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Cycloheptatrienyl bridged heterobimetallic complexes: synthesis, fluxional behaviour and X-ray crystal structure of *syn*-[(μ-η^3;η^2-C_7H_7)Fe(CO)$_3$Pt(η^2,σ^1-C_8H_{12}-C_5H_5)] ☆

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Abstract

The reaction of [(η^3-C_7H_7)Fe(CO)$_3$]$^-$ with [(η^4-C_8H_{12})(η^5-C_5H_5)Pt]$^+$ leads to the formation of *syn*-[(μ-η^3;η^2-C_7H_7)-Fe(CO)$_3$Pt(η^2,σ^1-C_8H_{12}-C_5H_5)] (**1**), a bridged cycloheptatrienyl complex with an Fe–Pt bond. In solution two structural isomers of **1** are present in roughly the same concentration, whereas in the solid only one isomer is detected. Both isomers are fluxional and undergo ring whizzing of the C_7H_7 ring. The slow-exchange limiting NMR spectrum of the cycloheptatrienyl unit cannot be reached even at low temperature (~173 K). The C_7H_7 ring has an uncoordinated double bond and the cyclopentadienyl unit is linked to the C_8H_{12} ring through an sp^2 carbon; the resulting cyclooctenyl unit is coordinated η^2,σ^1 to platinum. The C_5H_5 transfer, mediated by platinum, can be of interest in the synthesis of the skeleton of natural occurring products. Crystal data for *syn*-[(μ-η^3;η^2-C_7H_7)Fe(CO)$_3$Pt(η^2,σ^1-C_8H_{12}-C_5H_5)]: monoclinic, space group *C2/c* (No. 15), $a = 45.197(6)$, $b = 13.306(1)$, $c = 7.509(1)$ Å, $\beta = 92.96(1)°$, $V = 4509.8(9)$ Å^3, $Z = 8$, $R = 0.033$, $R_w = 0.080$.

Keywords: Crystal structures; Iron complexes; Platinum complexes; Cyclopentadiene complexes; Bridging cycloheptatrienyl complexes; Heterobimetallic complexes

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1. Introduction

Cycloheptatriene (C_7H_8) and cycloheptatrienyl (C_7H_7) complexes [1] are still being actively investigated [2] and among them the number of cycloheptatrienyl bridged bimetallic complexes reported, having all the seven carbons of the ring coordinated, is rapidly increasing [3–8]. Recently [9] we described the first case of a complex of the cycloheptatrienyl bridged bimetallic series, namely *syn*-[(μ-η^3;η^2-C_7H_7)Fe(CO)$_3$Pd(η^5-C_5H_5)] (**2**), having a double bond of the bridging C_7H_7 ring uncoordinated. Moreover **2** is the only complex, so far, which shows low-temperature limiting ^{1}H and ^{13}C NMR spectra [10]. The uncoordinated double bond in the C_7H_7 ligand in the cycloheptatrienyl bridged bimetallic complexes could be, however, present in other reported complexes, since Takats and co-workers [11] have shown very recently, by X-ray analysis, that *syn*-[(μ-C_7H_7)Fe(CO)$_3$Pd(η^3-C_3H_5)], for which a fully coordinated cycloheptatrienyl ligand (μ-η^3;η^4-C_7H_7) was suggested [8], also has a (μ-η^3;η^2-C_7H_7) moiety.

Here we describe the first example of this coordination in a cycloheptatrienyl bridged iron–platinum complex.

2. Experimental

All experimental procedures were performed in standard Schlenk glassware under an atmosphere of prepurified dinitrogen. Solvents were refluxed in dinitrogen with the appropriate drying agent and distilled just before use.

☆ This article is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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Iron pentacarbonyl (Ventron Corp.) was filtered on alumina before use. Cycloheptatriene (Aldrich) and 1,5-cyclooctadiene (Aldrich) were freshly distilled. Cyclopentadiene was obtained by cracking of bicyclopentadiene (Aldrich). Potassium tert-butoxide (Aldrich) was sublimed before use. Other reagents were used as received. $(\eta^4\text{-}C_7H_8)Fe(CO)_3$ [12], $K[(\eta^3\text{-}C_7H_7)Fe(CO)_3]$ [13], $[(\eta^4\text{-}1,5\text{-}C_8H_{12})PtCl_2]$ [14] and $[(\eta^4\text{-}C_8H_{12})(\eta^5\text{-}C_5H_5)Pt]Cl$ [15] were obtained by published procedures and characterised by comparison of the spectroscopic data with the published ones.

IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer in CaF_2 cells. NMR spectra were recorded on Bruker WP-80 or 200-AC spectrometers, the latter equipped with a 5 mm 'reverse' probe and BSV3 unit with a second synthesiser that allows decoupling and pulsing at ^{13}C (90° = 35 μs) or ^{195}Pt (90° = 30 μs) frequency, while observing ^1H. The temperature was controlled by the BVT1000 of the spectrometer. Benzene-d_6 and acetone-d_6 solutions were prepared using Schlenk techniques. A relaxation delay of 15 s was employed to ensure accurate integration ratios in the ^1H spectra. For the ^1H–^{13}C and ^1H–^{195}Pt reverse correlated experiments 256 f.i.d.s of 2K data points over a sweep width of 1800 Hz in F2 were recorded. In F1 the sweep widths were 9000 and 20 000 Hz for ^{13}C and ^{195}Pt, respectively.

Mass spectra were recorded on a Jeol SG-2S operating at 70 eV, using the direct inlet technique for the introduction of the sample.

2.1. *Preparation of syn-[(μ-η³;η²-C₇H₇)Fe(CO)₃-Pt(η²,σ¹-C₈H₁₂-C₅H₅)] (1)*

A solution of $K[(\eta^3\text{-}C_7H_7)Fe(CO)_3]$ (8 mmol) in 10 ml of dry THF was added dropwise to a cooled (−78 °C) and magnetically stirred solution of $[(\eta^4\text{-}C_8H_{12})(\eta^5\text{-}C_5H_5)Pt]Cl$ (3.2 g, ~8 mmol) in 10 ml of THF. After the addition was completed, the reaction mixture was stirred for 2 h. Solvent was removed from the reaction mixture under vacuum, at low temperature (~ −20 °C), and the reddish-brown residue was extracted with cold pentane (5×20 ml). The combined extracts were filtered, concentrated, and cooled to −20 °C to give a pure sample as dark red needles (yield ~35%). *Anal.* Calc. for $C_{23}H_{24}O_3PtFe$: C, 45.96; H, 4.31; Fe, 9.32. Found: C, 45.54; H, 4.17; Fe, 9.27%. Mass spectrum (70 eV, 120 °C): M^+ (599.38), $M^+ - n$CO (n = 1–3). IR (hexane): ν(CO) 2002vs, 1945s, 1930s cm^{-1}. ^1H NMR (benzene-d_6, 200.13 MHz, 298 K, ppm): isomer (a) δ 6.91 (dq, 1H, *H*C(Cp)), 6.35 (m, 1H, *H*C(Cp)), 6.02 (m, 1H, *H*C(Cp)), 3.46 (m, *H*Cσ(COD), *J*(H–Pt) = 90 Hz), 2.84 (m, 2H, H_2C(Cp)); isomer (b) δ 6.50 (m, 1H, *H*C(Cp)), 6.26 (m, 2H, *H*C(Cp)), 3.38 (m, *H*Cσ(COD), *J*(H–Pt) = 90 Hz), 3.23–2.84 (AB system, 2H, H_2C(Cp)); overlapping resonances 4.72 (m, *H*Cη²(COD), *J*(H–Pt) = 86 Hz), 4.279 and 4.275 (s, H_7C_7, *J*(H–Pt) = 7 Hz), 4.01 (m, *H*Cη²(COD), *J*(H–Pt) = 67 Hz), 3.5–3.3 (*H*C(COD)), 2.3–1.3 (H_2C(COD)); (acetone-d_6, 200.13 MHz, 280 K, ppm): isomer (a) δ 6.58 (dq, 1H, *H*C(Cp)), 6.34 (m, 1H, *H*C(Cp)), 6.02 (m, 1H, *H*C(Cp)), 2.92 (m, 2H, H_2C(Cp)); isomer (b) δ 6.38 (m, 1H, *H*C(Cp)), 6.24 (m, 2H, *H*C(Cp)), 3.15–2.75 (four signals, 2H, H_2C(Cp)), 5.48 (m, *H*Cη²(COD), *J*(H–Pt) = ~80 Hz), 5.02 (m, *H*Cη²(COD)), 4.928 and 4.921 (s, H_7C_7, *J*(H–Pt) = 7 Hz), 3.3–2.7 (*H*C(COD)), 2.4–1.7 H_2C-(COD)). ^{195}Pt NMR (benzene-d_6, 42.8 MHz, 308 K, ppm): isomer (a) δ 1459, isomer (b) 1407 (with respect to Ξ = 21.4000 MHz). ^{13}C NMR (benzene-d_6, 50.32 MHz, 298 K, ppm): isomer (a) 215.7 (CO), 151.8 (*C*(Cp)), 134.9 (H*C*(Cp)), 132.8 (H*C*(Cp)), 124.1 (H*C*(Cp)), 90.9 (H*C*η²(COD), *J*(C–Pt) = 142 Hz), 88.2 (C_7H_7, *J*(C–Pt) ~8–9 Hz), 85.2 (H*C*η²(COD)), *J*(C–Pt) = 144 Hz), 43.2 (H*C*(COD)), 42.6 (H*C*σ(COD), *J*(C–Pt) = 704 Hz), 40.8 (H_2C(Cp)); isomer (b) 211.4 (CO), 154.1 (*C*(Cp)), 131.9 (H*C*(Cp)), 130.4 (H*C*(Cp)), 125.3 (H*C*(Cp)), 91.0 (H*C*η²(COD), *J*(C–Pt) = 142 Hz), 88.2 (C_7H_7, *J*(C–Pt) ~8–9 Hz), 85.2 (H*C*η²(COD), *J*(C–Pt) = 144 Hz), 44.0 (H*C*(COD)), 43.9 (H*C*(COD)), 43.0 (H_2C(Cp)); 34.2, 34.1, 30.5, 28.9, 28.1, 27.6 (H_2C(COD)); (acetone-d_6, 50.32 MHz, 298 K, ppm): isomer (a) 217.2 (CO), 152.6 (*C*(Cp)); 135.6 (H*C*(Cp)), 132.8 (H*C*(Cp)), 124.8 (H*C*(Cp)); isomer (b) 211.8 (CO), 155.4 (*C*(Cp)), 133.3 (H*C*(Cp)); 130.5 (H*C*(Cp)), 125.7 (H*C*(Cp)); 93.0 (H*C*η²(COD), *J*(C–Pt) = 147 Hz), 89.9 (C_7H_7), 87.8 (H*C*η²(COD), *J*(C–Pt) = 143 Hz), 44.7, 44.4, 43.9, 43.5, 42.9, 41.4, 34.9.

2.2. *X-ray data collection, structure solution and refinement for syn-[(μ-η³;η²-C₇H₇)Fe(CO)₃Pt(η²,σ¹-C₈H₁₂-C₅H₅)] (1)*

A dark red–brown crystal of dimensions 0.25×0.10×0.10 mm was mounted on an Enraf-Nonius CAD-4 diffractometer, and 25 intense reflections having a θ value in the range 10.0–14.0° were centred using graphite-monochromatised Mo Kα radiation (λ = 0.71073 Å). Least-squares refinement of their setting angles resulted in the unit-cell parameters reported in Table 1, together with an orientation matrix relating the crystal axes to the diffractometer axes. A total of 3939 diffracted intensities (2739 with $I \geqslant 3\sigma(I)$) was collected at room temperature with variable scan speed (maximum scan time for each reflection 90 s), by exploring the quadrant of the reciprocal lattice with $-53 < h < 53$, $0 < k < 15$ and $0 < l < 8$, out to a maximum 2θ angle of 50°. Intensity was checked by monitoring three standard reflections every 180 min and a moderate crystal decay was observed, the drift corrections applied being in the range 0.94–1.00. The diffracted intensities were also corrected for Lorentz, polarisation and background effects. An empirical absorption correction was

Table 1
Summary of crystal data and structure refinement parameters for *syn*-[(μ-η^3;η^2-C_7H_7)Fe(CO)$_3$Pt(η^2,σ^1-C_8H_{12}-C_5H_5)]

Formula	$C_{23}H_{24}FeO_3Pt$
Formula weight	599.36
Crystal system	monoclinic
Space group	*C*2/*c* (No. 15)
a (Å)	45.197(6)
b (Å)	13.306(1)
c (Å)	7.509(1)
β (°)	92.96(1)
V (Å^3)	4509.8(9)
Z	8
F(000)	2320
Density (calc.) (g cm^{-3})	1.766
Temperature (K)	298(2)
Diffractometer	CAD4
Radiation (Mo Kα graphite-monochromated) (Å)	0.71073
Absorption coefficient (mm^{-1})	6.859
Crystal size (mm)	0.25 × 0.10 × 0.10
Scan method	ω
Scan interval (°)	1.3
Max. time per reflection (s)	90
θ Range (°)	3.0–25.0
Index ranges	$-53 \leq h \leq 53$, $0 \leq k \leq 15$, $0 \leq l \leq 8$
Reflections collected	3939
Crystal decay (%)	5
Absorption correction	ψ-scan
No. azimut reflections	3
Max. and min. transmission	1.00 and 0.35
Refinement method	full-matrix least-squares on F_o^2
Observed reflection criterion	$I > 3\sigma(I)$
Data/restraints/parameters	2739/0/254
Goodness of fit on F_o^2	1.146
Final *R* indices ($I > 3\sigma(I)$)	*R*1, 0.0331; *wR*2, 0.0799
R indices (all data)	*R*1, 0.0822; *wR*2, 0.1078
Largest difference peak and hole (e Å^{-3})	1.038 and −0.837

Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 54.1835P]$ where $P = (F_o^2 + 2F_c^2)/3$. $R1 = \Sigma\Delta F/\Sigma F_o$; $wR2 = [\Sigma w\Delta F^2/\Sigma wF_o^2]^{1/2}$.

[illegible]

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for *syn*-[(μ-η^3;η^2-C_7H_7)Fe(CO)$_3$Pt(η^2,σ^1-C_8H_{12}-C_5H_5)]

	x	*y*	*z*	U_{eq} [a]
Pt	0.351619(8)	0.28645(3)	0.11700(5)	0.04048(12)
Fe	0.31215(3)	0.18564(9)	0.2971(2)	0.0419(3)
O(1)	0.2856(2)	0.0776(6)	0.5863(11)	0.076(2)
O(2)	0.3534(2)	0.0174(6)	0.2556(13)	0.086(3)
O(3)	0.3370(2)	0.3515(6)	0.5112(9)	0.060(2)
C(1)	0.2957(2)	0.1191(7)	0.4719(13)	0.048(2)
C(2)	0.3380(2)	0.0852(8)	0.2681(14)	0.054(3)
C(3)	0.3294(2)	0.2859(7)	0.4194(12)	0.046(2)
C(4)	0.2729(2)	0.2809(9)	0.2513(13)	0.057(3)
C(5)	0.2735(2)	0.1922(9)	0.1446(14)	0.062(3)
C(6)	0.2948(2)	0.1767(9)	0.0214(13)	0.059(3)
C(7)	0.3119(2)	0.2502(9)	−0.0723(13)	0.060(3)
C(8)	0.3107(2)	0.3554(8)	−0.0548(13)	0.057(3)
C(9)	0.2946(2)	0.4151(8)	0.0621(14)	0.056(3)
C(10)	0.2789(2)	0.3838(8)	0.1960(14)	0.057(3)
C(11)	0.3897(2)	0.2549(7)	0.2788(12)	0.042(2)
C(12)	0.4037(2)	0.3568(7)	0.3281(13)	0.050(2)
C(13)	0.4042(2)	0.4289(8)	0.164(2)	0.062(3)
C(14)	0.3798(2)	0.4054(8)	0.0260(14)	0.056(3)
C(15)	0.3802(2)	0.3262(8)	−0.0962(13)	0.058(3)
C(16)	0.4028(3)	0.2518(10)	−0.1313(13)	0.072(4)
C(17)	0.4253(2)	0.2218(8)	0.0284(13)	0.059(3)
C(18)	0.4111(2)	0.1809(7)	0.1913(13)	0.052(3)
C(19)	0.4342(2)	0.1513(7)	0.3317(13)	0.050(2)
C(20)	0.4629(3)	0.1767(9)	0.352(2)	0.077(4)
C(21)	0.4768(3)	0.1270(11)	0.512(2)	0.097(5)
C(22)	0.4552(3)	0.0713(10)	0.584(2)	0.081(4)
C(23)	0.4281(3)	0.0818(9)	0.4798(14)	0.068(3)

[a] U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

applied by performing a ψ-scan correction [16]. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from Ref. [17].

The structure was solved by Patterson methods and refined by full-matrix least-squares against F_o^2. Weights assigned to individual observations are reported in Table 1. All non-hydrogen atoms were given anisotropic thermal parameters. The hydrogen atoms were placed in idealised positions following the pertinent carbon atoms' stereochemistry and refined riding on their parent atoms with a common refinable isotropic displacement parameter. The final values for the conventional *R* values are reported in Table 1. All the calculations were performed on a Personal Iris 4D/35 computer using SHELXL-93 [18].

The final position parameters are given in Table 2, together with their associated standard deviations. Selected bond distances and angles are to be found in Table 3.

3. Results and discussion

3.1. Fluxional behaviour of *syn*-[(μ-η^3;η^2-C_7H_7)-Fe(CO)$_3$Pt(η^2,σ^1-C_8H_{12}-C_5H_5)] (1)

The formation of *syn*-[(μ-η^3;η^2-C_7H_7)Fe(CO)$_3$-Pt(η^2,σ^1-C_8H_{12}-C_5H_5)] (**1**), by reaction of [(η^3-C_7H_7)-Fe(CO)$_3$]$^-$ with [(η^4-C_8H_{12})(η^5-C_5H_5)Pt]$^+$ was indeed unexpected since *syn*-[(μ-C_7H_7)Fe(CO)$_3$Pd(η^5-C_5H_5)], obtained by a very similar procedure, in the reaction of [(η^3-C_7H_7)Fe(CO)$_3$]$^-$ with [(η^4-C_8H_{12})(η^5-C_5H_5)-Pd]$^+$ [9,10], was the expected product even if the η^3;η^2-C_7H_7 coordination was unique. Some examples of transfer of C_5H_5 on other diolefins mediated by Pt have been reported, but these compounds are secondary products of the reaction [19], whereas **1** is obtained in discrete yield and is the only product of our reaction.

Whereas the IR spectrum (three terminal CO stretching bands at 2002, 1945, 1930 cm^{-1}) was indicative of

Table 3
Relevant bond lengths (Å) and angles (°) for *syn*-[(μ-η^3;η^2-C_7H_7)Fe$(CO)_3$Pt(η^2,σ^1-C_8H_{12}-C_5H_5)]

Bond lengths			
Pt–C(11)	2.098(9)	C(6)–C(7)	1.45(2)
Pt–C(14)	2.164(9)	C(7)–C(8)	1.41(2)
Pt–C(15)	2.175(9)	C(8)–C(9)	1.41(2)
Pt–C(7)	2.283(9)	C(9)–C(10)	1.329(14)
Pt–C(8)	2.384(9)	C(11)–C(12)	1.532(13)
Pt–C(3)	2.530(9)	C(11)–C(18)	1.550(13)
Pt-Fe	2.6569(13)	C(12)–C(13)	1.564(13)
Fe–C(3)	1.776(10)	C(13)–C(14)	1.508(14)
Fe–C(1)	1.778(10)	C(14)–C(15)	1.398(14)
Fe–C(2)	1.795(12)	C(15)–C(16)	1.46(2)
Fe–C(5)	2.039(10)	C(16)–C(17)	1.58(2)
Fe–C(6)	2.178(9)	C(17)–C(18)	1.511(13)
Fe–C(4)	2.194(10)	C(18)–C(19)	1.498(13)
O(1)–C(1)	1.136(11)	C(19)–C(20)	1.340(14)
O(3)–C(3)	1.154(11)	C(19)–C(23)	1.484(13)
O(2)–C(2)	1.145(12)	C(20)–C(21)	1.48(2)
C(4)–C(5)	1.43(2)	C(21)–C(22)	1.36(2)
C(4)–C(10)	1.461(14)	C(22)–C(23)	1.43(2)
C(5)–C(6)	1.38(2)		
Bond angles			
C(11)–Pt–Fe	99.0(2)	C(11)–Pt–C(7)	156.0(4)
C(11)–Pt–C(8)	168.9(4)	Et2*–Pt–Fe	176.3(2)
Et1*–Pt–Fe	79.0(1)	Et1*–Pt–C(11)	173.8(3)
Et1*–Pt–Et2*	97.3(1)	Et2*–Pt–C(11)	84.7(2)
Al*–Fe–Pt	94.6(3)	Al*–Fe–C(1)	104.0(3)
Al*–Fe–C(2)	125.0(3)	Al*–Fe–C(3)	117.8(3)
C(1)–Fe–Pt	160.8(3)	C(2)–Fe–Pt	81.8(3)
C(3)–Fe–Pt	66.2(3)	C(3)–Fe–C(1)	100.5(4)
C(3)–Fe–C(2)	110.6(4)	C(1)–Fe–C(2)	91.0(4)
O(1)–C(1)–Fe	178.5(9)	O(2)–C(2)–Fe	175.8(9)
O(3)–C(3)–Fe	170.5(8)	O(3)–C(3)–Pt	114.5(7)
Fe–C(3)–Pt	73.9(3)	C(5)–C(4)–C(10)	127.2(9)
C(6)–C(5)–C(4)	122.4(10)	C(5)–C(6)–C(7)	128.9(11)
C(8)–C(7)–C(6)	127.0(11)	C(7)–C(8)–C(9)	129.9(10)
C(10)–C(9)–C(8)	127.3(10)	C(9)–C(10)–C(4)	128.6(10)
C(12)–C(11)–C(18)	114.0(8)	C(11)–C(12)–C(13)	112.1(8)
C(14)–C(13)–C(12)	111.9(8)	C(15)–C(14)–C(13)	124.9(10)
C(14)–C(15)–C(16)	131.7(10)	C(15)–C(16)–C(17)	117.6(8)
C(18)–C(17)–C(16)	115.1(8)	C(19)–C(18)–C(17)	110.8(8)
C(19)–C(18)–C(11)	107.2(8)	C(17)–C(18)–C(11)	114.4(8)
C(20)–C(19)–C(23)	106.7(9)	C(20)–C(19)–C(18)	130.6(10)
C(23)–C(19)–C(18)	122.7(9)	C(19)–C(20)–C(21)	110.3(11)
C(22)–C(21)–C(20)	106.5(11)	C(21)–C(22)–C(23)	110.1(11)
C(22)–C(23)–C(19)	106.4(10)		
Torsional angles			
C(4)–C(5)–C(6)–C(7)	−25(2)	C(5)–C(6)–C(7)–C(8)	1(2)
C(6)–C(7)–C(8)–C(9)	4(2)	C(7)–C(8)–C(9)–C(10)	7(2)
C(8)–C(9)–C(10)–C(4)	−3(2)	C(9)–C(10)–C(4)–C(5)	−23(2)
C(10)–C(4)–C(5)–C(6)	39(1)	C(11)–C(12)–C(13)–C(14)	26(1)
C(12)–C(13)–C(14)–C(15)	−78(1)	C(13)–C(14)–C(15)–C(16)	−3(2)
C(14)–C(15)–C(16)–C(17)	27(2)	C(15)–C(16)–C(17)–C(18)	57(1)
C(16)–C(17)–C(18)–C(11)	−60(1)	C(17)–C(18)–C(11)–C(12)	−54(1)
C(18)–C(11)–C(12)–C(13)	80(1)		

Et1*, Al* and Et2* are the centre of mass of the ethylene (C_7–C_8), allyl (C_4–C_5–C_6) and ethylene (C_{14}–C_{15} moieties, respectively.

the presence of the expected $Fe(CO)_3$ unit, the ^1H NMR spectrum, both in benzene and in acetone solutions (Fig. 1), showed the presence of σ-bonded cyclopentadiene units [20]. The absence of Pt satellites however indicated that these moieties were not bound to the metal. The benzene spectrum presents five signals at $\delta = 6.89$ (a), 6.52 (b), 6.35 (c), 6.24 (d) and 6.01 (e) ppm, respectively. Three signals, namely a, c and e, are coupled to each other and coupled to a signal at 2.84 ppm (1:1:1:2 intensity ratio) as shown by a COSY-

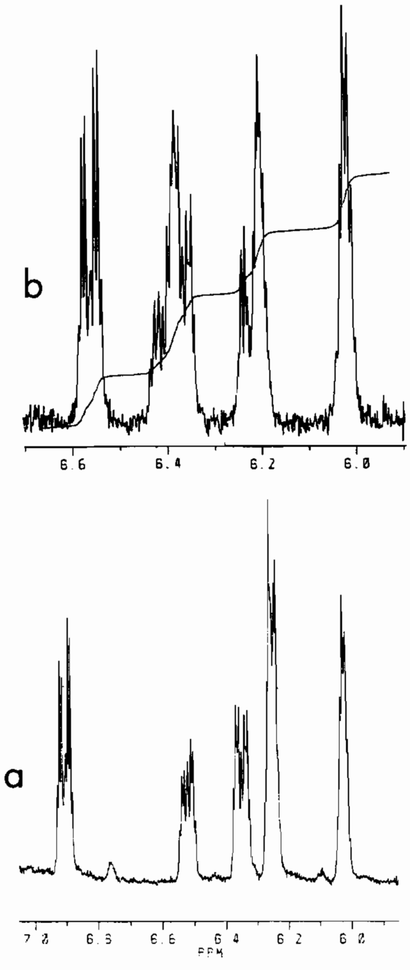

Fig. 1. Low field portion of the ^1H NMR spectrum (200.13 MHz) of (a) benzene-d_6 (298 K) and (b) acetone-d_6 (280 K) solutions of **1**.

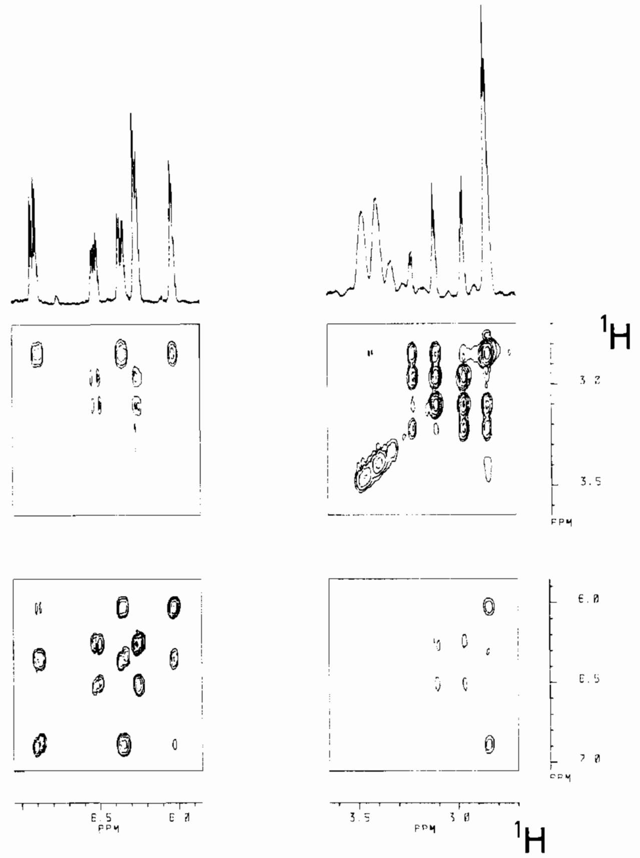

Fig. 2. Contour plots of selected regions of the ^1H COSY-45 spectrum of **1** (200.13 MHz, 308 K, benzene-d_6).

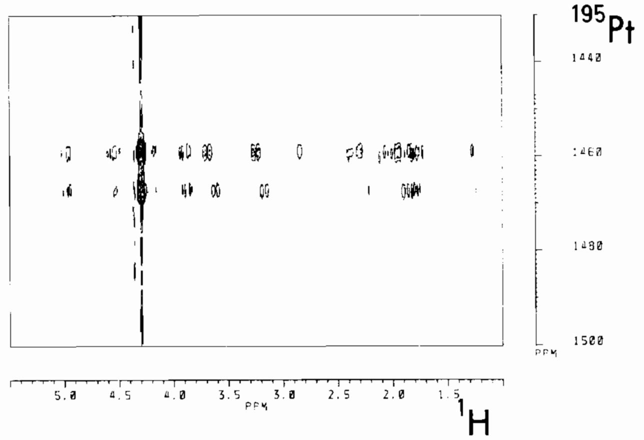

Fig. 3. Contour plot of the 2D ^1H–^{195}Pt reverse correlated experiment showing the presence of two species (308 K, benzene-d_6). No Pt decoupling was performed during the acquisition.

45 experiment (Fig. 2) and can be easily attributed to a cyclopentadiene unit [20] attached to an organic unit with an sp^2 carbon. The signals b and d are coupled together and to the four signals of an AB spin system at 3.23–2.84 ppm with an intensity ratio 1:2:1:1 and can be attributed to a similar cyclopentadiene of a second isomer. The relative amount of the two groups of signals of cyclopentadienes suggests an isomeric ratio about 55:45. Also for the C_7H_7 protons two very close signals are observed ($\delta = 4.279$ and 4.275, J(H–Pt) = 7 Hz) and their overall integrated intensity is what is expected for one C_7H_7 moiety for each set of the cyclopentadiene resonances. The presence in solution of two species differing only in the bonding mode of the C_5H_5 fragment is confirmed by a 2D ^1H–^{195}Pt reverse correlated experiment [21] (Fig. 3) which shows that the two compounds have very similar Pt environments (δ 1459 and 1467 ppm, respectively) and that, moreover, the resonances of the protons of the π-C_2H_2 and of the σ-CH groups of the cyclooctenyl ligands are almost overlapped in the ^1H spectrum: 4.72 (m, $HC\eta^2$(COD), J(H–Pt) = 86 Hz), 4.01 (m, $HC\eta^2$(COD), J(H–Pt) = 67 Hz); isomer (a) δ 3.46 (m, $HC\sigma$(COD), J(H–Pt) = 90 Hz); isomer (b) δ 3.38 (m, $HC\sigma$(COD), J(H–Pt) = 90 Hz).

The same pattern of ^1H signals is observed in acetone solutions although the signals of the two cyclopentadiene units are shifted and overlapping ($\delta = 6.58$ (a′), 6.38 (b′), 6.24 (c′), 6.00 (d′) ppm). A 2D COSY experiment showed that the signals a′, b′ and d′, are coupled to each other and also to a signal at 2.92 ppm. The signals of the second cyclopentadiene unit are found at 6.24 ppm (c′, 2 protons) and at 6.38 (b′, overlapping the signal of one proton of the first cyclopentadiene unit). Integration of the cyclopentadiene signals shows that in acetone the ratio between the two isomers is reversed, isomer (b) being slightly more abundant. As in benzene, the signals expected for the C_7H_7 rings are very close and a better resolution is achieved in the 80 MHz spectrum (δ=4.87 ppm). Both signals present the expected satellites originated by the coupling with platinum (Fig. 4). The variable temperature ^1H NMR spectra of **1** in acetone in the region of the cycloheptatrienyl signal clearly show the fluxional behaviour of both compounds, both undergoing a rapid ring whizzing of the C_7H_7 unit. We were not able to obtain the low-temperature limiting spectrum since at 203 K the signal is practically collapsed (Fig. 4) and at 173 K the limiting spectrum starts to grow up but the new signals are still very broad.

A 2D ^1H–^{13}C correlation experiment performed in the reverse mode and a ^{13}C 1D *J* modulated spectrum at room temperature allowed the unambiguous assignment of part of the ^{13}C resonances. While the carbonyl and the cyclopentadiene signals of the two isomers are well resolved and identified (C_6D_6, isomer (a) 215.7 (CO), 151.8 (*C*(Cp)), 134.9 (H*C*(Cp)), 132.8 (H*C*(Cp)), 124.1 (H*C*(Cp)), 40.8 (H_2*C*(Cp)); isomer (b) 211.4 (CO), 154.1 (*C*(Cp)), 131.9 (H*C*(Cp)), 130.4 (H*C*(Cp)), 125.3 (H*C*(Cp)), 43.0 (H_2*C*(Cp))), the signals of the cycloheptatrienyl and cyclooctenyl carbons are overlapped and only a partial assignment could be performed. The 2D ^1H–^{13}C correlation experiment clearly shows also that the two protonic signals of the cyclopentadiene fragment that are overlapped are bound to two different carbon atoms at 130.4 and 125.3 ppm, respectively.

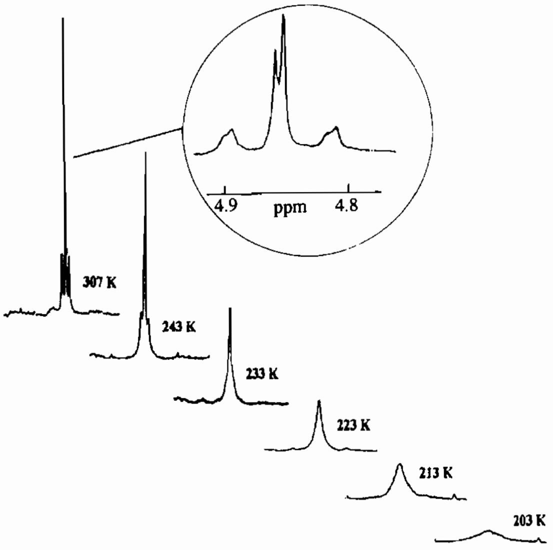

Fig. 4. The variable temperature ^1H NMR spectrum of the cycloheptatrienyl ring of **1**. Inset: the evidence of two isomers with the satellites due to coordination to platinum (80.13 MHz, acetone-d_6).

The ^{195}Pt chemical shifts of the two species are very close and fall in the range expected for Pt(II) complexes [22].

Platinum in complex **1** achieves a 16-electron configuration which is the preferred one in Pt(II) square planar complexes [23] whereas, in the similar reaction of palladium, an 18-electron configuration was obtained with complete substitution of the cycooctadiene ligand. The recent finding [11] that $[(\mu\text{-}C_7H_7)Fe(CO)_3Pd(\eta^3\text{-}C_3H_5)]$ [8] also has a $(\mu\text{-}\eta^3;\eta^2\text{-}C_7H_7)$ moiety suggests that Pd, at least in these bridged cycloheptatrienyl bimetallic complexes, also prefers a 16-electron configuration, when possible. Probably the uncommon η^3-C_5H_5 coordination [19,24] is forcing the 18-electron configuration in *syn*-$[(\mu\text{-}\eta^3;\eta^2\text{-}C_7H_7)Fe(CO)_3Pd(\eta^5\text{-}C_5H_5)]$ (**2**) [9,10].

So far in the series of cycloheptatrienyl bridged bimetallic complexes (Fe–M; M = Pd, Pt) [8–11] the low-temperature limiting NMR spectrum [9,10] has been achieved only for **2**. Considering that usually the activation energy of the fluxional movement of the polyolefinic rings bonded to transition metals increases in the same transition metal group with increasing atomic number (see for instance Refs. [25,26]), and that even in **1** the ring whizzing is still operating at 173 K, one can speculate that in the d^{10} transition metals the 18-electron configuration of the metal increases the activation energy of the ring whizzing.

The transfer of the cyclopentadiene unit to the cyclooctadiene ring, mediated by platinum, which produces **1**, may be of interest in the synthesis of the skeleton of natural occurring products and further work in this direction is being currently carried out.

3.2. Molecular structure of syn-$[(\mu\text{-}\eta^3;\eta^2\text{-}C_7H_7)Fe(CO)_3Pt(\eta^2,\sigma^1\text{-}C_8H_{12}\text{-}C_5H_5)]$ *(1)*

Two perspective views of the *syn*-$[(\mu\text{-}\eta^3;\eta^2\text{-}C_7H_7)Fe(CO)_3Pt(\eta^2,\sigma^1\text{-}C_8H_{12}\text{-}C_5H_5)]$ molecule, with the appropriate numbering scheme, are shown in Fig. 5. The molecule consists of an Fe–Pt heterobimetallic dimer bridged by a cycloheptatrienyl group in the rare $(\mu\text{-}\eta^3;\eta^2)$ coordination mode [9–11]. The coordination sphere around Fe is completed by three carbonyls in order to achieve the 18 Ve; at variance the Pt atom reaches only 16 Ve being bound in an uncommon σ,π mode to a substituted cyclooctene obtained by the metal assisted addition of the C_5H_5 ligand to one of the 1,5-cyclooctadiene's double bonds.

The π electrons of the C_7H_7 ring are partially localised into one 'allylic' (av. C–C 1.406 Å) and two 'ethylenic' (av. C–C 1.367 Å) moieties separated by long C–C bonds (av. C–C 1.442 Å); as result C_7H_7 is non-planar, the angle between the coordinated ethylenic and allylic moieties is 24(1)° while that between the two ethylenic moieties is 8(1)°. Noteworthy, one out of the two double

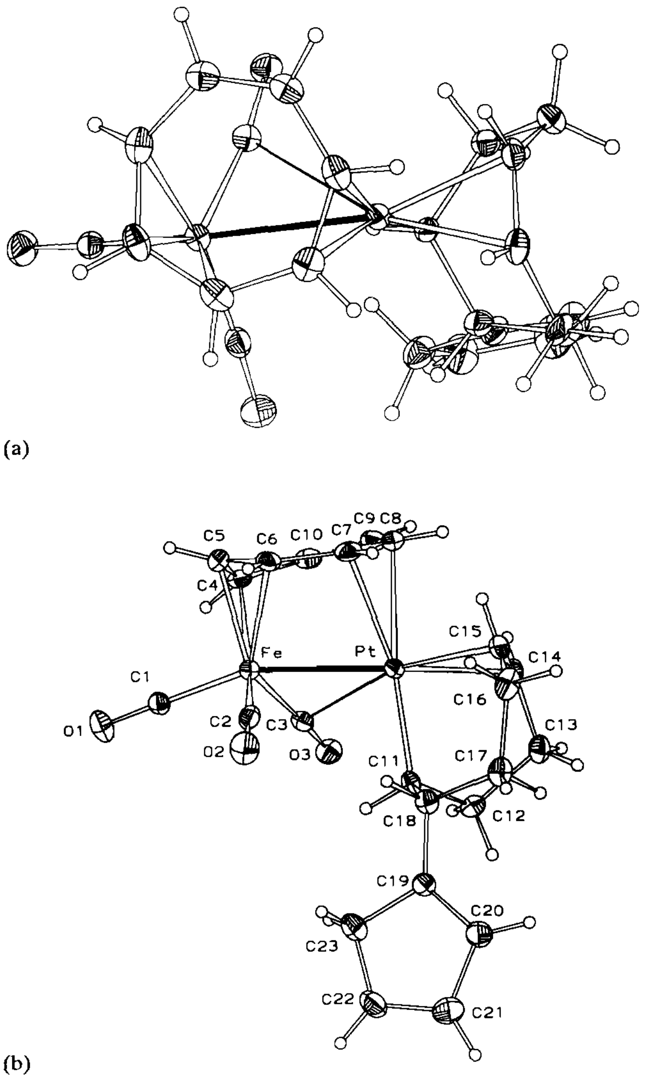

Fig. 5. ORTEP drawings (30% probability ellipsoids) of *syn*-[(μ-η^3;η^2-C_7H_7)Fe(CO)$_3$Pt(η^2,σ^1-C_8H_{12}-C_5H_5)] showing the molecule: (a) along the perpendicular of the C_7H_7 least-squares plane; (b) rotating the previous view by 90° about the Fe–Pt bond.

bonds is uncoordinated and, as a consequence, has a shorter C–C bond distance than the coordinated one (1.327(15) versus 1.407(16) Å).

The σ,π-coordinated cyclooctenyl has a skew-boat conformation, reminiscent of that of an η^4-coordinated cyclooctadiene, since the cyclopentadiene radical has attached one of the coordinated carbon atoms from the opposite side of the Pt metal. The σ-bonded C atom is hybridised sp^3 and a similar σ,π coordination has been observed before in a few compounds, e.g. [(η^2,σ^3-$C_3B_2Et_4Me$)Pt(η^2,σ^1-C_8H_{13})] [27] and [(η^5-C_5Me_5)Pt(η^2,σ^1-C_8H_{13})] [28]. The cyclopentadiene radical is bound through an sp^2 C atom as shown by the NMR spectra and by the pattern of the C–C bond distances which allow identification, unequivocally, of C23 as the sp^3 carbon atom.

The Fe environment is close to that found in **2** [10] and in *syn*-[(μ-η^3;η^2-C_7H_7)Fe(CO)$_3$Pd(η^3-C_3H_5)] [11], the average Fe–C(carbonyl) bond length (1.784, 1.786 and 1.771 Å, respectively) and the pattern of the Fe–C(ring) interactions (long–short–long) being similar. The Fe–Pt bond distance is also similar to the Fe–Pd ones (2.657(1), 2.653(1) and 2.666 Å, respectively); however the semibridging carbonyl ligand in **1** is more interacting with the adjacent metal than in **2** (Fe–C–O 170.4(8) versus 171.0(3)°; M···C 2.530(9) versus 2.653(4) Å). Interestingly, in the crystals of *syn*-[(μ-η^3;η^2-C_7H_7)Fe(CO)$_3$Pd(η^3-C_3H_5)] [11] there are two independent molecules with a different character of the semibridging carbonyl ligands, one being closer to **1**, the other to **2**. This suggests a definite role of packing forces in tuning the degree of asymmetrisation of such a coordination mode.

The 16-electron Pt atom is in a unique square planar environment of two *cis* π-bonded double bonds, a σ-bonded sp^3 carbon and the Fe atom. As expected the Pt–C_{sp^3} interaction (2.097(9) Å) is shorter than the Pt–(η^2-C_2) ones. Noteworthy, the two Pt–(η^2-C_2) interactions are markedly different, the average Pt–C bond lengths for the double bonds belonging to the cycloheptatrienyl and to the cyclooctenyl ligands being 2.333 and 2.169 Å, respectively. This cannot be related to 'aromaticity' of the cycloheptatrienyl ligand since the analogous interactions in **2** [9,10] were 2.151 Å (versus 2.333 Å). More reasonably, the markedly different bond distances are due to the different *trans*-influence of the Pt–Fe and Pt–C_{sp^3} bonds. A further indication of the role of the *trans*-influence is embedded in the individual Pt–C bond lengths; as a matter of fact C8, which is definitely more *trans* to the Pt–C_{sp^3} bond than C7, has a longer distance from the Pt atom than C7 (2.383(10) versus 2.283(10) Å).

4. Conclusions

The NMR data do not allow a definitive structural determination for the two isomers present in solution. However, since the main differences concern the signals of the σ-bonded cyclopentadiene moiety, we think that the two isomeric complexes probably differ in the location of the unique sp^3 carbon atom which could be in α position in one solution isomer (like in the crystal selected for the X-ray structure determination) and in β position in the second one.

5. Supplementary material

Tables S1 and S2 giving hydrogen atom coordinates and anisotropic thermal parameters (2 pages) for **1** are available from the authors on request.

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