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CATIONIC RUTHENIUM(II) COMPLEXES CONTAINING 1,4-BIS(DIPHENYLPHOSPHINO)BUTANE AND COORDINATED SOLVENT MOLECULES *

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Summary

Efforts to develop catalysts for asymmetric hydrogenation using ruthenium(II)-chelated ditertiary phosphine complexes have led to the synthesis of the complexes $[\{Ru(P-P)(CH_3CN)\}_2\mu\text{-}Cl_3]^+\ PF_6^-$, $[RuCl(P-P)(CH_3CN)_3]^+\ PF_6^-$, and $[RuCl(\eta^6\text{-toluene})(P-P)]^+\ PF_6^-$, where P–P = 1,4-bis(diphenylphosphino)butane. The characterization of the complexes, including X-ray data for the pseudo-tetrahedral toluene complex, is described. In preliminary tests, the tris(acetonitrile) complex has been shown to be a precursor for a catalyst that effects homogeneous hydrogenation of terminal olefins, CH_3CN, and imines.

Introduction

During attempts to develop synthesis of ruthenium(II) complexes containing one chelated ditertiary phosphine per metal, that is an $Ru^{II}(P-P)$ moiety, we discovered a route to make the mixed-valence dimers $Ru_2Cl_5(P-P)_2$ [1]. The ultimate interest in the $Ru^{II}(P-P)$ chemistry is the development of catalysts for asymmetric hydrogenation [2], analogous to the well-known $Rh^I(P-P)$ systems [3,4]. In donor solvents, the mixed-valence dimers were found to undergo disproportionation to Ru_2^{II} and Ru_2^{III} congeners, according to eq. 1 [1].

$$2Ru_2Cl_5(P-P)_2 \rightarrow [RuCl_3(P-P)]_2 + [RuCl_2(P-P)]_2 \qquad (1)$$

By carrying out corresponding disproportionation reactions in the presence of silver salts, dimeric and monomeric cationic ruthenium(II) complexes containing

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coordinated acetonitrile have been isolated and characterized; a toluene analogue was subsequently made. We initially investigated systems with P–P being dppe, dppb, and the respective chiral analogues, chiraphos and diop [5]. The synthetic procedures proved somewhat simpler with the dppb ligand and this, coupled with its lower cost compared to the chiral phosphines, led to the chemistry of Ru(dppb) systems becoming more well developed. This paper describes particularly dppb complexes, and notes also an observed hydrogenation of coordinated CH_3CN to amine, and also catalytic hydrogenation of acetonitrile and imines.

Results and discussion

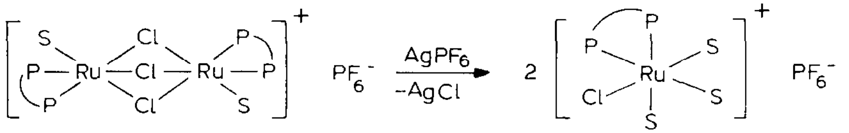
Synthesis and characterization of cationic complexes

The disproportionation of $Ru_2Cl_5(dppb)_2$ in CH_3CN solution in the presence of $AgPF_6$ takes place according to eq. 2 (cf. eq. 1).

$$2Ru_2Cl_5(dppb)_2 + AgPF_6 \rightarrow [RuCl_3(dppb)]_2 + \underset{(\mathbf{1})}{[Ru_2Cl_3(dppb)_2(CH_3CN)_2]^+ PF_6^-} + AgCl \qquad (2)$$

The ruthenium(II) cationic complex (**1**) has been isolated and well characterized by elemental analysis, conductivity and spectroscopic data. The $^{31}P\{^1H\}$ NMR in CD_2Cl_2 consists of an AB quartet (δ_A 49.6, δ_B 46.6 ppm, $^2J_{AB}$ 36.6 Hz); the data are consistent with a triply chloro-bridged structure (**1**), similar to that proposed previously for monodentate phosphine analogues containing π-acid ligands rather than coordinated CH_3CN [6], see eq. 3. In CH_3CN, **1** rapidly dissociates to monomeric species as suggested by the presence of just a singlet in the $^{31}P\{^1H\}$ NMR (δ 40.6 ppm), and a conductivity well above the range for a 1/1 electrolyte in this solvent [7]. The dissociation reaction was confirmed by a separate reaction of **1** with one equivalent of $AgPF_6$ to yield $[RuCl(dppb)(CH_3CN)_3]^+ PF_6^-$ (**2**), eq. 3. This complex was prepared more conveniently by reaction of the triply chloro-bridged species $Ru_2Cl_4(dppb)_2(acetone) \cdot acetone$ (**3**), with two equivalents of $AgPF_6$ in CH_3CN solution. Complex **3** will be described fully elsewhere [2,8].

The principal resonances in the $^{31}P\{^1H\}$ NMR spectrum of **2** at ambient temperature are a singlet (δ 40.6 ppm in CD_3CN, δ 41.2 ppm in CD_2Cl_2) and a high-field septet of the PF_6^- anion. The singlet is consistent with a *fac*-arrangement of CH_3CN ligands.



(3)

(**1**) (**2**)

(P—P = dppb, S = CH_3CN)

The $^{31}P\{^1H\}$ spectrum of **2** in CD_3CN also shows an AB quartet (δ_A 42.5, δ_B 35.7 ppm; $^2J_{AB}$ 34.2 Hz), corresponding to ~ 15% of the integrated intensity of the low field resonances. The quartet is attributed to the *mer*-isomer of **2**. In CD_2Cl_2, the $^{31}P\{^1H\}$ NMR shows an additional singlet at 38.7 ppm (~ 5% integrated intensity), which is assigned to a five-coordinate species arising from dissociation of an

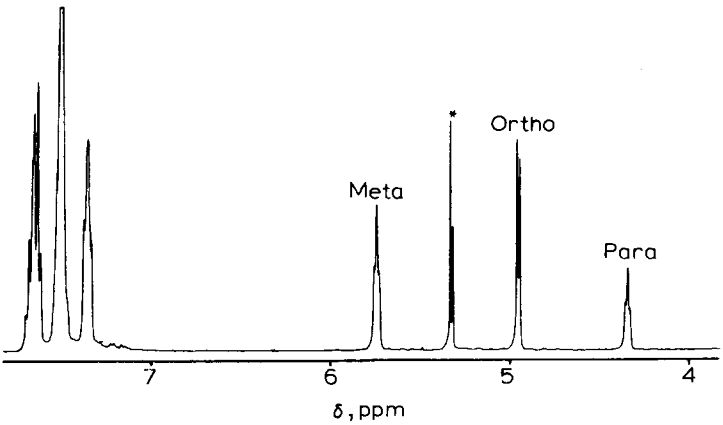


Fig. 1. Low-field region of the 400 MHz ^1H NMR spectrum of $[RuCl(dppb)(\eta^6\text{-toluene})]^+ PF_6^-$ in CD_2Cl_2; ★ represents $CHDCl_2/CH_2Cl_2$ impurities in the solvent.

acetonitrile ligand. Support for this comes from the noted disappearance of the singlet following addition of CD_3CN (~ 10% v/v) to the solution.

Attempts to generate a tris(acetone) analogue of **2**, using **3** as precursor and two equivalents of $AgPF_6$ in toluene/acetone, led instead to the isolation of $[RuCl(\eta^6\text{-toluene})(dppb)]^+ PF_6^-$ (**4**), which has been characterized crystallographically as well as spectroscopically. The presence of a π-bonded phenyl ring is evident in the ^1H NMR spectrum (Fig. 1); the resonances of the *ortho-*, *meta-*, and *para*-protons are shifted to higher field compared to free toluene, and are affected to varying degrees by the metal to give rise to well separated signals. The spectra may be interpreted on a first-order basis with assignment of the resonances at δ 5.74(t), 4.95(d) and 4.34(t) ppm to the *meta-*, *ortho-* and *para*-protons, respectively ($J_{om} = J_{pm} = 6$ Hz, $J_{op} = 0$ Hz). The shifts of these resonances relative to free toluene have been observed previously in hydridotriphenylphosphine analogues of **4** [9], and are thought [10] to arise from the following effects: withdrawal of π-electron density from the aromatic ring by the metal, quenching of ring currents by interaction with the metal, and by magnetic anisotropy of the rest of the complex. The relative intensity of the η^6-toluene is a quarter of that of the phosphine-phenyl resonances which appear at δ 7.3–7.7 ppm. The $^{31}P\{^1H\}$ NMR of **4** in CD_2Cl_2 consists of a singlet at 31.0 ppm which is invariant to temperature. This is consistent with the cation having a pseudo-tetrahedral geometry as found by X-ray analysis (vide infra).

Elemental analyses, conductivity and other spectroscopic data for complexes **1**, **2** and **4** are given in the Experimental. The IR reveals the expected ν(C≡N) and terminal ν(Ru–Cl) absorptions, and all three complexes exhibit bands due to non-coordinated PF_6^- at 840 and 570 cm^{-1}. The ^1H NMR resonances of CH_2 and CH_3 groups were broad and overlapping, and were of little value.

Reaction of $RuCl(dppb)(CH_3CN)_3]^+ PF_6^-$ *(2) with* H_2

Complexes **1** and **2** were found to be effective catalysts for the homogeneous hydrogenation of the terminal olefins hex-1-ene, styrene, and acrylamide in DMA solution at 50°C, 1 atm H_2 [2]. In attempts to detect a hydride intermediate, the reaction of **2** with H_2 was studied at catalytic conditions but in the absence of added

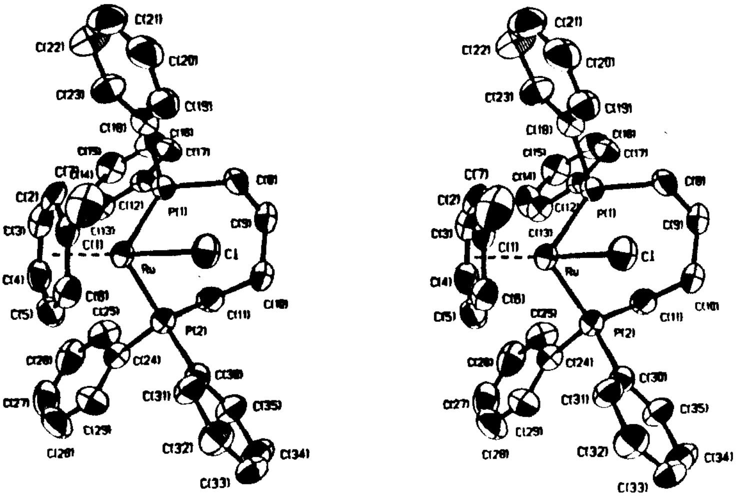


Fig. 2. Stereoview of the chloro(η^6-toluene)[1,4-bis(diphenylphosphino)butane]ruthenium(II) cation. 50% probability thermal ellipsoids are shown, hydrogen atoms being omitted for the sake of clarity.

olefin. The gas-uptake in a base-promoted reaction, using a slight excess of proton sponge, corresponded to 6.9 ± 0.1 mol of H_2 per Ru, which is consistent with hydride formation and hydrogenation of CH_3CN ligands, according to a reaction such as eq. 4:

$$RuCl(dppb)(CH_3CN)_3{}^+ + 7H_2 \xrightarrow{\text{base}} RuH(dppb)(C_2H_5NH_2)_3{}^+ + \text{base} \cdot HCl \qquad (4)$$

Attempts to isolate a pure tris(ethylamine) complex have been thwarted by anion exchange with the base · HCl generated. The IR of the crude product, however, does show absorptions in the 3300–3140 cm^{-1} region due to coordinated amine [11], and a strong absorption at 1997 cm^{-1} assignable to ν(Ru–H): attempts to find the high field NMR resonance of the hydride have failed because of low solubility. Following the above findings, we have shown in preliminary studies [2] that **2** is catalytically active for the H_2-reduction of CH_3CN and imine substrates under mild conditions (50°C, 1 atm total pressure in DMA). More detailed studies on these catalytic reductions, including the potential for asymmetric hydrogenation, are currently under investigation.

X-ray structure of [RuCl(η^6-toluene)(dppb)]$^+$ PF_6^- (4)

The crystal structure of $\{Cl(\eta^6\text{-}C_6H_5CH_3)[Ph_2P(CH_2)_4PPh_2]Ru\}(PF_6) \cdot C_3H_6O$ consists of discrete cations (Fig. 2), anion, and solvent molecules. Each cation is linked to a pair of PF_6^- anions via weak C–H...F hydrogen bonding [12] involving toluene ring H atoms (C(3)–H(3)...F(6) and C(6)–H(6)...F(3b), H...F = 2.39 and 2.38 Å, C...F = 3.233(8) and 3.22(3) Å, C–H...F = 145 and 144°). There are also three additional (toluene) H...F contacts in the range 2.50–2.54 Å. The solvent molecules are well separated from both cations and anions.

The ruthenium(II) atom in the complex cation is coordinated by an η^6-toluene ligand, in an approximately eclipsed orientation with respect to the two P atoms of the $Ph_2P(CH_2)_4PPh_2$ ligand and the chloride ligand. The coordination geometry may be described as a pseudooctahedral three-legged piano stool. The Ru–Cl distance of 2.399(2) Å and the Ru–P distances of 2.322(2) and 2.349(2) Å are normal. The Ru–C(π) distances range from 2.200(7) to 2.333(7) Å, mean 2.256 Å, the substituted ring atom being farthest from the metal. The distance from the metal to the centroid of the aromatic ring is 1.772(3) Å.

Although to our knowledge there are no other (η^6-toluene)ruthenium(II) structures in the literature, there are a number of (η^6-benzene)- and (η^6-aromatic)ruthenium(II) compounds that have been structurally characterized. The mean Ru–C(π) distances are generally around 2.20 Å, although two (η^6-benzene)ruthenium(II) complexes have mean Ru–C distances comparable to or longer than those observed here (e.g. (η^6-C_6H_6)[$CH_3CH(C_6H_5)N(H)PPh_2$]-(Cl_3Sn)Ru, 2.264 Å [13] and (η^6-C_6H_6)(Cl_3Ge)$_2$(CO)Ru, 2.29 Å [14]). Numerous (η^6-toluene) structures have been reported recently. The coordination mode ranges from symmetric, or nearly so, with a planar aromatic ring (e.g. 15, 16) to asymmetric with a non-planar ring, usually a flattened boat (e.g. 16,17). In the present structure the (η^6-toluene) ligand is slightly but significantly non-planar ($\chi^2 = 36.4$ for C_6; deviations from the mean plane = 0.008(7), 0.012(7), −0.019(7), −0.001(7), 0.026(8), −0.025(7), 0.001(8), and −1.7688(5) Å for C(1)–C(7) and Ru, respectively). Ring atoms C(6), C(1), C(2), and C(3) are coplanar to within 0.001(7) Å, with C(4) and C(5) displaced by 0.050(8) and 0.080(8) Å, from the plane away from the metal. This represents an irregular boat conformation (see Table 5). Bond lengths in the toluene ring range from 1.377(10) to 1.429(9) Å, mean 1.398 Å.

Bond lengths and angles in the remainder of the structure are generally as expected. The seven-membered chelate ring has an irregular chair conformation. The four phosphine phenyl rings are planar within experimental error.

Experimental

All synthetic reactions were carried out in Schlenk apparatus under an atmosphere of Ar using distilled and deoxygenated solvents. IR spectra were recorded on a Perkin–Elmer 598 spectrometer as Nujol mulls between CsI plates. $^{31}P\{^1H\}$ NMR spectra were measured at ambient temperatures on a Bruker WP-80 spectrometer and are referenced to 85% H_3PO_4, downfield shifts being positive. Conductivity measurements were made at 25°C under anaerobic conditions on solutions containing from $(0.15–3.0) \times 10^{-3}$ M of the complexes using a Thomas Serfass conductivity bridge and cell; the Onsager plots obtained were linear and the Λ_M values given (ohm^{-1} cm^2 mol^{-1}) are the limiting ones at infinite dilution, unless stated otherwise. The gas-uptake apparatus for determining gas stoichiometries and rates at constant pressure has been described previously [18]. Elemental analyses were performed by Mr. P. Borda of this department. The ruthenium source was $RuCl_3 \cdot 3H_2O$ on loan from Johnson, Matthey Ltd.

Preparation of [$Ru_2Cl_3(dppb)_2(CH_3CN)_2$]$^+$ PF_6^- (1)

To $Ru_2Cl_5(dppb)_2$ (1.0 g, 0.81 mmol) in CH_3CN (60 ml) was added $AgPF_6$ (0.103 g, 0.41 mmol) in CH_3CN (10 ml), and the mixture stirred for 0.5 h. The AgCl was filtered from the pink solution using Celite and the filtrate evaporated to a red oil. Addition of benzene (50 ml) and rapid stirring for 16 h caused precipitation of a solid that was filtered and washed with benzene. Recrystallisation from CH_2Cl_2/

hexane yielded a bright yellow solid (0.39 g, 70%). Anal. Found: C, 52.1; H, 4.5; N, 2.0; Cl, 7.7. $C_{60}H_{62}N_2Cl_3F_6P_5Ru_2$ calcd.: C, 51,89; H, 4.47; N, 2.02; Cl, 7.68%. IR, cm^{-1}: 2315, 2280, ν(CN). Λ_M, 59 (CH_2Cl_2), 240 (CH_3CN). The red dimer $[RuCl_3(dppb)]_2$ (cf. eqs. 1, 2) has been isolated from the benzene filtrate [1].

Preparation of $[RuCl(dppb)(CH_3CN)_3]^+\ PF_6^-$ *(2)*

To $Ru_2Cl_4(dppb)_2$(acetone)·acetone (1.0 g, 0.76 mmol) dissolved in CH_3CN (50 ml) was added $AgPF_6$ (0.385 g, 1.52 mmol) in CH_3CN (10 ml). The solution was stirred for 0.5 h, filtered through Celite, and the filtrate concentrated to 10 ml.

TABLE 1

CRYSTALLOGRAPHIC DATA [a]

Compound	$\{Cl(\eta^6\text{-}C_6H_5CH_3)[Ph_2P(CH_2)_4PPh_2]Ru\}(PF_6)\cdot C_3H_6O$
Formula	$C_{35}H_{36}ClF_6P_3Ru\cdot C_3H_6O$
Mol. wt.	858.2
Crystal system	monoclinic
Space group	$I2/a$
a	26.958(5)
b	10.816(1)
c (Å)	27.288(4)
α	90
β	108.70(1)
γ (deg)	90
V (Å^3)	7537(2)
Z	8
D_c (g/cm^3)	1.513
$F(000)$	3504
μ(Mo-K_α) cm^{-1}	6.6
Crystal dimensions (mm)	0.08×0.22×0.29
Transmission factors	0.836–0.955
Scan type	$\omega-2\theta$
Scan range (deg in ω)	$0.55+0.35\tan\theta$
Scan speed (deg/min)	0.75–6.71
Data collected	$+h, +k, \pm l$
$2\theta_{max}$ (deg)	50
Unique reflections	6607
Reflections with $I \geq 3\sigma(I)$	2803
Number of variables	461
R	0.038
R_w	0.037
S	1.332
mean Δ/σ (final cycle)	0.03
max Δ/σ (final cycle)	0.45 (U_{12} for C(36))
Residual density (e/Å^3)	0.84

[a] Temperature 22°C, Enraf–Nonius CAD4-F diffractometer, Mo-K_α radiation ($\lambda_{K_{\alpha1}}$ 0.70930, $\lambda_{K_{\alpha2}}$ (0.71359 Å), graphite monochromator, takeoff angle 2.7°, aperture $(2.0+\tan\theta)\times 4.0$ mm at a distance of 173 mm from the crystal, scan range extended by 25% on both sides for background measurement, $\sigma^2(I) = S+2B+[0.04\,(S-B)]^2$ (S = scan count, B = normalized background count), function minimized $\Sigma w|F_0|-|F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \Sigma||F_0|-|F_c||/\Sigma|F_0|$, $R_w = (\Sigma w(|F_0|-|F_c|)^2/\Sigma w|F_0|^2)^{1/2}$, $S = (\Sigma w(|F_0|-|F_c|)^2/(m-n))^{1/2}$. Values given for R, R_w, and S are based on those reflections with $I \geq 3\sigma(I)$.

TABLE 2. FINAL POSITIONAL (fractional $\times 10^4$; Ru, Cl, and P $\times 10^5$) AND ISOTROPIC THERMAL PARAMETERS ($U \times 10^3$ Å^2) (estimated standard deviations in parentheses) [a]

Atom	x	y	z	U_{eq}/U_{iso}
Ru	37347(2)	24066(6)	12106(2)	35
Cl	40940(7)	5826(17)	16950(7)	53
P(1)	32516(6)	26451(19)	17840(6)	40
P(2)	44360(7)	35465(17)	17417(7)	39
$P(3)^1$	50000	0	0	66
$P(4)^1$	25000	66019(27)	0	60
F(1)	5566(2)	430(6)	70(3)	137
$F(2)^2$	4801(4)	1387(7)	−66(6)	121
$F(3)^2$	5032(4)	54(11)	579(3)	124
F(4)	2313(2)	7642(4)	318(2)	83
F(5)	3062(2)	6578(4)	427(2)	87
F(6)	2311(2)	5550(4)	316(2)	81
C(1)	3416(3)	1129(7)	489(3)	42
C(2)	3017(3)	1900(8)	527(3)	47
C(3)	3088(3)	3190(8)	573(3)	51
C(4)	3553(4)	3717(7)	560(3)	50
C(5)	3951(3)	2948(8)	510(3)	52
C(6)	3900(3)	1681(7)	496(3)	46
C(7)	3357(3)	−253(7)	455(3)	76
C(8)	3506(3)	1997(6)	2440(3)	50
C(9)	3918(3)	2697(8)	2861(2)	65
C(10)	4437(3)	2937(7)	2756(3)	62
C(11)	4416(3)	3995(7)	2379(3)	49
C(12)	3010(2)	4173(6)	1876(2)	36
C(13)	3032(3)	5159(6)	1558(3)	42
C(14)	2809(3)	6285(7)	1590(3)	58
C(15)	2569(3)	6452(7)	1961(3)	61
C(16)	2553(3)	5508(9)	2293(3)	62
C(17)	2768(3)	4372(7)	2253(3)	47
C(18)	2647(3)	1767(7)	1520(3)	43
C(19)	2669(3)	483(8)	1483(3)	57
C(20)	2224(4)	−193(7)	1240(3)	71
C(21)	1746(4)	406(10)	1028(3)	77
C(22)	1709(3)	1664(9)	1057(3)	76
C(23)	2161(3)	2323(7)	1299(3)	59
C(24)	4526(3)	5044(6)	1468(3)	43
C(25)	4248(3)	6061(7)	1541(3)	57
C(26)	4294(3)	7187(8)	1314(3)	73
C(27)	4600(4)	7300(9)	1007(3)	78
C(28)	4885(4)	6317(10)	937(3)	77
C(29)	4846(3)	5173(8)	1163(3)	62
C(30)	5081(3)	2844(6)	1874(3)	41
C(31)	5166(3)	1880(7)	1578(3)	54
C(32)	5666(3)	1400(7)	1668(3)	61
C(33)	6078(3)	1850(9)	2065(3)	67
C(34)	5999(3)	2811(8)	2358(3)	69
C(35)	5507(3)	3316(7)	2266(3)	56
X(1)	934(6)	4682(13)	418(5)	276
X(2)	1273(5)	5340(16)	1164(5)	286
C(36)	1058(8)	5579(19)	636(8)	183
C(37)	1129(9)	6858(17)	521(9)	274
$F(2b)^3$	4650(10)	665(30)	−489(12)	108(8)
$F(3b)^3$	5018(10)	1145(28)	346(12)	92(8)

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[a] Superscripts refer to occupancy factors of 0.5, 0.75, and 0.25, respectively. Atoms labelled X were refined as oxygen.

Addition of diethyl ether (40 ml) with rapid stirring precipitated a yellow product that was filtered, washed with diethyl ether, and vacuum-dried. Recrystallisation from CH_2Cl_2/diethyl ether gave a yellow crystalline product (0.93 g, 72%). Anal. Found: C, 48.4; H, 4.5; N, 4.9; Cl, 4.0. $C_{34}H_{37}N_3ClF_6P_3Ru$ calcd.: C, 49.12; H, 4.46; N, 5.06; Cl, 4.27%. IR, cm^{-1}: 2268, ν(CN); 285 ν(RuCl). Λ_M 20 (at 2×10^{-3} *M* in CH_2Cl_2), 127 (CH_3CN). The carbon analysis is somewhat low, but the complex was hygroscopic; incorporation of one solvate water, for example, gives much better agreement.

*Preparation of [RuCl(η^6-toluene)(dppb)]$^+$ PF_6^- (**4**)*

To $Ru_2Cl_4(dppb)_2$(acetone)·acetone (1.0 g, 0.76 mmol) partially dissolved in toluene (40 ml) and acetone (30 ml) was added $AgPF_6$ (0.385 g, 1.52 mmol) in acetone (10 ml). The solution was stirred at ca. 40°C for 2 h and then filtered through Celite. The filtrate was concentrated to 10 ml and diethyl ether (40 ml)

TABLE 3

BOND LENGTHS (Å) (estimated standard deviations in parentheses) [a]

Bond	Length (Å)	Bond	Length (Å)
Ru-Cl	2.399(2)	C(8)-C(9)	1.520(10)
Ru-P(1)	2.349(2)	C(9)-C(10)	1.537(10)
Ru-P(2)	2.332(2)	C(10)-C(11)	1.528(9)
Ru-C(1)	2.333(7)	C(12)-C(13)	1.389(9)
Ru-C(2)	2.283(7)	C(12)-C(17)	1.399(8)
Ru-C(3)	2.200(8)	C(13)-C(14)	1.374(9)
Ru-C(4)	2.200(7)	C(14)-C(15)	1.376(10)
Ru-C(5)	2.247(8)	C(15)-C(16)	1.375(10)
Ru-C(6)	2.274(7)	C(16)-C(17)	1.378(10)
Ru-Ar	1.772(3)	C(18)-C(19)	1.396(10)
P(1)-C(8)	1.837(7)	C(18)-C(23)	1.392(9)
P(1)-C(12)	1.824(7)	C(19)-C(20)	1.379(10)
P(1)-C(18)	1.823(7)	C(20)-C(21)	1.391(11)
P(2)-C(11)	1.823(7)	C(21)-C(22)	1.369(11)
P(2)-C(24)	1.831(7)	C(22)-C(23)	1.383(10)
P(2)-C(30)	1.825(7)	C(24)-C(25)	1.381(9)
P(3)-F(1)	1.547(5)	C(24)-C(29)	1.385(9)
P(3)-F(2)	1.584(7)	C(25)-C(26)	1.390(10)
P(3)-F(3)	1.555(6)	C(26)-C(27)	1.357(12)
P(3)-F(2b)	1.54(3)	C(27)-C(28)	1.360(11)
P(3)-F(3b)	1.55(3)	C(28)-C(29)	1.402(11)
P(4)-F(4)	1.598(4)	C(30)-C(31)	1.381(9)
P(4)-F(5)	1.587(4)	C(30)-C(35)	1.391(9)
P(4)-F(6)	1.605(5)	C(31)-C(32)	1.391(10)
C(1)-C(2)	1.390(9)	C(32)-C(33)	1.368(10)
C(1)-C(6)	1.429(9)	C(33)-C(34)	1.370(11)
C(1)-C(7)	1.503(9)	C(34)-C(35)	1.381(10)
C(2)-C(3)	1.409(9)	X(1)-C(36)	1.131(14)
C(3)-C(4)	1.386(10)	X(2)-C(36)	1.40(2)
C(4)-C(5)	1.398(10)	C(36)-C(37)	1.44(2)
C(5)-C(6)	1.377(10)		

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[a] Here and elsewhere Ar refers to the centroid of the coordinated aromatic ring.

TABLE 4

BOND ANGLES (deg) (estimated standard deviations in parentheses) [a]

Bonds	Angle(deg)	Bonds	Angle(deg)
Cl–Ru–P(1)	86.30(7)	C(12)–C(13)–C(14)	122.2(7)
Cl–Ru–P(2)	89.35(7)	C(13)–C(14)–C(15)	118.8(7)
Cl–Ru–Ar	122.72(12)	C(14)–C(15)–C(16)	120.5(7)
P(1)–Ru–P(2)	92.30(6)	C(15)–C(16)–C(17)	120.5(7)
P(1)–Ru–Ar	126.86(13)	C(12)–C(17)–C(16)	120.1(7)
P(2)–Ru–Ar	127.21(13)	P(1)–C(18)–C(19)	119.6(6)
Ru–P(1)–C(8)	119.5(2)	P(1)–C(18)–C(23)	123.1(6)
Ru–P(1)–C(12)	119.4(2)	C(19)–C(18)–C(23)	117.0(7)
Ru–P(1)–C(18)	107.3(2)	C(18)–C(19)–C(20)	120.9(8)
C(8)–P(1)–C(12)	104.5(3)	C(19)–C(20)–C(21)	119.9(8)
C(8)–P(1)–C(18)	101.1(3)	C(20)–C(21)–C(22)	121.0(8)
C(12)–P(1)–C(18)	102.3(3)	C(21)–C(22)–C(23)	118.0(8)
Ru–P(2)–C(11)	117.8(2)	C(18)–C(23)–C(22)	123.3(7)
Ru–P(2)–C(24)	113.6(2)	P(2)–C(24)–C(25)	119.8(6)
Ru–P(2)–C(30)	115.7(2)	P(2)–C(24)–C(29)	121.5(6)
C(11)–P(2)–C(24)	101.6(3)	C(25)–C(24)–C(29)	118.5(7)
C(11)–P(2)–C(30)	103.9(3)	C(24)–C(25)–C(26)	120.3(8)
C(24)–P(2)–C(30)	101.9(3)	C(25)–C(26)–C(27)	120.8(9)
C(2)–C(1)–C(6)	118.2(7)	C(26)–C(27)–C(28)	119.9(9)
C(2)–C(1)–C(7)	122.1(8)	C(27)–C(28)–C(29)	120.2(8)
C(6)–C(1)–C(7)	119.6(8)	C(24)–C(29)–C(28)	120.1(8)
C(1)–C(2)–C(3)	120.9(8)	P(2)–C(30)–C(31)	121.6(5)
C(2)–C(3)–C(4)	120.3(8)	P(2)–C(30)–C(35)	119.8(5)
C(3)–C(4)–C(5)	119.0(7)	C(31)–C(30)–C(35)	118.5(6)
C(4)–C(5)–C(6)	121.5(8)	C(30)–C(31)–C(32)	120.7(7)
C(1)–C(6)–C(5)	119.9(8)	C(31)–C(32)–C(33)	120.2(7)
P(1)–C(8)–C(9)	120.1(5)	C(32)–C(33)–C(34)	119.5(7)
C(8)–C(9)–C(10)	115.4(6)	C(33)–C(34)–C(35)	120.9(7)
C(9)–C(10)–C(11)	114.4(6)	C(30)–C(35)–C(34)	120.1(7)
P(2)–C(11)–C(10)	115.9(5)	X(1)–C(36)–X(2)	110(2)
P(1)–C(12)–C(13)	121.3(5)	X(1)–C(36)–C(37)	138(2)
P(1)–C(12)–C(17)	120.8(5)	X(2)–C(36)–C(37)	111(2)
C(13)–C(12)–C(17)	117.8(6)		
F(1)–P(3)–F(2)	90.8(4)	F(4)–P(4)–F(5)	90.3(2)
F(1)–P(3)–F(3)	97.5(4)	F(4)–P(4)–F(6)	89.9(2)
F(1)–P(3)–F(1)′	180	F(4)–P(4)–F(4)″	90.5(4)
F(1)–P(3)–F(2)′	89.2(4)	F(4)–P(4)–F(5)″	91.0(3)
F(1)–P(3)–F(3)′	82.5(4)	F(4)–P(4)–F(6)″	179.5(3)
F(2)–P(3)–F(3)	89.2(4)	F(5)–P(4)–F(6)	89.2(3)
F(2)–P(3)–F(2)′	180	F(5)–P(4)–F(5)″	178.2(4)
F(2)–P(3)–F(3)′	90.8(4)	F(5)–P(4)–F(6)″	89.5(2)
F(3)–P(3)–F(3)′	180	F(6)–P(4)–F(6)″	89.7(4)
F(1)–P(3)–F(2b)	105.8(9)	F(2b)–P(3)–F(3b)	92.6(13)
F(1)–P(3)–F(3b)	81.2(9)	F(2b)–P(3)–F(2b)′	180
F(1)–P(3)–F(2b)′	74.2(9)	F(2b)–P(3)–F(3b)′	87.4(13)
F(1)–P(3)–F(3b)′	98.8(9)	F(3b)–P(3)–F(3b)′	180

[a] Primed and double-primed atoms have coordinates related to those in Table 2 by the symmetry operations: $1-x, y, z$ and $\frac{1}{2}-x, y, -z$, respectively.

added to precipitate a solid which was washed with benzene and diethyl ether. Slow recrystallisation from CH_2Cl_2/acetone (1/1 by volume) by precipitation with diethyl ether affords yellow crystals; acetone solvate could be removed by pumping (0.47 g, 40%). Anal. Found: C, 52.5; H, 4.7; Cl 4.7. $C_{35}H_{36}ClF_6P_3Ru$ calcd.: C, 52.53; H, 4.50; Cl, 4.55%. IR, cm^{-1}: 302 ν(RuCl). Λ_M 29 (at 2×10^{-3} M in CH_2Cl_2). The crystals obtained in this way as an acetone solvate were satisfactory for X-ray analysis.

X-ray crystallographic analysis of chloro(η^6-toluene)[1,4-bis-(diphenylphosphino)butane]ruthenium(II) hexafluorophosphate · acetone solvate

Crystallographic data appear in Table 1. Final unit-cell parameters were obtained by least-squares on 2 sin θ/λ values for 25 reflections (2θ = 25–32°) measured with Mo-K_{α_1} radiation. The intensities of three standard reflections, measured each hour during the data collection, showed only small random fluctuations in intensity. After data reduction [19], an absorption correction was applied using the Gaussian integration method [20,21].

The structure was solved by conventional heavy-atom methods; the coordinates of the Ru, Cl, and phosphine P atoms were determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent difference maps. The structure was found to contain two independent half-anions, one lying on a twofold-axis and the other situated at a centre of symmetry. The latter was found to be twofold disordered, the minor component (F(2b), F(3b)) being rotated by ~ 45° about the P(1)–F(1) bond and also tilted out of the F(2)F(3)P(1) plane by ~ 15°. As a result, the two F(1) positions were too close to resolve and this atom was refined with full occupancy. The occupancy factors of the split atoms F(2) and F(3) were estimated to be 0.75 and 0.25 from relative peak heights and were kept fixed in subsequent cycles of refinement. The appropriateness of the occupancy factors may be judged from the resulting U_{eq}/U_{iso} values in Table 2. The asymmetric unit also contains one molecule of solvent (probably acetone). This solvent molecule (atom X(1), X(2), C(36), C(37)) was originally refined with X(1) as an oxygen atom and the

TABEL 5

INTRA-ANNULAR TORSION ANGLES (deg) (standard deviations in parentheses)

Atoms	Value(deg)
P(2)–Ru–P(1)–C(8)	−62.7(3)
Ru–P(1)–C(8)–C(9)	81.3(6)
P(1)–C(8)–C(9)–C(10)	−60.6(8)
C(8)–C(9)–C(10)–C(11)	77.7(9)
C(9)–C(10)–C(11)–P(2)	−108.5(7)
Ru–P(2)–C(11)–C(10)	65.2(5)
P(1)–Ru–P(2)–C(11)	7.4(3)
C(6)–C(1)–C(2)–C(3)	−0.1(11)
C(1)–C(2)–C(3)–C(4)	2.5(13)
C(2)–C(3)–C(4)–C(5)	−1.0(12)
C(3)–C(4)–C(5)–C(6)	−3.0(13)
C(4)–C(5)–C(6)–C(1)	5.4(13)
C(2)–C(1)–C(6)–C(5)	−3.7(11)

remaining three positions as carbon atoms, all with full occupancy. This resulted in a low temperature factor for X(2), implying greater electron density at this point. This position was subsequently refined as oxygen. It is most likely that the solvent is acetone, apparently disordered over at least two sites which have the X(2) position in common. The minor components in this case have low occupancy (probably $< 10\%$) and were not resolved.

In the final stages of refinement all non-hydrogen atoms except the low-occupancy fluorine atoms were refined with anisotropic thermal parameters. Hydrogen atoms associated with the cation were included as fixed contributors in idealized positions (methyl proton positions based on observed positions, $C(sp^2)$–H 0.97 Å, $C(sp^3)$–H 0.98 Å), recalculated after each cycle of refinement. Neutral atom scattering factors and anomalous scattering corrections for Ru, Cl, and P atoms were taken from ref. 22. The final positional and equivalent isotropic thermal parameters ($U_{eq} = 1/3$ trace $U_{diagonalized}$) for the non-hydrogen atoms appear in Table 2. Bond lengths, bond angles, and intra-annular torsion angles are given in Tables 3–5, respectively. Tables of calculated hydrogen parameters, anisotropic thermal parameters, torsion angles, and structure factors are available from the authors.

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