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Synthesis of some bis(triphenylphosphine)(ethynylferrocenyl) platinum(II) complexes; molecular structure of [PtH($C\equiv C-C_5H_4FeC_5H_5$)(PPh_3)$_2$]

M.V. Russo and A. Furlani

Department of Chemistry, University "La Sapienza", P. le A. Moro 5, I-00185 Rome (Italy)

S. Licoccia

Department of Chemistry, University of Siena, Pian dei Mantellini 44, 53100 Siena (Italy)

R. Paolesse

Department of Chemical Sciences and Technologies, University of Rome "Tor Vergata", I-00173 Rome (Italy)

A. Chiesi Villa and C. Guastini

Istituto di Strutturistica Chimica, University of Parma, Viale delle Scienze, I-43100 Parma (Italy)

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Abstract

Substituted acetylidoplatinum(II) complexes *trans*-[PtX($C\equiv C-C_5H_4FeC_5H_5$)(PPh_3)$_2$] (X = H, Cl, $C\equiv CPh$ or $C\equiv C-C_5H_4FeC_5H_5$) have been prepared. Controlled basicity of the reaction solutions yields the different complexes. A single-crystal X-ray diffraction study of *trans*-[PtH($C\equiv C-C_5H_4FeC_5H_5$)(PPh_3)$_2$] indicates an alternating alignment of the ethynyl ligands between two centrosymmetric platinum atoms, resulting in the formation of a pseudo-polymeric structure.

Key words: Platinum; Ferrocene; Ethynyl; Acetylide; Crystal structure

1. Introduction

Syntheses of dialkynyl transition metal complexes have recently attracted renewed interest because these materials may often form liquid crystals [1]. Complexes of *trans*-bis(arylethynyl)bis(trimethylphosphine)-platinum(II) and -palladium(II) have been extensively investigated by Takahashi *et al.* as starting materials for the synthesis of rod-like metal poly(yne) polymers which are lyotropic liquid crystals [2–5]. Metal-containing organic polymers obtained from σ-dialkynyl complexes are also expected to have large third-order optical non-linearities [6].

A variety of acetylenes has been used in the preparation of σ-bonded metal acetylides, but only a few reports deal with complexes of ethynylferrocene (EFc). The reactions of EFc with Ni, Co or Ir carbonyls [7], leading to EFc complexes and dimers or trimers of EFc, was reported. The alcoholic protonation of *trans*-[PtH($C\equiv C-C_5H_4FeC_5H_5$)$_2$(PMe_2Ph)$_2$] has also been studied [8]. The synthesis from EFc and different halogenonucleosides, of metallocene nucleosides, which

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Correspondence to: Professor M.V. Russo.

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are possible cytotoxins, and their characterization have been reported [9]. Recently an interesting study [10] showed that *trans*-[(Pt(C≡CX)(C≡CY)$(PMe_2Ph)_2$] where X is a strong π-donor and Y is a strong π-acceptor, have large second-order optical non-linearities; unsymmetrical bis(acetylides) have especially large efficiencies.

In this paper we describe the reactivity of EFc with *cis*-[$PtCl_2(PPh_3)_2$] and with *trans*-[$PtHCl(PPh_3)_2$] under different reaction conditions some leading to asymmetrically substituted complexes. The molecular structure of the hydridoacetylide complex is also discussed.

2. Experimental details

All chemicals (Carlo Erba) were reagent grade and were used without further purification. EFc was prepared according to a published method [11]. IR spectra (Nujol mulls) were recorded on a Perkin Elmer 580 B spectrometer and UV spectra on a Perkin Elmer Lambda 5 spectrophotometer. NMR spectra were run on a Bruker AM400 instrument in $CDCl_3$ solutions. All chemical shifts are given in ppm referred to tetramethylsilane (TMS). FAB analyses were performed with a VG Quattro instrument, using 3-nitrobenzylalcohol as matrix. Elemental microanalyses were done by the Laboratorio di Microanalisi, University of Pisa.

2.1. Synthesis of the complexes

2.1.1. trans-[Pt(C≡C-$C_5H_4FeC_5H_5)_2(PPh_3)_2$] (1)

500 mg (0.6 mmol of *cis*-[$PtCl_2(PPh_3)_2$] was heated under reflux in 20 ml of $NH(C_2H_5)_2$ with 260 mg (1.2 mmol) of EFc (molar ratio 1:2) and 5 mg (2.6×10^{-2} mmol) of CuI, for 10 min. An orange compound precipitated from the reaction mixture; the complex was filtered off and crystallized from benzene/ethanol.

2.1.2. trans-[PtCl(C≡C-$C_5H_4FeC_5H_5)(PPh_3)_2$] (2)

500 mg (0.6 mmol) of *cis*-[$PtCl_2(PPh_3)_2$] was dissolved in 50 ml of $CHCl_3$ and 130 mg (0.6 mmol) of EFc (molar ratio 1:1) was added with 0.5 ml of $NH(C_2H_5)_2$. The reaction solution was heated under reflux for 1 h. Upon addition of absolute ethanol a light orange product precipitated. It was recrystallized twice from benzene/ethanol.

2.1.3. trans-[PtH(C≡C-$C_5H_4FeC_5H_5)(PPh_3)_2$] (3)

500 mg of *trans*-[$PtHCl(PPh_3)_2$] (0.66 mmol) dissolved in $CHCl_3$ (20 ml), was heated under reflux with 140 mg (0.66 mmol) of EFc in the presence of $NH(C_2H_5)_2$ (0.5 ml) for 30 min. The reaction solution was cooled to room temperature and ethanol added. Upon standing overnight at *ca*. 0°C, needle-like orange microcrystals precipitated. Crystallization from $CHCl_3$/ethanol gave complex **3** with 40% yield.

2.1.4. trans-[Pt(C≡C-$C_5H_4FeC_5H_5$)(C≡C-Ph)-$(PPh_3)_2$] (4)

(i) 500 mg (0.52 mmol) of complex **2** (obtained from the reaction detailed in section 2.1.2.) and 1.5 ml (9.5 mmol) of HC≡CPh were suspended in 20 ml of $NH(C_2H_5)_2$. The solution was heated under reflux for 4 h. The deep orange product was filtered off, washed with hot ethanol and crystallized from hot CH_2Cl_2/ethanol (yield 40%).

(ii) 500 mg (0.53 mmol) of complex **3** (obtained from the reaction detailed in section 2.1.3.) was dissolved in 25 ml of $CHCl_3$ and 1.5 ml (9.5 mmol) of H-C≡CPh added to the solution, which was heated under reflux for 1 h. Upon addition of ethanol, complex **4** precipitated, was filtered off and crystallized from hot CH_2Cl_2/ethanol.

TABLE 1. Experimental data for the X-ray diffraction studies on crystalline complex 3 [a]

formula	$C_{48}H_{40}FeP_2Pt$
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.947(1)
b, Å	11.378(1)
c, Å	9.094(1)
α, deg	108.34(1)
β, deg	96.90(1)
γ, deg	94.73(1)
V, Å^3	962.0(2)
Z	1
D_{calcd}, g cm^{-3}	1.605
mol wt	929.7
cryst dimens, mm	0.14×0.18×0.27
linear abs coeff, cm^{-1}	41.61
radiation	Graphite-monochromated Mo Kα (λ = 0.71069 Å)
2θ range, deg	6–50
reflcns measd	$\pm h \pm k\ l$
unique total data	3371
criterion for obsn	$I > 3\sigma(I)$
unique obsd data	3065
No. of variables	211
overdetermination ratio	14.5
max Δ/σ on last cycle	0.2
$R = \Sigma w \Vert F_o\vert - \vert F_c \Vert / \Sigma \vert F_o \vert$	0.034
$R_w = [\Sigma w(\vert F_o\vert - \vert F_c\vert)^2 / \Sigma w \vert F_o\vert^2]^{1/2}$	0.034
$GOF = [\Sigma(w \Vert F_o\vert - \vert F_c\Vert)^2/(N_o - N_v)]^{1/2}$	0.89

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 25 carefully centred reflections chosen from diverse regions of reciprocal space.

2.1.5. *Attempted preparations of complexes [$Pt(HC{\equiv}C{-}C_5H_4FeC_5H_5)(PPh_3)_2$] (5), and cis-[$Pt(C{\equiv}C{-}C_5H_4FeC_5H_5)_2(PPh_3)_2$] (6)*

To 400 mg of *cis*-[$PtCl_2(PPh_3)_2$] and 117 mg of EFc (molar ratio 1 : 1) dissolved in 25 ml of absolute ethanol, ~ 1 ml of hydrazine hydrate was added dropwise at room temperature until the solution cleared. The solution was then heated under reflux for 5 min and an orange-yellow precipitate was obtained. The IR spectrum of the crude product showed a medium intensity band at 1700 cm^{-1} and two bands at 2110 and 2010 cm^{-1}, suggesting the formation of the η^2-Pt complex **5** mixed with the hydrido-complex **3**. Recrystallization gave the complex **3** in low yield.

500 mg of *cis*-[$PtCl_2(PPh_3)_2$] and 130 mg of EFc (molar ratio 1:2) in absolute ethanol (25 ml) and hydrated ammonia (20 ml) were heated under reflux for 15 min until an orange product precipitated. The reaction mixture was left at room temperature for 6 h and the crude product filtered. IR spectroscopy showed the presence of the monochloroacetylide complex **2** in low yield.

2.2. *Crystal-structure determination of trans-[$PtH(C{\equiv}C{-}C_5H_4FeC_5H_5)(PPh_3)_2$]*

Crystal data and details associated with structure refinement are given in Table 1. The reduced cell was obtained with the use of TRACER [12]. Intensity data were collected at room temperature on a Philips PW1100 single crystal diffractometer. For intensities and background, individual reflection profiles were analyzed [13]. The structure amplitudes were obtained after the usual reflection profiles were analyzed [13]. The structure amplitudes were obtained after the usual Lorentz and polarization corrections [14*] and the absolute scale was established by the Wilson method [15]. Intensity data were corrected for absorption using a semiempirical method [16].

The function minimized during the least-squares refinement was $\Sigma w \mid F_o \mid - \mid F_c \mid^2$. A weighting scheme based on counting statistics was applied [14*]. Anomalous scattering corrections were included in all structure factor calculations [17b]. Scattering factors for neutral atoms were taken from ref. 17a for non-hydrogen atoms and from ref. 18 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

TABLE 2. Fractional atomic coordinates ($\times 10^4$)

Atom	x	y	z
Pt	0(–)	0(–)	0(–)
Fe	5000(–)	0(–)	5000(–)
P	–14(1)	2027(1)	109(1)
C(1)	4277(9)	710(9)	3314(12)
C(2)	4952(9)	1705(7)	4727(11)
C(3)	6293(8)	1479(7)	4964(9)
C(4)	6485(10)	403(9)	3786(12)
C(5)	5267(13)	–68(8)	2794(10)
C(6)	2965(14)	508(11)	2404(15)
C(7)	1871(11)	368(9)	1587(13)
C(11)	1064(3)	3246(3)	1747(3)
C(12)	541(3)	4295(3)	2636(3)
C(13)	1397(3)	5224(3)	3845(3)
C(14)	2776(3)	5104(3)	4164(3)
C(15)	3299(3)	4054(3)	3275(3)
C(16)	2443(3)	3126(3)	2066(3)
C(21)	530(4)	2295(3)	–1626(3)
C(22)	–107(4)	1507(3)	–3099(3)
C(23)	284(4)	1670(3)	–4452(3)
C(24)	1312(4)	2622(3)	–4332(3)
C(25)	1949(4)	3410(3)	–2859(3)
C(26)	1558(4)	3247(3)	–1506(3)
C(31)	–1694(3)	2545(3)	164(4)
C(32)	–2534(3)	2164(3)	1097(4)
C(33)	–3832(3)	2538(3)	1176(4)
C(34)	–4290(3)	3291(3)	322(4)
C(35)	–3451(3)	3672(3)	–612(4)
C(36)	–2153(3)	3298(3)	–690(4)

The site occupancy factor for C(6) and C(7) is 0.5.

Solution and refinement were based on the observed reflections. The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map. Refinement was first isotropical, then anisotropical for non-H atoms by full-matrix least-squares. The platinum and the iron atoms are on centres of symmetry. This requires a statistical distribution of the ethynyl group over the two centrosymmetric cyclopentadienyl rings and, at the same time, a statistical distribution between the ethynyl group and the hydridic hydrogen around platinum. The disorder resulted in very high thermal parameters for the ethynyl carbons (C(6) and C(7)). Consequently the C(6) and C(7) atoms were refined with anisotropic temperature factors and a site-occupation factor of 0.5. All the hydrogen atoms, except the hydridic H which was put in a geometrically calculated position, were located in a difference map and introduced in the final stages of refinement as fixed contributions with isotropic *U* fixed at 0.08 Å^2. The final difference map showed no peaks = 0.8 or –1.0e Å^{-3}, except in the immediate vicinity of the Pt atoms. The general background was about 0.4 eÅ^{-3}. During the refinement, all the Ph rings were constrained to be regular hexagons (C–C = 1.395 Å). Final atomic co-ordinates are listed in Table 2 for non-H atoms and in Table 3 for hydrogen atoms. Thermal parameters are given in Table 4, bond distances and angles in Table 5. Lists of atomic

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* Reference number with asterisk indicates a note in the list of references.

TABLE 3. Fractional atomic coordinates (×10^4) for hydrogen atoms

Atom	x	y	z
H(1)	−1397	−277	−1195
H(2)	4330	2356	5271
H(3)	7066	2086	5954
H(4)	7435	36	3910
H(5)	5160	−912	1750
H(12)	−414	4421	2538
H(13)	1046	6035	4515
H(14)	3449	5739	4994
H(15)	4252	4012	3415
H(16)	2862	2332	1586
H(22)	−963	882	−3191
H(23)	−231	1055	−5531
H(24)	1704	2741	−5206
H(25)	2627	4051	−2954
H(26)	2007	3871	−472
H(32)	−2233	1525	1542
H(33)	−4439	2097	1803
H(34)	−5259	3584	405
H(35)	−3759	4139	−1196
H(36)	−1473	3600	−1181

The site occupancy factor for H(1) is 0.5.

TABLE 5. Bond distances (Å) and angles (°)

Pt–P	2.278(1)	P–C(31)	1.818(3)
Pt–C(7)	2.137(10)	C(1)–C(2)	1.461(11)
Fe–C(1)	2.033(12)	C(1)–C(5)	1.403(15)
Fe–C(2)	2.035(9)	C(1)–C(6)	1.418(16)
Fe–C(3)	2.043(8)	C(2)–C(3)	1.384(12)
Fe–C(4)	2.052(11)	C(3)–C(4)	1.395(12)
Fe–C(5)	2.033(10)	C(4)–C(5)	1.377(14)
P–C(11)	1.834(3)	C(6)–C(7)	1.210(17)
P–C(21)	1.832(4)	Fe–Cp	1.653(11)
P–Pt–C(7)	94.1(3)	C(5)–C(1)–C(6)	120.4(10)
P(′)–Pt–P	180	C(2)–C(1)–C(6)	132.8(10)
C(4)–Fe–C(5)	39.4(4)	C(2)–C(1)–C(5)	106.4(9)
C(3)–Fe–C(4)	39.8(4)	Fe–C(2)–C(1)	68.8(5)
C(2)–Fe–C(3)	39.7(4)	C(1)–C(2)–C(3)	106.5(8)
C(1)–Fe–C(5)	40.4(4)	Fe–C(2)–C(3)	70.5(5)
C(1)–Fe–C(2)	42.1(4)	Fe–C(3)–C(2)	69.9(5)
Cp–Fe–Cp′	180	C(2)–C(3)–C(4)	109.4(8)
Pt–P–C(31)	113.8(1)	Fe–C(3)–C(4)	70.4(6)
Pt–P–C(21)	112.0(1)	Fe–C(4)–C(3)	69.8(5)
Pt–P–C(11)	118.5(1)	C(3)–C(4)–C(5)	108.7(9)
C(21)–P–C(31)	104.3(2)	Fe–C(4)–C(5)	69.6(6)
C(11)–P–C(31)	103.3(2)	C(1)–C(5)–C(4)	109.0(9)
C(11)–P–C(21)	103.5(2)	Fe–C(5)–C(4)	71.0(6)
Fe–C(1)–C(6)	130.8(8)	Fe–C(5)–C(1)	69.8(5)
Fe–C(1)–C(5)	69.8(6)	C(1)–C(6)–C(7)	176.9(13)
Fe–C(1)–C(2)	69.1(6)	Pt–C(7)–C(6)	175.2(10)

TABLE 4. Anisotropic thermal parameters $U_{i,j}$ (×10^4 Å^2). $U_{i,j}$ are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt	382(2)	235(2)	345(2)	123(1)	74(1)	59(1)
Fe	538(8)	410(7)	563(8)	230(6)	−154(6)	−27(6)
P	317(7)	258(6)	299(7)	115(5)	45(6)	47(5)
C(1)	726(54)	988(66)	1061(69)	806(60)	−372(51)	−237(49)
C(2)	877(60)	571(44)	1056(65)	506(46)	245(51)	252(41)
C(3)	737(52)	625(45)	758(52)	390(41)	−182(41)	−142(39)
C(4)	825(61)	976(67)	943(67)	562(58)	165(53)	217(51)
C(5)	1657(107)	615(52)	554(49)	222(41)	17(59)	−55(59)
C(6)	635(87)	385(63)	536(75)	229(56)	123(67)	40(57)
C(7)	376(63)	312(53)	481(65)	205(48)	−39(53)	99(45)
C(11)	437(31)	252(24)	295(26)	105(20)	98(23)	1(21)
C(12)	521(36)	343(29)	423(32)	76(25)	50(27)	65(25)
C(13)	666(44)	374(31)	521(37)	113(28)	87(32)	106(29)
C(14)	666(45)	502(37)	451(36)	127(30)	−25(32)	−158(32)
C(15)	403(34)	622(40)	466(36)	135(31)	19(28)	−56(29)
C(16)	362(31)	538(34)	382(31)	150(26)	68(25)	75(26)
C(21)	407(30)	322(26)	313(27)	121(22)	116(23)	130(22)
C(22)	477(34)	443(31)	325(29)	88(24)	76(26)	19(26)
C(23)	727(47)	565(39)	361(33)	113(29)	118(31)	74(34)
C(24)	746(46)	623(40)	426(36)	246(31)	255(33)	200(35)
C(25)	659(44)	625(41)	534(40)	312(33)	149(34)	−19(33)
C(26)	493(36)	440(32)	414(32)	162(26)	47(27)	−66(26)
C(31)	418(31)	243(24)	309(27)	62(20)	35(23)	47(21)
C(32)	487(36)	484(34)	525(36)	272(29)	150(29)	99(27)
C(33)	523(40)	626(41)	660(44)	270(35)	273(34)	152(32)
C(34)	365(34)	615(40)	651(42)	157(34)	142(31)	137(29)
C(35)	528(39)	415(33)	617(40)	164(29)	−35(32)	153(28)
C(36)	400(32)	365(28)	454(32)	141(25)	20(26)	92(24)

TABLE 6. Analytical and spectroscopic data for *trans*-ferrocenylacetylido Pt complexes

	Complex	Yield (%)	m.p. (°C)	UV λ_{max} (nm)	IR (cm^{-1})	FAB (*m/z*)	Elemental analyses (%)			
							Calcd.		Found	
							C	H	C	H
1	[Pt(C≡C–$C_5H_4FeC_5H_5$)$_2$(PPh_3)$_2$]	65	> 270 dec.	294	νC≡C 2110	1135	63.36	4.22	62.16	4.42
2	[PtCl(C≡C–$C_5H_4FeC_5H_5$)(PPh_3)$_2$]	80	210–212	310	νC≡C 2120 νPt–Cl 320	963	59.81	4.04	60.69	4.05
3	[PtH(C≡C–$C_5H_4FeC_5H_5$)(PPh_3)$_2$]	40	191–192	279, 330	νC≡C 2110 νPt–H 2010	929	62.03	4.30	61.17	4.27
4	[Pt(C≡C–$C_5H_4FeC_5H_5$)(C≡CPh)(PPh_3)$_2$]	40	> 270 dec.	338	νC≡C 2100	1029	65.33	4.27	65.86	4.88

coordinates, thermal parameters, etc. are also available from the Cambridge Crystallographic Data Centre.

3. Results and discussion

Analytical data for the complexes are reported in Table 6. The synthetic procedure leading to the formation of complex **1** is of quite wide applicability [19,20] for dialkynylplatinum complexes. Complex **1** is poorly soluble in most common organic solvents. Its characterization was by IR and FAB techniques. The IR spectrum of **1** shows a band at 2110 cm^{-1}, ν(C≡C), two bands at 1590 and 1570 cm^{-1} (ν(C=C) of the triphenylphosphine) and a triplet at 820, 810, 800 cm^{-1}, characteristic of the ferrocene. The absence of a band at 540 cm^{-1}, attributable to Pt–C and Pt–P stretching

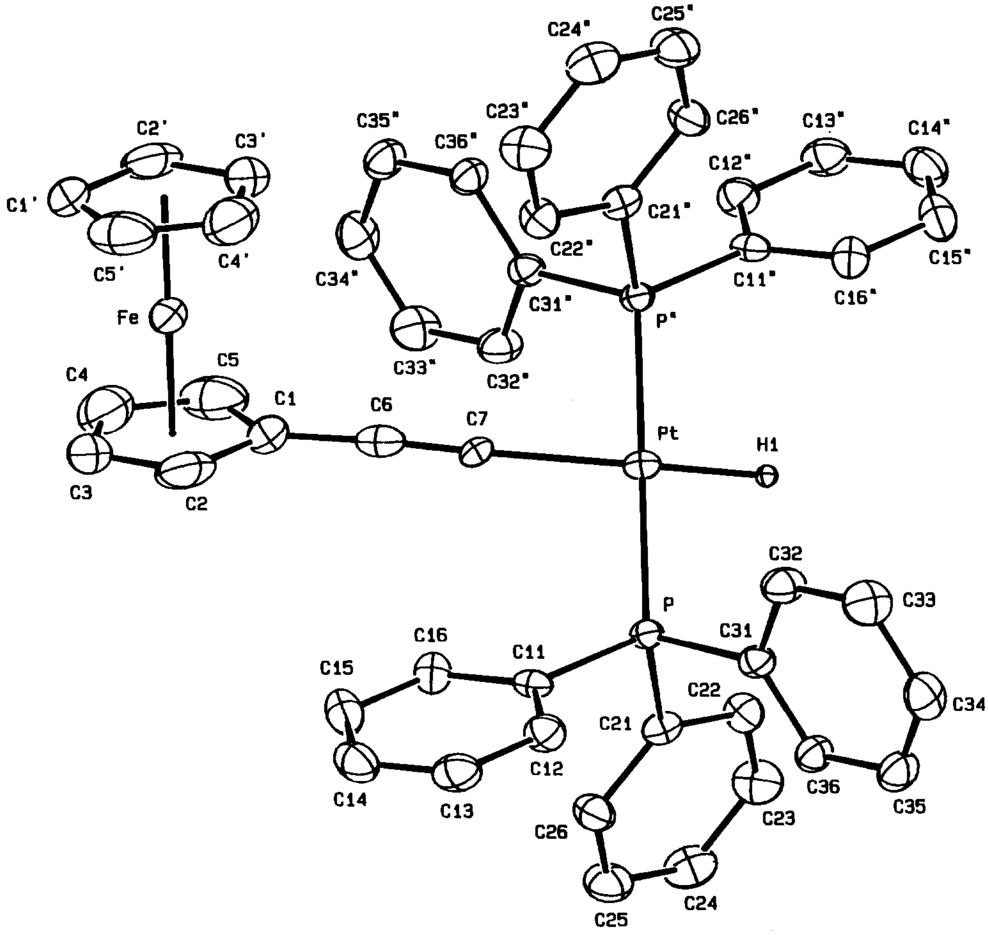

Fig. 1. ORTEP drawing of complex **3** (30% probability ellipsoids). Prime and double prime refer to transformations of $1-x$, $-y$, $1-z$ and $-x$, $-y$, $-z$ respectively.

vibrations of *cis* acetylidoplatinum complexes [21], suggests a *trans* configuration. Attempts to obtain the *cis* isomer by performing the reaction procedure already described for a series of monosubstituted acetylenes [22] (see part (ii) of section 2.1.5) were unsuccessful.

When the reaction solvent is $CHCl_3$ and only a small amount of base is present (see Section 2.1.2), the monochloroacetylide **2** is obtained. The characteristic IR bands are observed at 2121 cm^{-1}, ν(C≡C), and at 320 cm^{-1}, ν(Pt–Cl). The absence of the band at 540 cm^{-1} suggests a *trans* configuration. The mid-IR pattern (range 2000–600 cm^{-1}) of complex **2** is similar to that of complex **1**.

The standard procedure to obtain platinum hydridoacetylides [23] was followed to synthesize complex **3**. The IR spectrum shows a doublet at 2110 cm^{-1}, attributed to ν(C≡C) of the ferrocenylacetylene and a single band at 2010 cm^{-1} due to ν(Pt–H). The low value of (Pt–H) reflects the high *trans* effect of the acetylenic moiety, [23,24]. The ^1H NMR spectrum in the hydride region shows two triplets of triplets; the first is centred at τ 16.40 ppm (J(Pt–H) = 625 Hz; J(P–H) = 15.7 Hz) and may be assigned to the *trans* isomer. The Pt–H and P–H coupling constants are of the order of those already reported for a series of *trans* platinum hydridoacetylides [23]. The low J(Pt–H) value for a *trans* complex [25,26] is consistent with the expected high *trans* influence of the acetylido group. The second set of triplets is centred at $\tau = 26.23$ ppm (J(Pt–H) = 1210 Hz; J(P–H) = 13.5 Hz). The chemical shift and coupling constants are the same as the values reported for the *trans*-[$PtHCl(PPh_3)_2$] [27]. The formation of this complex may be ascribed to the reaction between complex **3** and hydrogen chloride generated by the photocatalyzed decomposition of deuteriochloroform according to the following scheme:

$$[(PtH(C{\equiv}C\text{-}C_5H_4FeC_5H_5)(PPh_3)_2)]$$
$$\Leftrightarrow [PtH_2Cl(C{\equiv}C\text{-}C_5H_4FeC_5H_5)(PPh_3)_2]$$
$$\Leftrightarrow [PtHCl(PPh_3)_2] + HC{\equiv}C\text{-}C_5H_4FeC_5H_5$$

A similar reaction has been proposed for the analogous complex *trans*-[$PtHCl(PEt_3)_2$] [28]. The intensities of the resonances suggest a molar ratio of 3 : 1 for complex **3** and [$PtHCl(PPh_3)_2$. The ratio of the two species varies with different commercial samples of $CDCl_3$ as solvent supporting the reaction scheme proposed. Owing to the poor solubility of complex **3**, it was impossible to obtain NMR spectra in other solvents.

Complex **3** can also be obtained from [$PtCl_2(PPh_3)_2$] in reaction with ethynylferrocene (1 : 1 molar ratio), by using ethanol as solvent and hydrazine hydrate as reducing agent. These reaction conditions usually yield complexes [$Pt(H\text{-}C{\equiv}C\text{-}R)(PPh_3)_2$] with the acetylene η^2-bonded to the Pt, or insertion products into the Pt–H bond [22]. With EFc the hydridoacetylide is formed.

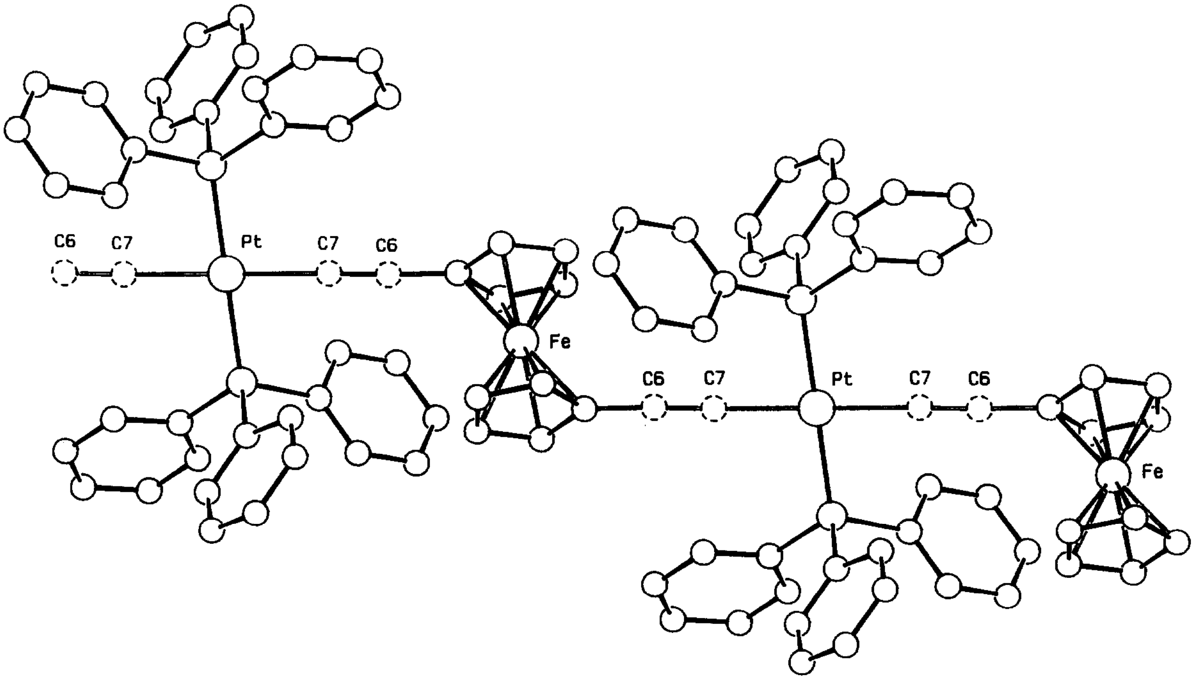

Fig. 2. ORTEP projection showing the pseudo polymeric structure of complex **3** (30% probability ellipsoids). The disordered carbon atoms are indicated by dotted circles.

Crystals of complex **3** suitable for X ray analysis were obtained by crystallization from $CHCl_3$/hexane; it consists of discrete [PtH(C≡C–$C_5H_4FeC_5H_5$)($PPh_3)_2$] molecules with the two metal atoms on crystallographic centres of symmetry (Fig. 1). Selected bond distances and angles are listed in Table 5. Coordination around platinum is square planar, involving two *trans* triphenylphosphines, a σ-bonded EFc molecule and a hydrogen atom. This atom could not be located directly by X-ray analysis for the reasons given in the Experimental section. However its presence can be deduced from the absence of appreciable electron density in the fourth coordination site, and it is supported by spectroscopic evidence. Coordination around platinum is rigorously planar. The Pt–P bond distance [2.278(1) Å] is consistent with the mean value of 2.273(5) found in [PtH(C≡CC(OH)Me_2)($PPh_3)_2$] [23]. These values are significantly shorter than those observed in *trans* acetylide derivatives containing chlorine instead of hydrogen, probably as a consequence of the small size of hydrogen [23].

The Pt–C(7) bond distance [2.173(10) Å] falls towards the upper end of the range usually found [23]. This may be related to the statistical distribution of the ethynyl between two centrosymmetric cyclopentadienyl rings, leading to a pseudo 'diethynyl'-ferrocene unit. This alternating arrangement gives two centrosymmetric platinum atoms. The situation also requires a statistical distribution of the H atom H(1)* bonded to C(1). H(1)* was ignored in calculations but it was taken into account to calculate the position of the hydridic H(1) atom, which was aligned with the Pt–C(7) bond at a Pt–H bond distance which would reduce this contact to unacceptably large van der Waals distances. The disorder distorts the real Pt–C and Pt–H distances as well as the packing of the molecules, resulting in the formation of a pseudo polymer (Fig. 2) running parallel to the [101] axis. This prevents an evaluation of the *trans* effect of the ethynyl. Intraligand steric interactions may also affect the Pt–C bond length, the shortest intramolecular contacts involving the ethynyl and a Ph ring [C(6) ··· C(16), 3.167(14), C(7) ··· C(16), 3.024(11) Å]. Intramolecular contacts between Ph and Cp rings are greater than 3.7 Å.

The ethynylferrocene unit is terminal, linearly bonded to platinum in the fashion usual for terminal alkynes [Pt–C(7)–C(6), 175.2(10), C(1)–C(6)–C(7), 176.9(13)°]. Its geometrical parameters are unexceptional. The C(6)–C(7) triple bond [1.210(17) Å] and the C(1)–C(6) distances [1.418(16) Å] fall in the usual range. The C(6) and C(7) ethynyl atoms are out of the cyclopentadienyl (Cp) ring plane by 0.142(13) and 0.324(11) Å, respectively in a direction opposite to iron. The Cp rings are planar within experimental error, with a mean length of the C–C bonds [1.404(13) Å] close to those found in other ethynyl ferrocene derivatives [29,30]. The two Cp are strictly parallel and staggered for symmetry requirements, iron lying on a centre of symmetry. They form a dihedral angle of 47.2(3)° with the coordination plane of the Pt atom. The Fe–Cp(centroid distance) [1.653(11) Å] compares very well with those observed in ref. 29 and 30. The geometry of the PPh_3 is as expected with the Pt–P–C angles greater than the tetrahedral values and C–P–C angles smaller. As usual the largest Pt–P–C angles involve the carbon atom closer to the coordination plane [out-of-plane distances (Å): C(11), 0.499(3), C(21), –1.659(3), C(31), 1.075(3)]. The Ph rings adopt a conformation leading to two above and below the coordination plane [Pt ··· H(32), 3.12 Å]. The direction of the Pt ··· H(32) line forms an angle of 37° with the normal to the coordination plane. Complexes **2** and **3** react with phenylacetylene giving [Pt(C≡C–Ph)(C≡C–$C_5H_4FeC_5H_5$)($PPh_3)_2$].

The IR spectrum of complex **4** is similar to that of complex **1** except for a band at 2100 cm^{-1}, due to the superimposition of ν(C≡C) of the ethynylferrocenyl moiety on that of phenylacetylide, usually very strong. A detectable enhancement of the band at 1600 cm^{-1} (due to ν(C=C) of the phenyl ring in Pt phenylacetylides) is also observed. Complexes **2** and **3** do not react with α-hydroxyacetylenes. If the complex [PtCl(C≡C–Ph)($PPh_3)_2$] is heated under reflux in the presence of EFc, complex **4** is not obtained. The *trans* effect of the electron-releasing ethynyl ferrocene group seems to be more effective that that of phenylacetylene, which in turn is more reactive than monosubstituted acetylenes bearing α-hydroxy groups.

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