two-dimensional correlation NMR spectroscopy $\{^1H,^1H\}$ (COSY) with phosphorus decoupling. Properties of these complexes have scarcely been studied; it was only established that metallation of complexes **22** and **23** with Bu^nLi involves only six C–H bonds of two internal Cp rings.[115]

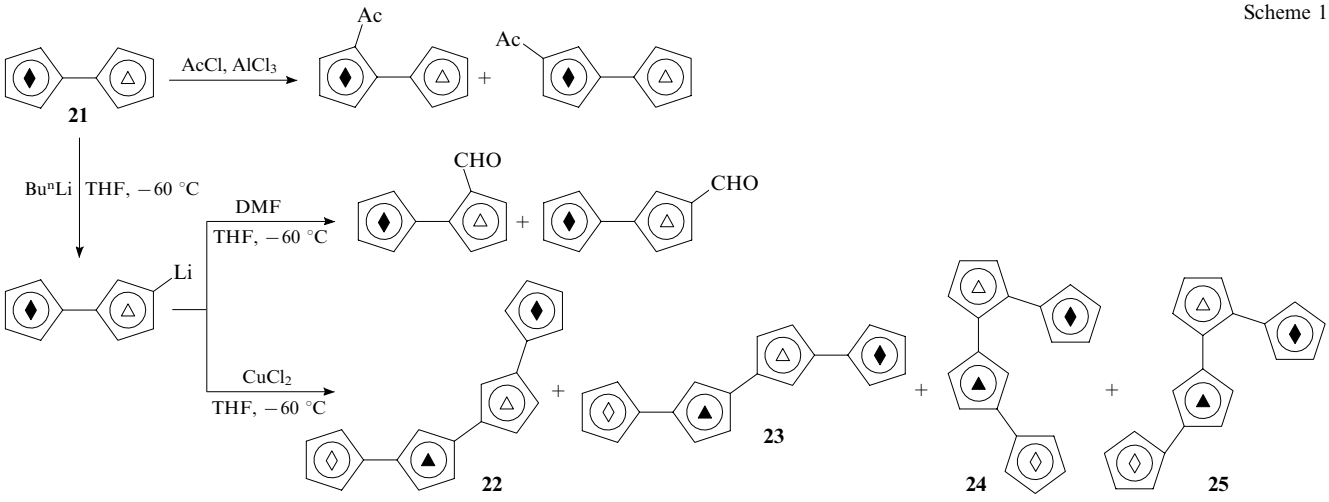
IV. 'Ladder'-type complexes

A relatively small group of bi- and polynuclear transition metal complexes containing one or several bridging η^1,η^5-Cp-ligands and a chain of two and more atoms of the same or different transition metal atoms is referred to as 'ladder' complexes (LC). The majority of the currently known LC have one or several fragments $(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_3$ (Cym).

First reports on the synthesis of LC appeared in 1977–1990 and are not cited here (for earlier publications see Refs 116–120 and a review [121]). 'Ladder' complexes are interesting in view of possible transfer of the electronic influence of metal-containing fragments along the chain metal–σ-bond–π-system–metal; therefore, they can serve as models for studies of intramolecular charge transfer. Important information on the structure and properties of these compounds can be obtained from studies of their electrochemical redox processes,[116] which allows modelling of the behaviour of polynuclear complexes in different chemical reactions.

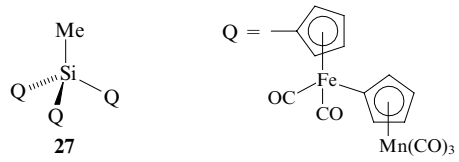
Polynuclear organometallic complexes can be considered as a model of catalytic systems for unique chemical transformations. In view of this, the synthesis and studies of the properties of new LC and other polynuclear complexes is of doubtless interest from the viewpoins of both the theory of chemical bonding and practical search for new

Scheme 1



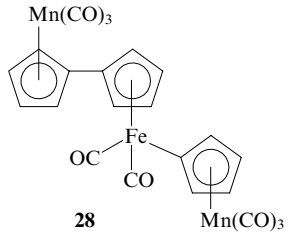
▲ and ♦ are the $Mn(CO)_3$ and $Mn(CO)_3PPh$ fragments, respectively, above the plane of the Cp ring;
△ and ◊ are the same fragments under the plane of the Cp ring.

efficient catalysts. The synthesis and investigations of new LC have got further impetus when it was found that the complex $(\eta^5\text{-}C_5H_5)(CO)_2FeCym$ is metallated with Bu^nLi at the $(\eta^5\text{-}C_5H_5)Fe$ ring.[121] The treatment of the lithium derivative with CO_2 or C_3F_7I resulted in the carboxylic acid $(\eta^5\text{-}HO_2CC_5H_4)(CO)_2FeCym$ (**26**) or the corresponding iodide. The use of $Cp(CO)_2FeI$ as an electrophile allowed chain elongation by successive introduction of new fragments $Cp(CO)_2Fe$, which, in turn, can further be metallated. The reaction of Cp_2MCl_2 (M = Ti, Zr) with 2 equiv. of sodium salt of acid **26** gave the pentanuclear complexes $[(Cym)Fe(CO)_2(\eta^5\text{-}C_5H_4CO_2)]_2\text{-}\mu\text{-}MCp_2$.[117] The reaction of $SiMeCl_3$ with 3 equiv. of lithium derivative $(\eta^5\text{-}LiC_5H_4)Fe(Cym)$ resulted in the hexanuclear complex $MeSi[(\eta^1,\eta^5\text{-}C_5H_4)(CO)_2Fe(Cym)]_3$ (**27**) characterised by X-ray diffraction.[118]



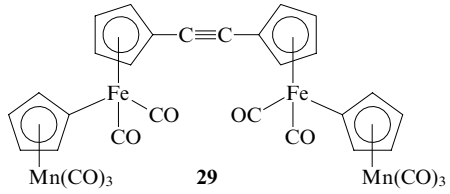
27

The reaction of the iodide $(\eta^5\text{-}IC_5H_4)(CO)_2Fe(Cym)$ with $Me_3SiC{\equiv}CSiMe_3$ (in a ratio of 2 : 1) in the presence of $Pd(MeCN)_2Cl_2$ resulted in the complex $\eta^5,\eta^5\text{-}I(CO)_2Fe(C_5H_4-C_5H_4)Mn(CO)_3$ instead of expected dimeric cross-coupling product. This resulted from migration of the iodine atom from the Cp ring to the Fe atom and of the group $(\eta^5\text{-}C_5H_4)Mn(CO)_3$, from the Fe atom to the Cp ring.[119] The reaction of the lithium derivative $(\eta^5\text{-}LiC_5H_4)Fe(CO)_2(Cym)$ with anhydrous $CuCl_2$ gave, instead of the expected dimerisation product, the trinuclear complex $(\eta^5\text{-}CymC_5H_4)Fe(CO)_2(Cym)$ (**28**);



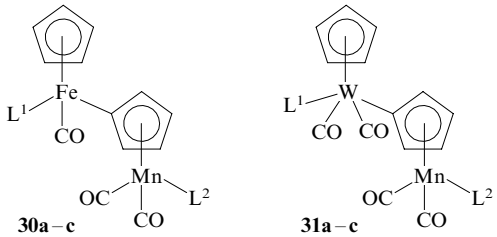
28

the reaction of the iodide $(\eta^5\text{-}IC_5H_4)Fe(CO)_2(Cym)$ with $Me_3SnC{\equiv}CSnMe_3$ in the presence of $Pd(MeCN)_2Cl_2$ yielded the expected cross-coupling product, *i.e.*, the dimeric complex $(Cym)(CO)_2Fe(\eta^5\text{-}C_5H_4C{\equiv}CC_5H_4\text{-}\eta^5).Fe(CO)_2(Cym)$ (**29**).[120]



29

Electrochemical and spectral studies of intramolecular charge transfer in bi- and polynuclear 'ladder' complexes were reported;[122] therein references are given to the synthesis of complexes **30** and **31**. Metallation of the phosphine complex **30b**, as well as complex **30a**, occurs at the $(\eta^5\text{-}C_5H_5)Fe$ ring to form $(\eta^5\text{-}LiC_5H_4)(CO)_2.Fe(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_2PPh_3$.[122]



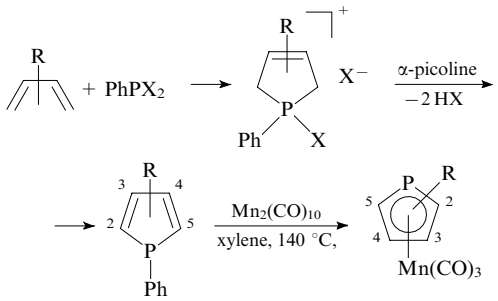
30a – c **31a – c**

$L^1 = L^2 = CO$ (**a**); $L^1 = CO$, $L^2 = PPh_3$ (**b**); $L^1 = PPh_3$, $L^2 = CO$ (**c**).

The reaction of the lithium derivative $(\eta^5\text{-}LiC_5H_4).Fe(CO)_2(Cym)$ with Ph_2PCl resulted in the phosphine complex $(\eta^5\text{-}Ph_2PC_5H_4)Fe(CO)_2(Cym)$ where one CO group at the W atom can be substituted in the reaction with $CpW(CO)_3Cl$ in the presence of Me_3NO to form the trinuclear LC $Cp(CO)_2ClW{\leftarrow}(\eta^5\text{-}PPh_2C_5H_4)(CO)_2.Fe(Cym)$, which was studied by X-ray diffraction. The $MeSi[(\eta^1,\eta^5\text{-}C_5H_4)(CO)_2Fe(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_2PPh_3]_3$ hexanuclear complex was synthesised by the reaction of $(\eta^5\text{-}LiC_5H_4)(CO)_2Fe(\eta^1,\eta^5\text{-}C_5H_4)Mn(CO)_2PPh_3$ with $SiMeCl_3$ (in the ratio of 3 : 1).[123] Electronic effects and rotational isomerism for this type complexes were studied by vibrational spectroscopy.[124, 125]

V. Phosphacymantrenes

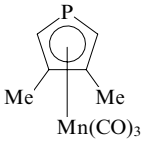
Phosphacymantrenes are complexes with the general formula $(\eta^5\text{-}C_4R_4P)Mn(CO)_3$ with a phospholyl ligand C_4R_4P isolobal to the cyclopentadienyl ligand (complexes with substituents 3,4-Me_2, Me_4 and 2,5-Ph_2 have been studied in the most detail). The first phosphacymantrene was synthesised in 1976. Prof. Mathey and co-workers made a great contribution to the development of chemistry of phosphacymantrenes and phosphaferrocenes, since untill 1996 – 1998, this group was virtually the only group working in this field. Phosphacymantrenes can be synthesised starting from dienes bearing substituents R. The condensation of a diene with $PhPX_2$ (X = Br, Cl) yields a cyclic ionic adduct, from which two HX molecules can be eliminated by the base (α-picoline) to form a substituted phosphole. The reaction of the latter with $Mn_2(CO)_{10}$ in boiling xylene (2 – 4 h) resulted in the target product, the corresponding phosphacymantrene. An improved procedure for the synthesis of phospholes has been suggested.[126]



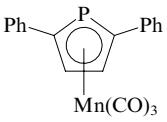
R = Alk, Ar; X = Cl, Br.

3,4-Dimethylphosphacymantrene (**32**) was synthesised from 3,4-dimethylbutadiene by this method; the reaction of 1,4-diphenylbutadiene with $PhPCl_2$ gives 1,2,5-triphenylphosphole (in this case, HCl elimination occurs spontaneously due to high reaction temperature), from which 2,5-diphenylphosphacymantrene (**33**) was obtained.[127] The

majority of publications concerning phosphacymantrenes dealt with compounds **32** and **33** because of relatively high accessibility of the corresponding phospholes.



32



33

Later, 2,3,4,5-tetramethyl-1-phenylphosphole and tetramethylphosphacymantrene were synthesised.[128] The mechanism of the thermal reaction of phospholes with $Mn_2(CO)_{10}$ is not established, but most probably, this reaction occurs by the radical route with the cleavage of the Mn—Mn bond in $Mn_2(CO)_{10}$ and the P—Ph bond in the parent phosphole. The recombination of the radicals gives the fragment $(CO)_5Mn(\eta^1\text{-}PC_4R_4)$, which under the conditions of thermal reaction (in refluxing xylene) undergoes elimination of two CO groups and $\sigma \rightarrow \pi$-rearrangement to give an η^5-phospholyl ligand.

A functionalised 1-phenylphosphole also reacts with $Mn_2(CO)_{10}$. The complex $(\eta^5\text{-}3,4\text{-}Me_2\text{-}5\text{-}CO_2EtC_4HP).Mn(CO)_3$, was obtained by this method from 5-ethoxycarbonyl-3,4-dimethyl-1-phenylphosphole; it can be hydrolysed to give the corresponding carboxylic acid.[129]

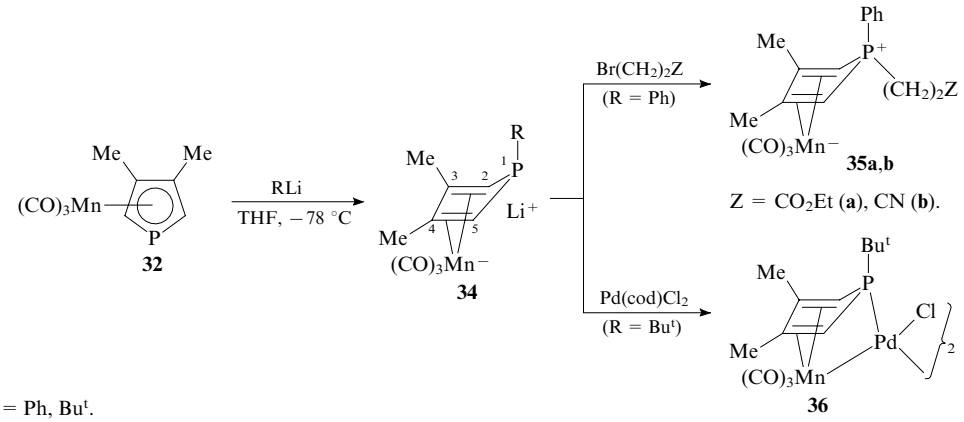
In the very first steps of investigations, the similarity of certain properties of cymantrene and phosphacymantrenes was observed, *viz*., yellow colour, faint camphor smell, close melting points, similar chromatographic mobilities, similar structural features, close or coinciding frequencies ν(CO) in the IR spectra. The similarity with cymantrene is not limited only to the physical properties. Phosphacymantrenes, like cymantrenes, readily undergo photochemical substitution of phosphines and phosphites for one or two CO ligands.[130] Complex **32** bearing only methyl substituents in the C_4P ring undergoes the electrophilic Friedel—Crafts acetylation[127] and benzoylation; the ketone, 2-benzoyl-3,4-dimethylphosphacymantrene, was characterised by the X-ray diffraction.[131] Mathey *et al*.[131] gave a brief review of early publications devoted to the phosphacymantrene chemistry. The similarity of chemical properties is not complete: for complex **32**, the attempts to perform other electrophilic reactions such as alkylation and formylation with dichloromethyl ether (Cl_2CHOMe) failed, whereas in the case of cymantrene these reactions occur readily. The P atom in the C_4P ring maintains its donor properties; for example, phosphacymantrenes add readily 16e fragments, $Fe(CO)_4$[127] and $W(CO)_5$ having vacant orbitals, to the phosphorus atom; the complex $(CO)_3Mn(\eta^5\text{-}2,5\text{-}Ph_2C_4H_2P) \rightarrow W(CO)_5$ was studied by X-ray diffraction.[132] Other differences in the properties were also found, *viz*., the P atom in the phospholyl ligand η^5-C_4P does not react with quaternising reagents and is not oxidised with iodine.[131]

The reaction of phosphacymantrenes with nucleophilic agents is of peculiar interest. Characteristic features of the phospholyl ligand and its distinction from cyclopentadienyl consists in that complex **32** is not metallated with Bu^nLi, whereas cymantrene is easily metallated with this reagent in THF at −60 °C. The reactions of phosphacymantrene **32** with strong nucleophiles like Bu^nLi, EtONa and Et_2NLi in THF and even with a weaker nucleophile NaCN in EtOH lead to complete destruction of the complex with the elimination of the $Mn(CO)_3$ fragment.[131] In the case of Bu^nLi, the Bu^n group adds the P atom to give 1-butyl-3,4-dimethylphosphole isolated as phosphole sulfide upon the treatment with sulfur.

The quantum chemical calculations confirm the preference of the nucleophilic attack to the P atom, because the low-lying LUMO is mainly localised on the phosphorus atoms.[133] According to the data from later calculations, in the case of phosphacymantrenes, the LUMO is an antibonding combination of the p_z-orbital of the P atom and d_{xz}-orbital of the Mn atom, which suggests that the nucleophilic attack ought to be directed to the phosphorus atom.[134]

The reaction of phosphacymantrenes with nucleophiles PhLi (Ref. 134) and Bu^tLi (Ref. 135) was reinvestigated. It was suggested that the nucleophilic attack on the P atom that can occur only from the *exo*-side leads to a change in the coordination mode of the phospholyl ligand to the manganese atom. In the parent phosphacymantrene, the C_4P ligand is η^5-bound to the Mn atom, the C—C bonds in the ring C_4P and the distances from the Mn atom to the C(2)—C(5) atoms are equalised. Presumably, nucleophiles (R) are attached to the *exo*-position of the phosphorus atom of complex **32** to form intermediate **34** where the phospholyl ligand is η^4-bound to the group $Mn(CO)_3$ by two 'double' bonds C=C (Scheme 2). This fragment is depicted in this way for clarity; actually, the lengths of the 'terminal' bonds C(2)—C(3) and C(4)—C(5) are only a little changed as compared to that of the 'middle' bond C(3)—C(4). A ^{31}P NMR study[134] of the reaction of complex **32** with PhLi confirmed that an intermediate is formed, which is insufficiently stable to be isolated, but which can be stabilised by the treatment with quaternising reagents like

Scheme 2

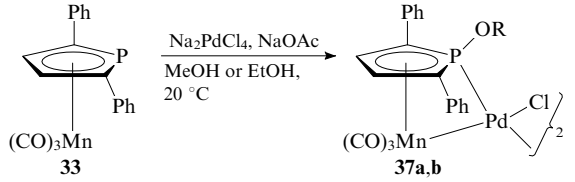


R = Ph, Bu^t.

$BrCH_2CH_2Z$ (Z = CO_2Et, CN) to form complexes **35a**,**b**. Compound **35a** was characterised by X-ray diffraction analysis; which shows minor changes in the coordination mode: the C−C bond distances in the phospholyl ligand are somewhat different, the C(2)−C(3) (1.447 Å) and C(4)−C(5) (1.449 Å) bonds being a little longer than the bond C(3)−C(4) (1.414 Å). The Mn−C bond lengths also differ: the Mn−C(2) and Mn−C(5) (2.150 and 2.156 Å, respectively) distances are a little longer than the Mn−C(3) and Mn−C(4) distances (2.099 and 2.093 Å).

In the reaction with Bu^tLi, the intermediate is also formed, which was identified by ^{31}P NMR spectroscopy. This intermediate reacts with $Pd(cod)Cl_2$ (cod is cycloocta-1,5-diene) and transforms to the stable dimeric complex **36** with the central fragment Pd_2Cl_2.[135] The structure of complex **36** was confirmed by X-ray diffraction analysis. The reactions of phosphacymantrenes with Pd^{II} and Pd^0 compounds were also investigated.[136]

The above-mentioned syntheses were performed in two steps. Recently, a new one-step reaction of conjugate alkoxypalladation under mild conditions has been found.[137] Dimeric complexes **37a**,**b** with the central Pd_2Cl_2 fragment were obtained in high yield by treatment of 2,5-diphenylphosphacymantrene (**33**) with sodium tetrachloropalladate (Na_2PdCl_4) in the presence of the base (NaOAc) (reactant ratio was 1 : 1 : 1) in MeOH or EtOH at room temperature. The structures of complexes **37a**,**b** were established by X-ray diffraction analysis.[138]



R = Me (**a**), Et (**b**).

All phosphacymantrenes with one substituent in position 2 or 3 of the C_4P ring are planar chiral because, from the stereochemical viewpoint, they are similar to cymantrene with two different substituents, the phosphorus atom playing the role of the second substituent. 3,4-Dimethyl- and 2,5-diphenylphosphacymantrenes are not chiral because their molecules have a plane of symmetry passing through the P atom, Mn atom and the middle of the C(3)−C(4) bond.

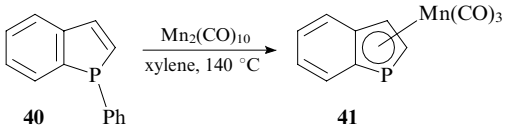
The reaction of enantiopure chiral 2,5-di[(−)-menthyl]-1-phenylphosphole with $Mn_2(CO)_{10}$ in boiling xylene resulted in the corresponding chiral 2,5-di[(−)-menthyl]-phosphacymantrene $\{\eta^5\text{-}CR(CH)_2CRP\}Mn(CO)_3$ [R is (−)-menthyl].[139]

It was mentioned above that the formylation of 3,4-dimethylphosphacymantrene was unsuccessful.[131] Later, it was found that the substitution of a donor ligand PPh_3 for one CO group at the Mn atom increases significantly the reactivity of the phospholyl ring in electrophilic substitution reactions. The complex (η^5-3,4-$Me_2C_4H_2P$)$Mn(CO)_2PPh_3$, unlike its tricarbonyl analogue **32**, readily enters the Vilsmeier formylation with $POCl_3$ and *N*-methylformanilide to give the corresponding aldehyde in high yield; this was reduced with $LiAlH_4$ to a primary alcohol and a methyl derivative.[129]

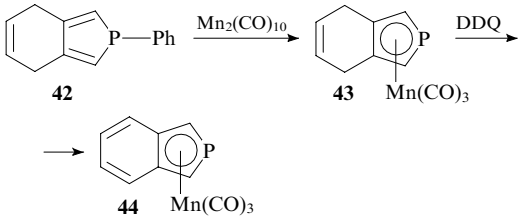
High stability of metallocenylcarbenium ions, ferrocenyl and cymantrenyl cations among them, is well-known.[81, 140] The substitution of the η^5-phospholyl ligand for one Cp-ligand in ferrocene does not markedly influence the ability of the ferrocenyl substituent to stabilise the cationic centre.[141] The secondary alcohol (η^5-2-MeC*H(OH)-3,4-Me_2C_4HP).$Mn(CO)_3$ (**39**) was prepared by reduction of the ketone (η^5-2-Ac-3,4-Me_2C_4HP)$Mn(CO)_3$ (**38**).[127, 131] Treatment of this alcohol with $AlCl_3$ in CH_2Cl_2 (0 °C, 2 h) in the presence of a substrate that is sufficiently reactive in electrophilic substitution (anisole or ferrocene) and subsequent hydrolysis resulted in the *para*-alkylation product of anisole, complex 4-MeC*H(Q)C_6H_4OMe, or MeC*H(Q)Fc in the case of ferrocene [the fragment (η^5-3,4-Me_2C_4HP)$Mn(CO)_3$ is denoted as Q]. Alkylation of 1,3-dimethoxybenzene under these conditions (the reactant ratio is 2 : 1) yielded the bisderivative 1,3-$(MeO)_2$-4,6-$[MeC^*H(Q)]_2C_6H_2$. The formation of these products suggests that the reaction with $AlCl_3$ affords a sufficiently stable carbocation $MeC^+H(Q)$, *i.e.* the phosphacymantrene residue stabilises the cationic centre approximately with the same efficiency as cymantrenyl does.[142] Both the alcohol **39** and alkylation products have a chiral centre at the α-C atom (asterisked) and exist as mixtures of two diastereomers due to the presence of two chiral elements, the chiral centre at the C* atom and the chirality plane at the η^5-phospholyl ligand with a substituent in position 2 (see above).

The reductive coupling of ketone **38** in the presence of $TiCl_4$ (3 equiv.) and zinc dust (6 equiv.) in boiling THF (18 h) resulted predominantly in the alkene (Q)C(Me)=C(Me)(Q) in the *Z*-configuration as a mixture of racemic and *meso*-diastereomers. Coupling of 2-benzoylphosphacymantrene[131] under the same conditions resulted predominantly in the alkene in the *E*-configuration.[143]

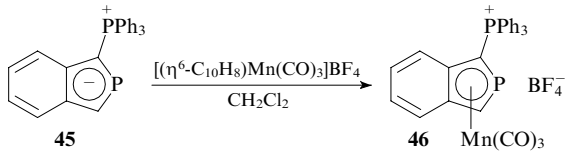
The methods for the synthesis of benzoannulated analogues of phospholes and phosphacymantrenes have been developed. Thus benzophosphacymantrene (**41**) was prepared from 1-phenylbenzophosphole (**40**) according to the standard procedure by the reaction with $Mn_2(CO)_{10}$ in boiling xylene.



Dihydroisobenzophosphole **42** was prepared, this reacts with $Mn_2(CO)_{10}$ to give complex **43**; it can be aromatised with 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone (DDQ) to yield isobenzophosphacymantrene (**44**).[144]



The reaction of 1-triphenylphosphoniobenzo[*c*]-phospholide (**45**) with the manganese cationic complex $[(\eta^6\text{-}C_{10}H_8)Mn(CO)_3]BF_4$ in CH_2Cl_2 (non-coordinating solvent) gave the cationic complex **46** due to the substitution of the naphthalene ligand.[145]



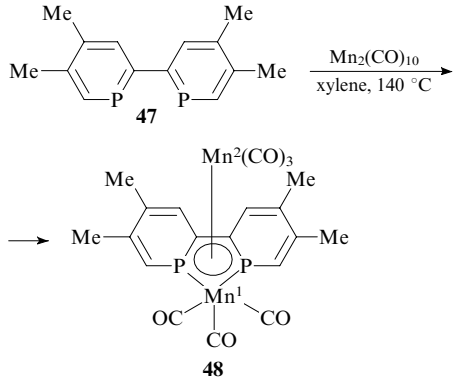
45 **46**

The structures of complexes **41**, **44** and **46** were established by X-ray diffraction analysis.

Due to donor properties of the phosphorus atom in phosphacymanteres, these compounds can play the role of peculiar phosphine ligands.[127,132] Two octahedral complexes $Ru(CO)_2Cl_2(PCym)_2$ and $RuCl_2(PCym)_4$ were synthesised by the reaction of ruthenium carbonyl halides with 3,4-dimethylphosphacymantrene (PCym) and studied by X-ray diffraction. In the former complex, two PCym ligands occupy the axial positions, while in the latter complex, four PCym ligands are in the equatorial plane.[146]

According to the concept of isolobal equivalence suggested and developed by Hoffmann in 1982,[147] the phosphorus atom can be considered as an isovalent and isolobal 'building block' that can substitute one or several groups CR (R = H, Alk, Ph) in unsaturated heterocycles. In accordance with this approach, in addition to above monophosphacymantrenes containing one P atom, compounds with two, three and five phosphorus atoms in the unsaturated η^5-ligand were synthesised.

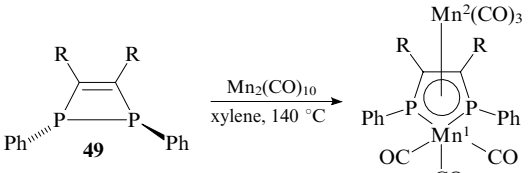
2,2′ -Biphosphinines and 1,4-diphosphadienes can play the role of 8e ligands with respect to two $Mn(CO)_3$ groups.[148] The reaction of 4,4′,5,5′-tetramethylbiphosphinine (**47**) with $Mn_2(CO)_{10}$ under standard conditions (refluxing in xylene for 4 h) gave complex **48** containing two fragments $Mn(CO)_3$ in high yield, the tricyclic system being virtually coplanar and the central $C_2P_2Mn(1)$ ring forming the planar diphosphamanganacyclopentadienyl ligand coordinated to the Mn(2) atom.



47 → **48**

The distance between the Mn(2) atom and the centre of the $C_2P_2Mn(1)$ ring is equal to 1.855 Å being somewhat larger than the similar distance in cymantrene (1.77 Å). The Mn(1)—Mn(2) distance in complex **48** is 2.8182(5) Å.

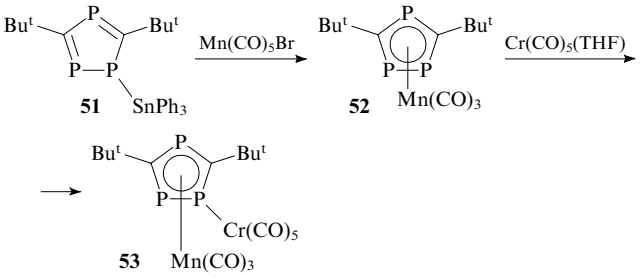
The reaction of 1,2-dihydro-1,2-diphosphetes **49** with $Mn_2(CO)_{10}$ under the same conditions yields complexes **50**, which can be considered as open analogues of complexes **48**; the structures of complexes **48** and **50** were established by X-ray diffraction.[148]



49 → **50**

R = Ph, Bu^t.

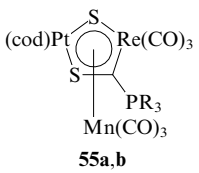
Triphosphacymantrene **52** was synthesised in high yield by the reaction of triphosphole **51** with a $SnPh_3$ substituent, with $(CO)_5MnBr$. Complex **52** is diamagnetic; its properties are similar to those of unsubstituted cymantrene (the CO frequencies in the IR spectrum are shifted by only $\sim$17 cm^{-1}). Like monophosphacymantrenes, complex **52** reacts as a phosphine ligand and adds the $Cr(CO)_5$ group to the phosphorus atom to form complex **53**.[149]



51 → **52** → **53**

Like cymantrene, complex **52** easily undergoes photochemical substitution of ligands PMe_3 and cyclo-$C_6H_{11}NC$ for the CO group.[150]

The reaction of potassium pentaphospholide, (cyclo-P_5)$^-$K$^+$, with $Mn(CO)_5Br$ in boiling DMF results in complex $(\eta^5\text{-cyclo-}P_5)Mn(CO)_3$ (**54**), which is isoelectronic with cymantrene because the anion (cyclo-P_5)$^-$ is isolobal to the cyclopentadienyl anion. In the IR spectrum of compound **54**, two ν(CO) bands at 1778 cm^{-1} (E mode) and 1960 cm^{-1} (A_1 mode) are strongly shifted to the low-frequency range as compared to similar bands of cymantrene ($\sim$1950 and 2025 cm^{-1}).[151] The reaction of the salt $Na_2[MnRe(CO)_6(S_2CPR_3)]$ with $Pt(cod)Cl_2$ gave complexes **55** where the $(CO)_3Mn$ group is coordinated to the analogue of the cyclopentadienyl anion, *viz.*, ligand η^5-(cod)PtSRe.$(CO)_3C(PR_3)S$ with the Pt—S—Re—C—S framework. Complex **55a** was characterised by X-ray diffraction; the five-membered ring is virtually planar [the largest out-of-plane deviation of $Re(CO)_3$ is 0.115(3) Å].



55a,b R = Pr^i (**a**), cyclo-C_6H_{11} (**b**).

The Mn atom is bound to all five atoms of the ring and is arranged symmetrically. The plane formed by the three C atoms of the fragment $Mn(CO)_3$ is almost parallel to the plane of the five-membered ring that can be considered as a dimetalladithia analogue of C_5H_5. The ν(CO) frequencies in the IR spectrum of complex **55** are 1971 and 2002 cm^{-1} and practically coincide with those for cymantrene.[152]

* * *

In the last decade, in addition to Mn and Fe derivatives, phosphametallocomplexes of both transition and non-transition metals, *viz*., Ti, Zr, Ge, Sn, Pb, W, Ru, Co, Rh, Ir, Ni, have been synthesised and intensively studied (see reviews [153, 154]).

In the present review, only the chemistry of Cp complexes with the $Mn(CO)_3$ fragment was considered, which is only a small part of the data on manganese Cp complexes. The chemistry of CO substitution products ligands and other compounds formed in the reactions changing the ligand environment of the metal was not included. In addition, such rapidly developing fields as chemistry of carbene, carbyne, vinylidene, cumulenylidene, borylene complexes, complexes with pyrazolylborate bridges, cymantrene anionic complexes and other binuclear complexes attract most interest. The cymantrene derivatives with free-radical ligands have not been reviewed either.

The chemistry of phosphametallocenyl complexes with other metals (besides Mn and Fe) being developed over the recent 6–10 years is also interesting. The appearance of reviews on the above and other fields of the chemistry of manganese Cp complexes is appreciated and, in our opinion, is but the matter of time.

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