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FERROCENE-CONTAINING METAL COMPLEXES

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CONTENTS

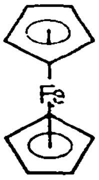
ABBREVIATIONS

acac	acetylacetonate ion
All	allyl
Ar	aryl
BPPFA	1,1′-bis(diphenylphosphino)-2-[(dimethylamino)ethyl]ferrocene
BPPFOH	1,1′-bis(diphenylphosphino)-2-(ethanol)ferrocene
COD	cyclooctadiene
Cp	η^5-C_5H_5
dmg	dimethylglyoxime anion
dppb	1,4-bis(diphenylphosphino)butane
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
Et	ethyl
FcH	Ferrocene, Cp_2Fe
Fc	ferrocenyl
FcN	*N*,*N*-(dimethylamino)methylferrocene
FcNP	1-[(dimethylamino)methyl]-2-(diphenylphosphino)ferrocene
Fdma	1,1′-bis(dimethylarsino)ferrocene
Fdpa	1,1′-bis(diphenylarsino)ferrocene
Fdpp	1,1′-bis(diphenylphosphino)ferrocene
Me	methyl
MPFA	1-[(dimethylamino)ethyl]-2-(dimethylphosphino)ferrocene

NBD	norbornadiene
Ph	phenyl
PPEF	1-ethyl-2-(diphenylphosphino)ferrocene
PPFA	1-[(dimethylamino)ethyl]-2-(diphenylphosphino)ferrocene
py	pyridine

A. INTRODUCTION

Since the first preparation of ferrocene (I) in 1951 this molecule has played a major role in organometallic chemistry [1,2]. The ease with which a wide variety of substituents may be introduced into the molecule has also led to the preparation of many ferrocene containing coordination compounds (vide infra). In this account we have attempted to include as wide a variety of transition metal complexes containing ferrocene ligands as possible and have excluded, for example, the well known lithiated and mercurated derivatives which have been discussed elsewhere [2]. Nevertheless, although the primary focus of this review is on transition metal coordination compounds we feel justified in adopting a flexible approach and including several sigma-bonded and metallated derivatives which are worthy of note. For ease of presentation the material in the text is organized in terms of the Group of the central atom(s) and summarized in the same manner in tabular form.



I

B. GROUP IV AND V METALS

Only a few Group IV and V metal complexes are reported. Ferrocene acetonitrile and *N*,*N*-dimethylaminomethylferrocene (FcN) both form 1 : 1 complexes with Group IV halides ($TiCl_4$, $TiBr_4$, $SnCl_4$, $ZrCl_4$) [3]. The infrared spectra of these compounds confirm that complexation has taken place since for the nitrile ligand the ν(CN) vibration moves to higher frequency (43–52 cm^{-1}) on formation of the compound, whilst the ν(N–CH_3) vibration of the amine shifts to lower frequency (~ 20 cm^{-1}). The vibrations associated with the ferrocene part of the ligand are largely unaffected by complexation (a result which is not atypical).

Treatment of dicyclopentadienyltitanium dichloride with ferrocenoyltrifluoroacetone yields an unstable dark violet compound of formula

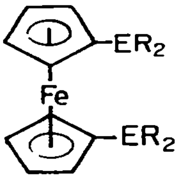
$TiCpCl(FcC(0)CHC(0)CF_3)_2$ whose structure has not yet been elucidated [4]; the equivalent hafnium and zirconium complexes have also been reported [5].

Sigma-bonded compounds have been formed by reaction of mono- and dilithioferrocene with dialkylaminotitanium bromides [6] and dicyclopentadienylmetal chlorides (metal = Ti, Zr, Hf) [7].

$$Fe(C_5H_4Li)_2 + 2(Et_2N)_3TiBr \rightarrow 2\ LiBr + Fe(C_5H_4Ti(NEt_2)_3)_2 \qquad (1)$$

Addition of $VOCl_3$ to ferrocene yields a dark blue compound of 1 : 1 stoichiometry [8]. By comparison of the relative intensities of the in and out of plane CH vibrations in the infrared for FcH, FcBr and $FcHVOCl_3$ and from the electronic spectra, the ionic structure $FcH^+ VOCl_3^-$ was proposed.

Photolysis of a THF solution of bis(diglyme)sodium hexacarbonylvanadate (or tantalate) and 1,1′-bis(diphenylphosphino)ferrocene (Fdpp, II) has



II

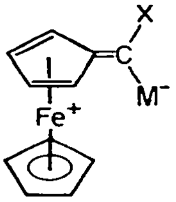
ER$_2$= PPh$_2$ (Fdpp)
= AsPh$_2$ (Fdpa)
= AsMe$_2$ (Fdma)

been used to obtain tetramethylammonium tetracarbonyl[1,1′-bis(diphenylphosphino)ferrocene]vanadate (or tantalate), as part of a wider study of the coordinating ability of Fdpp [9]. A vanadium complex of the arsenic analogue, Fdpa, has also been prepared [10].

C. GROUP VI METALS

A wide variety of ferrocene ligands have been used to form Group VI metal complexes. The electronic structure of a number of these derivatives has been of particular interest to many workers. Thus, Gubin and Khandkarova [11] prepared compounds of the type $Cr(CO)_3(Fc(CH_2)_nC_6H_5)(n = 0, 1)$ from $Cr(CO)_6$ and the appropriate ferrocene derivative. By measurement of the polarographic and potentiometric oxidation of the iron centre, which in ferrocene is particularly sensitive to the nature of any substituents on the cyclopentadienyl rings, and by calculation of a set of σ-constants for the $Cr(CO)_3C_6H_5$ group they were able to conclude that a considerable increase in the effective positive charge on the aromatic ring σ-orbitals takes place upon coordination with the $Cr(CO)_3$ group.

Connor et al. [12,13] prepared a variety of ferrocene carbene complexes of the type $M(CO)_5(C(Fc)X)$ ($M = Cr$, W; $X = OMe$, OEt, NH_2, NMe_2, NC_4H_8) and $Mn(CO)_2(C(Fc)OMe)(\eta^5\text{-}C_5H_4Me)$ by well established procedures utilizing ferrocenyllithium. The Group VI complexes are air stable in contrast to the manganese compound which is both air and light sensitive. Analysis of the NMR, IR, UV–VIS and the mass-spectra of these compounds led to the conclusion that the π-system of the ferrocene interacts very strongly with the sp^2 hybridised carbene carbon atom, ferrocene being a more potent electron donor than a phenyl group; thus the resonance canonical form (III) contributes to the representation of the carbene complexes. Similar structures are drawn to account for the stability of α-ferrocenylcarbonium ions [14]. Attempts to prepare β-ferrocenyl carbene complexes were unsuccessful [13].



III

The electrochemical oxidation of some of the above carbene complexes, ($M(CO)_5(C(Fc)OEt)$ ($M = Cr$, W) and $Mn(CO)_2(C(Fc)OMe)(\eta^5\text{-}C_5H_4Me)$, was studied by McCleverty et al. [15,16] as part of a wider investigation. Although the manganese derivative undergoes two one-electron oxidations as expected, only a single one-electron oxidation is observed for the Group VI compounds, this result led to the proposal that the highest occupied molecular orbital of the complexes may encompass both metal centres [16].

In contrast to this Pannell et al. [17] found two distinct oxidation waves in the cyclic voltamagram of $Fe(CO)_2Cp(Fc)$ (both waves irreversible) and $Fe(CO)_2Cp(COFc)$ (one irreversible) showing the lack of significant metal–metal interactions in these compounds.

Carbyne complexes have also been prepared by reacting aluminum or boron halides with the corresponding carbene complex, and studied by both electrochemical and spectroscopic techniques [18,19]. The structure of $CrBr(CO)_4CFc$ is shown in Fig. 1.

As might be expected, many Group VI complexes containing ferrocenylphosphine ligands have been reported. Preparation of compounds of the type $M(CO)_5(Fc_xPh_{3-x}P)$ ($M = Cr$, Mo, W) by direct reaction of the phosphine with the metal carbonyl [20,21] has enabled the σ-donating properties of ferrocenyl phosphine ligands to be estimated by study of the carbonyl region in the infrared spectra of the complexes. As the number of

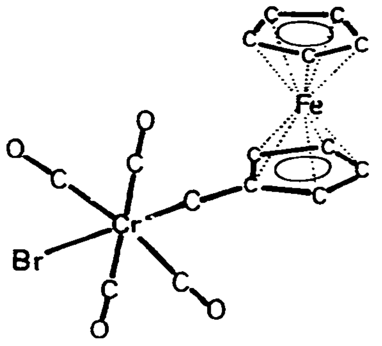


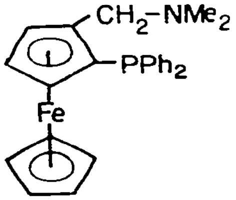
Fig. 1. The structure of $CrBr(CO)_4CFc$ [19].

TABLE I
Cyclic voltammetry data for the ferrocenylphosphines and some complexes from ref. 24

Compound	Ferrocenyl group redox waves E_{peak} (V vs. SCE)		Coordinated metal redox waves E_{peak}
	Anodic	Cathodic	(V vs. SCE)
Ferrocene	+0.59	+0.43	
$FcPh_2P$	+0.72	+0.41	
Fc_2PhP	+0.75	+0.62	
	+0.91	+0.79	
Fc_3P	+0.70	+0.59	
	+0.84		
	+0.91	+0.72	
$W(CO)_5(Ph_3P)$			+1.48
$W(CO)_5(FcPh_2P)$	+0.82	+0.70	+1.54
$W(CO)_5(Fc_2PhP)$	+0.78	+0.64	+1.52
	+0.96	+0.83	
$W(CO)_5(Fc_3P)$	+0.70	+0.58	+1.92
	+0.87	+0.77	
	+0.96	+0.84	
$Mo(CO)_5(FcPh_2P)$	+0.82	+0.65	+1.56
$Mo(CO)_5(Fc_2PhP)$	+0.69	+0.49	+1.35
	+0.88	+0.68	
$Mo(CO)_5(Fc_3P)$	+0.68	+0.54	+2.05
	+0.86	+0.72	
	+0.92	+0.76	
$Mo(CO)_4(FcPh_2P)_2$	+0.72	+0.55	+1.16
$W(CO)_4(Fc_2PhP)_2$	+0.76	+0.53	+1.32
	+0.91	+0.69	

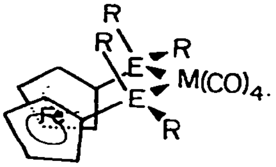
ferrocenyl groups is increased the A_1 and E bands progressively shift to lower frequency. This has been interpreted as resulting from an increasing σ-donor ability. Similar shifts in the ν(CO) frequency were also observed in $Cr(CO)_2(Fc_xPh_{3-x}P)(\eta^6\text{-}C_6H_6)$ complexes [22,23] and in iron carbonyl derivatives described below.

Some electrochemical studies on molybdenum and tungsten carbonyl compounds are summarised in Table 1 [24]. The ferrocenyl group oxidations are reversible and fall in the range $E_{\text{peak,anodic}} = +0.65-+1.10$ V for the ligands and are only increased significantly for the $FcPh_2P$ complex. The coordinating ability of the ligand does not seem to be appreciably altered upon oxidation. The irreversible oxidation of the Group VI metal takes place at higher potentials (+1.16–2.05 V). In a continuation of this work Kotz et al. [25] investigated the coordination chemistry of 1-(dimethylamino)methyl-2-(diphenylphosphino)ferrocene, FcNP, (IV) which forms the chelate complexes $M(CO)_4(FcNP)$ ($M = Cr$, Mo, W). The CH_2 protons are "diasteriomeric" in both the free ligand and its complexes because of the planar chirality of the η^5-bonded group. The electrochemical behaviour of FcNP is not simple and changes considerably upon chelation. In $Cr(CO)_4(FcNP)$ two reversible one electron redox waves are observed. The first is assigned to $Cr^{(0)} \rightarrow Cr^{(+)}$ and the second to $Fe^{2+} \rightarrow Fe^{3+}$. A third irreversible wave at very high anodic potential is ascribed to $Cr^{+} \rightarrow Cr^{n+}$. The molybdenum and tungsten analogues behave differently, since the $M^0 \rightarrow M^+$ ($M = Mo$, W) is irreversible in these compounds although the $Fe^{2+} \rightarrow Fe^{3+}$ oxidation is still reversible and indeed largely unchanged. This type of variation in the electrochemical properties of Group VI metal complexes has been noted for other ligands [16]. The Group VI metal in the $M(CO)_4(FcNP)$ complexes is oxidized at lower potential than the ferrocenyl group in contrast to the $M(CO)_{4,5}(Fc_xPh_{3-x}P)_{2,1}$ complexes where the opposite is the case. This difference probably arises because in the FcNP complexes a carbonyl group has been replaced by a donor (NMe_2) group that does not function as a π-acceptor. The electron density on the Group VI metal is thus higher and oxidation may occur at lower potentials. Finally, Kotz et al. [25] noted that in the $M(CO)_4(FcNP)$ complexes their electrochemical studies do not suggest any interaction between the metal centres.

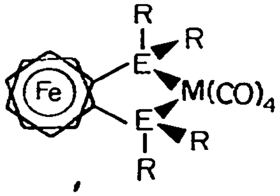


IV

1,1′-Bis(dimethylarsino)ferrocene(Fdma, II) and its diphenylarsino and diphenylphosphino analogues, Fdpa and Fdpp, have been used to form complexes of the Group VI metals [9,26]. All three ligands form the usual $M(CO)_4(L-L)$ derivatives upon direct reaction with the metal hexacarbonyl. Prolonged reaction of $Mo(CO)_6$ with Fdma yields μ-(Fdma)–$[Mo(CO)_3(Fdma)]_2$ and $Mo(CO)_3(Fdma)_2$. The latter compound has one bidentate and one monodentate ligand with the carbonyl groups in a meridional arrangement whilst the three carbonyl groups adopt a facial arrangement in the bridged complex. In principle there are two possible conformations for the chelate complexes, staggered (VI) and eclipsed (V).



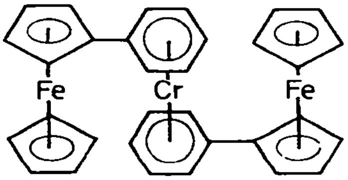
V



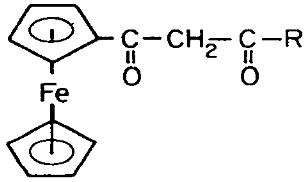
VI

The NMR spectra of the $M(CO)_4(Fdma)$ complexes indicates that the molecules are fluxional but limiting spectra were not obtained. The spectra of the bridged complex may be interpreted in terms of a fluxional (VI) or a static (V) chelate ring. The spectra of $(Fdma)_2Mo(CO)_3$ cannot be interpreted using either the static or the dynamic models.

One other chromium complex worth noting is 1,1′-diferrocenyldibenzenechromium which was prepared from the reaction of $CrCl_3$ and $AlCl_3/Al$ with phenylferrocene. The compound was identified by elemental analysis as the iodide of the corresponding cation, and structure (VII) proposed [27].



VII



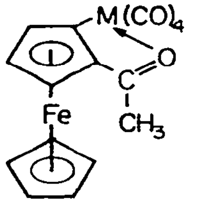
VIII

Finally chelates based on β-diketones of ferrocenes (VIII) form chromium complexes [28] which apparently have some potential as antistatic agents in gasoline.

D. GROUP VII

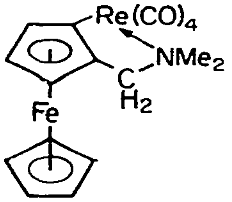
Few manganese containing derivatives have been reported, and usually these have been prepared as part of wider studies. Thus for example, the carbene complex $Mn(CO)_2(C(Fc)OMe)(\eta^5\text{-}C_5H_4Me)$ was prepared during the course of an investigation of the electrochemical oxidation of a variety of chromium and molybdenum compounds mentioned above [13,15]. Unlike those derivatives, the manganese complex was found to undergo two one-electron oxidations. Treatment with iodine gave what is thought to be, on the basis of its characteristic six line EPR signal, the cationic species.

Crawford et al. [29–31] have reacted acetylferrocene and *N,N*-dimethylaminomethylferrocene with $M(CO)_5Me$ ($M = Mn$, Re). The acetylferrocene is metallated by both manganese and rhenium (IX). The FcN is metallated in much the same way by $Re(CO)_5Me$ to give (X) but with $Mn(CO)_5Me$ metallation occurs on the nitrogen methyl group to give the unusual species shown in Fig. 2 whose structure was determined by X-ray crystallography [31]. The bonding in the three membered $Mn–N–CH_2$ ring can best be regarded as an aminomethylene group acting as a 3-electron donor to the manganese atom rather than as an iminium cation.

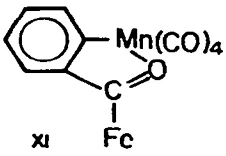


IX

M = Mn, Re



X



XI

When benzoylferrocene is treated with $Mn(CO)_5Me$ the benzene ring is metallated (XI) probably because the strain involved in fusing a five and a six-membered ring is less than when two five-membered rings are fused.

The remainder of the manganese complexes in the literature are derivatives of ferrocenylphosphines and are listed in Table 2.

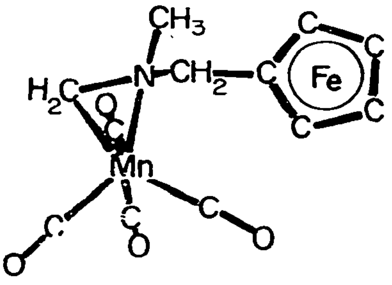


Fig. 2. The structure of $Mn(CO)_4(FcCH_2N(CH_3)CH_2)$ [31].

TABLE 2
Ferrocene containing metal complexes

		Ref.
Group IV		
MCp_2Fc_2	(M = Ti, Zr, Hf)	7
$M(FcCH_2CN)X_4$	(M = Ti, Zr, X = Cl, Br; M = Sn, X = Cl)	3
$M(FcN)X_4$	(M = Ti, Zr, X = Cl, Br; M = Sn, X = Cl)	3
$FcTi(NR_2)_3$	(R = Me, Et)	6
$Fe[(\eta^5\text{-}C_5H_4)Ti(NEt_2)_3]_2$		6
$MClCp(FcCO.CH.COCF_3)_2$	(M = Ti)	4
	(M = Ti, Zr, Hf)	5
Group V		
$FcH.VOCl_3$		8
$[M(CO)_4(Fdpp)][NEt_4]$	(M = V, Ta)	9
Group VI		
$M(CO)_5(C(Fc)R)$	(M = Cr, W, R = OMe, OEt, NMe_2, NC_4H_8)	12, 13, 15
$M(CO)_4(CFc)X$	(M = Cr, Mo, W, X = Cl, Br, I)	18, 19
$Cr(CO)_3(\eta^6\text{-}C_6H_5Fc)$		11
$Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2Fc)$		11
$[Cr(\eta^6\text{-}C_6H_5Fc)_2]^+I^-$		27
$M(CO)_5(Fc_3P)$	(M = Cr, Mo, W)	20
$Cr(CO)_2(\eta^6\text{-}C_6H_6)(Fc_xPh_{3-x}P)$	($x = 1, 2, 3$)	22, 23
$M(Fdpp)(CO)_4$	(M = Cr, Mo, W)	9
$M(CO)_4(FcNP)$	(M = Cr, Mo, W)	25
$M(Fdma)(CO)_4$	(M = Cr, Mo, W)	26
$M(Fdpa)(CO)_4$	(M = Cr, Mo, W)	26
$Cr(FcCO.CH.CO.CH_3)_3$		28
$Cr(FcCO.CH.CO.CH_3)(C_{17}H_{33}CO_2)_2$		28
$M(CO)_5(Fc_xPh_{3-x}P)$	(M = Mo, W, $x = 1, 2, 3$)	21, 24
$M(CO)_4(Fc_xPh_{3-x}P)_2$	(M = Mo, $x - 1$; M = W, $x = 2$)	24
$Mo(Fdma)(CO)_4$		26

		Ref.
$Mo(Fdma)_2(CO)_3$		26
$u\text{-}(Fdma)\text{-}[Mo(Fdma)(CO)_3]_2$		26
$W(FcCo.)(CO)_3Cp$		17
$M(Fc.CO.CH_2)(CO)_3Cp$	($M=Mo$, W)	17, 32
Group VII		
$M(CpFeC_5H_3CO.R)(CO)_4$	($M=Mn$, Re, $R=Me$; $M=Mn$, $R=Ph$)	29, 30
$Mn(CpFeC_5H_3COCH_3)(CO)_3(Ph_3P)$		30
$Mn(CO)_2(\eta^5\text{-}C_5H_4Me)(C(Fc)OEt)$		15
$Mn(CO)_4(FcCH_2N(CH_3)CH_2)$		29, 30, 31
$Mn(CO)_2Cp(Fc_xPh_{3-x}P)$	($x=1, 2, 3$)	22, 23
$Mn_2(CO)_9(Fc_3P)$		20
$Mn(CO)_4(Me)(Fc_3P)$		30
$Re(CO)_4(CpFeC_5H_3CH_2NMe_2)$		29, 30
Group VIII		
$Fe(CO)_4(FcCH.CHCOPh)$		35
$Fe(CO)_3(FcCHCHCOPh)$		35
$Fe(CO)_3(FcCHCHCOPh)(Me_2PhP)$		36
$Fe(CO)_2Cp(Fc)$		17
$Fe(CO)_2Cp(FcCH_2)$		17
$Fe(CO)_2Cp(Fc(CH_2)_2)$		33
$[Fe(CO)_2Cp(FcCH=CH_2)]BF_4$		34
$Fe(CO)_2Cp(FcCOCH_2)$		17
$Fe(FcN)_2X_2$	($X=Cl$, Br, I, NCS)	41
$Fe(CO)_4(Fc_3P)$		20, 37
$Fe(CO)_2(Fc_3P)_3$		37
$Fe(CO)_4(FcNP)$		25
$Fe(FcCOCHCOCH_3)_3$		28
$Co_2(CO)_6(FcCCFc)$		38
$Co_2(CO)_6(FcCCH)$		39
$CoCp(\eta^4\text{-}C_4RR'PhFc)$	($R=R'=Ph$; $R=CO_2CH_3$, $R'=Ph$; $R=Ph$, $R'=CO_2CH_3$)	40
$CoCp(\eta^4\text{-}C_4RR'PhFc)$	($R=CO_2CH_3$, $R'=Ph$; $R=Ph$,$R'=CO_2CH_3$; $R=R'=CO_2CH_3$)	40
$CoCp(\eta^4\text{-}C_4Ph_2Fc)$		40

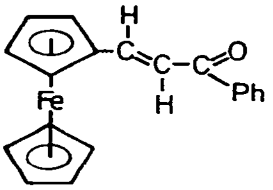
$Co(FcN)_2X_2$	$(X=Cl, Br, I, NCS)$	41
$Co(CpFeC_5H_3CH_2NMe_2.py)X_2$	$(X=Cl, Br, SCN)$	43
$Co(FcCH=N.NC(NH_2)S)_2$		42
$Co(dmg)_2(Me)(Fc_xPh_{3-x}P)$	$(x=1, 2)$	21
$[Co(CO)_3(FcPh_2P)_2]BPh_4$		21
$Co(Fdpp)X_2$	$(X=Cl, Br, I)$	9
$[Co(CO)_3(FcNP)]BPh_4$		25
$Rh(CO)Cl(Fc_3P)_2$		45
u-(Fdpp)-$[Rh_2(CO)_2(Fdpp)_2H_2]$		57
$[Rh(Fdma)_2X_2]PF_6$	$(X=Br, I)$	44
$[Rh(Fdma)_2HX]PF_6$	$(X=Cl, Br)$	44
$[Rh(Fdma)_2H_2]PF_6$		44
$[Rh(Fdma)_2L]PF_6$	$(L=CO, SO_2, CNCMe_3, S_2, (SCH_3)_2, O_2)$	44
[Rh(diene)(PPFA)]X	(diene=NBD, COD, $X=ClO_4^-$, PF_6^-)	47, 52
$[Rh(PAFA)(NBD)]ClO_4$		54
$[Rh(MAFA(NBD)]ClO_4$		54
$[Rh(Fdpp)(NBD)]ClO_4$		54
$[Rh(diene)(BPPFOH)]ClO_4$	(diene=NBD, COD)	55, 56
Rh(CO)Cl(PPFA)		52
$NiCp(CpFeC_5H_3Cl)(Ph_3P)$		91
$Ni(FcN)X_2$	$(X=Cl, Br, I, NCS)$	41
$Ni(Fdpp)_2X_2$	$(X=Cl, Br, I)$	9
$Ni(Fdma)_2Br_2$		59
$Ni(Fdma)(CO)_2$		59
u-(Fdma)-$[Ni(CO)_3]_2$		59
$Ni(Fdma)(CO)I_2$		59, 61
$Ni(Fdpa)_2I_2$		59
$Ni(Fdpa)_2(CO)I_2$		59
$Ni(Fdpa)(CO)_2$		59
$Ni(CO)_3(PPFA)$		52
$Ni(FcCO.CH.COCH_3)_2$		28
$PdCl_2(FcN)_2$		63
$[MX_4][FcCH_2NHMe_2]_2$	$(M=Pd, Pt. X=Cl, CN)$	63
$Pd_2(CpFeC_5H_3CH_2NMe_2)_2X_2$	$(X=Cl, I)$	64, 69, 71
$Pd(acac)(CpFeC_5H_3CH_2NMe_2)$		64, 69

		Ref.
$Pd(CpFeC_5H_3CH_2NMe_2)(L)$	$(L = Me_2PhP, Me_2PhAs, (OMe)_3P, Ph_3P)$	64
$Pd_2Cl_2(CpFeC_5H_3CH(CH_3)NMe_2)_2$		65, 70
$Pd(acac)(CpFeC_5H_3CH(CH_3)NMe_2)$		65
$Pd_2Cl_2(CpFeC_5H_3py)$		92
$Pd_2Cl_2(CpFeC_5H_3py)_2$		92
$Pd(Fdpp)Cl_2$		73
$PdCl_2(PPFA)$		98
$M(Fdma)_2X_2$	$(M = Pd, Pt, X = Cl, Br, I)$	59
$M(Fdpa)X_2$	$(M = Pd, X = Cl, Br, I; M = Pt, X = Cl)$	59
$[M(Fdma)_2X]PF_6$	$(M = Pd, X = Cl, Br; M = Pt, X = Cl, Br, I)$	59
$[M(Fdma)_2][PF_6]_2$	$(M = Pd, Pt)$	59
$Pd(FcCO.CHCOCF_3)_2$		4
$Pd(All)(FcCOCHCOCF_3)$		4
$PtCl(C_2Fc)(Me_2PhP)$		76
Group I		
$M_4(FcCH_2NMe_2)_4$	$(M = Cu)$	79
	$(M = Ag)$	80
$Cu(FcCHN.NCNH_2.S)_2$		42
$Cu_2(FcCHN.NCNH_2.S)_2$		42
$Cu(Fdpp)I$		9
$Cu(FcCOCHCOCH_3)_2$		28, 77
$Au(Fc)(Ph_3P)$		81, 82, 86
$Au(C_5H_4XFeC_5H_3X)(Ph_3P)$	$(X = H, Cl, OCH_3, CH_2NMe_2)$	86, 93
$Au_2((\eta^5\text{-}C_5H_4)_2Fe)(Ph_3P)_2$		94
$Au(FcS)(Ph_3P)$		84, 85, 86, 95
$[Au_2(Fc)(Ph_3P)_2]BF_4$		86, 95
$AuBr(Fc_xPh_{3-x}P)$	$(x = 1, 3)$	90
$[AuBr(FcPh_2P)][AuCl]$		90
$AuBr_3(FcPh_2P)$		90
$Au(R)(Fc_3P)$	$(R = Me, tolyl, m\text{-}FC_6H_4, p\text{-}CH_3C_6H_4)$	88
	$(R = PhCH{=}CH_2, PhCH{=}CHCO_2CH_3)$	89, 97
$[Au_2(R)(Fc_3P)_2]BF_4$	$(R = o\text{-}IC_6H_4, PhCH{=}CHCO_2CH_3)$	88, 89

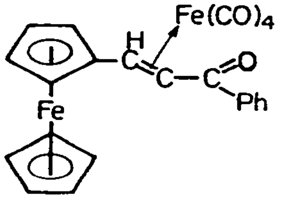
E. GROUP VIII

Very few iron complexes with ferrocene ligands have been described. Sigma bonded, Fc–C, iron derivatives of the type $Fe(CO)_2Cp((CH_2)_nFc)$ ($n = 0, 1, 2$) and $Fe(CO)_2Cp(COFc)$ have been prepared [17,32,33] by salt elimination reactions using $[Fe(CO)_2Cp]Na$ and the appropriate chlorinated ferrocene derivative. Electrochemical studies were carried out on the above compounds and any possibility of metal–metal interaction can be discounted since $Fe(CO)_2Cp(CH_2Fc)$ and $Fe(CO)_2Cp(COFc)$ both have two oxidation waves (one reversible in each case) whilst $Fe(CO)_2Cp(Fc)$ is destructively oxidized to ferrocene.

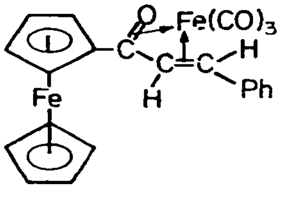
Reaction of $Fe(CO)_2Cp((CH_2)_2Fc)$ with Ph_3CBF_4 [33] produces a ferrocenium derivative rather than the anticipated hydride abstracted cationic π-olefin complex $[Fe(CO)_2Cp(CH_2=CHFc)]^+BF_4^-$ which has been obtained by other routes [34]. An interesting feature of some olefinic derivatives of ferrocene is that although an olefin such as (XII) possesses a symmetry plane, its iron carbonyl derivative (XIII) does not; with the result that C–H groups in the 2–5 and 3–4 positions are diasterotopic. This is seen in the ^{13}C NMR spectra of derivatives of this type [35]. The enone derivative (XIV) prepared from the enone and $Fe_2(CO)_9$ shows this effect in both its ^1H and ^{13}C NMR spectra [36].



XII



XIII

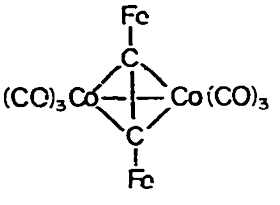


XIV

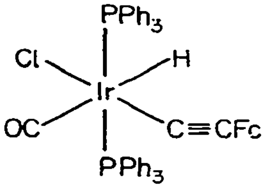
The thermal reaction of triferrocenylphosphine with $Fe(CO)_5$ yields $Fe(CO)_4(Fc_3P)$ [20] and in an analogous manner the aminophosphine complex $Fe(CO)_4(FcNP)$, where only the phosphorus is bonded to the iron, may be obtained [25]. The disubstituted derivative $Fe(CO)_3(Fc_3P)_2$ is not obtained directly from the thermal reaction but may be prepared by heating (with or without UV irradiation) the monosubstituted complex with excess ligand [37]. The photochemical reaction between Fc_3P and $Fe(CO)_5$ proceeds only at elevated temperatures and the first product is $Fe(CO)_4(Fc_3P)$. On further reaction the unusual trisubstituted complex $Fe(CO)_2(Fc_3P)_3$ is obtained by a disproportionation process not involving $Fe(CO)_3(Fc_3P)_2$. Another isomer of formula $Fe(CO)_2(Fc_3P)_3$ is obtained by heating the ligand with butadieneiron tricarbonyl. Its structure is unknown.

The iron (III) (and nickel (II)) complexes of ferrocenyl-β-diketones (VIII) have been prepared and can be used as initiators for the polymerisation of styrene [28].

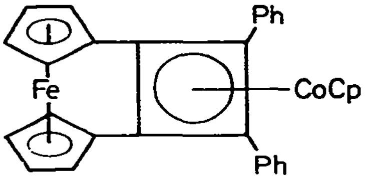
Diferrocenylacetylene reacts readily with $Co_2(CO)_8$ at room temperature to give (XV) [38] which is easily oxidized to give ferrocil, FcCOCOFc. A similar compound to (XV) can be isolated from ferrocenylacetylene [39]. It is apparently an intermediate in the trimerization reaction which affords 1,2,4-triferrocenylbenzene. Reaction of $FcC\equiv CH$ with *trans*-$Ir(CO)Cl(Ph_3P)_2$ gives the oxidative addition product (XVI) together with $FcCH=CH-C\equiv CFc$ and $FcCH=CHC(=CHFc)C\equiv CFc$. The iridium compound could not be obtained pure because of facile reductive elimination of ferrocenylacetylene [39].



XV

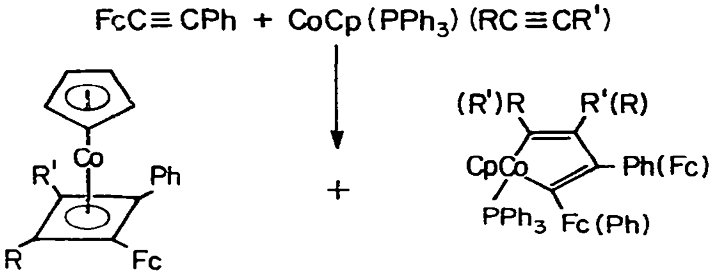


XVI



XVII

Yasufuku and Yamazaki [40] have reacted $FcC\equiv CPh$ with $CoCp(PPh_3)$ $(RC\equiv CR')$ (R, R' = Ph, CO_2CH_3) or $CoCp(PPh_3)_2$ and obtained a variety of ferrocenylcyclobutadienecobalt complexes (cf. eqns. 2 and 3). The products were identified by elemental analysis and NMR measurements. A similar reaction of 1,1'-bis(phenylethynyl)ferrocene gives (XVII). Some ad-



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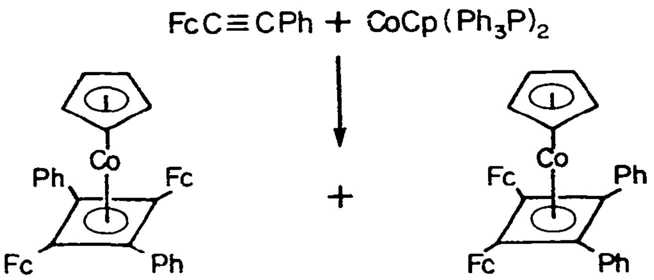
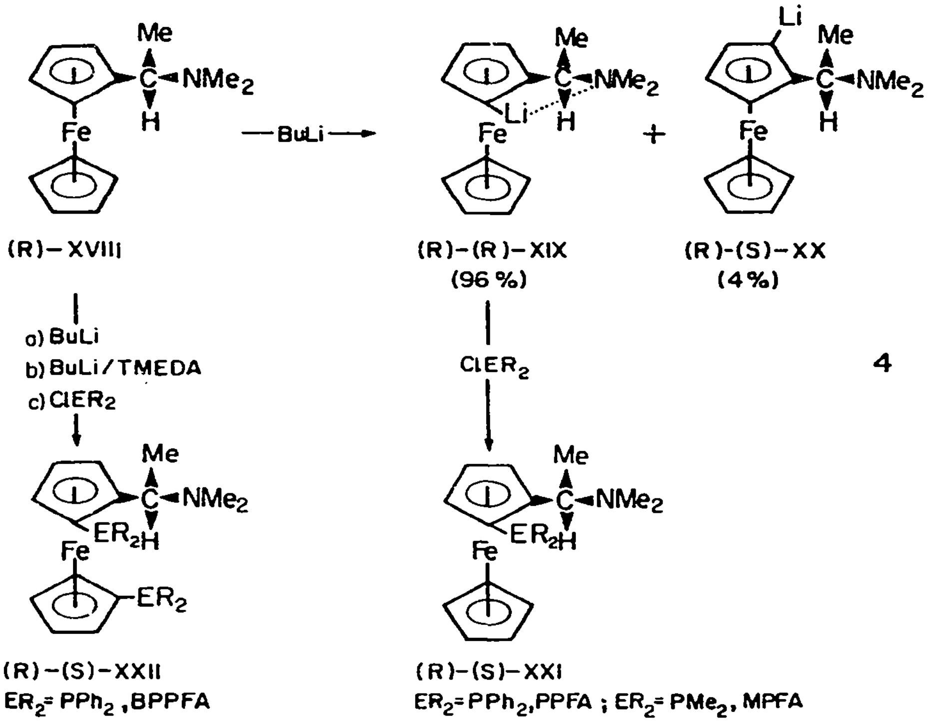


3

ducts of FcN with Group VIII MX_2 salts (M = Co, Ni; X = Cl, Br, I, CNS) have been prepared [41]. Formylferrocenethiosemicarbazole forms complexes with both Co(II) and Ni(II) [42]. Electrochemical studies revealed that the potential of the oxidation, $Fe^{2+} \rightarrow Fe^{3+}$ in the ligand, (0.45 V), was virtually unaltered upon complexation. Some phosphine complexes are known, thus $M(Fdpp)_2X_2$(M = Co, Ni, X = Cl, Br, I) were prepared by mixing the ligand and hydrated metal halide in hot 1-butanol [9]. The complexes are probably tetrahedral, an unexpected geometry in the case of the nickel derivatives. The ferrocenylphosphine complex $[Co(CO)_3(FcPh_2P)]BPh_4$ [21] is obtained from the ligand and dicobalt octacarbonyl. The potentially bidentate ligand FcNP is monodentate in a related derivative [25]. Ferrocenylphosphine adducts of the type $Co(dmg)_2(Me)L$ ($L = (Fc_xPh_{3-x}P)$ $x = 1, 2$,) have been prepared: steric hindrance apparently prevents complex formation by Fc_3P. (The ability to displace pyridine from $Co(dmg)_2(Me)py$ decreases as x increases). The cobalt–methyl resonance shifts to higher field as x increases although in general there is a poor correlation between δ(Co–Me) and the nature of the ligand.

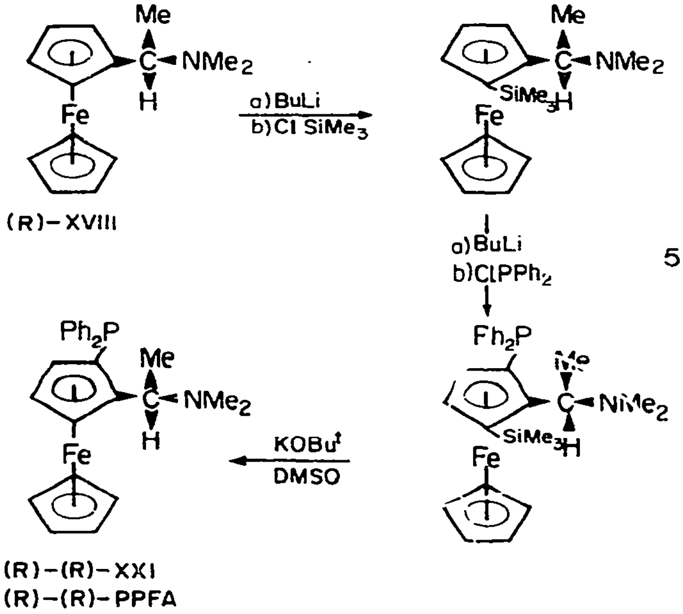
Mague and Nutt [44] have obtained several rhodium complexes of Fdma, these are listed in Table 2. The highly oxygen sensitive $[Rh(Fdma)_2]PF_6$, which forms a 1 : 1 adduct with O_2 even in the solid state, is readily prepared. Spectroscopic studies on the adducts formed by O_2, CO, SO_2 and $CNC(CH_3)_3$ indicate a considerable basicity for the Fdma ligand. Variable temperature NMR studies reveal that they are most probably fluxional, trigonal bipyramidal molecules; the rearrangements apparently coming about as a result of an opening of a chelate ring. Other adducts with CS_2, S_2 and $CF_3C \equiv CCF_3$ were prepared as was the dihydride $[RhH_2(Fdma)_2]PF_6$. This last compound, a *cis* isomer, does not react directly with hept-1-ene. Other six coordinate adducts are formed with CH_3I, CH_3SO_2Cl, Br_2, I_2 and HX, (X = Cl, Br, I). With HX (X = Cl, Br), there is evidence to suggest that a mixture of $RhH(Fdma)_2X^+$ and $Rh(Fdma)_2X_2^+$ is formed with the PF_6^- counterion being replaced, to some extent, by HX_2^-. Because of the ability of $Rh(Fdma)_2^+$ to abstract a proton from NH_4^+ a convenient way of preparing the pure HX adduct is to treat $Rh(Fdma)_2X$ with NH_4PF_6; although this procedure gives rise to two isomers depending on the reaction temperature. Triferrocenylphosphine has also been used to form a rhodium complex [45], $Rh(CO)Cl(Fc_3P)_2$, which, from its infrared spectrum, is entirely analogous to the Vallarino complex.

The remainder of the rhodium complexes have mainly been prepared for use as catalysts. Chiral ferrocenylphosphines are readily prepared by way of stereoselective lithiation of (+) or (−)-ferrocenylethyldimethylamine, eqn. 4 [46]. This lithiated derivative has been treated with a number of halophosphines [47,48] and haloarsines [47]. The resulting ligands have two



4

centres of chirality one being the asymmetric carbon atom and the other the planar element of chirality due to the ferrocene rings.



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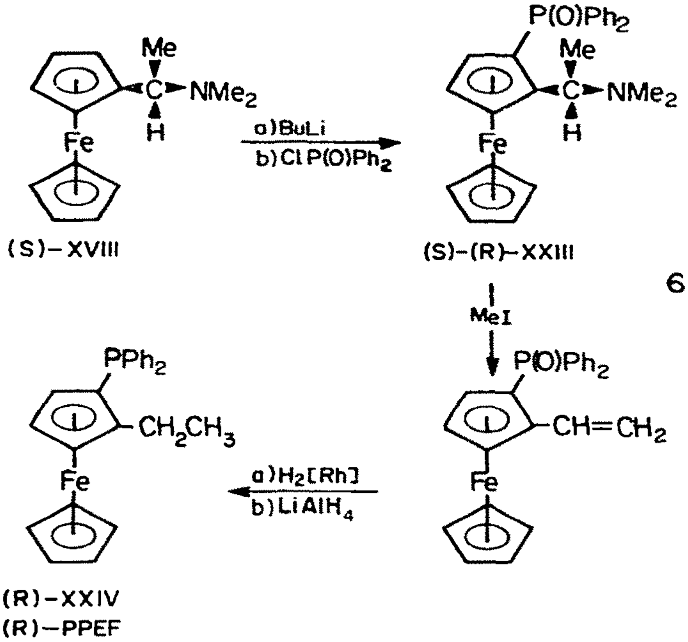
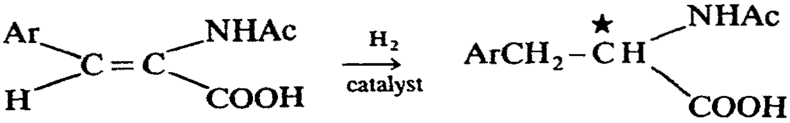
The principle ligands used to form complexes are shown in eqn. 4. Slight modification to the procedure allows the isolation of ligands containing other aryl phosphines, other amines, and the (*R*)–(*R*) (and (*S*)–(*S*)) isomers of (XXI) [49]. Modification of the alkyl group on the asymmetric carbon atom has also been reported [49,50]. A selection of these methods are illustrated in eqns. 5 and 6.



Hydrosilylation of ketones has been carried out using several of the ligands as "in situ" catalysts in the presence of $[RhCl(C_6H_{10})]_2$. Under mild conditions chemical yields as high as 89% with an optical excess of 49% were obtained using MPFA (XXI) (note the absence of phenyl groups) for the hydrosilylation of acetophenone [48]. PPFA and BPPFA (XXI and XXII) are less effective and the optical yield is lowest (5.2%) (chemical yield 88%) for the reaction of EtCOPh with Me_3SiH catalyzed by a rhodium complex of (*R*)-PPEF (XXIV) which contains only a planar element of chirality.

Reduction of α-acetamidoacrylic acids at 50 atm of H_2 occurs in 86–94% chemical yield with optical yields being as high as 93% when BPPFA (XXII) is used to prepare an in situ catalyst [51] (eqn. 7).



$$\mathrm{(Ar)(H)C{=}C(NHAc)(COOH)} \xrightarrow[\text{catalyst}]{H_2} \mathrm{ArCH_2{-}\overset{\star}{C}H(NHAc)(COOH)} \qquad (7)$$

Optical yields are lower when these substrates are hydrogenated under similar conditions using catalysts derived from modified BPPFA and PPFA

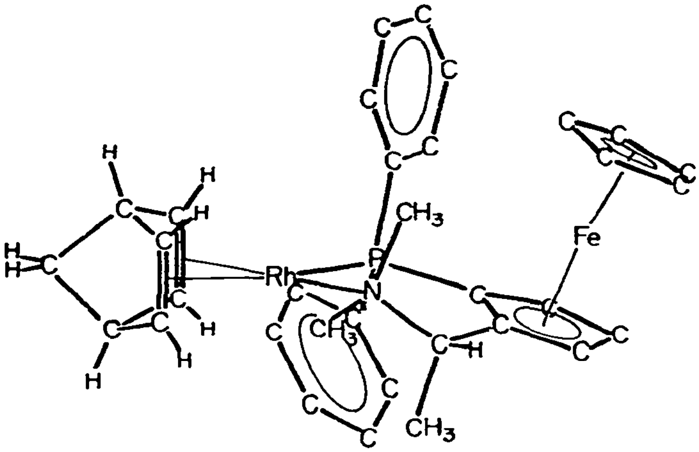


Fig. 3. The structure of [Rh(PPFA)(NBD)]ClO$_4$ [52].

(i.e. replacement of the methyl group on the chiral centre with a phenyl or an isopropyl group) [49]). When the substrate lacks an amido carbonyl group which can coordinate to the rhodium, the optical yields are very low e.g. 8% for $CH_2 = CPhCOOH$ in a Rh/BPPFA catalyzed hydrogenation at 20 atm.

Use of the complexes [Rh(diene)(+) or (−)-PPFA)]X (diene = COD, NBD; X = PF_6. BF_4, ClO_4) as catalyst precursors has enabled the reduction of α-acylaminocinnamic and acrylic acid derivatives to be carried out at 1 atm of H_2 and 32°C [47,52]. The crystal structure of $[Rh(NBD)(PPFA)]^+$ ClO_4^- has also been determined, Fig. 3, which shows that both the N and P are bound to the central metal. A mechanism was proposed to explain the chirality of the products [52] based on reaction paths offering least steric hindrance. However, in related systems, this type of argument has recently been shown to be ill-founded [53].

Recent studies on the catalytic ability of PAFA and MAFA (the arsenic analogues of PPFA and MPFA (XXI)) show that the arsines do not act as hydrogenation catalysts either in situ (in the presence of $[RhCl(NBD)]_2$) or when used as the cationic complexes [Rh(NBD)(L-L′)]ClO$_4$ [54].

A cationic complex [Rh((*R*)-(*S*)-BPPFA)(COD)]ClO$_4$ [55] has been used as the catalyst precursor in the reduction of some prochiral carbonyl compounds (the ligand is XXII with the NMe_2 group replaced by OH). At 50 atm of H_2 and 23°C, acetophenone is quantitatively reduced with an optical purity of 40%. The same catalyst is also effective in the reduction of pyruvic acid ($MeCOCO_2H$) with quantitative reaction and an optical yield of 83% being achieved in the presence of Et_3N [55]. It is believed that the OH group on the ligand is involved in the binding in the transition state although the discrimination is lower in the absence of Et_3N. Optically active

2-amino-1-arylethanols are obtained by asymmetric reduction of aminomethyl aryl ketones using the BPPFOH derived catalyst together with Et_3N [56]. An optical yield of 95% was achieved in one example.

The alcohol derived from PPFA (PPFOH) also acts as an in situ catalyst when mixed with $[RhCl(NBD)]_2$ for the hydrogenation (1 atm, 30°C) of acylaminocinnamic and -acrylic acids, but the optical yields are low (17% e.e. and 3% e.e. respectively) [54]. This result is not surprising since PPFOH is expected to be monodentate whereas PPFA is bidentate when bound to rhodium [52], Fig. 3.

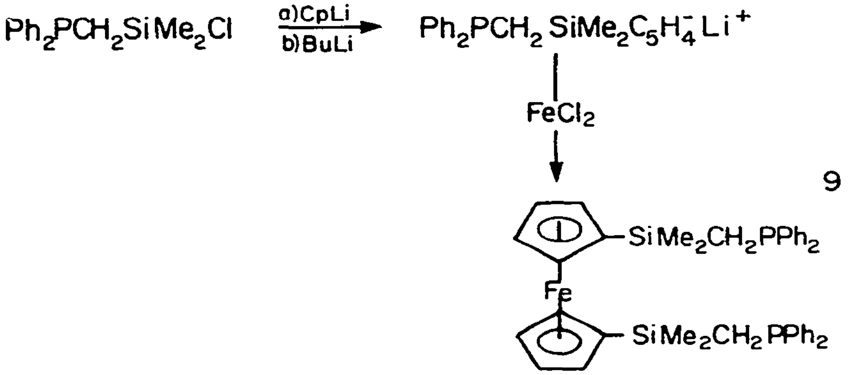
Finally Unruh et al. [57,58] have recently reported the use of in situ catalysts produced from 1,1′-bis(diarylphosphino)ferrocene (cf. IV) and rhodium complexes such as $[Rh(CO)_2Cl]_2$ (aryl = C_6H_5, p-$CH_3OC_6H_4$, p-ClC_6H_4, m-FC_6H_4, p-$CH_3C_6H_4$) as hydroformylation catalysts. It seems that the active species has three phosphorus atoms bound to each rhodium atom as would be present in the bridged species (P–P)Rh(CO)H-(P–P)Rh(CO)H(P–P). Higher rates and higher linear/branched ratios are obtained with the more basic ligands.

There are numerous examples of nickel, palladium and platinum complexes containing ferrocenyl ligands. In particular this group includes several ligands containing phosphorus or arsenic. Thus $Ni(Fdpp)X_2$ (X = Cl, Br, I) may be obtained by standard techniques [9] as described above under cobalt complexes. These compounds resemble the high spin pseudotetrahedral $Ni(Ph_3P)_2X_2$ complexes rather than the $Ni(dppe)X_2$ derivatives. The Fdma and Fdpa ligands (II) can be used to form $M(L{-}L)X_2$ complexes (M = Pd, Pt, X = Cl, Br, I) [59]. Only the Fdma complexes are easily converted to salts of the type $[M(Fdma)X]PF_6$. The NMR spectra of these Fdma derivatives are too simple for static systems and the absence of platinum satellites in some cases indicates that chemical exchange of the type shown in eqn. 8 is taking place. Treatment of anhydrous $NiBr_2$ with Fdma in hot butanol gave the unexpected derivative, $Ni(Fdma)_2Br_2$, as red brown paramagnetic crystals—suggesting a pseudo-octahedral symmetry. In contrast, the reaction of Fdpa with anhydrous NiI_2 in hot butanol gives $Ni(Fdpa)I_2$ which is paramagnetic with pseudo-tetrahedral geometry.

$$2Pt(Fdma)X^+ \rightleftharpoons Pt(Fdma)_2^+ + Pt(Fdma)X_2 + Fdma \qquad (8)$$

A related ligand (XXV) synthesized as shown in eqn. 9 yields chelated NiX_2 complexes (X = Br, Cl) which appear to be mixtures of the square planar (diamagnetic) and tetrahedral isomers [60].

The Fdma and Fdpa ligands have also been used to form chelated zero valent nickel complexes $Ni(L{-}L)(CO)_2$ by reaction with $Ni(CO)_4$ [59]. The amino-phosphine PPFA affords only the phosphorus coordinated $Ni(CO)_3(L{-}L')$ (although it is chelated in $RhCl(CO)(L{-}L')$ [52]).



XXV

When a stoichiometric amount of iodine is added to Ni(Fdpa)$(CO)_2$ in refluxing benzene the tetrahedral Ni(Fdpa)I_2 is obtained. At room temperature dark red Ni(Fdpa)$(CO)_2I_2$ and dark blue Ni(Fdma)(CO)I_2 are obtained from similar reactions [59]. These unusual complexes are examples of carbon monoxide bonded to nickel in the formal oxidation state of +2. A crystal structure determination of Ni(Fdma)(CO)I_2 shows the molecule to be a trigonal bipyramid with the chelating Fdma ligand occupying both an axial and equatorial position with the CO in the other axial position [61], Fig. 4. The ligand has the stepped conformation (IV) with a dihedral angle of 46.6° between the $NiAs_2$ and $FeAs_2$ planes. All four As–Me groups are inequivalent in the solid state although the solution NMR spectrum is simpler than that expected for this static system.

Other nickel complexes are known, for example the formylferrocenethiosemicarbazone previously mentioned [42], a FcN adduct [41] and a β-diketone complex [28].

Many interesting species containing palladium and platinum have been prepared; the majority seem to be compounds with amines in which the

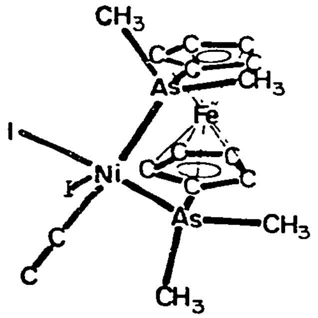
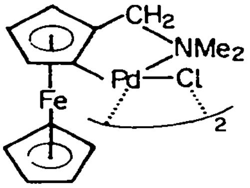


Fig. 4. The structure of Ni(Fdma)(CO)I_2 [61].

metal is bound to the nitrogen atom or has undergone a metallation reaction in addition to binding the nitrogen. Thus Moynahan et al. [63], by analogy with the work of Cope and Friedrich on benzylamine [62], attempted to prepare metallated derivatives of FcN by its reaction with K_2PdCl_4, but could only obtain the *trans*-dichlorodiaminepalladium(II) complex. Reaction of FcN as its hydrochloride salt in aqueous solution with $M_2[M'X_4]$ (M = Na, K; M' = Pd, Pt; X = Cl, CN; but not all combinations) gave compounds which were formulated as the $[FcCH_2NH(CH_3)_2]_2^+ M'X_4^{2-}$ salts on the basis of elemental analyses, IR, NMR and conductivity measurements. Gaunt and Shaw [64] later found that the expected σ-bonded species (XXVI)



XXVI

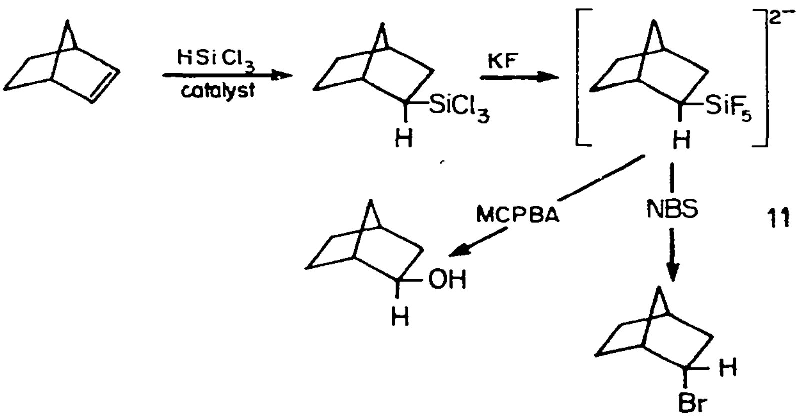
could be obtained by reaction of FcN with Na_2PdCl_4 in the presence of sodium acetate, (known to promote internal palladation). The chlorine bridged species readily reacts with thallous acetylacetonate and undergoes bridge splitting reactions with ligands such as Ph_3P but the data do not allow the distinction to be made between P *trans* to C, or *trans* to N. Following this work, Sokolov et al. reported the palladation of dimethylaminoethylferrocene (XVIII) by similar reactions [65]. If optically active amine is used the metallation occurs with a stereoselectivity of 85/15, which is rather less selective than the lithiation which goes 96/4 (eqn. 4). The optically pure palladium derivative was obtained from the mercurichloride which can be prepared via the lithiated species. Palladation of FcCHD–$N(CH_3)_2$ was also carried out to test if the chirality due to a deuterium atom is sufficient to cause stereoselectivity; only very low induction was detected [66]. It is worth noting that the optically active alcohol, which is the precursor for the amine, was obtained by enzymic reduction of the aldehyde (R = D) although the optical purity of the alcohol was not established. In eqn. 10 when R = CH_3 there is no reduction [67] but when R = CF_3, the reduction affords the alcohol in 80% yield but only 33% optical yield [67,68].

$$\text{Fc–C(O)R} \xrightarrow[\text{yeast}]{\text{fermenting}} \text{Fc–CHR–OH} \tag{10}$$

As mentioned above sodium acetate is used to catalyze palladation reactions. With this in mind Sokolov and Troitskaya [69] found that sodium salts of optically active acids such as lactic or mandelic catalyze the asymmetric cyclopalladation of FcN in low, 2.5–12.0%, enantiomeric excess. This is the first example of the introduction of planar chirality into an achiral molecule in an enantio-selective way and shows that the acid anion is directly involved in the reaction.

Several reactions of (XXVI) have been reported [70,71] and its use as an intermediate in the synthesis of 1,2-disubstituted ferrocenes proposed, however, there seems little advantage of this reagent over the lithium derivatives.

Mention has been made above of the asymmetric hydrogenation reaction catalyzed by rhodium derivatives of ferrocenyl phosphines. The palladium complex Pd((*R*)–(*S*)-PPFA)Cl_2 is a catalyst for the hydrosilylation of olefins [98]. This is a useful procedure since the products can be converted into optically active alcohols or bromides. The hydrosilylation shown in eqn. 11 proceeds in 53% chemical yield. The optical purity of the derived bromide is 53% and that of the alcohol is similar.



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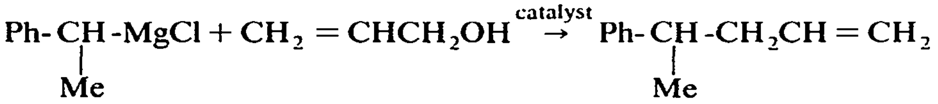
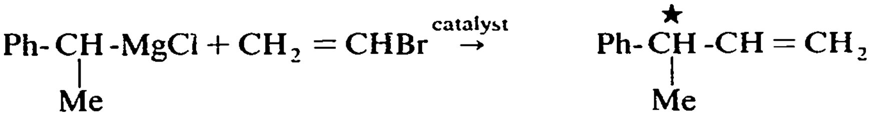
Palladium phosphine complexes are well known to catalyze cross coupling reactions between organometallic compounds and alkyl or aryl halides. Kumada and co-workers [72] have found that Pd(Fdpp)Cl_2 is particularly effective as a catalyst for coupling sec-butylmagnesium chloride with 2-bromopropene, bromobenzene or β-bromostyrene. The reactions go easily in high yield and are selective. The ligand apparently retards the β-elimination processes which result in side reactions and which occur when other Pd(L–L)Cl_2 complexes are used (L–L = dppb > dppp > dppe; the order being given in decreasing effectiveness). The same catalyst can be used to couple Grignard reagents with allylic alcohols [73] in high yield (91% for the example given) and without isomerization. Again the ferrocene derivative is better than others such as Pd(dppb)Cl_2. When other allyl alcohols such as 2-buten-2-ol are coupled with the same Grignard reagent a mixture is obtained indicating that coupling occurs through π-allyl palladium intermediates.



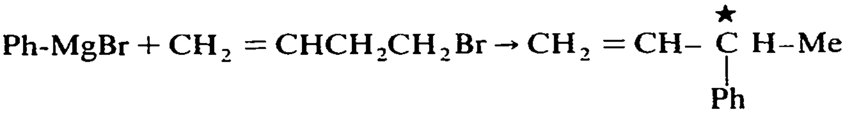
$$\text{Ph-}\underset{\text{Me}}{\underset{|}{\text{CH}}}\text{-MgCl} + CH_2=CHCH_2OH \xrightarrow{\text{catalyst}} \text{Ph-}\underset{\text{Me}}{\underset{|}{\text{CH}}}\text{-}CH_2CH=CH_2 \qquad (12)$$

In situ catalysts formed from $NiCl_2$ and optically active ligands such as PPFA can be used to couple Grignard reagents with vinyl bromides [74]. The chemical yield is high (> 83%) and the optical yield is also appreciable being in the range 52–83% for the ferrocene ligand containing both N and P. It is worth noting that only planar chirality is necessary since (*S*)-1-[(dimethylamino)methyl]-2-(diphenylphosphino)ferrocene (XXI with an achiral CH_2NMe_2 group) gives a product with 60% *S* configuration.



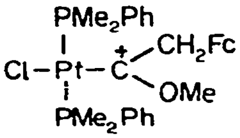
$$\text{Ph-}\underset{\text{Me}}{\underset{|}{\text{CH}}}\text{-MgCl} + CH_2=CHBr \xrightarrow{\text{catalyst}} \text{Ph-}\underset{\text{Me}}{\underset{|}{\overset{\bigstar}{\text{CH}}}}\text{-}CH=CH_2 \qquad (13)$$

Coupling reactions between a Grignard reagent and allyl bromide are also catalyzed by the same nickel-containing in situ catalysts [75]. The product is the same as in eqn. 13 but the optical yields (actually enantiomers are isolated) are halved for a given optically active ferrocene derivative as ligand.

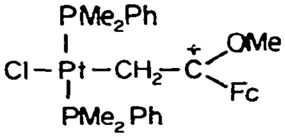


$$\text{Ph-MgBr} + CH_2=CHCH_2CH_2Br \rightarrow CH_2=CH\text{-}\underset{\text{Ph}}{\underset{|}{\overset{\bigstar}{\text{C}}}}\text{H-Me} \qquad (14)$$

Other complexes involving palladium or platinum include a *β*-diketone derivative [4] and *trans*-$PtCl(Me_2PhP)_2(FcC\equiv C)$ which was prepared [76] to enable a comparison of the relative thermodynamic stabilities of platinum and ferrocenyl stabilised carbonium ions (XXVII) and (XXVIII) which could be derived from it by reaction with HPF_6 in methanol. It seems that (XXVII) is the only product on the basis of NMR measurements.



XXVII

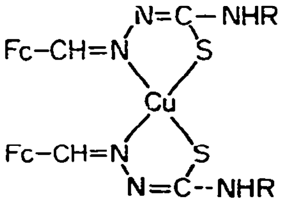


XXVIII

F. GROUP I

In 1958 Hauser and Cain [77] reported copper(II) complexes of the mono- and bis-*β*-diketones $FcCOCH_2COPh$ (VIII, R = Ph) and $Fe(C_5H_4$-

$COCH_2COPh)_2$. The 1 : 1 complex of the bis-diketone is monomeric. The mono-β-diketone complex is believed to have a similar structure to (XXIX) obtained from a range of formylferrocenethiosemicarbazones [78]. This type of ligand also gives (1 : 1) copper(II) complexes [42].



XXIX

Copper [79] or silver iodide [80] react with 2-lithio(dimethylaminomethyl)-ferrocene to give isostructural compounds of known crystal structure, Fig. 5. The metal atoms form an essentially planar square with the substituted cyclopentadienyl rings acting as bridging ligands through almost coplanar carbon atoms. The nitrogen atoms have little interaction if any, with the silver or copper atoms since, for example the shortest Ag----N distance is 2.94 Å. For the silver compound there is some possibility of Fe----Ag interaction since this distance, 3.09 Å, is not much longer than the sum of the single bonded radii (2.79 Å for Ag, 1.34 Å for Fe). However, the copper compound has a Cu–Fe distance of 2.94 Å; the sum of the radii being 2.69 Å. The Ag–Ag distance is 2.74 Å, considerably shorter than that seen in silver metal, and the Cu–Cu distance is 2.44 Å.

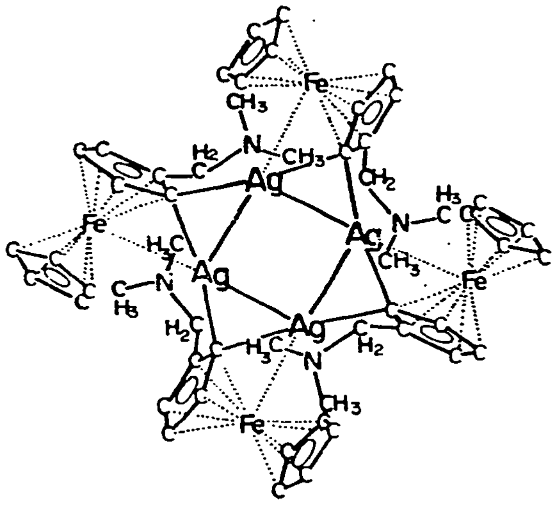
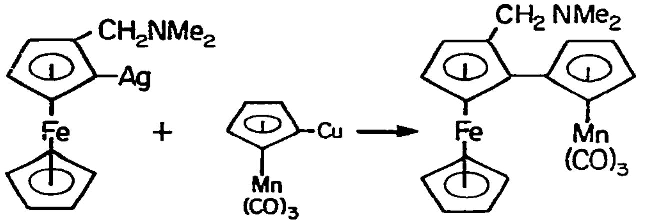


Fig. 5. The structure of $Ag_4(FcCH_2NMe_2)_4$ [80].

A number of reactions of both the silver and copper derivatives have been described, in particular their chemical decomposition in the presence of other metal derivatives which can lead to coupled products (for example eqn. 15).



15

Ferrocenyl(triphenylphosphine)gold may be obtained in 81% yield by reaction of ferrocenyllithium with chloro(triphenylphosphine)gold [81]. The air stable Au(Fc)(Ph_3P) reacts with HX (X = Cl, I, CN) to form ferrocene and Au(Ph_3P)X and with halogens to give haloferrocene [82]. Biferrocenyl is also formed during the reaction with chlorine and bromine, indicating that in these cases the iron is first attacked. Treatment of FcAu(PPh_3) with tetracyanoethylene affords ferrocenyltricyanoethylene and cyano(triphenylphosphine)gold [83].

In other studies with Au(Fc)(Ph_3P), Grandberg et al. [84] found that in benzene solution it reacts with $[CH_2=CHAuPPh_3-Au-PPh_3]^+BF_4^-$, a reagent that transfers the $Au-PPh_3^+$ group, to give [ferrocenyl(triphenylphosphine)gold]triphenylphosphinegold tetrafluoroborate in 89% yield. The struc-

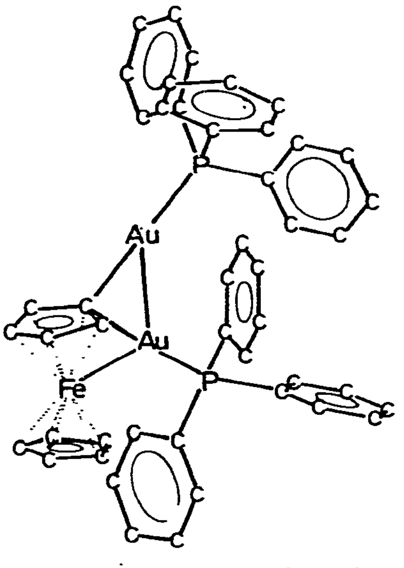
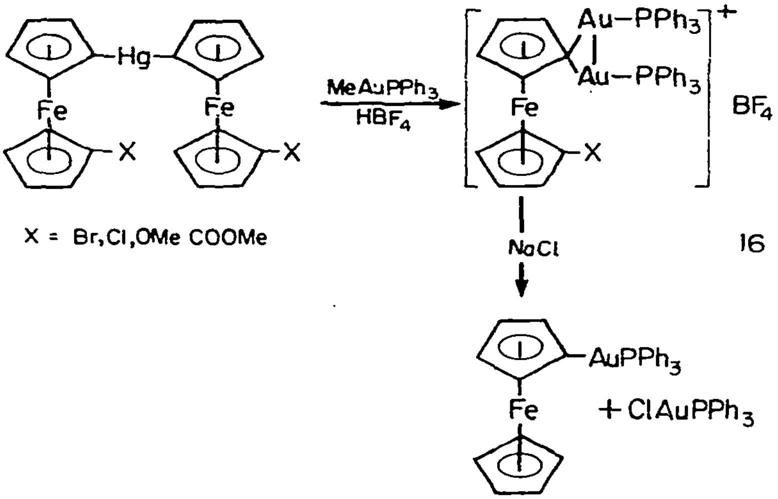


Fig. 6. The structure of the cation of $[Au_2(Fc)(Ph_3P)_2]BF_4$ [86].

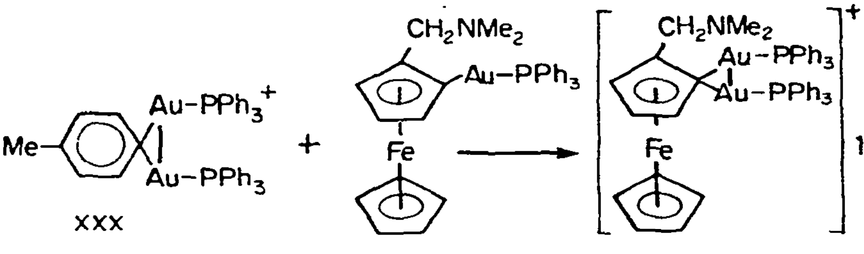
ture of this compound was determined by X-ray crystallography [85,86], Fig. 6. The unique features of this interesting compound are a gold atom which seems to be bonded to iron (Au–Fe bond distance 2.82 Å) and a C_5H_4 ring which acts as a bridge between the two gold atoms. The gold–iron interaction does not distort the ferrocene system very much either geometrically or electronically, the dihedral angle between the cyclopentadienyl rings being only 13°, whilst the Mössbauer shift of the iron is typical of ferrocene and its derivatives.

Direct auration of ferrocene using $[(Ph_3PAu)_3O]^+BF_4^-$ yields the same cation seen in Fig. 6 [96], and the unusual exchange of mercury by gold gives related complexes, eqn. 16. Cations with a second substituent on the gold substituted ring can be prepared by other $AuPPh_3^+$ transfer reactions, e.g. eqn. 17. The *p*-tolyl reagent (XXX) also reacts with the mercury derivative in eqn. 16 to give the same product. The methyl group of acetylferrocene is also aurated (5% yield) by treatment with $[(PPh_3Au)_3O]MnO_4$ [87].

Phosphorus ligands with more electron donor ability such as $FcPh_2P$ and Fc_3P can be used to replace Ph_3P in the gold complex $Au(Ar)(Ph_3P)$ [88].



16



17

The alkyl derivative Au(Me)(Fc_3P) has similar chemistry to the Ph_3P analogue [88]. It may also be reacted with vinyl mercury to give the appropriate vinyl gold compound without loss of configuration [89]. Compounds like AuBrL (L = Fc_2PhP, Fc_3P) are prepared by direct reaction of the phosphine with aurous bromide [90]. These complexes may be oxidised by treatment with Br_2 to $AuBr_3L$ or with chloroauric acid to the ferrecinium compound $[AuBrL]^+[AuCl]^-$.

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