Isolation and Crystal Structure of $[Rh(PPh_3)_3(MeCN)][BF_4]$, Acetonitriletris(triphenylphosphine)rhodium(I) Tetrafluoroborate†

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The salt $[Rh(PPh_3)_3(MeCN)][BF_4]$ has been isolated as one product of the reaction between $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ and PPh_3 (1 : 4), and its structure determined by single-crystal *X*-ray diffraction. The cation possesses an essentially square-planar co-ordination geometry, with the length of the Rh–P bond *trans* to the acetonitrile ligand [2.261(3) Å] significantly shorter than those of the mutually *trans* PPh_3 groups [2.311(3) and 2.367(3) Å]. Proton, ^{13}C, ^{19}F, and ^{31}P n.m.r. spectra have been recorded for this compound and, with reference to these properties and the crystallographic data, the relationship of $[Rh(PPh_3)_3(MeCN)][BF_4]$ to the hydrogenation catalyst precursor $[Rh(PPh_3)_3Cl]$ and to a material previously reported as $Rh(PPh_3)_3BF_4$ is discussed.

Rhodium–phosphorus chemistry has been widely investigated,[1] especially because $[Rh(PPh_3)_3Cl]$,[2] popularly known as 'Wilkinson's catalyst,' provided the first efficient route for the homogeneous hydrogenation of alkenes, alkynes, and other unsaturated organic molecules under ambient conditions.[3–5] As part of a study of the reactions of complexes containing a Rh_2^{4+} centre with phosphines, we report here that the reaction of $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$[6] with triphenylphosphine gives, as one product, $[Rh(PPh_3)_3(MeCN)][BF_4]$. This compound is of interest because of its similarity to Wilkinson's catalyst, and also because $Rh(PPh_3)_3BF_4$ was reported previously,[7] but not fully characterised.

Experimental

Preparation of Acetonitriletris(triphenylphosphine)rhodium(I) Tetrafluoroborate, $[Rh(PPh_3)_3(MeCN)][BF_4]$.—All solvents were dried and distilled under a dinitrogen atmosphere. Manipulations were carried out using standard Schlenk techniques.

Triphenylphosphine (1.04 g, 3.96 mmol) was added to a stirred solution of $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$[6] (0.49 g, 0.66 mmol) in methanol (40 cm^3). After *ca.* 2 h the orange solution was filtered to remove the precipitated $[Rh_2(O_2CMe)_2(PPh_3)_2(MeCN)_4][BF_4]_2$. Diethyl ether (30 cm^3) was added to the filtrate to ensure the complete precipitation of this orange product, which was removed by filtration. The resulting yellow filtrate was reduced in volume until a pale yellow powder precipitated. Diethyl ether was added to achieve further precipitation and the powder was collected by filtration and dried *in vacuo*. This powder was recrystallised from a warm methanol solution by cooling to *ca.* 20 °C. Small block-like crystals, suitable for *X*-ray crystallographic study, were obtained on controlled addition of diethyl ether to a concentrated solution of the material in methanol. Yield 0.39 g (*ca.* 30%).

Subsequently, a more rational synthesis of this compound was developed. The compound $[Rh(PPh_3)_3Cl]$[2] (0.4 g, 0.43 mmol) and $[Me_3O][BF_4]$ (0.19 g, 1.29 mmol) were stirred in MeCN (20 cm^3). The reaction mixture was stirred under N_2 for *ca.* 24 h when an orange solution had formed above a pale yellow precipitate. The solution was filtered, concentrated to 10 cm^3, and cooled to *ca.* 5 °C. An orange-yellow precipitate formed on standing. This was collected by filtration and recrystallised from methanol, when pale yellow crystals formed. Yield *ca.* 0.22 g (50%) (Found: C, 64.6; H, 4.6; N, 1.3; P, 8.9; Rh, 10.3. $C_{56}H_{48}BF_4NP_3Rh$ requires C, 66.1; H, 4.8; N, 1.4; P, 9.1; Rh, 10.1%).

Crystallography.—Crystal data. $C_{56}H_{48}BF_4NP_3Rh$, M = 1 017.6, orthorhombic, $a = 25.354(3)$, $b = 21.439(1)$, $c = 18.842(2)$ Å, U = 10 242 Å^3 (from 2θ values of 36 reflections centred at $\pm\omega$), T = 291 K, Mo-K_α radiation, λ = 0.710 69 Å, space group *Pbca*, $Z = 8$, D_c = 1.320 g cm^{-3} (all atoms in general positions); yellow block crystal, 0.2 × 0.4 × 0.45 mm, μ = 4.7 cm^{-1}.

Data collection and processing. Stoe-Siemens AED diffractometer, ω—θ scan mode with on-line profile fitting,[8] $2\theta_{max.}$ = 50°, all indices $\geqslant 0$, no absorption or extinction corrections, intensity decay of *ca.* 10% corrected from three standard reflections, 8 994 non-extinguished reflections, 4 552 with $I > 3\sigma(I)$.

Structure analysis and refinement. Patterson and difference syntheses, blocked-cascade refinement on *F*, $w^{-1} = \sigma^2(F) + 0.0026F^2$ optimised automatically, rigid idealised hexagons for Ph groups with C–C 1.395 Å, C–H 0.96 Å on C–C–C external bisectors, anisotropic thermal parameters for Rh, P, C, and N, $U_{iso}(H) = 1.2U_{eq}(C)$, rigid tetrahedral $[BF_4]^-$ with B–F 1.30 Å and common U_{iso} [refined to 0.309(5) Å^2], no H atoms for MeCN, R = 0.078, $R' = \Sigma w^{\frac{1}{2}}|\Delta|/\Sigma w^{\frac{1}{2}}|F_o|$ = 0.084 (observed reflections only), slope of normal probability plot = 1.32, scattering factors from ref. 9. Programs: SHELXTL,[10] diffractometer control program by W. C.

Atomic co-ordinates are given in Table 1, selected geometrical parameters in Table 2.

Instrumentation.—N.m.r. spectra were recorded for $[Rh(PPh_3)_3(MeCN)][BF_4]$ dissolved in CD_2Cl_2; the proton spectrum was obtained on a Varian SC300 spectrometer, and 20.1-MHz ^{13}C, 75.3-MHz ^{19}F, and 32.4-MHz ^{31}P spectra on a Brüker WP80 spectrometer. The ^{31}P data were recorded for solutions at *ca.* 200 and 303 K, the ^1H, ^{13}C, and ^{19}F n.m.r. spectra for solutions maintained at *ca.* 260, 230, and 290 K, respectively.

I.r. spectra were measured on a Perkin-Elmer 577 spectro-

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† *Supplementary data available* (No. SUP 56238, 6 pp.): H-atom co-ordinates, thermal parameters, other bond angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates (× 10^4) for $[Rh(PPh_3)_3(MeCN)][BF_4]$

Atom	*x*	*y*	*z*
Rh	1 336(1)	6 200(1)	7 265(1)
P(1)	1 720(1)	7 176(1)	7 209(2)
C(112)	933(3)	8 111(3)	7 305(3)
C(113)	630	8 554	7 663
C(114)	721	8 672	8 381
C(115)	1 116	8 347	8 741
C(116)	1 419	7 905	8 383
C(111)	1 328	7 787	7 665
C(122)	2 245(2)	7 858(3)	6 111(4)
C(123)	2 256	8 147	5 448
C(124)	1 826	8 094	4 991
C(125)	1 384	7 751	5 197
C(126)	1 373	7 461	5 860
C(121)	1 803	7 514	6 317
C(132)	2 623(3)	7 788(3)	7 775(4)
C(133)	3 089	7 798	8 166
C(134)	3 274	7 253	8 486
C(135)	2 992	6 698	8 413
C(136)	2 525	6 688	8 021
C(131)	2 341	7 233	7 702
P(2)	1 900(1)	5 755(1)	6 487(2)
C(212)	2 305(3)	6 386(4)	5 288(4)
C(213)	2 681	6 738	4 925
C(214)	3 150	6 907	5 262
C(215)	3 243	6 724	5 961
C(216)	2 867	6 372	6 324
C(211)	2 398	6 203	5 988
C(222)	2 330(3)	5 063(3)	7 598(4)
C(223)	2 689	4 655	7 913
C(224)	3 063	4 349	7 497
C(225)	3 079	4 451	6 766
C(226)	2 720	4 859	6 451
C(221)	2 346	5 165	6 867
C(232)	1 663(3)	4 868(3)	5 394(5)
C(233)	1 347	4 644	4 844
C(234)	885	4 960	4 660
C(235)	741	5 499	5 026
C(236)	1 057	5 722	5 576
C(231)	1 518	5 407	5 760
P(3)	886(1)	5 257(1)	7 512(2)
C(312)	1 309(4)	5 380(3)	8 871(5)
C(313)	1 442	5 184	9 554
C(314)	1 311	4 584	9 778
C(315)	1 048	4 179	9 319
C(316)	915	4 375	8 636
C(311)	1 045	4 976	8 412
C(322)	1 332(2)	4 116(3)	7 073(4)
C(323)	1 366	3 582	6 653
C(324)	990	3 473	6 127
C(325)	580	3 897	6 022
C(326)	547	4 431	6 442
C(321)	923	4 541	6 968
C(332)	−155(3)	5 155(4)	8 048(4)
C(333)	−694	5 290	8 053
C(334)	−907	5 680	7 535
C(335)	−583	5 936	7 012
C(336)	−45	5 801	7 007
C(331)	169	5 411	7 525
N(4)	783(4)	6 575(4)	7 904(5)
C(41)	433(6)	6 808(6)	8 169(9)
C(42)	−50(6)	7 089(8)	8 519(14)
B	−281(5)	7 235(6)	5 572(7)
F(1)	134	6 996	5 271
F(2)	−473	7 672	5 169
F(3)	−634	6 803	5 663
F(4)	−151	7 470	6 183

Table 2. Unconstrained bond lengths (Å) and selected bond angles (°) for $[Rh(PPh_3)_3(MeCN)][BF_4]$

Rh–P(1)	2.311(3)	Rh–P(2)	2.261(3)
Rh–P(3)	2.367(3)	Rh–N(4)	2.015(10)
P(1)–C(111)	1.855(7)	P(1)–C(121)	1.843(8)
P(1)–C(131)	1.830(8)	P(2)–C(211)	1.845(7)
P(2)–C(221)	1.840(8)	P(2)–C(231)	1.836(9)
P(3)–C(311)	1.845(9)	P(3)–C(321)	1.848(7)
P(3)–C(331)	1.848(8)	N(4)–C(41)	1.134(17)
C(41)–C(42)	1.516(23)		
P(1)–Rh–P(2)	94.9(1)	P(1)–Rh–P(3)	170.3(1)
P(2)–Rh–P(3)	94.1(1)	P(1)–Rh–N(4)	87.7(3)
P(2)–Rh–N(4)	175.2(3)	P(3)–Rh–N(4)	83.6(3)
Rh–N(4)–C(41)	169.5(11)	N(4)–C(41)–C(42)	177.2(14)

meter for the compound mulled in Nujol and held between NaCl discs. Conductivity measurements were performed for MeCN solutions at *ca.* 298 K, using a Phillips PW9504/00 conductivity bridge and platinum electrodes.

Results and Discussion

The compound $[Rh(PPh_3)_3(MeCN)][BF_4]$ crystallises as discrete $[Rh(PPh_3)_3(MeCN)]^+$ cations and $[BF_4]^-$ anions. The anion is probably disordered, as is commonly observed for such small, highly symmetrical counter ions: neither individual atomic co-ordinates nor anisotropic thermal parameters could be successfully refined. This disorder and the high thermal motion of some of the cation phenyl-ring carbon atoms are responsible for the high proportion of unobserved reflections.

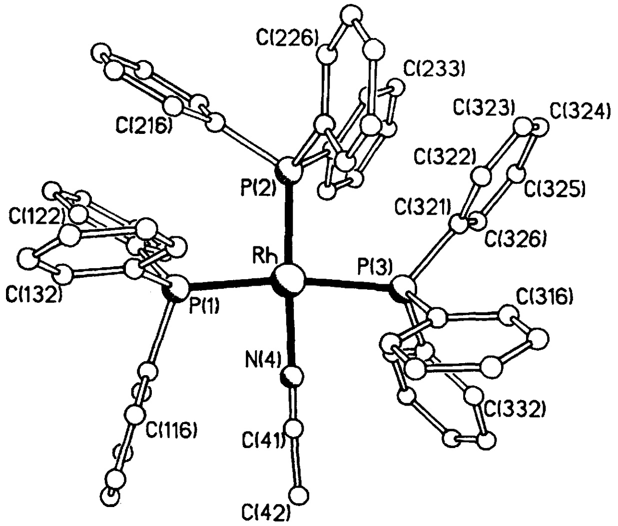

Figure 1. Structure of the cation of $[Rh(PPh_3)_3(MeCN)][BF_4]$ projected on the RhP_3N mean plane. All phenyl rings follow the same numbering scheme

In the cation (Figure 1) the rhodium(I) atom has an essentially square-planar P_3N co-ordination. In-plane deviations from ideal square-planar co-ordination consist of P–Rh–P angles greater than, and P–Rh–N angles less than, 90° as a result of the disparate steric bulk of the PPh_3 and MeCN ligands. An out-of-plane distortion towards tetrahedral co-ordination is very slight: deviations of the atoms from the mean RhP_3N plane are: Rh −0.002(2); P(1), 0.079(3); P(2),

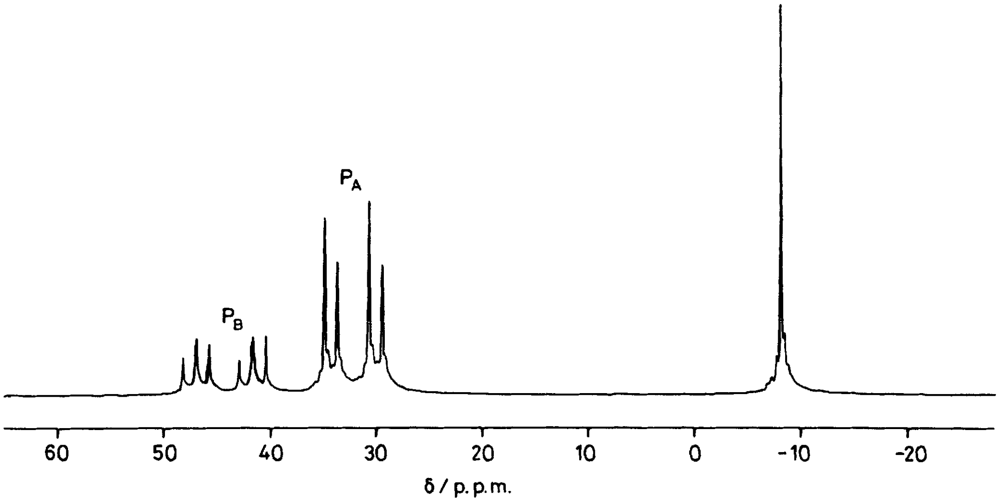

Figure 2. ^{31}P N.m.r. spectrum of $[Rh(PPh_3)_3(MeCN)][BF_4]$ plus PPh_3 in CD_2Cl_2 at 200 K

Table 3. Comparison of selected dimensions (distances in Å, angles in °) for the co-ordination of Rh in $[Rh(PPh_3)_3(MeCN)][BF_4]$ and the red and orange forms of $[Rh(PPh_3)_3Cl]$[11]

		$[Rh(PPh_3)_3Cl]$	
Dimension	$[Rh(PPh_3)_3(MeCN)][BF_4]$	Orange	Red
Rh–X[a]	2.015(10)	2.404(4)	2.376(4)
Rh–P *cis* to X	2.367(3)	2.338(4)	2.332(4)
	2.311(3)	2.304(4)	2.334(3)
Rh–P *trans* to X	2.261(3)	2.225(4)	2.214(4)
P–Rh–P *cis*	94.9(1)	97.7(1)	97.9(2)
	94.1(1)	96.4(2)	100.4(1)
P–Rh–P *trans*	170.3(1)	159.1(2)	152.8(1)
X–Rh–P *cis*	83.6(3)	84.5(1)	86.1(2)
	87.7(3)	85.3(1)	85.2(2)
X–Rh–P *trans*	175.2(3)	166.7(2)	156.2(2)
r.m.s. Δ[b]	0.071	0.272	0.426

[a] X = MeCN or Cl. [b] Root mean square deviation (unweighted) of the RhP_3N atoms from their mean plane.

−0.067(3); P(3), 0.080(3); and N(4), −0.090(10) Å. All three Rh–P bond lengths are significantly different: the shortest lies *trans* to the acetonitrile ligand, which forms an essentially linear Rh–N–C–C arrangement.

Wilkinson's catalyst, $[Rh(PPh_3)_3Cl]$, may be obtained in a red or an orange form, depending on the method of synthesis,[2,4] and the crystal structures of both have been determined.[11] The two forms differ in their packing arrangements, in the orientations of the phenyl rings, in the degree of distortion of the square-planar co-ordination towards tetrahedral, and in the closest Rh ··· H intramolecular contacts. Important features of the co-ordination in both forms and in $[Rh(PPh_3)_3(MeCN)]^+$ are compared in Table 3. The $[Rh(PPh_3)_3(MeCN)]^+$ cation shows much less out-of-plane distortion than either form of $[Rh(PPh_3)_3Cl]$, and a more orderly 'paddle-wheel' arrangement of the PPh_3 ligands: thus the three bonds P(1)–C(111), P(2)–C(211), and P(3)–C(321) lie approximately in the RhP_3N mean plane [subtending angles of 6.5(2), 4.9(2), and 13.0(2)° respectively with it], and the phenyl rings mesh together around the co-ordination plane (Figure 1). The difference in the P(1)–Rh–N(4) and P(3)–Rh–N(4) angles can also be ascribed to this arrangement of the ligand substituents.

The phenyl-ring arrangement brings several hydrogen atoms into close proximity with the Rh atom. Each PPh_3 ligand has one *ortho*-H atom within 2.85 Å of Rh: H(136), 2.80; H(236), 2.83; and H(312), 2.81 Å (for the purpose of these calculations, the C–H bonds were extended to 1.08 Å). All other Rh ··· H distances are >2.9 Å. This contrasts with the two forms of $[Rh(PPh_3)_3Cl]$, for each of which *one* particularly short *ortho*-H ··· Rh distance was observed.[11,12] Since an idealised geometry for phenyl rings was assumed in all three structure determinations, the significance of the hydrogen-atom positions is, however, questionable.

However, the overall co-ordination geometry at the rhodium in all three complexes is similar, despite the above, secondary, differences in detail.

The i.r. spectrum of $[Rh(PPh_3)_3(MeCN)][BF_4]$ mulled in Nujol clearly showed absorptions characteristic of $[BF_4]^-$ (1 160, 1 095, 1 055, and 1 000 cm^{-1}) and PPh_3 (1 435, 765, 745, and 700 cm^{-1}) moieties.

Conductivity measurements, as a function of concentration of a solution in dried, degassed MeCN, indicated that $[Rh(PPh_3)_3(MeCN)][BF_4]$ behaves as a 1:1 electrolyte in MeCN solution.

The u.v.–visible spectrum of $[Rh(PPh_3)_3(MeCN)][BF_4]$ in MeCN solution consists of features with $\lambda_{max.}$ (ε/l mol^{-1} cm^{-1}) of: 400 (1 433), 350 (3 604), 300 (9 000), 260 (16 000), and 226 nm (19 500). This profile is very similar to that observed for a solution of $[Rh(PPh_3)_3Cl]$ in MeCN.

The ^{1}H, ^{13}C, ^{19}F, and ^{31}P n.m.r. spectra recorded for $[Rh(PPh_3)_3(MeCN)][BF_4]$ in CD_2Cl_2 solution were consistent with the solid-state structure of the cation and anion being retained in solution. The ^{1}H n.m.r. spectrum consists of resonances due to MeCN (2.11 p.p.m.) and the two inequivalent PPh_3 groups (7.5 and 7.3 p.p.m., relative intensity 2:1 with shoulders to higher frequency on each resonance). The ^{13}C n.m.r. spectrum manifests signals at (128.3, 129.9), (130.1, 131.7), (132.2, 134.0), and (134.3, 134.5) p.p.m., which are assigned to the four inequivalent carbons on each phenyl ring, the doubling (as indicated) resulting from the two inequivalent PPh_3 groups. Resonances at 127.8 and 0.4 p.p.m. are assigned to the *C*N and *C*H_3, respectively, of MeCN, the former showing a significant shift from that (119 p.p.m.) of the free ligand in the sense observed[6] for $[M_2(O_2CMe)_2(MeCN)_6][BF_4]_2$ (M = Mo or Rh). The ^{19}F n.m.r. spectrum comprises a single resonance, 38 Hz in width, at −74 p.p.m. (referenced to CF_3CO_2H), consistent with the presence of $[BF_4]^-$.

The ^{31}P n.m.r. spectrum of $[Rh(PPh_3)_3(MeCN)][BF_4]$ in

CD_2Cl_2 at 200 K (Figure 2) consists of a doublet of doublets centred at 32.1 p.p.m. and a doublet of triplets (with the central peak of each triplet split by second-order effects[13]) centred at 44.3 p.p.m. This pattern is typical of an A_2BX system;[14,15] here, A are the mutually *trans* P atoms, B is the P atom *trans* to MeCN, and X = Rh, with $\delta(P_A) = 32.1$ p.p.m. and $\delta(P_B) = 44.3$ p.p.m. The coupling constants are: $J(Rh-P_A) = 136$, $J(Rh-P_B) = 170$, and $J(P_A-P_B) = 39$ Hz. Also, as shown in Figure 2, at 200 K in CD_2Cl_2, $[Rh(PPh_3)_3(MeCN)]^+$ does not undergo exchange with PPh_3 on the n.m.r. time-scale. However, at 303 K in CD_3CN the ^{31}P n.m.r. spectrum shows some indication for this exchange.

The reaction of $[Rh(PPh_3)_3(MeCN)][BF_4]$ with $P(OMe)_3$ has been investigated by ^{31}P n.m.r. spectroscopy. Upon addition of $P(OMe)_3$ to a solution of $[Rh(PPh_3)_3(MeCN)][BF_4]$ in CD_3CN at 303 K, the intensity of the doublet of triplets centred at 44.3 p.p.m. decreased and with a 1:1 molar ratio of the reagents the peaks were completely removed. Concomitantly, two peaks centred at 135 p.p.m. appeared and, at the 1:1 ratio, took on the appearance of a doublet of triplets. Therefore, we conclude that $P(OMe)_3$ selectively replaces the PPh_3 group *trans* to MeCN in $[Rh(PPh_3)_3(MeCN)]^+$.

The initial synthesis of $[Rh(PPh_3)_3(MeCN)][BF_4]$ involves cleavage of the Rh–Rh single bond of $[Rh_2(O_2CMe)_2(MeCN)_6][BF_4]_2$, upon reaction with PPh_3. This resembles the synthesis of a material of composition $Rh(PPh_3)_3BF_4$, which was isolated as a product of the protonation of $[Rh_2(O_2CMe)_4]$ by HBF_4, followed by reaction with PPh_3.[7] The conductance of solutions of this material in $MeNO_2$ solution was significantly less than expected for a 1:1 electrolyte and, therefore, co-ordination of the tetrafluoroborate anion to the metal was postulated. This contrasts with $[Rh(PPh_3)_3(MeCN)][BF_4]$ which behaves as a 1:1 electrolyte. An important difference in the two syntheses is that the route reported herein commenced with MeCN co-ordinated to the rhodium and this clearly clings tenaciously throughout the subsequent reaction and recrystallisation from MeOH.

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