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THE SYNTHESIS AND MOLECULAR STRUCTURE OF 1-(η^5-CYCLOPENTADIENYL)-1-TRIPHENYLPHOSPHINE-2,3,4,5-TETRAKIS(PENTAFLUOROPHENYL)RHODOLE

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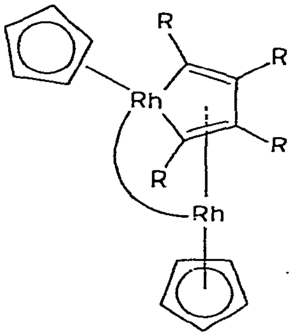
Summary

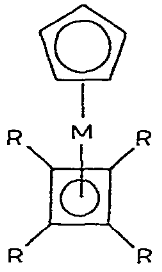
A reaction between π-cyclopentadienylcarbonyl(triphenylphosphine)rhodium and bis(pentafluorophenyl)acetylene in refluxing xylene has produced low yields of hexakis(pentafluorophenyl)benzene and 1-(η^5-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)rhodole. The metallocycle has been characterized by elemental analysis, spectral measurements and an X-ray diffraction study. Yellow crystals of the title compound from Skelly C are triclinic with a 11.715(4), b 14.015(6), c 20.420(6) Å and α 114.07(3), β 106.97(3), γ 107.28(3)°. The space group indicated by intensity statistics is $P\bar{1}$, and there are two molecules per unit cell. An ill-defined solvent molecule in the cell affects the agreement between the observed and calculated densities. A similar solvation was observed in the corresponding cobaltacycle which is isomorphous with the rhodium complex. The final residual R after least-squares refinement was 0.065 for the 5235 reflections with $I \geqslant 2\sigma(I)$ which were used in the analysis. The rhodium is σ-bonded to the two carbons of the butadiene-like fragment with Rh—C bonds of 2.060(12) and 2.067(11) Å. The C—C distances of 1.343(16), 1.457(16) and 1.354(15) Å indicate that the C_4 fragment is very similar to a butadiene group. The Rh—P distance of 2.293(2) Å is longer than the value of 2.234(3) Å found in the cobaltacycle, which is consistent with the larger size of Rh compared to Co.

Introduction

Reactions of $(\eta^5\text{-}C_5H_5)M(CO)_2$, where M = Co, Rh or Ir, with disubstituted acetylenes have been under extensive investigation in our laboratories [1—9] and elsewhere [10—18], and have been shown to yield a wide variety of novel organometallic complexes as well as acetylene trimerization products. In certain cases, stable binuclear products which contain a metallocyclopentadiene moiety are formed as in I, where R = CF_3 [13,14,16], C_6F_5 [2—4,9] and C_6H_5 [4,8]. In other instances, metallocyclopentadiene intermediates have been implicated, as in the formation of η^4-cyclobutadienemetal complexes (II) and η^4-cyclopentadienone-metal complexes (III) [3—7,12—14].



(I)



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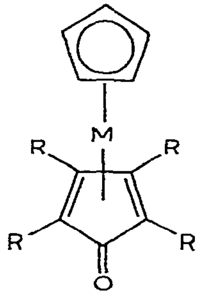
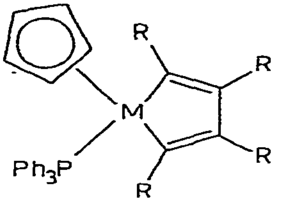


(III)

Several stable cobaltacycles have recently been reported which contain triphenylphosphine and η^5-cyclopentadienyl ligands. In the reaction of diphenylacetylene with $(\eta^5\text{-}C_5H_5)Co(PPh_3)I_2$ and isopropylmagnesium bromide, a product was obtained whose structure was assigned as IV on the basis of chemical reactions [19]. An analogous compound has been isolated from a reaction of $(\eta^5\text{-}C_5H_5)Co(CO)(PPh_3)$ with bis(pentafluorophenyl)acetylene, and has been characterized as V on the basis of spectroscopic and crystallographic analyses [20]. Therefore, in an attempt to isolate a stable rhodacyclopentadiene the reaction of $(\eta^5\text{-}C_5H_5)Rh(CO)(PPh_3)$ with bis(pentafluorophenyl)acetylene was investigated.

The following report is a description of the synthesis and structural characterization by spectral and X-ray diffraction techniques of 1-(η^5-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)rhodole (VI).



(IV) M = Co, R = C_6H_5
(V) M = Co, R = C_6F_5
(VI) M = Rh, R = C_6F_5

Experimental

η^5-Cyclopentadienylcarbonyl(triphenylphosphine)rhodium was prepared according to a literature method [21]. Bis(pentafluorophenyl)acetylene was prepared by a modification of a literature method [22,23]. Xylene, benzene and hexane were distilled under nitrogen from calcium hydride before use. NMR spectra were recorded on a Perkin—Elmer R-12A instrument, IR spectra were recorded on a Beckman IR-10 instrument, and mass spectra were obtained with a Perkin—Elmer—Hitachi RMU 6L instrument operating at an ionizing potential of 70 eV. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Mass. 01002. "Skelly C" is commercial heptane, b.p. 88—98° C.

Reaction of η^5-cyclopentadienylcarbonyl(triphenylphosphine)rhodium and bis(pentafluorophenyl)acetylene

A solution of bis(pentafluorophenyl)acetylene (2.14 g, 5.98 mmol) and π-cyclopentadienylcarbonyl(triphenylphosphine)rhodium (1.50 g, 3.27 mmol) in 25 ml of anhydrous xylene was refluxed for 85 h with magnetic stirring under nitrogen. The reaction mixture was cooled and filtered under nitrogen. A light tan solid was obtained which sublimed at 200—205° C/10^{-3} torr to give 0.027 g (1.3%) of hexakis(pentafluorophenyl)benzene. The product was identified by comparison with a known sample [2].

To the red filtrate was added 10 g of alumina (deactivated with 5% water) under nitrogen and the solvent removed. The coated alumina was added to a column of alumina (2 × 50 cm) packed dry under nitrogen. Elution with 4 : 1 hexane/benzene brought down a light yellow band which after removal of the solvent and sublimation at 90° C/10^{-3} torr gave unreacted bis(pentafluorophenyl)-acetylene (0.816 g, 38.3% recovery).

Further elution with 4 : 1 hexane/benzene brought down a yellow band. After the addition of 2 g of alumina the solvent was removed in vacuo. The coated alumina was added to a smaller alumina column (2 × 18 cm) in air and eluted with 4 : 1 hexane/benzene. A red band was obtained which after removal of the solvent gave 0.273 g (8% yield) of 1-(η^5-cyclopentadienyl)-1-(triphenylphosphine)-2,3,4,5-tetrakis(pentafluorophenyl)rhodole(VI). An analytical sample was prepared by recrystallization from Skelly C and drying in vacuo at 70° C; yellow crystals, m.p. 293—294° C. (Found: C, 53.22; H, 1.84. $C_{51}H_{20}CoF_{20}P$ calcd.: C, 53.42; H, 1.76%). The NMR spectrum in $CDCl_3$ consisted of a singlet at τ 4.83 ppm (5 H) and a multiplet centered between τ 2.5—3.0 ppm (15 H), assignable to the cyclopentadienyl and phenyl protons, respectively. An IR spectrum (KBr) exhibited the following major peaks: 1625w, 1460s, 1415(sh), 1095m, 1075s, 965s, 925m, 795m, 730m, 675s cm^{-1}. The mass spectrum exhibited the following principal peaks: *m/e* 1146 (8.5, M^+), 1081 (5.0, $RhP(C_6H_5)_3(C_6F_5C_2C_6F_5)_2^+$), 884 (10, $C_5H_5Rh(C_6F_5C_2C_6F_5)_2^+$), 819 (1.2, $Rh(C_6F_5C_2C_6F_5)_2^+$), 526 (2.7 $C_5H_5Rh(C_6F_5C_2C_6F_5)^+$), 461 (5.0, $Rh(C_6F_5C_2C_6F_5)_2^+$), 442 (1.0, $Rh(C_6F_5C_2C_6F_5) - F^+$), 358 (25, $C_6F_5C_2C_6F_5^+$), 262 (30, $P(C_6H_5)_3^+$), 168 (100, $C_5H_5Rh^+$), 103 (55, Rh^+).

Additional elution of the original column with 4 : 1 hexane/benzene gave a red band which contained unreacted π-cyclopentadienylcarbonyl(triphenylphos-

(*continued on p. 360*)

TABLE 1

THE FINAL ATOMIC PARAMETERS FOR NONHYDROGEN ATOMS OF 1-(η^5-CYCLOPENTADIENYL)-1-TRIPHENYLPHOSPHINE-2,3,4,5-TETRAKIS-(PENTAFLUOROPHENYL)RHODOLE. (All values are $\times 10^4$ except for those of Rh which are $\times 10^5$. The temperature factors are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	4527(7)	49168(7)	21247(4)	620(6)	630(6)	248(2)	543(10)	294(7)	443(6)
P(1)	1433(2)	6288(2)	3493(1)	71(3)	72(2)	26(1)	62(4)	38(3)	53(2)
C(1)	1546(9)	4003(8)	2101(5)	96(11)	71(8)	26(3)	77(16)	36(10)	49(9)
C(2)	2531(9)	4307(8)	1901(5)	87(10)	61(8)	26(3)	63(15)	41(10)	43(9)
C(3)	2825(8)	5370(8)	1872(5)	70(9)	68(8)	26(3)	66(15)	34(9)	48(9)
C(4)	2016(8)	5864(8)	2003(5)	72(9)	75(8)	26(3)	57(15)	27(9)	56(9)
C(11)	1091(9)	2877(8)	2092(6)	89(11)	73(9)	37(4)	84(16)	52(11)	63(10)
C(12)	1298(10)	2836(9)	2781(6)	94(11)	89(10)	42(4)	84(17)	55(12)	83(11)
C(13)	902(11)	1800(10)	2759(7)	127(14)	112(11)	56(5)	115(21)	80(14)	117(14)
C(14)	273(12)	735(10)	2027(8)	166(16)	83(10)	78(7)	131(22)	122(18)	125(15)
C(15)	35(12)	725(9)	1327(7)	147(15)	74(10)	57(6)	81(20)	92(16)	65(13)
C(16)	438(11)	1777(9)	1363(6)	132(13)	82(9)	44(5)	109(19)	84(13)	75(11)
F(12)	1952(6)	3850(5)	3520(3)	153(8)	98(6)	38(2)	96(11)	54(7)	72(6)
F(13)	1163(8)	1809(7)	3446(4)	210(11)	160(8)	68(4)	152(16)	101(10)	169(10)
F(14)	−143(9)	−293(6)	1990(5)	263(13)	100(7)	101(5)	162(16)	158(14)	149(10)
F(15)	−610(9)	−305(6)	602(5)	249(12)	72(6)	70(4)	86(14)	138(12)	52(8)
F(16)	188(7)	1725(5)	667(3)	188(9)	86(6)	39(3)	94(12)	79(8)	50(6)
C(21)	3231(9)	3588(8)	1667(5)	87(10)	74(9)	35(4)	86(16)	51(11)	58(10)
C(22)	4056(10)	3435(9)	2182(6)	118(13)	86(10)	41(5)	113(19)	60(13)	62(11)
C(23)	4706(11)	2768(11)	1945(8)	123(14)	114(12)	63(6)	157(22)	67(15)	99(15)
C(24)	4517(12)	2266(11)	1170(8)	137(15)	113(12)	65(6)	173(23)	98(16)	77(15)
C(25)	3684(12)	2412(10)	635(7)	156(15)	91(11)	45(5)	109(21)	100(15)	50(12)
C(26)	3043(10)	3059(9)	876(6)	100(11)	83(9)	41(4)	95(17)	66(12)	66(11)
F(22)	4288(7)	3912(6)	2963(4)	170(9)	147(7)	46(3)	204(14)	68(8)	101(8)
F(23)	5526(9)	2636(8)	2478(5)	228(12)	205(11)	80(4)	337(20)	98(12)	144(12)
F(24)	5155(9)	1657(8)	926(6)	233(13)	179(10)	101(5)	310(20)	180(14)	120(12)
F(25)	3478(8)	1910(7)	−144(4)	238(12)	148(8)	63(4)	200(17)	164(11)	90(9)
F(26)	2223(6)	3177(6)	332(3)	167(9)	118(6)	38(2)	150(13)	77(8)	75(7)
C(31)	3949(9)	5834(8)	1710(5)	94(11)	68(8)	34(4)	85(16)	51(11)	54(10)
C(32)	3746(10)	5826(9)	1002(6)	108(12)	89(10)	37(4)	91(18)	61(12)	69(11)
C(33)	4764(12)	6138(10)	805(7)	153(13)	106(11)	51(5)	125(22)	114(15)	96(13)
C(34)	6049(11)	6498(10)	1334(7)	123(13)	112(11)	69(6)	136(21)	144(16)	109(14)
C(35)	6327(10)	6544(10)	2048(7)	81(11)	100(10)	60(5)	104(8)	73(13)	87(13)
C(36)	5288(10)	6213(9)	2221(6)	94(11)	90(10)	37(4)	84(18)	42(12)	63(11)

F(32)	2468(6)	5439(6)	459(3)	122(7)	147(7)	40(3)	125(12)	56(7)	104(7)
F(33)	4482(8)	6073(7)	94(4)	212(11)	194(10)	65(4)	204(17)	166(11)	158(10)
F(34)	7059(8)	6827(8)	1164(6)	164(10)	208(10)	111(5)	198(17)	207(13)	203(13)
F(35)	7607(6)	6928(7)	2567(5)	88(7)	163(8)	84(4)	127(13)	76(9)	124(10)
F(36)	5597(6)	6265(6)	2930(4)	107(7)	152(7)	46(3)	127(12)	47(7)	105(8)
C(41)	2290(9)	7009(8)	2054(5)	80(10)	72(8)	32(4)	76(15)	53(10)	59(9)
C(42)	1474(10)	7113(9)	1470(6)	98(11)	83(9)	34(4)	88(17)	45(11)	67(10)
C(43)	1711(12)	8169(10)	1549(7)	150(15)	118(12)	50(5)	157(22)	84(15)	115(14)
C(44)	2786(12)	9217(10)	2252(7)	144(14)	91(11)	68(6)	128(21)	111(16)	113(14)
C(45)	3630(10)	9135(9)	2818(6)	103(12)	84(10)	45(5)	51(18)	64(13)	54(11)
C(46)	3405(9)	8064(8)	2722(6)	94(11)	73(9)	37(4)	72(16)	56(11)	65(10)
F(42)	402(6)	6129(5)	785(3)	127(7)	107(6)	38(2)	96(11)	30(7)	78(6)
F(43)	887(8)	8225(7)	964(5)	198(11)	165(9)	79(4)	204(16)	92(11)	179(10)
F(44)	3005(8)	10263(6)	2332(5)	236(12)	98(7)	100(5)	172(15)	144(13)	137(10)
F(45)	4715(7)	10148(5)	3495(4)	164(9)	73(6)	64(3)	31(12)	79(9)	47(7)
F(46)	4296(5)	8055(5)	3305(3)	100(6)	93(5)	37(2)	64(10)	29(6)	59(6)
C(51)	−1641(9)	4744(11)	1924(6)	63(10)	133(13)	43(5)	72(19)	27(12)	77(13)
C(52)	−1672(10)	3638(11)	1750(7)	66(11)	125(13)	56(6)	6(19)	16(13)	103(14)
C(53)	−1403(10)	3198(10)	1083(7)	77(11)	90(10)	48(5)	29(18)	1(12)	54(12)
C(54)	−1161(10)	4034(10)	847(6)	81(11)	108(11)	30(4)	73(18)	10(11)	41(11)
C(55)	−1339(9)	4970(10)	1355(6)	71(10)	104(11)	41(4)	62(17)	16(11)	69(12)
C(60)	188(9)	5980(9)	3869(6)	82(10)	108(10)	30(4)	75(17)	52(11)	71(11)
C(61)	−282(11)	4899(10)	3822(7)	126(14)	123(12)	50(5)	99(22)	88(14)	111(14)
C(62)	−1248(13)	4597(12)	4062(8)	162(17)	146(15)	67(7)	124(26)	124(18)	130(17)
C(63)	−1735(14)	5371(14)	4357(9)	159(18)	171(17)	74(7)	132(29)	136(20)	137(19)
C(64)	−1248(15)	6446(14)	4401(10)	188(20)	184(18)	91(9)	213(33)	196(23)	156(22)
C(65)	−311(12)	6748(11)	4152(7)	135(15)	137(13)	60(6)	147(24)	128(16)	99(15)
C(70)	2953(9)	6484(8)	4230(5)	73(10)	72(8)	29(4)	60(15)	26(10)	53(9)
C(71)	3141(11)	6760(10)	5001(6)	111(13)	118(12)	35(4)	70(20)	36(12)	81(12)
C(72)	4315(12)	6902(12)	5555(7)	123(14)	145(14)	42(5)	77(23)	26(14)	102(14)
C(73)	5271(12)	6770(11)	5344(7)	116(14)	130(13)	52(6)	84(23)	25(14)	101(15)
C(74)	5119(11)	6504(11)	4572(7)	109(14)	118(13)	52(6)	81(22)	20(14)	78(14)
C(75)	3938(9)	6368(9)	4025(6)	79(11)	91(10)	37(4)	72(17)	22(11)	59(11)
C(80)	1836(9)	7791(8)	3744(5)	91(11)	85(9)	32(4)	90(16)	56(11)	66(10)
C(81)	938(10)	7945(9)	3225(6)	117(13)	91(10)	37(4)	109(19)	65(12)	67(11)
C(82)	1146(12)	9094(10)	3420(7)	160(15)	91(10)	53(5)	135(21)	94(15)	89(13)
C(83)	2317(13)	10102(10)	4129(8)	158(16)	98(11)	58(6)	115(23)	101(17)	76(14)
C(84)	3211(12)	9921(10)	4638(7)	133(15)	91(11)	55(6)	85(21)	67(15)	70(13)
C(85)	2980(10)	8797(9)	4458(6)	106(12)	81(10)	42(5)	69(18)	54(12)	57(11)

phine)rhodium (0.781 g, 52% recovery). Subsequent elution with benzene and 1 : 1 benzene/ether produced several additional red or red-brown bands, each of which contained one or more compounds. Due to the minute quantities available, these were not characterized.

Crystal data and intensity measurement

Preliminary Weissenberg and precession photographs showed the yellow crystals to be triclinic and isomorphous with the corresponding cobalt complex [20]. A crystal 0.14 × 0.24 × 0.43 mm was mounted on a glass fiber and placed on a Syntex $P\bar{1}$ diffractometer in a random orientation. Crystal data: $RhC_{51}H_{20}F_{20}P$, M = 1146.56, a 11.715(4), b 14.015(6), c 20.420(6) Å, α 114.07(3), β 106.97(3), γ 107.28(3)°, V 2574.3(1.5), D_m 1.60 g/cm^3. The density calculated for 2 molecules per unit cell is 1.479 g/cm^3, however as noted below, there is an ill-defined molecule of solvent in the crystal and the calculated value should be nearer to 1.6 g/cm^3. The intensity collection and processing were identical to previously described procedures [20,24]. A total of 5235 reflections (out of 6766 possible) had an $I \geqslant 2.0\sigma(I)$ and were considered reliable and used in the analysis. The value of μ was calculated to be 4.7 cm^{-1} (Mo-K_α radiation) and absorption corrections were considered unnecessary.

Structure determination and refinement

The final parameters after isotropic thermal refinement of the cobalt complex were used as a starting set. A structure factor and difference Fourier synthesis confirmed the isomorphous nature of the Rh and Co complexes. The R factor ($= \Sigma||F_o| - |F_c||/\Sigma|F_o|$) was 0.17 at this point and was reduced to 0.11 after three cycles of refinement with isotropic thermal parameters. A block-diagonal approximation was used for the refinement with anisotropic thermal parameters and after 9 cycles, the R value was 0.065 and refinement was terminated. An ill-defined solvent molecule was evident in the difference Fourier syntheses, but all attempts to fit a C_7 or C_8 fragment were unsuccessful. The refinement procedures, scattering factors, and weighting scheme were identical to those given in a previous report [20].

The final positional and thermal parameters are given in Table 1 with the various bond distances and angles given in Tables 2, 3 and 4. A table of observed and calculated structure factors is available [25] or can be obtained from the authors on request.

Results and discussion

The reaction of (η^5-C_5H_5)Rh(CO)(PPh_3) and bis(pentafluorophenyl)acetylene produced mainly two products, hexakis(pentafluorophenyl)benzene and VI, in very small yields after 85 h in refluxing xylene. Under similar conditions, the cobalt analog is much more reactive [20]. Yellow crystals of VI were characterized by elemental analysis, IR, mass and proton NMR spectra. The unique nature of VI and the fact that rhodacyclopentadienes have been postulated as intermediates in the trimerization of acetylenes [26] prompted an X-ray structural study.

That VI is a rhodacyclopentadiene complex is easily seen from Fig. 1 which

TABLE 2

BOND DISTANCES (in Å) AND ANGLES (in degrees) IN 1-(η^5-CYCLOPENTADIENYL)-1-TRIPHENYLPHOSPHINE-2,3,4-5-TETRAKIS(PENTAFLUOROPHENYL)RHODOLE, EXCLUDING THE PENTAFLUOROPHENYL RINGS

Rh—C(1)	2.060(12)	C(1)—C(2)	1.343(16)	P—C(60)	1.858(12)
Rh—C(4)	2.067(11)	C(2)—C(3)	1.457(16)	P—C(70)	1.821(10)
Rh—P	2.293(2)	C(3)—C(4)	1.354(15)	P—C(80)	1.820(13)
Rh—C(51)	2.286(13)	C(1)—C(11)	1.498(17)	C(51)—C(52)	1.429(22)
Rh—C(52)	2.261(14)	C(2)—C(21)	1.497(16)	C(52)—C(53)	1.420(17)
Rh—C(53)	2.250(13)	C(3)—C(31)	1.478(16)	C(53)—C(54)	1.424(20)
Rh—C(54)	2.238(10)	C(4)—C(41)	1.492(17)	C(54)—C(55)	1.422(17)
Rh—C(55)	2.268(12)			C(55)—C(51)	1.431(18)

Rh—C(1)—C(2)	115.5(8)	C(21)—C(2)—C(3)	120.9(9)
C(1)—C(2)—C(3)	114.9(9)	C(31)—C(3)—C(2)	119.7(9)
C(2)—C(3)—C(4)	115.5(9)	C(31)—C(3)—C(4)	124.9(10)
Rh—C(4)—C(3)	114.8(8)	C(41)—C(4)—C(3)	120.3(9)
C(1)—Rh—C(4)	78.3(4)	C(41)—C(4)—Rh	124.9(7)
P—Rh—C(1)	101.6(3)	C(51)—C(52)—C(53)	108.3(12)
P—Rh—C(4)	93.3(3)	C(52)—C(53)—C(54)	108.8(11)
C(11)—C(1)—Rh	123.3(8)	C(53)—C(54)—C(55)	106.9(11)
C(11)—C(1)—C(2)	119.4(10)	C(54)—C(55)—C(51)	109.3(11)
C(21)—C(2)—C(1)	124.1(10)	C(55)—C(51)—C(52)	106.8(11)
C(60)—P—C(70)	103.5(5)	C(70)—P—C(80)	103.8(5)
C(60)—P—C(80)	101.8(5)		

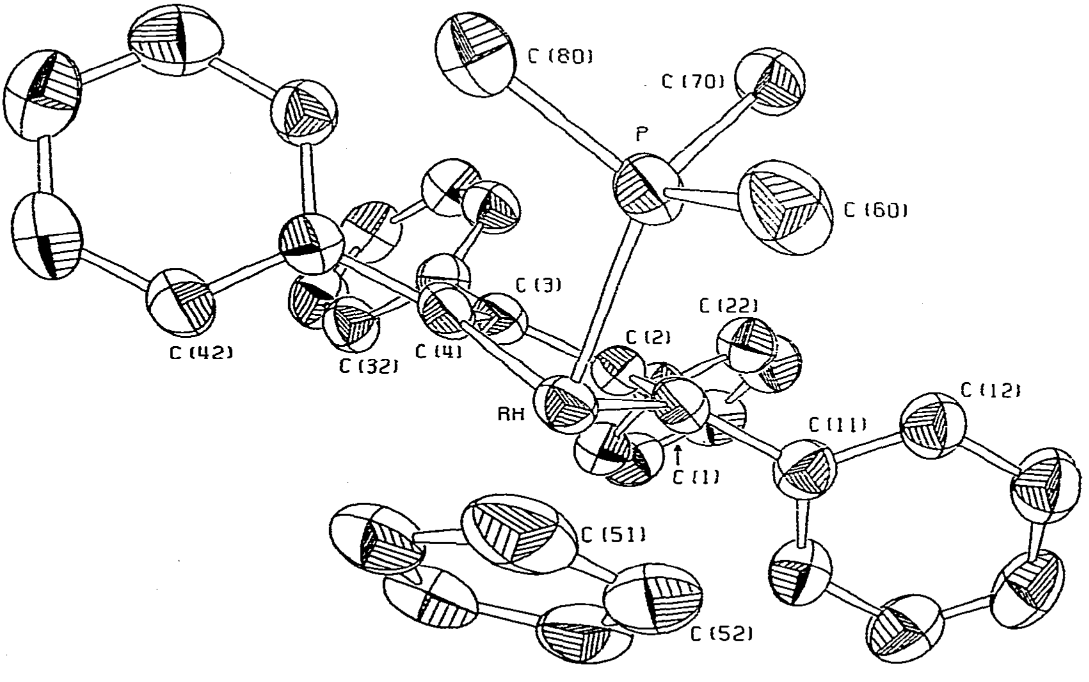


Fig. 1. The atomic numbering and thermal ellipsoids in 1-(η^5-cyclopentadienyl)-1-triphenylphosphine-2,3,4,5-tetrakis(pentafluorophenyl)rhodole. The pentafluorophenyl rings are numbered 1—4 and the fluorines have been omitted for clarity. Similarly, the three phenyl rings of the phosphine have been omitted with only the first atoms C(60), C(70) and C(80) being shown. The rhodacycle is best viewed as a cyclopentadiene with the double bonds between C(1)—C(2) and C(3)—C(4).

TABLE 3

BOND DISTANCES (in Å) AND ANGLES (in degrees) IN THE FOUR PENTAFLUOROPHENYL RINGS

	n			
	1	2	3	4
C(*n*1)—C(*n*2)	1.384(15)	1.342(16)	1.392(15)	1.385(15)
C(*n*2)—C(*n*3)	1.364(20)	1.400(20)	1.374(20)	1.351(20)
C(*n*3)—C(*n*4)	1.375(18)	1.358(18)	1.357(19)	1.389(18)
C(*n*4)—C(*n*5)	1.367(19)	1.365(20)	1.368(18)	1.355(19)
C(*n*5)—C(*n*6)	1.372(20)	1.373(19)	1.367(18)	1.362(19)
C(*n*6)—C(*n*1)	1.393(15)	1.389(14)	1.389(16)	1.386(14)
C(*n*2)—F(*n*2)	1.347(12)	1.354(12)	1.351(13)	1.344(12)
C(*n*3)—F(*n*3)	1.339(15)	1.341(18)	1.349(15)	1.348(16)
C(*n*4)—F(*n*4)	1.338(18)	1.337(19)	1.335(18)	1.340(18)
C(*n*5)—F(*n*5)	1.343(15)	1.358(14)	1.338(15)	1.357(14)
C(*n*6)—F(*n*6)	1.331(13)	1.343(14)	1.351(13)	1.342(13)
C(*n*1)—C(*n*2)—C(*n*3)	123.1(11)	122.4(12)	123.7(11)	122.9(11)
C(*n*2)—C(*n*3)—C(*n*4)	119.6(13)	119.3(13)	118.8(13)	120.2(13)
C(*n*3)—C(*n*4)—C(*n*5)	119.6(13)	119.3(14)	120.8(13)	117.9(13)
C(*n*4)—C(*n*5)—C(*n*6)	119.8(13)	120.6(13)	119.0(12)	121.4(12)
C(*n*5)—C(*n*6)—C(*n*1)	122.6(12)	121.1(11)	123.6(11)	122.0(11)
C(*n*6)—C(*n*1)—C(*n*2)	115.3(11)	117.3(11)	114.1(10)	115.4(10)
C(*n*)—C(*n*1)—C(*n*2)	124.2(10)	123.9(10)	123.1(10)	124.1(10)
C(*n*)—C(*n*1)—C(*n*6)	120.5(10)	118.8(10)	122.5(10)	120.5(10)
F(*n*2)—C(*n*2)—C(*n*1)	120.2(10)	121.3(11)	118.2(10)	119.4(10)
F(*n*2)—C(*n*2)—C(*n*3)	116.7(11)	116.4(11)	118.0(11)	117.7(11)
F(*n*2)—C(*n*3)—C(*n*2)	120.9(12)	120.7(13)	120.3(12)	120.8(12)
F(*n*3)—C(*n*3)—C(*n*4)	119.5(12)	120.0(13)	120.9(12)	119.0(12)
F(*n*4)—C(*n*4)—C(*n*3)	120.7(13)	121.3(14)	119.9(13)	119.9(12)
F(*n*4)—C(*n*4)—C(*n*5)	119.7(13)	119.4(13)	119.3(12)	122.1(13)
F(*n*5)—C(*n*5)—C(*n*4)	120.9(13)	120.1(13)	119.6(12)	118.8(12)
F(*n*5)—C(*n*5)—C(*n*6)	119.4(12)	119.3(12)	121.4(12)	119.8(11)
F(*n*6)—C(*n*6)—C(*n*5)	117.7(11)	119.0(11)	117.6(11)	117.9(10)
F(*n*6)—C(*n*6)—C(*n*1)	119.7(11)	119.9(10)	118.9(10)	120.1(10)

TABLE 4

BOND DISTANCES (in Å) AND ANGLES (in degrees) IN THE THREE PHENYL RINGS OF THE PHOSPHINE GROUP

	n		
	6	7	8
P—C(*n*0)	1.858(12)	1.821(10)	1.820(13)
C(*n*0)—C(*n*1)	1.400(21)	1.387(14)	1.395(16)
C(*n*1)—C(*n*2)	1.382(22)	1.399(19)	1.413(20)
C(*n*2)—C(*n*3)	1.379(25)	1.347(21)	1.413(19)
C(*n*3)—C(*n*4)	1.396(30)	1.405(18)	1.406(21)
C(*n*4)—C(*n*5)	1.367(25)	1.403(18)	1.380(21)
C(*n*5)—C(*n*0)	1.377(20)	1.368(16)	1.404(15)
P—C(*n*0)—C(*n*1)	117.4(9)	121.4(9)	118.5(9)
P—C(*n*0)—C(*n*5)	122.2(10)	119.5(8)	122.3(9)
C(*n*0)—C(*n*1)—C(*n*2)	120.1(13)	120.3(12)	121.0(11)
C(*n*1)—C(*n*2)—C(*n*3)	119.7(15)	120.3(14)	119.5(12)
C(*n*2)—C(*n*3)—C(*n*4)	119.2(16)	120.8(14)	118.2(13)
C(*n*3)—C(*n*4)—C(*n*5)	121.8(17)	118.2(13)	122.0(13)
C(*n*4)—C(*n*5)—C(*n*0)	118.8(14)	121.3(11)	120.1(12)
C(*n*5)—C(*n*0)—C(*n*1)	120.4(12)	119.1(11)	119.1(11)

also gives the atomic numbering. The Rh—C distances in the RhC_4 ring (2.060(12) and 2.067(11) Å) are only slightly longer than the corresponding Co—C distances (average of 1.994(11) Å) found in the analogous Co complex. An average Rh—C distance of 2.062(22) Å was reported in two rhodium complexes where no Rh—ligand π-bonding was possible [27]. The rhodacyclopentadiene can be formulated as a normal diene with single Rh—C σ-bonds to the C_4 fragment. The C—C bonds in the RhC_4 ring (see Table 2) are very nearly identical to the distances of 1.344 and 1.467 Å found in gaseous butadiene [28], indicating the localized nature of the two π-bonds in the ring. The Rh—C distances of 2.004 [29], 2.022 [30] and 1.98 Å [31] found in other rhodacycles are very nearly the same which suggests that, to a large extent, the RhC_4 ring is a localized diene system and that there is little or no Rh—C π-bonding in these complexes. A similar conclusion was reached in the case of the cobalt analog of VI [20]. The Rh atom is displaced by 0.239 Å from the plane defined by C(1) to C(4) in the direction of the C_5H_5 or Cp ring. The Cp ring is planar but tipped by 36.6° relative to the C(1) to C(4) plane. The Rh—C (to the Cp ring) distances show a large significant variation 2.286(13) to 2.238(10) Å, with an average of 2.261(8) Å. The average value is at the upper end of the reported values which range from 2.19 to 2.26 Å [24].

The Rh—P distance of 2.293(2) Å is longer than the Co—P distance of 2.234(3) Å in the cobalt analog [20] by 0.059 Å. A similar difference (0.073 Å) was found in the M—C distances in the two complexes. For comparison, the distances of 2.235(5) and 2.304(5) have been reported [27] in another rhodium(I) complex. An examination of some reported Rh—P bond distances [29,32] indicates that the Rh—P bond length is very sensitive to the *trans* group. For example, the Rh^{III}—P bond length varies from about 2.25 to 2.4 Å depending on the nature of the *trans* ligand *. Similar effects have been noted with Pd, Pt and other second and third row transition metals.

The distances and angles in the Cp, phenyl and pentafluorophenyl rings are comparable to the dimensions found in numerous other studies. There are no unusual features which could be related to the stability of these intermediates. The isolation and characterization of VI supports the arguments that a rhodacyclopentadiene moiety may be an intermediate in trimerization of acetylenes catalyzed by rhodium complexes. The sterically hindered nature of the rhodacycle can be appreciated from Fig. 1 even though the fluorine atoms were not included in the illustration. The isolation of the fluorinated intermediate is probably possible because of the steric problems which an attacking acetylene would encounter. Since the distances and angles in VI are sufficiently similar to related compounds, electronic factors due to the fluorine atoms do not appear to be significant.

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* The range of Rh—P distances can be appreciated by scanning the various issues of BIDICS compiled by I.D. Brown, McMaster University, Hamilton, Ontario, Canada.

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