

Journal of Organometallic Chemistry, 181 (1979) 169–182
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

**THE *trans*-INFLUENCE IN POLYENYL–METAL COMPLEXES;
THE CRYSTAL AND MOLECULAR STRUCTURE OF HYDRIDO-
(η -PENTAMETHYLCYCLOPENTADIENYL)BIS(TRIPHENYLPHOSPHINE)-
RHODIUM(III) HEXAFLUOROPHOSPHATE ***

D. MICHAEL P. MINGOS * and PETER C. MINSHALL

*Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR
(Great Britain)*

M.B. HURSTHOUSE, K.M.A. MALIK and S.D. WILLOUGHBY

*Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS (Great
Britain)*

(Received May 29th, 1979)

Summary

The structure of $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{H}(\text{PPh}_3)_2]\text{PF}_6$ has been determined by ^1H NMR studies and a single-crystal X-ray analysis. The compound crystallises in the orthrhombic space group $P2_12_12_1$ with lattice constants a 12.926(3), b 15.216(3) and c = 20.957(4) Å, with Z = 4. The structure was determined using diffractometer data and by least-squares techniques to R = 0.0887 based on 2805 independent reflections with $F_o > 4\sigma(F_o)$. The geometry about the metal atom may be inferred to be a “piano-stool” arrangement with the C_5Me_5 ring representing the seat and the PPh_3 and H ligands the legs, although the hydrogen atom was not directly located in the crystallographic analysis. The observed distortions in the C_5Me_5 ring may be attributed to the large *trans*-influence of the hydrido ligand.

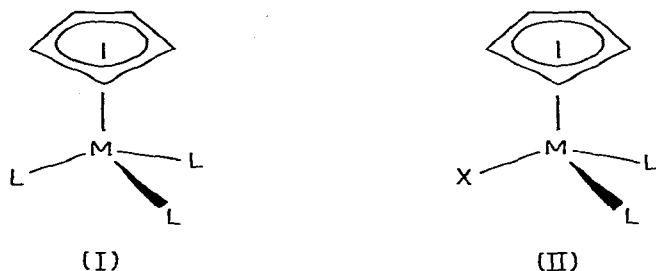
Introduction

Much of our current understanding of the *trans*-effect and *trans*-influence [1] in simple transition metal coordination compounds has arisen from research initiated by Professor Chatt and his coworkers [2] in the ICI laboratories in the 1950's. The observation that ligands such as CO, C_2H_4 and PR_3 exhibited a high *trans*-effect and also had the potential to act as π -acid ligands when coordinated to electron rich transition metals led to a general theory of the *trans*-

* Dedicated to Professor Joseph Chatt on the occasion of his 65th birthday.

effect based on a π -bonding model [3]. The synthesis of stable alkyl and hydrido complexes of the platinum metals in the ICI laboratories permitted their investigation by a wide range of spectroscopic and structural techniques [4–6] and resulted in the recognition that such ligands not only exhibited high *trans*-effects [7] but also gave rise to a considerable lengthening of the *trans*-metal–ligand bond. The study of these *trans*-influences using NMR and structural techniques has continued to attract the interest of chemists to this date, although there is still some controversy as to the electronic forces responsible for the *trans*-influence and its relationship to the *trans*-effect [8,9].

The structural implications of having ligands of high *trans*-influence on a polyene also coordinated to the same metal have not been investigated in a systematic fashion, however. Early structural studies by Dahl, Mason and their coworkers [10,11] gave some indication that if the axial symmetry of a metal–ligand fragment were removed, for example by a substitution such as that illustrated in I and II then distortions in the metal polyene unit resulted.



The variation in C–C distances in such complexes was consistent with an “ene-enyl” localisation as indicated in III, and was attributed to unequal populations of the C_5H_5 e_1 molecular orbitals. However, there was no attempt to evaluate the influence of the electronic characteristics of the ligand X on the observed distortion. In this context it is perhaps worth noting that an alternative type of distortion has been reported for cyclopentadienyl complexes of the type $M(C_5R_5)(L)_2$ and is illustrated in IV [12].



The structural analysis reported in this paper of $[Rh(\eta-C_5Me_5)H(PPh_3)_2]PF_6$, is the first in a series of such studies aimed at elucidating the structural distortions arising from the coordination of ligands of high *trans*-influence to cyclopentadienylmetal fragments.

Experimental

Unless otherwise stated the reactions were performed under anaerobic conditions and the solvents were purified and distilled under nitrogen before use.

Infrared spectra were recorded on a Perkin—Elmer 577 spectrophotometer. Elemental analyses were performed by Butterworth Microanalytical Laboratories. The proton magnetic resonance spectra were recorded on a Varian HA100 and Bruker HX90 spectrometers.

[Rh(η -C₅Me₅)Cl₂]₂ was prepared by standard literature methods [13] and converted into Rh(η -C₅Me₅)(NO₃)₂(PPh₃). The details of the preparation of Rh(η -C₅Me₅)(NO₃)₂(PPh₃) and single crystal structural analysis of this compound will be given in a subsequent publication [14].

Hydrido(triphenylphosphine)(η -pentamethylcyclopentadienyl)rhodium(III) hexafluorophosphate

Triphenylphosphine (0.38 g, 1.48 mmol) was added to a suspension of Rh(η -C₅Me₅)(NO₃)₂(PPh₃) (0.46 g, 0.74 mmol) in methanol (30 cm³) and air was slowly bubbled through the mixture at 55°C for 0.5 h. The mixture was cooled to room temperature and filtered. Concentration of the filtrate to 15 cm³ and addition of NH₄PF₆ (0.30 g, 1.8 mmol) gave yellow crystals of [RhH(η -C₅Me₅)(PPh₃)₂]PF₆ (0.32 g, 48%). The sample was recrystallised from acetone/ether to give an analytically pure sample, m.p. 192–194°C (dec.). (Found: C, 59.0; H, 4.9; P, 10.2, RhC₄₆H₄₆P₃F₆ calcd.: C, 60.8; H, 5.1; P, 10.2%) Λ_m (10⁻³ solution in nitrobenzene) 22.8 ohm⁻¹ cm² mol⁻¹, which is consistent with its formulation as a 1/1 electrolyte.

Hydridobis(triphenylphosphine)(η -pentamethylcyclopentadienyl)rhodium(III) tetraphenylborate

This compound was prepared similarly using NaBPh₄ instead of NH₄PF₆ in 51% yield, m.p. 158–159°C (dec.). (Found: C, 78.1; H, 6.0. RhC₇₀H₆₆BP₂ calcd.: C, 77.7; H, 6.1%). Λ_m (~10⁻³ solution in nitrobenzene) 20.2 ohm⁻¹ cm² mol⁻¹.

Hydridobis(triphenylphosphine)(η -pentamethylcyclopentadienyl)rhodium(III) perchlorate

Triphenylphosphine (0.92 g, 3.51 mmol) was added to a solution of Rh(η -C₅Me₅)(C₂H₄)₂ (0.51 g, 1.73 mmol) in dry benzene (25 cm³) and the mixture was stirred at 60°C for 1 h. HClO₄ (0.35 g, 3.5 mmol) in methanol (25 cm³) was added to the reaction mixture with stirring. Addition of ether to the yellow solution gave crystals of [Rh(η -C₅Me₅)H(PPh₃)₂]ClO₄ (1.22 g, 82%). (Found C, 62.8; H, 5.1. RhC₄₆H₄₆ClO₄P₂ calcd.: C, 64.0; H, 5.3%).

The spectroscopic data for the complexes [Rh(η -C₅Me₅)H(PPh₃)₂]X, where X = PF₆, ClO₄ and BPh₄, are summarised in Table 1. Preliminary examination of the crystals from the above reactions suggested that the PF₆ salt would be most suitable for a three dimensional single crystal analysis.

Collection and reduction of diffraction data

[Rh(η -C₅Me₅)(H)(PPh₃)₂]PF₆ was recrystallised from CHCl₃/petroleum (40–60°C) as yellow transparent irregular blocks. A single crystal with overall dimensions 0.40 × 0.30 × 0.30 mm was selected for the crystallographic analysis and mounted on the end of a fine glass fibre. Preliminary oscillation and

TABLE I
SPECTROSCOPIC DATA FOR $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{H})(\text{PPh}_3)_2]\text{X}$ (X = PF₆, BPh₄ or ClO₄)

Compound	$\nu(\text{Rh}-\text{H})$ cm ⁻¹	C ₅ Me ₅	Rh-H	Other
$[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{H})(\text{PPh}_3)_2]\text{PF}_6$	2050	1.37(m)	-11.05(dt) ^b J(Rh-H) 18 Hz 2J(P-H) 30 Hz	7.2-7.6 complex (Ph, PPh ₃)
$[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{H})(\text{PPh}_3)_2]\text{BPh}_4$	2050	1.35(m)	-11.00(dt) ^a J(Rh-H) 18 Hz 2J(P-H) 28 Hz	7.2-7.4 complex (Ph, PPh ₃ and BPh ₄)
$[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{H})(\text{PPh}_3)_2]\text{ClO}_4$	2050	1.40(m)	-11.02(dt) ^a J(Rh-H) 18 Hz J(P-H) 30 Hz	7.2-7.4 complex (Ph, PPh ₃)

^a m = multiplet, ^b dt = doublet of triplets.

TABLE 2

SUMMARY OF CRYSTAL DATA FOR $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{H})(\text{PPh}_3)_2]\text{PF}_6$

F.W.	908
a 12.926(3) Å	
b 15.216(3) Å	$\alpha = \beta = \gamma = 90^\circ$
c 20.957(4) Å	
Volume 4122 Å ³	
Systematic absences $h00$ for h odd; $0k0$ for k odd; $00l$ for l odd	
Space group $P2_12_12_1$	
$Z = 4$	
$d(\text{calcd.})$	1.468 g cm ⁻³
$d(\text{found})$	1.45(2) g cm ⁻³ (by flotation)
$F(000)$	1860
$\lambda(\text{Mo-K}\alpha)$	0.7107 Å
2805 symmetry independent reflections $1.5 \leq 2\theta \leq 28^\circ$	
Crystal dimensions 0.40 × 0.30 × 0.30 mm	

Weissenberg photographs taken with $\text{Cu-K}\alpha$ (λ 1.51418 Å) radiation showed the complex to crystallise in the orthorhombic system in a cell of dimensions, a 12.93 Å, b 15.22 Å and c 20.96 Å. The observed systematic absences were consistent with the space group $P2_12_12_1$ (D_2^4-19) [15], and the measured and calculated densities suggested that $Z = 4$.

After these preliminary analyses the crystal was carefully set on a Nonius CAD 4 automatic diffractometer and the setting angles of 15 strong reflections were used to determine the unit cell parameters accurately. These together with the other relevant crystallographic data are summarised in Table 2. All the reflections used in the crystallographic analysis were given a fast prescan and those with a net count greater than 5 in the prescan were subjected to a slow scan to yield a total count of 3000, but with the maximum time for measuring any reflection set at 60 s. The slow scan was made over the range of $0.70 + 0.30 \tan \theta$ in 96 steps, the first and last 16 being considered as left and right backgrounds, respectively, and the intermediate 64 steps as the peak. The aperture width was determined from the expression $4.00 + 0.30 \tan \theta$ mm.

The net intensity and its estimated standard deviation were calculated from the equations:

$$I_{\text{obs}} = [c - 2(B_L + B_R)]S$$

$$\sigma(I_{\text{obs}}) = [c + 4(B_L + B_R)]^{1/2}S$$

where C is the peak count, B_L and B_R are the two background counts and S is the scale factor which includes the Lorentz and polarization effects and a correction for the time taken to measure a reflection.

The intensity data was collected in the range $1.5 \leq \theta \leq 28^\circ$ with two intensity control reflections being measured every 50 reflections. The crystals showed no indications of decomposition during data collection. A total of 4392 reflections were measured 2805 of which satisfied the condition $|F_0| \geq 4\sigma(|F_0|)$ and were symmetry independent.

The structure was solved and refined using conventional Patterson, Fourier and least squares methods. A computed three-dimensional Patterson map indi-

(Continued on p. 177)

TABLE 3

FRACTIONAL COORDINATES (Rh X 10⁵; others X 10⁴) OF NON-HYDROGEN ATOMS IN [Rh(η -C₅Me₂(PPh₃)₂)]PF₆

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Rh	32852(3)	-4990(3)	42695(3)	C(122)	3239(8)	1755(7)	3563(5)
P(1)	1981(3)	536(3)	4215(2)	C(123)	3428(8)	2559(7)	3265(5)
P(2)	4031(3)	-108(3)	5227(2)	C(124)	2677(8)	3218(7)	3278(5)
P(3)	1248(5)	3729(4)	7587(3)	C(125)	1739(8)	3073(7)	3589(5)
F(1)	3431(13)	5325(8)	2755(8)	C(126)	1550(8)	2269(7)	3887(5)
F(2)	2662(14)	6652(13)	2639(12)	C(121)	2300(8)	1610(7)	3874(5)
F(3)	4060(17)	7244(10)	2426(10)	C(132)	848(12)	-10(9)	5236(7)
F(4)	4879(14)	5964(14)	2512(12)	C(133)	320(12)	63(9)	5814(7)
F(5)	3628(24)	6062(13)	1898(7)	C(134)	305(12)	863(9)	6139(7)
F(6)	3900(21)	6501(12)	3285(8)	C(135)	819(12)	1590(9)	5886(7)
C(1)	3152(16)	-1983(10)	4253(10)	C(136)	1348(12)	1517(9)	5309(7)
C(2)	2539(11)	-1626(10)	3742(9)	C(131)	1362(12)	718(9)	4983(7)
C(3)	3252(15)	-1159(11)	3328(7)	C(212)	6047(10)	-226(7)	5755(5)
C(4)	4298(15)	-1268(11)	3601(8)	C(213)	7115(10)	-103(7)	5732(5)
C(5)	4196(13)	-1739(11)	4123(9)	C(214)	7585(10)	160(7)	5164(5)
C(11)	2728(17)	-2585(14)	4748(10)	C(215)	6986(10)	301(7)	4619(5)
C(21)	1445(16)	-1804(14)	3550(11)	C(216)	5918(10)	178(7)	4643(5)
C(31)	3066(22)	-794(15)	2670(9)	C(211)	5448(10)	-85(7)	5211(5)
C(41)	5315(18)	-1064(16)	3225(11)	C(222)	3957(9)	1701(7)	5142(4)
C(51)	5067(15)	-2165(12)	4490(10)	C(223)	3871(9)	2560(7)	5369(4)
C(112)	-49(9)	-80(8)	3894(6)	C(224)	3658(9)	2711(7)	6012(4)
C(113)	-845(9)	-229(8)	3458(6)	C(225)	3531(9)	2004(7)	6429(4)
C(114)	-716(9)	0(8)	2819(6)	C(226)	3616(9)	1145(7)	6202(4)
C(115)	209(9)	879(8)	2615(6)	C(221)	3529(9)	994(7)	5659(4)
C(116)	1006(9)	529(8)	3051(6)	C(232)	2700(8)	-777(7)	6140(6)
C(111)	877(9)	299(8)	3690(6)	C(233)	2348(8)	-1396(7)	6581(6)
				C(234)	2967(8)	-2113(7)	6741(6)
				C(235)	3939(8)	-2212(7)	6460(6)
				C(236)	4291(8)	-1594(7)	6020(6)
				C(231)	3672(8)	-876(7)	5860(6)

TABLE 4

ANISOTROPIC VIBRATIONAL AMPLITUDES ($\text{\AA}^2 \times 10^4$) OF NON-HYDROGEN ATOMS IN $[\text{RhH}(\eta\text{-C}_5\text{Me}_5)(\text{PPh}_3)_2]\text{PF}_6$ (estimated standard deviations in parentheses)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rh	605(10)	294(6)	383(7)	-111(7)	-248(8)	189(8)
P(1)	245(23)	358(20)	339(23)	-21(25)	28(21)	-13(21)
P(2)	262(26)	284(23)	322(27)	10(20)	-29(21)	20(20)
P(3)	770(45)	447(31)	548(37)	38(28)	-7(32)	46(31)
F(1)	1654(151)	495(84)	1871(165)	30(93)	720(141)	-151(98)
F(2)	1249(152)	1508(172)	3141(297)	-434(195)	-438(181)	1046(143)
F(3)	2525(343)	596(97)	2248(225)	16(122)	237(205)	-675(128)
F(4)	965(130)	1606(172)	2547(234)	-147(168)	-88(148)	338(124)
F(5)	4093(386)	1475(166)	628(107)	-254(102)	-85(172)	664(225)
F(6)	3724(338)	1169(146)	934(126)	-288(108)	-682(175)	642(192)
C(1)	751(153)	286(80)	525(110)	170(95)	-51(138)	8(97)
C(2)	1(78)	311(94)	738(136)	-160(94)	141(87)	-228(71)
C(3)	461(112)	479(97)	265(89)	-193(81)	-205(96)	65(105)
C(4)	564(131)	305(93)	363(106)	37(87)	-180(97)	32(93)
C(5)	346(110)	311(91)	578(135)	-235(95)	-148(100)	-74(85)
C(11)	779(170)	698(145)	753(160)	274(137)	125(141)	-320(131)
C(21)	528(154)	754(146)	935(176)	-491(132)	175(128)	-187(120)
C(31)	1420(240)	915(179)	388(121)	151(115)	147(151)	203(182)
C(41)	644(152)	996(187)	679(156)	-85(141)	217(131)	40(146)
C(51)	518(133)	541(120)	806(167)	-268(111)	-173(113)	404(106)
C(112)	182(100)	457(108)	1047(171)	-487(116)	35(108)	-84(89)
C(113)	325(129)	728(164)	1357(239)	-387(159)	-108(145)	255(113)
C(114)	1215(246)	982(195)	579(162)	-280(150)	-449(165)	484(181)
C(115)	1205(222)	880(180)	805(178)	248(154)	-850(164)	-246(180)
C(116)	725(142)	505(113)	468(115)	-83(111)	-345(107)	144(131)
C(111)	285(101)	250(93)	542(115)	-17(78)	-209(88)	-32(75)
C(122)	448(120)	487(105)	388(103)	-144(85)	-138(105)	-108(110)
C(123)	740(163)	721(141)	440(115)	185(107)	158(123)	-573(135)
C(124)	1690(301)	315(119)	1034(214)	6(138)	-681(221)	-215(169)
C(125)	860(187)	476(135)	1308(234)	85(139)	-327(198)	335(150)
C(126)	238(112)	453(107)	720(131)	-67(99)	-160(99)	41(94)
C(121)	199(99)	330(93)	487(108)	-4(83)	-122(84)	-180(80)
C(132)	828(184)	1522(245)	166(107)	395(132)	75(116)	40(174)
C(133)	327(143)	2225(345)	976(235)	878(253)	77(158)	369(179)

TABLE 4 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(134)	887(213)	2302(395)	239(127)	7(183)	73(133)	696(250)
C(135)	565(174)	2256(352)	514(181)	-283(203)	-176(138)	336(204)
C(136)	787(180)	1478(233)	320(123)	-568(142)	-196(115)	569(164)
C(131)	494(138)	1037(197)	375(113)	187(121)	-41(97)	219(128)
C(212)	616(147)	584(127)	524(133)	-126(116)	-271(125)	27(106)
C(213)	619(149)	555(116)	474(123)	-192(121)	1(125)	146(106)
C(214)	481(136)	401(132)	1034(193)	-146(126)	-94(145)	13(107)
C(215)	812(179)	434(126)	760(154)	69(106)	459(137)	-125(116)
C(216)	581(145)	436(114)	552(135)	-80(98)	58(114)	-143(104)
C(211)	346(107)	329(98)	473(122)	-122(93)	18(97)	25(86)
C(222)	407(117)	299(96)	466(116)	100(88)	61(97)	-1(91)
C(223)	341(120)	467(121)	566(136)	7(102)	181(102)	-38(99)
C(224)	558(147)	208(94)	1153(199)	-164(111)	99(132)	95(94)
C(225)	1000(195)	435(115)	572(138)	-110(102)	221(134)	302(128)
C(226)	208(108)	384(103)	998(173)	-188(133)	193(107)	-284(87)
C(221)	414(113)	396(101)	264(98)	-11(74)	56(81)	237(90)
C(232)	508(131)	524(123)	393(110)	13(95)	35(99)	87(102)
C(253)	258(108)	699(131)	517(122)	133(108)	65(96)	74(106)
C(234)	515(142)	690(140)	549(130)	109(115)	149(112)	-93(116)
C(235)	590(151)	548(126)	645(143)	349(110)	10(121)	121(115)
C(236)	519(129)	371(100)	507(118)	292(89)	285(99)	243(94)
C(231)	388(103)	297(77)	167(90)	29(66)	90(75)	48(71)

TABLE 5

SELECTED DISTANCES (Å) AND ANGLES (°) FOR RhH(η -C₅Me₅)(PPh₃)₂PF₆ (Estimated standard deviations in parentheses).

Rh—C(1)	2.265(15)	C(1)—C(2)—C(3)	106.3(1.4)
Rh—C(2)	2.254(16)	C(2)—C(3)—C(4)	107.2(1.4)
Rh—C(3)	2.212(15)	C(3)—C(4)—C(5)	106.9(1.6)
Rh—C(4)	2.246(18)	C(4)—C(5)—C(1)	113.4(1.7)
Rh—C(5)	2.245(17)	C(5)—C(1)—C(2)	106.3(1.5)
Rh...C(11)	3.407(16)	P(3)—F(1)	1.539(20)
Rh...C(21)	3.445(16)	P(3)—F(2)	1.527(20)
Rh...C(31)	3.391(16)	P(3)—F(3)	1.569(20)
Rh...C(41)	3.523(17)	P(3)—F(4)	1.528(20)
Rh...C(51)	3.457(16)	P(3)—F(5)	1.486(20)
C(1)—C(2)	1.429(26)	F(1)—P(3)—F(2)	95.11(1.2)
C(2)—C(3)	1.451(24)	F(1)—P(3)—F(4)	89.72(1.2)
C(3)—C(4)	1.477(26)	F(1)—P(3)—F(5)	89.66(1.2)
C(4)—C(5)	1.314(25)	F(1)—P(3)—F(6)	91.57(1.2)
C(1)—C(5)	1.426(27)	F(2)—P(3)—F(6)	87.70(1.2)
C(1)—C(11)	1.488(28)	F(3)—P(3)—F(6)	87.57(1.2)
C(2)—C(21)	1.496(26)	F(4)—P(3)—F(6)	92.79(1.2)
C(3)—C(31)	1.506(26)	F(1)—P(3)—F(3)	83.79(1.2)
C(4)—C(41)	1.563(29)	F(3)—P(3)—F(5)	89.66(1.2)
C(5)—C(51)	1.510(26)	F(2)—P(3)—F(5)	92.95(1.2)
Rh—P(1)	2.309(4)	F(4)—P(3)—F(5)	86.45(1.2)
Rh—P(2)	2.306(5)	F(3)—P(3)—F(4)	91.39(1.2)

cated the Rh—Rh vectors between symmetry related atoms. A difference Fourier synthesis based on the parameters of the Rh atom revealed the two phosphorus atoms coordinated to the metal. Two cycles of full matrix least squares refinement on these positions gave a discrepancy index, R , of 0.31 and located most of the remaining non-hydrogen atoms including the disordered PF₆⁻ ion. A further four cycles of refinement on all these positions with the phenyl rings constrained to be regular hexagons (C—C distance 1.395 Å) and treated as rigid groups reduced R to 0.15. At this stage, anisotropic temperature factors were introduced to the Rh, P and F atoms which further reduced R to 0.11. In the final refinement, the hydrogen atoms belonging to the PPh₃ groups were allowed to ride on the parent carbon atoms in the calculated positions (C—H fixed at 1.08 Å) and anisotropic temperature factors were assigned to all the carbon atoms. The model chosen for the disordered F₆ group was one in which the six anisotropic atoms occupied the most populated octahedral sites. The weighting scheme used was $\omega = 1/(\sigma^2 F_0 + 0.00070 F_0^2)$ and gave a satisfactory analysis of variance with parity groups, $\sin \theta$ and $(F_0 | F_{\max})^{1/2}$. The refinement finally converged to $R_1 = 0.0887$ and $R_2 = 0.0924$ where R_1 and R_2 are as defined in the usual fashion. The final non-hydrogen atomic fractional coordinates are listed in Table 3, and their anisotropic vibrational amplitudes in Table 4. Intramolecular interatomic distances and interbond angles are tabulated in Table 5*.

* Lists of observed and calculated structure factors are available from the authors on request.

All calculations were performed on the Queen Mary College ICL1904S and University of London CDC 7600 computers with the programs SHELX-76 [16] (structure determination and refinement) and PLUTO [17] (diagrams). Neutral atom scattering factors were taken from reference 18 (H) and 19 (others) with those of the heavier elements being modified for anomalous dispersion taking the $\Delta f'$ and $\Delta f''$ values from ref. 20.

Description of the structure

The structure of $[\text{RhH}(\eta\text{-C}_5\text{Me}_5)(\text{PPh}_3)_2]\text{PF}_6$ consists of discrete anions and cations with the geometry of the cation being a distorted pseudo-octahedron. The labelling scheme used in the following discussion is indicated on the illustration of the molecular structure of the cation shown in Fig. 1.

Despite the partial disorder, the refined PF_6^- anion has nearly octahedral symmetry. Considering the problem of disorder and the asymmetric environment of the anion, the distortions from idealised octahedral symmetry are not significant. The *cis*-F—P—F angles range between 84 and 95° (see Table 5) suggesting that the model chosen for the anion is acceptable. The shortest intermolecular contacts involving fluorine atoms are with the phenyl hydrogen atoms with a minimum distance of 2.47 Å.

Not surprisingly, the small hydrido ligand in close proximity to the rhodium atom was not directly detected by the X-ray crystal analysis. Its presence has nonetheless been demonstrated by the spectroscopic data summarised in Table 1. Its presence is also suggested by the angle subtended by the P(1)—Rh—P(2) with the C_5 ring plane (ca. 79°, see Table 6). Therefore it can reasonably be

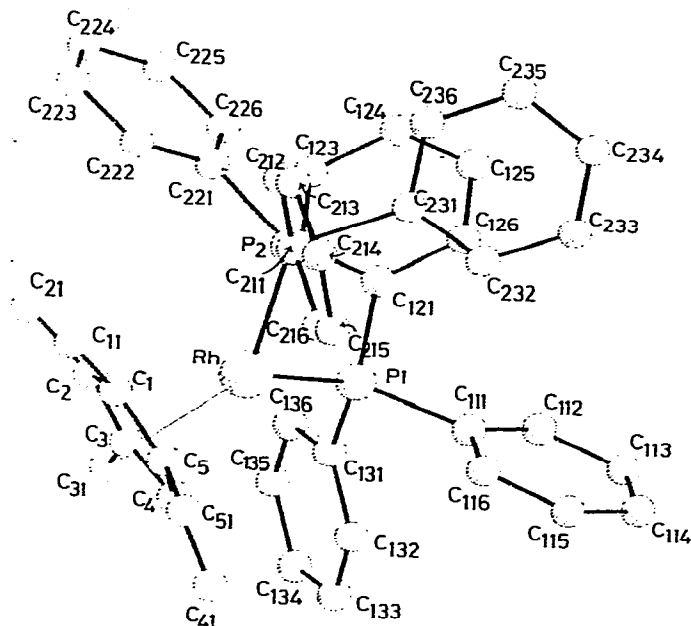


Fig. 1. Molecular structure of $[\text{RhH}(\eta\text{-C}_5\text{Me}_5)(\text{PPh}_3)_2]^+$.

TABLE 6

SELECTED LEAST-SQUARES PLANES IN $[\text{RhH}(\eta\text{-C}_5\text{Me}_5)(\text{PPh}_3)_2]\text{PF}_6$

Equations are of the form $px + qy + rz = s$. σ (Å) is the root mean square standard deviation; atomic deviations (Å) are in square brackets.

Plane 1 (through atoms Rh, P(1), P(2))

<i>p</i>	<i>q</i>	<i>r</i>	<i>s</i>
7.9561	9.5020	-10.0763	-2.1618

Plane 2 (through atoms C(1), C(2), C(3), C(4) and C(5))

<i>p</i>	<i>q</i>	<i>r</i>	<i>s</i>	σ
-1.6595	12.7273	11.1660	1.6963	0.0049

[C(1), 0.0054; C(2), -0.0069; C(3), 0.0059; C(4), -0.0027; C(5), -0.0017; C(11), -0.1384; C(21), -0.2684; C(31), -0.2344; C(41), -0.3315; C(51), -0.2785; Rh, 1.8903]

Plane 3 (through atoms C(11), C(21), C(31), C(41) and C(51))

<i>p</i>	<i>q</i>	<i>r</i>	<i>s</i>	σ
1.4357	12.8903	10.8893	1.2941	0.0440

[C(1), 0.2281; C(2), 0.220; C(3), 0.2699; C(4), 0.2754; C(5), 0.2520; C(11), 0.0513; C(21), -0.0615; C(31), 0.0495; C(41), -0.0170; C(51), -0.0224; Rh, 2.1397]

Angles between normals to planes

Plane 1 and Plane 2	79.21°
Plane 1 and Plane 3	77.83°
Plane 2 and Plane 3	1.39°

implied that the hydrido ligand, together with the two phosphine ligands represent the three legs of the piano-stool geometry. The isoelectronic complex $[\text{RuH}(\text{PPh}_3)_2(\eta\text{-C}_6\text{H}_5\text{PPh})]\text{BF}_4$ has a closely related geometry [21].

The C_5 ring of the cation is planar but not coplanar with the carbon atoms of the Me_5 ring. It is clear from Table 6 that the Me groups are bent away from the rhodium atom to a very significant extent; the ring defined by the methyl carbon atoms is ca. 0.25 Å further from the rhodium atom than the C_5 ring. The extent of bending back in this complex is substantially greater than in $\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{dba})^*$ where the $\text{Me}_5\text{-C}_5$ ring separation is reported [24] to be ca. 0.10 Å. It seems possible that this departure from the idealised planar geometry of the $\eta\text{-C}_5\text{Me}_5$ ligand is due to steric effects introduced by the presence of the two triphenylphosphine ligands.

Discussion

The *trans*-influence of the ligands L and X in complexes of the type $\text{M}(\eta\text{-C}_5\text{R}_5)\text{L}_2\text{X}$ can have two distinct geometric manifestations. Firstly the combined *trans*-influence of the ligands L and X is likely to be reflected in the distance of the metal atom from the plane of the C_5 ring and secondly the difference in the *trans*-influences of the ligands L and X could be reflected in an asymmetry of the $\text{C}_5\text{R}_5\text{-M}$ distance parameters.

* dba = dibenzylideneacetone

The distance of the rhodium atom from the centre of the C_5 ring in $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{H}(\text{PPh}_3)_2]\text{PF}_6$ of 1.890 Å is significantly longer than that observed in the following related complexes: $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ (1.756 Å) [22]; $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Br}_2]_2$ (1.769 Å) [22]; $\{\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{Cl}_2\}_2\text{HCl}$ (1.777 Å) [23]; $\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{NO}_3)_2$ (1.745 Å) [14] and $\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{NO}_3)_2(\text{PPh}_3)$ (1.815 Å) [14] and approximately the same as that reported for $\text{Rh}(\eta\text{-C}_5\text{Me}_5)(\text{dba})$ (1.899 Å) [24]. In this series of complexes the $\text{Rh}\text{-C}_5\text{Me}_5$ distance appears to reflect the combined *trans*-influence of the non-cyclopentadienyl ligands, with ligands of high *trans*-influence as H^- and PPh_3 causing a lengthening of this distance compared with ligands of low *trans*-influence such as Cl^- and NO_3^- . Such an effect is consistent with either an electrostatic or covalent view of the metal cyclopentadienyl bonding, since the combined inductive effects of the tertiary phosphine and hydrido ligands will serve to increase the electron density on the rhodium atom.

The C—C distances in the cyclopentadienyl ring (see Table 5) of $[\text{Rh}(\eta\text{-C}_5\text{Me}_5)\text{H}(\text{PPh}_3)_2]\text{PF}_6$ show a variation which is consistent with a degree of localization in carbon—carbon bonding, which can be represented approximately by the “ene-enyl” form illustrated in III. A similar localization has been reported for $[\text{Rh}_2(\eta\text{-C}_5\text{Me}_5)_2(\text{acac})_2](\text{BF}_4)_2$, where the cyclopentadienyl rings are *trans* to two oxygen atoms and a carbon atom of the bridging acetylacetonate ligands [25]. The short C—C bond of the cyclopentadienyl ligand lies *trans* to the carbon atom of acetylacetonate ligand which has a high *trans*-influence.

In an ML_2X fragment the d_{xz} and d_{yz} components of the e frontier orbital set illustrated below [26] are no longer degenerate and interact in different fashion



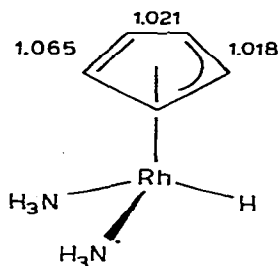
with the components of the cyclopentadienyl e_1 orbitals illustrated in VI and VII.



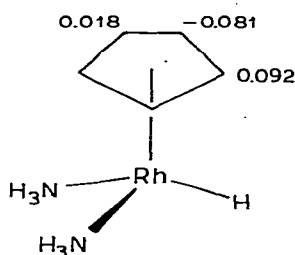
Extended Hückel molecular orbital calculations, details of which are given in the Appendix; on the ions $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{HL}_2]^+$ (where $\text{L} = \text{NH}_3$ or PH_3), suggest that the asymmetry resulting from this loss of symmetry depends on the conformation of the $[\text{M}(\eta\text{-C}_5\text{H}_5)\text{HL}_2]^+$ ion with an “ene-enyl”-localization resulting from conformation illustrated in VIII and a “diene” localization resulting from conformation illustrated in IX. The degree of localization sug-

gested by the calculated overlap populations is greater for the amine than the phosphine complex reflecting the greater difference in *trans*-influence between H^- and NH_3 . The calculated localization effects are considerably smaller than those reported previously [27] for the complexes $[L_2PtB_{11}H_{11}]^{2-}$. The calculated overlap populations and charges are given in VIII and IX. It is noteworthy

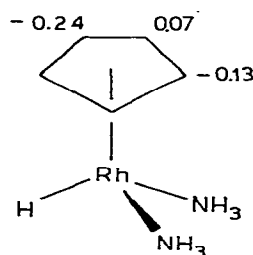
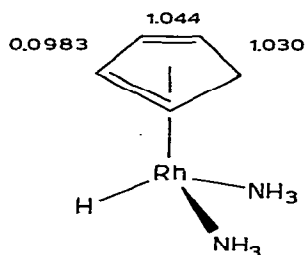
Overlap populations



Calculated charges



(VIII)



(IX)

that the calculated charges reflect in a precise fashion the nodal characteristics of the cyclopentadienyl e_1 orbitals illustrated in VI and VII.

Appendix

All calculations were performed on the ICL 1906A computer at Oxford using the extended Hückel (ICON 8) programs developed by Prof. R. Hoffmann and his coworkers at Cornell University [28]. The following geometric parameters were used in the calculations: Rh-P 2.308 Å; Rh-N 2.150 Å; P-H 1.200 Å; N-H 1.012 Å; Rh-C 2.2522 Å; C-H 1.09 Å; Rh-H 1.70 Å.

Tetrahedral angles about the nitrogen and phosphorus atoms were assumed.

The electronic parameters used in the calculation are summarised below:

Orbital	Exponent	H_{ii} (eV)
Rh 5s	2.135	-8.00
Rh 5p	2.100	-4.50
P 3s	1.600	-18.60
P 3p	1.600	-14.00
N 2s	1.95	-26.00
N 2p	1.95	-13.40
C 2s	1.625	-21.40
C 2p	1.625	-11.40
H 1s	1.360	-13.60

Orbital	Exp. 1	Coeff. 1	Exp. 2	Coeff. 2	H_{ii} (eV)
Rh 4d	4.290	0.5807	1.970	0.5685	-12.50

References

- 1 M.L. Tobe, *Inorganic Reaction Mechanisms*, Nelson, London, 1972, p. 42-68.
- 2 J. Chatt, *Advan. Organometal. Chem.*, 12 (1974) 1.
- 3 J. Chatt, L.A. Duncanson and L.M. Venanzi, *J. Chem. Soc.*, (1955) 4456.
- 4 J. Chatt and B.L. Shaw, *J. Chem. Soc.*, (1959) 705.
- 5 J. Chatt, L.A. Duncanson and B.L. Shaw, *Proc. Chem. Soc.*, (1957) 343.
- 6 J. Chatt, Tilden Lecture, *Proc. Chem. Soc.*, (1962) 318.
- 7 F. Basolo, J. Chatt, H.B. Gray, R.G. Pearson and B.L. Shaw, *J. Chem. Soc.*, (1961) 2207.
- 8 A. Pidcock, R.E. Richards and L.M. Venanzi, *J. Chem. Soc. (A)*, (1966) 1707.
- 9 J. Burdett, *Inorg. Chem.*, 12 (1977) 3013.
- 10 L.F. Dahl and C.H. Wei, *Inorg. Chem.*, 2 (1963) 713.
- 11 M.J. Bennett, M.R. Churchill, M. Gerloch and R. Mason, *Nature*, 201 (1964) 1318.
- 12 V.W. Day, K.J. Reimer and A. Shaver, *J. Chem. Soc. Chem. Commun.*, (1975) 403.
- 13 P.M. Maitlis and J.W. Keay, *J. Amer. Chem. Soc.*, 90 (1968) 3259.
- 14 M.B. Hursthouse, K.M.A. Malik, D.M.P. Mingos and S.D. Willoughby, unpublished results.
- 15 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, 1952, Vol. I.
- 16 The SHELX Crystal Structure Analysis Program, G. Sheldrick, University of Cambridge, 1976.
- 17 The PLUTO plotting routine program, W.D.S. Motherwell, University of Cambridge.
- 18 R.F. Stewart, E.R. Davison and W.T. Simpson, *J. Chem. Phys.*, 42 (1965) 3175.
- 19 D.T. Cromer and J.B. Mann, *Acta Cryst.*, A, 24 (1968) 321.
- 20 D.T. Cromer and D. Liberman, *J. Chem. Phys.*, 53 (1970) 1891.
- 21 J.C. McConway, A.C. Skapski, L. Phillips, R.T. Young and G. Wilkinson *J. Chem. Soc. Chem. Commun.*, (1974) 327.
- 22 M.R. Churchill and S.A. Julis, *Inorg. Chem.*, 13 (1978) 3011.
- 23 M.R. Churchill and S.W.Y. Ni, *J. Amer. Chem. Soc.*, 95 (1973) 2150.
- 24 J.A. Ibers, *J. Organometal. Chem.*, 73 (1974) 389.
- 25 W. Rigby, H.B. Lee, P.M. Bailey, J.A. McCleverty and P.M. Maitlis *J. Chem. Soc. Dalton*, (1979) 387.
- 26 M. Elian, M.M.L. Chen, D.M.P. Mingos and R. Hoffmann, *Inorg. Chem.*, 15 (1976) 1148.
- 27 D.M.P. Mingos, *J. Chem. Soc. Dalton*, (1977) 602.
- 28 R. Hoffmann, *J. Chem. Phys.*, 39 (1963) 1397.