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ORGANOMETALLIC INTRAMOLECULAR-COORDINATION COMPOUNDS CONTAINING A CYCLOPENTADIENYL DONOR LIGAND

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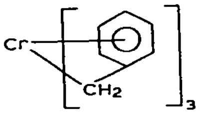
A. INTRODUCTION

Organometallic intramolecular-coordination compounds $\overset{\longleftarrow}{\mathrm{M}\!-\!(\mathrm{C})_n\!-\!\mathrm{Y}}$ (Y = coordination group or atom; $n \geqslant 1$) can be classified into two groups with respect to the M–Y bond, viz. σ-coordination or π-coordination compounds [1–7]. The author has written several reviews on σ-coordination in which Y is O [1,4], S [2], N [3], P [5] or As [7] and on π-coordination compound in which Y is a carbon–carbon double bond [6].

This review concerns π-coordination compounds where Y is a cyclopentadienyl ring and also includes dicyclopentadienyl intramolecular-coordination compounds having another cyclopentadienyl donor ligand at the M–C bond side, that is, bridged metallocenes. Intramolecular η^6-phenyl metal compounds such as the chromium compounds (**1**) [8] also have very similar structures to these cyclopentadienyl intramolecular-coordination compounds. However, this review does not include such compounds.



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The purpose is to survey organometallic intramolecular-coordination compounds containing a cyclopentadienyl donor ligand, to show what kinds of structure in these compounds are strain-free, and to show synthetic methods, spectroscopic data and chemical properties.

B. MONOCYCLOPENTADIENYL INTRAMOLECULAR-COORDINATION COMPOUNDS

In the organometallic intramolecular-coordination compounds, the σ-coordination compounds having a M–Y σ-bond generally tend to form the 5-membered ring structure (**2**).

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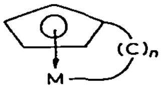

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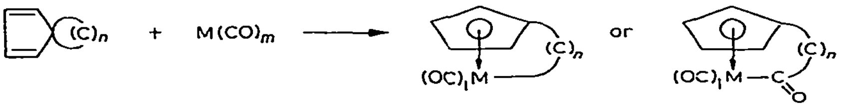
However, the Y moiety of the compounds described in this review is not an atom but a cyclopentadienyl group. Therefore, it is exceptionally interesting to know which number of bridged carbon atoms in these compounds (**3**) in comparison with compounds (**2**) is most favourable for the synthesis of such compounds.

Eilbracht and co-workers [9–19] have reported organometallic intramolecular-coordination compounds containing a cyclopentadinyl donor ligand (**4**) and (**5**) synthesized by the ring opening reaction of spiro compounds (of cyclopentadiene and cycloalkanes) or their derivatives with metal carbonyls as shown in eqn. (1).



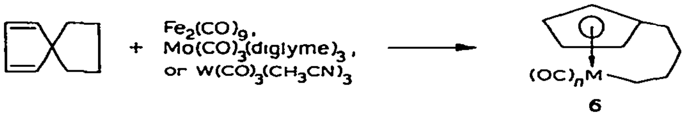
4 **5**

(1)

The size of the ring in these products is varied depending upon the size of the cycloalkane ring. In the case of a small ring size, ring opening tends to proceed, accompanying carbonyl insertion, because the product seeks to reduce strain by ring-expansion, to afford the corresponding bridge ketone (**5**).

Ring opening reactions have been reported with various metals such as iron [9], molybdenum [9], tungsten [10], nickel [11], etc. in metal carbonyl compounds as shown in eqns. (2)–(4).

For example, in the reaction of spiro-cyclopentane (eqn. (2)) or spiro-cyclopropane (eqn. (3)) with di-iron nonacarbonyl, the former affords the ordinary ring opened products (**6**) and the latter, having a small ring affords



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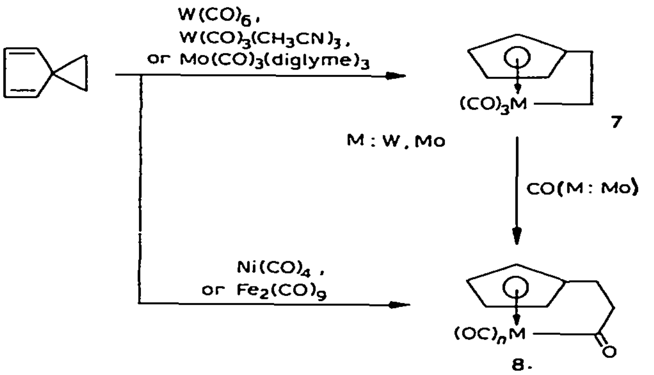
M(CO)$_n$: Fe(CO)$_2$, Mo(CO)$_3$, W(CO)$_3$

(2)



7

(3)

8.

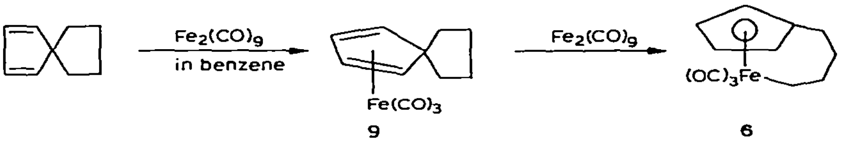
(4)

M(CO)$_n$: Ni(CO), Fe(CO)$_2$, Mo(CO)$_3$

the carbonyl inserted product (8). Reactive molybdenum or tungsten carbonyls are capable of affording the ordinary ring opened products (7) even with spiro-cyclopropane. The compounds (7) are presumed to have much strain and cannot be prepared by the reaction of iron or nickel carbonyl compounds. It is presumed that formation of the two-carbon bridged products (7) with molybdenum or tungsten carbonyls is also sterically more advantageous than that of (7) with iron or nickel carbonyl because the atomic covalent radii of the former atoms are larger than those of the latter. The strain of (7) is easily understood by the fact that (7) easily reacts with carbon monoxide to afford the carbonyl inserted products (8) [12].

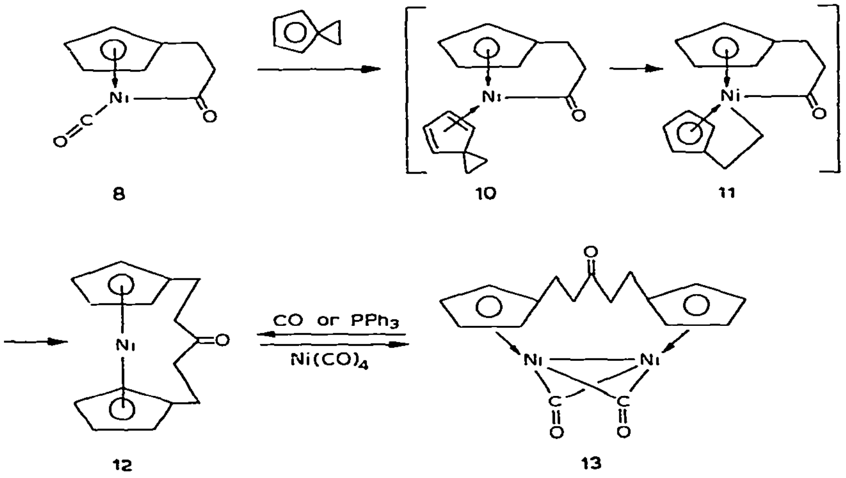
The strain of spiro-cyclopropane ring opened products (7) is also considerable, because the ^{13}C NMR spectra of the bridge carbons or the cyclopentadienyl carbon bonded by the bridged carbons in (7) are remarkably shifted compared with those of the corresponding carbons in spiro-cyclopentane ring opened products (6) or non-bridged η^5-cyclopentadienyl metal carbonyl compounds, e.g. (η^5-C_5H_5)(Me)M(CO_3)(M: Mo, W) [16].

The reaction shown in general formula (1) is presumed to proceed via the formation of η^4-cyclopentadienyl metal compounds such as compound (9); in fact, as the reactivity of the spiro-cyclopentane is low, its reaction with di-iron nonacarbonyl in boiling benzene gives primarily the rather stable η^4-cyclopentadienyl metal intermediate (9) and minor amounts of ring opened product (6) [9]. The stable intermediate (9) is further heated in benzene to form the final product (**6**) by a ring opened reaction. Complex (**6**) is also produced by photochemical reaction of the intermediate (**9**) or a mixture of spiro-cyclopentane and iron pentacarbonyl [9].



(5)

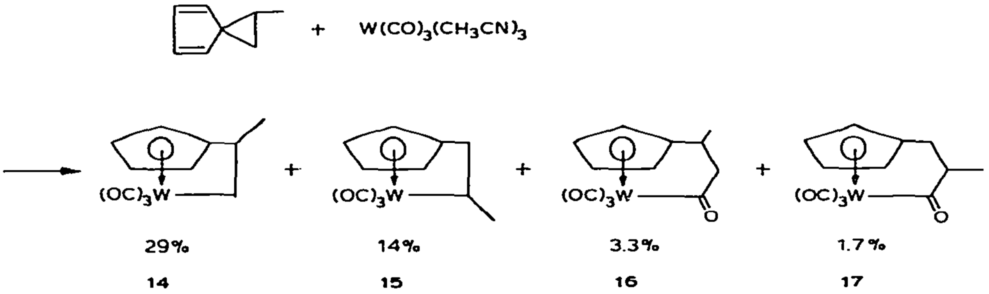
The reaction of a carbonyl inserted nickel product (**8**) with another spiro-cyclopropane gives the di-cyclopentadienyl intramolecular-coordination compound, i.e. a bridged metallocene (**12**), described in the next section. This reaction is also speculated to go via a η^4-cyclopentadienyl metal intermediate (**10**) [17] similar to (**9**).



(6)

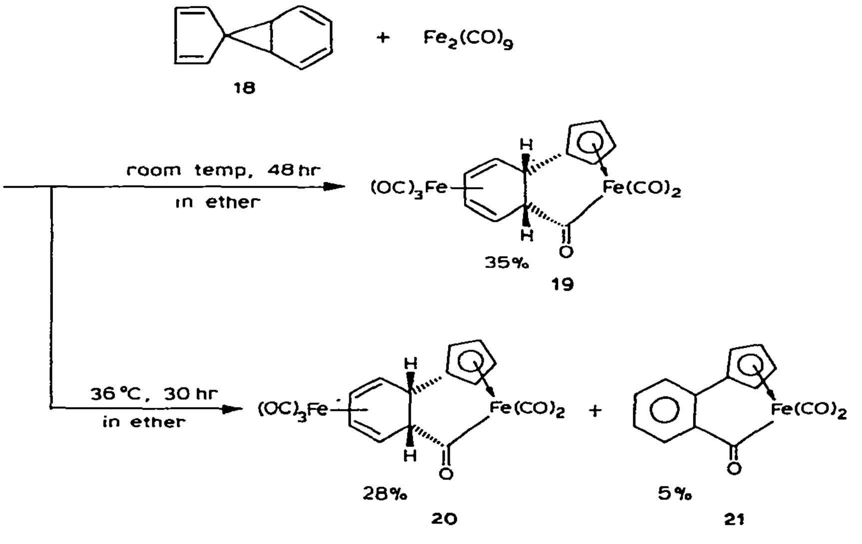
The reaction between nickel carbonyl and spiro-cyclopropane yields approximately the same amount of dinuclear nickel compounds (**13**) as the usual carbonyl inserted product (**8**) [11]. The treatment of (**13**) with carbon monoxide or triphenylphosphine yields the above bridged compound (**12**), and (**12**) can give (**13**) again by heating it with nickel tetracarbonyl in benzene [11,12].

The spiro-cycloalkane derivatives of cyclopentadienyl compounds such as methyl [12,17], vinyl [18] and 2,3-cyclohexadienyl derivatives [19] also react with metal carbonyls similar to the reaction of spiro-cycloalkane as shown in general formula (1). For example, the reaction of the spiro-cyclopropane methyl derivative with a tungsten carbonyl compound mainly affords the ring-opened reaction products (**14**, **15**) and small amounts of carbonyl inserted products (**16**, **17**); both of these two sets of compounds are isomeric with respect to the methyl position (eqn. (7)) [12].



(7)

The reaction of spiro-cyclopropane 2,4-cyclohexadienyl derivatives (**18**), formally, spiro[2,4-cyclopentadiene-1,7′-norcara-2′,4′-diene] with di-iron nonacarbonyl at room temperature yields the product (**19**) by a ring opening reaction of the cyclopropane, followed by carbonyl insertion (eqn. (8)). At slightly higher temperature, the reaction yields (**20**) a stereoisomer of (**19**), alternate position of the Fe(CO)$_3$ group with respect to the cyclohexadiene group and a small amount of the compound (**21**) obtained by dehydrogenation and elimination of the iron tricarbonyl group from the η^4-cyclohexadienyl iron coordinating moiety in (**19**) or (**20**) (eqn. (9)) [19].



(8)

(9)

The structure of (**20**) is determined unambiguously by means of an X-ray structural analysis [20]. The η^5-cyclopentadienyl ring coordinates symmetrically to one iron atom, individual distances ranging from 2.068 to 2.128 Å (Fig. 1).

Weiss and co-workers [21–25] have synthesized various kinds of η^5-cyclopentadienyl coordination compounds by the reaction of fulvene compounds with metal carbonyls. The reactions, at first step, are thought to proceed through the η^4-cyclopentadienyl iron intermediate, e.g. the intermediate (**22**) in the reaction of dimethylfulvene with di-iron nonacarbonyl (eqn. (10)) similar to the spiro-cyclopentane or spiro-cyclopropane reactions

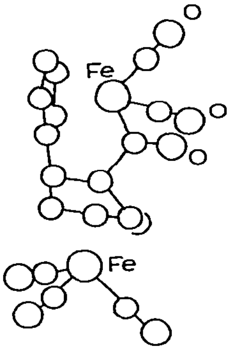
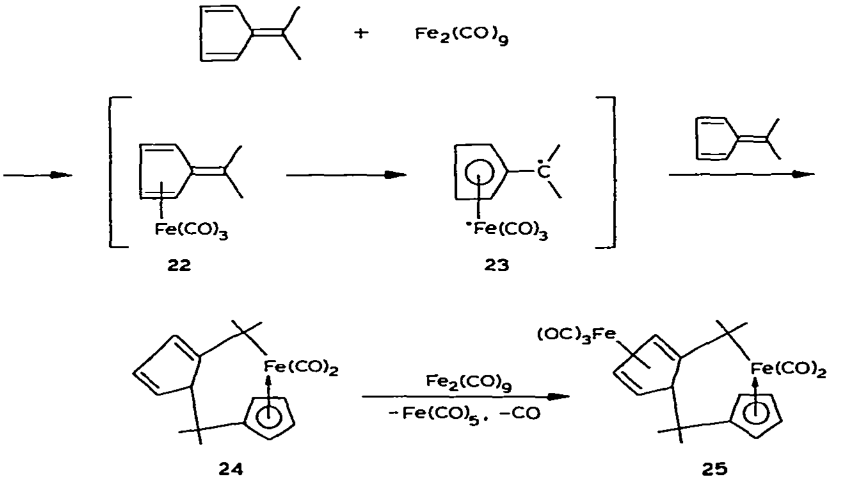


Fig. 1. The structure of the reaction product (**20**) between di-iron nonacarbonyl and spiro[2,4-cyclopentadiene-1,7′-norcara-2′,4′-diene].

(eqns. (5) or (6)) which proceed via the η^4-cyclopentadienyl metal carbonyl intermediate. Fission of one bond in the double bond corresponding to one ring in the spiro-cycloalkane compound forms the biradical (**23**). The biradical then reacts with another fulvene compound to form the intramolecular-coordination compound (**24**). Finally (**24**) is coordinated by another metal carbonyl moiety to give the product (**25**) having an η^4-cyclopentadienyl iron bond [23].



(10)

The intramolecular-coordination structure of (**25**) is determined by single-crystal X-ray diffraction studies (Fig. 2) [23]. The covalent single-bond

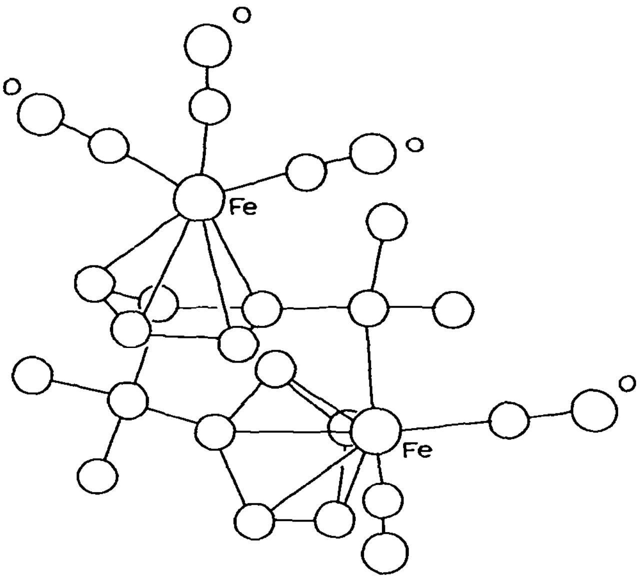
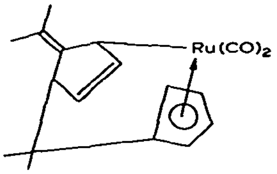


Fig. 2. The structure of bis(dimethylfulvene)pentacarbonyl di-iron (25).

radius of iron in the η^5- and η^4-cyclopentadienyl iron groups is 1.38 Å. In addition to (**25**), several compounds with complicated structures having an Fe–Fe bond have been observed, and some structures have also been determined [22,23].

Weiss and co-workers [24] studied the reaction between ruthenium carbonyl and fulvene and considered it to parallel the above iron reaction (**25**). However, the ruthenium product has been found by X-ray diffraction studies [25] to have a cyclopentenyl bridge (**26**) instead of a cyclopentadienyl bridge (**25**).



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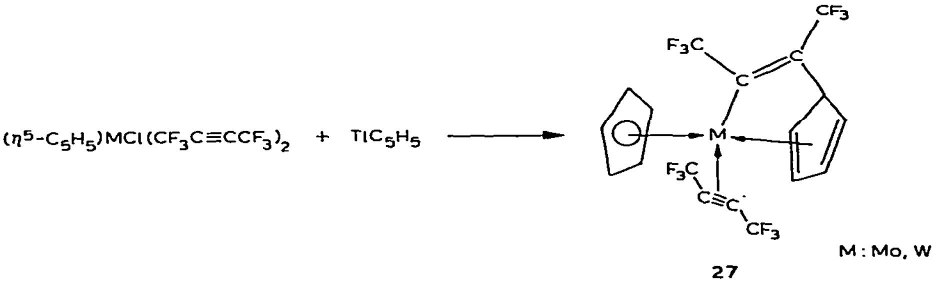
Monocyclopentadienyl intramolecular-coordination compounds are also synthesized by reaction between metal compounds and acetylenes, olefins or high strain compounds such as benzvalenes.

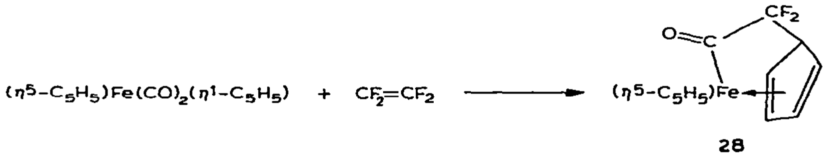
As shown in eqn. (11), an acetylene complex of a cyclopentadienyl molybdenum carbonyl chloride reacts with cyclopentadienylthallium to afford the intramolecular compounds (**27**) by substitution of cyclopentadienyl for Cl in the labile Mo–Cl bond, followed by insertion to one acetylene–metal bond.



(11)

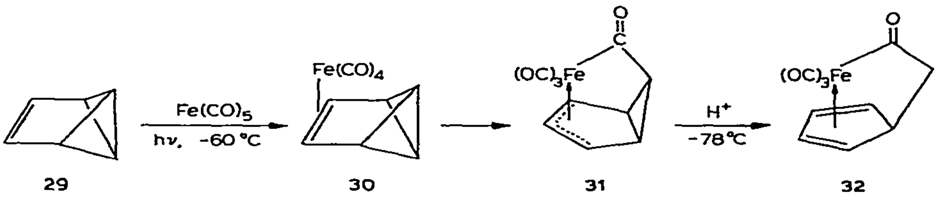
The ethylene bridge bond between molybdenum and cyclopentadienyl ring in (**27**) has much strain; the cyclopentadienyl metal bond forms a η^4-bond in place of a η^5-bond. This four-electron coordination structure of the cyclopentadienyl ring to molybdenum is determined by X-ray crystallography (Fig. 3) [26].

Tetrafluoroethylene reacts with an η^1-cyclopentadienyl iron compound to afford the product (**28**) by carbonyl and difluoromethyl insertions to the metal-η^1-cyclopentadienyl bond, where the difluoromethyl arises from carbon–carbon double bond fission [27] of the tetrafluoroethylene. The number of bridge carbon is two, and (**28**) is also found by X-ray diffraction study to form an η^4-cyclopentadienyl iron bond similar to (**27**) [28].



(12)

Photochemical reaction of benzvalene with iron pentacarbonyl at a low temperature affords the η^2-cyclopentadienyl iron compound (**30**). Complex (**30**) can be warmed at 10°C or above to yield the intramolecular η^3-cyclopentadienyl compound (**31**) by carbonyl insertion. Finally, protonation at a low temperature affords the η^4-cyclopentadienyl iron compound (**32**) by fission of the cyclopropane ring [29].



(13)

The reaction of dimethyl acetylene with palladium chloride in the presence of aryl mercury yields the monocyclopentadienyl intramolecular-coordination compound (**37**) as shown in Scheme 1 [30–33]. Further, in order

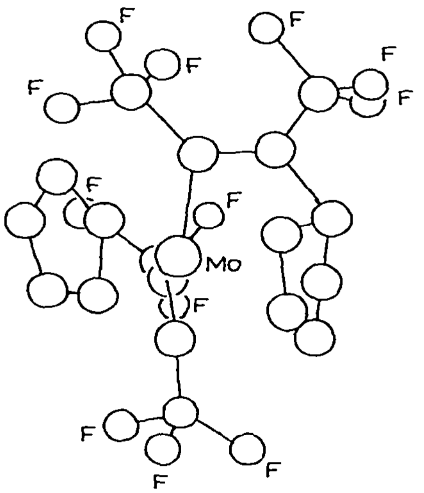
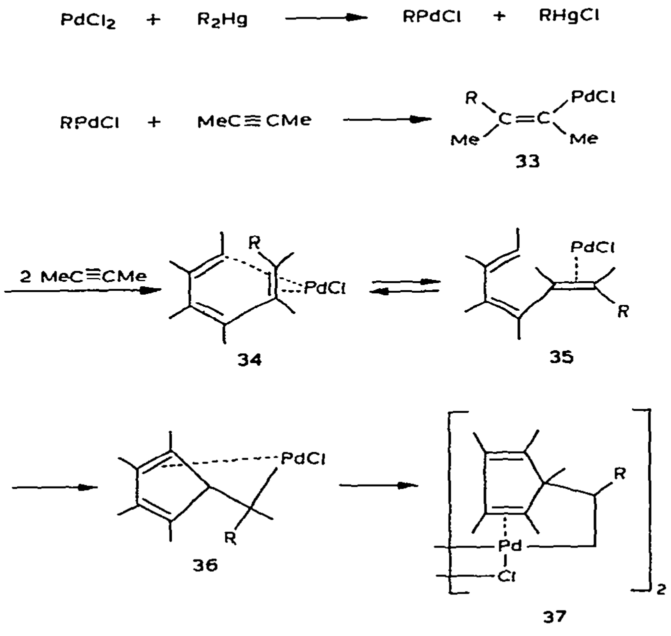


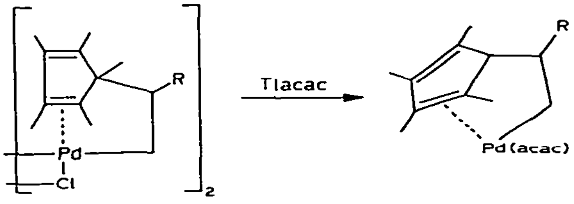
Fig. 3. The structure of [$Mo(CF_3C_2CF_3)(\eta^5-C_5H_5)\{C(CF_3)=C(CF_3)(\eta^4-C_5H_5)\}$] (27).



R : Ph, p-Tolyl

Scheme 1

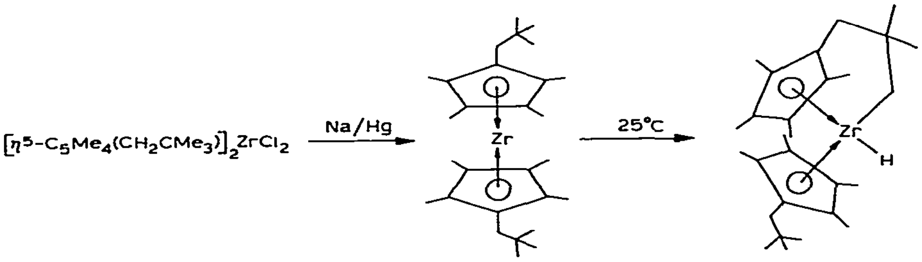
to clarify the coordination structure of (**37**), the chloro-bridge was eliminated



37 38 (14)

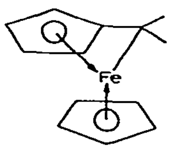
by reaction with thallium acetylacetonate to give (**38**). This η^2-cyclopentadienyl palladium structure has been determined by X-ray analysis (Fig. 4) [30,31]. The number of bridge carbons in (**38**) is two; however, as reported in a previous review [6], (**38**) has the same structure as the strain-free 5.5-membered ring structure in the organometallic intramolecular-coordination compounds containing a carbon–carbon double bond donor ligand, therefore it is presumed to be strain-free. Maitlis and co-workers [30,31] pointed out that this bridge bond length and bond angle are normal, and there is no strain in this chelate ring.

Other monocyclopentadienyl intramolecular-coordination compounds have been produced via facile insertion of zirconium into a ligand C–H bond by treatment [34] of pentylzirconocene dichloride with sodium amalgam (eqn. (15)), and by thermolysis [35] of cyclopentadienyl cobalt compounds.



39 40 (15)

In monocyclopentadienyl intramolecular-coordination compounds, where the number of carbon atoms bonded between cyclopentadienyl ring and metal is one, it is presumed that the formation of stable compounds is difficult because their strain is too great. However, the ferrocenylcarbenium ion is extraordinarily stable, e.g. it shows the same stability as triphenylmethyl cation [36–39]; structures such as (**41**), (**42**) and (**43**) are presumed [39–45]. The single crystal X-ray analysis [44] of ferrocenyldiphenyl-



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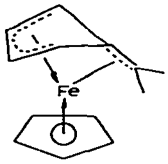

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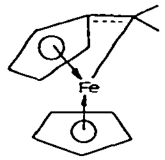

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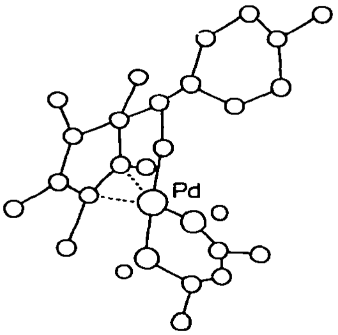
carbenium tetrafluoroborate shows a slight bend of the carbenium group towards the iron (angle 20.7°); the distance between the iron and the carbenium group is 2.715 Å (cf. Fe–C in ferrocene ring: 2.009–2.095 Å) as shown in Fig. 5. Behrens [44] proposed an interaction between iron and the carbenium group. Gleiter and Seeger [41] predicted an angle of 40° in structure (**43**) but this value would be somewhat too large. Similarily this bent structure is also found in α,α-diferrocenylmethylium tetrafluoroborate [45], ferrocenyldiphenylcyclopropenium tetrafluoroborate [46], a fulvene chromium compound $(OC)_3Cr(\eta^5\text{-}C_5H_4=CPh_2)$ [47], and $[(\eta^4\text{-}C_4Ph_4)\text{-}Co(\eta^5\text{-}C_5H_4CPh_2)]^+PF_6^-$ [47a].



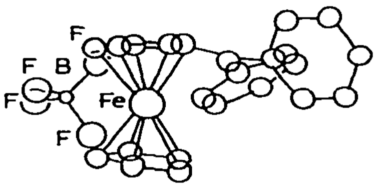
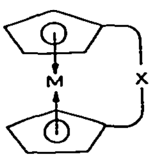


Fig. 4. The structure of η^2-cyclopentadienyl palladium compound (**38**).

Fig. 5. The structure of ferrocenyldiphenylcarbenium tetrafluoroborate.

C. DICYCLOPENTADIENYL INTRAMOLECULAR-COORDINATION COMPOUNDS (BRIDGED METALLOCENES)

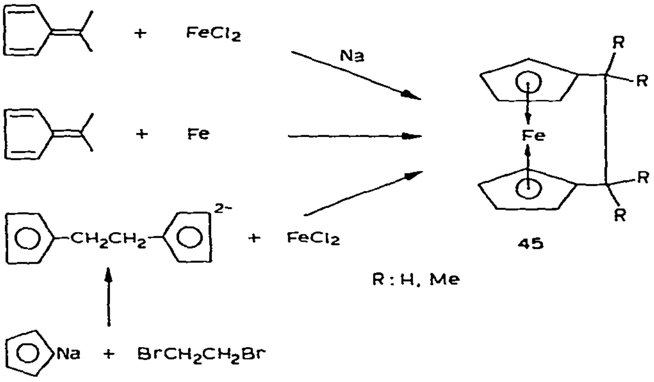
This section deals with π,π-coordination compounds having two cyclopentadienyl rings, that is, dicyclopentadienyl intramolecular-coordination compounds (bridged metallocene) as shown in general formula (**44**).



M : Fe
X : $-(C)_n-$
n : 1–10

44

Trimethylene bridges ($n = 3$) have primarily been reported in these bridged metallocenes, because these syntheses are facile. [2]Ferrocenophane and its tetramethyl derivative (**45**) ($n = 2$), are prepared by reaction of 6,6-dimethylfulvene with ferrous chloride in the presence of Na [48] or with iron vapor [49] directly, or by reaction of ferrous chloride with the 1,2-dicyclopentadienylethane dianion obtained from the reaction of 1,2-dibromoethane with sodium cyclopentadienide [50,51].



(16)

The bond length between the two cyclopentadienyl rings in ferrocene is 3.32 Å [52]. However, the bond length of an ordinary carbon–carbon single bond is 1.54 Å [53], therefore, the separation between the two cyclopentadienyl rings in ferrocene should be shortened by 1.78 Å in order to link these two cyclopentadienyl rings with two carbons. Hence these compounds should form a ring-tilt structure having significant strain; this strain is indicated by unusual values in measurements of ^{1}H NMR spectra [51], electronic spectra [54,55], polarographic half-wave potentials [56], etc. compared with those data for non-bridged alkyl ferrocenes and [3]- or [4]ferrocenophanes. Lentzner and Watt [51] have reported that the electronic spectra of ethylene-bridged ferrocene and its alkyl derivatives contain two broad relatively weak absorptions around 325 and 440 nm. There is general agreement [57] that these bands represent symmetry-forbidden transitions of electrons from non-bonding e_{2g} and a_{1g} levels respectively to the antibonding e_{1g} level. Ring-tilt induced reordering of the non-bonding levels produces corresponding changes in absorption characteristics and the 440 nm band is particularly sensitive to molecular distortion of this nature [55]. Thus, in the spectra of the [2]ferrocenophanes, the intensity of this band ($\epsilon \approx 450$) is increased over fourfold compared with that found for non-bridged analogues, e.g. 1,1′-diethylferrocene ($\lambda_{max} = 438$ nm; $\epsilon = 105$) (Table 1). Further, the absorption maximum is bathochromically shifted by ca. 30 nm, accounting for the characteristic red colour of these ferrocenophanes.

TABLE 1

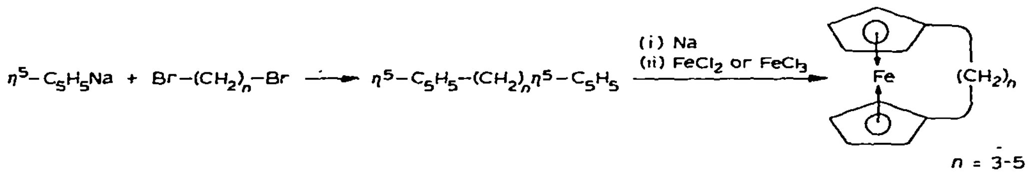
Absorption maxima of alkylferrocenes and [*m*]ferrocenophanes [51, 55]

Ferrocenes	Band I λ_{max} (nm)	ϵ	Band II λ_{max} (nm)	ϵ
Ferrocene	325	50	440	90
1,1'-Dimethylferrocene	325	60	437	100
1,1'-Diethylferrocene	325	70	438	105
[2]Ferrocenophane	328	100	472	450
1,1,2,2-Tetramethyl[2]ferrocenophane	326	105	466	460
[3]Ferrocenophane	319	85	442	185
[4]Ferrocenophane	323	70	433	100
[5]Ferrocenophane	329	110	448	110

The chemical reactivity of [2]ferrocenophanes, e.g. Friedel–Crafts acetylation, protonation, etc., also shows peculiarities compared with non-bridged ferrocenes such as 1,1'-dialkylferrocenes and [*m*]ferrocenophanes ($m = 3$, 4) [58].

The [2]ferrocenenophane structure was determined in 1,1,2,2-tetramethylethylferrocene by X-ray diffraction [59] as shown in Fig. 6. The two η^5-cyclopentadienyl rings are tilted by 23° with respect to one another. The strain in the molecule is apparent also in the fact that the dihedral angles in the bridge are only about 26°, and that the exocyclic bonds are bent by 11° from the ring planes. The bond distances in the bridge are slightly greater (1.584 Å) than normal.

[*m*]ferrocenophanes ($m = 3$–5) [48,58,60] having a higher number of bridged carbon atoms than [2]ferrocenophane can be prepared in low yields by reaction of cyclopentadienyl sodium and α,ω-dibromoalkane, followed by reaction of the resulting α,ω-dicyclopentadiene alkane (46) with sodium, and then with ferrous chloride or ferric chloride.



46 47 (17)

Generally, [*m*]ferrocenophanes (47) have been prepared by cyclization of ferrocene-ω-carboxylic acids.

[3]Ferrocenophanes, as shown in eqn. (18), are prepared in a high yield by heteroannular cyclization of β-ferrocenic propionic acid (48), followed by

reduction of the ketone (**49**) with lithium aluminium hydride–aluminium chloride [61–64]. However, γ-ferrocenylbutylic acid or δ-ferrocenylvaleric acid affords homoannularly cyclized products (**50**) ($n = 3, 4$), and ε-ferrocenyl capronic acid affords only polymer by the cyclization [62,65].

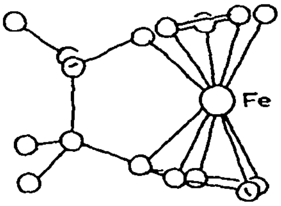
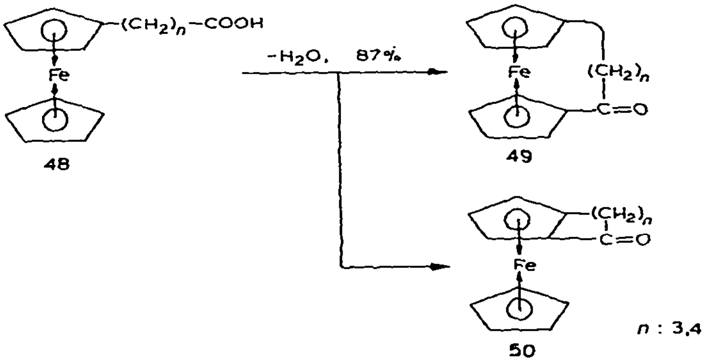


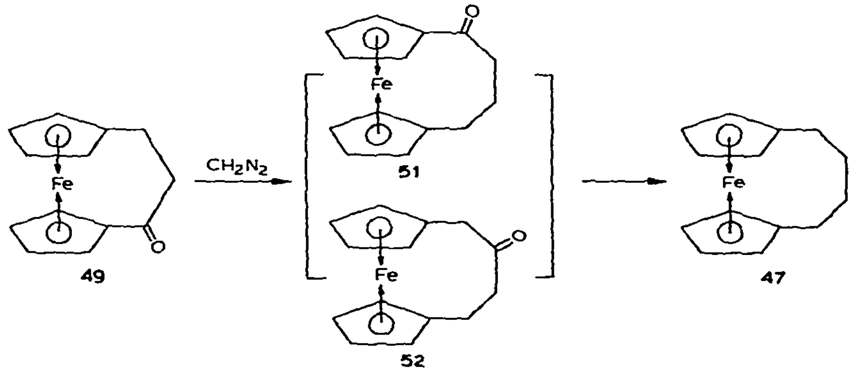
Fig. 6. The structure of 1,1′-tetramethylethyleneferrocene (**45**).



(18)

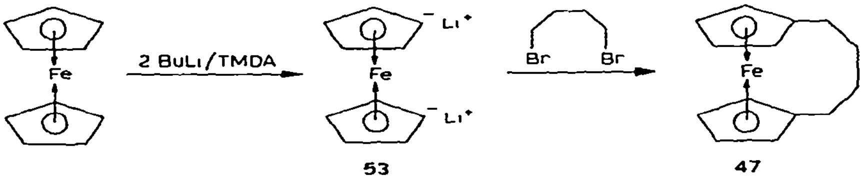
(19)

[4]Ferrocenophanes are conveniently prepared from the [3](1,1′)ferrocenophane-6-one (**49**) as shown in eqn. (20): the diazomethane ring expansion reaction of the [3]ferrocenophane (**49**) affords a mixture the ring-expanded ketones (**51**, **52**), and the [4]ferrocenophanes are produced from both (**51**) and (**52**) by Wolf–Kishner reduction or reduction with lithium aluminium hydride–aluminium chloride [66].



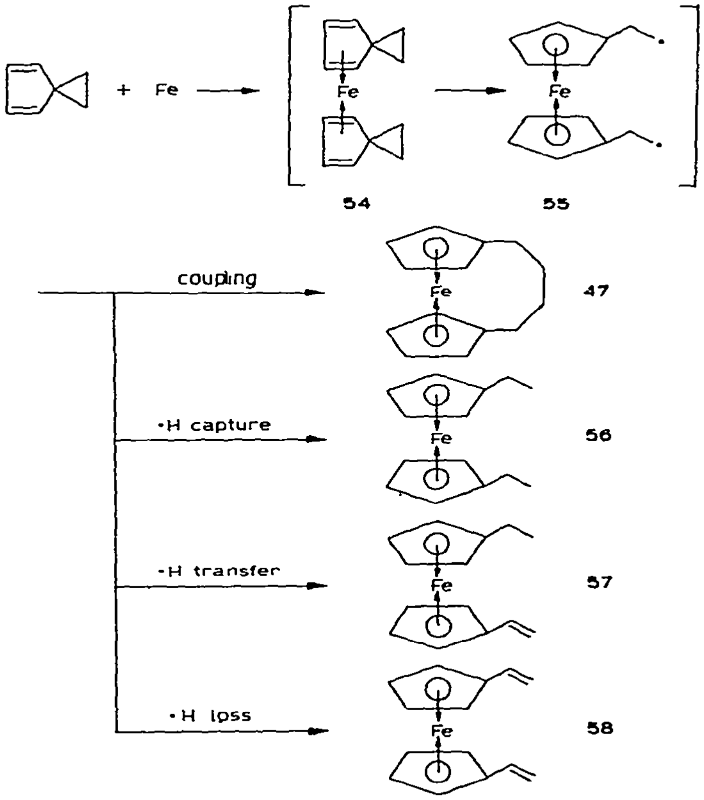
(20)

The [4]ferrocenophane (**47**) can also be prepared in a low yield by reaction of the ferrocene dialkali metal compound (**53**) with α,ω-dibromoalkylene as shown in eqn. (21); this process shows a better yield than from reaction of α,ω-dibromoalkylene with cyclopentadienyl sodium as shown above (eqn. (17)).



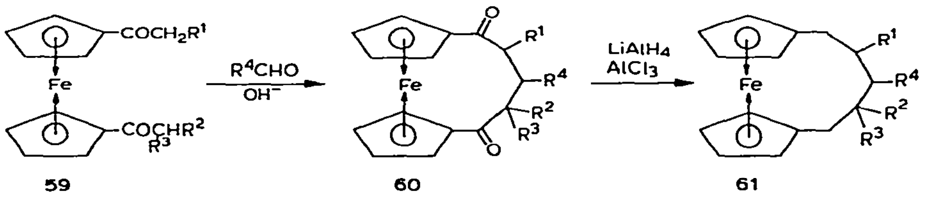
(21)

In the previous section we described the formation of monocyclopentadienyl intramolecular-coordination compounds from the reaction between spiro-cyclopropane compounds and metal carbonyls (eqns. (3) and (4)); however, this spiro-cyclopropane also reacts directly with iron vapour to afford [4]ferrocenophane, but only in a low yield, via a ring opened reaction, biradical formation and coupling reaction as shown in eqn. (22). This reaction affords mainly the ·H transfer reaction product (**57**), and the ratios of the coupling (**47**), ·H capture (**56**), ·H transfer (**57**) and ·H loss reaction products (**58**) are 17:14:62:6 [67].



(22)

[5]Ferrocenophane can be prepared in poor yield directly from the species (**46**) and ferrous or ferric chloride as shown in eqn. (17). A convenient route to ferrocenes bridged by a five-carbon chain involves base-catalysed condensation of 1,1′-diacylferrocenes (**59**) with aromatic or aliphatic aldehyde as shown in eqn. (23) [60,68–71].

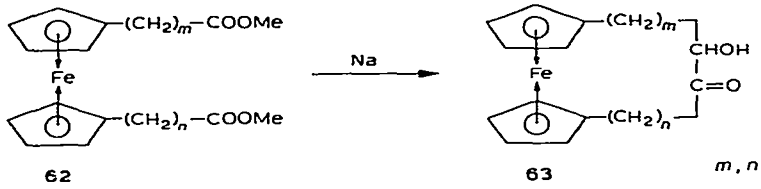


(23)

R^1-R^3 : H, Me, Et, Ph

R^4 : H, Me, Et, Ph, n-Pr, i-Pr, i-Bu, o-ClC_6H_4, 2-furyl, m-$O_2NC_6H_4$, etc.

The acyloin condensation of heteroannularly substituted diester (**62**) has provided, further, larger [*m*]ferrocenophanes ($m = 6$–10) shown in eqn. (24) [60,63,72].



(24)

m, *n* : 1–4

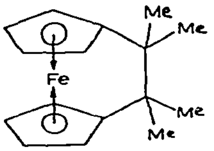
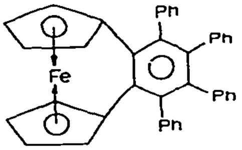
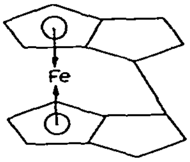
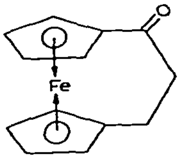
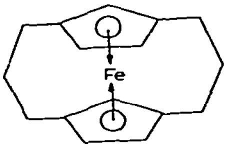
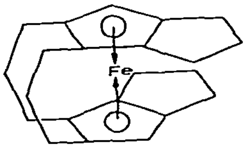
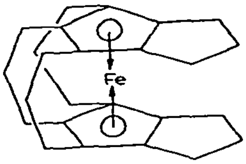
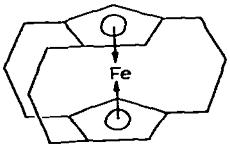
As described above, [*m*]ferrocenophanes ($m = 2$–10) have been reported; however, [1]ferrocenophane has not been synthesized yet. Germanium [73,74], silicon [74–76] or phosphorus [73,74] bridged ferrocenes, which do not belong to the organometallic intramolecular-coordination compounds (M–(C)$_n$Y) [1–7], have been synthesized and the structures of some of these bridged ferrocenes have been determined; the two cyclopentadienyl rings tilt by 16.6°, 19.2° and 26.7°, respectively.

[3]Ferrocenophane is also slightly strained. The tilt angles of the two cyclopentadienyl rings of [2]- and [3]ferrocenophanes are shown in Table 2. [2]Ferrocenophanes tilt by 23–24°. [3]Ferrocenophanes tilt by about 10°; the tilt structures are similar with both mono- and di-bridged ferrocenophanes. In the case of [3](1,1′)[3](2,2′)[3](4,4′)ferrocenophane (**69**) [84], the formation of a tilt structure is difficult; therefore the distance (3.15 Å) between the rings is significantly short (0.17 Å) than that of ferrocene (3.32 Å) [52].

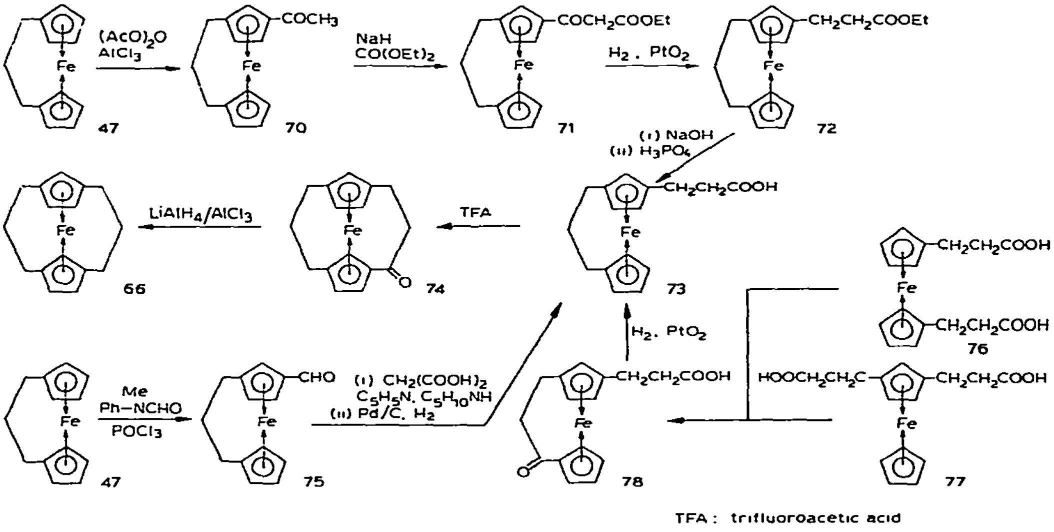
[4]Ferrocenophane and [5]ferrocenophane evidently have no strain since their electronic spectra show almost the same characteristics as ferrocene.

TABLE 2

The dihedral angle between two cyclopentadienyl rings in bridged ferrocenes

Number of bridge carbon	Ferrocenes	Dihedral angle	Refs.
2	 45	23.2°	56
	 64	23.7°	77–79
	 65	23.6°	80
3	 49	8.8°	81
	 66	9°	82
	 67	11.1°	83
	 68	12.5°	84
	 69	2.4°	85

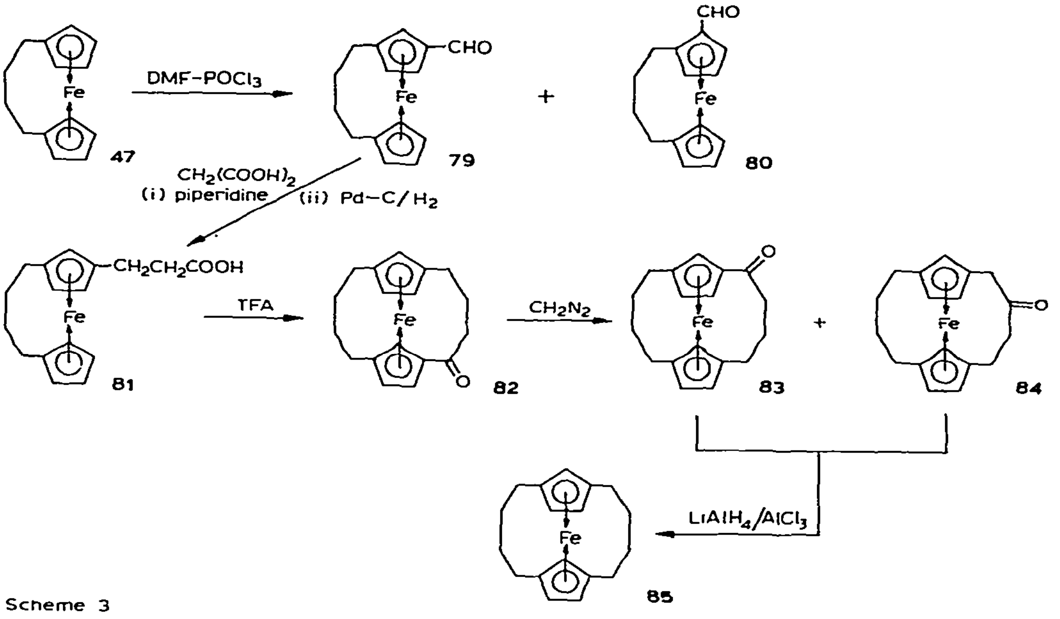
The di-bridged ferrocenes such as (**66**) in Table 2, have been prepared, e.g. by the method shown in Scheme 2 [85–88]. The general reaction route is as follows: Friedel–Crafts acylation of [3]ferrocenophanes with acetic acid anhydride in the presence of aluminium chloride leads to the acetyl compound (**70**); carbethoxylation of (**70**) with diethyl carbonate, employing a dispersion of sodium hydride in hydrocarbon solvent; hydrogenolysis of the resulting *β*-keto ester (**71**) over platinum oxide; saponification of the propionate ester (**72**); cyclization of the propionic acid (**73**) with trifluoroacetic anhydride (TFA) in carbon tetrachloride; and reduction of the bridged ketone (**74**) to form the final di-bridged ferrocene (**66**) with lithium aluminium hydride–aluminium chloride [86]. [3]Ferrocenophane-3-propionic acid (**73**) in the formation of di-bridged ferrocenes is also prepared by the following process: formylation of mono-bridged ferrocene (**47**) to an aldehyde (presumably [3]ferrocenophane-3-carboxaldehyde), which was converted via condensation with malonic ester in the Doebner reaction and subsequent hydrogenation to (**73**). Further, (**73**) is also prepared from 1,3- or 1,1′-ferrocenedipropionic acid (**76**) or (**77**) as shown in Scheme 2.



Scheme 2

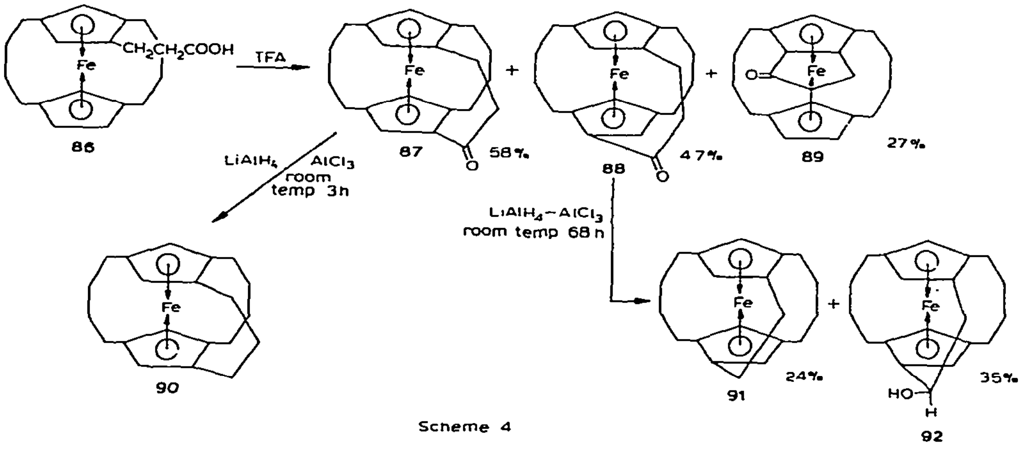
Similarily tri- [86,87,89] and tetra-bridged [89] ferrocenes have been prepared. In these bridges ferrocenes, di- [82,90] and tri-bridged [83,84,90] structures have been determined by X-ray diffraction studies.

On the other hand, di-bridged ferrocenes having two tetramethylene bridges, that is, [4],[4]ferrocenophane (**85**) is prepared by a diazomethane ring expansion reaction (eqn. (20)) as shown in Scheme 3 [66,91].

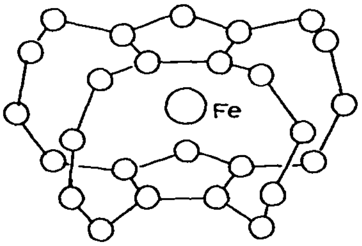


Scheme 3

The propionic acid derivatives (**86**) of [4],[4]ferrocenophane are cyclized with trifluoroacetic acid anhydride (TFA) to give two kinds of heteroannular compounds (**87**, **88**) and one homoannular compound (**89**) [66]. The reduction of the heteroannular product (**87**) with lithium aluminium hydride–aluminium chloride affords easily, almost quantitatively, the tri-bridged hydrogenated product (**90**), but the reduction of twist-bridged ketone (**88**) is more difficult, and affords [4](1,1′)[4](3,3′)[3](4,5′)ferrocenophane (**91**) in a low yield together with the endo-16-hydroxyferrocenophane (**92**) even if the reduction is carried out for a longer reaction time.



Scheme 4



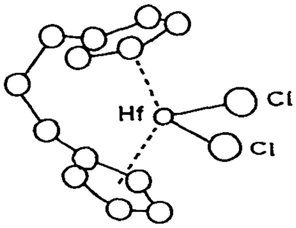


Fig. 7. The structure of [4],[4],[4],[4]ferrocenophane.

Fig. 8. The structure of (1,1'-trimethylenedicyclopentadienyl)hafnium chloride.

Hisatome and co-workers [66,92] prepared the tetra-bridged ferrocene by the processes shown in Schemes 2–4 and determined the structures of [4],[4],[4],[3]ferrocenophane [93] and [4],[4],[4],[4]ferrocenophane (Fig. 7) [94]. Further, they are attempting to prepare and determine the perferrocenophane, that is, penta-bridged ferrocenophane [94a].

The compounds shown as general formula $(CH_2)_3(\eta^5\text{-}C_5H_5)MCl_2$ (M: Ti [95], Zr [96], Hf [97]) have similar structures to [3]ferrocenophanes, but the central metal of these compounds forms a distorted tetrahedral structure and they have no strain, in spite of the tilt of the two cyclopentadienyl rings, e.g. the hafnium compound (Fig. 8) [97]. These three compounds form approximately the same structure.

Heating ferrocene in the presence of $AlCl_3$ affords various kinds of cyclopentylene bridged compounds of ferrocene [98–102] determined by X-ray diffraction studies [98–100]. Various kinds of synthesis [103–111], acetylation [112], photochemical reaction [113], etc. [114–116] concerning bridged ferrocenes have also been reported.

D. CONCLUDING REMARKS

Organometallic intramolecular-coordination compounds containing a cyclopentadienyl donor ligand can be classified into two groups of monocyclopentadienyl intramolecular-coordination compounds having a σ,π-coordination bond (M–C σ-bond and M–cyclopentadienyl π-bond) and dicyclopentadienyl intramolecular-coordination compounds having a π,π-coordination bond (two M–cyclopentadienyl π-bonds).

The former compounds are mainly η^5-cyclopentadienyl coordination compounds, and include some η^4- and η^2-coordination compounds.

The former compounds, with two bridging carbon atoms, have significant strain and tend to react with carbonyl insertion to form the ring-expanded product during their preparation or under a carbon monoxide atmosphere.

However, the compounds having η^2-coordination have almost no strain even if the number of their bridged carbon is two, because such compounds can form an ordinary 5.5-membered ring [6].

In the latter compounds, [2]ferrocenophanes have much strain and the two cyclopentadienyl rings tilt by 23–24°. [3]Ferrocenophanes have slight strain and the rings tilt by about 10°. [4]- and [5]ferrocenophane have no strain.

1,2,4-Tri-bridged ferrocenes, even trimethylene bridged ferrocene, cannot tilt but must be almost planar; the distance of two cyclopentadienyl rings is then shortened by 0.17 Å compared with that of ferrocene.

In multibridged ferrocenes, tetra-bridged ferrocenes have been synthesized step by step and their structures have been determined by X-ray diffraction studies, but synthesis of perferrocenophane, that is, penta-bridged ferrocene has not yet succeeded.

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