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Synthesis of a ruthenium bis(diisopropylamino-(isocyano)borane) complex from the activation of an amino(cyano)borane†

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The reactivity of the amino(cyano)borane $^{i}Pr_2NBH(CN)$ (**2**) towards $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**3**) was investigated. Our study reveals that the formation of the bis(isocyanoborane) ruthenium complex $[RuH(CN)(CN\text{-}BHN^{i}Pr_2)_2(PCy_3)_2]$ (**6**) occurs *via* the intermediacy of the bis(σ-B–H) ruthenium complex $[RuH(CN)(H_2BN^{i}Pr_2)(PCy_3)_2]$ (**5**). This transformation involves BCN linkage isomerisation in **2**. The diisopropylaminoborane ligand in **5** can be displaced to ultimately produce the bis(σ-borane) complex $[RuH_2(\eta^2{:}\eta^2\text{-}H_2BN^{i}Pr_2)(PCy_3)_2]$ (**4**) as a by-product.

Introduction

Isonitriles (R–N≡C:) are well known organic molecules and their role as ligands in coordination chemistry has been well documented.[1–4] Often considered as CO analogues, isonitriles coordinate to transition metal centers *via* a σ/π synergistic bonding scheme. They generally exhibit a more pronounced σ-donor ability[5] than CO, although the π-acceptor character is strongly influenced by the nature of the substituent at the nitrogen atom.[6] 'Functionalized' isocyanides have received little attention.[7] In particular, introduction at nitrogen of a *pull* group such as a boryl substituent,[8–11] likely to stabilize the lone pair in the adjacent position, has been rarely explored (Fig. 1).

Fig. 1 Functionalized isocyanide complexes.

As a result, boron substituted isocyanide metal complexes of general formulation $L_nM(C{\equiv}N\text{-}BR^1R^2)$ are scarce and mostly limited to group 6 transition metals (Cr, Mo, W).[12–14] Their syntheses are restricted to salt elimination from organometallic nucleophiles $[M(CO)_5(CN)]^-$ and suitable haloboranes,[12,13] or to isomerization of the BCN linkage of a B-cyanoborane upon coordination to chromium.[12,14,15]

As part of our ongoing program on the chemistry of σ-complexes and more particularly on bis(σ-borane) and agostic borane complexes,[16–20] we addressed the synthesis of the amino(cyano)borane $^{i}Pr_2NBH(CN)$ (**2**) and its reactivity with the ruthenium precursor $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**3**). We report here the isolation and the characterization of a new cyano ruthenium bis(isocyano)borane complex. The reaction takes place *via* the intermediacy of a bis-σ borane complex. Our study shows that isomerization of the BCN linkage in **2** drives the reaction by displacement of the diisopropylaminoborane fragment.

Results and discussion

The strategy for the synthesis of cyanoborane **2** was first based on the dehydrogenation of the amine-borane precursor **1**. The stoichiometric reaction of diisopropylammonium chloride with sodium cyanoborohydride did not lead to **1** but to the corresponding ammonium borohydride ion pair ($^{i}Pr_2NH_2$, BH_3CN), even after a prolonged reaction time in refluxing THF. **1** could be cleanly obtained by the reaction of diisopropylamine with oligomeric cyanoborane according to a modified literature procedure developed by Spielvogel *et al.*[21,22] Unfortunately, and despite all our efforts, cyanoborane **2** could not be

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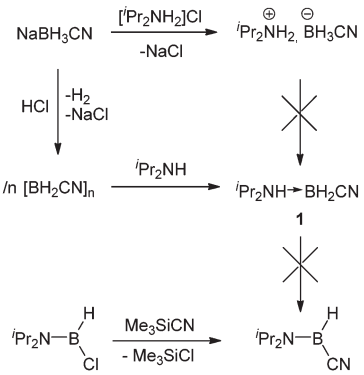


Scheme 1 Synthesis of diisopropylamine-cyanoborane **1** and diisopropylamino-(cyano)borane **2**.

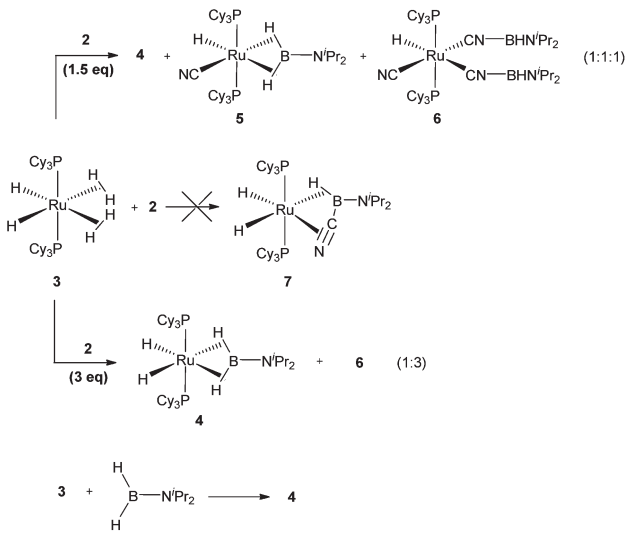
cleanly generated by a simple dehydrogenation from **1**. The cyano/halogen exchange reaction from $^{i}Pr_2NBHCl$ and Me_3SiCN[23] circumvented the problem and afforded **2** that was isolated in 85% yield and characterized by multinuclear NMR spectroscopy (Scheme 1).

The ^{11}B NMR spectrum of **2** displays a doublet at δ 24.7 (**1**: δ −23.8, t) with a J_{BH} coupling constant of 143 Hz. In the $^{13}C\{^{1}H\}$ NMR spectrum, the cyano carbon atom exhibits a broad quartet at δ 125.30 with a coupling constant of 98 Hz, indicative of the B–CN linkage in **2**. The IR spectrum of **2** exhibits a peak at 2200 cm^{-1} in the expected region for the nitrile CN vibration.[14]

The reaction of **2** (1.5 equiv.) with $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**3**), in C_6D_6 at room temperature, led to the complete disappearance of the starting ruthenium complex and the formation of complexes **4**, **5** and **6** in a 1 : 1 : 1 integration ratio, respectively, according to $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra. In the presence of 3 equiv. of **2**, only complexes **4** and **6** were observed in a 1 : 3 integration ratio, respectively (ESI Fig. S1–S5†). No cyanoborane ruthenium complex such as **7** could be observed in the reaction mixture (Scheme 2).

The bis(σ-B–H) diisopropylamino ruthenium complex $[RuH_2(\eta^2\text{:}\eta^2\text{-}H_2BN^{i}Pr_2)(PCy_3)_2]$ (**4**) was clearly identified by NMR spectroscopy by comparison with the data of an authentic sample prepared independently from diisopropylaminoborane ($^{i}Pr_2NBH_2$) and $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**3**).[18]

Complex $[RuH(CN)(CN\text{-}BHN^{i}Pr_2)_2(PCy_3)_2]$ (**6**) was fully characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction. The $^{31}P\{^{1}H\}$ NMR spectrum of **6** shows a singlet at δ 56.40 for the two magnetically equivalent PCy_3. The $^{11}B\{^{1}H\}$ NMR spectrum displays a signal at δ 22.6. The ^{1}H NMR spectrum exhibits a triplet hydride resonance at δ −7.56 that sharpens into a singlet upon phosphorus decoupling. The hydride atom is *cis* to two PCy_3 ligands, as indicated by the small coupling constant value ($^{2}J_{HP}$ = 22.7 Hz). The presence of two signals at δ 4.46 and 4.38 that sharpen upon boron decoupling is indicative of two non-equivalent uncoordinated BH groups. The presence of two sets of two septets at δ 4.55 and δ 4.17, and at δ 2.97 and δ 2.86, respectively, and of two sets of two doublets at δ 1.13 and δ 1.01, and at δ 1.05 and δ 0.97, respectively, is in favour of two non-equivalent $B(H)N^{i}Pr_2$ containing ligands at ruthenium. In solution, the geometry around the metal center in **6** was supported by $^{13}C\{^{31}P\}$, $^{13}C\{^{1}H;^{31}P\}$ (ESI Fig. S6–S9†) and $[^{13}C\{^{1}H\}, ^{1}H]$-HMBC experiments (Fig. 2). The $^{13}C\{^{1}H\}$ NMR spectrum exhibits a well-resolved triplet at δ 141.27 for the cyano ligand *cis* to two PCy_3 as indicated by the small J_{CP} coupling constant of 15 Hz. Two isocyano CNB resonances appear as deshielded triplets at δ 196.55 and 195.86 with a small *cis* J_{CP} coupling constant of 12 Hz and 7 Hz, respectively. These isocyanide values are comparable to those reported by Caulton *et al.* for the mono isocyanide hydrido chloro Ru(II) complex $[RuHCl(CN\text{-}Et)(P^{i}Pr_3)_2]$ (δ 182, *cis* $^{2}J_{PC}$ = 12 Hz).[24] The same authors reported that, when monitoring by ^{31}P NMR the reaction of methylisocyanide with $[RuHCl(P^{i}Pr_3)_2]_2$, the bis isocyanide species $[RuHCl(CN\text{-}Me)_2(P^{i}Pr_3)_2]$ was transiently observed prior to the mono isocyanide complex $[RuHCl(NC\text{-}Me)(P^{i}Pr_3)_2]$.[24]



Scheme 2 Reactivity of **2** with complex **3**.

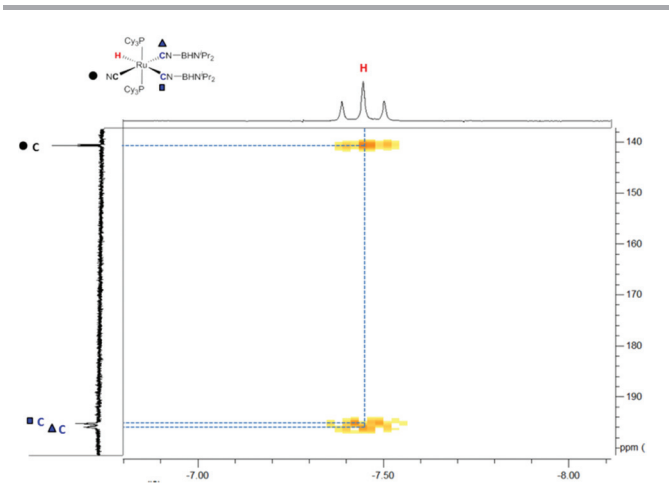


Fig. 2 $[^{13}C\{^{1}H\}, ^{1}H]$-HMBC NMR experiment of **6** in C_6D_6.

Complex **5** was fully characterized by multinuclear NMR spectroscopy from a C_6D_6 solution of **4**, **5** and **6** in equimolar ratio. The data obtained for **5** are in agreement with a diisopropylaminoborane unit bis(σ-B–H) coordinated to the 14 valence electron $[RuH(CN)(PCy_3)_2]$ fragment. In the $^{31}P\{^1H\}$ NMR spectrum, **5** shows a singlet at δ 61.3 for the two equivalent PCy_3 ligands, more shielded than in **4** (δ 77.8). The $^{13}C\{^1H\}$NMR spectrum exhibits a well-resolved triplet at δ 141.73 ($^2J_{CP}$ = 17.5 Hz) for the cyano group (ESI Fig. S6†). In the ^1H NMR spectrum, in the hydride zone, a set of three signals in a 1 : 1 : 1 integration ratio was observed: two broad signals at δ −4.10 and δ −11.79, and a triplet of doublets at δ −11.60. The broad signals sharpened upon boron decoupling whereas the other one collapsed into a doublet upon phosphorus decoupling allowing the measurement of a $^2J_{HH}$ coupling constant value of 6 Hz (ESI Fig. S2, S3†). Complex **5** displays NMR data similar to those reported for the ruthenium complex $RuHCl(\eta^2{:}\eta^2\text{-}H_2BNMe_2)(PCy_3)_2$.[25]

The X-ray structure of **6** was determined at 110 K. As illustrated in Fig. 3, the asymmetric unit contains two independent molecules $[RuH(CN)(NC\text{-}BHN^iPr_2)_2(PCy_3)_2]$ (**6a** and **6b**) in a head-to-tail disposition and presents similar geometrical features (Table 1). The structure of **6a** is enlarged for clarity (Fig. 3).

The Ru atom is in a distorted octahedral environment with the PCy_3 ligands in pseudo axial positions bent away from the isocyanoboranes to reduce steric repulsion (P–Ru–P: 156.151(4)° (**6a**), 159.151(4)° (**6b**)). The coordination sites in the equatorial plane of the ruthenium atom are occupied by one hydride and three coplanar carbon atoms with the cyano ligand *cis* to the hydride. The Ru–C (**6a**: 2.088(4); **6b**: 2.088(4)) and the terminal C–N bond distances (**6a**: 1.108(5) Å; **6b**: 1.121(5) Å) are comparable to those reported in monomeric Ru(II) $[CpRuL_2(CN)]$ complexes.[26–28] The structure is almost collinear through the B1–N1–C1–Ru1 linkage (B1–N1–C1: 169.1(4)° (**6a**); 172.7(4)° (**6b**); N1–C1–Ru1: 173.4(4)° (**6a**); 174.9(3)° (**6b**)) *cis* to the cyano ligand. This geometrical feature is in favour of sp hybridization for both N1 and C1. On the contrary, the B2–N3–C8–Ru1 linkage *trans* to the cyano ligand reveals a substantial deviation from linearity at the N3 nitrogen atom (B2–N3–C8: 155.4(4) (**6a**); 155.2(4) (**6b**); N3–C8–Ru1 178.2(3) (**6a**); 177.8(4) (**6b**)). A shortening of the Ru1–C8 bond (**6a**: 1.920(4); **6b**: 1.925(4)) accompanies this angular variation, when compared to the near-linear B1–N1–C1–Ru1 group (Ru1–C1: 1.972(4) (**6a**); 1.964(4) (**6b**)). The N3–C8 (**6a**: 1.184(5); **6b**: 1.186(5)) and N1–C1 (**6a**: 1.178(5); **6b**: 1.173(5)) bond lengths are however similar, and are set at the upper limit for a coordinated isocyano CN group when compared with those in the only two reported crystal structures $R^2R^1BNCCr(CO)_5$ ($R^2R^1B = C_4H_4N(Et)B$ (NC = 1.153(4) Å),[14] $((Me_3Si)_2CH)_2B$ (NC = 1.159(5) Å [13]) and Ru(II) isocyanide complexes (NC ~ 1.15–1.16 Å).[29–32] They both exhibit a partial C–N triple bond character. The isocyano carbon ruthenium distances Ru1–C1 and Ru1–C8 are shorter than the sum of the single-bond covalent radii (2.00 Å),[33] thus suggesting a partially double bond character[34–39] as a result of the metal-to-ligand π-back bonding that takes place more effectively towards the isocyanoborane *trans* to the cyano group and involving a deviation from linearity of the CN–B axis at the N atom. The nitrogen boron distances in **6a**/**6b** (1.335 < NB <

Table 1 Selected geometrical parameters (distances in Å, angles in °) for the experimental and calculated structures **6a**/**6b** and **6′**, respectively

	Experimental **6a**/**6b**	Computed **6′**
Ru1–P1	2.3478(10)/2.3488(11)	2.398
Ru1–P2	2.3629(11)/2.3617(11)	2.405
Ru1–C15	2.088(4)/2.088(4)	2.063
Ru1–C8	1.920(4)/1.925(4)	1.911
Ru1–C1	1.972(4)/1.964(4)	1.958
Ru1–Hy1	1.69(4)/1.56(6)	1.642
C15–N5	1.108(5)/1.121(5)	1.174
C1–N1	1.178(5)/1.173(5)	1.190
N1–B1	1.449(6)/1.454(6)	1.442
B1–N2	1.385(6)/1.356(7)	1.397
B1–H1	1.11(4)/1.09(5)	1.196
C8–N3	1.184(5)/1.186(5)	1.198
N3–B2	1.477(6)/1.458(6)	1.442
B2–N4	1.371(6)/1.388(6)	1.398
B2–H2b	1.15(5)/1.24(4)	1.197
P1–Ru1–P2	156.15(4)/159.51(4)	157.40
Ru1–C1–N1	173.4(4)/174.9(3)	174.23
Ru1–C8–N3	178.2(3)/177.8(4)	176.14
C1–N1–B1	169.1(4)/172.7(4)	179.99
C8–N3–B2	155.4(4)/155.2(4)	159.96
Ru1–C15–N5	178.5(4)/177.6(4)	176.23
N1–B1–N2	120.0(4)/121.6(5)	121.72
N3–B2–N4	122.1(5)/121.2(4)	122.84

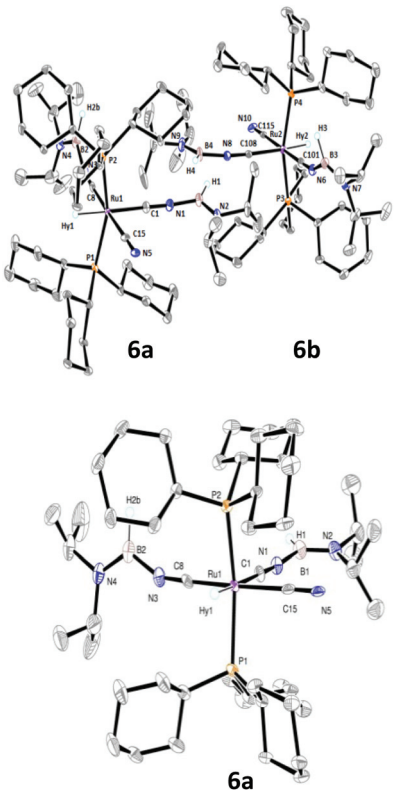


Fig. 3 X-ray crystal structure of **6**.

1.495 Å) are in the range of values observed for amino substituted trigonal-planar boron groups.[14,20,40–45]

The title compound was optimized by DFT (B3PW91) calculations (**6′**). The cyano C–N and the Ru–P distances are computed slightly too long but the other geometrical parameters are in good agreement with the X-ray data (see Table 1), and more importantly, the hydride location by X-ray diffraction in **6a**/**6b**, which can always be subjected to controversy, was confirmed by the DFT optimization[18,19,46,47] of **6′** with the Ru–H bond computed to be 1.642 Å (Ru–H = 1.69(4) Å (**6a**), 1.56(6) Å (**6b**)). The isocyanoborane *trans* to the hydride is computed linear (C1–N1–B1: 179.99° (**6′**) *vs.* 169.1(4)° (**6a**), 172.7(4)° (**6b**)) and the deviation from linearity in the one *cis* to the hydride is well reproduced (C8–N3–B2: 159.96° (**6′**) *vs.* 155.4(4)° (**6a**), 155.2(4)° (**6b**)). The small angular variations in **6′** when compared with **6a**/**6b** probably result from too long Ru–P distances, thus affecting the steric repulsions.

Conclusions

In this study, we have shown that the reaction of $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**3**) with an excess diisopropylamino(cyano)borane $^iPr_2NBH(CN)$ (**2**) led to the formation of the hydrido cyano bis(diisopropylamino(isocyano)borane) ruthenium complex $[RuH(CN)(CN\text{-}BHN^iPr_2)_2(PCy_3)_2]$ (**6**) as the major compound. **6** was fully characterized by multinuclear NMR spectroscopy and single-crystal X-ray diffraction. This reaction occurred *via* the intermediacy of $[RuH(CN)(H_2BN^iPr_2)(PCy_3)_2]$ (**5**), a compound formulated as a bis(σ-B–H) species on the basis of NMR data. In the presence of a large excess of **2**, complex **5** was not observed in the reaction medium. The formation of **6** is likely resulting from diisopropylaminoborane displacement at ruthenium and BCN linkage isomerisation in **2**.

Experimental

Materials and methods

All experiments were performed under an atmosphere of dry argon using standard Schlenk and glove box techniques. Unless stated all chemicals were purchased from Aldrich and used without further purification. Diisopropylaminoborane,[48] diisopropylaminochloroborane,[19] $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$[49] were prepared according to a literature procedure. THF was freshly distilled under argon from Na/benzophenone. All other solvents were purified and dried through an activated alumina purification system (MBraun SPS-800). NMR solvents were dried using appropriate methods and degassed prior to use. NMR samples of sensitive compounds were prepared under an argon atmosphere. Nuclear magnetic resonance spectra were recorded on Bruker AV 300, 400 or 500 spectrometers operating at 300.13, 400.13 or 500.33 MHz, respectively for ^1H, 121.5, 162 or 202.5 MHz, respectively for ^{31}P, 75.48 or 100.62 MHz, respectively for ^{13}C and 96.29 or 128.38 MHz, respectively for ^{11}B. ^1H and ^{13}C chemical shifts are reported in ppm referenced internally to residual protio-solvent, while ^{31}P are relative to 85% H_3PO_4, and ^{11}B are relative to $BF_3{\cdot}OEt_2$ external references. Chemical shifts are quoted in δ (ppm) and coupling constants in Hertz. The following abbreviations are used: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were performed by the 'in house' service of the Laboratoire de Chimie de Coordination, Toulouse.

Synthesis of diisopropylamine-(cyano)borane (**1**). $NaBH_3CN$ (2.69 g, 41.5 mmol) was suspended in Et_2O (60 mL), cooled to 0 °C and a 1.0 M ethereal HCl solution (42 mL, 42 mmol) was added dropwise (*ca.* 1 h) with stirring. After warming up to room temperature, the solution was refluxed for 1 h, cooled again, and filtered. Diisopropylamine (6.2 mL, 42.8 mmol) was added to the supernatant and the resulting solution refluxed for 12 h. After filtration and aqueous work-up, the ethereal phase was dried over $MgSO_4$, filtered and evaporated to dryness. The resulting white powder was crystallized in ether at 0 °C affording **1** as a colourless solid (1.63 g, 28% yield). ^1H NMR (400.13 MHz, C_6D_6) δ 5.42 (br s, 1 H, NH), 2.89 (heptd, $^3J_{CHCH}$ = 6.6 Hz, $^3J_{CHNH}$ = 3.7 Hz, 2 H, CH ^{i}Pr), 2.21 (qd, $^1J_{BH}$ = 103 Hz, $^3J_{CHNH}$ = 2.5 Hz, 2 H, BH_2), 1.00 (d, $^3J_{HH}$ = 6.6 Hz, 12 H, CH_3 ^{i}Pr). ^{11}B NMR (128.38 MHz, C_6D_6) δ −23.8 (t, $^1J_{BH}$ = 103 Hz, BH_2). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$) δ 136.64 (m, CN), 52.18 (s, CH ^{i}Pr), 20.21, 18.90 (s, CH_3 ^{i}Pr). IR (cm^{-1}) ν(BH) 2447, 2414; ν(CN) 2198. Anal. Calc for $C_7H_{17}BN_2$: C, 60.04; H, 12.24; N, 20.00. Found: C, 60.10; H, 10.80; N, 20.00.

Synthesis of diisopropylamino(cyano)borane (**2**). Me_3SiCN (2.11 mL, 16.8 mmol) was added to neat $^iPr_2NBHCl$ (2.48 g, 16.8 mmol) and the mixture was stirred for 24 h at room temperature. Me_3SiCl was then removed at room temperature under reduced pressure (30 mbar) and **2** was purified by trap-to-trap distillation and isolated as a colourless liquid (1.96 g, 85% yield). ^1H NMR (300.13 MHz, C_6D_6) δ 3.98 (q, $^1J_{BH}$ = 143 Hz, 1 H, HB), 3.87, 2.80 (hept, $^3J_{HH}$ = 6.7 Hz, 1 H, CH ^{i}Pr), 0.81, 0.78 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH_3 ^{i}Pr). ^{11}B NMR (96.29 MHz, C_6D_6) δ 24.7 (d, $^1J_{BH}$ = 143 Hz, BH). $^{13}C\{^1H\}$ NMR (100.62 MHz, C_6D_6) δ 125.30 (q, $^1J_{CB}$ = 98 Hz, BCN), 54.08, 48.79 (s, CH ^{i}Pr), 26.13, 22.53 (s, CH_3 ^{i}Pr). IR (cm^{-1}) ν(BH) = 2553; ν(CN) = 2208.

$[RuH(CN)(H_2BN^iPr_2)(PCy_3)_2]$ (**5**). **2** (1.5 equiv., 0.058 mmol) in C_6D_6 (1.5 mL) was added to a C_6D_6 solution (0.5 mL) of **3** (25.8 mg, 0.039 mmol). The solution was stirred for 3 h at room temperature prior to NMR analysis. Complex **5** was not isolated from the solution containing **4**, **5** and **6** in a 1 : 1 : 1 ratio. Selected NMR data: ^1H NMR (400.13 MHz, C_6D_6) δ 3.76, 2.95 (sept, $^3J_{HH}$ = 6.5 Hz, 1 H, CH ^{i}Pr), 1.13, 1.07 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH_3 ^{i}Pr), −4.10 (bs, 1 H, RuHB (*cis* to CN)), −11.60 (td, $^2J_{HP}$ = 21 Hz, $^3J_{HH}$ = 6 Hz, 1 H, RuH), −11.79 (br, 1 H, RuHB (*trans* to CN)). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6) δ 61.3 (s, PCy_3). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 141.73 (t, $^2J_{CP}$ = 17.5 Hz, RuCN), 51.08, 46.14 (s, CH ^{i}Pr), 25.57, 22.90 (14 (s, CH_3 ^{i}Pr)). $^{11}B\{^1H\}$ NMR (128.38 MHz, C_6D_6) δ 29 (br, BH).

Synthesis of $[RuH(CN)(CNBHN^iPr_2)_2(PCy_3)_2]$ (**6**). A pentane solution (0.5 mL) of **2** (0.1 mmol, 3 equiv.) was added to a stirred suspension of $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (**3**) (23 mg, 0.03 mmol) in pentane (3 mL). The stirring was stopped and after 24 h without stirring, colourless crystals of **6** (6.1 mg,

21% yield) could be isolated from the solution. ^{1}H NMR (400.13 MHz, C_6D_6) δ 4.55, 4.17 (sept, $^{3}J_{HH}$ = 6.6 Hz, 1 H, CH ^{i}Pr), 4.46 and 4.38 (br, 1 H, BH), 2.97 and 2.86 (sept, $^{3}J_{HH}$ = 6.8 Hz, 1 H, CH ^{i}Pr), 1.30–2.70 (m, 66 H, PCy_3), 1.13 and 1.01 (d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, CH_3 ^{i}Pr), 1.05 and 0.97 (d, $^{3}J_{HH}$ = 6.6 Hz, 6 H, CH_3 ^{i}Pr), −7.56 (t, $^{2}J_{HP}$ = 22.7 Hz, 1 H, RuH). ^{11}B NMR (128.38 MHz, C_6D_6) δ 22.6 (br, BH). $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6) δ 56.40 (s, PCy_3). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) δ 196.55 (t, $^{2}J_{CP}$ = 12 Hz, BNCRu), 195.88 (t, $^{2}J_{CP}$ = 7 Hz, BNCRu), 141.27 (t, $^{2}J_{CP}$ = 15 Hz, RuCN), 49.44, 49.02, 45.56 and 45.45 (s, CH ^{i}Pr), 37.23 (m), 30.30, 28.85 (m), 27.86 (PCy_3), 26.97, 26.85, 22.65, 22.56 (s, CH_3 ^{i}Pr). IR (cm^{-1}): 2103 (w, νCN); 2053 and 1971 (vs, RuH(CN)(CNB) coupled modes), 1899 (w, νRuH). Anal. Calc for $C_{51}H_{97}B_2N_5P_2Ru$: C, 63.48; H, 10.13; N, 7.26. Found: C, 64.52; H, 10.37; N, 6.33.

X-ray diffraction analyses

Data were collected at low temperature (110 K) on a Bruker Kappa Apex II diffractometer[50] using a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems Cryostream Cooler device. The structure was solved by the direct method using SIR92,[51] and refined by means of least-squares procedures on an F^2 with SHELXL97[52] (a program included in the software's package WinGX version 1.63).[53] The atomic scattering factors were taken from International Tables for X-ray Crystallography.[54] Except for Hy1 and Hy2, all hydrogen atoms were placed geometrically, and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ where $P = (Fo^2 + 2Fc^2)/3$. It was not possible to resolve diffuse electron-density residuals (enclosed solvent molecule). Treatment with the SQUEEZE facility from PLATON[55] resulted in a smooth refinement. Since a few low order reflections are missing from the data set, the electron count will be underestimated. Thus, the values given for D(calc), F(000) and the molecular weight are only valid for the ordered part of the structure. Drawing of molecules was performed with the program ORTEP32[56] with 30% probability displacement ellipsoids for non-hydrogen atoms. Crystal data of **2** are available as ESI† (CCDC number 894081).

Computational details

All the calculations have been performed with the Gaussian 09 package at the B3PW91 level of hybrid density functional theory.[57–59] For the optimization of geometry, the ruthenium atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis sets,[60] augmented by an f polarization function.[61] The phosphorus atom was represented by RECP from the Stuttgart group and the associated basis set,[62] augmented by a d polarization function.[63] The remaining atoms (C, H, N, B) were represented by a 6-31G(d,p) basis set.

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