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Rhodium(I) complexes of the type $[Tp^{3R,5R}Rh(LL)]$ (LL = 2 CO, NBD, COD) with trifluoromethyl substituted tris(pyrazolyl)borate ligands and their dynamic behaviour in solution. The X-ray crystal structure of $Tp^{CF_3,Me}Rh(CO)_2$

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Abstract

Three series of Rh(1) complexes of the type $Tp^{3R,5R}$ Rh(LL), with LL=2 CO (1), norbornadiene (NBD) (2) and 1,5-cyclooctadiene (COD) (3) and the tris(pyrazolyl)borate (Tp) ligands 3R = 5R = Me (a), $3R = CF_3$, 5R = Me (b); and $3R = 5R = CF_3$ (c) were synthesized and fully characterized by IR and multinuclear NMR spectroscopy. Three isomeric forms were identified in solutions of these complexes: two square-planar isomers with a κ^2 -Tp^{3R,5R} ligand, the uncoordinated pyrazolyl ring occupying either an equatorial position (type A), or an axial position (type B), and a five-coordinate species with a κ^3 -Tp^{3R,5R} ligand (type C). In the carbonyl complexes 1 the dynamic equilibria between these isomers are solvent dependent. Interestingly, solutions of complex 1c contained all three isomers simultaneously. ¹⁰³Rh and ¹³C NMR spectral studies indicate that the NBD compounds, 2, preferentially form square-planar complexes when Tp^{CF3,Me} and Tp^{CF3,CF3} are present, while for the COD complexes, 3, square-planar complexes are preferred for all three Tp-type ligands. The X-ray structure of Tp^{CF3,Me}Rh(CO)₂ (1b) was determined (space group C2/c, a = 21.271(9), b = 11.004(3), c = 21.563(9) Å, $\beta = 114.93(3)^\circ$, V = 4577(3) Å³, Z = 8, R = 3.41, $R_w = 4.70$). Its structure is of type B, with the third pyrazolyl ring axially placed, the N(4) being almost directly above the Rh atom but exerting only a weak Rh–N interaction.

Keywords: Rhodium complexes; Crystal structures; Tris(pyrazolyl)borate complexes; Carbonyl complexes; Norbornadiene complexes; Cyclooctadiene complexes

1. Introduction

Poly(pyrazolyl)borates of the type $[H_{4-n}B(pz)_n]^-$ (pz = pyrazole, n = 2-4) have been widely used for the synthesis of transition-metal complexes $[1,2]^{-1}$. The tris(pyrazolyl)borates, the class most often employed, are potentially tridentate ligands and, normally, coordinate facially in a tripodal fashion, although complexes with d⁸metal centres often contain an η^2 -bonded Tp-type ligand and

* This paper is dedicated to Professor F. Basolo.

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display fluxional behaviour which can vary depending on the nature of the Tp and the co-ligands [3].

Some Rh(I) and Ir(I) complexes with substituted tris(pyrazolyl)borates, $Tp^{3R,4R,5R}$, have received considerable attention because of their ability to activate C-H bonds [4,5].

Variation of poly(pyrazolyl)borate denticity can easily occur in Rh(I) and Ir(I) complexes which may exist either as 16e⁻ or 18e⁻ species. Thus, the compounds pzTpRh(LL) (pzTp = (tetrakis(pyrazolyl)borate) were shown [6] to exist in the solid state as 16e⁻ complexes with κ^2 -pzTp when LL was norbornadiene (NBD) and 1,5-cyclooctadiene (COD), and as an 18e⁻ species with κ^3 -pzTp when LL was duroquinone. However, all these complexes were assigned five-coordination in solution [7]. Furthermore, recent studies

¹ The nomenclature for tris(pyrazolyl)borate ligands and their complexes, as proposed by Trofimenko in Ref. [1], is used throughout this publication.



Fig. 1. Proposed structures for isomer forms A, B and C of complexes of the type TpRh(LL).

showed that complexes of the type $Tp^{3R,4R,5R}Rh(LL)$ (LL=2CO, NBD, COD) [8,9] and $Tp^{3R,4R,5R}Ir(COD)$ [10,11], in solution, give rise to the equilibria shown in Fig. 1.

The 16e⁻ square-planar κ^2 -Tp^{3R,4R,5R} complexes, which can be of type **A** or **B**, appear to be favoured (i) when large substituents are present in the 3-positions of the pyrazolyl rings and (ii) in complexes with sterically demanding LL coligands. The 18e⁻- κ^3 -Tp^{3R,4R,5R} forms (type **C**) are favoured by small substituents on the pyrazolyl rings, and less bulky co-ligands, e.g. NBD as opposed to COD [9].

It has also been established that, in the square-planar complexes, unless very bulky substituents in the 3-positions are present: (i) the uncoordinated ligands appear to prefer the pseudoaxial, as in form **B**, to pseudo-equatorial positions, as in form **A**; (ii) substituents in the 5-positions of the pyrazolyl rings enhance this preference [9].

A recent study evidenced $\kappa^2 - \kappa^3$ isomerism in Rh(I) complexes with analogous tris(pyrazolyl)borate ligands having (i) a B-CH₃ instead of the normal B-H moiety and (ii) a non-coordinating substituent with comparable steric requirements instead of the potentially free, third pyrazolyl ring, i.e. [MePhB(3-Me-pz)₂]⁻ [12]. However, the influence of electronic effects of the co-ligand and of the substituents of the pyrazolyl rings on the equilibrium shown in Fig. 1 was not investigated. Thus, it seemed of interest to study the influence of electron-withdrawing substituents such as trifluoromethyl groups on the coordination chemistry of Tp-type ligands.

It has recently been proposed [9] that 103 Rh, 15 N and 13 C NMR chemical shift data can be employed to obtain estimates of the position of the equilibria between the fast exchanging isomers of types **B** and **C**.

¹⁰³Rh NMR spectroscopy was used to assign the denticity of the Tp^{3R,4R,5R} ligands [9]: it was shown that while symmetry considerations in the ¹H and ¹³C spectra allowed the identification of complexes of type **A**, when the intermolecular rearrangement between isomers **A** and **B** was sufficiently slow, the ¹⁰³Rh NMR parameters allowed the differentiation between forms **B** and **C**. As shown by the data for the bis(pyrazolyl)borate complexes [12], the δ (¹⁰³Rh) values of four-coordinate NBD complexes are around 1360 ppm, while those of the four-coordinate COD complexes are near 1130 ppm. Furthermore, one of the isomers of compound Tp^{Me}Rh(COD) which, on the basis of ¹H and ¹³C NMR spectroscopy, was unambiguously assigned a square-planar structure of type **A**, gave a δ ⁽¹⁰³Rh) of 1107 ppm, while the corresponding species of type **B** absorbed at 1106 ppm.

¹⁵N NMR spectroscopy proved to be useful for isomer identification. Thus, in free pyrazolylborates, the $\delta(^{15}N)$ shifts of the N² donor have values which are ~50–70 ppm higher than those of N¹ [9]. Furthermore, large changes in the ¹⁵N chemical shifts of N(2), from -75 to ~ -138 ppm, occur upon coordination of a pyrazolyl ring of a pyrazolylborate to rhodium. Therefore, in the κ^2 -bonded form of the complex the value for this parameter, in the case of fast exchange between two coordinated and one free ligand arm, should be close to -117 ppm [12]. Thus, more negative values of the observed chemical shifts can be taken to indicate increasing proportions of the κ^3 - relative to the κ^2 -bonded form of the complex.

¹³C NMR spectroscopy has also been used for structural assignments in complexes of this type with the olefinic coligands NBD and COD. It has been shown that the ¹³C chemical shift of the olefinic carbons is sensitive to the coordination number of the metal, the lower values being indicative of five-coordination [9]. While the averaged solid-state δ value of Tp^{Me}Rh(NBD), whose X-ray structure shows it to be distorted trigonal-bipyramidal, is 32 ppm [9], the typical values for four-coordinate forms, in CDCl₃ solution, range from 51 to 57 ppm.

This paper describes the preparation of three series of complexes of the type Tp^{3R,5R}Rh(LL), with LL = 2CO (1), NBD (2) and COD (3) and Tp ligands where 3R, 5R = Me, Me (a), 3R, 5R = CF₃, Me (b) and 3R, 5R = CF₃, CF₃ (c). Their characterization by IR and multinuclear NMR spectroscopy and, for Tp^{CF₃,Me}Rh(CO)₂, by X-ray diffraction are also reported. Finally, aspects related to $\kappa^2 - \kappa^3$ isomerisms, their solvent dependence, and the dynamic processes occurring in solution, as evidenced by IR and one- and two-dimensional NMR spectroscopy, are described.

2. Experimental

2.1. Materials

Commercial solvents, of 'puriss. p.a. absolute' grade, were used as purchased. The organometallic starting materials $Rh_2Cl_2(CO)_4$ [13], $Rh_2Cl_2(NBD)_2$ [14], $Rh_2Cl_2(COD)_2$ [15] and Rh₂Cl₂(COE)₄ [16] were prepared as described in the appropriate references; the former two were also purchased from Aldrich. The ligands Na[Tp^{Me2}] [9], $Na[Tp^{CF_3,Me}]$ [9] and $M[Tp^{CF_3,CF_3}]$ (M=Na, Tl) [17] were available from other studies. TlCl₃, K[BH₄] and [PPh₄]Cl were obtained from Aldrich, while Na₂[PtCl₆] · 6H₂O was kindly provided by B. Lippert. [PPh₄]₂[PtCl₆] was precipitated from an aqueous solution of Na₂[PtCl₆] · 6H₂O (0.1 M) by addition of a stoichiometric amount of a [PPh₄]Cl (0.35 M) solution.

2.2. NMR spectroscopy

The one-dimensional ¹H, ¹¹B, ¹³C and ¹⁹F and two-dimensional HMQC (¹³C-¹H, ¹⁵N-¹H and ¹⁰³Rh-¹H) NMR spectra were recorded on Bruker AMX 500, AC 250 and AC 200 spectrometers. The chemical shift scales are relative to internal TMS (¹H and ¹³C) and external BF₃·Et₂O (¹¹B), CFCl₃ (¹⁹F), CH₃HO₂ (¹⁵N) and Ξ =3.16 MHz (¹⁰³Rh). ¹⁵N-¹H and ¹⁰³Rh-¹H HMQC experiments were optimized for long-range couplings. All experiments were recorded in phase-sensitive mode using TPPI, processed with cosine-square windows in both dimensions, zero-filling, double Fourier-transformation and phase-correction. Processing of the long-range correlation experiments involved final magnitude calculation in the ω_2 dimension [18].

2.3. Analytical and other physical measurements

C, H, N and F microanalyses were performed by the Microanalytical Laboratory of the ETH Zürich. IR spectra were recorded as KBr pellets, or as CHCl₃ and CH₃CN solutions in NaCl cells, on Perkin-Elmer model 883 and Perkin-Elmer FT-IR Paragon 1000 spectrometers.

2.4. Syntheses of Tp^{3R,5R}Rh(LL) complexes

2.4.1. General procedure

As the preparation of **1a** as described by Bucher et al. [9] was unsuccessful, this and the other complexes described here were prepared by the following modified procedure. To a solution of the appropriate $Rh_2Cl_2(LL)_2$ (LL = 2CO, NBD, COD) compound (0.2 mmol in 5 ml of MeCN), at -30 °C, two equivalents of the solid tris(pyrazolyl)borate were added at once. The mixture was stirred for ~ 3 h while the temperature was allowed to rise to 25 °C (compounds with Tp^{Me2} must be stirred for less than 1 h and the temperature kept below 0 °C to avoid decomposition and the formation of byproducts). The solvent was then removed using a rotary evaporator, the residue extracted with 5 ml CH₂Cl₂ and the solution filtered through Celite to remove MCl (M = Na, Tl). The solvent was removed on a rotary evaporator and the residual product, after drying in vacuo for 3 h, proved to be analytically pure. Yields, analytical, IR spectroscopic (KBr pellets) and NMR spectroscopic data (CDCl₃) are as follows.

2.4.2. $Tp^{Me_2}Rh(CO)_2$ (1a)

Yield 173 mg, 94%. IR (cm⁻¹): 2509 s (B–H str). ¹H NMR: 5.79 (s, 3H, H(4)), 4.58 (br, BH), 2.39 (s, 9H, Me(3)), 2.33 (s, 9H, Me(5)). ¹³C NMR: 189.9 (d, ¹J(Rh, C) = 69 Hz, CO), 149.7 (s, C(3)), 144.5 (s, C(5)), 105.9 (s, C(4)), 15.3 (s, Me(3)), 12.8 (s, Me(5)). ¹⁵N NMR: -157.3 (N(1)), -134.3 (N(2)).

2.4.3. $Tp^{CF_{3,Me}}Rh(CO)_{2}(1b)$

Yield 207 mg, 84%. Anal. Found: C, 33.05; H, 2.19; N, 13.60; F, 27.37. Calc. for $C_{17}H_{13}N_6BO_2F_9Rh$: C, 33.04; H, 2.12; N, 13.60; F, 27.66%. IR (cm⁻¹): 2571 s (B–H str). ¹H NMR: 6.41 (s, 3H, H(4)), 4.80 (br, BH), 2.41 (s, 9H, Me(5)). ¹⁹F NMR: -60.19 (CF₃). ¹³C NMR: 182.9 (d, ¹J(Rh, C) = 72 Hz, CO), 146.6 (C(5)), 144.0 (q, ²J(F, C) = 38 Hz, C(3)), 120.8 (q, ¹J(F, C) = 269 Hz, CF₃), 106.3 (q, ³J(C, F) = 2 Hz, C(4)), 13.0 (Me(5)). ¹⁵N NMR: -150.6 (N(1)), -128.3 (N(2)). ¹¹B NMR: -8.99 (d, ¹J(B, H) = 101 Hz, BH).

2.4.4. $Tp^{CF_3, CF_3}Rh(CO)_2$ (1c)

Yield 259 mg, 81%. Anal. Found: C, 26.61; H, 0.48; N, 11.62; F, 42.87. Calc. for $C_{17}H_4N_6BO_2F_{18}Rh$: C, 26.18; H, 0.52; N, 10.78; F, 43.84%. IR (cm⁻¹): 2645 w (B–H str). ¹H NMR: 7.06 (s, 3H, H(4)), 5.07 (br, BH). ¹⁹F NMR: -60.35, -59.58 (CF₃). ¹³C NMR: 181.2 (d, ¹J(Rh, C) = 73 Hz), 145.4 (q, ²J(F, C) = 39 Hz, C(3)), 141.1 (q, ²J(F, C) = 44 Hz, C(5)), 119.6 (q, ¹J(F, C) = 270 Hz, CF₃), 118.7 (q, ¹J(F, C) = 271 Hz, CF₃), 108.5 (br, C(4)). ¹⁵N NMR: -156.1 (N(1)), -118.1 (N(2)).

2.4.5. $Tp^{Me_2}Rh(NBD)$ (2a)

Yield 167 mg, 85%. IR (cm^{-1}) : 2509 (B-H str). ¹H NMR: 5.69 (s, 3H, H(4)), 2.49 (s, 9H, Me), 2.24 (s, 9H, Me), see Ref. [9].

2.4.6. Tp^{CF3,Me}Rh(NBD) (2b)

Yield 227 mg, 87%. Anal. Found: C, 40.51; H, 3.15; N, 12.75; F, 26.32. Calc. for $C_{22}H_{21}N_6BF_9Rh$: C, 40.40; H, 3.24; N, 12.85; F, 26.14%. IR (cm⁻¹): 2489 s (B–H str). ¹H NMR: 6.40 (s, 3H, H(4)), 4.72 (br, BH), 3.90 (4H, H^{o1}), 3.47 (s, 2H, H^{brh}), 2.20 (s, 9H, Me(5)), 1.08 (2H, H^{br}). ¹⁹F NMR: -59.98 (CF₃). ¹³C NMR: 146.2 (C(5)), 143.2 (q, ²J(F, C) = 38 Hz, (C(3)), 121.2 (q, ¹J(¹⁹F, ¹³C) = 269 Hz, CF₃), 106.3 (q, ³J(F, C) = 2 Hz, C(4)), 62.4 (d, ³J(Rh, C) = 7 Hz, C^{br}), 57.5 (d, ¹J(Rh, C) = 10 Hz, C^{o1}), 50.1 (d, ²J(Rh, C) = 3 Hz, C^{brh}), 12.9 (Me(5)). ¹⁵N NMR: -148.9 (N(1)). ¹⁰³Rh NMR: 1261.

2.4.7. Tp^{CF₃,CF₃}Rh(NBD) (2c)

Yield 287 mg, 88%. Anal. Found: C, 32.06; H, 1.87; N, 10.14; F, 41.23. Calc. for $C_{22}H_{12}N_6BF_{18}Rh$: C, 32.38; H, 1.48; N, 10.30; F, 41.90%. IR (cm⁻¹): 2576 (B–H str). ¹H NMR: 7.05 (s, 3H, H(4)), 4.92 (br, BH), 4.06 (4H, H^{ol}), 3.52 (2H, H^{brh}), 1.16 (2H, H^{br}). ¹⁹F NMR: -59.80, -60.35 (CF₃). ¹³C NMR: 144.2 (q, ²J(F, C) = 39 Hz, C(3)), 140.2 (q, ²J(F, C) = 45 Hz, C(5)), 120.1 (q, ¹J(F, C) = 270 Hz, CF₃), 118.9 (q, ¹J(F, C) = 271 Hz, CF₃), 108.5 (br, C(4)), 63.1 (d, ³J(Rh, C) = 7 Hz, C^{br}), 58.9 (d, ¹J(Rh, C) = 10 Hz, C^{ol}), 50.1 (d, ²J(Rh, C) = 2 Hz, C^{brh}). ¹⁵N NMR: -154.1 (N(1)). ¹⁰³Rh NMR: 1244.

Table 1

2.4.8. $Tp^{CF_3, CF_3}Rh(COD)$ (3c)

Yield 59 mg, 71%. IR (cm⁻¹): 2586 (B–H str). ¹H NMR: 7.05 (s, 3H, H(4)), 4.85 (br, BH), 4.29 (4H, H^{ol}), 2.03 (4H, H^{exo}), 1.67 (4H, H^{endo}). ¹⁹F NMR: -59.5 (2 CF₃). ¹³C NMR: 144.6 (q, ²J(F, C) = 39 Hz, C(3)), 140.9 (br, C(5)), 120.1 (q, ¹J(F, C) = 270 Hz, CF₃), 119.0 (q, ¹J(F, C) = 270 Hz, CF₃), 109.0 (br, C(4)), 83.3 (d, ¹J(Rh, C) = 13 Hz, C^{ol}), 29.1 (s, CH₂). ¹⁵ N NMR: -154.3(N(1)). ¹⁰³Rh NMR: 1129.

2.5. X-ray crystallography

A yellow plate of $Tp^{CF_3,Me}Rh(CO)_2$ (1b), of size 0.4× 0.3×0.3 mm, was used for the structure determination. Crystals suitable for X-ray analysis were obtained from a CH₂Cl₂ solution upon addition of CH₃CN. Details of the X-ray data collection are as follows: C₁₇H₁₃BF₉N₆O₂Rh, M = 618.1, monoclinic, space group C2/c, a = 21.271(9), b = 11.004(3), c = 21.563(9) Å, $\beta = 114.93(3)^{\circ}, V =$ 4577(3) Å³, Z=8, μ = 0.847 mm⁻¹, T=293 K, F(000) = $2432, D_c = 1.794 \text{ M gm}^{-3}$; Syntex P21 diffractometer, graphite crystal monochromated Mo K α radiation (0.71073 Å) and ω -scan mode. Accurate unit-cell parameters were obtained by least-squares fits of the 2θ values of the high order reflections. A total of 2380 reflections $(3.0^{\circ} <$ $2\theta < 40.0^{\circ}$) was collected, of which 2153 were independent, with index ranges $-20 \le h \le 18$, $0 \le k \le 10$ and $0 \le l \le 20$. These gave 1807 observed $(F > 4.0\sigma(F))$ reflections. No absorption correction was applied.

The structure was solved by direct methods [19] and refined by full-matrix least-squares methods (328 parameters, the function minimized was $[\Sigma w(F_o - F_c)^2]$), with anisotropic thermal ellipsoids for all non-hydrogen atoms. Extinction corrections were deemed to be unnecessary. The hydrogen atoms were introduced into the calculated positions with a riding model with fixed isotropic U. The final values R (observed data) = 3.41, $R_w = 4.70$, GOF = 1.26, with weighting scheme $w^{-1} = \sigma^2(F) + 0.0010(F)^2$ were obtained. Maximum and minimum peaks were 0.45 (located on Rh) and -0.26 e Å⁻³; largest and mean $\Delta/\sigma = 0.343$ and 0.013. The final coordinates and U_{eq} values are listed in Table 1. See also Section 5.

3. Results and discussion

3.1. Syntheses

As a continuation of an earlier study [9] of complexes of the types $Tp^{Me_2}Rh(CO)_2$ (1a), $Tp^{Me_2}Rh(NBD)$ (2a) and $Tp^{Me_2}Rh(COD)$ (3a), in order to investigate the influence of electron-withdrawing substituents on the pyrazolyl rings on the properties of their complexes, the Rh(I) compounds with the recently described anionic ligands $Tp^{CF_3, Me}$ [9] and Tp^{CF_3, CF_3} [17] were prepared. The sodium or thallium salts of the tris(pyrazolyl)borates $Tp^{3R, 5R}$ (a-c) reacted in dry acetonitrile with the rhodium complexes $Rh_2Cl_2(LL)_2$ (LL = 2CO, NBD, COD) according to Eq. (1):

$$Rh_2Cl_2(LL)_2 + MTp^{3R,5R}$$

$$2Tp^{3R,5R}Rh(LL) + 2MCl$$
 (1)

	LL	3R	5R
1a	2CO	CH ₃	CH
1b	2CO	CF ₃	CH
lc	2CO	CF ₃	CF ₃
2a	NBD	CH ₃	CH ₃
2b	NBD	CF ₃	CH
2c	NBD	CF ₃	CF ₃
3a	COD	CH ₃	CH ₃
3b	COD	CF ₃	CH ₃
3c	COD	CF ₃	CF ₃

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 $a = Tp^{Me_2}, b = Tp^{CF_3, Me}, c = Tp^{CF_3, CF_3}, M = Na, Tl.$

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coerdinates	ffi
cients ($Å^2 \times 10^3$)	

	x	у	Z	$U_{\rm eq}{}^{\rm a}$
Rh(1)	2173(1)	149(1)	1592(1)	55(1)
B(1)	1312(4)	-2095(6)	601(3)	49(3)
N(1)	1115(2)	-841(4)	255(2)	48(2)
N(2)	1487(3)	191(4)	542(2)	53(2)
N(3)	1056(2)	-2239(4)	1165(2)	48(2)
N(4)	1273(3)	-1411(5)	1680(3)	61(2)
N(5)	2111(2)	-2264(4)	893(2)	47(2)
N(6)	2567(3)	-1396(4)	1292(2)	51(2)
C(1)	1229(3)	1072(6)	69(3)	55(3)
C(2)	691(3)	619(7)	-506(3)	65(4)
C(3)	626(3)	-576(6)	-377(3)	53(3)
C(4)	1517(5)	2326(7)	187(4)	80(4)
C(5)	113(3)	-1483(7)	-819(3)	74(3)
C(6)	993(3)	-1785(6)	2094(3)	57(3)
C(7)	601(3)	-2821(6)	1861(3)	61(3)
C(8)	651(3)	-3093(5)	1262(3)	52(3)
C(9)	1130(5)	- 1076(9)	2720(4)	92(5)
C(10)	333(3)	-4130(6)	793(4)	76(3)
C(11)	3199(3)	-1795(6)	1406(3)	57(3)
C(12)	3164(4)	-2898(6)	1098(3)	63(3)
C(13)	2470(4)	-3188(5)	778(3)	54(3)
C(14)	3832(4)	-1060(9)	1784(5)	89(5)
C(15)	2146(4)	-4290(6)	376(3)	72(4)
F(1)	1256(3)	3004(4)	542(3)	107(3)
F(2)	2191(3)	2369(4)	515(3)	104(3)
F(3)	1341(3)	2894(4)	-411(3)	113(3)
F(4)	840(4)	-1534(7)	3084(3)	177(4)
F(5)	1778(3)	-937(7)	3123(3)	158(4)
F(6)	917(5)	54(6)	2599(3)	178(5)
F(7)	3998(2)	-895(5)	2427(3)	120(3)
F(8)	4359(3)	-1508(7)	1727(3)	177(4)
F(9)	3771(3)	92(6)	1555(3)	156(4)
C(16)	2774(4)	143(6)	2495(4)	70(3)
C(17)	1893(4)	1587(7)	1822(4)	85(4)
0(1)	3119(3)	150(5)	3071(3)	100(3)
O(2)	1715(4)	2446(6)	2003(4)	145(5)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. The yellow to orange solid products were obtained in high yields and proved to be stable under normal laboratory conditions. Attempts to synthesize $Tp^{CF_3,CF_3}Rh(COE)_2$ (COE = cyclooctene), using either NaTp^{CF_3,CF_3} or TlTp^{CF_3,CF_3}, were unsuccessful: the 500 MHz ¹H NMR spectra of the brownish materials obtained in both cases did not show B–H resonances and, therefore, the tris(pyrazolyl)-borate anions had decomposed.

3.2. Carbonyl complexes $Tp^{3R,5R}Rh(CO)_2(1)$

3.2.1. Solution studies

The ν (CO) stretching frequencies (sym and asym) of the carbonyl derivatives **1a**-c in solution are given in Table 2, together with the corresponding values for some related complexes. Some representative IR spectra are shown in Fig. 2.

Earlier work from this laboratory showed that CHCl₃ solutions of Tp^{Me2}Rh(CO)₂ (**1a**), at room temperature, contain the five-coordinate isomer with a κ^3 -bonded pyrazolylborate ligand with characteristic ν (CO) bands at 2055 and 1980 cm⁻¹ [9]. However, Purwoko and Lees [4a] report that, in CH₂Cl₂ solution, there is an equilibrium between a κ^2 - and the κ^3 -bonded species, the former showing characteristic ν (CO) vibrations at 2078 and 2009 cm⁻¹.

The IR spectrum of $Tp^{CF_3,Me}Rh(CO)_2$ (1b), in CHCl₃, showed four carbonyl stretching vibrations of similar intensities at $\nu = 2100$, 2088, 2037 and 2022 cm⁻¹ (see Table 2 and Fig. 2(a)). Their energies are in the range characteristic for four-coordinate rhodium complexes, as can be seen by comparing these values with those of corresponding bis(pyrazolyl)borate complexes [9,12]. Interestingly, while for some complexes of the type $Tp^{3R,4R,5R}Rh(CO)_2$, a remarkable shift towards the five-coordinate form on replac-



Fig. 2. IR spectra showing the carbonyl stretching modes of $Tp^{CF_3,Me}Rh(CO)_2$ (1b) in $CHCl_3$ (a) and CH_3CN (b); $Tp^{CF_3,CF_3}Rh(CO)_2$ (1c) in $CHCl_3$ (c) and CH_3CN (d).

ing CHCl₃ with CH₃CN occurred [9], the IR spectra of **1b** in CH₃CN (see Table 2 and Fig. 2(b)) remained almost unchanged, apart from the appearance of a weak shoulder at ~ 1980 cm⁻¹, the range characteristic for a five-coordinate form. Thus, the two forms present in these solutions were assigned the κ^2 -bonded structures **A** and **B**.

The IR spectra of $\text{Tp}^{\text{CF}_3,\text{CF}_3}\text{Rh}(\text{CO})_2$ (1c), in CHCl₃, showed five bands in the region 1900–2200 cm⁻¹, those of highest intensity being at 2095 and 2028 cm⁻¹ (see Table 2 and Fig. 2(c)). The IR spectra of 1c, in CH₃CN, also showed five bands (see Table 2 and Fig. 2(d)). However, in addition to the absorptions at $\nu = 2095$ and 2026 cm⁻¹, due to the major isomer, here a five-coordinate species responsible for the bands at 2068 and 1991 cm⁻¹ was also present. A com-

Table 2

Carbonyl stretching bands for complexes of the type Tp^{3R,5R}Rh(CO)₂ and related compounds

Compound	CHCl ₃		MeCN		KBr (isolated from CHCl ₃) ^c		KBr (isolated from CH ₃ CN)	
	$\nu_{\rm sym}$	$\nu_{\rm asym}$	$ u_{\rm sym}$	$ u_{ m asym}$	$\nu_{\rm sym}$	$ u_{\rm asym}$	ν _{sym}	ν_{asym}
1a	2055 vs	1980 vs ª	2056 vs	1980 vs *	2108 w 2083 w 2051 vs	2073 sh 2012 s 1972 vs	2052 vs	1973 vs
1b	2100 s 2088 s	2037 s 2022 s	2100 s 2087 s	2036 s 2019 s	2082 vs	2016 vs 2001 br	2085 vs	2017 vs 1988 w
1c	2110 m 2095 vs 2066 w	2051 m 2028 vs	2049 sh 2095 vs 2068 s	2026 vs 1991 s	2096 vs	2038 vs	2095 vs	2035 vs
$Tp^{Me}Rh(CO)_2^a$	2085 s 2060 s	2019 s 1988 s	2087 w 2062 vs	2019 w 1988 vs				
MeTp ^{Me} Rh(CO) ₂ ^b	2083 s 2056 s	2017 s 1980 s	2083 w 2056 vs	2019 w 1980 vs				

* See Ref. [9].

^b See Ref. [12].

^c 1a isolated from CH₂Cl₂.

Table 3	
Selected 103Rh,	¹⁵ N and ¹³ C NMR data for complexes of the type Tp ^{3R,5R} Rh(LL) ₂ and related compounds

Compound	δ(¹⁰³ Rh)	¹⁵ N	$\delta(^{13}C(\text{olefinic}))$	
		$\delta(N^1)$	$\delta(N^2)$	
la		- 157.3	- 134.3	
1b		- 150.6	- 128.3	
1c		- 156.1	-118.1	
2a	1777 °			35.1 ^{a,b}
2b	1261	- 148.9	n.d.	57.5
2c	1244	- 154.1	n.d.	58.9
{BBN(3-Me-pz) ₂ }Rh(NBD) *	1374			53.5, 51.0
{PhMeB(3-Me-pz) ₂ }Rh(NBD) ^c	1340	- 140.2	- 137.8	57.1, 51.7
3a	1107 ^a			75.2 °
3b	1129 *			
3c	1129	- 154.3	n.d.	83.3
$\{PhMeB(3-Me-pz)_2\}Rh(COD)^{\circ}$	1136	- 140.4	-139.8	
{BBN(3-Me-pz) ₂ }Rh(COD) ^a	1205			78.3, 75.1
{BBN(pz) ₂ }Rh(COD) ^a		-131	-136	81.1, 79.1

* See Ref. [9].

^b Solid state: 30-35 ppm.

parison of the spectra in the two solvents allows the assignment of the weak absorption at 2066 cm⁻¹ in the CHCl₃ solution to the ν_{sym} absorption of the five-coordinate form C, whereas the shoulder at 2049 cm⁻¹, in the CH₃CN solution, is assigned to the ν_{asym} vibrations of the four-coordinate species which are found at $\nu = 2110$ and 2051 cm⁻¹ in CHCl₃.

It is noteworthy, that the carbonyl compound 1c is the only complex of this type, where all three isomeric forms can be simultaneously observed in solution. Furthermore, also 1cshows solvent-dependent equilibria between them, one of the four-coordinate forms being the major isomer in CHCl₃ as well as in CH₃CN, the equilibria being shifted towards the other four-coordinate form in the former and to form C in the latter solvent.

In contrast to the recently studied carbonyl complex $Tp^{iPr,4Br}Rh(CO)_2$ [9], where one could clearly detect by NMR the inequivalent pyrazolyl rings, in a 2:1 ratio, of isomeric form **A**, the ¹H and ¹³C spectra of **1a–c** showed the equivalence of the three pyrazolyl rings. Low temperature experiments were also performed on $Tp^{CF_3,Me}Rh(CO)_2$ (1b) but no spectral change was observed even at -80 °C. Thus, in the new carbonyl complexes described here, i.e. 1b and 1c, the exchange between the three forms is fast on the NMR time scale.

Additionally, the $\delta({}^{15}N)$ chemical shift values of the carbonyl complexes **1a-1c** were measured to obtain another estimate of the position of the equilibrium between species of types **B** and **C**. The relevant data are summarized in Table 3. The $\delta({}^{15}N^2)$ values of compounds **1a-c** (-134.3, -128.3 and -118.1 ppm, respectively) clearly indicate that the tendency to form five-coordinate species decreases in the order **1a** to **1c**. Assuming that the chemical shift of N² in the fivecoordinate complex is not much different from that of the four-coordinate species [12], one estimates that solutions of **1c** contain almost exclusively the κ^2 -bonded form, as the N²-shift observed for **1c** (-118.1 ppm) is in good agreement with the value calculated for a κ^2 -bonded form (-117 ppm), while solutions of **1a** and **1b** may contain both five- and four-coordinate species.

While the relative amounts of the isomeric forms of 1a and of 1c estimated by this method are in good agreement with those obtained from IR spectroscopy, the relative amounts of κ^2 - and κ^3 -bonded species of 1b in solution obtained by the two methods differ significantly. The reason for this discrepancy is not apparent.

As an indirect detection [20] of the ¹⁰³Rh resonances by ¹H observation was employed during this study, ¹⁰³Rh chemical shift values could only be obtained for olefinic complexes, where suitable long-range couplings $^nJ(Rh, H)$ are observable. In principle couplings to pyrazolylborate protons could also be used as, for example, in the case of some tungsten complexes [21]. However, in complexes 1–3, where there are $\kappa^2 - \kappa^3$ equilibria involving cleavage of Rh-N bonds, these couplings and the associated double-quantum coherences disappear.

3.2.2. Solid state

The solid-state IR spectra of complex $Tp^{Me_2}Rh(CO)_2$ (1a), reported in the literature [9], indicated the presence of only the five-coordinate species in the solid state. However, it was found in this study that for **1a**-c the solids obtained by evaporating the solvent to dryness contained different isomers. Thus, while compound **1a**, obtained from a CH₃CN solution, contained, as expected, only the κ^3 -bonded species, the material similarly isolated from a CHCl₃ solution, also

[°] See Ref. [12].

showed the bands due to the two κ^2 -bonded species **A** and **B** (see Table 2).

Although the compositions of solutions of $Tp^{CF_3,Me}Rh(CO)_2$ (1b) and $Tp^{CF_3,CF_3}Rh(CO)_2$ (1c) showed no solvent dependence (see Table 2), complex 1b always gave a solid which contained one of the κ^2 -bonded forms as the major isomer and some five-coordinate form as deduced from the presence of a weak absorption at 1988 cm⁻¹. However, exclusively one of the four-coordinate forms was observed in the case of 1c.

Thus, the structural information obtained from single crystal X-ray crystal structure analyses for complexes of this type may not be generally usable as, depending on the solvent employed, and the isolation procedure, different or additional species might be present in the solid state. Thus, not only subtle electronic and steric effects, but also solubility factors and the crystal packing, may determine whether these complexes form four- or five-coordinate species even in the solid state.

3.2.3. X-ray crystal structure of $Tp^{CF_3,Me}Rh(CO)_2$ (1b)

The structure of 1b was determined by X-ray diffraction and an ORTEP view of the molecule is shown in Fig. 3. The crystal contains discrete molecules separated by normal van der Waals distances. A selection of bond lengths and angles is given in Table 4. The Rh atom is four-coordinate and bonded to the two carbonyl co-ligands and to nitrogen atoms of two of the pyrazole rings of the tris(pyrazolyl)borate anion. The coordination geometry at rhodium is approximately square-planar. There do not appear to be structures of closely related complexes in the literature except [Rh{ κ^2 - $HB(pz^{Me_2})_2(pz^{Me_2}H)\}(CO)_2][BF_4]$ (1d), obtained by protonating 1a [22]. The Rh coordination sphere, i.e. the square-planar coordination, of 1b and 1d are quite similar; e.g. the Rh-N distances are 2.070(4), 2.093(4) Å in 1d and 2.116(4), 2.114(5) Å in **1b**, while the Rh–C distances are 1.848(5), 1.867(6) Å in 1d and 1.824(7), 1.832(9) Å in 1b. These Rh-C, as well as the C-O distances, are also in



Fig. 3. ORTEP plot of Tp^{CF3,Me}Rh(CO)₂ (1b).

Table 4 Selected distances (Å) and angles (°) for 1b

Rh(1)-N(2)	2.116(4)	Rh(1)-N(6)	2.114(5)
Rh(1) - N(4)	2.636(5)	Rh(1)-C(16)	1.824(7)
B(1)-N(1)	1.540(8)	Rh(1)-C(17)	1.832(9)
B(1) - N(5)	1.555(9)	B(1)-N(3)	1.534(11)
C(17)–O(2)	1.145(12)	C(16)-O(1)	1,146(9)
N(2)-Rh(1)-N(6)	82.7(2)	N(2)-Rh(1)-C(16)	178.7(3)
N(6)-Rh(1)-C(16)	97.7(3)	N(2)-Rh(1)-C(17)	96.6(3)
N(6)-Rh(1)-C(17)	173.8(3)	C(16)-Rh(1)-C(17)	82.8(3)
N(1)-B(1)-N(3)	111.2(6)	N(1)-B(1)-N(5)	109.4(5)
N(3)-B(1)-N(5)	111.0(4)	B(1)-N(1)-N(2)	122.3(4)
Rh(1)-C(16)-O(1)	176.1(9)	Rh(1)-C(17)-O(2)	175.4(8)
N(4)-Rh(1)-N(2)	84.1(3)	N(4)-Rh(1)-N(6)	83.8(3)
N(4)-Rh(1)-C(16)	97.1(3)	N(4)-Rh(1)-C(17)	102.4(3)

good agreement with those reported in the square-planar complex $[NMe_4][Rh(ox)(CO)_2]$ (ox = oxalato) [23].

However, there are significant differences in the overall structures of 1b and of the above protonated derivative 1d. While the latter is a typical example of a four-coordinate species of type B, 1b represents an intermediate between the four-coordinate form B and a five-coordinate square-pyramidal form. As can be seen from Fig. 3, the uncoordinated pyrazolyl ring occupies an axial position and is placed approximately above the coordination plane, as expected for a κ^3 -Tp coordination. The N(4) atom is not placed exactly above the rhodium atom but slightly displaced towards the two coordinated nitrogen atoms, as can be seen from the N(4)-Rh(1)-N(2) and N(4)-Rh(1)-N(6) angles which are ~84° and the N(4)-Rh(1)-C(16) and N(4)-Rh(1)-C(17) angles which are ~97° and 102°, respectively. Presumably, given the square-planar coordination at rhodium, this is as close as N(4) can approach the metal centre given the bonding constraints of the Tp^{CF₃,Me} ligand.

However, there does not appear any significant bonding between the N(4) atom of this ring and the Rh atom, the Rh– N(4) distance being 2.636(5) Å, while an Rh–N distance of 2.157 Å had been considered being at the long end of the normal Rh–N range [24]. Interestingly, all the five-coordinate Tp^{3R,4R,5R}M(LL) (M=Rh and Ir) complexes, at least with LL=diene, which have been structurally characterized to date, show geometries which are intermediates between trigonal-bipyramidal and square-pyramidal [6,9,10,12].

3.3. Norbornadiene complexes Tp^{3R,5R}Rh(NBD) (2)

In view of the interesting properties of the carbonyl compounds discussed above and the differences between solids and solutions, the corresponding series of NBD and COD derivatives 2a-c and 3a-c were also examined.

The ¹H and ¹³C NMR spectra of $Tp^{CF_3,Me}Rh(NBD)$ (2b) and $Tp^{CF_3,CF_3}Rh(NBD)$ (2c), recorded in CDCl₃ at room temperature, indicated in each case the presence of only one type of molecule, i.e. that showing a spectrum with dynamically averaged pyrazole rings, as found in the related compound $Tp^{Me_2}Rh(NBD)$ (1a) [9]. However, as shown earlier for the carbonyl complexes, the appearance of magnetic equivalence in the ¹H and ¹³C NMR spectra does not necessarily imply the presence of only κ^3 -bonded tris(pyrazolyl)-borate ligands.

The ¹⁰³Rh shifts of Tp^{CF₃,Me}Rh(NBD) (**2b**) and Tp^{CF₃,CF₃Rh(NBD) (**2c**) (1261 and 1244 ppm, respectively), indicate that only four-coordinate isomers of these complexes exist in solution (see Table 3). However, it is not possible to establish whether, in each case, one or both of the square-planar forms are present. In contrast, complex Tp^{Me₂}Rh(NBD) (**2a**), with δ (¹⁰³Rh) = 1777 ppm, exists predominately in form C [9].}

The observed ¹³C NMR chemical shift values of the olefinic C atoms in complexes **2b** and **2c**, also given in Table 3, indicate that both complexes exist in their κ^2 -bonded form in CDCl₃ solution. These data are in good agreement with the results from the ¹⁰³Rh NMR study, which indicated the absence of κ^3 -bonded forms.

3.4. Cyclooctadiene complexes Tp^{3R,5R}Rh(COD) (3)

The ¹⁰³Rh shift recorded for Tp^{CF₃,CF₃Rh(COD) (**3c**), in CDCl₃, was 1129 ppm (see Table 3). As the COD complexes Tp^{Me2}Rh(COD) (**3a**) and Tp^{CF₃,MeRh(COD) (**3b**), showing δ (¹⁰³Rh) values of 1107 and 1129 ppm, respectively, were assigned square-planar coordination [9], the value for **3c** was taken to indicate that also this complex exists in its four-coordinate form in solution.}}

The observed ¹³C NMR shift of the olefinic C atoms in 3c, 83.3 ppm, is in good agreement with the values typical for four-coordinate bis(pyrazolyl)complexes and thus this result also supports the conclusions based on the ¹⁰³Rh NMR data.

Regrettably, the ¹⁵N NMR resonances for the N² atoms could not be detected in the complexes having NBD and COD ligands.

3.5. Intramolecular pyrazole rearrangement and other reactions

A previous publication [9] described the formation of the borotropic migration product [$\{HB(3-iPr-4-Br-pz)_2(5-iPr-4-Br-pz)\}Rh(COD)$] when a CDCl₃ solution of Tp^{iPr,4Br}Rh(COD) was heated to 70 °C for 30 min. As the complexes **1b**, **2b** and **3b** have different C substituents on the pyrazolyl rings, it should also be possible to detect borotropic migrations by NMR spectroscopy. Therefore, CDCl₃ solutions of **1b** and **2b** were similarly studied. However, in both cases neither migration nor decomposition products were found.

Related studies showed that the reaction of $Tp^{Me_2}Ir(COD)$ with K[BH₄] in MeOH gave $Tp^{Me_2}Ir(H)(1\sigma,4,5-\eta^2-cyclooctenyl)$ [10]. Thus, attempts were made to produce the $Tp^{CF_3,CF_3}Rh$ analogue by reacting $Tp^{CF_3,CF_3}Rh(COD)$ (3c) with K[BH₄] in MeOH. However, upon addition of K[BH₄] to 3c there was immediate formation of black metallic rhodium, as found for $Tp^{CF_3,Me}Ir(COD)$ [10]. Finally, attempts were made to oxidize complexes 1 and 2 with TlCl₃ or $[PPh_4]_2[PtCl_6]$ in order to obtain, for example, the corresponding complexes of the type $[Ph_4P]$ - $[Tp^{3R,4R,5R}RhCl_3]$ [25] as these anionic complexes allowed the preparation of the dihydrogen complexes of the type $Tp^{3R,4R,5R}RhH_2(H_2)$ [26]. However, so far, these attempts have been unsuccessful: either the organometallic starting materials were recovered unchanged or decomposition of the $Tp^{3R,4R,5R}$ ligand occurred.

4. Conclusions

The carbonyl, norbornadiene and 1,5-cyclooctadiene Rh(I) complexes with two new tris(pyrazolyl)borate ligands, having the C-3 or the C-3 and C-5 positions substituted with CF₃ groups, i.e. Tp^{CF₃,Me}Rh(LL) and Tp^{CF₃,CF₃Rh(LL), were prepared. The $\kappa^2 - \kappa^3$ isomerism in} these complexes was studied by IR and multinuclear NMR spectroscopy. All COD complexes 3 were assigned squareplanar geometries, while the analogous NBD and CO derivatives also formed the corresponding five-coordinate isomers, depending on the substituents on the pyrazolyl rings. It was found that, generally, the presence of CF₃ substituents favoured the formation of the four-coordinate complexes, while in the complexes with the corresponding Me₂-substituted ligand the five-coordinate form was preferred. Although it is still arguable whether these differences are caused by steric or electronic effects, given that (i) larger substituents in the 3positions disfavour the formation of form C, (ii) substituents in the 5-positions on the pyrazole rings destabilize form A due to steric repulsions, and (iii) form A is present at least in 1c, the changes induced by CF₃ as opposed to CH₃ substituents are more likely to be due to electronic rather than steric effects.

5. Supplementary material

Tables of structure determination summary, anisotropic displacement coefficients, H atom coordinates, and an extended list of bond distances and angles may be obtained from author V.G. upon request.

6. Note added in proof

The authors are indebted to Dr S. Trofimenko and to a Referee for the information that the X-ray crystal structure of $[Tp^{CF_3,Me}Rh(CO)_2]$ had previously been determined by R.G. Ball and M. Cowie and reported by R. Krentz (*Ph.D. Thesis*, University of Alberta, 1989). However, the bonding parameters for this complex are not available to them at this stage. Dr Trofimenko also kindly sent us the X-ray crystal structural data for the related compound $[Tp^{CF_3,Th}Rh(CO)_2]$ (Th = thienyl), determined by J. Calabrese (E.I. Du Pont,

Wilmington, DE). The coordination geometry of this complex is closely analogous to that reported here.

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