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[Tris(1-pyrazolyl)hydroborato]ruthenium chemistry: preparation and reactions of {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(X)} (X = H, Cl). The X-ray crystal structure of {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(PMe$_3$)}PF$_6$

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Abstract

Treatment of RuH(Cl)(CO)(PPh$_3$)$_3$ with sodium tris(1-pyrazolyl)hydroborate(III) in refluxing toluene gave {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(H)} (**1**) in high yield. The corresponding chloride {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(Cl)} (**2**) was obtained by treating **1** with chloroform in dichloromethane. Reactions of **2** with CO, CN^{t}Bu, P(OMe)$_3$, or PMe$_3$ in methanol in the presence of ammonium hexafluorophosphate gave cations of the general formula {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(L)}PF$_6$ (**3–6**) respectively. The X-ray crystal structure of {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(PMe$_3$)}PF$_6$ (**6**) has been determined.

Introduction

The tris(1-pyrazolyl)hydroborato anion is isoelectronic with the cyclopentadienyl anion and both are potentially tridentate ligands. These properties have led to the preparation of a large number of tris(1-pyrazolyl)hydroborato analogues selected from an even larger stable of cyclopentadienyl compounds [1]. Ruthenium complexes are limited to the mixed sandwich {Ru(η^5-C$_5$H$_5$)(η^3-HB[1-pyrazolyl]$_3$)} [2], the complexes {Ru(η^3-HB[1-pyrazolyl]$_3$)(CO)$_2$X} [3], and the vinyl complexes {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(CR=CHR)} [4].

Two major differences exist between the tris(1-pyrazolyl)hydroborate and cyclopentadienyl ligands; the tridentate (η^3) tris(1-pyrazolyl)hydroborato ligand is non-fluxional and this provides additional spectroscopic handles in its complexes, and its cone angle is 184° whilst that of the cyclopentadienyl ligand is 100° [5]. Both of these properties suggest that in six coordinate compounds the possibility of

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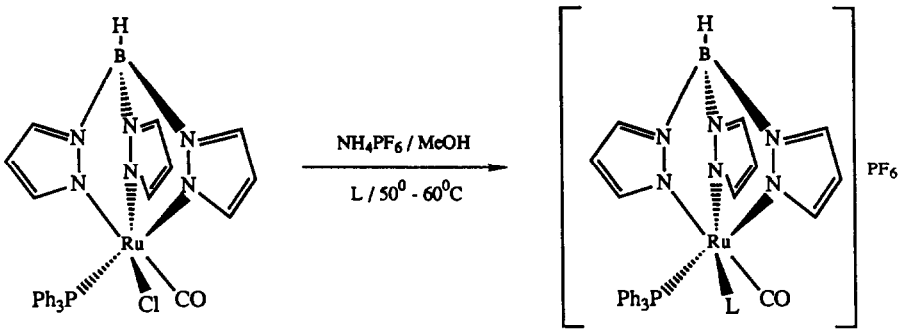
trans effects may be observable for metal tris(1-pyrazolyl)hydroborate compounds which are normally averaged out in the corresponding cyclopentadienyl compounds. Jones has reported that the eight coordinate lanthanide compounds {Ln(η^3-HB[1-pyrazolyl]$_3$)$_2$(acac)} are fluxional on the ^{1}H NMR timescale but this appears to be an isolated example [6].

We have a longstanding interest in compounds of the type {RuL$_3$(L')(L")(X)} recognising that they are potentially chiral at the metal and are susceptible to electrophilic attack [7,8]. In order to determine the stereochemical course of such an attack we sought to make use of the desirable properties of the {η^3-tris(1-pyrazolyl)hydroborato} ligand to prepare suitable compounds for a future determination. Our initial results with this ligand are reported below.

Results and discussion

Our first synthesis efforts were directed towards the reaction of RuCl$_2$(PPh$_3$)$_3$ or RuCl$_2$(PPh$_3$)$_4$ with sodium tris(1-pyrazolyl)hydroborate(III) in refluxing toluene. We were unable to cleanly isolate a well defined product after variation of the reaction time over the range 5–72 h. Hill had demonstrated that RuH(Cl)(CO)(PPh$_3$)$_3$ was a good synthon for the preparation of the vinyl complexes {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(CR=CHR)} [4] and we turned our attention to this ruthenium starting material. Treatment of RuH(Cl)(CO)(PPh$_3$)$_3$ with a small excess of sodium tris(1-pyrazolyl)hydroborate(III) in toluene under reflux for 18 h produced colourless crystals on work-up which were identified as {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(H)} (**1**). In particular the infrared spectrum of **1** contained bands at 2480, 1985, and 1922 cm^{-1} assignable to the B–H, Ru–H, and C≡O stretching modes, respectively. The ^{1}H NMR spectrum of **1** in C$_6$D$_6$ contained a doublet a δ −11.14 [J(PH) = 27 Hz] due to the metal hydride ligand. The hydride **1** could be converted to {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(Cl)} (**2**) by refluxing in a dichloromethane/chloroform solution. All nine pyrazolyl protons were inequivalent and resolved in the ^{1}H NMR spectrum of **2** in CDCl$_3$ while the resolution was incomplete in the case of **1** in C$_6$D$_6$; use of CD$_3$NO$_2$ gave good dispersion for **1**.

The cyclopentadienyl complexes [Ru(η^5-C$_5$H$_5$)(L)(L')(Cl)] are easily converted into cationic derivatives by means of a halide acceptor such as the ammonium ion in the presence of a donor ligand [9]; this reactivity was also present in **2**. Accordingly, reaction of **2** with CO, CN^{t}Bu, P(OMe)$_3$, and PMe$_3$ in methanol containing NH$_4$PF$_6$ gave the crystalline salts **3**–**6**. The rate of reaction of **2** closely mirrored that found for the cyclopentadienyl analogue [7]. The major infrared bands of compounds **1**–**6** are shown together with their cyclopentadienyl analogues in Table 1. There are very small differences in carbonyl stretching frequencies associated with replacing the cyclopentadienyl group with the {η^3-tris(1-pyrazolyl)hydroborato} group except in the case of the trimethylphosphine cations. Curtis [10] has shown that the {η^3-tris(1-pyrazolyl)hydroborato} group is a better π-donor than the cyclopentadienyl group and that both are poor π-acceptors, further the {η^3-tris(1-pyrazolyl)hydroborato} ligand uses its σ-donor orbitals to form strong π-bonds to a metal centre. The limited data of Table 1 show that the electron donating abilities of the two ligands is very similar since the differences in ν(C≡O) are minimal.



(2)

(3) L = CO
(4) L = CN^tBu
(5) L = $P[OMe]_3$
(6) L = PMe_3

Table 2 summarises the ^1H NMR chemical shifts for compounds **1–6**; in those compounds containing three different monodentate ligands, we expect nine signals for the pyrazolyl protons while for **3**, six signals in two groups (2:1) of three are expected. Homonuclear decoupling experiments permitted the grouping of the protons on each particular ring but did not permit each ring to be unambiguously assigned. We have followed the suggestion of Trofimenko [1] and Stone [3] in distinguishing the chemical shifts of the H_a and H_b ring protons. It is possible that further data allowing consideration of anisotropic effects might permit full unambiguous labelling of each ring.

Solid state structure of 6

The structure of **6** in the solid state contains a cation–anion pair and two partially occupied solvent sites. The structure of the cation in **6** is shown in Fig. 1 and demonstrates the octahedral geometry of the metal centre. Selected bond lengths and angles are given in Table 4. The three ruthenium–nitrogen bond lengths are identical within experimental error illustrating that despite the variation of σ-donor/π-acceptor abilities of the trimethylphosphine, triphenylphos-

Table 1

Comparison of the carbonyl stretching frequencies of {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(X)} and {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(L)}PF_6, and their cyclopentadienyl analogues

	(η^5-C_5H_5)	(η^3-HB[1-pyrazolyl]$_3$)
H	1973 [a], 1931	1985 [a], 1922
Cl	1958	1965
CO^+	2075, 2030	2095, 2033
CN^tBu^+	2186 [b], 2014	2189 [b], 2021
$P(OMe)_3^+$	–	2004
PMe_3^+	1995	1975

[a] ν(Ru–H). [b] ν(C≡N).

Table 2

300.13 MHz ^{1}H NMR spectroscopic data for compounds **1–6**

Compound	Pyrazolyl δ (ppm) [c]	Phenyl δ (ppm)	Other δ (ppm)
1 [a]	7.83, 6.90, 6.05, 7.80, 7.74, 6.22, 7.70, 6.65, 5.79	7.47–7 20	−11.90d J(PH) = 26 Hz Ru–*H*
2 [b]	7.96, 7.53, 6.17, 7.64, 6.88, 5.87, 7.59, 6.29, 5.73	7.40–7.20	
3 [b]	7.88, 6.71, 6.07 [d], 7.79, 7.75, 6.33	7.56, 7.45, 7.05	
4 [b]	7.79, 6.52, 5.99, 7.77, 6.83, 6.04, 7.69, 7.64, 6.31	7.51, 7.39, 7 03	1.42s CN^t*Bu*
5 [b]	7.90, 7.49, 6.20, 7 77, 6.55, 5.94, 7.75, 7 71, 6.31	7.44, 7.33, 7.12	3.30d J(PH) = 11 Hz P(O*Me*)$_3$
6 [a]	8.00, 6.87, 6.14, 7.95, 7.89, 6.39, 7.89, 6.39, 6.00	7.60–7.45	1.30d J(PH) = 9.7 Hz P*Me*$_3$

[a] CD_3NO_2 solvent. [b] $CDCl_3$ solvent. [c] Chemical shifts in the order H_a, H_c, H_b for each ring. H_a and H_b signals were approximate doublets J(HH) ≈ 2 Hz, H_c signals were approximate triplets J(HH) = 2 Hz. [d] The first group of signals is of double intensity relative to the second group.

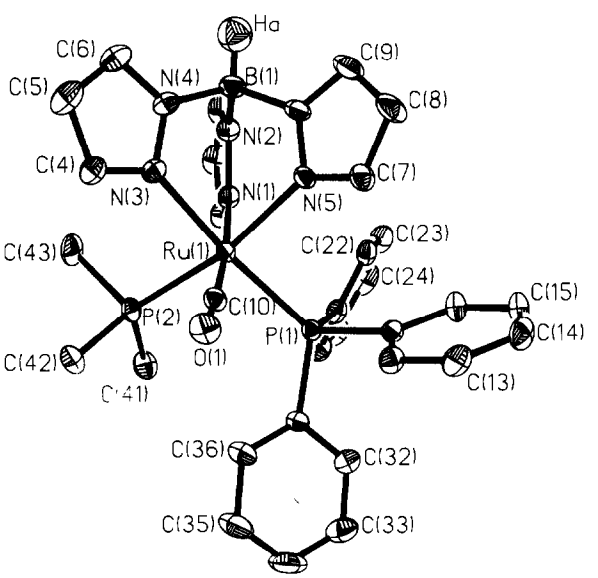


Fig. 1. Molecular structure of the cation in {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh$_3$)(CO)(PMe$_3$)}PF$_6$ shown with 30% probability thermal ellipsoids.

phine, and carbonyl ligands there is no evidence of a *trans* labilising effect. This is in contrast to the clear evidence found for such an effect in the compounds {Mo(η^3-HB[1-pyrazolyl]$_3$)(COMe)(CO)(P[OMe]$_3$)} and {Mo(η^3-HB[1-pyrazolyl]$_3$)(COMe)(CO)(PEt_3)} which possess octahedral coordination with a weak metal to acyl oxygen interaction [13]. In particular the molybdenum–nitrogen bond *trans* to the carbonyl group was longer than the other metal–nitrogen bonds. The bond to the bulky triphenylphosphine ligand Ru(1)–P(1) (2.364(1) Å) is lengthened in comparison with an analogous cationic cyclopentadienylruthenium complex, for example [(η^5-C_5H_5)Ru(PPh_3)(CO)(CN^{t}Bu)]PF_6 where the equivalent bond length is 2.328(1) Å [14]. It is conceivable that this is a steric consequence of the much larger ligand cone angle of the tridentate (η^3) tris(1-pyrazolyl)hydroborato ligand. Unfortunately, few other suitable crystal structures have been reported which allow observation of *trans* effects in η^3-pyrazolylborate complexes and we believe that the degeneracy observed in **6** is either serendipitous or the three ligands chosen are not sufficiently dissimilar in electronic nature. Further work with more extreme ligand sets is clearly required.

Experimental

All reactions and preparations were carried out under nitrogen by standard Schlenk-tube techniques. Diethyl ether, toluene, and light petroleum ether (b.p. 40–60°C) were dried over sodium wire and distilled. Dichloromethane was dried over phosphorus pentoxide and distilled. Chloroform was dried over magnesium sulphate in the dark immediately prior to use. Analar grade methanol was used as supplied. Infrared spectra were recorded on a Perkin–Elmer 1710 FTIR instrument. Nuclear magnetic resonance spectra were recorded on Jeol EX90 (89.56 MHz, ^{1}H; 36.25 MHz, ^{31}P) and Bruker AC300 (300.13 MHz, ^{1}H; 121.49 MHz, ^{31}P; 75.47 MHz, ^{13}C) spectrometers. Elemental analyses were by Butterworth Laboratories, London. Fast atom bombardment (FAB) mass spectra were obtained on a Kratos Concept S1 spectrometer. Ru(H)Cl(CO)(PPh_3)$_3$ [11] and Na[HB(1-pyrazolyl)$_3$] [12] were prepared by literature procedures.

{Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh_3)(CO)(H)} (1)

A mixture of Ru(H)Cl(CO)(PPh_3)$_3$ (1.79 g, 1.88 mmol) and Na[HB(1-pyrazolyl)$_3$] (0.80 g, 3.39 mmol) in toluene (60 cm^3) was heated under reflux for 16 h. The cooled solution was treated with petroleum ether (30 cm^3) and filtered. Removal of solvent from the colourless filtrate under reduced pressure gave a colourless solid which was dissolved in diethylether (15 cm^3). Addition of petroleum ether (15 cm^3) and cooling (−30°C) overnight gave colourless crystalline **1**, yield 1.0 g (92%). Anal. Found: C, 56.93; H, 4.84; N, 12.70. $C_{28}H_{26}BN_6OPRu$ calcd.: C, 55.55; H, 4.33; N, 13.88%. IR (Nujol): ν_{max} 2480m (BH), 1985m (RuH), 1922vs (CO) cm^{-1}. ^{31}P{^{1}H} NMR [C_6D_6]: δ 65.6 ppm. MS [FAB]: m/z 605 $[M]^+$.

{Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh_3)(CO)(Cl)} (2)

{Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh_3)(CO)(H)} (**1**) (1.0 g, 1.65 mmol) in chloroform (25 cm^3) was heated under reflux for 5 h. Removal of the solvent under reduced pressure and crystallisation of the pale yellow residue from dichloromethane/petroleum ether (1:1, 20 cm^3 total) at −78°C gave pale yellow blocks of **2**, yield

0.8 g (90%). Anal. Found: C, 52.17; H, 3.93; N, 12.43. $C_{28}H_{25}BClN_6OPRu$ calcd.: C, 52.56; H, 3.94; N, 13.13%. IR (Nujol): ν_{max} 2487m (BH), 1965vs (CO) cm^{-1}. $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 203.5 (d, $J(PC) = 16$ Hz, CO), 145.9, 143.6, 143.3 (s, C_a), 136.2, 135.1, 134.6 (s, C_c), 134.2 (d, $J(PC) = 10$ Hz, C_{ortho}), 132.1 (d, $J(PC) = 44$ Hz, C_{ipso}), 128.1 (d, $J(PC) = 9$ Hz, C_{meta}), 130.0 (s, C_{para}), 106.0, 105.9, 105.6 (s, C_b) ppm. $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 40.5 ppm. MS [FAB]: m/z 640 $[M]^+$.

{Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh_3)($CO)_2$}PF_6 (3)

A solution of {Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh_3)(CO)(Cl)} (**2**) (0.2 g, 0.21 mmol) and NH_4PF_6 (0.25 g, 1.5 mmol) in methanol (30 cm^3) was pressurised under carbon monoxide (200 psig) in a Fischer–Porter bottle. The reactants were stirred at 80°C for 36 h. The solvent was removed under reduced pressure and the residue extracted into dichloromethane (25 cm^3). Concentration (*ca.* 5 cm^3) and addition of diethylether (*ca.* 15 cm^3) followed by cooling (−30°C) gave colourless microcrystalline **3**, yield 0.18 g (76%). Anal. Found: C, 43.80; H, 3.37; N, 9.88. $C_{29}H_{25}BF_6N_6O_2P_2Ru$ calcd.: C, 44.81; H, 3.24; N, 10.81%. IR (Nujol): ν_{max} 2539m (BH), 2095, 2033vs (CO) cm^{-1}. $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 193.5 (d, $J(PC) = 13$ Hz, CO), 144.8 * 144.7 (s, C_a), 138.0 * 137.1 (s, C_c), 133.2 (d, $J(PC) = 10$ Hz, C_{ortho}), 132.5 (s, C_{para}), 129.7 (d, $J(PC) = 9$ Hz, C_{meta}), 127.5 (d, $J(PC) = 51$ Hz, C_{ipso}), 107.7 107.6 * (s, C_b), ppm. $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 34.5 ppm. MS [FAB]: m/z 633 $[M - PF_6]^+$.

{Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh_3)(CO)(L)}PF_6 (4–6)

These salts were prepared by a common method: a solution of **2** (0.3–0.6 g, 0.47–0.94 mmol) in methanol (*ca.* 40 cm^3) containing NH_4PF_6 (0.35 g, 2 mmol) and the ligand (L) (*ca.* 5–10 mmol) was stirred at 60°C for 16 h. The solvent was removed under reduced pressure and the residue extracted into dichloromethane (25 cm^3). Concentration (*ca.* 5 cm^3) and addition of diethylether (*ca.* 10 cm^3) followed by cooling (−30°C) gave microcrystalline products.

{Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh_3)(CO)(CN^tBu)}PF_6 (4). Yield 45%. Anal. Found: C, 46.71; H, 4.34; N, 10.50. $C_{33}H_{34}BF_6N_7OP_2Ru$ calc.: C, 47.61; H, 4.12; N, 11.78%. IR (Nujol): ν_{max} 2492m (BH), 2189s (CN), 2021vs (CO) cm^{-1}. $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 198.2 (d, $J(PC) = 13$ Hz, CO), 144.7 144.3 143.5 (s, C_a), 137.2 136.9 136.4 (s, C_c), 133.4 (d, $J(PC) = 10$ Hz, C_{ortho}), 131.7 (s, C_{para}), 129.2 (d, $J(PC) = 10$ Hz, C_{meta}), 107.3 107.2 106.9 (s, C_b), 60.1 (s, CMe_3), 30.2 (s, CMe_3) ppm. $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 39.5 ppm. MS [FAB]: m/z 688 $[M - PF_6]^+$.

{Ru(η^3-HB[1-pyrazolyl]$_3$)(PPh_3)(CO)(P{OMe}$_3$)}PF_6 (5). Crystallised with 1 mol of CH_2Cl_2 per mole, yield 62%. Anal. Found: C, 39.90; H, 3.92; N, 7.80. $C_{31}H_{34}BF_6N_6O_4P_3Ru$. CH_2Cl_2 calcd.: C, 40.04; H, 3.75; N, 8.76%. IR (Nujol): ν_{max} 2494m (BH), 2004vs (CO), 1051vs (PO) cm^{-1}. $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 199.3 (dd, $J(PC) = 13$, 22 Hz, CO), 146.0 145.2 144.3 (s, C_a), 137.5 136.9 136.6 (s, C_c), 133.9 (d, $J(PC) = 9$ Hz, C_{ortho}), 131.1 (s, C_{para}), 128.5 (d, $J(PC) = 10$ Hz, C_{meta}), 107.1 106.9 106.8 (s, C_b), 54.1 (d, $J(PC) = 9$ Hz, P{O*Me*}$_3$) ppm. $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 124.7 (d, $J(PP) = 50$ Hz, P{OMe}$_3$), 34.8 (d, $J(PP) = 50$ Hz, PPh_3) ppm. MS [FAB]: m/z 729 $[M - PF_6]^+$.

* Denotes resonances for the two equivalent pyrazole rings.

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **6**.

	x	y	z	U_{eq} [a]
Ru(1)	2645(1)	1018(1)	157(1)	24(1)
B(1)	2451(5)	−497(5)	1353(4)	42(2)
N(1)	1986(3)	1212(3)	964(2)	34(1)
N(2)	1957(3)	453(4)	1395(2)	39(2)
C(1)	1455(4)	1899(5)	1107(3)	41(2)
C(2)	1072(4)	1559(6)	1625(3)	52(2)
C(3)	1398(4)	661(6)	1786(3)	52(2)
N(3)	2093(3)	−411(3)	50(2)	34(1)
N(4)	2057(3)	−922(3)	617(3)	40(2)
C(4)	1778(4)	−991(4)	−502(3)	42(2)
C(5)	1560(5)	−1887(5)	−275(4)	60(3)
C(6)	1737(4)	−1813(5)	433(4)	51(2)
N(5)	3656(3)	307(3)	948(2)	34(1)
N(6)	3419(3)	−259(4)	1421(3)	42(2)
C(7)	4524(4)	193(5)	1075(3)	42(2)
C(8)	4840(4)	−455(6)	1616(4)	57(2)
C(9)	4113(5)	−708(6)	1828(4)	60(3)
P(1)	3385(1)	2525(1)	361(1)	27(1)
C(12)	4978(4)	2085(4)	124(3)	39(2)
C(13)	5883(4)	1950(5)	300(4)	49(2)
C(14)	6385(4)	2167(5)	957(4)	52(2)
C(15)	6007(4)	2520(5)	1444(3)	47(2)
C(16)	5108(3)	2648(4)	1291(3)	40(2)
C(11)	4581(3)	2425(4)	627(3)	31(1)
C(22)	3316(4)	2822(5)	1724(3)	39(2)
C(23)	3073(5)	3315(5)	2253(4)	53(2)
C(24)	2603(5)	4151(6)	2120(4)	62(3)
C(25)	2351(5)	4526(5)	1456(4)	54(3)
C(26)	2607(4)	4062(4)	920(3)	41(2)
C(21)	3106(3)	3208(4)	1052(3)	35(2)
C(32)	3723(4)	4315(5)	−168(4)	47(2)
C(33)	3755(5)	4981(6)	−695(4)	62(3)
C(34)	3397(7)	4746(7)	−1377(5)	78(4)
C(35)	2994(7)	3864(6)	−1559(4)	68(3)
C(36)	2985(5)	3174(5)	−1041(3)	46(2)
C(31)	3323(3)	3408(4)	−339(3)	34(2)
P(2)	1352(1)	1567(1)	−635(1)	32(1)
C(41)	1034(4)	2828(5)	−645(3)	46(2)
C(42)	1218(4)	1323(5)	−1554(3)	44(2)
C(43)	406(4)	944(6)	−499(4)	51(2)
C(10)	3142(3)	745(4)	−566(3)	31(1)
O(1)	3419(3)	546(4)	−1019(2)	49(2)
P(3)	1219(1)	6899(1)	2352(1)	47(1)
F(1)	208(4)	6707(5)	2310(4)	117(3)
F(2)	1499(6)	5870(4)	2682(4)	121(4)
F(3)	1022(4)	6430(5)	1584(3)	93(2)
F(4)	923(3)	7932(4)	1989(3)	85(2)
F(5)	1350(7)	7322(6)	3105(3)	157(4)
F(6)	2178(3)	7087(6)	2321(4)	135(3)
C(51)	3939(6)	6182(14)	1730(5)	232(18)
Cl(1)	3363(3)	6504(3)	855(2)	114(2)
Cl(2)	5009(3)	6693(5)	2024(3)	157(3)
C(52)	338(3)	9287(10)	3578(3)	267(25)
Cl(3)	28(4)	9104(4)	4370(4)	162(4)
Cl(4)	1452(3)	9641(3)	3706(3)	138(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table 4

Selected bond lengths (Å) and bond angles (°)

Ru(1)–N(1)	2.157(5)	Ru(1)–N(3)	2.139(4)
Ru(1)–N(5)	2.157(4)	Ru(1)–C(10)	1.856(6)
Ru(1)–P(1)	2.364(1)	Ru(1)–P(2)	2.355(1)
C(10)–O(1)	1.137(8)		
N(1)–Ru(1)–N(3)	85.3(2)	N(1)–Ru(1)–N(5)	86.1(2)
N(3)–Ru(1)–N(5)	82.1(2)	N(1)–Ru(1)–P(1)	94.8(1)
N(3)–Ru(1)–P(1)	173.9(1)	N(5)–Ru(1)–P(1)	91.8(1)
N(1)–Ru(1)–P(2)	86.8(1)	N(3)–Ru(1)–P(2)	88.0(1)
N(5)–Ru(1)–P(2)	168.3(1)	P(1)–Ru(1)–P(2)	98.0(1)
N(1)–Ru(1)–C(10)	174.4(2)	N(3)–Ru(1)–C(10)	89.3(2)
N(5)–Ru(1)–C(10)	94.7(2)	P(1)–Ru(1)–C(10)	90.7(2)
P(2)–Ru(1)–C(10)	91.5(1)	Ru(1)–C(10)–O(1)	176.9(5)

$(Ru(\eta^3\text{-}HB[1\text{-}pyrazolyl]_3)(PPh_3)(CO)(PMe_3)\}PF_6$ (6). Crystallised with 1.5 mol of CH_2Cl_2 per mole, yield 52%. Anal. Found: C, 41.71; H, 3.98; N, 8.46. $C_{31}H_{34}BF_6N_6OP_3Ru \cdot 3/2\ CH_2Cl_2$ calcd.: C, 40.97; H, 3.91; N, 8.82%). IR (Nujol): ν_{max} 2495m (BH), 1975vs (CO) cm^{-1}. $^{13}C\{^1H\}$ NMR [CD_3NO_2]: δ 203.4 (t, J(PC) = 15 Hz, CO), 146.2 145.7 145.6 (s, C_a), 139.2 138.5 138.4 (s, C_c), 135.1 (d, J(PC) = 9 Hz, C_{ortho}), 132.6 (s, C_{para}), 130.4 (d, J(PC) = 10 Hz, C_{meta}), 108.4 108.2 107.5 (s, C_b), 17.3 (d, J(PC) = 34 Hz, PMe_3) ppm. $^{31}P\{^1H\}$ NMR [CD_3NO_2]: δ 42.2 (d, J(PP) = 29.5 Hz, PPh_3), 1.1 (d, J(PP) = 29.5 Hz, PMe_3) ppm. MS [FAB]: m/z 681 $[M - PF_6]^+$.

X-Ray structure of 6

Well-shaped colourless blocks were obtained by crystallisation from a dichloromethane/diethyl ether mixture. A suitable crystal specimen was mounted on a glass fibre with epoxy resin. Precession photographs and intensity data were collected on a Nicolet R3m/V diffractometer using graphite monochromatized Mo-K_α X-rays.

Crystal data. $C_{31}H_{34}BN_6OF_6P_3Ru \cdot 1.5\ CH_2Cl_2$, $M = 952.8$, monoclinic, space group $P2_1/c$, $a = 15.929(4)$, $b = 13.746(3)$, $c = 19.872(5)$ Å, $\beta = 105.65(2)°$, $U = 4190(2)$ Å^3, $D_c = 1.51$ g cm^{-3} for $Z = 4$. $F(000) = 1924$, μ(Mo-K_α) = 7.32 cm^{-1}, $T = -42°C$, crystal size $0.35 \times 0.30 \times 0.25$ mm^3. Cell dimensions were obtained from 41 centred reflections with 2θ values from 18.3° to 35.4°. Intensity data in the range $3° < 2\theta < 60°$ were collected using a 2θ–θ scan technique. The intensities of three reflections measured periodically showed a decrease of less than 1% over the data collection. An empirical absorption correction was applied using an azimuthal scan technique. A total of 13,170 reflections were collected of which 12,276 were independent, and 7302 for which $I > 4\sigma(I)$ were used in the refinement. The structure was solved by standard heavy atom routines and refined by full matrix least squares methods. All non-hydrogen atoms were given anisotropic temperature factors. Hydrogen atoms were placed in the model at calculated positions and allowed to ride on their respective carbon atoms. The two solvent molecules were disordered and could not be fully modelled, their site occupancies were refined and found to be equal. Chemical and spectroscopic analysis confirmed 1.5 molecules of dichloromethane per molecule of complex and the site occupancies were each

fixed at 0.75. Each dichloromethane molecule was confined geometrically with C–Cl bond distances of 1.790 Å and an angle of 114.4° at carbon.

The highest peaks in the final difference map were < 2.12 e Å^3 and associated with the disordered solvent molecules. At convergence $R = 6.30\%$ and $wR = 9.51\%$, $w = [\sigma^2(F) + 0.008F^2]^{-1}$, $S = 1.00$ for a data/parameter ratio 14.7 : 1.

Calculations were performed using SHELXTL-PLUS on a Micro VAX II. The final positional parameters are given in Table 3. Structure factors, a complete list of bond lengths and angles, and hydrogen atom coordinates are available from the author.

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