Journal of Organometallic Chemistry, 438 (1992) 229–239
Elsevier Sequoia S.A., Lausanne
JOM 22807

Pentafluorophenyl compounds of rhodium(III) with bidentate phosphorus or nitrogen ligands

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(Received January 31, 1992)

Abstract

Treatment of $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2]$ with tertiary diphosphine ligands gives anionic compounds of the type $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3L_2]$ (L_2 = (bis(diphenylphosphino)methane (I), bis(diphenylphosphino)amine (II) and bis(diphenylphosphino)ethane (III)) and neutral compounds of stoichiometry $[Rh(C_6F_5)_3L_2]$ (IV–VI); dichloromethane solutions of IV–VI react with carbon monoxide or tert-butyl isocyanide yielding complexes of the type $[Rh(C_6F_5)_3L'_2]$ (L' = CO or ^tBuCN) (VII–X)). In a similar way, addition of nitrogen ligands to solutions of $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2]$ or $[Rh(C_6F_5)_3(OEt_2)_x]$ gives dinuclear complexes $[\{Rh(C_6F_5)_3\}_2L_2]$ (L_2 = 2,2′-bipyrimidine (XIII), L = 4,4′-bipyridine (XIV)) and mononuclear complexes $[Rh(C_6F_5)_3L_2]$ (L_2 = 1,10-phenanthroline (XV) or 2,2′-biimidazole (XVI)).

Introduction

We have recently reported the synthesis of the first homoleptic anionic pentafluorophenyl derivative of rhodium $[P(CH_2Ph)Ph_3]_2[Rh(C_6F_5)_5]$ [1]; this compound reacts with HCl to give the homobinuclear complex $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2]$ from which cleavage of the chloro-bridges, or treatment with thallium(I) acetylacetonate or silver perchlorate and addition of monodentate neutral ligands gives a variety of neutral and anionic five-coordinated mononuclear complexes of rhodium(III) [2]. Diethyl ether solutions of the species $[Rh(C_6F_5)_3(OEt_2)_x]$ are of particular interest because the ether can be easily displaced by neutral ligands.

To investigate the ability of the "RhR_3" unit to form mono- or bi-nuclear compounds we studied the reaction of $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2]$ and $[Rh(C_6F_5)_3(OEt_2)_x]$ with bidentate ligands such as tertiary diphosphine ligands and *N*-donors. Tertiary diphosphines have being increasingly used in coordination chemistry [3], and bis(diphenylphosphine)methane (dppm) has been the subject of

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much recent work, mainly because of its ability to form homo- or hetero-metallic binuclear bridged complexes with or without metal–metal bonds [4]; similar systems such as the isoelectronic bis(diphenylphosphino)amine (dppa) [5] and bis(diphenylphosphino)ethane (dppe) [3] have received less attention. However, neutral mononuclear species with the dppm and the dppa ligands are rare [6]. Here we describe the synthesis and characterization of several neutral and anionic mononuclear rhodium diphosphine complexes. We have also investigated nitrogen ligands such as 2,2′-bipyrimidine (bipym), 4,4′-bipyridine (bipy), 2,2′-biimidazole (H_2bim) and 1,10-phenanthroline (phen) [7–10].

Results and discussion

Analytical, colour, molecular weight or conductance and yields for the new complexes are listed in Table 1; ^{19}F NMR parameters are summarized in Table 2 and ^{1}H and $^{31}P\{^{1}H\}$NMR parameters in Table 3.

Complexes with bidentate phosphorus ligands (Scheme 1)

The addition of solid bis(diphenylphosphino)methane (dppm), bis(diphenylphosphino)ethane (dppe) or bis(diphenylphosphino)amine (dppa) to dichloromethane solutions of the complex $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2$ [2] (2 : 1 ratio) cleaves the chloro-bridges and after a few minutes forms the anionic complexes $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3L]$ (L = dppm (I) dppa (II); dppe (III)) (Scheme 1, (a)); if the reaction mixture is stirred for longer periods, the chlorine is displaced and neutral compounds of the formula $[Rh(C_6F_5)_3L]$ (L = dppm (IV); dppa (V); dppe (VI) can be isolated (Scheme 1, (c)). Compounds IV, V and VI can also be obtained by addition of the bases to diethyl ether solutions of the solvated species $[Rh(C_6F_5)_3(Et_2O)_x]$ (Scheme 1, (e)); these complexes are not stable in air, in solution or in the solid state. When the addition is made in the presence of carbon monoxide (Scheme 1, (f)), the orange solutions became almost colourless and the IR spectra of the solutions show ν(CO) at ~2100 cm^{-1}. After work up, white solids of stoichiometry $[Rh(C_6F_5)_3(CO)L]$ (L = dppm (VII); dppa (VIII); dppe (IX)) were isolated; a similar compound $[Rh(C_6F_5)_3(^tBuCN)(dppm)]$ (X) is prepared when 1 equiv. of ^{t}BuCN is added to a diethyl ether solution of $[Rh(C_6F_5)_3(dppm)]$; complexes VII–X are stable in air, in solution or in the solid state. Complexes are 1 : 1 electrolytes in acetone solutions (5×10^{-4} *M*) [11].

The IR spectra of the complexes show the characteristic bands near 1510, 1050, and 950 cm^{-1} of the pentafluorophenyl group [12]; the anionic compounds I–III have absorptions arising from ν(Rh–Cl) at about 280 cm^{-1} (see Experimental section); ν(NC) of the ^{t}BuCN ligand in complex X occurs at 2215 cm^{-1} in the solid state and at 2210 cm^{-1} in dichloromethane solution, consistent with its coordination to Rh^{III} [13]; bands in the 600-400 cm^{-1} region confirm the presence of the phosphines.

The ^{1}H NMR spectra of the complexes are in agreement with the proposed formulae. The ^{19}F NMR spectra of all the complexes (Table 2) show time-averaged signals at around room temperature. Most of the spectra consist of a broad signal for the *o*-fluorine atoms of the pentafluorophenyl groups and two unresolved multiplets for the *m*- and *p*-fluorine atoms; this behaviour is similar to that found for the complexes $[Rh(C_6F_5)_3L_2]$ (L = monodentate ligand) [2]; as with those

Table 1

Analysis, colour, yields and molecular weight or conductance for the new complexes

Compound	Analysis [b]			Colour	Yield (%)	M_w [b,c] / Λ_M [d]
	%N	%C	%H			
Q[Rh(C_6F_5)$_3$Cl(dppm)] (I) [a]	–	59.70 (59.38)	3.40 (3.07)	Pale yellow	65	92 (1 : 1)
Q[Rh(C_6F_5)$_3$Cl(dppa)] (II)	1.04 (1.02)	57.40 (58.38)	3.75 (3.15)	Pale yellow	70	94 (1 : 1)
Q[Rh(C_6F_5)$_3$Cl(dppe)] (III)	–	60.84 (60.47)	3.78 (3.61)	Pale yellow	60	87 (1 : 1)
[Rh(C_6F_5)$_3$(dppm)] (IV)	–	52.00 (52.25)	2.30 (2.24)	Pale orange	75	[e]
[Rh(C_6F_5)$_3$(dppa)] (V)	1.32 (1.41)	50.21 (50.98)	2.97 (2.14)	Pale orange	60	[e]
[Rh(C_6F_5)$_3$(dppe)] (VI)	–	52.50 (52.72)	2.15 (2.41)	Pale yellow	80	[e]
[Rh(C_6F_5)$_3$(dppm)(CO)] (VII)	–	51.17 (51.99)	2.20 (2.18)	Pale yellow	68	803 (1016.47)
[Rh(C_6F_5)$_3$(dppa)(CO)] (VIII)	1.33 (1.37)	50.73 (50.76)	2.26 (2.08)	Pale yellow	62	987 (1017.46)
[Rh(C_6F_5)$_3$(dppe)(CO)] (IX)	–	52.04 (52.45)	2.81 (2.35)	White	75	1381 (1030.49)
[Rh(C_6F_5)$_3$(dppm)(^{t}BuCN)] (X)	1.36 (1.30)	53.29 (53.80)	3.27 (2.92)	White	60	
Q_2[{Rh(C_6F_5)$_3$Cl}$_2$(μ-bipym)] (XI)	2.72 (2.61)	51.36 (51.53)	2.77 (2.25)	Yellow	75	207 (2 : 1)
[{Rh(C_6F_5)$_3$}$_2$(μ-bipym)] (XIII)	4.38 (4.10)	38.83 (38.68)	0.84 (0.64)	Orange	82	[f]
[{Rh(C_6F_5)$_3$(μ-4,4'bipy)}$_2$] (XIV)	3.70 (3.68)	42.93 (44.23)	2.77 (2.35)	Yellow	93	[f]
[Rh(C_6F_5)$_3$(1,10-phen)] (XV)	3.93 (3.57)	46.69 (45.95)	0.79 (1.02)	Yellow	82	[f]
[Rh(C_6F_5)$_3$(H_2-biim)]THF (XVI)	6.78 (6.91)	39.38 (41.50)	1.59 (0.99)	Orange	50	950 (810.33)

[a] $Q^+ = [P(CH_2Ph)Ph_3]^+$. [b] Calculated values are given in parentheses. [c] In $ChCl_3$. [d] Λ_M (Ω^{-1} cm^2 mol^{-1}) ≈ 5×10^{-4} mol dm^{-3} acetone solutions. [e] Not stable in solution. [f] Insoluble in acetone.

compounds, on cooling, the rotation and isomerization processes slow yielding spectra with distinct signals for all (or most) of the *o*-fluorine atoms. For the anionic complexes, I–III, three *ortho*-F resonances ($2F_o:2F_o:2F_o$) are found (at low temperature for **I** and **III** and at room temperature for **II**). It is noteworthy

Table 2

^{19}F chemical shifts for the new complexes [a]

	T (°C)	∂*o*-F (ppm)	∂*m*-F (ppm)	∂*p*-F (ppm)
I	20 ($CDCl_3$)	−105.8 (4F, m), −120.2 (2F, m)	−164.3 (2F, ft), −168.7 (4F, M)	−161.4 (1F, ft) −167.3 (2F, m)
	−80 (HDA)	−93.6 (2F, m, b), −107.9 (2F, m, b) −111.9 (2F, m, b)	−165.9 (4F, m), −167.1 (2F, m)	−163.8 (1F, ft) −165.4 (2F, ft)
II	20 (HDA)	−101.9 (2F, m), −102.1 (2F, m), −116.6 (2F, m)	(−162.6 ··· −168.8, 9F, *m*- and *p*-F)	
	−80 (HDA)	−92.6 (1F, m), −96.9 (1F, m) −103.4 (2F, m), −109.5 (2F, m)	(−161.5 ··· −166.2, 9F, *m*- and *p*-F)	
III	20 ($CDCl_3$)	−119.3 (6F, m, b)	−164.3 (6F, ft)	−161.4 (3F, ft)
	−80 (HDA)	−86.9 (2F, m), −102.2 (2F, m), −103.3 (2F, m)	(−160.4 ··· 166.5, 9F, *m*- and *p*-F)	
IV	20 (HDA)	−117.9 (6F, m)	−164.3 (6F, ft)	−161.5 (3F, ft)
	−80 (HDA)	−88.4 (1F, m), −104.0 (1F, m), −104.5 (1F, m), −105.8 (1F, m), −109.7 (1F, m), −117.0 (1F, m),	(−160.1 ··· −164.4, 9F, *m*- and *p*-F)	
V	20 (HDA)	116.5 (6F, m)	−164.7 (6F, ft)	−162.2 (3F, ft)
VI	20 (HDA)	−119.0 (6F, m)	−166.0 (6F, ft)	−163.9 (3F, ft)
	−80 (HDA)	−92.6 (1F, m), −103.2 (1F, fd), −105.2 (1F, m), −115.8 (1F, m), −116.9 (1F, m), −127.9 (1F, m),	(−160.1 ··· −165.6, 9F, *m*- and *p*-F)	
VII	20 ($CDCl_3$)	−98.3 (2F, m), −104.8 (2F, m) −106.6 (2F, m)	(−160.1 ··· −164.3, 9F, *m*- and *p*-F)	
	−80 (HDA)	−87.6 (1F, fd), 96.5 (1F, m) −103.8 (1F, fd), −104.6 (2F, fd), −107.2 (1F, m)	(−158.8 ··· −163.4, 9F, *m*- and *p*-F)	
VIII	20 (HDA)	−98.6 (4F, m), −104.4 (1F, m) −105.5 (1F, m)	−163.3 (4F, ft), −164.1 (2F, m)	−160.6 (1F, ft) −159.4 (2F, ft)
	−80 (HDA)	−90.0 (1F, m), −95.8 (1F, m) −103.7 (1F, fd), −104.7 (3F, m)	(−159.2 ··· −163.7, 9F, *m*- and *p*-F)	
IX	20 ($CDCl_3$)	−98.4 (2F, m, b), −104.6 (4F, m)	−163.8 (4F, m), −166.3 (2F, m)	−160.8 (2F, ft) −162.5 (1F, ft)
	−80 (HDA)	−87.1 (1F, m), −100.1 (2F, m), −102.9 (1F, fd), −105.8 (2F, m)	(−159.1 ··· −165.5, 9F, *m*- and *p*-F)	
X	20 ($CDCl_3$)	−101.0 (4F, m, b), −107.8 (1F, m) −111.0 (1F, m)	−164.4 (4F, m), −165.2 (2F, m)	−161.4 (2F, ft) −163.5 (1F, ft)
	−50 ($CDCl_3$)	−88.1 (1F, fd), −102.2 (1F, fd), −105.6 (1F, m), −106.2 (1F, fd), −108.2 (1F, m), −111.1 (1F, fd).	−162.6 (2F, ft), −164.4 (2F, ft) −165.1 (2F, ft)	−160.1 (1F, ft) −161.1 (1F, ft) −163.1 (1F, ft)
XI	20 ($CDCl_3$)	−114.4 (2F, m, b), −117.1 (2F, m, b) −118.7 (2F, m, b)	(−161.8 ··· −166.0, 9F, *m*- and *p*-F)	
	−50 ($CDCl_3$)	−115.0 (2F, m), −119.5 (2F, m), −122.4 (2F, m)	−165.5 (6F, m)	−162.8 (3F, m)

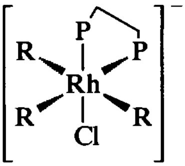
Table 2 (continued)

	T (°C)	∂o-F (ppm)	∂m-F (ppm)	∂p-F (ppm)
XIII	20 (HDA)	−115.0 (2F, m, b), −121.5 (2F, m, b), −127.5 (2F, m, b)	−164.7 (6F, m, b)	−161.5 (1F, m), −163.1 (2F, m)
	−40 (HDA)	−111.1 (2F, m), −115.8 (2F, m), −118.5 (2F, m)	−164.3 (2F, ft), −164.7 (2F, m) −165.2 (2F, ft)	−162.1 (1F, ft) −162.9 (2F, ft)
XIV	20 (HDA)	−122.2 (6F, m)	−163.7 (6F, ft)	−160.9 (3F, ft)
	40 (HDA)	−118.5 (6F, m, b)	−164.3 (6F, m, b)	−162.1 (3F, m, b)
XV	20 (HDA)	−114.3 (2F, m, b), −122.6 (2F, m, b), −128.8 (2F, m, b)	−164.4 (6F, m, b)	−161.6 (3F, m, b)
	−40 (HDA)	−111.8 (2F, m), −117.2 (2F, m) −120.9 (2F, m)	−164.3 (2F, ft), −164.7 (2F, ft) −165.5 (2F, ft)	−162.7 (2F, ft), −163.0 (1F, ft)
XVI	20 ($CDCl_3$)	−117.5 (2F, m, b), −125.5 (2F, m, b) −133.4 (2F, m, b)	−165.9 (6F, m, b)	−162.2 (3F, m, b)

[a] m, multiplet; b, broad; ft, false triplet; fd, false doublet.

that, in the neutral complexes IV–X, the ^{19}F NMR spectra at low temperature show six signals for the *o*-fluorine atoms, two of the signals being at a very low field (around −90 ppm). This has also been observed for the compounds $[Rh(C_6F_5)_3L_2]$ ($L = PEt_3$ or $AsPh_3$) and may be associated with the fact, established by X-ray structural studies, that two pentafluorophenyl rings are orientated so that one of the *ortho*-fluorine atoms of each ring is located at a short non-bonding distance from the rhodium, probably donating some electron density to the metal. The ^{19}F NMR spectra of IV–X seem to indicate that such weak *o*-F ··· Rh interactions may also be present.

The $^{31}P\{^1H\}$ NMR spectra (Table 3) of compounds I–III show a resonance due to the $[P(CH_2Ph)Ph_3]^+$ at ~23 ppm. Compounds I and II show a very broad signal at room and at low temperature so that there is probably an equilibrium in solution, between the I, II and I′, II′ forms (Scheme 1, (b)) although the spectroscopic data do not completely exclude the possibility of I and II having the following structure:



Compound III exhibits a doublet of multiplets (41.9 ppm, $^2J(Rh–P) = 82.7$ Hz) which can be assigned to two equivalent phosphorus atoms coupling to the rhodium and to the *o*-F atoms of the pentafluorophenyl groups [14]. For compounds IV–VI, the ^{31}P NMR spectra also reveal the presence of two equivalent phosphorus atoms coupling to the rhodium and to the *o*-F atoms of the pentafluorophenyl groups.

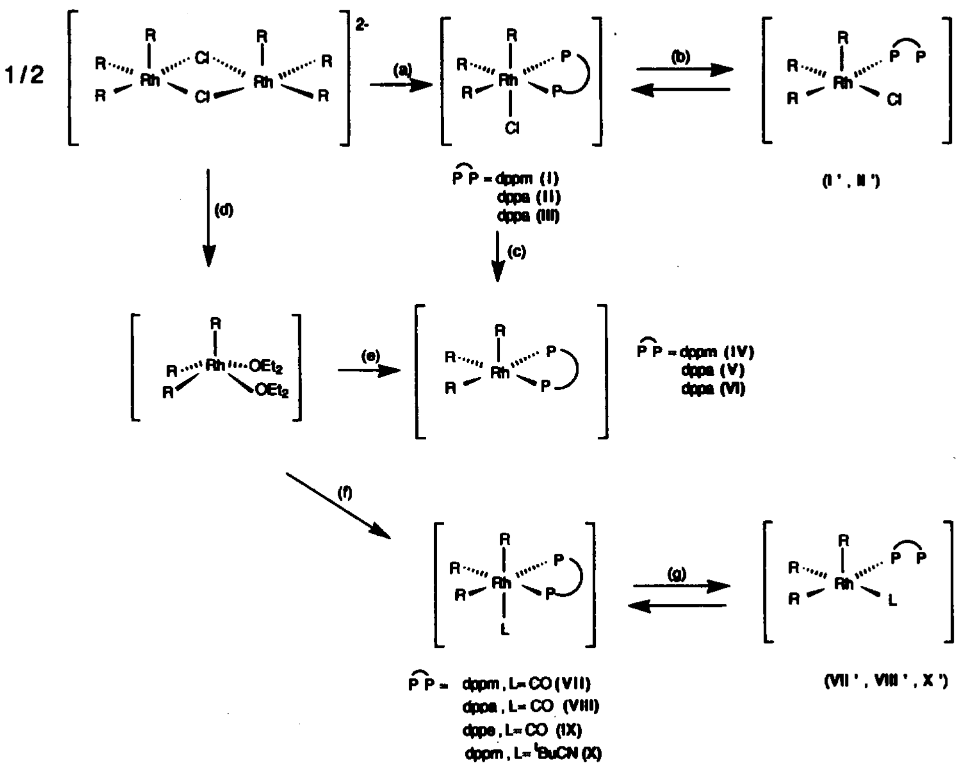
Whereas the ^{19}F NMR spectra of complexes VII–X are all very similar, the $^{31}P\{^1H\}$ spectra show clear differences; for compound IX at room temperature, the

Table 3

^{1}H and ^{31}P chemical shifts for the new complexes [a]

	T (°C)	^{1}H	^{31}P
I	20 ($CDCl_3$)	7.7–6.8 (40 H, phenyl), 4.7 (2H, $-CH_2-(Q^+)$, ^2J(H–P) = 14.16) 5.2 (1H, $-CH_2-$(dppm), m, b), 3.3 (1H, $-CH_2-$(dppm), m, b)	24.5 (s, 1P, Q^+), −23.3 (2P, m, dppm, b)
	−80 (HDA)		25.0 (s, 1P, Q^+), −23.1 (2P, m, dppm, b)
II	20 (HDA)	7.9–7.1 (40 H, phenyl), 5.1 (2H, $-CH_2-(Q^+)$, ^2J(H–P) = 15.14) 3.8 (1H, N–H, dppa)	23.4 (s, 1P, Q^+), 37.4 (2P, m, dppa, b)
	−80 (HDA)		23.4 (s, 1P, Q^+), 37.4 (2P, m, dppa, b)
III	20 ($CDCl_3$)	7.8–7.0 (40 H, phenyl), 4.7 (2H, $-CH_2-(Q^+)$, ^2J(H–P) = 14.16) 3.8 (4H, $-CH_2-$dppe, m)	23.9 (s, 1P, Q^+), 41.9 (2P, dm, dppe, b, ^2J(P–Rh) = 90.3)
	−60 ($CDCl_3$)		23.9 (s, 1P, Q^+), 44.4 (2P, dm, dppe, b, ^2J(P–Rh) = 84)
IV	20 (HDA)	7.8–7.1 (20H, phenyl), 4.9 (2H, *t*, ^2J(H–P) = 10.39)	−16.3 (dm, ^2J(P–Rh) = 82.7)
V		7.6 (20 H, phenyl)	37.6 (dm, ^2J(P–Rh) = 82.7)
VI		7.8–7.0 (20 H, phenyl), 3.2 (4H, m)	42.5 (dm, ^2J(P–Rh) = 91.6)
VII	20 (HDA)	7.4–7.1 (20 H, phenyl), 4.9 (2H, $-CH_2$ dppm, tm, ^2J(H–P) = 10.1)	−28.3 (Δ_m = 100 Hz), −39.3 (Δ_m = 118 Hz)
	−80 (HDA)		−28.2 (Δ_m = 115 Hz), −39.9 (Δ_m = 133 Hz)
VIII	20 (HDA)	7.4–7.1 (20H, phenyl), 9.1 (1H, NH dppa, s)	25.9 (Δ_m = 134 Hz), 37.3 (Δ_m = 109 Hz)
	−80 (HDA)		24.9 (Δ_m = 109 Hz), 36.4 (Δ_m = 94 Hz)
IX	20 ($CDCl_3$)	7.8–7.0 (20 H, phenyl), 3.4 (2H, $-CH_2-$dppe, m), 3.1 (2H, $-CH_2-$dppe, m)	38.9 (dm, dppe, b, ^2J(P–Rh) = 72.6)
	−80 (HDA)		42.1 (ddm, dppe, b, $^2J(P_a-Rh)$ = 74.7, $^2J(P_b-Rh)$ = 68.8)
X	20 ($CDCl_3$)	7.4–7.1 (20H, phenyl), 4.8 (2H, $-CH_2$ dppm), 1.4 (9H, $-CH_3$, ^{t}BuCN)	−25.6 (b), −37.3 (b)
	−80 (HDA)		−25.6 (b), −37.0 (b)
XI	20 ($CDCl_3$)	9.04 (4 H_b, d, $^3J(H_b-H_a)$ = 5.2), 4.72 (4H, $-CH_2-(Q^+)$, ^2J(H–P) = 14.16), 7.7–6.8 (20H, phenyl)	
XIII	20 (HDA)	9.58 (4 H_b, d, $^3J(H_b-H_a)$ = 5.4), 8.3 (2H_a, *t*, $^3J(H_b-H_a)$ = 5.4)	
XIV	20 (HDA)	8.2 (4H, AB system, $\Delta\nu$ = 141.07 Hz, ^3J = 5.17)	
XV	20 (HDA)	9.4 (2H, dm, ^3J = 5.0, H2, 9), 8.9 (2H, dd, ^3J = 8.2, ^4J = 1.4, H4, 7) 8.3 (2H, s, H5, 6), 8.2 (2H, dd, ^3J = 8.2, ^3J = 5.0, H3, 8)	
XVI	20 ($CDCl_3$)	11.06 (2H, m, H-acid-), 7.26 (2H, m, H_a or H_b), 7.14 (2H, m, H_a or H_b), 3.91 (4H, m, THF), 2.0 (4H, m, THF)	

[a] m, multiplet; b, broad; s, singlet; t, triplet; tm, triplet of multiplets; dm, doublet of multiplets, ddm, double doublet of multiplets; dd, doublet of doublets.



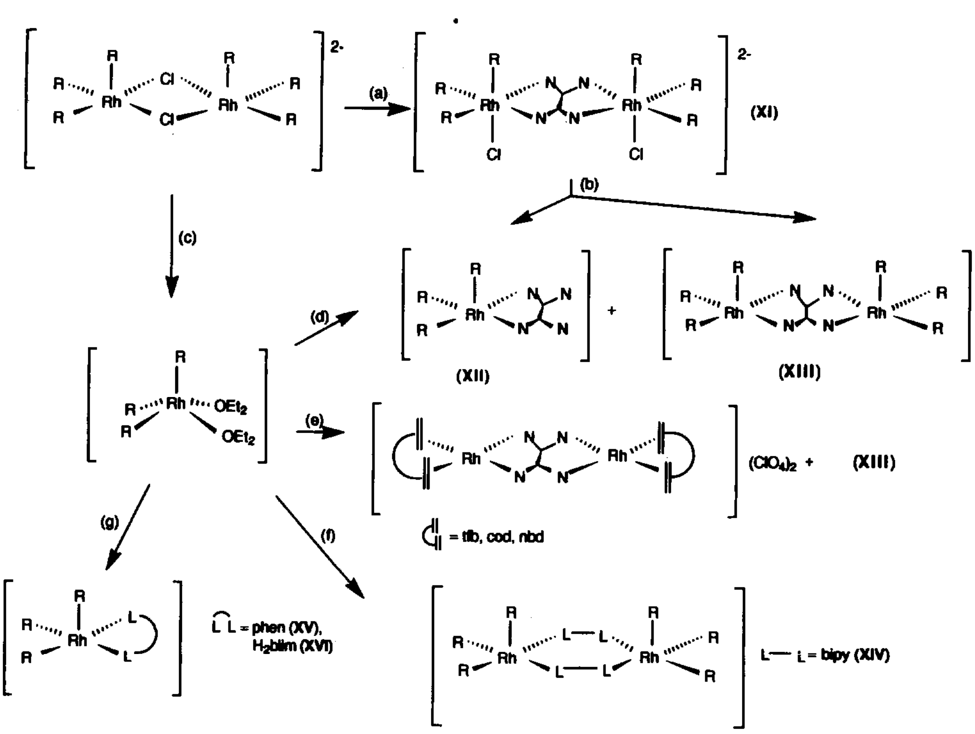
Scheme 1. a = $\widehat{PP}$; c = $-[P(CH_2Ph)Ph_3]Cl$; d = $AgClO_4$, $-AgCl$, $-[P(CH_2Ph)Ph_3]ClO_4$; f = L + $\widehat{PP}$.

spectrum shows a doublet of multiplets (38.9 ppm, $^2J(Rh-P) = 72.6$ Hz), which at −80°C becomes a doublet of doublets of multiplets. For compounds VII, VIII, and X there are two broad separate multiplets which do not change much from +60 to −80°C. Because the dppe chelates more easily than the other two phosphines [4], it is probable that compound IX is hexacoordinate using both P atoms whereas in compounds VII, VIII and X, the two types of phosphorus indicate that, in solution, an equilibrium between the hexacoordinate and pentacoordinate forms (VII, VIII, X and VII', VIII', X', respectively) may be present, even at −80°C (Scheme 1, (g)).

All these data do not exclude the possibility that these compounds are binuclear with the phosphines bridging two rhodium atoms. Compounds VII–IX were investigated with fast atom bombardment (FAB) mass spectroscopy [15] with nitrobenzyl alcohol as matrix. Complex VIII has the highest peak with *m/z* at 1017, corresponding to the parent peak, and peaks at *m/z* at 822, 655, and 488 corresponding to $Rh(C_6F_5)_2(dppa)$, $Rh(C_6F_5)(dppa)$, and Rh(dppa), respectively. For the other two complexes, no parent peak was observed, but only fragments. These data support the formulation of the compounds as mononuclear.

Complexes with bidentate nitrogen donors (Scheme 2)

From solid 2,2′-bipyrimidine and a dichloromethane solution of $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2]$, the orange solution obtained after stirring for a few



Scheme 2. a = d = 2,2′-bipyrimidine; b = $-[P(CH_2Ph)Ph_3]Cl$; c = $AgClO_4$, $-AgCl$, $-[P(CH_2Ph)Ph_3]$; e = $[Rh(bibym)(diolet)]ClO_4$; f = 4,4′-bipyridine; g = L_2.

minutes, gave on evaporation to dryness, an oily residue. Treatment with hexane gave a solid identified as the binuclear $[P(CH_2Ph)Ph_3]_2[\{Rh(C_6F_5)_3Cl\}_2(bipym)]$ (XI) (Scheme 2, (a)). Its IR spectrum shows only one absorption in the 1600 cm^{-1} region (1580 cm^{-1}) assigned to the ring stretching modes of the bipyrimidine [16]. Bands due to the C–H bending mode, appear together with those of the phenyl groups of the cation and the pentafluorophenyl groups. The absorption around 660 cm^{-1} ascribed to the ring bending mode is absent in this complex. These data, together with the elemental analyses and the conductivity in acetone ($\Lambda_M = 205$ ohm^{-1} cm^{-1}, 2:1 electrolyte) [11], confirm that the complex is binuclear and anionic, with the bipym bridging between two rhodium atoms. If the reaction mixture is stirred longer, the chlorine atom is displaced (Scheme 2, (b)), but in this case the solid obtained is a mixture of the neutral mononuclear $[Rh(C_6F_5)_3(bipym)]$ (XII) and the binuclear $[\{Rh(C_6F_5)_3\}_2(\mu\text{-bipym})]$ (XIII). We have not been able to isolate the pure mononuclear compound which has only been characterized in the IR and ^{1}H NMR spectra of the mixture. The dinuclear product is obtained pure by recrystallizing the mixture from acetone/diethylether. Compound XIII is less soluble than XII and gives orange crystals. The absorption due to the ring stretching modes of the bipym appears at 1590 cm^{-1} in the IR spectrum. The low solubility of complex XIII in chloroform or benzene prevents its molecular weight determination.

To prepare binuclear asymmetric Rh^{III}–Rh^{I} compounds with the bipyrimidine bridging, we explored the reaction of $[Rh(bipym)(diolefin)]ClO_4$ [17] [diolefin =

tetrafluorobenzobicyclo(2,2,2)octatriene (tfb), 1,5-cyclooctadiene (cod), or bicyclo(2,2,1)heptadiene (nbd)] with $[Rh(C_6F_5)_3(Et_2O)_x]$ (ratio 1:1) (Scheme 2, (e)). However, redistribution reactions took place, to give $[\{Rh(diolefin)\}_2(bipym)](ClO_4)_2$ and $[\{Rh(C_6F_5)_3\}_2(bipym)]$ (XIII). When the diolefin is tfb, both products can be separated because of their different solubilities in acetone, but with cod or nbd only mixtures of both compounds were obtained.

The reaction of $[Rh(C_6F_5)_3(Et_2O)_x]$ with 4,4′-bipyridine (bipy) (Scheme 2, (f)) gives the neutral binuclear $[\{Rh(C_6F_5)_3(bipy)\}_2]$ (XIV), an air-stable, microcrystalline solid. This is not soluble enough in chloroform or benzene to measure its molecular weight. The IR spectrum shows, together with the absorptions assigned to the pentafluorophenyl groups, bands characteristic of the bipy [18] at $\underline{1610}$, 1015, 810 and $\underline{635}$ cm^{-1}; the underlined frequencies are somewhat shifted with respect to the frequencies of the free bipy. Related binuclear rhodium(I) compounds have been reported [19].

Finally, when 1,10-phenanthroline (phen) or 2,2′-biimidazol (H_2bim) were added to diethyl ether solutions of $[Rh(C_6F_5)_3(Et_2O)_x]$ (Scheme 2, (g)), mononuclear complexes of formula $[Rh(C_6F_5)_3L_2]$ (L_2 = phen (XV); $L_2 = H_2bim$ (XVI)) were prepared. The IR spectra of the complexes show absorptions of the pentafluorophenyl groups together with bands assigned to the ligands (XV, 1600, 1620 and 850 cm^{-1} due to phenanthroline ligand [20]; XVI, absorptions at 3740–3600 broad, 3500–3120 broad, 1550 and 760 cm^{-1} corresponding to the N–H, C–N, ring stretchings and C–H bending out of plane, respectively, of the biimidazole ligand [21]).

The ^1H NMR (Table 3) spectra of complexes XI–XV are in agreement with the proposed formulae. The ^{19}F NMR (Table 2) spectra show three broad signals for the *ortho*-fluorine atoms and unresolved multiplets for the *meta*- and *para*-fluorine atoms of the pentafluorophenyl groups, both at room and at low temperature.

Experimental

All solvents were distilled and dried by standard methods [22]. Reactions were carried out under dinitrogen by standard Schlenk techniques and at room temperature. ^1H, ^{19}F and ^{31}P NMR spectra were recorded on a Varian XL-200 spectrometer operating at 200.057, 188.220 and 80.984 MHz, respectively (in deuterochloroform, $CDCl_3$, or acetone, $-d_6$ HDA, as solvents) chemical shifts are relative to $CFCl_3$, $SiMe_4$, and 85% H_3PO_4 as external references. IR spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 783 spectrophotometer using Nujol mulls between polyethylene sheets or in solution in NaCl cells. Elemental analyses were carried out with a Perkin–Elmer 240B microanalyser. Molecular weights were determinated with a Knauer osmometer using chloroform solutions. Mass spectra were made in a VG Autospec using a caesium FAB with nitrobenzyl alcohol as matrix. $[P(CH_2Ph)Ph_3]_2[\{Rh(\mu\text{-}Cl)(C_6F_5)_3\}_2]$ (1) was prepared according to the reported method [2].

Preparation of $[P(CH_2Ph)Ph_3][RhCl(C_6F_5)_3L]$ *(L = dppm (I), dppa (II), dppe (III))*

Addition of solid base (0.1 mmol) to solutions of 1 (100 mg, 0.05 mmol) in dichloromethane (10 cm^3) led to orange solutions which were left to react for 5 min. Evaporation of the solvent to ~ 1 ml, and addition of diethyl ether, for I and II, or n-hexane for III, gave yellow solids which were filtered, washed with hexane or diethyl ether, and vacuum dried.

Preparation of $[Rh(C_6F_5)_3L]$ *(L = dppm (IV), dppa (V), dppe (VI))*

To a yellow suspension of 1 (100 mg, 0.05 mmol) in dry diethyl ether (10 cm^3) with exclusion of light, silver perchlorate (20.8 mg, 0.1 mmol) was added. After 60 min the white solid formed was filtered off. The appropriate L (0.1 mmol) was added to the yellow solution of $[Rh(C_6F_5)_3(OEt_2)_x]$ and allowed to react for 30 min. Evaporation of the orange solutions under vacuum to 1 cm^3 and addition of n-hexane gave the complexes which were washed with n-hexane, vacuum dried and kept under dinitrogen.

Preparation of $[Rh(C_6F_5)_3L(CO)]$ *(L = dppm (VII), dppa (VIII), dppe(IX))*

The preparation was similar to that described for the complexes IV–VI but before isolating the complexes, carbon monoxide was bubbled through the orange solutions for ~ 15 min. The solutions became almost colourless and by addition of n-hexane, white stable solids were isolated. These compounds have the following ν(CO): (Nujol mulls): 2095s (VII), 2070s (VIII), and 2090 (IX); dichloromethane solutions: 2085s (VII), 2080s (VIII), and 2085s (IX) cm^{-1}; ν(NH) for complex VIII = 3370m cm^{-1}.

Preparation of $[Rh(C_6F_5)_3(dppm)({}^tBuCN)]$ *(X)*

This was prepared as above, with $[Rh(C_6F_5)_3(dppm)]$ and the stoichiometric amount of ^{t}BuCN. The solution became colourless and by addition of n-hexane, a white stable solid was isolated. ν(C≡N) (Nujol mull): 2215s; ν(C≡N) (dichloromethane solution): 2210s cm^{-1}.

Preparation of $[P(CH_2Ph)Ph_3]_2[\{RhCl(C_6F_5)_3\}_2(\mu\text{-}2,2'bipym)]$ *(XI)*

To a solution of 1 (100 mg, 0.05 mmol) in dichloromethane (10 cm^3), 2,2'bipyrimidine (7.96 mg, 0.05 mmol) was added. After stirring for 15 min the orange solution was evaporated to dryness giving an oily residue which was washed twice with n-hexane (1 cm^3) and stirred in n-hexane (10 cm^3) for 30 min. The resulting yellow solid was filtered, washed with n-hexane, and vacuum dried.

Preparation of $[\{Rh(C_6F_5)_3\}_2(\mu\text{-}L_2)]$ *(L_2 = 2,2'bipym (XIII); L = 4,4'bipy (XIV))*

To a solution of $[Rh(C_6F_5)_3(OEt_2)_x]$ in dichloromethane (10 cm^3) the solid base was added in the ratio $1Rh/1/2L_2$; complex XIII precipitated. The mixtures were reduced to 1 cm^3 under vacuum and addition of diethyl ether produced the complexes which were separated by filtration, washed with diethyl ether and vacuum dried.

Preparation of $[Rh(C_6F_5)_3(L)]$ *(L = 1,10-phen (XV);* H_2Biim *(XVI))*

To a solution of 0.1 mmol $[Rh(C_6F_5)_3(OEt_2)_x]$ in dichloromethane (10 cm^3) (for XV) or in a mixture of dichloromethane/THF (1 : 2) (20 cm^3) (for XVI) (0.1 mmol) of L was added. Complex XV was isolated after 30 min of stirring, filtered, washed with diethyl ether and vacuum dried. For complex XVI the reaction mixture was heated under reflux with stirring for 24 h. The solution was then concentrated under reduced pressure to ~ 1 cm^3 and needle-like crystals were obtained by slow diffusion of THF into a n-hexane solution at −20°C. Complex XVI crystallizes with a molecule of THF.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (Spain) (Project PB 88-0386) for financial support.

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