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Organometallic complexes of heterocycles. I. σ,π-Complexes of five-membered monoheterocycles

Alexander P. Sadimenko
Department of Chemistry, National University of Lesotho, P.O. Roma 180 (Lesotho)
Alexander D. Garnovskii
Research Institute of Physical Organic Chemistry, 344104 Rostov-on-Don (Russia)
Negussie Retta
Addis Ababa University, P.O. Box 1176, Addis Ababa (Ethiopia)

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CONTENTS

1. INTRODUCTION

The objective of this review is to provide a comprehensive literature survey on organometallic compounds containing heterocycles covering the period 1960–1991 (sometimes earlier papers are cited). σ,π-Metal-carbonyl and π-sandwich complexes of five-membered heterocycles are considered.

During recent decades there has been an increasing interest in the chemistry of heterocycles attached to transition metals, such as iron, chromium and manganese and, to a lesser extent, some noble transition metals.

Although the review attempts to be exhaustive, we do not claim to comment here on every aspect of the compounds considered.

2. GENERAL COMMENTS ON THE DONOR PROPERTIES OF HETEROCYCLES

Classification of heteroaromatic compounds enables detailed interpretation of the data on the basis of their reaction and complexing ability. One of the important

Correspondence to: A.P. Sadimenko, Department of Chemistry, National University of Lesotho, P.O. Roma 180, Lesotho.

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features may be the degree of aromaticity [1,2], which allows one to follow the most general trends in coordination. Existing experimental data lead to the following aromaticity series [1,2]: porphyrins > six-membered ring monoheterocycles > azines > azoles > five-membered ring monoheterocycles. It is therefore not surprising that porphyrins and pyridine and its derivatives are the most extensively studied ligands among the heterocycles [3-8]. The stability of porphyrin and phthalocyanine complexes and their role in biological systems may be explained by π-electron delocalization. The ease of synthesis, high tendency to undergo complex-formation (basically of σ-type) and relatively good π-donor properties stem from the aromatic nature of the hetero-rings [9].

Five-membered monoheterocycles are compounds with the least donor properties. Such systematization may be used only for the most general description of their properties but cannot be used for the purpose of predicting the most probable ways of complex formation.

The degree of aromaticity alone cannot be used as the basis for classification of different heterocycles. There can be two ways of classifying them, the first being based upon the relative number of chemical bonds in the π-conjugation chain, and the number of π-electrons [10] (heterocycles are subdivided into π-excessive and π-deficient), while the second has its origin in the Lewis acid–base classification [11], the polarization properties of electrophilic and nucleophilic species (the concept of hard and soft acids and bases, the HSAB concept). This clarifies the tendency of a definite site in a heteroaromatic ligand to act as a donor and/or acceptor [12].

The classification of heterocycles into π-excessive or π-deficient is fundamental, since it covers both electrophilic and nucleophilic substitution [13–15] and the ability to form complexes [16–19].

π-Excessive heterocycles are compounds in which the number of π-electrons in the conjugated system exceeds the number of atoms forming the cycle. The classical examples are five-membered monoheterocycles, pyrrole, phosphole, arsole, furan, thiophene, selenophene, tellurophene, all of which contain a heteroatom that can supply two electrons to the ring (six electrons per five atoms) [12,13]. This also includes benzofuran, benzothiophene, indole, dibenzofuran, dibenzothiophene, carbazole.

The features of the π-excessive heterocycles are negative net π-electron charge of the hetero-ring and the average π-charge per carbon atom. This principally means a predominant π-donor function, which is probably followed by the formation of radicals and π-type radical-ions (high energy of the highest occupied molecular orbital, HOMO).

Furan is considered to be a heterocycle of low aromaticity [1]. It is characterized by low resonance energy (6.7 kJ mol^{-1} according to one of the estimates) [20]. Bond lengths correspond to those in the polyenes, and the chemical properties resemble those of 1,3-dienes (in particular, the Diels–Alder reaction [21]). In addition, it is also formally classified as a π-excessive ligand. Thus, according to ab initio

calculations (on the basis of the double-exponent Slater functions [22]), the net π-electronic charge of the hetero-ring is -0.001, and the average π-electronic charge per carbon atom is negative (-0.062).

The electronic structure and spectra of these heterocycles has been discussed in some detail, e.g. furan [23–26], thiophene [26–35], thiophene-1,1-dioxide [36,37], selenophene and tellurophene [38,39], pyrrole [20,24,40–42] and the reader is referred to these references for detailed comment.

Phosphole has not yet been synthesized. However its simplest 1-methyl derivative is known. This heterocycle is non-planar. According to the data of the computation on the basis of the linear combination of the Gauss functions, phosphole is the least aromatic of the five-membered monoheterocycles and much less aromatic than phosphorine (the six-membered P-containing analogue of pyridine) [27], which in turn is more stable than benzene and pyridine. Phosphole is most stable in the non-planar (pyramidal) configuration. It is this configuration for which definite aromatic stabilization has been noted. In the process of transfer from planar phosphole to pyramidal, the HOMOs, $1a_2$ and $3b_1$, interchange their positions. The two most stable orbitals in phosphole are the same as in butadiene-1,3, which is one more piece of evidence of its non-aromatic character. The calculated ionization potential of phosphole is 9.38 eV.

The aromaticity of the silacyclopentadienyl anion [43] based upon ab initio calculations in the basis STO-2G with complete geometry optimization was quantified. The symmetry relative to the cyclopentadienyl anion is partially violated. The negative charge is not delocalized over the whole system and is accumulated at the silicon atom.

Pentaphenylborole is unstable. The conjugation between the boron atom and the dienylidene system leads to destabilization of the π-system [44]. The non-coordinated borole is a very reactive partner in the Diels–Alder reaction, interacting even with such dienophiles as diphenylacetylene at 298 K.

Benzannelated derivatives of the five-membered monoheterocycles (benzofuran, benzothiophene, indole) are aromatic [20]. Their isoconjugated analogues (isobenzofuran, isobenzothiophene, and isoindole) are less stable and take part in Diels–Alder reactions. The electronic distribution in benzofuran has been calculated by a non-empirical method on the basis of the linear combination of the Gauss functions [45]. The π-donor constituent in this compound is less than in furan, i.e. it is even less aromatic than furan. The influence of the heteroatom is limited by the five-membered heterocycle. The oxygen atom in benzofuran is a much stronger σ-acceptor and a weaker π-donor than in furan. The net π-electron charge in benzofuran is $+0.004$ and the average π-electron charge per carbon atom is -0.025. The corresponding data for benzene and furan rings separately are -0.103, -0.017 and $+0.038$, -0.042, respectively. This heterocycle is generally less π-excessive than furan, suggesting that the benzene and furan rings are fairly independent. Other aspects of the electronic

structures of benzofuran [24,45,46], and benzothiophene [30,45] can be found in the references cited.

Indole is less aromatic than pyrrole but more aromatic than benzofuran. It does not favour cycloaddition reactions. The electronic distribution in the indole molecule obtained by a non-empirical method [45] made it possible to elucidate some peculiarities of this heterocycle. The polarization of the bonds in the five-membered heterocycle is different from that in pyrrole. The NH grouping is the weak σ-acceptor, spreading its action only onto the proximate carbon atoms; it is a moderate π-donor. More detailed aspects of the electronic structure of indole are discussed elsewhere [24,45,47–51].

Isobenzofuran is much more stable than benzofuran. The addition of any reactant to the 1 or 3 position leads to a considerable increase of resonance energy (approximately by 75 kJ mol^{-1}) so that the benzene ring is quinoidal in isobenzofuran but benzene-like in the adduct [20]. The resonance energy data for isobenzofuran are analogous to those for isobenzothiophene and isoindole, the difference in stabilities in comparison with representatives of the normal series being much less. Thus, isoindole [20] is considered as an aromatic system. Bond lengths are different from those in the polyene chains. Combined analysis of the data of photoelectron spectroscopy and quantum-chemical calculations by Hückel and INDO method has shown that the first ionization potential of *N*-methylisoindole has $\pi(^2A_2)$ nature and is equal to 7.22 eV (experiment), 7.54 eV (Hückel MO) and 9.09 eV (INDO) [47].

Dibenzo derivatives of furan, thiophene and pyrrole are aromatically stable [20]. The first ionization potentials of these compounds are π in nature [52]. The HOMO–LUMO transition in dibenzofuran corresponds to 4.87 eV, while in dibenzothiophene it amounts to 4.70 eV and in carbazole it is equal to 4.80 eV, which reflects in all cases dienic character, i.e. refers to the five-membered ring [24].

These selected data on aromaticity and π-electronic character give some information on the donor ability of the five-membered heterocycles that do not contain substituents with noticeable electronic effects. In the case of benzannelated systems, the benzene ring may be an alternative π-donor, the ligand functions of the five- and six-membered cyclic systems being relatively independent. They can behave separately as a function of acceptors. Non-aromatic systems such as furan, isobenzofuran and others should not even form π-complexes. The absence of the cyclically conjugated ring should lead to its destruction during interaction with potential π-complex-forming agents. However the formation of cycloadducts of isobenzofuran followed by an increase in resonance energy may serve as an indicator for the possibility of an analogous interaction process with π-acceptors, such as metal carbonyls and metals in the zero oxidation. Other examples of extremely low aromaticity are the phospholes and their analogues. Low aromaticity is a consequence of acoplanarity of the ligands. It is possible that complex-formation may lead to flattening of the ligand and thereby abruptly increasing resonance energy or, in other words, metalloaromaticity is achieved.

A study of the electronic structure of π-complexes of cyclobutadiene, cyclopentadiene and benzene [53] is interesting in relation to the present review.

Cyclobutadiene is considered an anti-aromatic compound which exists in inert gas matrices, but has not yet been isolated in the free state. Its π-complexes, e.g. $C_4H_4Fe(CO)_3$, are however fairly stable [54]. This leads to the proposal that the coordinated cyclobutadiene behaves as an aromatic rather than anti-aromatic compound. Theoretical substantiation of this proposal has been presented in the framework of the Fenske–Hall non-empirical method [53]. The quantum-chemical features of metalloaromaticity are, firstly, the system $C_4H_4Fe(CO)_3$ obeys the Hückel rule owing to the two additional d_π-electrons, d_{xz} and d_{yz}. The latter overlap rather significantly with the e_g-orbitals and have similar energies. Secondly, substantial delocalization of the electron density over the π-system C_4H_4Fe takes place. The fact that the metal atom does not lie in the same plane as the cyclobutadiene framework is not important. Inclusion of the d_π-electrons of the metal in the aromatic system satisfies the classical π-electron delocalization scheme. The geometry of the complexes is such that it is possible to consider interactions between the metal and cyclobutadiene and the metal and carbonyl, separately. If these interactions compete ($C_4H_4M(CO)_4$, M = Cr, Mo, W) or filling of anti-bonding MO-levels takes place ($C_4H_4Ni(CO)_3$), metalloaromaticity is not observed. Evidence for the metalloaromaticity of $C_4H_4Fe(CO)_3$ is the possibility for acylation and other electrophilic substitutions of the cyclobutadiene ring [55].

On the other hand, classical aromatic molecules (benzene) show different behaviour in π-complex formation. Transfer of some of the π-electron density from the bonding to the π-anti-bonding benzene levels takes place. The aromatic character of the benzene ring is thus substantially distorted, causing a reduced tendency towards electrophilic substitution [56]. Substituent effects are not transmitted through the ring [57].

The properties of the cyclopentadienyl complexes are characteristic of aromatic compounds. For example, ferrocene undergoes electrophilic substitution better than benzene. Quantum-chemical data suggest that the aromatic ring of the cyclo-pentadienyl anion is stabilized by an ionic interaction with the metal [53].

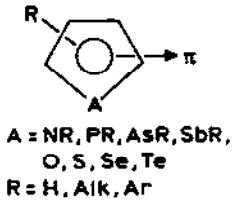
However, generalizations about metalloaromaticity should be used with caution. The criteria given for $C_4H_4Fe(CO)_3$ may not be met by other metalloaromatic compounds. For example, acylation of the cyclobutadiene ring in a π-complex is likely to occur more easily than acylation of a cyclopentadienyl ring under similar conditions. This follows from a study of the complex $C_4H_4CoC_5H_5$ in which the four-membered ring is the first to be acylated [58]. Thus the grouping C_4H_4Co is more aromatic than the cyclopentadienyl ring.

Analogous calculations for complexes of the five-membered heterocycles may also be of interest. However, the electronic structures of the free ligands make it possible to predict the basic trends in metalloaromaticity for the corresponding π-complexes and to compare the different five-membered heterocycles. Those com-

pounds, which are heteroaromatic, should be similar to π-complexes of the cyclopentadienyl anion. Compounds of the phosphole type should give organometallic π-complexes as a result of flattening of the ligands. The same is possible for ligands of the isobenzofuran type.

An alternative approach to classification of the five-membered monoheterocycles is given by the HSAB concept [12].

Unsubstituted five-membered monoheterocycles are n,π-ambidentate donors containing hard (nitrogen and oxygen heteroatoms) or soft (phosphorus, arsenic, antimony, sulphur, selenium, tellurium, π-system of the hetero-ring) nucleophilic sites. These π-excessive systems have mainly π-donor properties forming complexes of the π,v-type with soft acids (**1**) [59–62]. Examples are metal-carbonyl complexes of pyrrole (**2**, A = NR) [63–65], thiophene (**2**, A = S) [66,67], selenophene (**2**, A = Se) [67], tellurophene (**2**, A = Te) [68], azaferrocene (**3**) [69,70] and azacymantrene (**4**) [71]. On the other hand, with the pyrrole ring as the heteroaromatic system, there is formation of a metal–nitrogen bond (**5**) with salts of the hard metals of groups I and II [72,73]. The soft–soft π-excessive heterocycles (phosphole, arsole, stibole) are interesting in the way that they form two groups of complexes: n,v- (**6**) and π,v-types (**7**) [19,74]. Thus, the HSAB concept subdivides the ligands into the soft (thiophene, selenophene, tellurophene and benzo-analogues), hard–soft n,π- (pyrrole, indole, carbazole) and soft–soft n,π-donors (phosphole, arsole and stibole).



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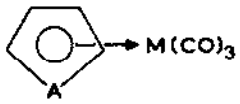

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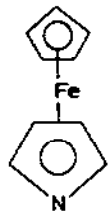

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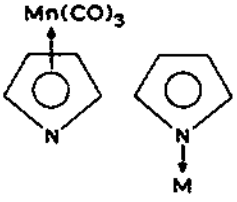

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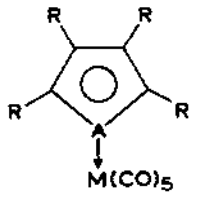

R = C_6H_5, A = P, As, Sb

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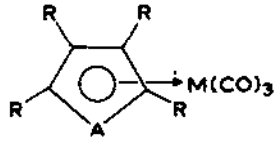


R = C_6H_5, A = P, As, Sb

7

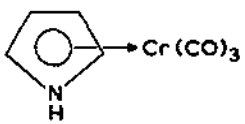
3. π-COMPLEXES

The most commonly encountered complexes with these five-membered monoheterocycles are the metal carbonyls (2) and the sandwich complexes (3) [75]. The formation of a π-complex followed by the elimination of a substituent from the 1-position is characteristic of heterocycles containing a group V atom (the corresponding π-complexes are called π-pyrrolyl, π-phospholyl, π-arsolyl, e.g. 4). Alternatively, when such elimination is absent, the π-complexes are known as π-pyrrole, π-phosphole, π-arsole, e.g. 8.

The π-complexes of condensed heterocycles may coordinate via the benzene or hetero-ring, usually the former. If there are several condensed rings, coordination takes place via the benzene ring which is the most remote from the heteroaromatic one. These general rules often have exceptions, which will be considered later.

4. σ,π-COMPLEXES OF THIOPHENES

Chromium tricarbonyl complexes of substituted thiophenes may be obtained through the substitution reaction of acetonitrile complexes $(CH_3CN)_3Cr(CO)_3$ [76–79]. Product 9 yields are higher than those obtained by the direct interaction of chromium hexacarbonyl with the thiophene derivatives [66,67,80–83]. According to ^1H NMR spectroscopy [77], compounds of type 9 are characterized by enhanced electron density at the α-carbon atom. The π- and σ-systems of thiophene are modified by complex formation. Complete delocalization among the four carbon atoms is followed by greater polarization of the β-carbon atoms.



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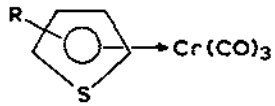
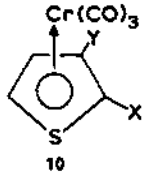


9

According to X-ray structural analysis [84], the sulphur atoms of the thiophene ring in this complex are in the trans position relative to one of the three carbonyl groups. The structure is consistent with a qualitative model, in which the chromium atom is attached to the hetero-ring via three centres, viz. the sulphur atom and two double bonds. This corresponds to octahedral coordination. The complex is isomorphous with benzenechromiumtricarbonyl, the benzene and thiophene rings being oriented in the elementary cell in a similar manner. Vibrational data have been reported [85].

The synthesis of complexes 10 included reaction of $(py)_3Cr(CO)_3$ with thiophenes in the presence of boron trifluoride etherate in boiling ether [86]. IR and UV spectra showed that the substituent electronic effects may be transmitted towards the terminal carbonyl groups through the metal atom. The interpretation of the data

is based upon existence of two canonical resonance forms (**11**,**12**). The influence of electron-donor substituents is better described in terms of structure **12**.



10

X	Y	X	Y	X	Y
OCH_3	H	H	CH_3	H	Br
H	OCH_3	H	H	CO_2CH_3	H
CH_3	H	Br	H	H	CO_2CH_3

$$X{-}M{-}C{\equiv}O \leftrightarrow {}^{+}X{=}M{=}C{=}O^{-}$$

11 **12**

The mass-spectral fragmentation pattern of tricarbonylchromium thiophene involves successive elimination of the three CO groups (**13**) [87]. The probability of formation of CrS^+ implies that, alongside with π-coordination of type **14**, $C_4H_4SCr(CO)_n^+$ ($n = 0$–2) is σ-coordinated (**15**) at least partly, or σ- and π-coordination are realized simultaneously (**16**).

$$C_4H_4SCr(CO)_3^+ \xrightarrow{-CO} C_4H_4SCr(CO)_2^+ \xrightarrow{-CO} C_4H_4SCr(Co)^+$$

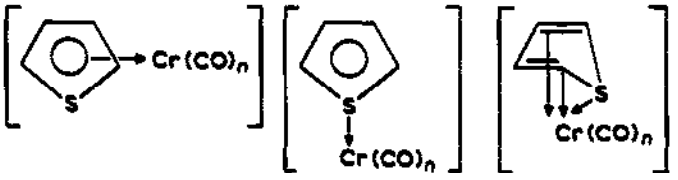
$$\downarrow -CO$$

$$Cr^+ \xleftarrow{-CO} C_4H_4SCr^+ \qquad C_4H_4S^+ \qquad CrS^+$$

13

The π-complex **17** was obtained by condensation of chromium hexacarbonyl with the thiophene σ-derivative of ironcyclopentadienyldicarbonyl (**18**) [87,88]. The presence of the electron-donor iron-containing substituent facilitates π-coordination.

Known reactions of tricarbonylchromiumthiophene include electrophilic isotope H,D-exchange [90] and metallation with *n*-butyllithium [91]. The latter reaction takes place instantaneously and quantitatively in THF at 220 K. In the three-fold excess of *n*-butyllithium and by decomposition of the reaction mixture using D_2O, D_2-thiophenechromiumtricarbonyl is formed, as indicated from mass-spectral analysis. The ^1H NMR spectra clearly show that, in excess *n*-butyllithium, both α-hydrogen



14 15 16

atoms in the thiophene ligand are substituted by the lithium atoms. Treatment of the reaction mixture by trimethylchlorosilane gives bis(trimethylsilyl)thiophene-chromiumtricarbonyl [90]. If an equimolar mixture of the chromium complex and *n*-butyllithium is used, only one hydrogen atom is substituted.

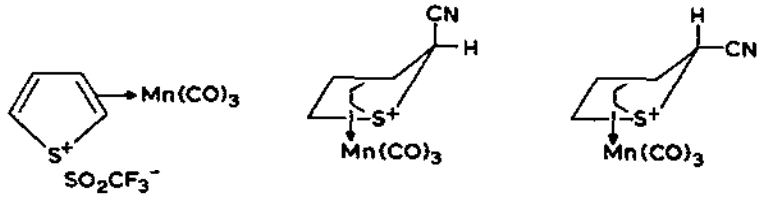
17 18

If one α-hydrogen atom in thiophene is substituted by the methyl group, reaction also proceeds with ease but demands more rigid conditions (reflux in excess reactant [92] or in the presence of tetramethylethylenediamine [93]).

The CNDO/2 calculations favour formation of $[Mo(CO)_5(\eta^1\text{-thiophene})]$ [94]. However, in the case of $[Mo(CO)_3(\eta^5\text{-thiophene})]$, stabilization is higher than that for the η^1-complex.

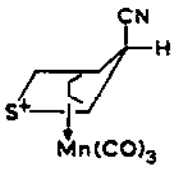
Cationic π-complexes of thiophene and its methyl derivatives (2-, 3-methyl-, 2,5-dimethyl-, 2,3,5-trimethyl- and tetramethylthiophene) with $Mn(CO)_5Cl$ in the presence of $AlCl_3$ or $AlBr_3$ in petroleum ether have been obtained [95]. The structure of the complexes $[(C_4H_{4-x}(CH_3)_xS)Mn(CO)_3]^+$ is based on IR analyses.

By boiling $Mn(CO)_5$ in thiophene, the stable complex **19** is obtained [96]. In excess potassium cyanide, an additional product is formed, represented as one of the isomers **20–23**. X-ray data are indicative of the predominance of structure **20**, the unsaturated carbon atom being above the hetero-ring plane at a distance of 0.0597 nm. The fragment of the three co-planar carbon atoms is described as the allyl system, over which the π-electron density is delocalized. The sulphur atom may be included, but not to such a degree as in the unsubstituted thiophene heterocycle.



19 20 21

The initial thiophene complex **19** reacts reversibly with tri-*n*-butylphosphine in acetone followed by formation of the complex **24**. The less basic phosphines, such as methyldiphenylphosphine, add to the thiophene complex **19** with much more difficulty.



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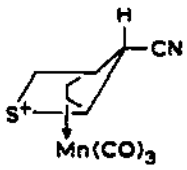

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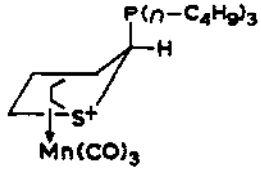
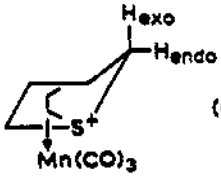


24

The reaction of **19** with the hydride anion (BH_4^-, $HFe(CO)_4^-$, $HW(CO)_5^-$) followed by formation of **25** has also been studied in detail. When the hydride anion is $HFe(CO)_4^-$, the reaction is complicated by formation of by-products **26** and **27**.



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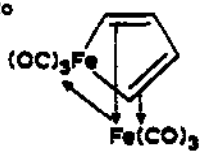

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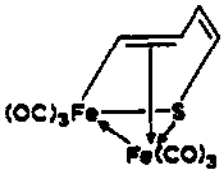
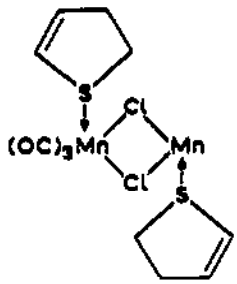


27

Passage of gaseous hydrogen chloride through a solution of **19** causes formation of the reduced forms, for which structures **28** and **29** have been postulated on the basis of IR and ^1H NMR spectroscopy.

28



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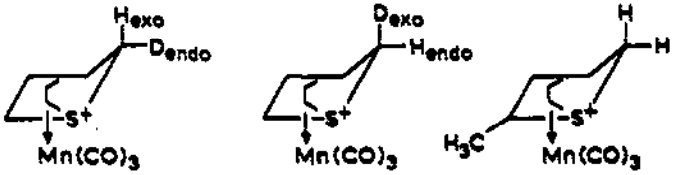
All the transformations observed are indicative of enhanced reaction ability of the coordinated thiophene in **19**, which reacts with nucleophiles under quite mild conditions. Nucleophilic addition distorts the aromatic stability of the heterocyclic ring.

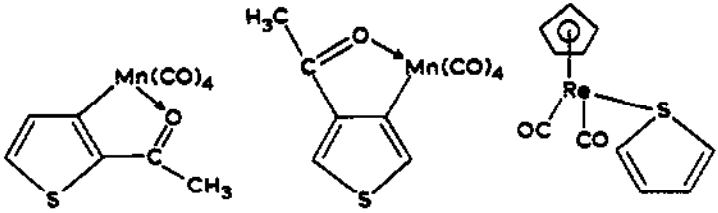
Addition of the deuteride anion to **19** is achieved by BD_4^- and $DFe(CO)_4^-$ and

leads to a mixture of endo (**30**) and exo (**31**) species alongside the product of hydride addition (**32**) [97]. Treatment of the mixture of **30** and **31** by $[(C_6H_5)_3C]BF_4$ leads to regeneration of the cation **25**. Reaction of $Mn(CO)_5OSO_2CF_3$ with 2-methylthiophene and 2,5-dimethylthiophene leads to the corresponding methylated analogues of **19**. They undergo substitution reactions with the coordinating solvents (acetone, acetonitrile) followed by formation of the complexes $Mn(CO)_3$ (solvent)$^+$. The 2-methylthiophene complex adds hydride anion **32**, whereas 2,5-dimethylthiophene does not enter this kind of reaction [97].



30 **31** **32**

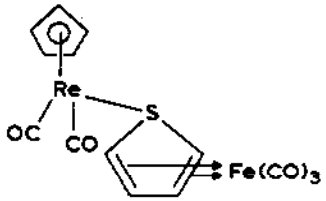
When acetylthiophenes and furans are subjected to orthomanganation, formation of the 2,3- **33** or 3,4- **34** metallocycle is observed [98]. The complex **33** contains two co-planar five-membered heterocycles with octahedral manganese. The complex **34** is also planar. In both cases, substantial delocalization of π-electron density follows from the structural parameters (X-ray).



33 **34** **35**

$(C_5Me_5)(CO)_2Re(THF)$ forms the complex **35** upon reaction with thiophene [99]. Similar reactions are known for 2- and 3-methyl-, 2,5-dimethyl-, tetramethylthiophene and dibenzothiophene [100]. Thiophene in **35** is S-coordinated, and the sulphur atom is pyramidal. Treatment of **35** with $Fe_2(CO)_9$ produces **36**. According to X-ray structural analysis of **36**, the thiophene ligand is bridge-coordinated via the sulphur atom to rhenium and four carbon atoms of the dienic system with iron. The pyramidal nature of the sulphur atom is preserved. The η^4-coordination of thiophene separates the dienic and sulphur counterparts of the ligand and decreases π-electron delocalization which leads to enhanced basicity of the sulphur atom.

On the other hand, reaction of selenophene with $(C_5Me_5)(CO)_2Re(THF)$ yields complex **37** containing the η^2-coordinated ligand. The non-coordinated selenium atom appears to be able to form a bond with the $W(CO)_5$ framework, the product



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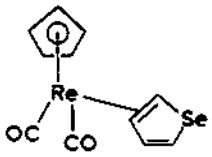

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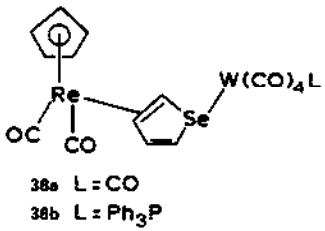
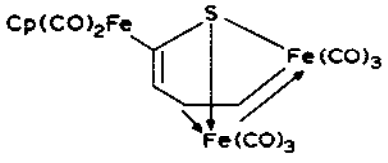


being **38a** [101]. The triphenylphosphine derivative (**38b**) is obtained from **37** and $W(CO)_4(PPh_3)(THF)$ (X-ray structural analysis).

The reaction of thiophene with iron carbonyls has peculiarities. At elevated temperatures, elimination of the sulphur atom from the heterocycle and substitution by the iron atom takes place (**26**) [102–105].

Recently, it was shown that thiaferroles (**27**) serve as precursors for ferroles [106]. Analogous complexes of 2-methyl- and 2,5-dimethylthiophene were obtained. Thiaferrole may be obtained from the compound $CpFe(CO)_2(C_4H_3S)$ [88,89,107] containing a 2-thienyl ligand σ-bonded to the iron atom **18**. The latter interacts with $Fe_3(CO)_{12}$ and complex **39** is formed.

Interaction of the iron metal atoms with thiophenes (thiophene, 2-methyl- and 2,5-dimethylthiophene) in the vapour phase of 77 K with subsequent heating in a carbon monoxide atmosphere also leads to formation of **26** [108,109]. The iron cyclopentadienyl ring is planar, all the bonds having multiple character. In addition, desulphurization takes place during reaction with chromium vapour. However, attempts to isolate and to establish the nature of the product of the latter reaction have been unsuccessful.



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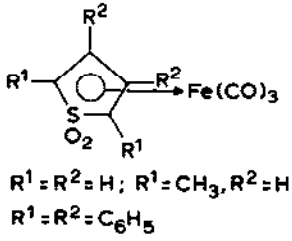


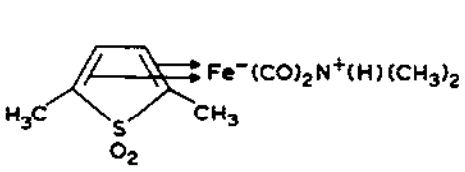
40

In contrast to thiophene and its derivatives, thiophene-1,1-dioxide is not subject to desulphurization. Thus, the structure of tricarbonyliron(η^4-3,4-dimethylthiophene-1,1-dioxide) has been determined [110]. The ligand is coordinated to the iron atom via the dienic system similar to that of butadiene in $LFe(CO)_3$. The sulphur atom is out of the dienic system. Three CO groups are directed towards the centres of the

maximum electron density of the ring. One CO and one SO_2 group are in the staggered conformation relative to each other.

Photochemical synthesis of $LFe(CO)_3$ (L = thiophene-1,1-dioxide, its 2,5-dimethyl- and tetraphenyl derivatives) has been successful (**40**) [111].

Decomposition of the complex **40** by trimethylamine oxide in aprotic medium proceeds via the intermediate **41** [112].



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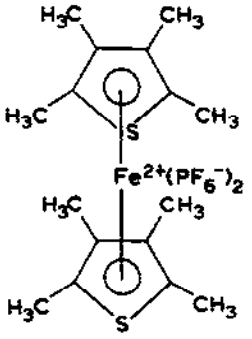


42

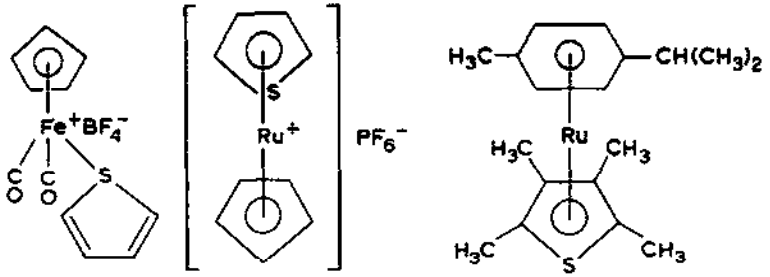
Irradiation of 3,4-dibromo-2,5-dimethylthiophene-1,1-dioxide in the presence of iron pentacarbonyl yields iron tricarbonyl complexes containing one or two bromine atoms [113,114].

Complexes containing the cyclopentadienyl framework, such as $(C_5H_5)Fe(CH_3CN)_2(\eta^5\text{-}C_4H_4S)$ [115,116] or $(\eta^5\text{-}C_4H_4S)Fe(\eta^5\text{-}C_5H_5)^+$ [117,118] have been reported.

The first thiophene π-complex **42** with charge +2 containing two heterocyclic molecules coordinated to a transition metal atom has been obtained [119]. According to cyclic voltammetry, the complex is reduced reversibly in two one-electron steps. Such electrochemical behaviour reveals the possibility of isolation of bis(tetramethylthiophene) iron(0).

Thiophenes are weak σ-donors. Only a few S-bonded complexes of thiophene and 2,5-dimethylthiophene are known. They are poorly described because of their extreme lability. For example, the only postulated σ-complex was $[Fe(\eta^1\text{-}C_4H_4S)(CO)_2(Cp)][BF_4]$ [120]. On the other hand, isobutene substitution in $[Fe(\eta^2\text{-}H_2C{=}C(CH_3)_2(CO)_2(Cp)][BF_4]$ by thiophene gives the complex **43** [121]. The S-coordination was rather reliably proven using IR, ^1H- and ^{13}C-NMR spectroscopy. Thiophene in this complex is quantitatively substituted by CD_3NO_2.

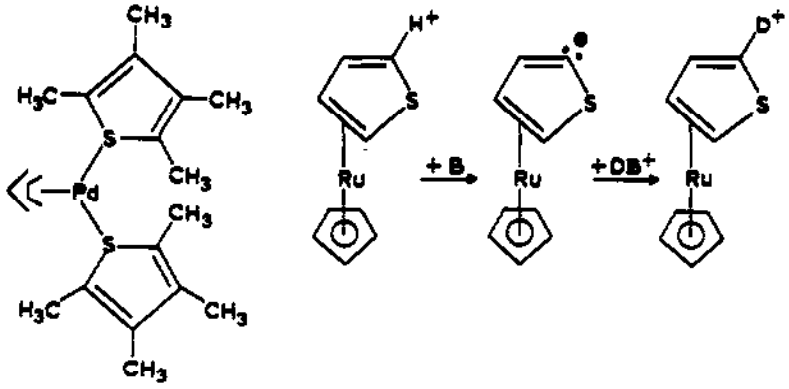
The reaction of $(\eta^5\text{-}C_5H_5)Ru(P(C_6H_5)_3)_2Cl$ with $AgBF_4$ and thiophene in methanol gives $[(\eta^5\text{-}C_4H_4S)Ru(\eta^5\text{-}C_5H_5)][BF_4]$ [122–124] together with **44**. The cation $[(\eta^5\text{-}C_4H_4S)Ru(\eta^5\text{-}C_5H_5)]^+$ appeared to be air- and moisture-stable but undergoes very slow substitution of thiophene by benzene, $(n\text{-}C_4H_9)_3P$, CH_3CN, and $t\text{-}C_4H_9NC$, which is an indicator of a rather strong thiophene → metal bond. The complexes $(\eta^5\text{-}C_4H_4S)M(P(C_6H_5)_3)_2^+$ (M = Rh, Ir) were also reported [125].



43 44 45

Thiophene in π-complexes may be an η^4 or η^5 donor. Data from reactivity and NMR spectroscopy reveal that η^5 coordination is predominant.

Treatment of di-μ-chlorobis[chloro(*p*-cymene)ruthenium(II)] with tetramethylthiophene in the presence of $AgPF_6$ leads to the formation of **45**. Reaction of di-μ-chlorobis[2-methylpalladium(II)] with tetramethylthiophene in the presence of $AgPF_6$ probably leads to **46** containing the η^1-coordinated ligand. The η^1-coordination of thiophene was also proposed in some ruthenium and iridium complexes [126–128], e.g. $[(\eta^5\text{-}C_5H_5)Ru(P(C_6H_5)_3)_2(\eta^1\text{-}C_4H_4S)]^+$.

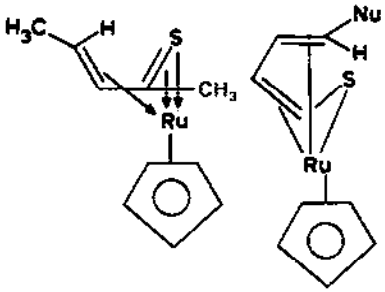


46 47 48

Kinetic studies of the base-promoted H,D-exchange of $[CpRuL]^+$, where L is thiophene, 2-methyl, 3-methyl and 2,5-dimethylthiophene, showed that the OH^- group of the base induces elimination of a proton from thiophene as the rate-determining step [129,130]. Then rapid D^+ transfer from the solvent (CD_3OD) to the intermediate **47** takes place, leading to the deuterated product **48**. H,D-Exchange is the most rapid process relative to the 2 and 5 positions, then exchange relative to the 3 and 4 positions takes place, and finally exchange relative to the methyl substitution occurs.

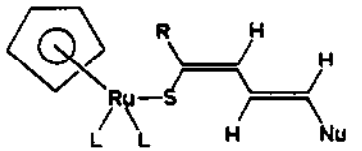
Reaction of the cationic complex $[(Cp)Ru(\eta^5\text{-}2,5\text{-}(CH_3)_2C_4H_2S][PF_6]$ with metal hydrides such as $LiAlH_4$, $Na[(CH_3OCH_2CH_2O)_2AlH_2]$ and $NaBH(C_2H_5)_3$

leads to the formation of the hydride adduct [131]. The reaction is followed by cleavage of the C–S bond and formation of the butadienethiolate ligand **49**. The ruthenium atom is coordinated to all four carbon atoms and the sulphur atom. Analogous hydride addition to the related complexes $[CpRu(\eta^5\text{-}SC_4HR^1R^2R^3)]$ ($R^1 = R^2 = R^3 = H$; $R^1 = 2\text{-}CH_3$, $3\text{-}CH_3$, $R^2 = R^3 = H$, $R^1 + R^2 = 2,3\text{-}(CH_3)_2$, $R^3 = H$, $R^1 + R^2 + R^3 = 2,3,5\text{-}(CH_3)_3$) gives similar butadienethiolate complexes.



Nu = OCH_3^-, SCH_3^-, $SC_2H_5^-$, $S(i\text{-}C_3H_7)^-$, $CH(CO_2CH_3)_2$

49 50



R = H, CH_3; L_2 = dppe, L = $P(CH_3)_3$, $P(CH_3)(C_6H_5)_2$

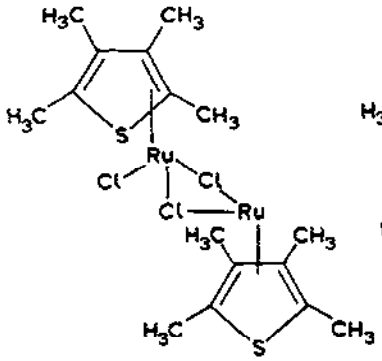
51

π-Complexation of thiophene in compounds of the type **44** activates the heterocycle relative to other nucleophiles, namely, OCH_3^-, SCH_3^-, $SC_2H_5^-$, $S(i\text{-}C_3H_7)^-$ and $CH(CO_2CH_3)_2^-$. The products **50** include the ring-opened butadiene–thiolate framework. Reactions of **50** with excess $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$ (dppe) in benzene lead to formation of the new compound **51**. The same property of formation of the S-coordinated butadienethiolate complexes was discovered for trimethyl- and methyldiphenylphosphine.

Thermal arene exchange of tetramethylthiophene with $[(p\text{-cymene})RuCl_2]_2$ affords **52** [132] which, by reaction with $AgBF_4$ and excess tetramethylthiophene yields **53**. The Ru–S thiophenic cluster **54** was synthesized by reaction of **52** with $(Me_3Si)_2S$ followed by anionic metathesis and formation of the PF_6 salt. The coordination geometry around each metal atom is pseudo-octahedral (X-ray).

The complex $[(\eta^5\text{-}C_5(CH_3)_5)Ir(\eta^5\text{-}C_4H_4S)]$ was obtained from $[(\eta^5\text{-}C_5(CH_3)_5)Ir(acetone)_3][BF_4]_2$ [133]. It appeared to be much more stable to ligand-substitution reactions than the Ru-analogue.

An attempt to synthesize the monomeric adduct $[Rh(C_5(CH_3)_5)Cl_2L]$ (L = thiophene) under normal conditions has been unsuccessful [134,135]. Thiophene is also non-reactive towards $[(Rh(C_5H_5)Cl_2)_2]$ in the presence of a reductant (sodium carbonate in ethanol). Similar attempts to synthesize the thiophene complexes by substitution of the solvent in $[M(C_5H_5)(sol)_3]^{2+}$ (M = Rh; sol = acetone, acetonitrile) also failed. However, 2,5-dimethylthiophene and especially tetramethylthio-



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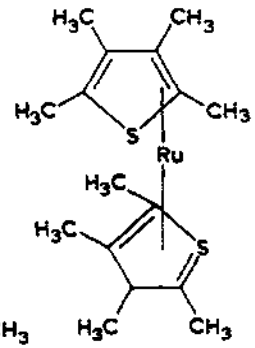

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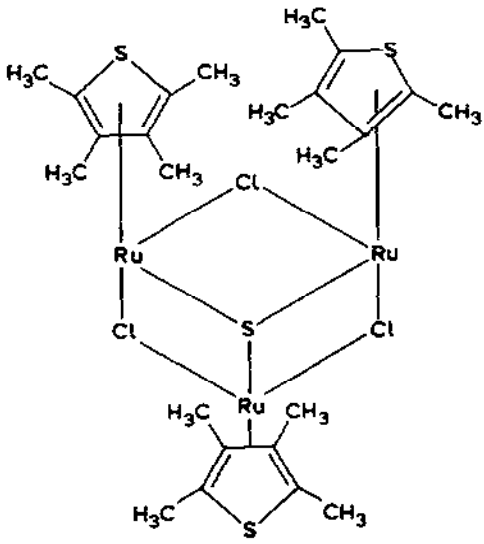

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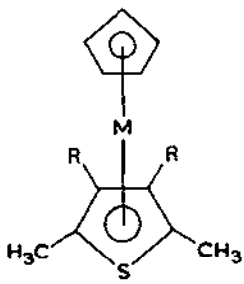
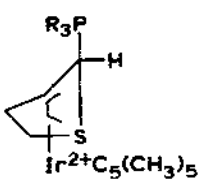
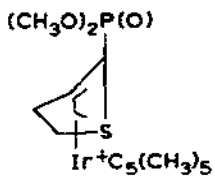


55a M = Rh, R = CH_3
55b M = Ir, R = CH_3
55c M = Ir, R = H



R_3 = $(CH_3)_3$, $(C_6H_5)_2CH_3$, $(C_6H_5)_3$

56



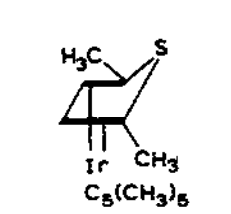
57

phene react with $[M(C_5H_5)(sol)_3]^{2+}$. Formation of similar complexes is observed with other representatives of group VIII elements.

Reaction of the rhodium and iridium tris-acetone complexes with tetramethylthiophene lead to **55a** and **55b**, while 2,5-dimethylthiophene yielded only the iridium complex **55c**. The complexes **55**, particularly the complex **55b**, are active hydrogenation catalysts [134,135].

Activation of the thiophene ring was studied in the iridium complex $[(\eta^5\text{-}C_5(CH_3)_5Ir(\eta^5\text{-}C_4H_4S)[BF_4]_2$ [136]. The compound undergoes reaction with trimethyl-, methyldiphenyl- and triphenylphosphine followed by formation of the η^4-complexes **56**. Reaction with trimethoxyphosphine leads to **57**. Reaction with $NaB(C_2H_5)_3H$ does not lead to hydride addition to the thiophene ligand but rather a two-electron reduction of the iridium complex followed by formation of the neutral complex $[\eta^5\text{-}C_5(CH_3)_5Ir(\eta^4\text{-}C_4H_4S)]$.

Two-electron reduction of $[C_5(CH_3)_5Ir(\eta^5\text{-}2,5\text{-dimethylthiophene})]$ produces **58** where the heterocycle is coordinated only via the four carbon atoms [137,138]. The isomer **58** is thermodynamically unstable with respect to the open-cycle isomer **59** (X-ray analysis) and is converted to it in the presence of basic alumogel or amines as catalysts. The sulphur atom in the η^4-complex possesses unusual donor properties and **58** forms the BH_3 adduct **60** extremely easily. The η^2-isomer **59** reacts with BH_3, followed by ring closure and formation of the same adduct (**60**). The complex **59** also reacts with P-donor ligands and carbon monoxide yielding the 18-electron adducts (**61a–f**) (NMR and mass spectra, microanalysis). The structure of (**61b,c**) follows from X-ray analysis, which shows that the six-membered ring is no longer



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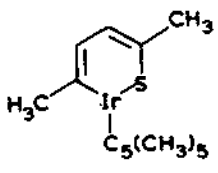

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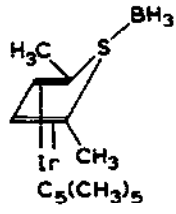

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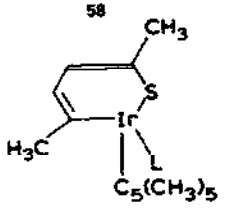
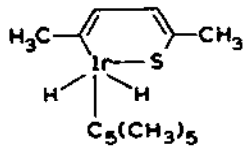


L = 61a $P(CH_3)_3$
61b $P(CH_3)_2C_6H_5$
61c $P(CH_3)(C_6H_5)_2$
61d $P(C_6H_5)_3$
61e $P(OC_6H_5)_3$
61f CO



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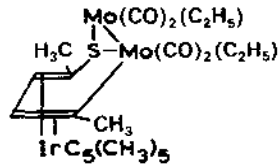
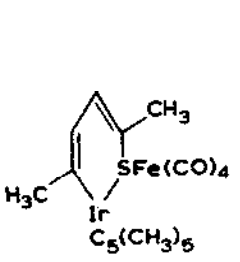


63

planar as in **59**. In addition, **59** undergoes oxidative addition of hydrogen, resulting in dihydride (**62**) formation. The same products (**61f** and **62**) are formed in similar reactions with **58**.

Complex **58** reacts with $(C_5H_5)Mo(CO)_3$ and forms **63** as the major product [139]. The bridging thiophene ligand preserves its η^4-coordination relative to the iridium atom while both molybdenum atoms are bonded via the sulphur atom of the heterocycle. These conclusions follow from X-ray structural analysis.

Both isomers, **58** and **59**, react with $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ followed by formation of a variety of products [140]. In **64**, the heterocycle is η^4-coordinated relative to the iridium atom and η^1-coordinated relative to the iron atom and thus serves as a bridge. The geometry around the iron atom is trigonal-bipyramidal (X-ray analysis, IR and NMR spectroscopy). In **65**, the thiophene derivative is η^4-coordinated to iridium and S-coordinated to two iron atoms. Several other products are described in ref. 140.



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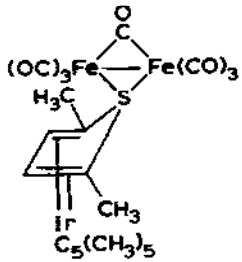

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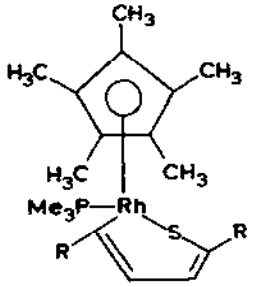
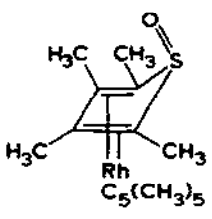


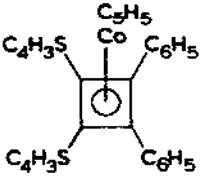
66

Thiophene and 2,5-dimethylthiophene react with $(C_5Me_5)Rh(PMe_3)(Ph)H$ to give the rhodium(III) complex **66** [141–143]. The dienic group and the sulphur atom are planar but the rhodium atom is above the plane. A localized dienic structure is observed in the six-membered ring metallocycle.

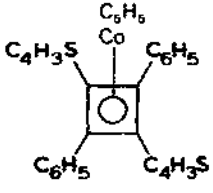
Another specific reaction occurs between the product of the two-electron reduction of **55a** and dry oxygen. The S-oxide complex **67** is formed [144], where the heterocyclic ligand is non-planar and there is a reduced Rh(I) centre.



67



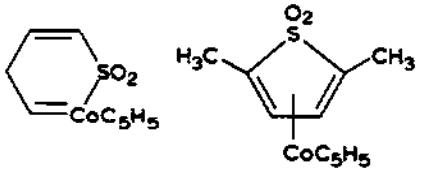
68



69

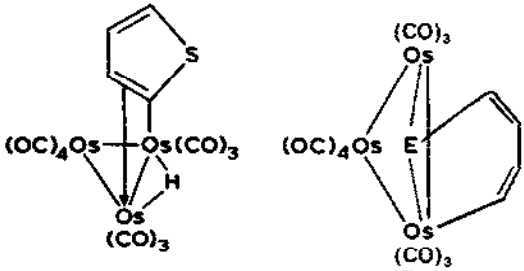
The products of reaction of η^5-cyclopentadienylcobalt with phenyl-2-thienylacetylene are **68** and **69** [145].

Photolysis of $(C_5H_5)Co(CO)_2$ with 2,5-dimethylthiophene-1,1-dioxide in hot benzene gives **70**, while flash-vacuum pyrolysis gives **71** and **72** and other products [146].



70 71 72

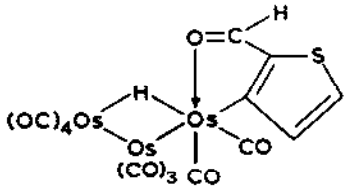
$[Os_3(CO)_{10}(CH_3CN)_2]$ reacts with thiophene forming the hydride product of oxidative addition **73** [147], the sulphur atom occupying the exo-position relative to the $Os(CO)_4$-group. Despite the predominance of the exo-species, NMR spectroscopy indicates rapid equilibrium of the exo and endo isomers. This suggests an intermediate S-bonded thienyl complex. Meanwhile, selenophene and tellurophene yield **74a** and **74b** under similar circumstances. Indeed, X-ray analysis of **74a** unequivocally shows cleavage of the selenium–carbon bond and donation of six electrons by the selenophene ring.



73

74a E = Se
74b E = Te

Interaction of thiophene and 2-formylthiophene with $[Os_3(CO)_{12}]$ or $[Os_3(CO)_{12}(CH_3CN)_2]$, respectively, gives clusters containing di- and tri-bridged ligands in which σ-type carbon–osmium bonds are formed [148]. The C_2 atom takes part in this bond in complex **75**, and both C_2 and C_3 atoms participate in coordination in **76** (X-ray).



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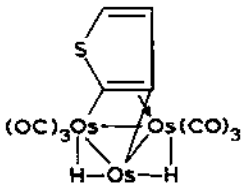


76

5. σ,π-COMPLEXES OF PYRROLES

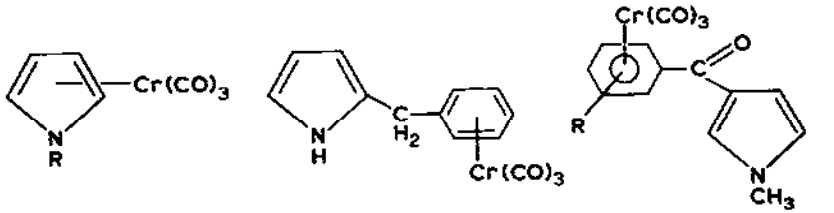
Data available in the literature [149] made it possible to examine the correlation between the π-donor properties of the pyrrolyl and cyclopentadienyl rings. The cyclopentadienyl ligands in the complexes $M(C_5H_5)_4$ ($M = Ti^{4+}$, Zr^{4+}, U^{4+}) are coordinated differently, depending on cation size. The small Ti^{4+} ion coordinates to the two ligands through the π-mode and to the remaining two ligands through the σ-mode, while the intermediate Zr^{4+} ion coordinates to the three ligands via the π-mode and to the remaining ligand via the σ-mode. The U^{4+} ion, with higher size, coordinates to all four ligands through π-bonds.

Interaction of $(\eta^5\text{-}C_5H_5)_2MCl_2$ (M = Ti, Zr) with sodium pyrrolyl in THF at room temperature leads to the formation of the air-stable complexes $(\eta^5\text{-}C_5H_5)_2M(\eta^1\text{-}NC_4H_4)_2$. In the complex $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}NC_4H_4)_2$, the mode of σ-bonding of the pyrrolyl group differs from that of the σ-cyclopentadienyl groups in $Ti(C_5H_5)_4$. X-ray structural analysis reveals that the σ-C_5H_5-group is bonded to the titanium atom through the sp^3-hybridized carbon atom, the Ti–C–centre angle of the cyclopentadienyl ring is 140°, while the Ti–N–centre angle of the pyrrolyl ring is 166° (which is characteristic of an sp^2-hybridized nitrogen atom). The Ti–N (0.2085 nm) bond length is indicative of a noticeable contribution of the $d_\pi \rightarrow p_\pi$ constituent. The titanium atom is in a distorted tetrahedral configuration. The structure of the zirconium complex is similar [149,150]. The pyrrolyl and cyclopentadienyl ligands are planar in both complexes. However, bond lengths in the pyrrolyl ligands imply localization of π-electron density. The cyclopentadienyl ligands in the zirconium complex can easily be eliminated to form an octahedral hexapyrrolylzirconium anion in $[Na(THF)_6]_2[Zr(\eta^1\text{-}NC_4H_4)_6]$ [149,150]. These data indicate less π-donor nature and more σ-donor property of the pyrrolyl ion in comparison with the cyclopentadienyl ion.

The effect of the steric and electronic environment on π-coordination was studied [151] by employing sterically hindered 2,5-dimethylpyrrole, which however has resulted in σ-coordination. In the cyclopentadienylbis(2,5-dimethylpyrrolyl) zirconium(IV) complex, which was obtained by direct interaction of $NaNC_4H_2(CH_3)_2$ with $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in THF, the methyl groups weaken the Zr–N bond.

The synthesis and X-ray structural analysis of the complex $[C_4H_4NCH_3Cr(CO)_3]$ are given in ref. 152. Pyrrole and 1-phenylpyrrole form the π-$Cr(CO)_3$ complexes **77** while 2-benzylpyrrole produces the η^6-$Cr(CO)_3$ complex **78** [153].

Interaction of chromium hexacarbonyl and 2-benzoylpyrrole leads to the σ-complex 2-(π-benzylchromiumtricarbonyl)pyrrole (**78**) [154], while reaction with 3-benzoylpyrrole gives only the π-complex in which the $Cr(CO)_3$ framework is bonded to the benzene ring (**79**) [155].



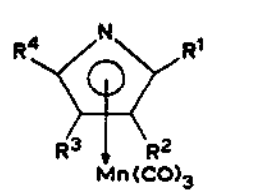
Radical anions of these complexes are obtained by treating **78** with potassium [156]. The radical anions were studied by ESR spectroscopy; the basic spin density is concentrated at the benzene ring, especially in the ortho and para positions. Large spin density belongs to the CrCO groups. The ESR data indicate substantial conjugation in the system containing the benzene ring and the $Cr(CO)_3$ groups.

Reaction between $[(W{\equiv}CR)Cl(CO)_2(pyridine)_2]$ ($R = C_6H_5$, CH_3) with the anionic chelating Schiff base pyrrole-2-carboxaldehydemethyliminate in THF yields the anionic complexes $[N(C_2H_5)_4][W(RCCO)(NN)_2(CO)]$ (where NN is the dianion of the pyrrole ligand). These complexes react with methylfluorosulphate, forming the neutral acetylenic complexes $[W(NN)_2(CO)(RC{\equiv}COCH_3)]$ [157] (X-ray). One of the pyrrolic Schiff bases is coordinated via the pyrrole and imino nitrogen atoms, another one only via the imino nitrogen atom.

Tricarbonylmanganese derivatives of pyrrole (**80**) are obtained both as a result of direct interaction and of interaction of $BrMn(CO)_5$ with the potassium salt of the corresponding pyrrole [65,69]. Complexes of the unsubstituted pyrrole are much more stable than the cyclopentadienyl analogues. Their boiling points are lower, but other physical properties such as colour, solubility and IR spectra are similar. The pyrrole complexes have a low pK_a value, e.g. $R^1 = R^2 = R^3 = R^4 = H$, $pK_a = 1.6$.

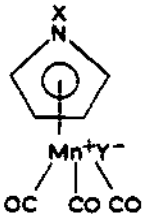
The weakly-basic manganese complex does not react with methyl iodide under mild conditions. The salt **81** ($X = CH_3$, $Y = I$) is obtained by reacting halogenmanganesetricarbonyl with *N*-methylpyrrole in the presence of aluminium chloride.

Comparison of the IR spectra of π-cyclopentadienyl ($L = C_5H_5$) and π-pyrrolyl ($L = C_4H_4N$) derivatives $LMn(CO)_2E(C_6H_5)_3$ (E = P, As, Sb) [158] shows a decrease

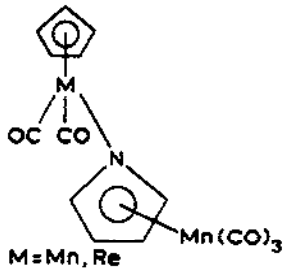


$R^1=R^2=R^3=R^4=H$;
$R^1=CH_3, R^2=R^3=R^4=H$;
$R^1=R^3=CH_3, R^2=R^4=H$

80



81



82

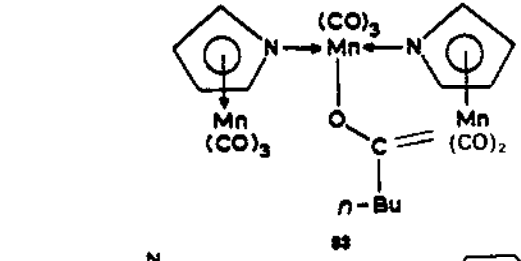
of the metal–carbon bond orders, as well as in the negative charge on the metal atom in the pyrrolyl derivative and that the pyrrolyl derivative is a better σ-acceptor than cyclopentadienyl.

The nitrogen atom in π-pyrrolylmanganesetricarbonyl has been found to form a donor–acceptor bond with transition metals. New complexes, in which the pyrrolyl ring behaves as the π-ligand for the manganese atom and an n-donor for the other metal, have been synthesized **82** [159]. Both metals in the binuclear rhenium complex have an octahedral configuration. The π-pyrrolyl and π-cyclopentadienyl ligands are tridentate. The nitrogen atom uses its lone pair to form a donor–acceptor bond with the rhenium atom.

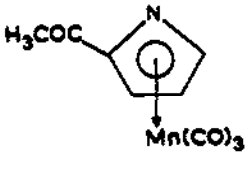
The binuclear heterobimetallic complexes of chromium, molybdenum and tungsten hexacarbonyls with π-pyrrolylmanganesetricarbonyl were synthesized [160]. n-Coordination of the framework $M(CO)_5$ (M = Cr, Mo, W) takes place via the nitrogen atom. It has been shown by IR spectroscopy that, in acidic medium, the complex $(OC)_5W \cdot C_4H_4NMn(CO)_3$ is protonated at the tungsten atom, which is indicative of the high donor property of azacymantrene as a ligand.

π-Pyrrolyltricarbonylmanganese was treated with *n*-butyllithium, then the reaction mixture was decomposed with heavy water to locate the position of the lithium atom. It appeared that lithium attacks not the pyrrolyl but the carbonyl group followed by formation of the trinuclear complex **83** not containing deuterium [161–163]. This fact was unequivocally proven by X-ray structural analysis.

Acylation of azacymantrene by acetic anhydride in the presence of phosphoric acid gives **85** rather than **84** [164,165]. The Mn^1 atom in **85** is in a near-octahedral configuration. The π-pyrrolyl ligand occupies three coordination positions. Bond lengths in the unsubstituted hetero-nucleus are such that the π-electron density delocalization may be considered to be complete. The Mn^2 atom in **85** has a somewhat distorted octahedral configuration. The five-membered metallocycle is practically planar and forms the whole planar system together with the hetero-ring. The distribution of bond lengths in the 2-substituted pyrrolyl ring differs from that



83



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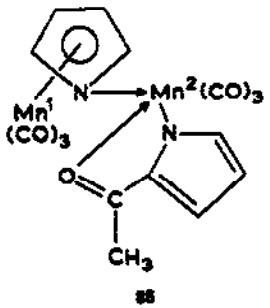
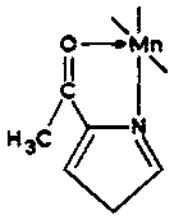
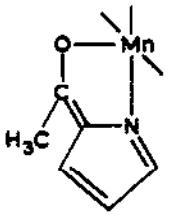


85

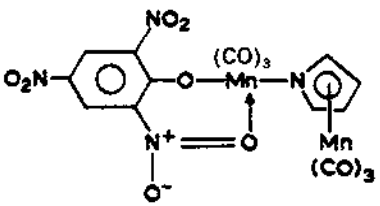
of the unsubstituted pyrrolyl in the system where all the bonds are similar, which may be predominantly due to the mesomeric structure of **86a** over **86b**.



86a



86b



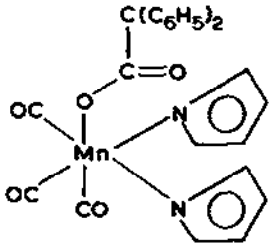
87

The complex **85** contains π-, σ-, donor–acceptor and chelate bonds with the azacymantrene molecule as a two-electron ligand.

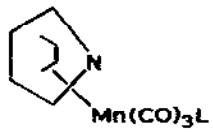
When π-pyrrolyltricarbonylmanganese reacts with trifluoroacetic acid, the nitrogen and manganese atoms may be the protonation centres. To elucidate the nature of this centre, an attempt was made to obtain a crystalline product from the interaction of the manganese complex with a protic acid [166]. Among different acids, picric acid gave **87** (X-ray).

Interaction of azacymantrene with diphenylketene in a boiling THF/water mixture leads to *N*-diphenylacetylpyrrole and **88** [167] (X-ray) with octahedral manganese. The structural parameters of the cis-oriented frameworks in **88** are near to the geometric characteristics of a monodentate N-donor azacymantrene.

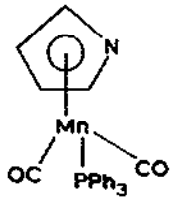
Substitution reactions at the carbonyl group in azacymantrene and its (2,5- and 3,4-dimethyl) derivatives proceed through intermediate **89** [168]. The pyrrolyl



88



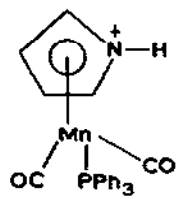
89



90

compound reacts much faster than the cyclopentadienyl compound owing to the electron donor effect of the nitrogen atom [169–171]. The role of the aza-allyl intermediate **89** was understood from X-ray structural analysis of the azacymantrene analogues containing 2,5- and 3,4-dimethylpyrroles as ligands.

Reaction of azacymantrene with triphenylphosphine yields the monosubstitution product of the carbonyl group (**90**) [172]. Attack of an electrophile on **90** may be directed towards a series of centres of basicity: the pyrrolic nitrogen atom, the manganese atom, etc. As a result of dissolution in trifluoroacetic acid, the product of proton addition over the pyrrolic nitrogen, **91**, is obtained. Reaction of **90** with aprotic acids, HgX_2 (X = Cl, $OCOCH_3$), $M(OCOCF_3)_2$ (M = Hg, Cd), ZnX_2, AlX_3, SnX_4 (X = Cl, Br), $GaCl_3$, and $SbCl_3$ leads to coordination of the latter again via the pyrrolic nitrogen (**92**). The same situation is realized in the case of $PdCl_2$, which gives **93** (X-ray). The palladium atom has a trans-square planar coordination via the two chlorine and two nitrogen atoms. The pyrrolyl rings are coordinated to the manganese atoms by the η^5-mode and are planar.



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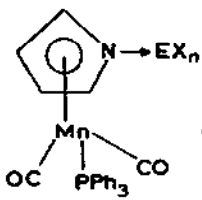

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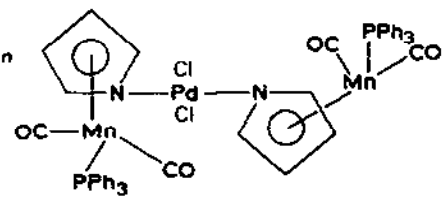
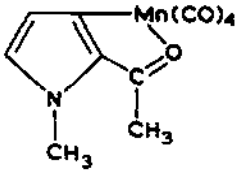


93

For the substituted pyrroles, π-complex-formation is limited owing to stabilization of the σ-complexes. Complexes of manganese-containing pyrroles bearing the acetyl group, such as $Mn(CO)_3L$, have been synthesized, where L = 3-acetyl-2-methylpyrrolyl [173], and the o-manganated species of 2-acetyl-1-methylpyrrole (**94**) has been isolated [98].

Unlike the chromium complex **78**, which coordinates via the phenyl ring of 2-benzylpyrrole, interaction of $Mn(CO)_5Br$ with the potassium salt of the pyrrole derivative leads to 2-benzyl-*n*-pyrrolylmanganesetricarbonyl (**95**) [154,174].



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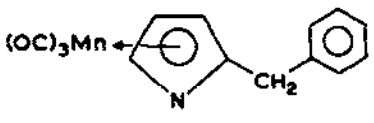


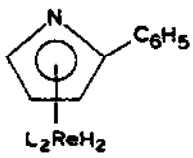
95

96

Rhenium heptahydride $((C_6H_5)_3P)_2ReH_7$, reacts with pyrrole in the presence of 3,3-dimethyl-1-butene in boiling THF followed by formation of **96** [175]. In this complex, not only does substitution of the hydride anions by other ligands take place, but also C_2-substitution on the pyrrole ring is possible so that a variety of π-pyrrolyl half-sandwich complexes may be obtained (**96**).

Treatment of **96** with one equivalent of iodine in excess potassium carbonate at room temperature gives **97**, which reacts with phenyllithium in THF to form **98** with subsequent formation of **99**. Attempts to introduce the third phenyl group were unsuccessful.

97



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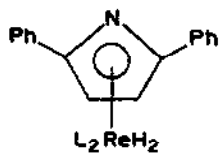
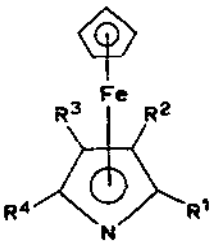


99

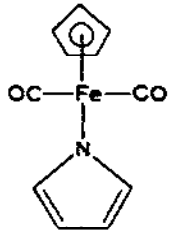
Dicarbonylcyclopentadienylironiodide reacts with pyrrolyl potassium to form azaferrocene (**100**) [69,70], which is isomorphous to ferrocene. The pK_a value (**100**, $R^1 = R^2 = R^3 = R^4 = H$) in water–ethanol medium (4.5) is similar to that of quinoline (4.65).



$R^1=R^2=R^3=R^4=H$
$R^1=CH_3, R^2=R^3=R^4=H$
$R^1=R^4=CH_3, R^2=R^3=H$

100

101

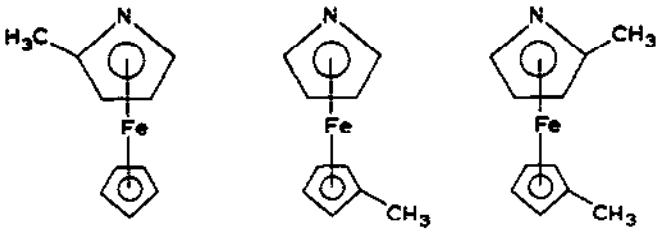


102

Azaferrocene is very soluble in dilute aqueous picric acid, giving the crystalline picrate **101** (X = H, Y = $C_6H_2(NO_2)_3O^-$), which reacts with methyl iodide to form the rather unstable salt **101** (X = CH_3, Y = I).

During the formation of **100**, it is possible to anticipate the existence of an intermediate σ-pyrrolyl complex (**102**), which then eliminates CO to give the π-complex [176]. The intermediate can be isolated if the reaction is conducted under mild conditions. This, in particular, is demonstrated in the case of π-(3-acetyl-2,4-dimethylpyrrolyl)-π-cyclopentadienyliron [158]. The mass spectrum of azaferrocene shows that the ability of the nitrogen-containing rings to act as a polydentate ligand is lower [177]. Comparison of the ^{1}H NMR spectra of ferrocene and azaferrocene leads to the conclusion that, in the pyrrolyl derivatives, the charge on the metal atom is less than in the π-cyclopentadienyl complex. The ^{1}H NMR spectra of solid azaferrocenes have been reported as a function of temperature [178].

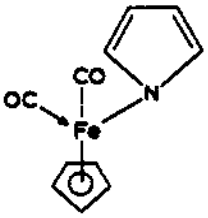
Azaferrocene is easily methylated by *n*-butyllithium in THF at 220 K with subsequent treatment with methyl iodide, resulting in formation of **103–105** [179]. It was possible to separate the products by chromatography and fractional distillation. According to ^{1}H NMR spectral data, the pyrrolyl and cyclopentadienyl rings are methylated rapidly, the process being more facile for the former.



103 104 105

Similar results were obtained when a mixture of heavy water and trimethylchlorosilane were used instead of methyl iodide. However, the monosubstituted trimethylsilylazaferrocenes are unstable and decompose into the corresponding ferrocenes instantaneously. The substituted trimethylsilylazaferrocene (analogue of **105**) is more stable.

The chemistry of ferrocene and azaferrocene is considerably different [180]. Ferrocene is rather stable while azaferrocene gives rise to ferrocene, and the metal ion is subject to carbonylation. The latter reaction includes a $\pi \rightarrow \sigma$ rearrangement of the pyrrolyl ligand and is reversible. The analogous process occurs under the influence of other π-acidic ligands: PF_3, R_2NPF_2 (R = CH_3, C_2H_5), $CH_3N(PF_2)_2$, *t*-C_4H_9NC, *n*-C_3H_7NC, i-C_3H_7NC, $(CH_3)_2N(CH_2)_2NC$, and C_6H_5NC. Derivatives of type **106** are easily isolated and purified except when L = PF_3, or $CH_3N(PF_2)_2$. The σ-donor ligands (phosphines and arsines) cause decomposition of azaferrocenes to the metal ion and a small amount of ferrocene. This takes place without the $\pi \rightarrow \sigma$ rearrangement.



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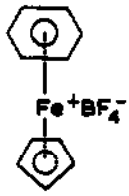

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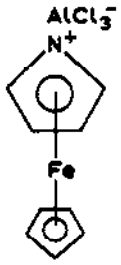

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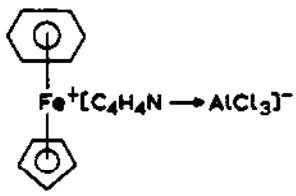
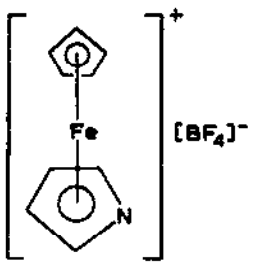


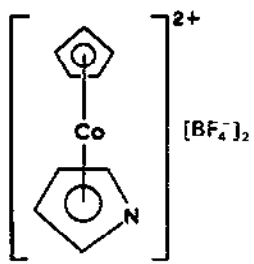
109

Azaferrocene reacts with aromatic hydrocarbons in the presence of aluminium chloride at 310–320 K, giving rise to cationic complexes of the type (η^6-arene)(η^5-cyclopentadiene)iron (1+) isolated as BF_4^- salts (**107**) [175]. Exchange of η^5-pyrrolyl and η^6-arene is likely to occur, although such a reaction does not necessarily mean that the bond between η^5-pyrrolyl and iron is weaker than the bond between η^5-cyclopentadienyl and iron. Labilization of the first bond is caused by formation of the adduct of azaferrocene with aluminium chloride (**108**) and is one more example of the basic properties of azaferrocene. The electrophile attacks at the basic nitrogen atom, weakening the bond between pyrrolyl and iron and facilitates decomposition of **109** to **108**.

The complex (**110a**), obtained by reaction of the sulphane complex $[(C_5H_5)(S(CH_3)_2)_3][BF_4]$ with pentamethylpyrrole, is stable in solution and in the solid phase. X-ray and ^{13}C NMR structural analysis reveal its metallocene character. This complex enters into substitution reactions with other neutral ligands upon photoexcitation. The isoelectronic complex **110b** is obtained in a similar manner [181].

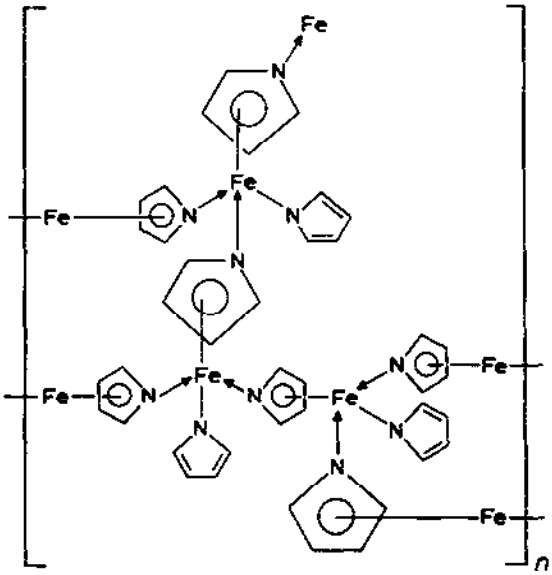


110a



110b

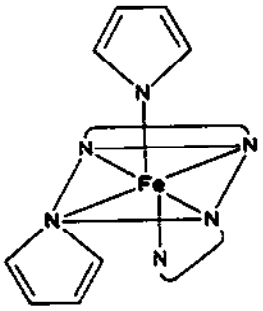
Using two synthetic routes, i.e. interaction of iron with pyrrole in the vapour phase at 77 K and reaction of ferrous chloride with sodium pyrrolyl in boiling THF, Reagen and Radonovich [182] obtained $Fe_x(pyrrolyl)_y$, for which they proposed the model **111**. It includes the π-pyrrolyl ligand simultaneously acting as the σ-donor ligand. The pyrrolyl ligand can act both as a π- and a σ-ligand. Indeed, reaction with excess sodium cyclopentadienyl leads to the corresponding ferrocenes, while reaction with excess 2,2'-bipyridine or 3,4,7,8-tetramethyl-1,10-phenanthroline results in formation of complexes of the type **112**.



111

A similar model was proposed for the cobalt complex [183]. This complex is synthesized as a result of co-condensation of cobalt vapours with pyrrole in vacuum followed by formation of a frozen matrix which is subsequently warmed to room temperature. An oligomer or a polymer is formed in which the σ- and π-donor functions are realized simultaneously. The model proposed differs from that for the Fe/pyrrolyl complex by inclusion of the Co–Co bonds to attain the 18-electron configuration.

The complex $[\eta^1\text{-}C_4(CH_3)_4N)_2Fe \cdot 2THF]$, obtained by reaction of $FeCl_2$ with $C_4(CH_3)_4Li$ in tetrahydrofuran, contains the N-coordinated pyrrolyl ligands as follows from ^{13}C NMR data. This compound is stable as a solid in argon atmosphere and also in THF at 230 K. However, it decomposes in solution after several hours, THF being liberated. The decomposition is accelerated by traces of water and the stable adduct **113** is formed. X-ray analysis reveals that the η^5-pyrrolyl ligands lie in parallel planes, the nitrogen atoms being in anti-positions [184,185]. Each of the η^5-coordinated ligands is H-bonded to the additional tetramethylpyrrole molecule,



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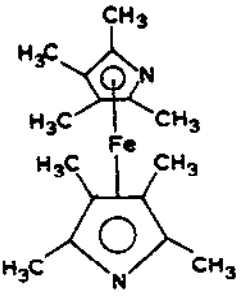

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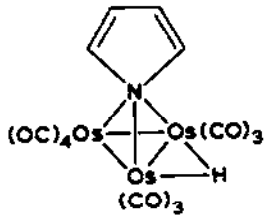
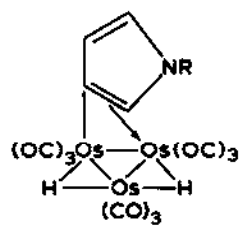


114

the plane of which is almost perpendicular to the ligand plane. All the C_4N rings are planar. Intermolecular hydrogen bonds are so tight that they are not exchanged in excess tetramethylpyrrole.

Dodecacarbonyltriosmium $[Os_3(CO)_{12}]$ and its diacetonitrile substitution product $[Os_3(CO)_{11}(NCCH_3)_2]$ are known to react with primary amides to form μ-amido complexes of the type $[Os_3H(CO)_{10}(NHR)]$. The amine ligand is a three-electron donor. If pyrrole behaves in a similar fashion, one would expect a complex such as **114** characterized by a tetrahedral environment of the pyrrole nitrogen atom followed by removal of π-electron delocalization. However, reaction of dodecacarbonyltriosmium and pyrrole in boiling decalin forms the dihydride **115**, confirmed by IR and NMR data [186,187]. Exchange between the hydride ligands in the methyl derivative occurs more rapidly than in the unsubstituted pyrrole complex.



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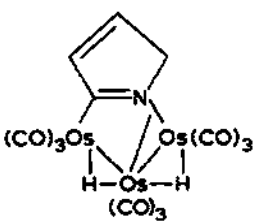

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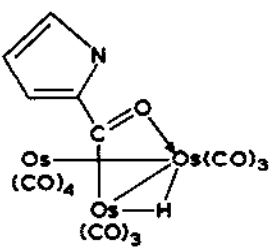


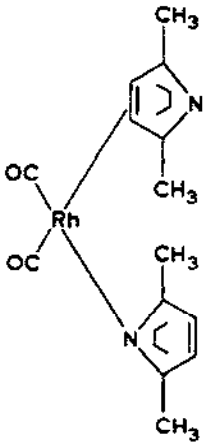
117

The structure **115** was later confirmed [188] by using 1-methylpyrrole as a ligand. The unsubstituted pyrrole complex of the type **115**, initially formed, isomerises as a result of proton transfer with the formation of a new stable isomer **116**. The

latter undergoes rapid and complete (N)H,D-exchange when treated by $D_2O/CDCl_3$ in the presence of catalytic amounts of triethylamine. In excess D_2O, $[Os_3H_2(CO)_9(C_4H_2ND)]$ gradually transforms to $[Os_3HD(CO)_9(C_4H_3N)]$ and probably to **114**. The ligand in these complexes is non-aromatic.

2-Formylpyrrole reacts with $[Os_3(CO)_{10}(NCCH_3)_2]$ giving rise to the product **117** followed by rupture of the C–H bond of the formyl group [188,189]. The complex obtained easily decomposes to form **115**, the product of direct interaction of the unsubstituted pyrrole and **116**.

Attempts to synthesize the pyrrolyl complexes of cobalt, (η^5-2,5-dimethylpyrrole)cobaltdicarbonyl and the 3,4-dimethyl analogue, have been unsuccessful [190]. Reaction of lithium-2,5-dimethylpyrrolide with $[RhCl(CO)_2]_2$ in THF leads to formation of **118**. This is the first example of the heterocyclic bridged ligand between two metals, where the σ- and η^2-π coordination is realized, and formation of the distorted metal–olefin framework takes place [169,170]. Reaction of **118** with nucleophiles, such as triphenylphosphine and triphenylarsine, leads to formation of **119**. This complex (E = P) is characterized by a square-planar coordination unit with a trans-mutual disposition of the phosphine ligands. The iridium analogues of **118** and **119** have also been synthesized.



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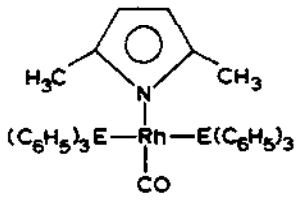


E = P, As

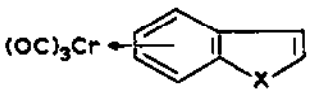
119

6. σ,π-COMPLEXES OF BENZANNELATED FIVE-MEMBERED MONOHETEROCYCLES

The existing view of the electronic distribution of benzannelated five-membered heterocycles [191,192] is that π-electron delocalization embraces only the carbocyclic constituent of the molecule. Thus, one may expect that coordination of metal carbonyls should occur via the π-conjugated system and that the hetero-nucleus should take part in π-complex formation only with difficulty. This should be true not only as a result of π-delocalized dienic structure (benzo-, dibenzo-, and naphthofurans

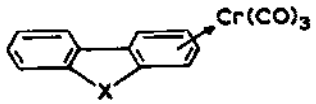
and -thiophenes) but also due to the existence of the competing donor site, the pyrrole-type nitrogen atom (indole, carbazole).

Chromium tricarbonyl complexes with condensed heterocycles — benzofuran, benzothiophene, 7-methylbenzothiophene and indole, dibenzofuran, dibenzothiophene **120** and carbazole **121**, benzo[b]naphtho[2,3-d]furan (**122**) and benzo[b]naphtho[2,1-d]thiophene (**123**) have been studied [193–197].



X = O, S, NH

120



X = O, S, NH

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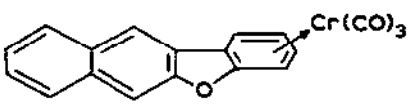

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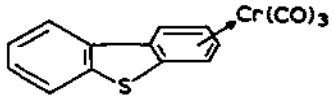
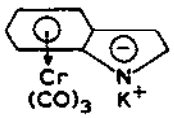


123

The two synthetic routes are usually described as direct interaction of chromium hexacarbonyl with the heterocycle [193–198] and, in the case of indole, interaction between this heterocycle and $(NH_3)_3Cr(CO)_3$ [193]. The indole and carbazole complexes are deprotonated by t-C_4H_9OK followed by formation of the η^6-arene (**124**,**125**), which does not isomerize to the η^5-species. The complexes **124** and **125** react with electrophiles (CH_3I, CH_3COCl, p-$CH_3C_6H_4SO_2N(NO)CH_3$) with addition occurring via the nitrogen atom, e.g. **126**.



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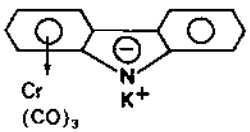

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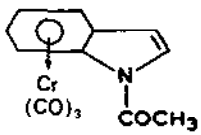
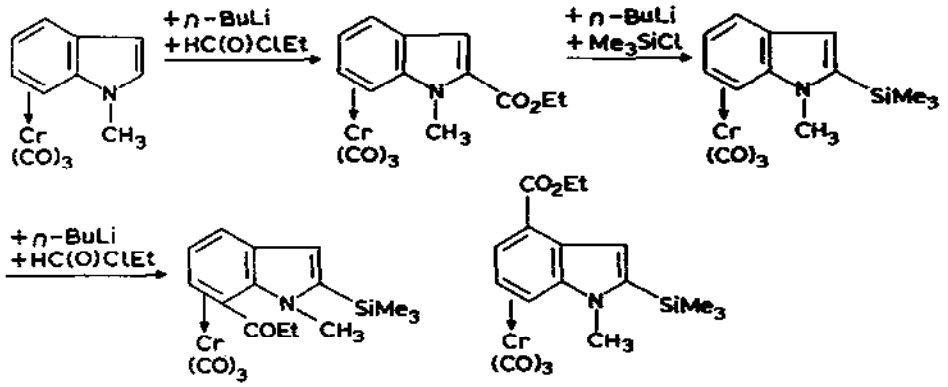


128

The sequence of transformations of the π-complex of 1-methyl-indole leads to the complexes **127** and **128** [199]. The scheme shows the sequence of deprotonation centres of indole, i.e. 2, 4, and 7 positions. X-ray structural analysis has shown that of the last two deprotonation centres, the more preferable is the γ position.

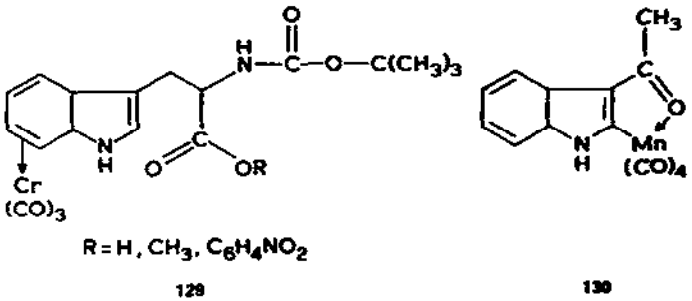
Nucleophilic addition of $LiCH_2CN$ and others to $Cr(CO)_3L$ (L = benzofuran, indole) occurred preferentially at the 4 position [200,201]. The selectivity correlates with the magnitude of the LUMO for indole [202].

Tricarbonylchromium(benzo[*b*]thiophene) was treated with an equimolar quantity of *n*-butyllithium and the product was methylated by methyl iodide to give tricarbonylchromium(2-methylbenzo[*b*]thiophene) [203]. When *n*-butyllithium was



used in a four-fold excess, tricarbonylchromium(2,7-dimethylbenzo[*b*]thiophene) was isolated as the basic product.

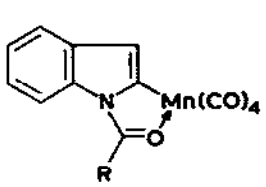
Reaction of chromium hexacarbonyl with the derivative of tryptophan yields **129** ($R = CH_3$), which is hydrolyzed to **129** ($R = H$) and transformed into **129** ($R = C_6H_4NO_2$) when reacted with *p*-nitrophenol and dicyclohexylcarbodiimide [204].



The pyrrole ring of 3-acetylindole reacts with $C_6H_5CH_2Mn(CO)_5$ forming the *o*-manganated product **130** [98].

Treatment of *N*-acetyl- and *N*-benzylindole by $C_6H_5CH_2Mn(CO)_5$ gave complexes **131** in which the $Mn(CO)_4$ group is bonded to the ligand via the Mn–O and Mn–C bonds [205]. This was confirmed by IR, ^1H and ^{13}C NMR spectroscopy and, in the case of $R = CH_3$, by X-ray structural analysis.

Reaction of benzothiophene with $Fe_3(CO)_{12}$ given benzothiaferrole, **132** [106]. X-ray structural analysis of the monophosphine derivative of this complex substantiates the $(CO)_6$ structure, contrary to the $(CO)_5$ structure proposed earlier [99,104]. Iron and cobalt carbonyls such as $Fe(CO)_5$, $Fe_2(CO)_9$, $C_5H_5Co(CO)_2$ do not react with benzothiophene. $Ru_3(CO)_{12}$ and benzothiophene form the complex analogous to **132**.



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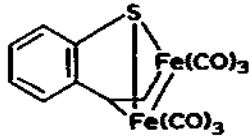
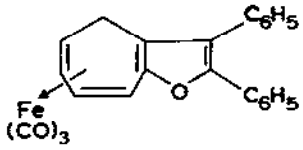


132

The reaction leading to **133** was also reported [206]. Two carbonyl groups and two double bonds of the dienic framework form the plane of the pyramidal base and the third carbonyl group is in the apex of the square-pyramid.



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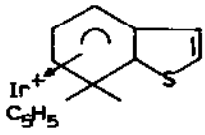

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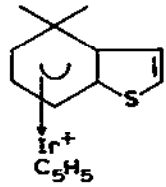
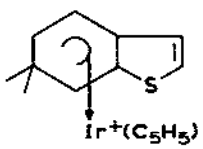


135

The ruthenium and iridium complexes $[(C_5(CH_3)_5)ML]X_2$ (M = Ru, Ir; L = benzothiophene, 2-methyl-, 3-methyl- and 2,3-dimethylbenzothiophene; X = PF_6, BF_4) were obtained as a result of interaction of $[(C_5(CH_3)_5)RuCl_2]$, $AgPF_6$ and benzothiophene, or $[C_5(CH_3)_5Ir(acetone)_3][BF_4]_2$ with various benzothiophenes [132,133]. The structure of the dicationic complexes was confirmed using X-ray analysis. The monocationic complexes $[(C_5H_5)RuL]X$ (L = benzothiophene or 3-methylbenzothiophene; X = BF_4, PF_6) were also synthesized. The η^6-coordination via the benzene ring takes place in all the complexes mentioned.

Dicationic iridium complexes react with hydrides, such as $NaBH_4$, to form four isomers (**134–137**), the relative content of which is decreased in the sequence: **134** > **135** > **137** ≫ **138**, irrespective of the nature of the ligand (benzothiophene or methylbenzothiophene). Hydride attacks the benzothiophene ring predominantly via the 7 position and noticeable amounts of the isomers are formed due to attack at the 5 and 6 positions. Interaction of $[(C_5H_5)Ru(benzothiophene)][PF_6]$ with $NaB(C_2H_5)_3H$ leads to the product **136**.



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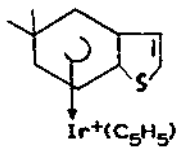
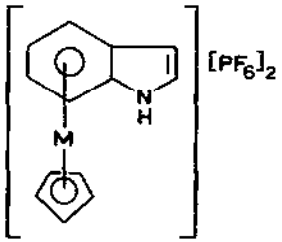


137

The dicationic iridium complexes and monocationic ruthenium complexes abstract the hydride anion under the action of $HBF_4 \cdot (C_2H_5)_2O$ [132]. The iridium

dications react with nucleophiles followed by formation of $[(C_5(CH_3)_5Ir(L \cdot Nu)]^+$ (L = benzothiophene, 3-methylbenzothiophene; $Nu = OCH_3^-$, $CH(CO_2CH_3)_2^-$, $SC_2H_5^-$). Four isomers of the type **134–137** are again formed with practically the same relative content. Excess $[(C_6H_5)_3C][BF_4]$ leads to immediate regeneration of the initial dication. The same kind of reaction takes place between the dications and trimethylphosphine, which predominantly adds at the 7 position of the condensed ring.

Reaction of tris(acetone) complexes with indole leads to the η^6-indole complexes **138** (IR, ^1H and ^{13}C NMR spectroscopy) [207,208]. None of these deprotonates easily in acetone but the iridium complex loses a proton in reaction with bases (Na_2CO_3 in water, t-C_4H_9OK in acetone) to form the η^5-indolyl complex **139**. This reaction is easily reversed in the presence of small amounts of trifluoroacetic acid.



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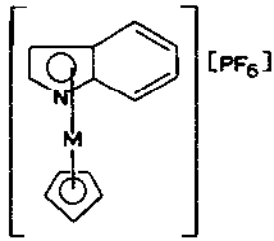
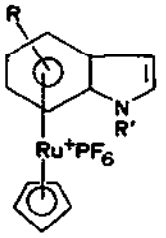


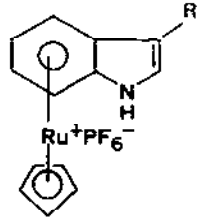
139

New indole complexes (**140**) were obtained by heating the corresponding indole with $[(C_5H_5)Ru(CH_3CN)_3][PF_6]$ [209]. The complexes, where R = 5-Cl, 4-Cl, R′ = CH_3, undergo nucleophilic substitution of chlorine by $(RCO_2)CH$ (R = CH_3, C_2H_5), CH_3O, $C_6H_5CH_2O$, HO_2CCH_2S, CH_3NH groups under mild conditions.



R=5-Cl, 5-CH_3, 5-Br, 4-Cl;
R′=H, CH_3

140



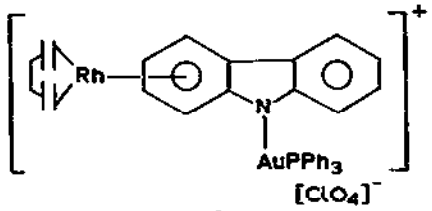
R=$CH_2CH(CO_2C_2H_5)(NHCOCH_3)$, $CH_2CH_2NH(COCH_3)$, CH_2CH_2OH

141

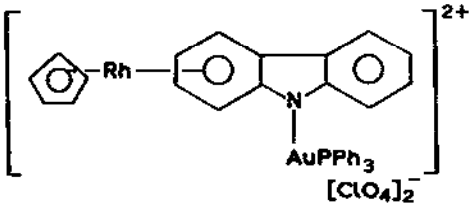
The cyclopentadienylruthenium complexes **141** were obtained by heating the indole substrate and $[(C_5H_5)Ru(CH_3CN)_3][PF_6]$ in dichloroethane under nitrogen [210].

$[(cod)Rh(acetone)_x]ClO_4$ reacts with carbazole followed by formation of the η^6-coordinated derivative, $[(cod)RhL]ClO_4$ [211]. Reaction of $ClAuP(C_6H_5)_3$ with

the potassium salt of carbazole forms the *N*-carbazolyl complex, which can form η^6 donor species towards Rh(I) or Rh(III) as the acetone-solvated species **142** and **143**.



142



143

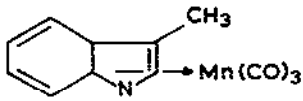
Unusual π-complex compounds were obtained when reacting Yb(fod)$_3$ or Ag(fod) with 9-vinylcarbazole [212]. The ^{1}H NMR spectrum of 9-vinylcarbazole in deuterochloroform in the presence of Yb(fod)$_3$ and Ag(fod) as the lanthanide shift reagent was interpreted in such a way that Ag(fod) forms a bridge between Yb(fod)$_3$ and 9-vinylcarbazole. This bridge simultaneously forms the π-complex with the double bond of the vinyl group.

The carbocycle in cyclopentadienyltricarbonylmanganese may be substituted by the indolyl anion. The structure of the corresponding complex **144** was proposed on the basis of X-ray analysis [213]. The manganese atom is almost symmetrical relative to the carbon atoms of the hetero ring. The indole system is non-planar, while the benzene ring preserves planarity. The π-electrons of the benzene ring are less polarizable than the π-electrons of the hetero-ring so that the manganese atom predominantly coordinates via the atoms outside the benzene ring. In the system, delocalization of electron density is directed towards π-azoallyl.

Tricarbonyl-π-(2-methylindolyl)manganese is also known [167]. Indolylsodium reacts with manganese pentacarbonyl in a more complicated way to give $C_9H_8Mn(CO)_5$.

The synthesis of cyclopentadienylironindolyl proceeds through formation of **145** [169]. Transformation into the π-complex occurs at elevated temperatures. Carbazole forms only the *N*-carbazolyl complex **146** under these circumstances.

$RuCl_2(P(C_6H_5)_3)_2$ reacts with 4-R_2P-dibenzothiophene and forms **147** in which, according to X-ray data, the dibenzothiophene ligand is coordinated to ruthenium via the phosphorus and sulphur atoms [214].



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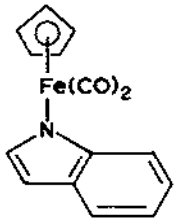

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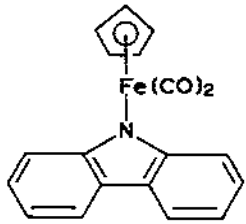
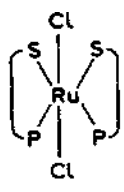


146

Reaction between [RhCl(nbd)(Haz)] (Haz = 7-azaindole) and $[Rh(acac)_2(CO)_2]$ yields the complex [(nbd)Rh(μ-az)(μ-CO)RhCl(CO)] [215].

7. σ,π-COMPLEXES OF PHOSPHOLES, ARSOLES AND STIBOLES

Neutral phospholes, arsoles and stiboles may formally be considered as two-electron donors, where only the lone pairs of phosphorus, arsenic and antimony take part in coordination (**148**). They also behave as four-electron donors, when the diolephinic part of the system coordinates to a metal-carbonyl framework (**149**). If both functions operate simultaneously, the cyclic system is a formal six-electron donor (**150**) [216–219].



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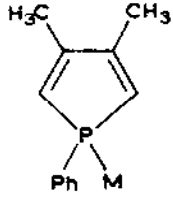

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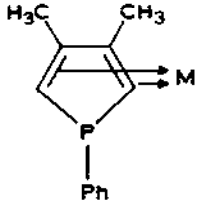

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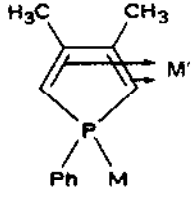
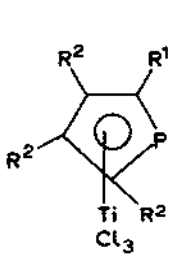


150

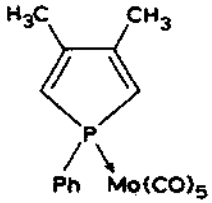
In compounds containing an ordinary chemical bond between phosphorus (arsenic, antimony) and a transition metal of the metalcarbonyl framework, phosphole, arsole and stibole are one-electron donors. However, they behave as three-electron donors when the heteroatom acts as a bridge. Phosphole, arsole and stibole can also act as formal five-electron donors similar to cyclopentadiene and pyrrole. Phosphole is sometimes known to be a formal seven-electron donor [216–219].

The complex bis(η^5-3,4-dimethylphospholyl)zirconiumdichloride has been synthesized and characterized [220]. The synthesis of the corresponding derivative of 2,3,4,5-tetramethylphospholyl was confirmed using ^{1}H, ^{13}C and ^{31}P NMR, mass spectroscopy and X-ray analysis [221].

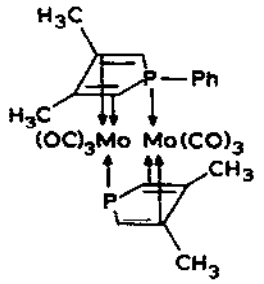
Direct synthesis of (η^5-phospholyl)MCl_4 (M = Ti, Zr) by reaction of lithium phospholide with metal tetrachloride is successful only in the case of zirconium, but not titanium, when 3,4,3′,4′-tetramethylphospholyl is isolated [222]. This is likely to be the consequence of one-electron reduction of $TiCl_4$ by the phospholide anion followed by pairing of the resultant phospholyl radicals. Other precursors of the titanium complexes are 1-trimethylsilylphospholes obtained from 1-phenylphosphole and lithium, then aluminium chloride and finally trimethylstannylchloride. They give rise to the complexes **151**. The $TiCl_3$ grouping possesses a substantial electron-acceptor effect.



151



152

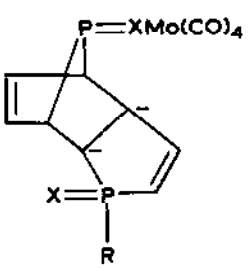


153

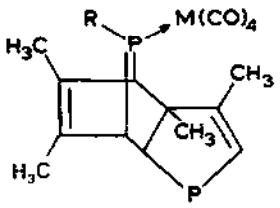
1-Phenyl-3,4-dimethylphosphole is characterized by the transfer of the phenyl group and a [1,5]-hydrogen shift at temperatures higher than 420 K. As a result, it is in equilibrium with 5-phenyl-3,4-dimethyl-2H-phosphole [223]. At temperatures lower than 420 K, the ligand reacts as the 1-phenylderivative. At 413 K in an argon atmosphere, the classical σ-complex **152** is formed with molybdenum carbonyls. If the reaction is conducted for a longer time, **153**, in which both σ- and π-bonding occur, is formed.

λ^5-Phospholes tend to dimerize at low temperatures (**154**). In contrast to λ^5-phospholes, the λ^3-derivatives are not dimerized under normal conditions. [2 + 2] Head-to-tail dimerization of 1,2,5-triphenyl-phosphole by UV radiation is possible

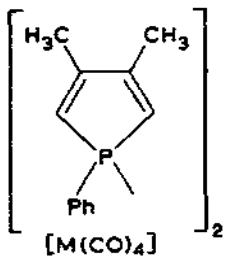
only in one case. However, during a study of the reaction of 1-phenyl-3,4-dimethylphosphole with molybdenum hexacarbonyl, [4 + 2] dimerization leading to the exo-phosphole Diels–Alder dimers has been noted [224,225].



154



155

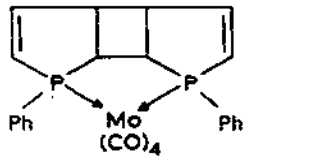


156a M = Cr
156b M = Mo

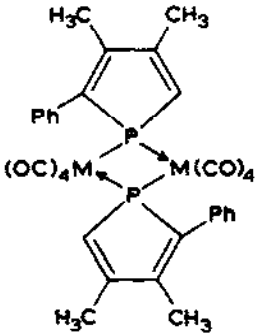
Thus, reaction of 3,4-dimethylphospholes with chromium, molybdenum and tungsten hexacarbonyls at room temperature in THF under UV radiation resulted in the two complexes **152** and **155**. The first complex of type **152** corresponds to the composition $LM(CO)_5$, while the second (**155**) has $L_2M(CO)_4$ (M = Cr, R = C_6H_5; M = Mo, R = CH_3, t-C_4H_9, C_6H_5; M = W, R = C_6H_5). The ^1H and ^{31}P NMR spectra show that the complexes **155** are derivatives of Diels–Alder dimers with an unusual exo-configuration. They have a cis configuration around the molybdenum atom. Phospholes themselves do not dimerize under UV radiation in THF at room temperature. Dimerization into **155** takes place only if a metal is coordinated. The first step includes formation of **156**, in which dimerization occurs as a result of proximity of the two phosphole nuclei. The cis complex (**156a**) was isolated along with **152** and **155**. Dimerization in this case is inhibited because of the small size of the chromium atom and the lesser tendency to be chelated by the phosphole dimer.

The second step of dimerization (intramolecular dimerization), like the first, is promoted by UV irradiation. Indeed, thermal reaction of 1-phenyl-3,4-dimethylphosphole with $(C_5H_{10}NH)Mo(CO)_4$ leads to **156b** and not to **155** (M = Mo, R = C_6H_5). Complex **156b** leads to **155** (M = Mo, R = C_6H_5) under UV irradiation. However, from the viewpoint of the Woodward–Hoffmann rules and on the basis of the study of UV dimerization of 1,2,5-triphenylphosphole, it is highly probable that [2 + 2]

dimers are the initial products of dimerization and [4 + 2] dimers are the final results of thermally allowed intramolecular rearrangement of [2 + 2] dimers. This hypothesis is substantiated by the data obtained from reaction of 1-phenylphosphole with molybdenum hexacarbonyl under UV radiation. The "head-to-head" structure of the complex **157** was proven by ^{1}H and ^{31}P NMR and mass spectra. The structure of the complex **155** (M = Mo, R = C_6H_5) was established from X-ray structural analysis.



157



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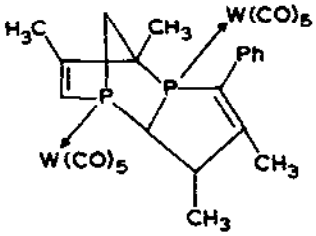


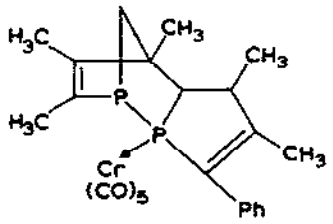
159

If the reaction temperature is raised to 430 K and the carbon monoxide pressure to 3 atm, coordination of the molybdenum atom in the rearrangement product occurs via the phosphorus atom (**158**) [223]. Reaction with tungsten and chromium hexacarbonyls occurs similarly. Along with this product at 420 K, formation of the dimer of 5-phenyl-3,4-dimethyl-2H-phosphole (**159**) (the σ-complex) is possible as a consequence of [4 + 2] cycloaddition reactions. Chromium hexacarbonyl in turn forms phosphidobridged complexes of the P-donor type (**160**).

At 420 K in excess 2,3-dimethylbutadiene, a transformation reaction **161** → **162** takes place [226].

A number of papers are devoted to the reaction ability of $W(CO)_5$ σ-complexes of type **152** [227–231]. The complex **163** is the first known η^5-phospholyl complex studied by X-ray analysis. The tungsten atoms have a coordination number of 9, and the carbon atoms of the phospholyl ring are co-planar. The phosphorus atom deviates from the plane of the carbon atoms by 0.015 nm. The basic difference between the η^5-cyclopentadienyl and η^5-phospholyl complexes is the existence of a low-lying LUMO localized mainly at the phosphorus atom.

Acylation of the carbon atoms of **152** becomes possible only after blocking the phosphorus atom by complex-formation with $Mo(CO)_6$. A series of complexes (**164–166**) was described.



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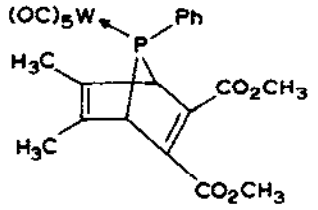

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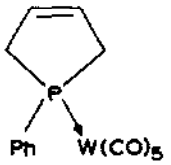

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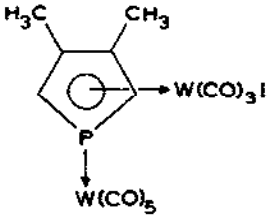

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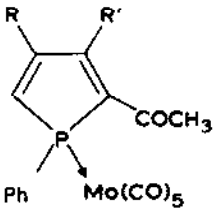

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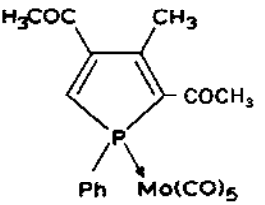

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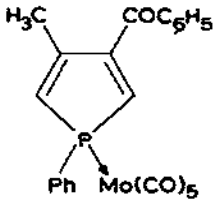

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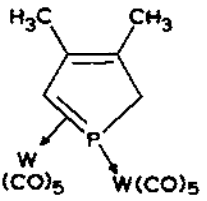

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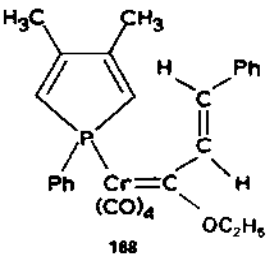


168

Another consequence of blocking the lone pair of phosphorus by group VI metal hexacarbonyls (particularly, tungsten hexacarbonyl) is interaction of the aromatic cyclopentadienyl cycle or the ferrocene molecule with the diene system of phosphole [232], yielding the 2-arylphospholene complexes.

An example of η^1,η^2-coordination is complex **167**, according to which the P–C bond length is intermediate between those of P–C and P=C [233].

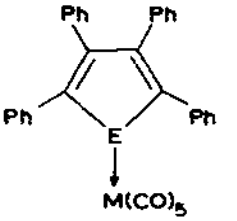
Dibenzophosphole (DBP) σ-complexes of the type $(DBP)_nM(CO)_{6-n}$ (M = Cr,

Mo, W; $n = 1–3$) were reported [234,235]. The complex $(DBP)_2Cr(CO)_4$ has a cis structure and $(DBP)_3Cr(CO)_3$ has a mer structure in the solid state.

The facile route for introduction of the phosphole ring into the coordination sphere of the chromium vinylcarbene complex is via [4 + 2] intramolecular cycloaddition of the phosphole dienic system to the C=C carbene double bond [236]. The intermediate complex **168** was proposed, where the phosphole behaves as a classical P ligand.

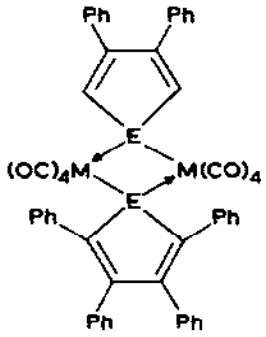
The existence of σ-complexes of triphenylarsolepentacarbonyls of manganese and rhenium [237] was identified on the basis of the $[(C_6H_5)_4C_4AsM(CO)_5]^+$ ions in the mass spectrum. These ions lose all the CO groups one by one. The most intense lines correspond to the $[(C_6H_5)_4C_4AsM(CO)_3]^+$ and $[(C_6H_5)_4C_4AsM]^+$ ions.

The σ-complexes of 2,3,4,5-tetraphenylarsole and -phosphole of composition $[M(CO)_5(EC_6H_5)_4]$ (**169**) and $[(M(CO)_4EC_4(C_6H_5)_4)_2]$ (**170**) transform rapidly into the corresponding monomeric tricarbonyl derivatives (**171**) at elevated temperatures [238]. It is quite probable that the transformation **169** → **171** proceeds through dimer formation via **170**.



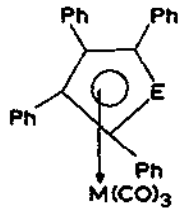
E = P, As; M = Mn, Re

169



E = P, As; M = Mn, Re

170



M = P, As; M = Mn, Re

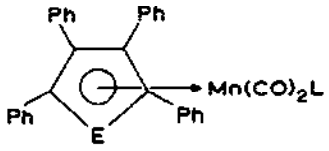
171

The structure of **171** (E = As) contains the arsole ring, where each phenyl group is rotated from the C_4As plane through 40–60°. The plane of the carbonyl groups containing the three carbon atoms is parallel to the hetero ring. Delocalization of electron density in the arsolyl ring takes place although phosphole and arsole themselves are characterized by lack of aromatic stabilization.

Phospholyl and arsolylmanganesetricarbonyls **171** (M = Mn) may be obtained by first forming the σ-complex and bridged dimers [238]. A second reaction may proceed through coordination of silylarsole to $Mn(CO)_5Cl$ followed by substitution of carbon monoxide and subsequent elimination of trimethylchlorosilane (**171**, M = Mn, E = As). Reaction with the organotin analogue proceeds similarly, although in

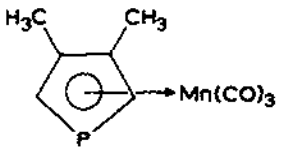
rather low yield. Moreover, the reaction is complicated by the formation of $[Mn(CO)_5Sn(CH_3)_3]$.

The π-complexes of tricarbonylmanganese (**171**) may be subject to a series of substitution reactions of carbon monoxide by L to yield **172** [238]. In cyclohexane and under UV irradiation, 3,4-dimethylphosphacymantrene (**173**) forms monosubstituted products with various phosphines and trimethylphosphite **174**. A disubstituted derivative was also obtained in the case of trimethylphosphite (**175**) [239].



E=P, As; L=$P(C_6H_5)_3$
E=As; L=$(C_6H_5)_2C{=}C(C_6H_5)_2$

172



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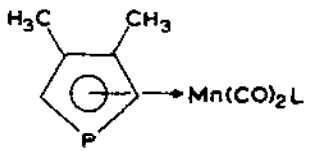
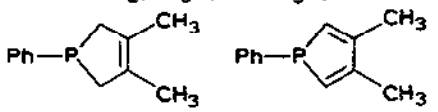


L=$PhPMe_2$, Ph_3P, $(MeO)_3P$,



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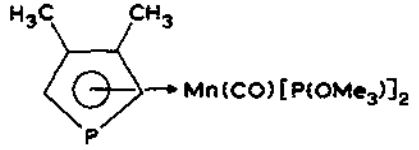

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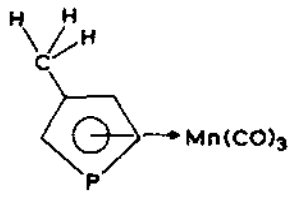

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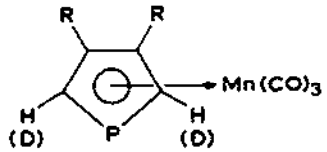


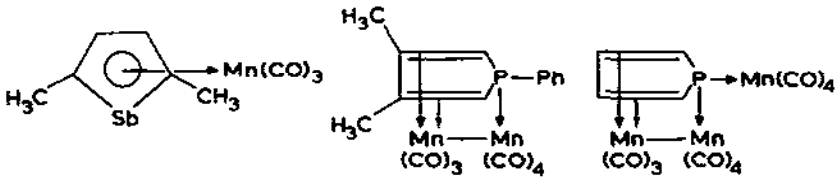
177

The phospholyl ring of phosphacymantrene is planar, as inferred from ^1H NMR measurements in nematic solvent. The following conformations of 3-methylphosphacymantrene (**176**) were considered [240–242]: (a) the C–H bond of the

methyl group is in the plane of the cycle; (b) it is perpendicular to the cycle; (c) the methyl group rotates freely. The optimum conformation is (b), i.e. the C–H bond of the methyl group is orthogonal to the plane of the ring.

The IR and Raman spectra of phosphacymantrene and its deutero- and 3,4-dimethylderivatives (**177**) have been measured [243]. Valence force fields of the C_5H_5 rings in cymantrene and C_4H_4P in phosphacymantrenes were compared. The phospholyl rings were shown to be more electrophilic and weaker π-donors than the cyclopentadienyl rings.

The stibacyclopentadienyl anion was synthesized for the first time by Ashe and Diephouse [244] and behaves as a six-electron donor to transition metals. Thus, treatment of this anion by bromomanganesetricarbonyl at 410 K gives 2,5-dimethylstibacymantrene (**178**).

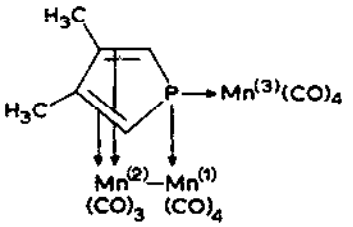


178 **179** **180**

UV radiation and heating of $Mn_2(CO)_{10}$ in the presence of phospholes gives rise to the σ-complexes $L_xMn_2(CO)_{10-x}$ ($x = 1, 2$) as unstable orange oils and to the σ,π-complexes (**179**) as stable orange-red crystals in which the ligands are tridentate [245]. When **179** is irradiated further in the presence of dimanganese decacarbonyl, the P–C_6H_5 bond is broken. As a result, $L'Mn_3(CO)_{12}$ is formed (L' = 3,4-dimethylphospholyl, **180**), where the P–C_6H_5 bond is replaced by P–$Mn(CO)_5$. The product is stable; its mass spectrum shows that it decomposes mainly into $L'Mn(CO)_3$ (**173**). Pyrolysis of the product at 420 K in vacuum yields **173** as indicated by ^1H NMR spectroscopy; subsequently, it was shown that the structure **180** proposed on the basis of its mass spectrum was erroneous. When complex **179** is heated, it gives decomposition products **181** (minor) and **173** (major).

The complexes $LMn_2(CO)_7$, where L = 1-butyl-3,4-dimethylphosphole (**182**) and (3,4-dimethylphospholyl)undecacarbonyltrimanganese (**181**), were studied by X-ray structural analysis [246,247]. Each manganese atom has an 18-electron configuration in **182**. The phosphorus atom in **181** forms a strong bond with the $Mn^{(3)}$ atom and weaker bonds with $Mn^{(1)}$ and $Mn^{(2)}$. Such a mode of interaction is absent in **182**. However, an increased interaction between $Mn^{(2)}$ and P and weak bonding between $Mn^{(1)}$ and $Mn^{(2)}$ in **182** exists relative to **181**. This is due to the more pronounced tendency of **182** to form the π-aromatic complex **173**. The dienic system of the phosphole ligand forms π-bonds with the $Mn^{(2)}$ atom. The $Mn^{(2)}$ and $Mn^{(3)}$ atoms are formally hexacoordinate, and the $Mn^{(1)}$ has a coordination number of 7. Each manganese atom has the configuration of an inert gas. The phosphorus atom

lies out of the plane of the three manganese atoms, with the angle between this plane and the plane passing through the four carbon atoms of the dienic system being 85.9°. The geometry of the phosphole ring changes slightly in the process of ligand coordination.



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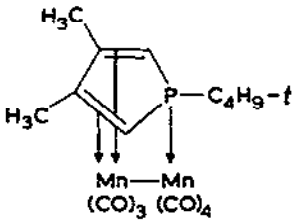

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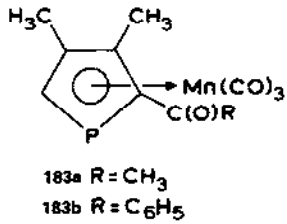


183a R = CH_3
183b R = C_6H_5

The basic purpose of a study of the phosphacymantrenes is to ascertain the existence of aromaticity of the phospholyl nucleus as a result of the three-coordination of phosphorus. In the free anions, electrophilic attacks proceed via the phosphorus atom since the heteroatom has a high negative charge. The π-complexes of phospholes have been chosen as references [248] to study the influence of π-complex formation on aromaticity of the phosphole nucleus.

C-acylation of **172** by CH_3COCl–$AlCl_3$ proceeds easily at room temperature in methylene chloride to give **183a** [248,249], while C-benzoylation (C_6H_5COCl–$AlCl_3$) yields **183b**. C_2H_5Br–$AlCl_3$ does not react in boiling methylene chloride, while attempts to obtain 2-formylderivatives by reaction of **183** with $Cl_2CHCOCH_3$–$AlCl_3$ in boiling tetrachloroethane were also unsuccessful.

Thus, electrophilic substitution via the carbon atoms of phospholyl is, in principle, possible. The reactivity of phospholyl towards electrophiles is considerably less than that of the cyclopentadienyl ring in cymantrene. The nucleophilicity of the phosphorus atom in the complex **173**, whether maintained or not as a result of quarternization and oxidation, was investigated (reactions with benzylbromide and iodine) and the phosphorus atom was found to have lost nucleophilicity upon coordination [248].

Reaction of **173** with *n*-butyllithium in THF at 320 K leads to nucleophilic attack at the phosphorus atom followed by rupture of the bond between phospholyl and manganese to form 1-*t*-butyl-3,4-dimethylphosphole [248]. The high electrophilicity of the phosphorus atom in **173** is substantiated by reactions with sodium

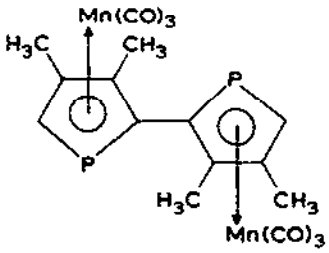
ethylate in THF, diethylaminelithium in THF, and sodium cyanide in ethanol. Free phospholes also react with nucleophiles, but only powerful ones.

IR and ^{13}C NMR data show that phospholyl is a weaker electron donor than cyclopentadienyl towards the $Mn(CO)_3$ group. The electron density at the cyclic carbon atoms is much less in 1-*t*-butyl-3,4-dimethylphosphole than in cymantrene. Although the phosphorus atom takes part in the delocalization in the phospholyl ring, it also plays the role of an electron withdrawer.

X-ray structural analysis of **183b** [250] has shown that the phospholyl ring is not strictly planar. The phosphorus atom is out of the plane of the four carbon atoms at a distance of 0.048 nm from the side opposite to the manganese atom. Three C—C bonds in the ring are equivalent, while the P—C bonds are not, a consequence of the different environments of the C_2 and C_5 atoms. The ketone and benzene frameworks are strictly planar with a dihedral angle near 30°.

In addition to what has been reviewed so far, it is worth mentioning the reaction between 2,2'-biphosphole and dimanganese decacarbonyl under different conditions [251]. In boiling xylene and under inert atmosphere, the main product is the isomeric bis-(η^5-diphospholyl)complex **184** and complexes **185** and **186** are also produced. When performing the reaction in a closed vessel at autogenic pressure of carbon monoxide and at 420 K, the new π-complex **187** is formed.

Interaction of pentaphenylphosphole with iron pentacarbonyl gives rise to



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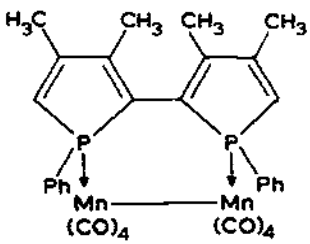

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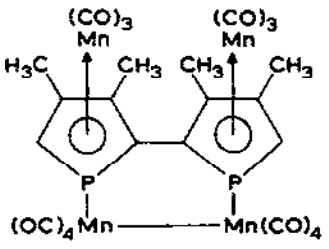

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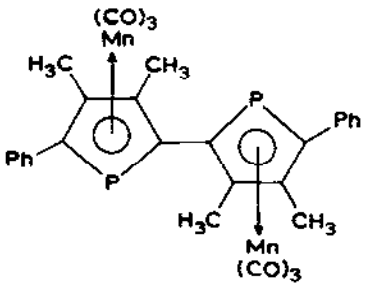
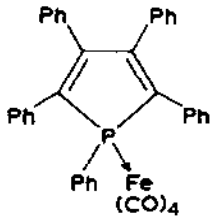


187

σ-complex-formation **188** [252–254]. On the other hand, the reaction with $Fe_3(CO)_{12}$ leads to formation of the π-complex **189** and σ,π-complex **190**. Thus, phospholes belong to one of the numerous kinds of non-aromatic conjugated dienes which easily react with iron carbonyls. This facile complex formation as well as the nature of the bond are inconsistent with the view that the lone pair of the phosphorus atom participates in the aromatic sextet. Note that complexes with pyrroles having substantial aromatic character are unknown.



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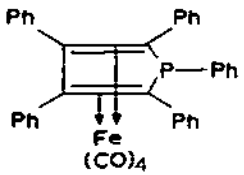

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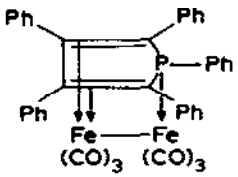

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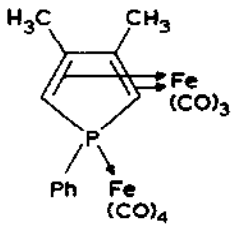
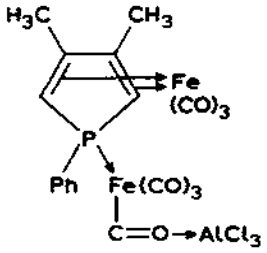


191

Pentaphenylarsole reacts with iron pentacarbonyl to form pentaphenylarsoleirontricarbonyl. Interaction of 1-phenyl-3,4-dimethylphosphole with di-iron-nonacarbonyl gives rise to a complex, in which $Fe(CO)_3$ is η^4-coordinated to the diene, while $Fe(CO)_4$ is η^1-coordinated to the phosphorus atom (**191**) [255]. Reaction with aluminium trichloride followed by treatment with ammonia leads to formation of **192**. The mononuclear complex **193** is formed through an intermediate product (**192**). The complex **193** reacts with hydrogen peroxide to give **194**, with sulphur to give **195**, and with benzyl bromide and methyl iodide to produce **196**. The π-complex also possesses properties of the normal phosphole and takes part in ring expansion with benzoyl chloride, water and triethylamine to give **197** [255,256]. In the presence of phenylnitrilepalladium dichloride, it loses carbon monoxide followed by formation of the sandwich complex **198**. When interacting with pentacarbonyltungstentetrahydrofuran, it yields bimetallic complexes in which the tungsten atom is coordinated via the phosphorus lone pair (**199**) [255].

The coordination chemistry of phospholes towards iron carbonyls has been studied in detail [257]. Reaction of 1-*t*-butyl-3,4-dimethylphosphole with $Fe_3(CO)_{12}$ at 380 K in boiling toluene leads to complexes containing the Fe—Fe bond (**200**).



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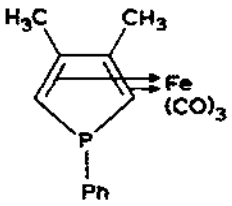

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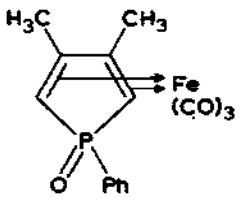

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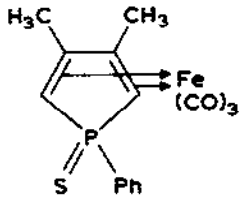

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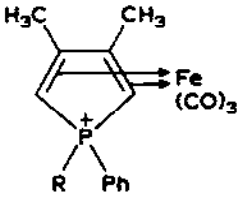
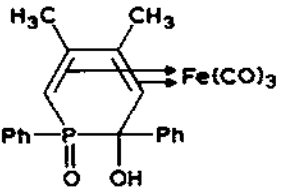


R = CH_3, $C_6H_5CH_2$

196



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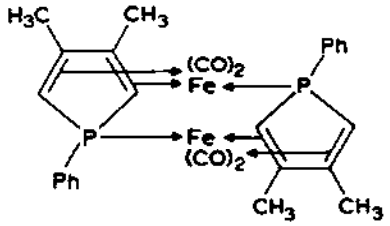

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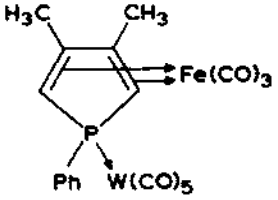
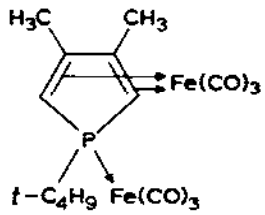


199

The IR bands corresponding to the bridged carbonyl are absent, which was the reason for assignment of structure **200**. However, noting that the structure of ferrole (**201**) has a semi-bridged carbonyl group yet shows no corresponding band in its IR spectrum, one can possibly assign structure **202** in place of **200**. This reaction also gave a complex with the proposed structure **203b** identical to **203a**. Complex **203b** is the side product vs. the basic product **203a** obtained by reaction of 1-phenyl-3,4-dimethylphosphole with $Fe_3(CO)_{12}$ and it disappears if the reaction is conducted at 420 K in boiling xylene. It may seem that **203b** decomposes, giving rise to **202** in boiling xylene and therefore an analogous decomposition reaction has been attempted for **203a**. Heating in xylene at 420 K for 24 h actually gives a new complex having the unexpected structure **204a**, justified by X-ray structural analysis.

The crystal structure of **204a** indicates that it is, in fact, the dimer of mononuclear complex $LFe(CO)_2$. The distance between the iron atoms (0.393 nm) is so great that direct interaction between these atoms is excluded. The distance between P and Fe (0.276 nm) is such that direct interaction is possible. The bond lengths in



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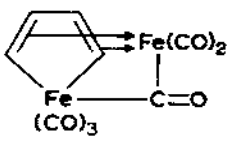

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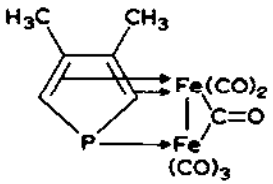

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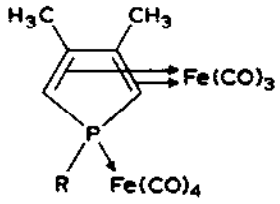
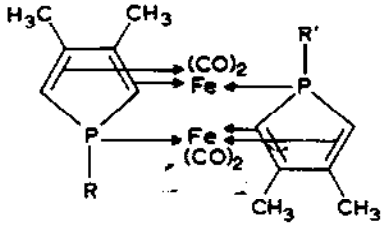


203a R = C_6H_5

203b R = t-C_4H_9



204a R = R' = C_6H_5

204b R = R' = t-C_4H_9

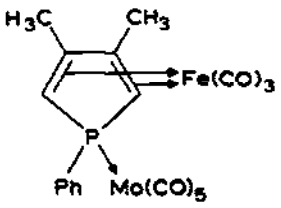
204c R = C_6H_5, R' = t-C_4H_9

the phosphole ring show no cyclic conjugation but still account for formation of the π-complex with the dienic system, which increases the electronegativity of the cyclic carbon atoms and induces polarity of the phosphorus–carbon bonds.

The following reactions were reported: 1-phenyl-3,4-dimethylphosphole + **203a** → **204a**; 1-*t*-butyl-3,4-dimethylphosphole + **200** → **204b**. In the reactions given below, the bond between the iron atoms is broken: 1-*t*-butyl-3,4-dimethylphosphole with **203a** and 1-phenyl-3,4-dimethylphosphole with **210**, both leading to **204b**. Reaction of **152** with (benzylideneacetone)iron tricarbonyl gives rise to the bimetallic complex **205**, which reacts further with the free phosphole to form the bimetallic heteronuclear sandwich **206** in good yield. The preferable coordination of the molybdenum atom to the dienic system of the second phosphole nucleus is rather unusual. The molybdenum atom is believed to have a higher tendency to coordinate via the trivalent phosphorus atom rather than via the dienic system. Proof of the proposed structure for **206**, which contains two non-equivalent phosphorus atoms and two non-equivalent dienic systems was based on NMR analysis.

In complexes **204b** and **206**, a strong $^{31}P \cdots {}^{31}P$ interaction is observed. Hence it is necessary to consider such factors as the cis disposition of the phosphorus atoms around the metal atoms and the direct through-space interaction of the iron and phosphorus atoms in **204a**.

There are some indications that ruthenium(II) carbonylchloride reacts with 1,2,5-triphenylphosphole and 1-phenylbenzophosphole, and that $Fe_2(CO)_9$ reacts with $(C_6F_5)_2PC{\equiv}CC_6H_5$ to yield **207** [258,259].



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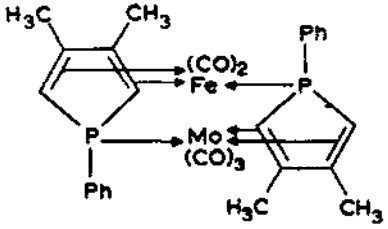

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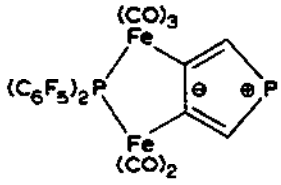

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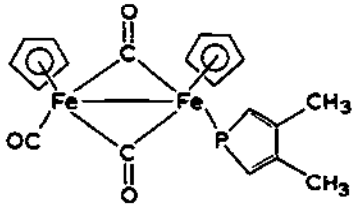


208

Treatment of pentaphenylphosphole sulfide with iron carbonyls gives only pentaphenylphospholeirontetracarbonyl (**188**), while pentaphenylphospholeoxide reacting with iron pentacarbonyl gives pentaphenylphospholeoxideirontricarbonyl [252].

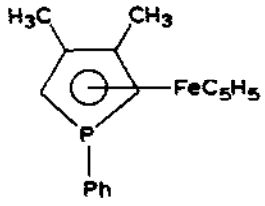
In boiling benzene, 1-phenyl-3,4-dimethylphosphole reacts with dicyclopentadienylirondicarbonyl to give mainly the classical σ-complex (**208**) in which the heterocyclic ligand substitutes one terminal CO group [260].

A synthetic route for 2-phenyl-3,4-dimethyl-1-phosphaferrocene (**209**) from 3,4-dimethyl-1-phenylphosphole and dicyclopentadienylirondicarbonyl at 430 K and 3 atm was reported [223]. 2-Phenyl-1-phosphaferrocene (**210**) was obtained under identical conditions. The same reaction with 1-phenylphosphole gives phosphaferrocene and a mixture of 2- and 3-phenylphosphaferrocenes.

Nucleophilic attack of the phospholyl anion on the metastable acetylacetonate of cyclopentadienyliron leads to **211** [261] (X-ray). The electrochemical properties of phosphaferrocenes were compared with those of the ferrocenes using different electrodes and solvent systems. One-electron reduction of **211** in propylenecarbonate takes place at −2.55, −2.15, and −2.33 V, and for that of ferrocene at −2.93 V. One-electron oxidation takes place at potentials similar to those of ferrocene to give phosphaferricenium cations which are less stable than ferricenium itself. An ESR study of the radical-cation showed that the unpaired electron is localized at the iron atom.

One more synthetic route for phosphaferrocene (**212**), which gives an additional product (**213**), was reported and will be discussed later.

The iron-containing derivatives $[Fe(CO)_2(\eta\text{-}C_5H_5)(EC_4(C_6H_5)_4]$ (E = P, As)



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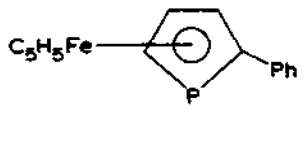

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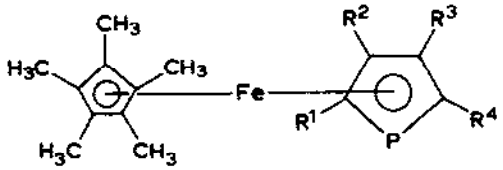
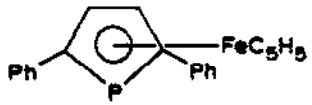


211a $R^1 = R^4 = H$, $R^2 = R^3 = CH_3$
211b $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$
211c $R^1 = R^2 = R^3 = R^4 = C_6H_5$



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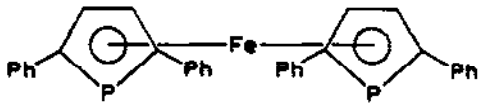
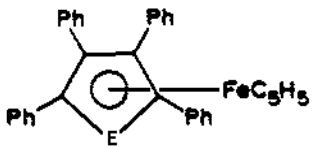


213



E = P, As

214

have greater thermal stability than the corresponding σ-complexes of manganese and rhenium. Continuous heating of these compounds causes abstraction of carbon monoxide and formation of phospha- and arsaferrocenes (**214**) [238].

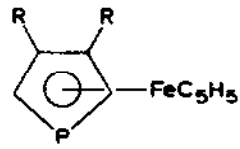
According to ^1H NMR, mass spectroscopy and study of the reactivity, the phospholyl group in phosphaferrocene is aromatic compared with the free ligand. It will be shown below that, if phosphole acylation proceeds via the phosphorus atom, phosphaferrocene is acetylated via the carbon atoms of the phospholyl nucleus.

The question arises whether the electrophilic character of the phosphorus atom in the complex causes delocalization of its lone pair. In order to answer this, a low-temperature X-ray diffraction study of dimethylphosphaferrocene has been undertaken. The ironcyclopentadienyl and ironphospholyl systems are symmetric. The phosphole ring is planar. The phosphorus atom deviates by 0.05 nm from the plane

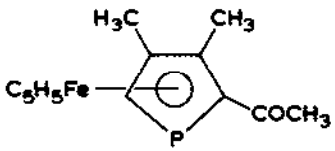
of the carbon atoms opposite from the metal. The carbon atoms of the cyclopentadienyl framework form a regular pentagon whose plane is not strictly parallel to the plane of the phosphole ring but forms an angle of 3.5° [262].

According to X-ray diffraction data, the d_{z^2}, d_{xy} and $d_{x^2-y^2}$ orbitals of iron are more populated than the d_{xz} and d_{yz} orbitals. In this sense, phosphaferrocene is quite similar to ferrocene. The phosphorus lone pair is in proximity to the five-membered cycle. Hence, the phosphorus atom is in a two-coordinate site and does not take part in direct bond formation with the iron atom. The lone pair is localized on the phosphorus atom yet nevertheless loses its nucleophilicity.

The phosphaferrocenes **215** were synthesized [262,263]; complex **215b** was studied by X-ray structural analysis and may be selectively acetylated via the phosphole ring leading to **216**.

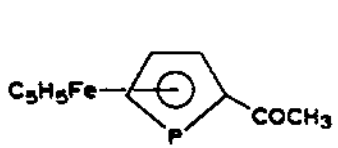


215a R = H
215b R = CH_3



216

The unsubstituted phosphaferrocene is acetylated at the 2 and 3 positions (**217** and **218**, respectively) as indicated by ^1H, ^{13}C, ^{31}P NMR and mass spectroscopy [260].



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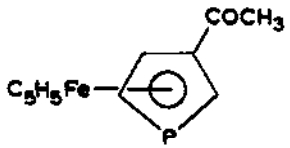

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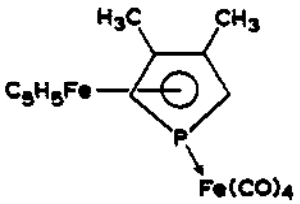


219

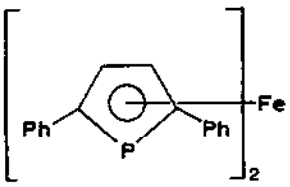
Reaction of $Fe_2(CO)_9$ in boiling benzene with phosphaferrocene leads to the corresponding P complex (**219**) [264].

The ability of phosphaferrocenes to form the classical P complexes led to a further study on the influence of P complex formation on the phosphaferrocene

aromaticity and nature of the bond between metal and phosphorus with respect to π back-donation. Indeed, the phosphorus atom has electron-acceptor character.

X-ray structural analysis of **219** showed that the bond lengths of the three bonds in the phosphole ring are equal and coincide with those in the initial phosphaferrocene [265]. The phosphole ring remains completely aromatic. This has two interesting consequences. Firstly, the lone pair of the phosphorus atom does not take part in the delocalization in the phosphole ring of the free phosphaferrocenes. Secondly, the possibility of C-electrophilic substitution via the phosphole ring still remains even after P complex formation. The geometry of the $P \rightarrow Fe(CO)_4$ grouping is trigonal-bipyramidal, the phosphorus atom being in the apex.

The synthesis, chemical properties and structural analysis of 1,1'-diphosphaferrocenes have been described [266–269]. The basic synthetic scheme includes preliminary splitting of the phosphorus–phenyl bond by alkali metals. The product **220** was not used for further studies because of its low solubility. The product **221a** is more soluble and more readily subject to C-electrophilic substitutions. X-ray structural analysis of **221a** revealed that the phosphole rings are not strictly parallel. The carbon atoms of the rings are disposed in one plane. The phosphorus atoms deviate from these planes by 0.011 and 0.0084 nm from the side opposite the iron atom.



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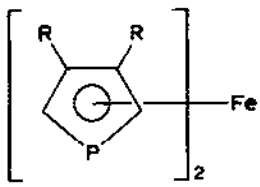
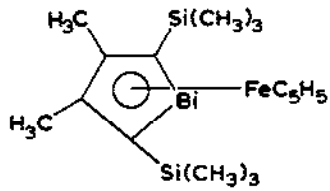


221a R = H
221b R = CH_3



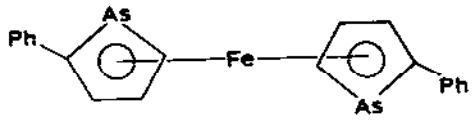
222

Diphosphaferrocene (**221b**) is subject to reversible one-electron reduction (−2.33 V) and one-electron oxidation (0.53 V) in propylenecarbonate [270]. It reduces more easily than ferrocene by 0.60 V, but oxidation is more difficult by 0.10 V. This is a consequence of substitution of the CH groups by the donor phosphorus atoms (the net result of weak σ-donor and strong π-acceptor functions of the phosphorus atom). The complex **221b** undergoes a second irreversible two-electron oxidation (1.8 V).

Reaction of 1-phenyl-2,5-bis(trimethylsilyl)-3,4-dimethylbismol with lithium

yields the corresponding bismolyl. The latter, when reacting with $AlCl_3$ and then with LiC_5H_5 and $FeCl_2$ produces a mixture of ferrocene and bismaferrocene (**222**) [271]. X-ray structural analysis of this sandwich confirmed its metallocenic nature, and revealed the multiple character of the Bi–C bonds and equality of the C–C bond lengths.

1,1′-Diarsaferrocene (**223**), which undergoes electrochemical oxidation and reduction, has been obtained from 1-phenylarsole [272]. Substitution of the two CH groups by the two arsenic atoms leads to anodic shifts of the redox potentials (+0.24 V for oxidation and −0.74 V for reduction). The arsacyclopentadienyl ring is more effective in accepting electron density from the metal which stabilizes the HOMO of **223** and adds charge to the LUMO. The complex **223** is subject to a rapid acid-catalyzed H,D exchange and to the C acetylation at position 2.



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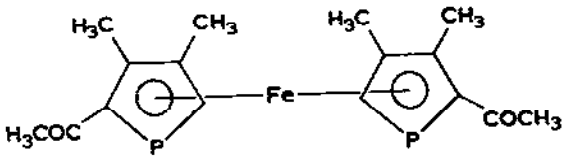


224

Reaction of the stibacyclopentadienyl ion with ferrous chloride gives a 2:1 mixture of bis(2,5-dimethylstibacyclopentadienyl)iron and 2,2′,5,5′-tetramethylstibolyl, which were separated by fractional sublimation [244].

Friedel–Crafts acetylation of **221b** using stoichiometric amounts of CH_3COCl–$AlCl_3$ or C_6H_5COCl–$AlCl_3$ in methylene dichloride was performed at room temperature [266,273]. The compound **221b** is more reactive towards electrophiles than 3,4-dimethylphosphacymantrene, the latter being benzoylated only at 380 K. On the other hand, since the yield of acetylation is greater than that of the analogous monophosphaferrocene, **221b** is more stable. This is substantiated by the fact that **221b** as ferrocene gives the diacetylated product **224** with excess CH_3COCl–$AlCl_3$ in good yield. Complex **224** is a mixture of two diastereomers.

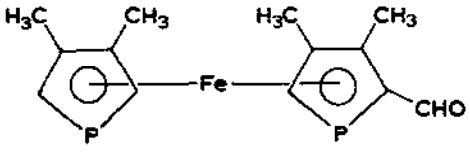
Attempts at Vielsmeier hydroformylation of **221b** gave monoaldehyde (**225**) in good yield, but attempts to obtain the dialdehyde appeared to be unsuccessful. Secondary and tertiary alcohols were obtained as a result of reaction of monoacetyl derivatives **224** and **225** with lithium aluminium hydride or borohydride. The secondary alcohol **226** is a mixture of two diastereomers. The tertiary alcohol **227** was

obtained from the reaction of the acetyl derivative **224** with Grignard reagent. Reaction of the complex with $(AlH_3)_n$ gave the ethyl derivative **228**. Reaction with *n*-butyllithium did not lead to formation of the 2-lithium derivative. The phosphorus atom in phosphaferrocenes loses its nucleophilicity.

In the phosphorus(III) compounds, the HOMO is represented by the lone pair of the phosphorus atom. In phosphacymantrenes, the lone pair contributes only to the fourth occupied MO. The LUMO in phosphaferrocene is located mainly on the phosphorus atom. In 1,1′-diphosphaferrocenes, the electrophilicity of the phosphorus atom is decreased to such a degree that these species are not destroyed by a nucleophilic attack. *n*-Butyllithium in the presence of methyliodide does not cause metallation at the α-CH-group.

Reactions of the alkyl and aryl derivatives of lithium with 1,1′-diphosphaferrocene were studied [274].

Reaction of 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene with *t*-butyllithium at



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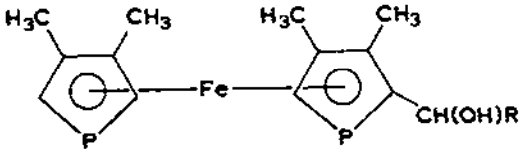

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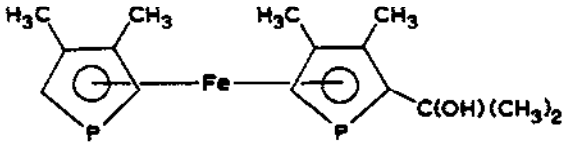

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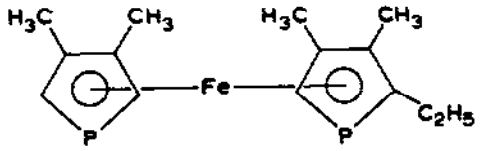
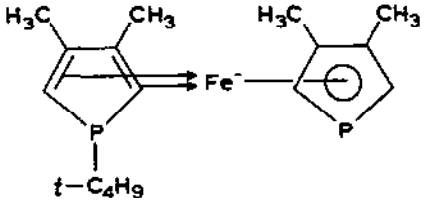


228

190 K in THF most probably yielded **229**. Subsequent addition of one, two, three or more equivalents of *t*-butyllithium does not lead to changes in the ^{31}P NMR spectra. The phospholyl in structures **229** and **230** loses its electrophilicity and the iron atom bears a considerable negative charge.



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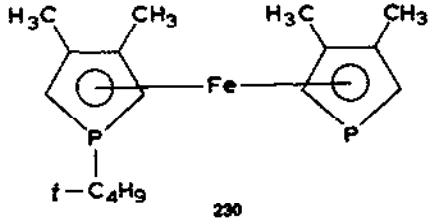
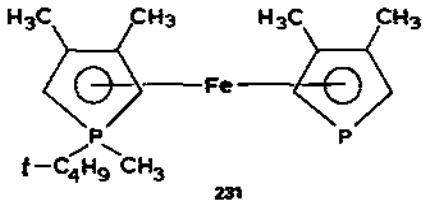


230

Addition of one gram-equivalent of *t*-butyllithium followed by one gram-equivalent of methyl iodide to **221b** leads to rearrangement of **221b**, which can be explained by spontaneous decomposition of **231** through **232**. However, it was not possible to isolate a stable monocation [274]. If two equivalents of *t*-butyllithium and three equivalents of methyl iodide are added to a THF solution of **221b** at 190 K, it was possible to isolate the chromatographically stable, water soluble monocation **233**, which has the structure bis(η^4-diene)iron (X-ray).



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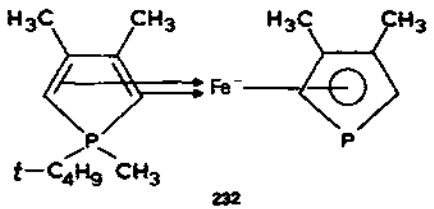
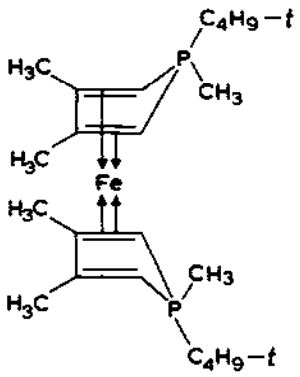


232

The large distances between P and Fe (0.269 nm) exclude the possibility of bond formation between the iron and phosphorus atoms. Therefore the phosphole



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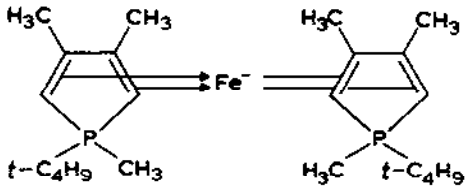


234

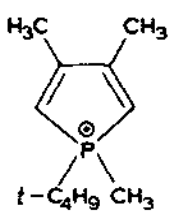
groups in **233** are η^4-ligands acting through their dienic systems. Formally, **233** contains the 17-electron iron atom forming a sandwich between two phosphole groups (**234**).

The phosphole rings are not planar. The dihedral angles between the planes C_1–C_4 and C_1–P–C_4 are 30.9° as a consequence of the η^4-coordination. Such a conformation is characteristic of π-complexes of the dienic hydrocarbons and is explained by distortion of the p orbitals of the α-carbon atoms, allowing better overlap with the metal atom. Although cyclic delocalization in the phospholium cycle is excluded, the intracyclic P–C bonds are considerably shorter than the exocyclic P–C bond, a consequence of the η^4-coordination.

The complex **233** reacts easily with an aqueous solution of hydrochloric acid with the formation of phospholium **235**. The stability of such an unusual group is explained by partial delocalization of the negative charge to the phospholium ligands or by the steric volume of the phospholium groups. Indeed, similar experiments with *n*-butyllithium and methyllithium led to isolation of the complexes **236**. Their yields decrease in the sequence **233** > **236a** ≫ **236b**, coinciding with the sequence of steric volume of the substituent.

The logical sequence of formation reactions of **233** is such that firstly, four bonds between phosphorus and carbon are formed simultaneously and attack on the second phosphorus atom begins only after neutralization of the first negative charge. Secondly, methyl iodide is reduced by **237**, a strong reducing agent in spite of its 18-electron configuration. If benzyl bromide is used instead of methyl iodide, **238** is formed. If the proposed scheme is correct, benzyl bromide should also act as an oxidizing agent for compounds of type **237**.

In a similar reaction, when *t*-butyllithium is replaced by phenyllithium, a different complex was obtained (**238**). Addition of only one gram-equivalent of phenyllithium and excess methyl iodide to a THF solution of **221b** at 190 K gives a covalent diamagnetic complex **239**, which was studied by X-ray structural analysis.



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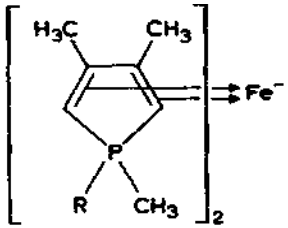
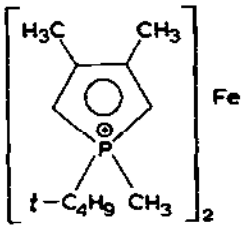


R = CH_3 , t-C_4H_9

236



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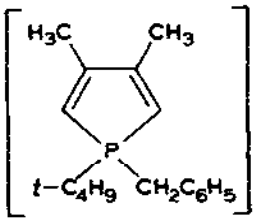
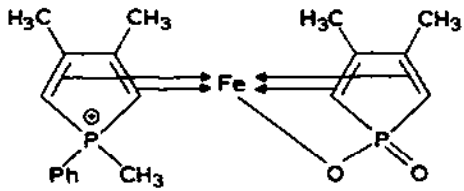


238



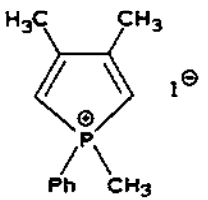
239

The phospholium cycle has a configuration similar to that of **233**, the dihedral angle being even greater (34.3°). The dihedral angle in phospholium (**233**) decreases to 10.4°, which leads to a decrease of overlap of the p orbitals of the α-carbon atoms with the metal orbitals. Its dienic system is coordinated to the iron atom to a lesser degree.

Coordination of the phospholium oxygen to the iron atom in **239** was proven on the basis of the Fe···O (0.215 nm) bond length. The distance between Fe and P^+ (0.273 nm) excludes the possibility of any bond formation between Fe and P^+. The complex **239** was formed as a result of spontaneous oxidation of a transient form analogous to **232**. The phosphole group in this complex is the η^4-donor. Treatment of **239** by an aqueous solution of hydrogen iodide yields the phospholium salt **240** and the unstable free acid **241**.

The complex **239** is the first example of a complex where the phosphole acid tends to chelate and act as a five-electron ligand.

The complex **220** is easily dissolved in concentrated sulphuric acid [275]. ^1H



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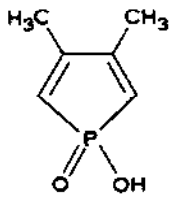

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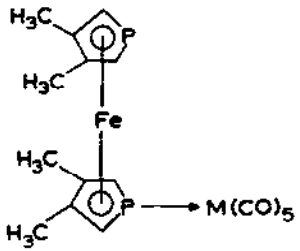


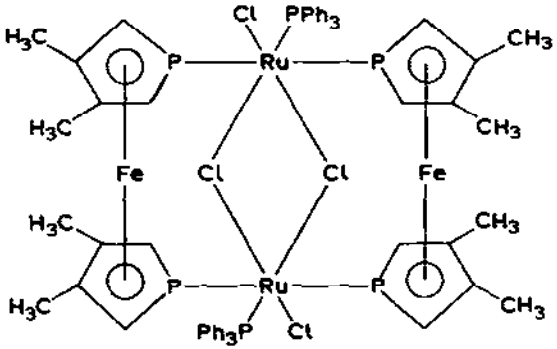
242

NMR spectroscopy indicates protonation at the iron atom. Sulphonation is more favourable at the phenyl rather than the five-membered cycle. The latter is deactivated with respect to electrophilic attack by the phosphorus atom. The strongest of the known protic acids, trifluoromethanesulphonic acid, having neither oxidizing nor sulphonating properties, causes protonation at the iron atom. The ^{31}P NMR spectrum excludes P protonation. In addition, protonation embraces the phenyl rings (Mössbauer spectroscopy). Oxidation of **220** by $FeCl_3$, H_2O_2, CCl_3COOH leads to decomposition and liberation of the ferric ions as a result of the phosphorus atom weakening the iron–ligand bond. In **221b**, protonation occurs at the five-membered ring.

According to ^{31}P NMR spectroscopy [276,277], protonation by means of trifluoroacetic acid proceeds via the iron atom in the unsubstituted diphosphaferrocenes, acetyl derivatives are protonated at the oxygen atoms of the C=O group, and in the case of the secondary alcohols the α-carbenium ions are formed. This view is supported by Mössbauer spectroscopy.

Diphosphaferrocene, $Fe(C_4H_2(CH_3)_2P)_2$ (Q) is a potential bidentate ligand [278,279]. However, reaction with $M(CO)_5(THF)$ (M = Cr, Mo, W) leads to formation of the monometallic complexes $M(CO)_5Q$ (**242**). Reaction of $M(CO)_5Q$ with $M(CO)_5(THF)$ leads to homo- and hetero-bimetallic complexes of trinuclear nature, $(OC)_5M(\mu\text{-}Q)M'(CO)_5$ (M/M′ = W/W, Mo/Mo, Cr/Cr, Mo/Cr, Mo/W, Cr/W). Reaction of Q with $Co_2(CO)_8$ gave no coordination product, while $Mn_2(CO)_{10}$ with Q gave $QMn_2(CO)_9$ and $Q[Mn_2(CO)_9]_2$. Reaction of Q with $RuCl_3 \cdot 3H_2O$ yields Q_4RuCl_2 when refluxed in methanol, where Q acts as a monodentate ligand. Interaction of Q with L_3RuCl_2 produces the dimer $[(L)Ru(Q)Cl(\mu\text{-}Cl)]_2$ (L = $P(C_6H_5)_3$) (**243**) containing the bridging ligand and the terminal chlorine atoms.

X-ray structural analysis of the dimer has shown that each ruthenium atom has a distorted octahedral environment. The phosphine ligands, the terminal chlorine and the two bridging chlorine atoms are in equatorial planes. Both axial positions are occupied by the phosphorus atoms of the two bridging ligands. The P–Ru–P fragments are nearly linear (172°), and the phosphole rings are almost parallel (the dihedral angle between ring planes is 5°). The Q ligand forms stronger bonds between the ruthenium and phosphorus atoms than the phosphine ligand. Calculation of the force constants of the CO stretching vibrations showed that Q is a stronger σ-donor and a slightly weaker π-acceptor than 1-phenyl-3,4-dimethylphosphole.



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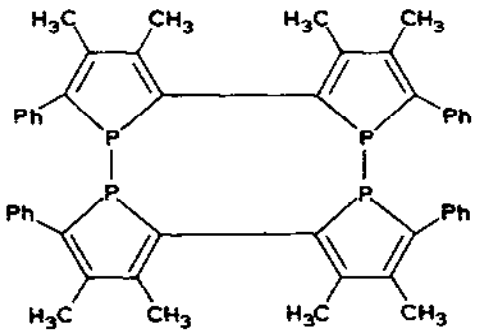
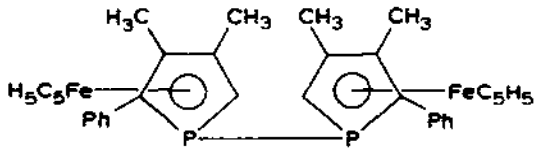


244

1-Phenyl-3,4-dimethylphosphole isomerises into 2-phenyl-3,4-dimethyl-5H phosphole at 440 K, giving then an unstable two-coordinate compound which transforms into **244** containing four phosphole units. It reacts with $[(C_5H_5)Fe(CO)_2]_2$ at 420 K in xylene leading to **245**, the P analogue of biferrocene [280]. Similarly, reaction of **246** with $MgBr_2$ followed by $FeCl_2$ leads to the bis(fulvalene)diiron analogue **247**.

Biphospholyl (**248**) undergoes splitting of exocyclic bonds of P–C_6H_5 through the action of lithium in THF [251]. As a result, a dianion is formed. The latter is the initial reagent for bimetallic η^5-complexes. Thus, reaction with anhydrous ferrous



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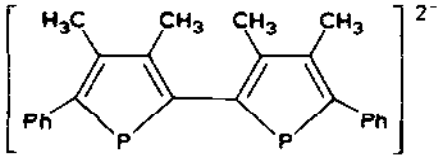

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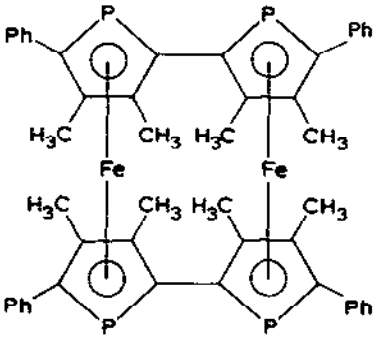

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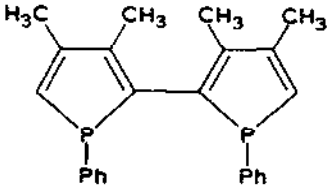


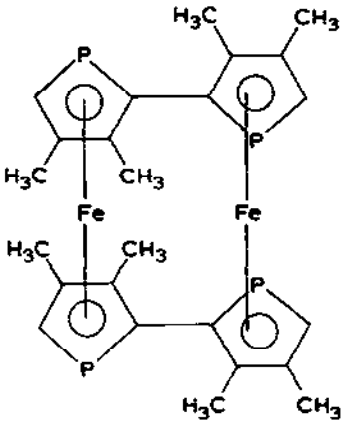
248

chloride gives the bis(diphosphafulvalene)diiron complex as a mixture of the two isomeric forms, one of which is the "head-to-tail" isomer **249** [251].

The complex cation [(cyclopentadienyl)(diacetonitrile)(η^1-2,5-dimethylthiophene)iron] with one equivalent of 3,4-dimethyl-1-phenylphosphole gives the σ-complex **250** on photolysis [281].

2,2',5,5'-Tetraphenylbiphospholyl reacts with $Co_2(CO)_8$ in refluxing toluene to give **251**, catalytically active in the cyclooligomerization of acetylenes [282].

η^5-Cyclopentadienyl(triphenylphosphine) cobaltocyclopentadienyl reacts with phosphites and forms complexes of 1-alkoxyphosphole oxides (**252**) through a step involving (η^5-cyclopentadienyl) (phosphite)cobaltocyclopentadienyls [283]. NMR spectra are indicative of the existence of two isomers, **252a** and **252b**, which are in some cases separable by chromatography. When $R^5 = CH_3$, C_2H_5, C_6H_5, irreversible isomerization of **252a** into **252b** is observed upon heating to 550–600 K. According to existing data, isomer **252b** is thermodynamically more stable. X-ray structural analysis of the complex **252b** ($R^{1-4} = C_6H_5$, $R^5 = CH_3$) shows that it is the exo-1-methoxy isomer. The phosphorus atom deviates from the plane of the ring by 0.632 nm, and the 1-methoxy group occupies the exo position relative to the cobalt atom.



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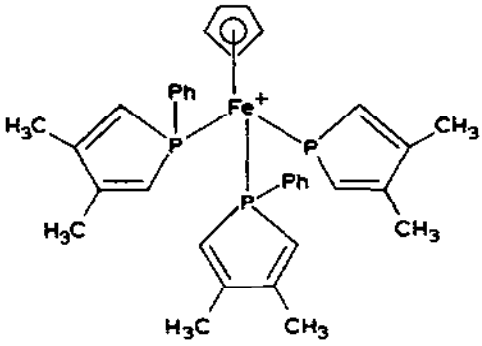

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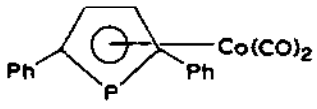

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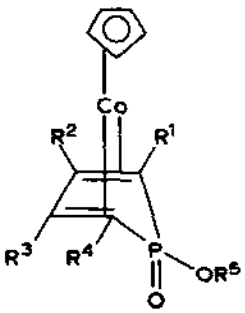
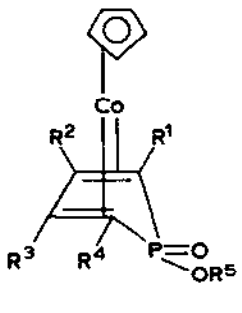


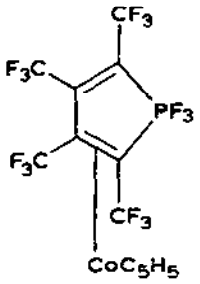
252a



252b

$(\pi\text{-}C_5H_5)Co(PF_3)_2$ reacts with hexafluorobut-2-yne and **253** is formed which hydrolyzes into **254** [284,285] (X-ray). The five-membered ring has the envelope conformation in which the carbon atoms are co-planar, and the phosphorus heteroatom deviates from this plane in the direction opposite from the cobalt atom. As a result, the bond lengths between metal and heteroatom increase. If the 18-electron rule is applied, the heterocycle is a four-electron donor relative to the cobalt atom. Interaction between the metal and heteroatom is not necessary for formation of the metal closed shell.

Upon carbonylation of $RuCl_3 \cdot 3H_2O$ in boiling 2-methoxyethanol and subsequent addition of 3,4-dimethylphosphole (L) under CO, **255** is formed [286]. If dibenzophosphole (L') is dissolved in chloroform or methylene chloride and then



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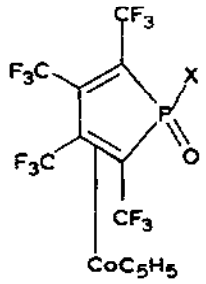
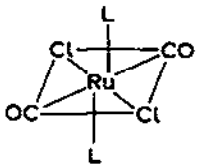


X = F, OH

254



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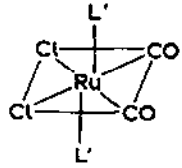

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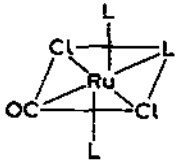

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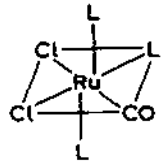


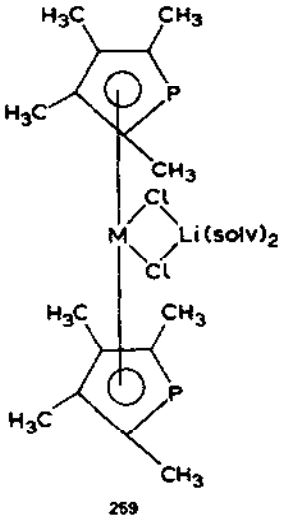
258

added to $[RuCl_2(CO)_2]_n$, one may obtain **256**. The isomeric structures are as indicated (**255**, **256**) in accordance with IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy. Reactions of ligand redistribution and isomerization were monitored using ^{31}P NMR spectroscopy. Thus, **255** is stable below 425 K and at 430 K ligand distribution process starts leading to a mixture of **257**, **258** and **256**, (L instead of L'). The temperature rise is followed by a rapid increase of the last component. Many other similar reactions are described.

Reaction of lithium 2,3,4,5-tetramethylphospholide with non-aqueous yttrium and lutetium trichlorides yields bis(phospholyl) complexes **259** [287]. The η^5-coordination follows from ^{31}P and ^{89}Y NMR spectroscopy. $LaCl_3$ does not enter this type of reaction.

8. SOME OTHER π-COMPLEXES

The attempted synthesis of the σ,π-complexes of furan is very difficult because of decomposition of the related ligands. Only rare representatives of complexes of furan are known.



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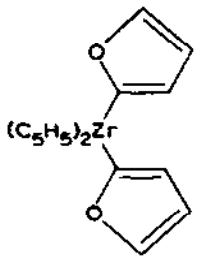

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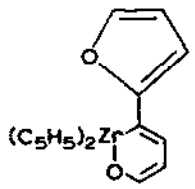


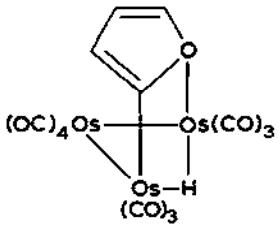
261

Bis(η-cyclopentadienyl)zirconium dichloride and 2-furyllithium react to form **260**, which at elevated temperatures rearranges into **261** [288].

Furan may oxidatively add to an Os_3 cluster, coordination via the oxygen atom and ortho-metallation being realized, and the μ-2-furyl cluster **262** being obtained [289]. Dehydrogenation across the α and β positions yields **263**. Ortho-metallation and subsequent η^2-coordination of the furyl group in the reaction of $[Os_3(CO)_{10}(CH_3CN)_2]$ with excess furan gives **264**. Upon addition of excess $(CH_3)_3NO$ to a solution of **264**, decarbonylation takes place, and formation of **263** is a result of the H transfer from ligand to metal and subsequent elimination of the CO ligand. X-ray analysis of **264** confirms the $\mu\eta^2$-bridged geometry. π-Complexes of five-membered monoheterocycles containing other heteroatoms are known [290–293].

Because of the similarity between the cyclopentadienyl anion and siloles, the syntheses of the silacyclopentadienyl anion and η^5-silacyclopentadienyl ligand are of basic interest. The latter was proposed on the basis of mass-spectral data [294–296]. However, this was not further substantiated. None of the possible synthetic routes considered leads to the expected η^5-complexes [295,297]. The η^4-coordination was found to be typical. In fact, the free silole ring is almost planar, but in the complexes, dihedral angles between the SiC^2C^5 and diene framework appear to be 20–32°.

Thermal reactions of 1,1-dimethylsilole and 1,1,3,4-tetramethylsilole and -germole with (η^4-1,5-cyclooctadiene)$M^{VI}(CO)_4$ (M^{VI} = Cr, Mo, W) lead to formation of chromium, molybdenum and tungsten complexes (**265** and **266**) [298,299]. Both



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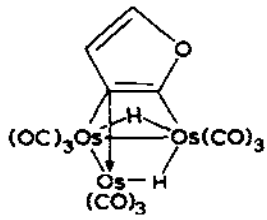

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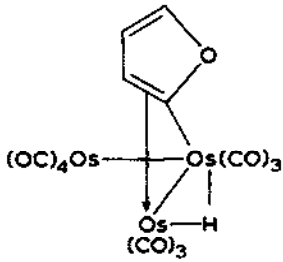

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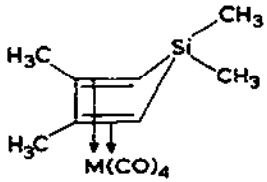
types of complex are formed, in case of tungsten only as a function of the nature of the solvent.



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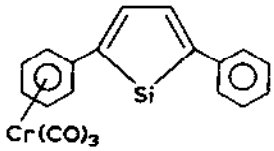

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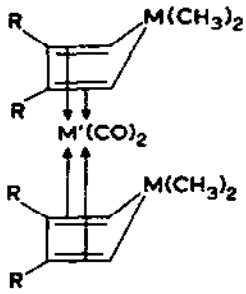


M = Si, R = H, CH_3, M' = Mo, W
M = Ge, R = CH_3, M' = Mo

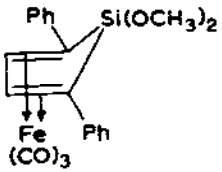
266

1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene reacts differently with $Mo(CO)_6$ and $Cr(CO)_6$. Prolonged reaction with molybdenum hexacarbonyl gives **266**, while reaction with chromium hexacarbonyl gives **267**, where $Cr(CO)_3$ is coordinated via the arene cycle [300–302].

[η^6-1-Methyl-1-(trimethylsilyl)dibenzosilacyclopentadiene]tricarbonylchromium is also known [303]. According to ^{1}H NMR spectroscopy, it is a mixture of the exo and endo isomers in the ratio 4:1.

Siloles predominantly play a role as η^4-donors in organometallic complexes of

group VIII metals [304–318]. Thus, treatment of 1,1-dimethoxy-2,5-diphenylsilacyclopentadiene with one equivalent of $Fe_2(CO)_9$ in toluene at 320 K gives (η^4-1,1-dimethoxy-2,5-diphenylsilacyclopentadiene)irontricarbonyl (**268**) [318]. Reduction of **268** with $(i\text{-}C_4H_9)_2AlH$ gives the stable dihydrocomplex **269**. Silole reacts with $Co_2(CO)_8$ to form the monosubstituted η^4-silacyclopentadiene complex **270**. The latter reacts with excess silole to form the corresponding disubstituted derivative **271**. Treatment of **271** with iodine in carbon tetrachloride gives **272**.



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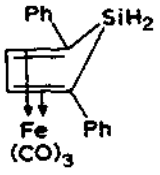

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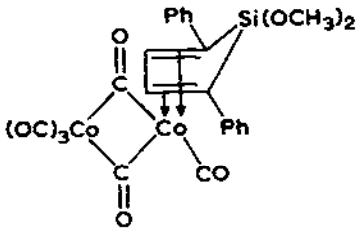


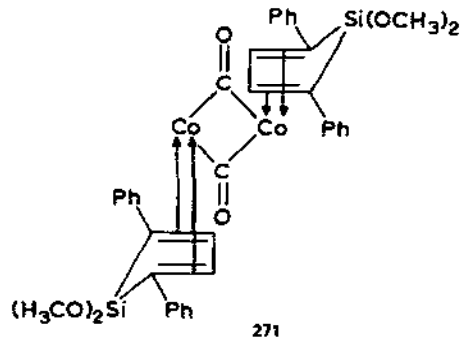
270

The availability of the new Si-disubstituted (η^4-silole) derivatives makes it possible to compare the relative reaction ability of the exo and endo substituents at one silicon atom by directly using the complex **269**. Reaction with PX_5 (X = Cl, Br) leads to **273a**, while reaction with $(C_6H_5)_3C^+BF_4^-$ leads to **273b**; again, reaction with water yields **274** and reaction with alcohols, ROH ($R = CH_3$, $p\text{-}CH_3OC_6H_4$), yields **273c**. Thus, irrespective of the nature of reactant, the exo isomer is selectively formed [317]. Si–H bond cleavage occurs with retention of configuration at the silicon atom. Nucleophilic substitution is governed not by steric hindrance of the metal-containing groups but by ring strain.

If one uses **275** as the reference complex, then substitution occurs via the Si–H bond [319]. Substitution reactions of **275** lead to the products **276**: **276a** was obtained by reaction with PCl_5, and **276b** by reaction with CH_3OH and H_2O. Substitution reactions with **276a** refer to the silicon–chlorine bond. The product of the reaction of **276a** with $LiAlH_4$ is **276c**, while with C_2H_5MgBr it is **276d**.

Retention of configuration may be used for the synthesis of the intramolecular carbene complexes [320]. Methyl or phenyllithium, or di-iso-propylaminolithium react with **277** leading to new cyclic carbenes, again with retention of configuration (**278**) (X-ray (**278b**)). The silole in **278b** is very near to planar.

Treatment of (1,1-difluoro-2,5-diphenylcyclopentadiene)tricarbonyliron with one



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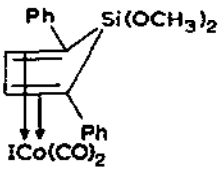

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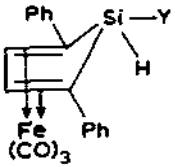
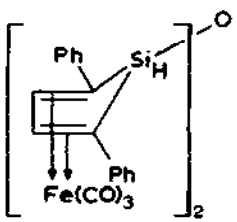


273a Y = Cl
273b Y = F
273c Y = OCH_3



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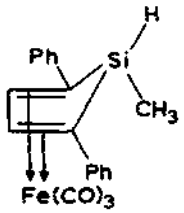

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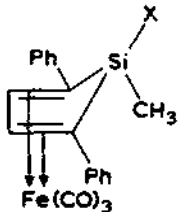
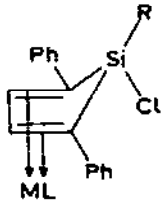


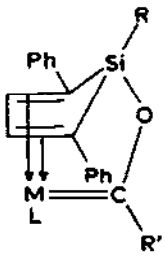
276a X = Cl
276b X = OR
276c X = H
276d X = C_2H_5

equivalent of a mixture of potassium fluoride and 18-crown-6 gave **279** [321,322]. X-ray structural analysis of **279** shows that the silicon atom has a trigonal-bipyramidal environment. Reaction between $Ru_3(CO)_{12}$ and 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene gave **280** [259], while reaction between 1-methyl-1-trimethylsilyl-dibenzosilole and $Cr(CO)_6$ gave **281** [241]. Treatment of **281** with methyllithium followed by oxidation by iodine gives 1,1-dimethyldibenzosilole.

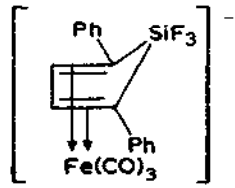
1H-Boroles are 4π-electron systems with a small HOMO–LUMO energy gap. The most satisfactory route for the synthesis of the η^5-borole complexes is reaction of dihydroboroles (2-borolenes, 3-borolenes) with metal carbonyls. An alternative method of synthesis includes formation of the borole adducts with ammonia (**282**)



277a R = CH_3, ML = $Fe(CO)_3$
277b R = i-C_3H_7, ML = $Cr(CO)_4$



278a R = R' = CH_3, ML = $Fe(CO)_3$
278b R = CH_3, R' = Ph, ML = $Fe(CO)_3$
278c R = CH_3, R' = $(i\text{-}C_3H_7)_2N$, ML = $Fe(CO)_3$
278d R = i-C_3H_7, R' = Ph, ML = $Cr(CO)_4$



[K^+(18-crown-6)]

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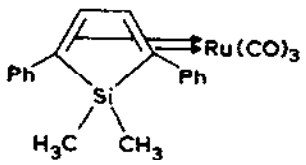

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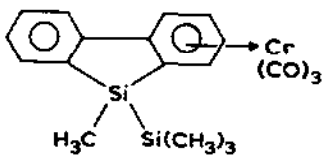

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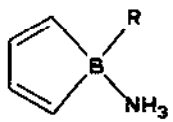
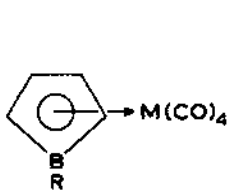


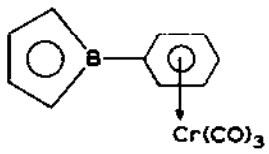
282a R = CH_3
282b R = Ph

[323]. Thermal reaction of **282b** with excess amounts of the THF derivatives of $M(CO)_6$ (M = Cr, Mo, W) gives **283b–283d** together with $M(CO)_6$, $M(CO)_5(NH_3)$ and traces of the binuclear complex **284** in the case of M = Cr. ^{13}C NMR data are indicative of π-electron delocalization over the borole ring. X-ray structural analysis of **283b** and **283c** shows a definite role for M → L back bonding, which is a peculiarity of boroles in comparison with siloles, a consequence of participation of the borole LUMO in the bond.

The reaction of 2-borolenes and 3-borolenes, C_4H_6BR (R = C_6H_5, CH_3, C_6H_{11}, OCH_3) with $Mn_2(CO)_{10}$, leads to complex formation followed by dehydrogenation and formation of the simple C-unsubstituted (η^5-borole)metal complexes **285**, which represent the so-called triple-decker complexes [324,325]. Thus, the general



283a M = Cr, R = CH_3
283b M = Cr, R = Ph
283c M = Mo, R = Ph
283d M = W, R = Ph



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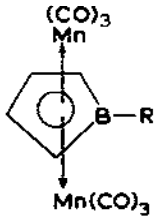
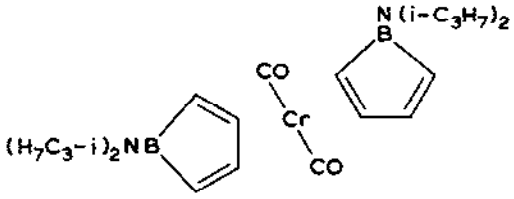


285

synthetic route consists of interaction of derivatives of transition metals with 1-R-2,5-dihydroborole followed by isomerization of LH_2 into the corresponding 2,3-dihydroborole and then dehydrogenation and formation of the η^5-metallocomplexes.

The exocyclic π-donor substituents of the boron atom influence electron delocalization in the cyclic conjugated boron-containing heterocycles via the p_z orbitals of the boron atom. Thus, the influence of the di-iso-propylamino substituent in the complexes **286** and **287** was probed on the basis of X-ray structural data, NMR and IR spectroscopy [326].



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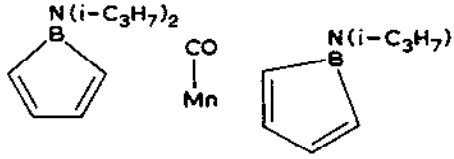

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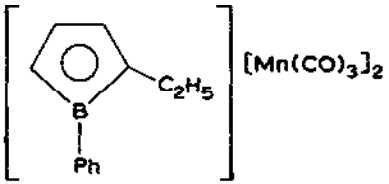
The structure of **286** contains the cis-$Cr(CO)_2$ framework. In contrast to the 1-methyl- and 1-phenylboroles, the ligand is distorted. Aminoborole is coordinated as the dienic ligand and direct interaction between the chromium and boron atoms is very weak. Interaction of the dienic system with the manganese atom is stronger in **287** than that of the dienic system with the chromium atom in **286**.

The basic product of the reaction of 1-phenyl-4,5-dihydroborepine with $Mn_2(CO)_{10}$ in boiling mesytylene is **288** [327]. The borole ligand serves as a bridge between the two manganese atoms (X-ray). The complex **288** represents the pentagonal-bipyramidal metallocarborane cluster of the closo type. The apical positions are occupied by the $Mn(CO)_3$ groups. The carbon and boron atoms occupy the equatorial site.

Analogous synthesis using $Fe(CO)_5$ gives the half-sandwich complexes **289** [328]. Sandwiches of the type **290** are mentioned [329]. Interaction of borolenes with $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $RuCl_2(P(C_6H_5)_3)_2$, $RuHCl(P(C_6H_5)_3)_3$, $OsCl_2(P(C_6H_5)_3)_3$, $[Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$, $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$, $[Ru(\eta^6\text{-}$



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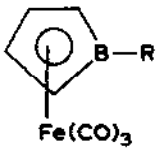

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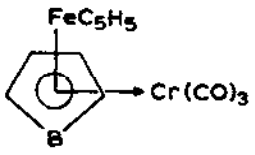

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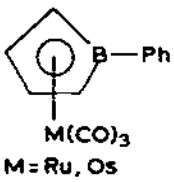
$C_6(CH_3)_6)Cl_2]_2$ leads to formation of the (η^5-borole) metallic complexes of ruthenium and osmium (**291–293**) [324, 330] (X-ray, (**292**)).



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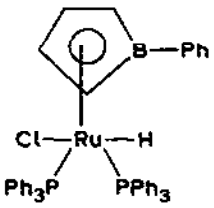

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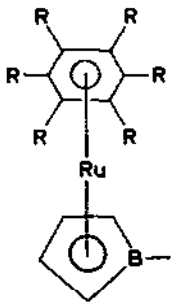

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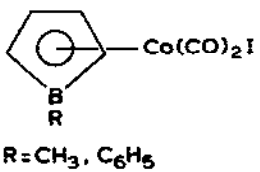
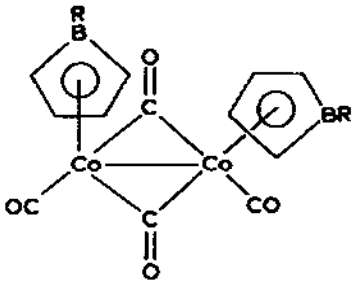


294

Pentaphenylborole reacts with $Fe_2(CO)_9$ yielding $^{-}(OC)_3(\eta^5$-pentaphenylborole)iron, and with excess $Ni(CO)_4$ yielding $(OC)_2(\eta^5$-pentaphenylborole)nickel [331]. Another synthetic route is based on 1-phenyl-4,5-dihydroborepine, which is subject to ring contraction in the process of complex formation. The borole ligands are bonded to a metal as the pentahapto-four-electron ligands. The B–M bond resists abstraction of the phenyl group at the boron atom.

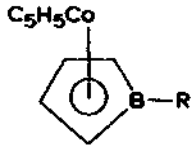
The complex **294** was described in ref. 323. If excess ammonia is introduced to the THF solution of **294**, then **295** is formed. The latter complexes serve as the starting material for the sandwich **296**, triple-deckers (**297** and **298**), binuclear complexes **299**, and salts **300** [330]. Anions of the latter salts easily form the triple-decker (**301**, **302**) or tetra-decker complexes (**303**). The complex **301** undergoes regiospecific H/D exchange in the α-position relative to the boron atom and acetylation with

$CH_3COCl/SnCl_4$ in methylene dichloride followed by formation of the 2-acetylderivative. In **297** ($R = CH_3$) the rings are almost coplanar (X-ray).



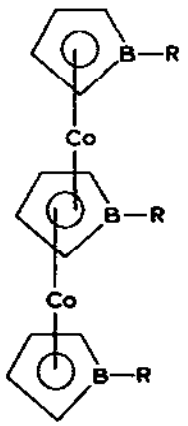
$R = CH_3, C_6H_5$

295



$R = CH_3, C_6H_5$

296



$R = CH_3, C_6H_5$

297

The ammonia adducts of 1H-boroles react with $M(cod)_2$ (M = Ni, Pd, Pt) followed by formation of the mixed-ligand complexes **304** [332]. Thermolysis of the latter gave the bis(ligand) complexes **305**, the free cyclooctadiene-1,4 and the metal.

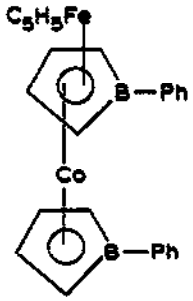
Complex-formation with the Wilkinson catalyst $RuCl(P(C_6H_5)_3)_3$ gives **306** [328]. The reaction with $[Rh(\eta^2\text{-}C_2H_4)_2Cl]_2$ gives the triple-decker complexes **307** [333]. Their interaction with sodium cyclopentadienyl gives the neutral complexes **308**, undergoing fast exchange at the α-position relative to the boron atom.

The synthetic method used for the η^5-complexes of boroles [324] is applied for the boroles containing amino substituents at the boron atom. Thus, the series of complexes **309–311** is known [146]. A platinum π-complex of pentaphenylborole similar to **304** has been reported [334].

9. CONCLUSION

The coordination chemistry of the five-membered monoheterocycles is mainly the chemistry of the π-complexes.

Furan, being almost a non-aromatic heterocycle, does not form π-complexes



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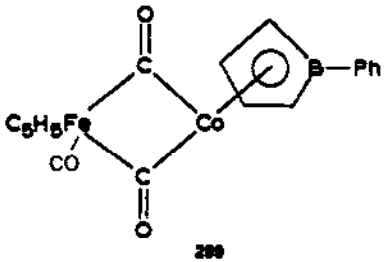

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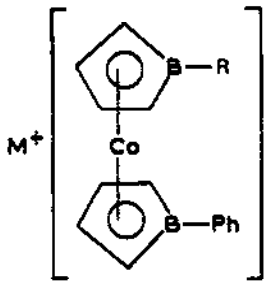
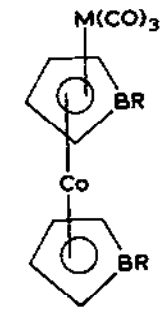
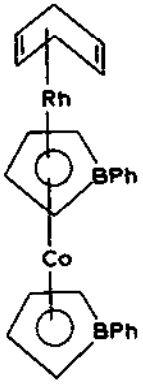


300a M = Na^+; R = CH_3, C_6H_5
300b M = $N(CH_3)_4$; R = CH_3, C_6H_5
300c M = Cs; R = C_6H_5



M = Mn, R = CH_3, C_6H_5
M = Cr, R = C_6H_5

301



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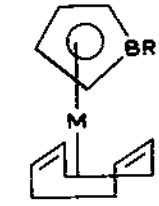
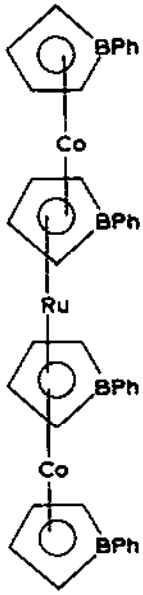


M = Ni, R = CH_3, C_6H_5
M = Pd, Pt, R = C_6H_5

304



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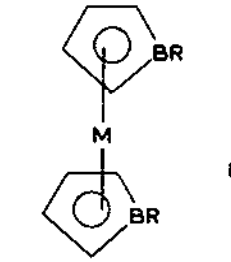
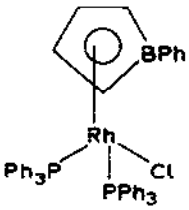


M = Ni, R = CH_3, C_6H_5
M = Pd, Pt, R = C_6H_5

305



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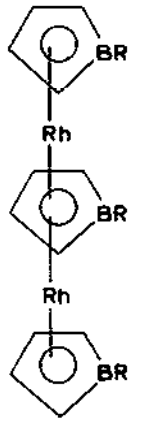
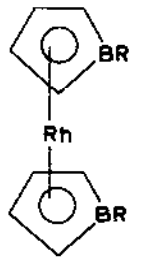


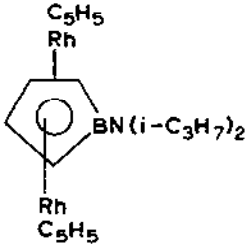
R = CH_3, C_6H_5

307



R = CH_3, C_6H_5

308



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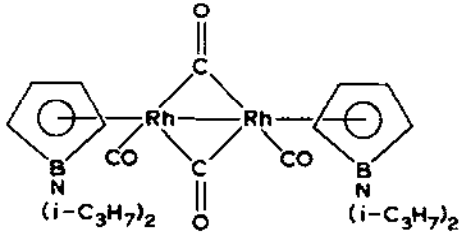

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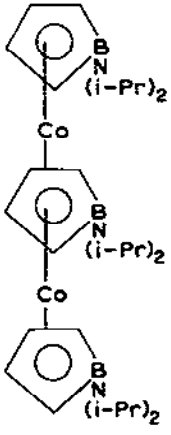

311

in spite of its π-excessive character. Attempts at synthesis led to destruction of this ligand system. Sometimes, its π-complexes are postulated as intermediates [335].

π-Complex formation by thiophene, selenophene and pyrrole occurs according to the classical scheme, although it is somewhat difficult.

According to current opinion, derivatives of phospholes, arsoles, stiboles, bismoles and boroles are non-aromatic compounds. However, these ligands acquire expressed aromaticity in many π-complexes, particularly in phosphaferrocenes, phosphacymantrenes, their As, Sb and Bi analogues, sandwiches and multiple-deckers in boroles. Phospholes and their analogues are soft–soft donors and, in addition to the π-system, the heteroatom may be a donor site.

Siloles are to be considered as typical η^4-donors, although there is a route proposed for the synthesis of complexes where siloles should act as η^5-ligands.

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