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Poly(azolyl)chelate chemistry.
V ☆. Synthesis of bis(benzotriazolyl)borato complexes of rhodium(I)

Stephen Anderson, Alan Harman, Anthony F. Hill *

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

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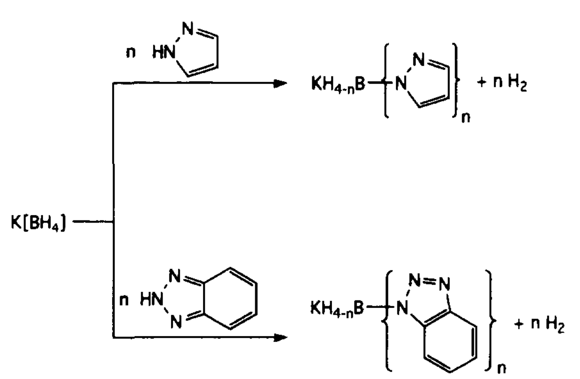
Abstract

The reaction of K[$H_2B(bta)_2$] (bta = benzotriazol-1-yl) with [RhCl(CO)($PPh_3)_2$] provides [Rh{κ^2-$H_2B(bta)_2$}(CO)($PPh_3)_2$], the carbonyl ligand of which is labile and readily replaced by $CNC_6H_3Me_2$-2,6 to provide [Rh{κ^2-$H_2B(bta)_2$}($CNC_6H_3Me_2$-2,6)($PPh_3)_2$]. The formation of the isonitrile derivative appears to proceed via an associative mechanism involving a blue intermediate complex formulated as [Rh{κ^1-$H_2B(bta)_2$}(CNR)(CO)($PPh_3)_2$]. [Rh{κ^2-$H_2B(bta)_2$}(CS)($PPh_3)_2$] may be prepared by the corresponding reaction of K[$H_2B(bta)_2$] with [RhCl(CS)($PPh_3)_2$]. All the complexes show dynamic behaviour (^1H, ^{13}C NMR) at room temperature.

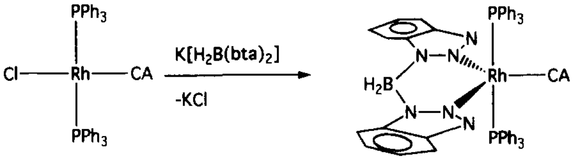
Keywords: Rhodium; Fluxionality; Benzotriazole; Chelate; Thiocarbonyl; Boron

1. Introduction

Interest in the poly(pyrazol-1-yl) borate chemistry of Group 9 metals currently centres on observations of C–H activation processes, e.g. for the complexes [$Rh(CO)_2${$HB(pzMe_2$-3,5$)_3$}] [2]. The recent independent discoveries of the poly(benzotriazolyl)borates K[$H_xB(bta)_{4-x}$] [bta = benzotriazol-1-yl: $x = 2$ (**1a**), 1 (**1b**), 0 (**1c**)] (Scheme 1) by Lalor et al. [3] and Shiu et al. [4] offer the possibility of extending this type of reaction to other poly(azolyl)chelates. We have recently been interested in the chemistry of poly(pyrazolyl)borato complexes of metals from Groups 8 and 9, and have begun to extend this study to include the poly(benzotriazolyl)borate chelates [1,5]. We describe below the simple and high yield synthesis of the complexes [Rh(CA){$H_2B(bta)_2$}($PPh_3)_2$] (A = O or S) by the reaction of the salt K[$H_2B(bta)_2$] (Scheme 2) with [RhCl(CA)($PPh_3)_2$], and also the subsequent formation of [Rh($CNC_6H_3Me_2$-2,6){$H_2B(bta)_2$}($PPh_3)_2$]. A preliminary report covering aspects of this work has appeared previously [5].



Scheme 1. Synthesis of poly(pyrazolyl)borates and poly(benzotriazolyl)borates.



Scheme 2. Synthesis of [Rh(CA){$H_2B(bta)_2$}($PPh_3)_2$] (A = O, S).

2. Experimental details

All experiments were carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk-tube techniques. Hydrocarbon solvents were

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[*] Corresponding author.

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dried by distillation from sodium/potassium alloy in the presence of triglyme/benzophenone indicator. Dichloromethane was dried by distillation from calcium hydride and all solvents were saturated with nitrogen prior to use. The complexes [RhCl(CO)(PPh_3)$_2$] [6] and [RhCl(CS)(PPh_3)$_2$] [7] and the salt K[H_2B(bta)$_2$] [3b] were prepared according to published procedures. The isonitriles $CNC_6H_3Me_2$-2,6 (Aldrich) and $CNCMe_3$ (Aldrich) were obtained commercially. IR, NMR and MS spectra were obtained using Perkin Elmer 1720-X, Bruker WH-400, Perkin Elmer R34, Jeol JNM-EX270 and Kratos MS 80 instruments. Microanalytical data were obtained commercially from Medac Ltd, Brunel University, Middlesex, UK. Ligand substitution reactions of the complex [Rh{H_2B(bta)$_2$}(CO)(PPh_3)$_2$] were followed by tlc (Silica-gel) and by monitoring the disappearance of the carbonyl-associated band at 1998 cm^{-1}. Light petroleum refers to that fraction of boiling point range 40–60°C. Characteristic data for the new complexes are collected in Tables 1–3.

2.1. Preparation of [Rh{κ^2-H_2B(bta)$_2$}(CO)(PPh_3)$_2$]

A mixture of [RhCl(CO)(PPh_3)$_2$] (3.00 g, 4.34 mmol) and K[H_2B(bta)$_2$] (1.28 g, 4.50 mmol) in dichloromethane (250 cm^3) was stirred for 24 h and the solution was then filtered through Kieselguhr to remove precipitated KCl. The solvent was removed from the filtrate under reduced pressure and the residue triturated ultrasonically with diethyl ether (100 cm^3). The bright yellow solid was isolated by filtration, washed with diethyl ether (20 cm^3) and light petroleum (20 cm^3), and dried in vacuo. Yield 3.50 g (83%). Anal. Calc. for $C_{49}H_{40}BN_6OP_2Rh$: C, 65.0; H, 4.5; N, 9.3; P, 6.9%. Found: C, 64.5; H, 4.5; N, 9.8; P, 6.9%.

Table 1
IR data [a] (cm^{-1}) for the complexes [Rh] = Rh(PPh_3)$_2${H_2B(bta)$_2$}

Compound	ν(CA) [b]	ν(BH)	other
[Rh](CO)	2006 (1999)	2413	1311w, 1282w, 1265w, 1235w, 1209w, 1176s, 1150s, 1131vs, 1107s, 944w, 920w, 863w
[Rh](CS)	1372	2413	1264w, 1232w, 1209w, 1176s, 1150s, 1132vs, 1109s, 943w, 920w, 863w
[Rh]($CNC_6H_3Me_2$-2,6)	2115 (2120)	2412	1462 (CN), 1310w, 1286w, 1264w, 1225w, 1130s, 929w, 861w
[Rh]($CNC_6H_3Me_2$-2,6)(CO)	2141 2006	2413	

[a] Data were obtained from nujol mulls between KBr discs in the range 4000–400 cm^{-1}, IR data characteristic of triphenylphosphine ligands not listed. Values given in parentheses were obtained from dichloromethane solutions.
[b] A = O, S or NR.

Table 2
FAB mass spectroscopic data [a] for the new complexes [Rh] = Rh(PPh_3)$_2${H_2B(bta)$_2$}

Compound	M_{max} (Intensity%)[Assignment]
[Rh](CO)	904 (1.7) [M]$^+$, 655 (11.8) [M–H_2B(bta)$_2$]$^+$, 627 (27.6) [M–H_2B(bta)$_2$-CO]$^+$, 550 (1.3) [M–H_2B(bta)$_2$-CO-C_6H_5]$^+$, 393 (3.6) [M–H_2B(bta)$_2$-PPh_3]$^+$
[Rh](CS)	920 (1.8) [M]$^+$, 670 (54.8) [M–H_2B(bta)$_2$]$^+$, 409 (39.4) [M– H_2B(bta)$_2$-PPh_3)]$^+$
[Rh]($CNC_6H_3Me_2$-2,6)	1008 (4.1) [M]$^+$, 889 (100) [M–bta]$^+$, 758 (21.6) [M–H_2B(bta)$_2$]$^+$, 627 (48.5) [M–H_2B(bta)$_2$-CNR]$^+$, 496 (33.9) [M–H_2B(bta)$_2$-PPh_3]$^+$, 419 (11.7) [M–H_2B(bta)$_2$-PPh_3-C_6H_5]$^+$, 365 (2.9) [RhPPh_3]$^+$

[a] Data collected from matrices of the complexes in nitrobenzyl alcohol. Isotope patterns consistent with formulation of [M]$^+$.

Table 3
^{31}P-{^{1}H} and ^{1}H NMR data for the complexes [a] [Rh] = Rh(PPh_3)$_2${H_2B(bta)$_2$}

Compound	^{31}P-{^{1}H} [b] [J (RhP)]	^{1}H(δ) [c]
[Rh](CO)	31.4 [128.8]	4.13 [s(br), 2 H, BH_2], 6.94–7.68 [m(br), 38 H, PC_6H_5 and $C_6H_4N_3$: Resolves into 11 multiplets at −40°C]
[Rh](CS)	32.8 [142.4]	4.11 [s(br), 2 H, BH_2], 6.91–7.76 [m(br) × 6, 38 H, PC_6H_5 and $C_6H_4N_3$]
[Rh]($CNC_6H_3Me_2$-2,6)	30.4(br) 29.9(s) [d]	1.58 [s, 6 H, $C_6H_3(CH_3)_2$], 4.2 [s(v.br), integ. not reliable, BH_2], 6.88–7.70 [m × 7, 47 H, C_6H_5, C_6H_4-N_3 and C_6H_3]

[a] From saturated solutions of the complex in $CDCl_3$ at ambient temperature. Chemical shifts are given in ppm, coupling constants in Hz.
[b] Relative to external H_3PO_4 (δ 0.00). [c] Relative to internal $SiMe_4$ (δ 0.00). [d] Not resolved presumably due to dynamic processes.

2.2. Preparation of $[Rh\{\kappa^2\text{-}H_2B(bta)_2\}(CS)(PPh_3)_2]$

A solution of $[RhCl(CS)(PPh_3)_2]$ (3.00 g, 4.20 mmol) in degassed dichloromethane (150 cm^3) was treated with solid $K[H_2B(bta)_2]$ (1.24 g, 4.30 mmol) and the mixture stirred for 18 h. Examination of the mixture by tlc (silica gel/CH_2Cl_2) then showed that some starting material remained, and addition of a further 0.5 equivalents of $K[H_2B(bta)_2]$ did not cause the reaction to proceed to completion. The mixture was filtered through Kieselguhr to remove KCl and the filtrate was freed of volatiles. The residue was chromatographed on a water-cooled column loaded with silica gel to provide the starting material (eluant: CH_2Cl_2) and then a red zone (eluant thf: CH_2Cl_2 1:3), the eluate from which was evaporated to leave a residue which was crystallised from a mixture of dichloromethane and ethanol. Yield 3.42 g (94% based on consumed $[RhCl(CS)(PPh_3)_2]$; 0.40 g starting complex recovered).

2.3. Preparation of $[Rh\{\kappa^2\text{-}H_2B(bta)_2\}(SO_2)(PPh_3)_2]$

A solution of $[Rh\{H_2B(bta)_2\}(CO)(PPh_3)_2]$ (0.13 g, 0.13 mmol) in dichloromethane (10 cm^3) was treated with a stream of sulphur dioxide for 2 s. The flask was then stoppered and the mixture stirred for 20 min. Light petroleum (20 cm^3) was then added and the solvent volume reduced (rotary evaporator) to ca. 10 cm^3. The yellow-green solid was isolated by filtration and washed with light petroleum (10 cm^3), and dried in vacuo. Yield 0.11 g (84%).

2.4. Preparation of $[Rh\{\kappa^2\text{-}H_2B(bta)_2\}(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$

A solution of $[Rh\{H_2B(bta)_2\}(CO)(PPh_3)_2]$ (1.00 g, 1.0 mmol) in dichloromethane (50 cm^3) was treated with 2-xylyl isocyanide (0.26 g, 1.0 mmol) and the mixture stirred for 30 min. Ethanol (50 cm^3) was added and the solution concentrated under reduced pressure to ca. 20 cm^3. The yellow product was filtered off, washed with light petroleum, and dried in vacuo. Yield 0.94 g (83%). Anal. Calc. for $C_{57}H_{34}BN_7P_2Rh$: C, 67.9; H, 4.9; N, 9.7%. Found: C, 68.1; H, 5.3; N, 9.9%. Similar treatment with CN^tBu provide $[Rh\{H_2B(bta)_2\}(CN^tBu)(PPh_3)_2]$ in 76% yield.

Alternatively, the same reaction may be carried out in diethyl ether with comparable yields, however a reaction time of 3 d is necessary owing to the rapid formation and slow decomposition of $[Rh\{H_2B(bta)_2\}(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$ to give the desired complex.

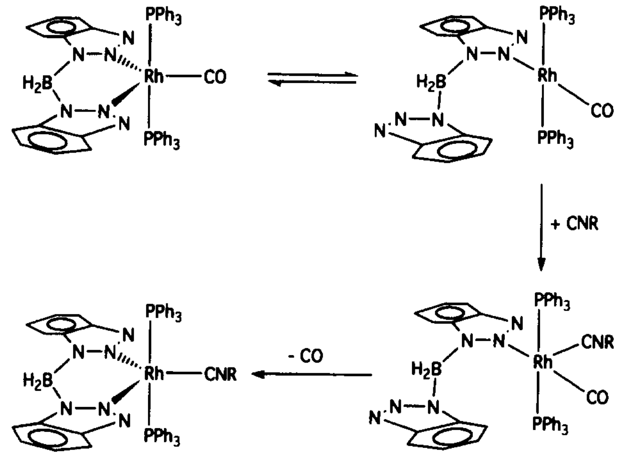
2.5. Preparation of $[Rh\{\kappa^1\text{-}H_2B(bta)_2\}(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$

A suspension of $[Rh\{H_2B(bta)_2\}(CO)(PPh_3)_2]$ (0.50 g, 0.56 mmol) and 2-xylyl isonitrile (0.80 g, 0.60 mmol) in diethyl ether was stirred for 15 min and the product was filtered off, washed with diethyl ether, and dried briefly in vacuo. Yield 0.50 g (88%). The complex is unstable with respect to CO elimination in solution, but solid samples were found to be stable for at least 3 years.

3. Results and discussion

The reaction of $[RhCl(CO)(PPh_3)_2]$ [6] with the salt $K[H_2B(bta)_2]$(**1a**) in dichloromethane leads to the clean, rapid and high yield formation of a yellow complex (Scheme 2). The IR spectrum (Nujol) of this complex shows, in addition to a strong carbonyl peak at 2006 cm^{-1} (2006 cm^{-1} in CH_2Cl_2), activity which may be attributed to the triazolyl groups of the bis(benzotriazol-1-yl)borato ligand, at 1176, 1150, 1131 and 1107 cm^{-1}, in addition to weaker bands in the regions 1200–1300 and 850–950 cm^{-1}. A weak structured band at 2413 cm^{-1} is assigned to $\nu(BH_2)$ stretching. The fine structure is lost in solution [CH_2Cl_2: 2430 cm^{-1}]. The FAB–MS spectrum of the complex shows a molecular ion at m/z 904 with the correct isotope pattern for the bis(phosphine) complex $[Rh(CO)\{H_2B(bta)_2\}(PPh_3)_2]$, in addition to fragmentations due to sequential loss of the borate ligand (m/z 655) and carbon monoxide (m/z 627). The formulation is supported by elemental microanalysis (C,H,N,P), but solution NMR data [^1H and ^{13}C] are equivocal owing to an apparent dynamic process which leads to broadening of all aromatic resonances. It is not clear whether this involves reversible dissociation of a phosphine ligand or one arm of the benzotriazolyl chelate. The stereochemistry at rhodium is indicated by the appearance of a doublet resonance in the ^{31}P NMR spectrum [J (RhP) 128.8 Hz], consistent with a *trans* disposition of the two phosphines in a trigonal bipyramid. It was not possible to confirm this from the ^{13}C NMR data owing to the broadness of the signal from the carbonyl ligand [δ 190.3 ppm], which precluded resolution of the coupling to rhodium and phosphorus.

The thiocarbonyl complex $[Rh(CS)\{H_2B(bta)_2\}(PPh_3)_2]$ may be similarly obtained from the reaction of Wilkinson's prototypical thiocarbonyl complex $[RhCl(CS)(PPh_3)_2]$ [7] with $K[H_2B(bta)_2]$ in dichloromethane (Scheme 2). The orange product of this reaction also appears to undergo a phosphine-based fluxional process at room temperature, leading to broad and poorly resolved ^1H and ^{13}C NMR spectra. However, the spectroscopic data are, in general, similar to those for the carbonyl derivative, with one notable exception: whilst the FAB–MS spectrum of the carbonyl compound showed a strong peak resulting from borate and CO loss from the parent molecular ion, no such peak is present in the spectrum of the thiocarbonyl derivative. Rather, loss of borate is followed by loss of a phosphine



Scheme 3. Synthesis of $[Rh\{H_2B(bta)_2\}(CNR)(PPh_3)_2]$, R = $C_6H_3Me_2$-2,6,CMe_3.

ligand. This is a reflection of the enhanced strength of metal–carbon bonds to thiocarbonyl ligands relative to those to carbonyls [8]. The thiocarbonyl ligand gives rise to an IR band at 1327 cm^{-1}.

The apparent fluxionality of the two complexes suggested that coordinatively unsaturated species were present in their solutions, either as a result of phosphine dissociation ($[Rh(CO)\{H_2B(bta)_2\}(PPh_3)]$) or dissociation of one arm of the $H_2B(bta)_2$ chelate ($[Rh(CO)\{\kappa^1\text{-}H_2B(bta)_2\}(PPh_3)_2]$). Accordingly, reactions with ligands capable of trapping such species were investigated. In these reactions, however it is the carbonyl ligand which is ultimately lost from the coordination sphere.

The isocyanides CNR (R = $C_6H_3Me_2$-2,6, CMe_3) react rapidly with $[Rh(CO)\{H_2B(bta)_2\}(PPh_3)_2]$ in dichloromethane solution via substitution of the carbonyl ligand to provide the yellow isonitrile complexes $[Rh\{H_2B(bta)_2\}(CNR)(PPh_3)_2]$ in spectroscopically (IR) quantitative yields (Scheme 3). Spectroscopic data for the $CNC_6H_3Me_2$-2,6 derivative are similar to those for the precursor, indicating once again that dynamic processes occur in solution at room temperature (^1H, ^{13}C NMR). The FAB–MS spectrum for this complex shows, in addition to a molecular ion [m/z 1008], fragmentations due to loss of the borate chelate [m/z 758], followed by that of the isonitrile ligand [m/z 627] or triphenylphosphine [m/z 496]. In contrast to the spectra for the derivatives discussed above the most abundant peak appears to result from loss of benzotriazole [m/z 889]. It is not clear why the presence of the isonitrile ligand should facilitate this particular fragmentation.

There is no evidence for the formation of an intermediate when the reaction is carried out in dichloromethane, but if the reaction between $[Rh\{H_2B(bta)_2\}(CO)(PPh_3)_2]$ and xylyl isonitrile is carried out in diethyl ether a dark blue compound precipitates immediately. This compound is converted instantaneously and quantitatively into $[Rh\{H_2B(bta)_2\}(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$ upon dissolution in dichloromethane, even when prewashed extensively with diethyl ether and petroleum ether (to remove any phosphine liberated). The solid state IR spectrum of this intermediate shows absorbances due to borate [$\nu(BH_2)$: 2413 cm^{-1}], isonitrile (2141 cm^{-1}) and carbonyl (2006 cm^{-1}) ligands.

In view of the propensity of dihydrobis(pyrazolyl) borate ligands to stabilise coordinative unsaturation by agostic coordination of a B–H bond to a metal centre, an alternative mechanism involving dissociation of a carbonyl or phosphine ligand with formation of an albeit weak B–H–Rh interaction was originally more attractive, and thus the presence of carbonyl, isonitrile and both phosphine ligands in the intermediate is suprising. The appearance of the carbonyl band in the IR spectrum of the intermediate at a value indistinguishable from that for the starting material was initially suspicious, but the relative intensities of carbonyl and isonitrile absorbances was invariant for a number of preparations of "$[Rh(CO)(CNC_6H_3Me_2\text{-}2,6)\{H_2B(bta)_2\}(PPh_3)_2]$" independent of the granularity of the sample of $[Rh(CO)\{H_2B(bta)_2\}(PPh_3)_2]$ used in the reaction suspension. Extensive washing of the blue intermediate with diethyl ether and light petroleum failed to extract any free triphenylphosphine. Since no triphenylphosphine appears to be liberated during the formation of this intermediate, we assume that the reaction proceeds via an unusual dissociation of one arm of the bis(benzotriazolyl)borate chelate (Scheme 3) to provide a complex $[Rh\{\kappa^1\text{-}H_2B(bta)_2\}(CO)(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$. We have been unable to obtain any spectroscopic data for this intermediate in solution owing to the extreme rapidity of its conversion into $[Rh(CNC_6H_3Me_2\text{-}2,6)\{H_2B(bta)_2\}(PPh_3)_2]$ (2–3 s) upon dissolution. We have previously had cause to suggest monodentate coordination of the $H_2B(bta)_2$ ligand [1].

We are currently investigating the further substitution and oxidative addition chemistry of these complexes.

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