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TRANSITION METAL DERIVATIVES OF 1,1'-DICHLOROFERROCENE

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SUMMARY

Complexes of the general formula $[Cl_2Fc]_nML$, ($Cl_2Fc = ClC_5H_4FeC_5H_3Cl$; $ML = Fe(CO)_2C_5H_5$, $AuP(C_6H_5)_3$, $Mn(CO)_5$ or $Ir(CO)[P(C_6H_5)_3]_2$ when n = 1; $ML = Ti(C_5H_5)_2$ when n = 2) have been prepared from a salt elimination reaction between 1,1'-dichloro-2-lithioferrocene and transition metal halide complexes. Spectroscopic properties of the compounds are reported. The titanium complex exists in *meso* and *dl* forms.

Studies on the chemistry of metal to carbon σ-bonds have occupied an important place in transition metal chemistry because of the role such linkages play in many catalytic processes. In recent years particular success has been achieved in obtaining stable metal alkyl complexes by the use of ligands such as the trimethylsilylmethyl group. Ligands of this type impart good thermal stability to the complexes by hindering or even precluding several common decomposition pathways. Two of the factors contributing to the increased stability of complexes involving the trimethylsilylmethyl ligands are the steric size of the group and the inability of the group to undergo β-elimination reactions.[1] Metallocene ligands possess both these features and they also offer the possibilities of forming σ-bonds to elements using one or both of the C_5 rings, in a monodentate or chelating linkage.

In the case of some gold complexes of ferrocene it has been shown that when the ring attached to the gold atom carries a substituent in the 2-position, an enhanced stability over the unsubstituted complex results.[2] As part of a general study of metallocene chemistry[3-6] we have prepared some transition metal derivatives of 1,1'-dichloroferrocene.

RESULTS AND DISCUSSION

In contrast to bromo- and iodoferrocene derivatives, chloroferrocene compounds react with n-butyl lithium to undergo metal hydrogen exchange rather than metal halogen exchange. It has been shown that an n-butyl lithium and N,N,N',N'-tetramethylethylenediamine mixture in hexane dilithiates 1,1'-dichloroferrocene at the 2- and 2'-positions.[7] We have studied the lithiation of 1,1'-dichloroferrocene in tetrahydrofuran and find that this is a convenient way of producing a monolithiated product in good yield. Deuteration of the lithiation mixture and examination of the ^1H n.m.r. spectrum of the product showed that metallation had occurred at the 2-position. A typical product composition of a deuteration experiment, determined by mass spectroscopy, was 1,1'-dichloromonodeuteroferrocene (88%), 1,1'-dichloroferrocene (6%), and approximately equal amounts (2%) of di-, tri- and tetradeuterated 1,1'-dichloroferrocene.

All the compounds were prepared by the same general method, namely addition of the transition metal halide complex to a tetrahydrofuran solution of 1,1'-dichloro-2-lithioferrocene. They were all sufficiently stable to be purified by dry-column chromatography[8] on alumina and were isolated as crystalline solids. The gold, manganese and titanium complexes were stable in air whereas the iron and iridium complexes were found to be mildly air-sensitive. This contrasts with the unstable nature of ferrocene complexes of gold and titanium.[2,9] Reaction yields, melting temperatures, colours and analytical data are listed in Table I.

With the exception of the iridium complex, which undergoes decomposition before volatilisation, the compounds all show a molecular ion in the mass spectrometer; the observed isotopic patterns being in

TABLE I

REACTION YIELDS, PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR 1,1'-DICHLOROFERROCENE COMPLEXES

Compound	Yield/%	Melting temperature/°C	Colour	Analysis Results[(a)]			
				C	H	Cl	P
$Cl_2FcAuPPh_3$	74	163-166	Orange	47.1(47.2)	3.4(3.1)	10.2(9.9)	4.5(4.3)
$Cl_2FcMn(CO)_5$	49	82-83	Orange	40.9(40.1)	1.7(1.6)	15.9(15.8)	
$Cl_2FcFe(CO)_2Cp$	32	106-107	Orange	47.5(47.4)	3.0(2.8)	16.7(16.5)	
$Cl_2FcIr(CO)(PPh_3)_2$	10	117-119 dec.[(b)]	Orange-brown	56.2(56.5)	4.0(3.7)	7.4(7.1)	6.2(6.2)
$(Cl_2Fc)_2TiCp_2$	59	60-80[(c,d)]	Very dark blue-green	52.4(52.5)	3.8(3.5)	20.9(20.7)	

Cl_2Fc = 1,1'-dichloroferrocenyl $Cp = \eta\text{-}C_5H_5$ $Ph = C_6H_5$

(a) calculated figures are in parenthesis. (b) sealed under vacuum. (c) the material sinters before melting.

(d) *meso/dl* mixture.

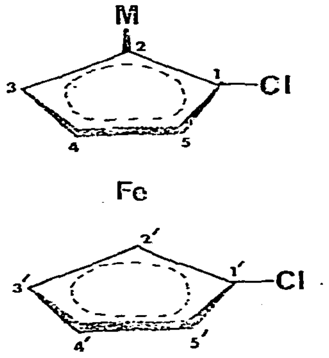

Fig. 1. Numbering scheme for the 1,1'-dichloroferrocene derivatives.

good agreement with theory. The structures of the compounds are straightforward, with the metal atom bonded to the 2-position of the 1,1′-dichloroferrocene group (Fig. 1). However, the introduction of a substituent at the 2-position makes the resulting molecule asymmetric and thus the gold, manganese, iron and iridium complexes should be racemic mixtures, and there are two possible isomers of the titanium complex, a *meso* and a *dl* form (Fig. 2).

^{1}H and ^{13}C n.m.r. data for the complexes and for 1,1'-dichloroferrocene are listed in Tables II and III respectively using the numbering scheme shown in Fig. 1. The assignments have been made by a combination of intensity measurements, analogies to 1,1'-dichloroferrocene, and selective ^{1}H decoupling measurements. In the ^{13}C n.m.r. spectra of all the compounds the influence of the metal atom causes downfield shifts of the signals of the carbon atoms of the ring bonded to the metal. The C_2 signal generally experiences the largest shift but there is considerable variation in the magnitude of this shift amongst the complexes, ranging from 9 ppm for the manganese compound to 55 ppm for the titanium isomers. There is much less variation in the shifts experienced by the C_1 and C_3 signals. In any given complex both signals experience a similar shift which ranges from an

TABLE II

^1H N.M.R. DATA FOR 1,1'-DICHLOROFERROCENYL TRANSITION METAL COMPLEXES[a,b,c]

Compound	Chemical Shifts (δ/ppm)					
	H_3	H_4	H_5	$H_{2',5'}$	$H_{3',4'}$	Other signals
$(C_5H_4Cl)_2Fe$	4.14(t)	4.14(t)	4.44(t)	4.44(t)	4.14(t)	
$Cl_2FcAuPPh_3$	4.00	4.22	4.57	4.42	4.11	C_6H_5 : 7.4 - 7.8
$Cl_2FcMn(CO)_5$	3.87	4.28	4.62	4.37	4.02	
$Cl_2FcFe(CO)_2Cp$[d]	3.78	4.09	4.45	4.27	3.94	C_5H_5 : 4.61(s)
$Cl_2FcIr(CO)(PPh_3)_2$	4.27	4.36	4.57	4.10	3.92	C_6H_5 : 7.0 - 7.7
meso-$(Cl_2Fc)_2TiCp_2$	3.54	4.10	4.42	4.42	4.10	C_5H_5 : 6.18(s), 6.62(s)
dl-$(Cl_2Fc)_2TiCp_2$	3.98	4.10	4.42	4.42	4.10	C_5H_5 : 6.35(s)

Cl_2Fc = 1,1'-dichloroferrocenyl Cp = η-C_5H_5 Ph = C_6H_5 .

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[a] $CDCl_3$ solution unless otherwise stated, δ(TMS) = 0. [b] All signals were complex multiplets unless otherwise stated; (s) = singlet, (t) = triplet. [c] Signal intensities were all in accordance with theory. [d] CD_2Cl_2/C_6D_6 (3:1 v/v) solution.

TABLE III

^{13}C N.M.R. DATA FOR 1,1'-DICHLOROFERROCENYL TRANSITION METAL COMPLEXES[a]

Compound	Chemical shifts[b]								Other signals
	C_1	C_2	C_3	C_4	C_5	$C_{1'}$	$C_{2',5'}$	$C_{3',4'}$	
$(C_5H_4Cl)_2Fe$[c]	93.1	69.9	68.3	68.3	69.9	93.1	69.9	68.3	
$Cl_2FcAuPPh_3$	101.7	104.8 (122)	76.9 (4)	70.6 (6)	70.9 (5)	93.5	69.2,69.5	68.0,68.0	C_6H_5 : C_1 131.1 (52); $C_{2,6}$ 134.6 (14); $C_{3,5}$ 129.4 (11); C_4 131.5 (2)
$Cl_2FcMn(CO)_5$[d]	104.2	79.3	80.2	69.4	72.2	93.1	71.6,71.7	69.8,71.0	CO: 209.4[30 °C]; 207.7(*trans*) 209.1(*cis*) [-55 °C]
$Cl_2FcFe(CO)_2Cp$[d]	105.4	84.9	80.3	70.5	71.3	93.5	69.7,71.5	70.2,70.8	CO: 215.8, 216.0; C_5H_5: 86.0
meso-$(Cl_2Fc)_2TiCp_2$[d]	99.8	125.3	75.4	-	-	93.2	$C_{5,2',5'}$ $C_{4,3',4'}$	69.1,71.0,72.2 69.2,69.5,70.0	C_5H_5 : 115.6, 116.4
dl-$(Cl_2Fc)_2TiCp_2$[d]	100.2	124.4	73.3	-	-	93.3	$C_{5,2',5'}$ $C_{4,3',4'}$	69.1,71.0,72.2 68.7,69.0,69.9	C_5H_5 : 117.1

Cl_2Fc = 1,1'-dichloroferrocenyl Cp = η-C_5H_5 Ph = C_6H_5

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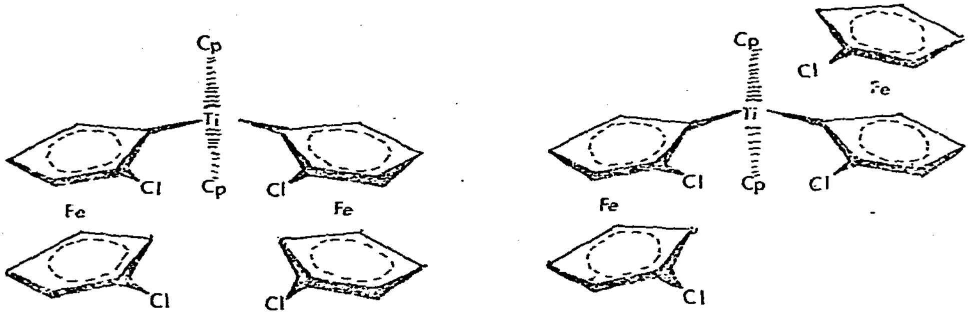
[a] CH_2Cl_2/C_6D_6 (3:1 v/v) solution unless otherwise stated. [b] Values are in ppm downfield from TMS; figures in brackets are coupling constants, $J(^{31}P-^{13}C)$/Hz. [c] $CDCl_3$ solution. [d] $Cr(acac)_3$ (25 mg) was added to the solution.



meso form

dl form

Fig. 2. Diastereoisomers of $(Cl_2Fc)_2TiCp_2$

average of 6 ppm for the *dl* titanium compound to 12 ppm for the iron compound. In all the complexes the C_4 and C_5 signals experience very small shifts of only one or two ppm.

<u>$Cl_2FcAuPPh_3$</u>

The ^1H n.m.r. spectrum (cyclopentadienyl region) of the gold complex is shown in Fig. 3. In the ^{13}C n.m.r. spectrum C_2, C_3, C_4 and C_5 are coupled to the phosphorus atom with C_2 showing the largest coupling (122 Hz).

<u>$Cl_2FcMn(CO)_5$</u>

Here the distortion from regular C_{4v} symmetry is indicated by the infrared spectrum in the carbonyl region (hexane solution) showing five bands; 2120 (medium), 2057 (weak), 2027 (strong), 2024 (shoulder), 2000 (strong) cm^{-1}. The magnitude of the E mode splitting (3 cm^{-1}) is similar to that shown by other complexes of this type.[10] In the ^{13}C n.m.r. spectrum at 30 °C the carbonyl groups showed a broad signal at 209.4 ppm. On cooling the solution to −55 °C this signal was resolved into peaks at 209.1 and 207.7 ppm corresponding respectively to the carbonyl groups *cis* and *trans* to the 1,1'-dichloroferrocenyl group. Behaviour of this type has been observed for benzylpentacarbonylmanganese and has been attributed to thermal decoupling of the quadrupolar manganese nucleus.[11]

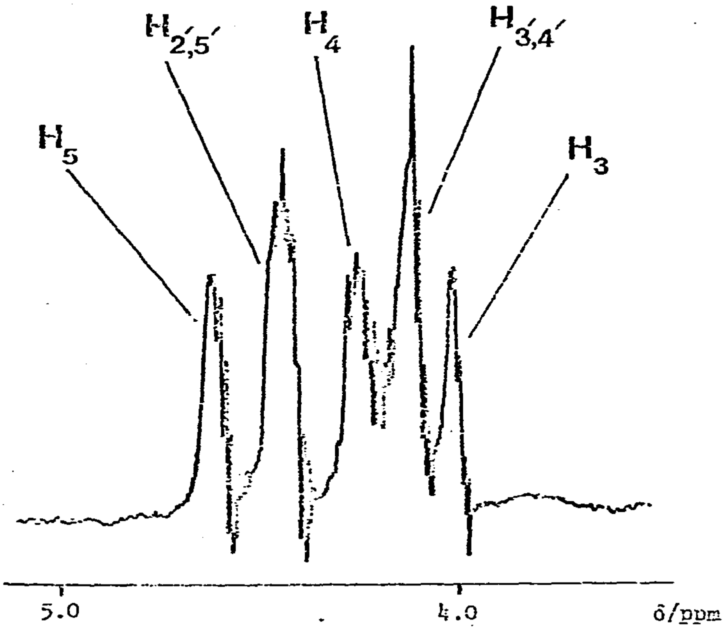


Fig. 3. Cyclopentadienyl signals in the ^{1}H n.m.r. spectrum of $Cl_2FcAuPPh_3$.

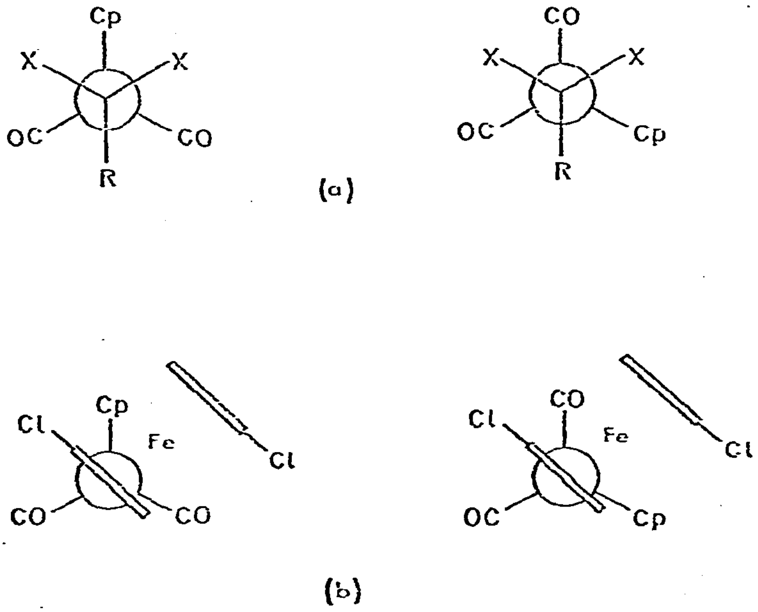


Fig. 4. Conformational isomers of

a) $Cp(CO)_2FeAX_2R$ and b) $Cp(CO)_2FeCl_2Fc$

$Cl_2FcFe(CO)_2Cp$

The infrared spectrum of this compound (hexane solution) showed two strong carbonyl bands (2029 and 1979 cm^{-1}) which is a common property of compounds of this type.[12] However, four carbonyl bands have been observed in the infrared spectra of compounds such as $Cp(CO)_2FeAX_2R$ (A = C, X = H, R = C_6H_5, $CH_2C_6H_5$ or $SiMe_3$; A = Si or Ge, X = Cl, R = Me) and it is considered that such compounds exist in solution as a mixture of rapidly interconverting conformational isomers[13] (Fig. 4a). Similar isomerism is possible for $Cp(CO)_2FeCl_2Fc$ (Fig. 4b) but the infrared spectrum does not provide any evidence for its occurrence. ^{13}C n.m.r. data have been published for a number of complexes of type $Cp(CO)_2FeX$, but in all cases only a single carbonyl chemical shift was observed.[14] However, for $Cp(CO)_2FeCl_2Fc$ carbonyl signals were seen at 215.8 and 216.0 ppm, arising from the lack of a plane of symmetry relating the two carbonyl groups.

In a study of eighteen compounds of the general formula $Cp(CO)_2FeX$, the carbonyl ^{13}C n.m.r. chemical shift was found to be linearly dependent on both the carbonyl infrared stretching frequencies and on the Taft σ_1 inductive reactivity value of the group X.[15] Extending this study to include $Cp(CO)_2FeCl_2Fc$ the correlations between $\delta(^{13}C)CO$ and the carbonyl i.r. stretching frequencies were found to hold, and the values of the relevant parameters indicated that the inductive nature of Cl_2Fc was close to that of *p*-ClC_6H_4, with $\sigma_1 = 0.15$.

$(Cl_2Fc)_2TiCp_2$

Because of the chiral nature of the 2-substituted 1,1'-dichloroferrocenyl group, the titanium compound can exist in *dl* and *meso* forms (Fig. 2), which are easily distinguished by differences in the ^1H n.m.r. spectra of the η-C_5H_5 groups; in the *meso* case the two η-C_5H_5 groups are not equivalent and so two signals are observed. Under the preparative conditions used the product was a mixture of approximately equal amounts of the two forms, but by extraction of the mixture with hexane-dichloromethane (9:1 v/v) it was possible to leach out most of the more soluble *dl* isomer.

EXPERIMENTAL

^{1}H n.m.r. spectra were recorded at 100 MHz using a Jeol MH 100 spectrometer. ^{13}C n.m.r. spectra were recorded at 25 MHz using a Jeol PS/PFT 100 spectrometer. Mass spectra were recorded on a Hitachi-Perkin Elmer RMU 6 instrument. Solution infrared spectra were recorded on a Perkin Elmer 357 spectrophotometer. Analyses were obtained from the Exeter University departmental service or from Butterworth Laboratories, Teddington, Middlesex. All solvents were dried and degassed before use and all reactions were carried out under purified nitrogen.

1,1'-dichloroferrocene was prepared by a literature method.[16]

Lithiation of 1,1'-dichloroferrocene and subsequent deuteration

1,1'-dichloroferrocene (255 mg, 1.0 mmol) was dissolved in tetrahydrofuran (15 cm^3) in a Schlenk tube (50 cm^3). n-Butyl lithium (1.22 mmol) was syringed into the stirred solution and an immediate colour change from yellow to orange was observed. After 80 minutes, deuterium oxide (0.2 cm^3, 11 mmol) was added and the solution stirred for 10 minutes. The solution was dried over $MgSO_4$, filtered, and the solvent removed under vacuum. The solid residue was dissolved in hexane, subjected to dry-column chromatography, (Al_2O_3 Grade II), followed by crystallisation from hexane (95% recovery).

Preparation of transition metal derivatives

$Cl_2FcAuPPh_3$

1,1'-dichloroferrocene (255 mg, 1.0 mol) was dissolved in THF (25 cm^3) in a Schlenk tube (100 cm^3) and n-butyl lithium (1.0 mmol) was added to the stirred solution. After one hour the solution was cooled to −78 °C and chloro(triphenylphosphine)gold(I) (0.40 g, 0.81 mmol) was added. The mixture was allowed to warm to room temperature and stirred for a further 20 hours. The resulting dark orange-brown solution was poured into benzene (50 cm^3), washed several times with water, dried over K_2CO_3, filtered, and evaporated to leave an orange-brown oil. The oil was purified by dry-column chromatography, (Al_2O_3 Grade II) using hexane as eluent. After 1,1'-dichloroferrocene had been eluted, an orange band was scraped from the column and the product extracted into benzene. Evaporation of the benzene and recrystallisation of the residue from hexane gave the product as orange needles. Yield 426 mg (74%).

$Cl_2FcMn(CO)_5$

A solution of 1,1'-dichloro-2-lithioferrocene (2.0 mmol), prepared as described above, was stirred and cooled to -78 °C. Bromopentacarbonylmanganese(I) (0.65 g, 2.4 mmol) was added to the solution which was stirred for 18 hours after it had warmed to room temperature. The reaction mixture was worked-up as described above and the crude product was purified by dry-column chromatography (Al_2O_3 Grade II). Hexane eluted a yellow band containing 1,1'-dichloroferrocene and decacarbonyldimanganese(0), followed by an orange band containing the product which was crystallised from hexane. Yield 438 mg (49%).

$Cl_2FcFe(CO)_2Cp$

The iron complex was prepared from 1,1'-dichloro-2-lithioferrocene (1.0 mmol) and dicarbonyl-(η-cyclopentadienyl)iodoiron(II) (335 mg, 1.1 mmol) as described above. The crude product was purified by dry-column chromatography (Al_2O_3 Grade II). Hexane eluted 1,1'-dichloroferrocene and a mixture of hexane:benzene (4:1, v/v) eluted an orange band containing the product (found to be light-sensitive whilst on the column), which was crystallised under a nitrogen atmosphere from hexane. Yield 138 mg (32%).

$Cl_2FcIr(CO)(PPh_3)_2$

The iridium complex was prepared from 1,1'-dichloro-2-lithioferrocene (2.0 mmol) and *trans*-carbonylchlorobis(triphenylphosphine)iridium(I) (1.56 g, 2.0 mmol) as described above for the preparation of the iron complex, with the exception that diethylether was used to elute the product from the column instead of benzene:hexane. Crystallisation from diethylether under a nitrogen atmosphere gave 207 mg (10%) of light orange-brown mildly air-sensitive crystals.

$(Cl_2Fc)_2TiCp_2$

A mixture of the *dl* and *meso* isomers was prepared from 1,1'-dichloro-2-lithioferrocene (4.0 mmol) and dichlorobis(η-cyclopentadienyl)titanium(IV) (450 mg, 1.8 mmol) as described above. The crude product was purified by dry-column chromatography (Al_2O_3 Grade II). Hexane eluted 1,1'-dichloroferrocene, then a mixture of hexane:benzene (7:3, v/v) was used to elute a diffuse dark blue band containing the product. Crystallisation from hexane gave a very dark blue-green (almost black) solid. Yield 731 mg (59%).

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