Notes

Synthesis and Structural Studies of some 1,1′-Dichloroferrocene Derivatives of Platinum(II). Crystal and Molecular Structure of 2,2-μ-[(1—2,5—6-η-*cis,cis*-Cyclo-octa-1,5-diene)platinio]-bis(1,1′-dichloroferrocene)†

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The synthesis and characterisation of complexes of platinum, of the general formula [Pt(cod)-{Fe(C_5H_4Cl)(C_5H_3Cl)}L] [cod = *cis,cis*-cyclo-octa-1,5-diene; L = Cl, Br, I, CH_3, CH_2Ph, or Fe(C_5H_4Cl)(C_5H_3Cl)], are reported. A single-crystal *X*-ray structure determination of [Pt-(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$] (*R* = 0.0485 for 2 553 independent reflections) showed a DL arrangement of the ferrocenyl groups, with a single crystal consisting of molecules of one enantiomer.

Following the recognition of the β-hydrogen elimination decomposition pathway, particular success in obtaining stable metal–alkyls has been achieved by using β-hydrogen-free ligands such as benzyl or trimethylsilylmethyl.[1] Metallocene ligands should show a much reduced tendency to undergo β-hydrogen elimination compared with alkyl groups and they also offer the possibilities of forming σ bonds to metals using one or both of the cyclopentadienyl rings, *i.e.* in a monodentate or chelate linkage. We now report the synthesis and reactions of a series of mono- and bis-1,1′-dichloroferrocenyl derivatives of platinum(II) and the crystal and molecular structure of 2,2-μ-[(η-*cis,cis*-cyclo-octa-1,5-diene)platinio]-bis(1,1′-dichloroferrocene).

Results and Discussion

The compounds [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}L] [L = Fe(C_5H_4Cl)(C_5H_3Cl), CH_3, or CH_2Ph; cod = *cis,cis*-cyclo-octa-1,5-diene] were prepared by salt-elimination reactions between 2-lithio-1,1′-dichloroferrocene and halogenoplatinum complexes. They were all sufficiently stable to be purified by dry-column chromatography and were isolated as orange crystalline solids. In the mass spectra the compounds all show molecular ions, often as the most abundant species, and always with good agreement of the isotope pattern with theory. The reaction yields, melting temperatures, and analytical data for the compounds are listed in Table 1.

The mono-1,1′-dichloroferrocenyl platinum compounds, [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}X] (X = Cl, Br, or I), were best prepared from [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$]. Addition of hydrogen chloride, generated *in situ*, to [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$] produced [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}Cl]; the bromo-derivative was then readily prepared by a metathetical reaction with potassium bromide. The iodo-compound was best prepared by the reaction of iodine with [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$]. This type of reaction with iodine has been observed[2] for compounds of the type [Pt(cod)R_2] where R is a bulky group, *e.g.* R = CH_2SiMe_3.

A previous report[3] of some ferrocenyl platinum compounds described the reaction of [Pt(cod)Cl_2] with trimethylstannylferrocene, which yielded the compound [Pt(cod){Fe(C_5H_5)(C_5H_4)}Cl] even when an excess of the tin reagent was used. This contrasts with our results where the bis-1,1′-dichloroferrocene compound is the preferred product.

All the ^1H n.m.r. spectra contain a number of complex multiplets in the range δ 3.45—5.0 for the cyclopentadienyl protons, and in each case the H^3 proton is coupled to platinum (^3J = 20—32 Hz). In the cyclopentadienyl ring to which Pt is attached, C^1, C^2, and C^3 experience downfield shifts compared with 1,1′-dichloroferrocene; C^2 shows the largest shift, being in the range 19.06—26.8 p.p.m. The C^1–C^5 atoms are all coupled to platinum, the largest coupling being to C^2 with $J(^{195}Pt–C)$ in the region of 1 200 Hz. This compares with values in the region of 1 100 Hz observed for some related aryl complexes.[3]

For the complex [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$] there exists the possibility of *meso* and DL isomers. Whilst the relative simplicity of the n.m.r. spectra indicate that only one isomer is present, the overall symmetry of the molecule does not allow a definite conclusion to be drawn as to which isomer was formed. The compound was reacted with several chelating ditertiary phosphines (L–L), *viz.* 2,2-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)ethane (dppe), and bis(diphenylphosphino)methane (dppm), to displace the cod and to produce the compounds [Pt(L–L){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$], Table 1. However, only in the case of the dppp complex was any conclusive structural information obtained. In the ^1H n.m.r., [Pt(dppp){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$] showed one triplet signal, $^3J(^{31}P–H)$ = 29 Hz, for the ligand methyl groups, indicating the DL configuration for the 1,1′-dichloroferrocenyl groups. Molecular models gave no indication why the DL isomer should be formed preferentially.

We have investigated the reactions of some 1,1′-dichloroferrocene derivatives with iodomethane in an attempt to obtain 1,1′-dichloroferrocenyl derivatives of platinum(IV), but no such compounds were obtained. Up to the reflux temperature there was no sign of reaction between [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$] and iodomethane. However, under more forcing conditions, *e.g.* 100 °C in a sealed tube, the solid products

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† *Supplementary data available* (No. SUP 56199, 7 pp.): H-atom co-ordinates, thermal parameters, geometry of mean planes, ^1H and ^{13}C n.m.r. data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Reaction yields, physical properties, and analytical data for some 1,1′-dichloroferrocene complexes

Compound	Yield (%)	Melting Temperature (°C)	Analysis (%)[a]			Mass spectrum[a,b]
			C	H	Cl	
$[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}_2]$	42	197—200 (dec.)	41.70 (41.50	3.30 (3.20)	17.4 (17.50)	508 (508)
$[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}Cl]$	61	186—187 (dec.)	36.55 (36.50)	3.30 (3.25)	17.80 (17.95)	592 (592)
$[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}Br]$	55	188—189 (dec.)	33.50 (33.95)	3.00 (3.00)		636 (636)
$[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}I]$	48	183—184 (dec.)	31.60 (31.60)	2.90 (2.80)	10.05 (10.35)	684 (684)
$[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}(CH_2Ph)]$	60	108—110 (dec.)	46.25 (46.30)	3.95 (4.05)		648 (648)
$[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}Me]$	76	108—111 (dec.)	40.40 (39.90)	4.15 (3.90)	12.40 (12.40)	572 (572)
$[Pt(dppp)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}_2]$	22	223—226 (dec.)	50.95 (50.60)	3.55 (3.60)		1 116 (1 116)
$[Pt(dppm)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}_2]$	48	220—223 (dec.)	49.35 (49.70)	3.45 (3.35)		1 091[c] (1 087)
$[Pt(dppe)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}_2]$	57	235 (dec.)	50.45 (50.15)	3.75 (3.50)		1 105[c] (1 101)

[a] Calculated values in parentheses. [b] Base peak of molecular ion. [c] Molecular ion not observed; molar mass determined osmometrically in benzene.

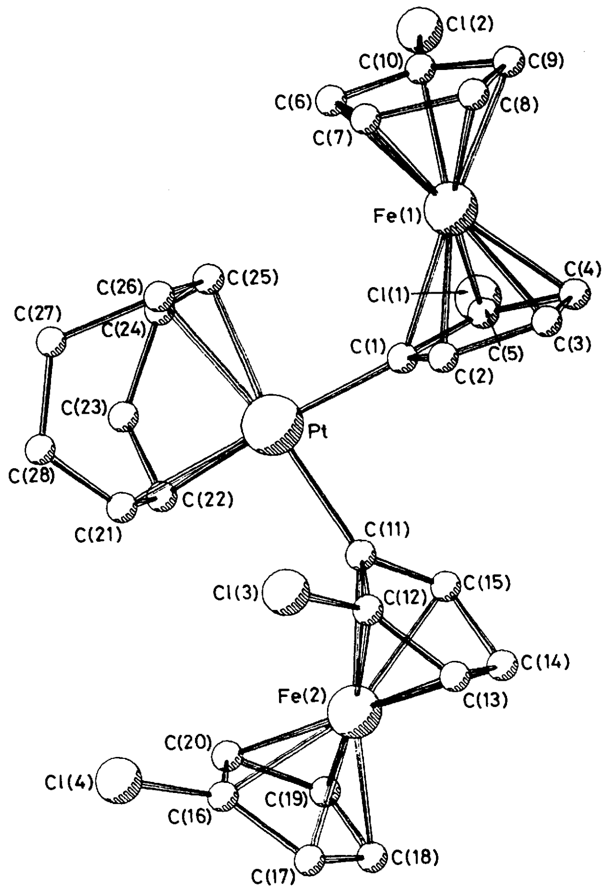

Figure. A molecule of $[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}_2]$ showing the numbering scheme used in the crystallographic results

isolated were $[Pt(cod)I_2]$ and tetrachlorodiferrocenyls. Under similar conditions $[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}Me]$ and iodomethane produced $[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}I]$ and methyl-1,1′-dichloroferrocene. These results are in contrast to the ease with which $[Pt(cod)Me_2]$ reacts with iodomethane, but in agreement with the non-reaction of analogues involving the more bulky groups benzyl or trimethylsilylmethyl.[2]

The structure of $[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}_2]$ was determined by *X*-ray diffraction. An individual crystal consists of single molecules of one enantiomer of $[Pt(cod)\{Fe(C_5H_4Cl)(C_5H_3Cl)\}_2]$, the bulk sample being a racemic mixture. The molecule is shown in the Figure.

The environment of the Pt atom is the expected square plane with σ bonds to the two 1,1′-dichloroferrocene ligands and π bonds to the cod ligand. The Pt–C σ bonds are equal within experimental error and the geometry of the cod ligand is similar to that previously reported,[4] in that it is twisted with respect to the mean plane of the four ligating carbon atoms [C(21), C(22), C(25), and C(26)].

The overall conformation adopted by the two ferrocene groups is that of an eclipsed geometry in which the chlorine substituents also eclipse one another within each ferrocene ligand. The absence of a molecular plane of symmetry arises because the chlorine substituents are on opposite sides of the platinum square plane in the two ferrocenyl ligands. The cyclopentadienyl planes within the ferrocenyl ligands are approximately orthogonal to the platinum square plane so, although there may be a potential overlap between the ferrocenyl π-system and the metal *d* orbitals, the two Pt–C σ bond lengths of 2.003(19) and 2.042(16) Å are not unexpectedly short. A representative value for the Pt–C_{sp^3} single bond length when *trans* to cyclo-octa-1,5-diene may be taken to be 2.068(8) Å, as reported[4] for the Pt–C(methyl) bond in $[Pt(cod)(\eta^1\text{-}C_5H_5)Me]$. After allowing for the contraction in the covalent radius of carbon from 0.77 Å in sp^3 hybridisation to 0.75 Å in sp^2 hybridisation, the two Pt–C σ bonds *trans* to cyclo-octa-1,5-diene in the present study both fall in the normal range.

Within the cod ring there appear to be anomalous bond lengths for the formally olefinic C(25)–C(26) [1.54(4) Å] and the single bond C(27)–C(28) [1.41(3) Å], both of which are outside their expected values, although there is no chemical basis for this.

Experimental

Hydrogen-1, carbon-13, and phosphorus-31 n.m.r. spectra were recorded at 100, 25, and 40.5 MHz respectively. All solvents were dried and degassed before use and all reactions were carried out under purified nitrogen. Chromatography was dry-column on Al_2O_3 (grade II). Only representative preparations are reported.

2,2-μ-[(η-cis,cis-*Cyclo-octa-*1,5-*diene*)*platinio*]-*bis*(1,1′-*dichloroferrocene*).—1,1′-Dichloroferrocene (1.53 g, 6.0 mmol) was dissolved in tetrahydrofuran (50 cm^3) and n-butyl-lithium (6.0 mmol) added to the stirred solution, causing an immediate colour change from yellow to orange. After 1 h the solution was cooled to −78 °C and (*cis,cis*-cyclo-octa-1,5-diene)di-iodoplatinum(II) (1,5 g, 2.8 mmol) was added. The mixture was warmed to room temperature and stirred for a further 20 h. The resulting dark orange-brown solution was poured into benzene (50 cm^3), washed several times with water, dried over potassium carbonate, filtered, and evaporated to leave an orange-brown oil. Chromatography using hexane as eluant produced 1,1′-

Table 2. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt	−2 092	−233	−2 500 *
Fe(1)	−876(1)	−1 711(2)	−567(4)
Fe(2)	−3 759(1)	−823(1)	−2 582(7)
Cl(1)	−1 396(3)	−1 908(4)	−4 955(8)
Cl(2)	155(3)	−1 497(5)	−3 906(10)
Cl(3)	−3 057(3)	−306(7)	1 416(9)
Cl(4)	−4 111(4)	1 077(5)	−931(17)
C(1)	−1 731(8)	−1 286(10)	−1 529(28)
C(2)	−1 732(8)	−1 615(12)	308(28)
C(3)	−1 540(9)	−2 447(13)	309(28)
C(4)	−1 390(9)	−2 675(12)	−1 512(33)
C(5)	−1 483(7)	−1 948(10)	−2 511(45)
C(9)	−41(8)	−2 203(15)	−487(36)
C(10)	−65(8)	−1 492(17)	−1 553(39)
C(8)	−222(8)	−1 916(18)	−1 299(31)
C(7)	−348(8)	−1 041(17)	1 218(36)
C(6)	−234(8)	−770(15)	−593(38)
C(11)	−2 857(8)	−906(10)	−2 330(78)
C(12)	−3 174(8)	−951(14)	−462(30)
C(13)	−3 571(9)	−1 638(14)	−501(40)
C(14)	−3 517(8)	−2 019(11)	−2 202(59)
C(15)	−3 054(7)	−1 584(11)	−3 289(31)
C(16)	−4 220(8)	242(12)	−2 387(86)
C(17)	−4 599(9)	−430(14)	−2 068(51)
C(18)	−4 594(9)	−929(18)	−3 597(45)
C(20)	−3 989(10)	199(17)	−4 191(41)
C(19)	−4 209(10)	−571(19)	−4 985(37)
C(21)	−2 543(10)	992(11)	−2 760(39)
C(22)	−2 488(8)	667(13)	−4 486(30)
C(23)	−2 020(9)	961(19)	−5 841(31)
C(24)	−1 411(10)	643(22)	−5 598(45)
C(25)	−1 244(9)	242(15)	−3 780(38)
C(26)	−1 335(8)	644(14)	−1 874(39)
C(27)	−1 577(10)	1 531(13)	−1 808(53)
C(28)	−2 196(9)	1 641(15)	−1 938(41)

* This value is indeterminate in *Pna*2_1 and was therefore constrained to have a fixed value.

Table 3. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

Pt–C(1)	2.003(19)	Cl(1)–C(5)	1.78(3)
Pt–C(11)	2.042(16)	Cl(2)–C(10)	1.77(3)
Pt–C(21)	2.222(20)	Cl(3)–C(12)	1.73(2)
Pt–C(22)	2.226(19)	Cl(4)–C(16)	1.72(4)
Pt–C(25)	2.261(20)	C(21)–C(22)	1.36(3)
Pt–C(26)	2.262(17)	C(21)–C(28)	1.43(3)
Fe(1)–C(1)	2.163(20)	C(22)–C(23)	1.52(3)
Fe(1)–C(2)	2.041(18)	C(23)–C(24)	1.48(3)
Fe(1)–C(3)	2.013(18)	C(24)–C(25)	1.51(4)
Fe(1)–C(4)	2.052(19)	C(25)–C(26)	1.54(4)
Fe(1)–C(5)	2.001(22)	C(26)–C(27)	1.53(3)
Fe(1)–C(9)	2.048(19)	C(27)–C(28)	1.41(3)
Fe(1)–C(10)	1.998(20)		
Fe(1)–C(8)	2.030(21)	Pt–pi(1)	2.116
Fe(1)–C(7)	2.062(22)		
Fe(1)–C(6)	2.094(20)	Pt–pi(2)	2.128
Fe(2)–C(11)	2.050(20)		
Fe(2)–C(12)	2.036(20)	Fe(1)–cp(1)	1.672
Fe(2)–C(13)	2.040(20)		
Fe(2)–C(14)	2.015(19)	Fe(1)–cp(2)	1.658
Fe(2)–C(15)	2.072(17)		
Fe(2)–C(16)	2.007(18)	Fe(2)–cp(3)	1.637
Fe(2)–C(17)	2.036(21)		
Fe(2)–C(18)	2.034(20)	Fe(2)–cp(4)	1.649
Fe(2)–C(20)	2.078(25)		
Fe(2)–C(19)	2.055(23)		
C(1)–Pt–C(11)	83.0(10)	pi(2)–Pt–C(1)	97.0
pi(1)–Pt–pi(2)	86.1	pi(2)–Pt–C(11)	176.9
pi(1)–Pt–C(1)	176.2	cp(1)–Fe(1)–cp(2)	175.6
pi(1)–Pt–C(11)	93.8	cp(3)–Fe(2)–cp(4)	174.9

pi(1), pi(2) and cp(1)—cp(4) are the centres of the cod double bonds and the centroids of the cyclopentadienyl rings respectively.

dichloroferrocene, and using hexane–benzene (3:1) as eluant produced the product which was crystallised from dichloromethane–hexane. Yield 0.947 g (42%).

1,1′-*Dichloro*-2-[*chloro*(η-cis,cis-*cyclo-octa*-1,5-*diene*)-*platinio*]*ferrocene*.—Acetyl chloride (0.02 cm^3, 0.25 mmol) in dichloromethane (5 cm^3) was added to a stirred solution of [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$] (0.20 g, 0.25 mmol) in dichloromethane (30 cm^3) and methanol (8 cm^3). After 1 h the solvent was removed under vacuum to leave a pale yellow solid which was purified by chromatography. Hexane elution produced 1,1′-dichloroferrocene, then hexane–benzene (2:1) elution produced a small amount of [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$], and finally elution with benzene–chloroform (1:1) produced the product as an orange oil which was subsequently crystallised from hexane–dichloromethane. Yield 90 mg (61%).

1,1′-*Dichloro*-2-[(η-cis,cis-*cyclo-octa*-1,5-*diene*)*iodoplatinio*]-*ferrocene*.—Iodine (0.07 g, 0.59 mmol) in dichloromethane (20 cm^3) was added to a stirred solution of [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$] (0.23 g, 0.28 mmol) in dichloromethane (20 cm^3). After 5 h the solvent was removed under vacuum to give a dark brown oil which was subjected to chromatography. Hexane elution produced a small amount of iodo-1,1′-dichloroferrocene, identified by mass spectroscopy, hexane–benzene (3:1) elution produced [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$], and finally benzene elution produced the product which was crystallised from dichloromethane–hexane. Yield 92 mg (42%).

2,2-μ-{[2,2-*Bis*(*diphenylphosphino*)*propane*]*platinio*}-*bis*(1,1′-*dichloroferrocene*).—2,2-Bis(diphenylphosphino)propane (0.16 g, 0.40 mmol) was added to a stirred solution of [Pt(cod){Fe(C_5H_4Cl)(C_5H_3Cl)}$_2$] (0.25 g, 0.31 mmol) in toluene (30 cm^3). The mixture was refluxed for 16 h, cooled, filtered, and the solvent evaporated to produce a dark orange oil which was subjected to chromatography. Hexane–benzene (3:1) eluted small amounts of the starting materials and benzene eluted the product which was crystallised from dichloromethane–hexane. Yield 75 mg (22%).

Crystal data.—$C_{28}H_{26}Cl_4Fe_2Pt$, M = 810.9, orthorhombic, a = 22.600(4), b = 16.048(2), c = 7.239(2) Å, U = 2 625.6 Å^3, D_m = 2.0 g cm^{-3} (by flotation), Z = 4, D_c = 2.05 g cm^{-3}, F(000) = 1 567.7, space group *Pna*2_1, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 65.5 cm^{-1}.

Data Collection and Processing.[5]—Hilger and Watts Y290 diffractometer, θ/2θ scan, symmetrical 0.8° scan in θ with 1.2-s counts at 0.03° intervals, graphite-monochromated Mo-K_α radiation; 4 010 reflections measured ($25 \leqslant \theta \leqslant 25°$) giving 2 553 with $I > 2.5\sigma(I)$. No absorption correction. No significant fluctuation in standards.

Structure Analysis.—Heavy-atom method (no solution in *Pnma*). Co-ordinate of Pt atom fixed at 0.25. Full-matrix least-squares refinement (no blocking), all non-hydrogen atoms anisotropic and 22 hydrogens in calculated positions with thermal parameter fixed at $U = 0.07$ Å^2. Unit weights used. Both enantiomers refined to convergence as above giving $R = 0.0528$, $R' = 0.0585$ (positive signs for Pt co-ordinates) and $R = 0.0485$, $R' = 0.0538$ (negative signs for Pt co-ordinates). Initial data reduction on the University of Nottingham ICL 1906A computer, subsequent calculations on the Trinity College, Dublin DEC 2060 system.

Atomic co-ordinates are given in Table 2 and bond lengths and angles in Table 3.

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