Triphenylcyanoborate Complexes of Rhodium. A Nitrogen-15 NMR Study of $[Rh(NCBPh_3)(PPh_3)_3]$ and $[Rh(CNBPh_3)(PPh_3)_3]$ and Their Derivatives

Laurence Carlton* and Rosemarie Weber

Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, Johannesburg, Republic of South Africa

Received February 8, 1996[⊗]

The isomeric compounds $[Rh(NCBPh_3)(PPh_3)_3]$ (**1**) (prepared from $[RhCl(PPh_3)_3]$ and $K[NCBPh_3]$) and $[Rh(CNBPh_3)(PPh_3)_3]$ (**2**) (prepared from $[Rh(CN)(PPh_3)_3]$ and BPh_3) undergo ligand exchange with pyridine (py) to give *cis*-$[Rh(NCBPh_3)(PPh_3)_2(py)]$ and *trans*-$[Rh(CNBPh_3)(PPh_3)_2(py)]$ and with L = ethylene (reversibly), carbon monoxide, and 2,6-xylyl isocyanide (XNC) to give *trans*-$[Rh(X)(PPh_3)_2(L)]$ (X = $NCBPh_3$, $CNBPh_3$) and oxidative addition with hydrogen (reversibly) and triphenyltin hydride to give $[Rh(X)(H)_2(PPh_3)_3]$ and $[Rh(X)(H)(SnPh_3)(PPh_3)_2]$, respectively; triphenylsilane combines with **1** (reversibly) but not with **2**. By heating **1** to 100 °C in an inert solvent, the rearrangement of **1** to **2** is observed. Complex **1** in DMSO combines with oxygen to yield a product formulated as a sulfonium salt, although in CH_2Cl_2 it is unreactive toward oxygen unlike **2** which forms an O_2 adduct. In a solution of toluene containing pyridine or substituted pyridines in the presence of oxygen, **1** forms *cis*-$[Rh(NCBPh_3)(O_2)(PPh_3)_2(py)]$ while **2** loses BPh_3 to give $[Rh(CN)(O_2)(PPh_3)_2(py)]$. Hydrogen is bound reversibly by *trans*-$[Rh(CNBPh_3)(PPh_3)_2(py)]$ and irreversibly by *cis*-$[Rh(NCBPh_3)(PPh_3)_2(py)]$. A comparison of the properties of **1** and **2** and their derivatives shows the N-bonded isomers to be the more electrophilic and the N−B bond to be significantly more labile than the C−B bond. Nitrogen-15 NMR data are reported for complexes enriched to 99% in ^{15}N.

Introduction

Complexes of the trihydrocyanoborate ion were first isolated approximately 25 years ago in studies of the reaction of transition metal chloro or perchlorate complexes with $Na(BH_3CN)$[1] and of the reaction of transition metal salts with this reagent in the presence of tertiary phosphines.[2] In view of the bonding possibilities offered by these compounds, much subsequent work has focused on elucidation of structure, with the characterization of complexes in which BH_3CN^- is bound in either a terminal[3] or a bridging[4] mode. The trihydrocyanoborate ion exists in the two forms $[NCBH_3]^-$ and $[CNBH_3]^-$ which have been prepared as sodium salts.[5] With the triphenylcyanoborate ion, which has more restricted bonding options, the derivatives $[Cu(NCBPh_3)(PPh_3)_3]$,[1c] $[M(Cp)(CO)_2(NCBPh_3)]$ (M = Fe, Ru),[6] and $[Rh(C_5Me_5)(S_2PMe_2)(NCBPh_3)_3]$[7] are known and have been assigned an N-bonded structure on the basis of infrared data. Our interest in the triphenylcyanoborate ligand arises from studies of complexes with N-donor ligands and of complexes that can activate E−H (*e.g.*, E = Si, Sn) bonds. We report the preparation, some chemistry, and a nitrogen-15 NMR study of $[Rh(NCBPh_3)(PPh_3)_3]$ and $[Rh(CNBPh_3)(PPh_3)_3]$.

Experimental Section

$[RhCl(PPh_3)_3]$ was prepared by the method of Wilkinson *et al*.,[8] and $[Rh(CN)(PPh_3)_3]$ by the method of Favero and Rigo.[9] $KC^{15}N$ (99% enriched) and BPh_3 were purchased from Aldrich. CH_2Cl_2 was distilled from P_2O_5 and toluene, benzene, and pyridine were dried over CaH_2; other solvents and reagents were of the highest available purity and were used without further treatment. All reactions other than those involving H_2, CO, O_2, and C_2H_4 were carried out under an argon atmosphere. NMR spectra were recorded on Bruker AC 200 and DRX 400 spectrometers; IR spectra were recorded on a Bruker IFS 25 spectrometer. Nitrogen-15 NMR spectra were obtained by direct observation with inverse-gated ^1H decoupling and a relaxation delay of 20 s or, for complexes having a hydrogen available for polarization transfer, by the INEPT[10] method.

Preparation of $[Rh(NCBPh_3)(PPh_3)_3](CH_2Cl_2)$ (1). A mixture of KCN (0.014 g, 0.21 mmol) and BPh_3 (0.052 g, 0.21 mmol) in EtOH (3 mL) at room temperature was stirred for 1 h to give a clear solution. $[RhCl(PPh_3)_3]$ (0.150 g, 0.16 mmol) was added, and the mixture was stirred for a further 16 h at 80 °C (taking care not to exceed this temperature) giving a yellow-orange suspension. The solid was filtered, washed with benzene (3 mL), and dried to yield an orange powder (0.165 g, shown by ^{31}P NMR to have no phosphorus-containing impurities), which was recrystallized from CH_2Cl_2/hexane. Yield: 0.107 g (53%). IR (Nujol): ν(CN) 2184 (m) cm^{-1} (the ^{15}N-enriched complex gave $\nu(C^{15}N)$ 2154 cm^{-1}). Anal. Calcd for $C_{74}H_{62}BCl_2NP_3Rh$: C, 71.51; H, 5.03; N, 1.13. Found: C, 70.98; H, 4.89; N, 1.24.

Preparation of $[Rh(NCBPh_3)(PPh_3)_2(CO)](CH_2Cl_2)$. Carbon monoxide was bubbled for 2 min through a solution of **1** (0.045 g, 0.039

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

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S0020-1669(96)00129-2 CCC: $12.00

mmol) in dichloromethane (2 mL) at room temperature. The solution was treated with hexane and allowed to stand at room temperature to give yellow crystals. Recrystallization from dichloromethane/hexane yielded 0.031 g (79%). IR (Nujol): ν(CN) 2196 (m), ν(CO) 2006 (s) cm^{-1} (the ^{15}N-enriched complex gave $\nu(C^{15}N)$ 2166, ν(CO) 2006 cm^{-1}). Anal. Calcd for $C_{57}H_{47}BCl_2NOP_2Rh$: C, 67.88; H, 4.70; N, 1.39. Found: C, 68.07; H, 4.73; N, 1.47.

Preparation of [Rh(NCBPh$_3$)(PPh$_3$)$_2$(XNC)](CH$_2$Cl$_2$). A solution of **1** (0.050 g, 0.043 mmol) in dichloromethane (2 mL) at room temperature was treated with 2,6-xylyl isocyanide (0.006 g, 0.046 mmol). The product was obtained as yellow crystals upon addition of hexane and recrystallized from the same solvent to yield 0.036 g (75%). IR (Nujol): ν(CN) 2118 (s) cm^{-1}. Anal. Calcd for $C_{65}H_{56}BCl_2N_2P_2Rh$: C, 70.19; H, 5.07; N, 2.52. Found: C, 69.78; H, 4.84; N, 2.57.

Preparation of [Rh(NCBPh$_3$)(H)(SnPh$_3$)(PPh$_3$)$_2$]. A mixture containing **1** (0.070 g, 0.060 mmol) and excess Ph_3SnH (0.06 g, 0.16 mmol) in toluene (2 mL) was warmed to 50−60 °C for 1−2 min to produce an orange solution. The product was obtained as orange crystals upon addition of hexane. Yield: 0.065 g (86%). IR (Nujol): 2196 (m), 2044 (m) cm^{-1}. Anal. Calcd for $C_{73}H_{61}BNP_2RhSn$: C, 70.34; H, 4.93; N, 1.12. Found: C, 69.88; H, 4.86; N, 1.25.

Preparation of [Rh(CNBPh$_3$)(PPh$_3$)$_3$](0.5CHCl$_3$) (2). A mixture of $[Rh(CN)(PPh_3)_3]$ (0.105 g, 0.115 mmol) and BPh_3 (0.029 g, 0.120 mmol) was dissolved in chloroform (2 mL) at room temperature to give a red solution. The product was obtained as orange crystals upon addition of hexane. Yield: 0.107 g (76%). IR (Nujol): 2144 (s) cm^{-1} (the ^{15}N-enriched complex gave $\nu(C^{15}N)$ 2110 cm^{-1}). Anal. Calcd for $C_{73.5}H_{60.5}BCl_{1.5}NP_3Rh$: C, 72.50; H, 5.01; N, 1.15. Found: C, 73.02; H, 5.07; N, 1.39.

Preparation of [Rh(CNBPh$_3$)(PPh$_3$)$_2$(CO)](0.5CH$_2$Cl$_2$). Carbon monoxide was bubbled for 2 min through a solution of **2** (0.050 g, 0.043 mmol) in dichloromethane (2 mL) at room temperature. The solution was treated with hexane and allowed to stand at room temperature to give yellow crystals. Recrystallization from dichloromethane/hexane yielded 0.036 g (75%). IR (Nujol): ν(CN) 2180 (m), ν(CO) 2016 (s) cm^{-1}. Anal. Calcd for $C_{56.5}H_{46}BClNOP_2Rh$: C, 70.24; H, 4.80; N, 1.45. Found: C, 70.61; H, 4.86; N, 1.68.

Preparation of [Rh(CNBPh$_3$)(PPh$_3$)$_2$(XNC)](0.5CH$_2$Cl$_2$). A mixture of **2** (0.040 g, 0.034 mmol) and 2,6-xylyl isocyanide (0.006 g, 0.046 mmol) in dichloromethane (2 mL) at room temperature was treated with hexane to give yellow crystals. The product was recrystallized from the same solvent to give 0.024 g (65%). IR (Nujol): ν(CN) 2113 (s) cm^{-1}. Anal. Calcd for $C_{64.5}H_{55}BClN_2P_2Rh$: C, 72.41; H, 5.18; N, 2.62. Found: C, 72.48; H, 5.13; N, 2.72.

Preparation of [Rh(CNBPh$_3$)(H)(SnPh$_3$)(PPh$_3$)$_2$]. A mixture containing **1** (0.030 g, 0.026 mmol) and excess Ph_3SnH (0.03 g, 0.08 mmol) in toluene (1 mL) was warmed to 50−60 °C for 1−2 min to give an orange solution. The product was obtained as orange crystals upon addition of hexane. Yield: 0.017 g (53%). IR (Nujol): 2168 (m) cm^{-1}. Anal. Calcd for $C_{73}H_{61}BNP_2RhSn$: C, 70.34; H, 4.93; N, 1.12. Found: C, 70.36; H, 4.93; N, 1.14.

Results and Discussion

[Rh(NCBPh$_3$)(PPh$_3$)$_3$] and [Rh(CNBPh$_3$)(PPh$_3$)$_3$]. The triphenylcyanoborate ion, formed from CN^- (as the potassium salt) and triphenylboron in ethanol, readily replaces the chloride of $[RhCl(PPh_3)_3]$ to give the N-bonded triphenylcyanoborate complex $[Rh(NCBPh_3)(PPh_3)_3]$ (**1**); the two reactions conveniently are carried out in the same solution to give the product as a yellow-orange microcrystalline powder. Washing with benzene gives the spectroscopically (^{31}P NMR) pure product (used in most of the subsequent work) in *ca.* 80% yield, while recrystallization from dichloromethane affords 53% of the CH_2Cl_2 solvate, with the presence of 1 CH_2Cl_2 confirmed by ^1H NMR. The complex was prepared in both unenriched and 99% ^{15}N-enriched forms. From the $^{15}N\{^1H\}$ NMR spectrum (Figure 1a, consisting of a doublet of doublets of triplets: coupling of

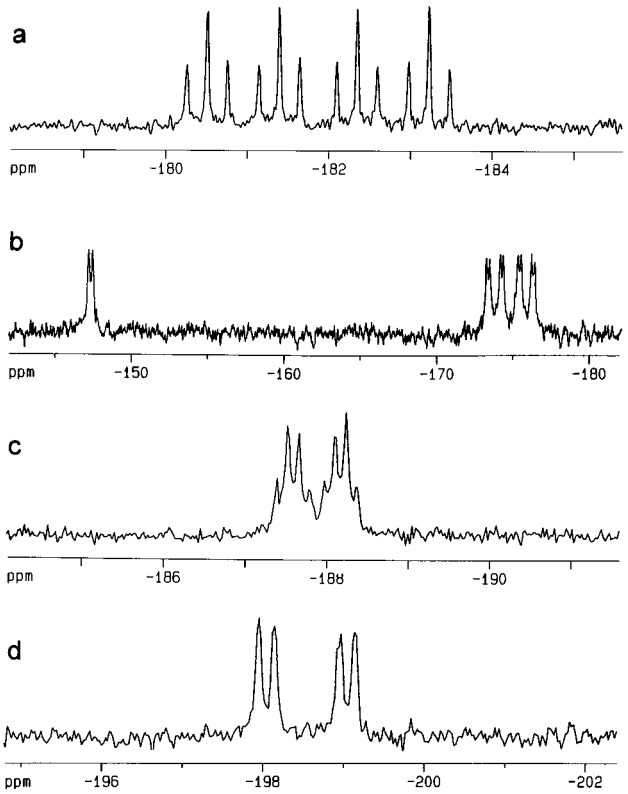

Figure 1. $^{15}N\{^1H\}$ NMR spectra (20.28 MHz). (a) $[Rh(^{15}NCBPh_3)(PPh_3)_3]$ (0.04 M) in chloroform, 22 °C. (b) Signals from *trans*-$[Rh(C^{15}NBPh_3)(PPh_3)_2(py)]$ (*ca.* 0.01 M) and *cis*-$[Rh(^{15}NCBPh_3)(PPh_3)_2(py)]$ (*ca.* 0.03 M) in 10% pyridine/toluene, −25 °C. (c) $[Rh(^{15}NCBPh_3)(H)_2(PPh_3)_3]$ (0.03 M) in toluene, 22 °C. (d) *cis*-$[Rh(^{15}NCBPh_3)(O_2)(PPh_3)_2(py)]$ (0.02 M) stabilized with PPh_3 (0.3 M) in 10% pyridine/toluene, −25 °C.

^{15}N to ^{103}Rh and to *trans* and *cis* phosphines), it is clear that in **1** the cyanoborate is bonded to rhodium *via* nitrogen and not carbon because $J(^{103}Rh-^{15}N)$ and $J(^{31}P-^{15}N$*trans*) (Table 1) have values that indicate coupling over one and two bonds, respectively.[11] The $^{31}P-^{15}N$ coupling is also seen in the $^{31}P\{^1H\}$ NMR spectrum (Figure 2a) superimposed on the doublet of triplets and doublet of doublets found for nominally square planar tris(phosphine)Rh(I) complexes.

The C-bonded isomer $[Rh(CNBPh_3)(PPh_3)_3]$ (**2**) is prepared from $[Rh(CN)(PPh_3)_3]$[9] and triphenylboron in chloroform, crystallizing readily in good yield. It is also formed by the reaction described above for **1** if the temperature is allowed to exceed 80 °C by more than a few degrees, constituting up to 40% of the product. Nitrogen-15 NMR data relating to the C-bonded isomer and its derivatives were obtained from these mixtures, since the method by which $[Rh(CN)(PPh_3)_3]$ is prepared is very wasteful of cyanide thereby prohibiting, on grounds of cost, its use for the preparation of a ^{15}N-enriched form. The $^{31}P\{^1H\}$ NMR spectrum of **2** (Figure 2b) shows the two phosphorus environments to be very similar, phosphorus *trans* to carbon having a chemical shift differing by only 1.5 ppm from phosphorus *trans* to phosphorus, with the consequence that second-order distortions are seen in the intensities of the lines. A solution of **1** in chlorobenzene (chosen as an alternative to toluene, in which **1** is only sparingly soluble) when heated to 90 °C gives broadened ^{31}P NMR signals. After the solution is cooled to room temperature, the spectrum shows the presence of a small amount of **2** (2−3% after 10−15 min at 90 °C). After 10−15 min at 110 °C, the extent of conversion is greater (*ca.* 40%) while at 120 °C conversion is complete within 15 min; in all cases there is evidence of decomposition, the extent of which can be reduced by the presence of triphenylphosphine.

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Table 1. ^{15}N NMR Spectral Data

complex[a]	signal	δ[b]	$J(^{103}Rh-^{15}N)$[c]	$J(^{31}P-^{15}N$*trans*$)$	$J(^{31}P-^{15}N$*cis*$)$
$[Rh(^{15}NCBPh_3)(PPh_3)_3]$[d]	ddt	−181.9	18.1	37.8	5.1
cis-$[Rh(^{15}NCBPh_3)(PPh_3)_2(py)]$[e,f]	ddd	−175.1	17.8	41.6	4.0
cis-$[Rh(^{15}NCBPh_3)(PPh_3)_2(4\text{-}Me_2Npy)]$[e−g]	ddd	−173.1	17.2	41.9	4.0
cis-$[Rh(^{15}NCBPh_3)(PPh_3)_2(4\text{-}CNpy)]$[e−g]	ddd	−175.3	18.4	41.0	3.9
trans-$[Rh(^{15}NCBPh_3)(PPh_3)_2(CO)]$[d,f,h]	dt	−188.6	18.3		5.4
trans-$[Rh(^{15}NCBPh_3)(PPh_3)_2(XNC)]$[d]	dt	−184.7	17.8		5.2
trans-$[Rh(^{15}NCBPh_3)(PPh_3)_2(C_2H_4)]$[g]	dt	−187.6	21.9		4.4
$[Rh(^{15}NCBPh_3)(H)_2(PPh_3)_3]$	dq	−187.8	11.9		2.7
$[Rh(^{15}NCBPh_3)(H)_2(PPh_3)_2(py)]$[e]	dt	−174.2	11.5		2.5
$[Rh(^{15}NCBPh_3)(H)_2(PPh_3)_2(4\text{-}Me_2Npy)]$[e]	dt	−173.4	11.3		2.4
$[Rh(^{15}NCBPh_3)(H)_2(PPh_3)_2(4\text{-}CNpy)]$[e]	dt	−174.7	11.7		2.5
cis-$[Rh(^{15}NCBPh_3)(O_2)(PPh_3)_2(py)]$[e,i]	dd	−198.5	20.2		4.1
cis-$[Rh(^{15}NCBPh_3)(O_2)(PPh_3)_2(4\text{-}Me_2Npy)]$[e,i]	dd	−197.1	20.0		3.9
cis-$[Rh(^{15}NCBPh_3)(O_2)(PPh_3)_2(4\text{-}CNpy)]$[e,f,i]	dd	−199.7	19.9		3.3
$[Rh(^{15}NCBPh_3)(H)(SiPh_3)(PPh_3)_2]$[d,f,j]	dt	−174.6	14.7		3.0
$[Rh(^{15}NCBPh_3)(H)(SnPh_3)(PPh_3)_2]$[d]	dt	−175.3	15.3		3.1
$[Rh(C^{15}NBPh_3)(PPh_3)_3]$[d]	dd	−147.7	3.9	6.7	
trans-$[Rh(C^{15}NBPh_3)(PPh_3)_2(py)]$[e,f]	d	−147.3	5.0		
trans-$[Rh(C^{15}NBPh_3)(PPh_3)_2(CO)]$[d]	d	−138.9	4.1		
trans-$[Rh(C^{15}NBPh_3)(PPh_3)_2(XNC)]$[d]	d	−143.0	4.2		
$[Rh(C^{15}NBPh_3)(H)_2(PPh_3)_3]$[d,f]	d	−149.3	1.5		
$[Rh(C^{15}NBPh_3)(H)(SnPh_3)(PPh_3)_2]$[d]	d	−142.8	3.2		

[a] Solution in toluene (*ca*. 0.03 M); temperature 27 °C unless otherwise specified. [b] Chemical shifts in ppm from CH_3NO_2 (negative values to low frequency) uncorrected for bulk susceptibility effects. [c] Coupling constants (absolute magnitude) in hertz. [d] Solution in chloroform. [e] Solution in 0.3 M pyridine (or substituted pyridine)/toluene. [f] Recorded at −25 °C. [g] Signal poorly resolved. $J(P-N$*cis*$)$ measured from ^{31}P NMR spectrum. [h] At 27 °C, the signal (δ −187.5 ppm) is broadened and P−N coupling is poorly resolved. [i] Stabilized with PPh_3 (0.06 M). [j] Solution containing Ph_3SiH (0.64 M).

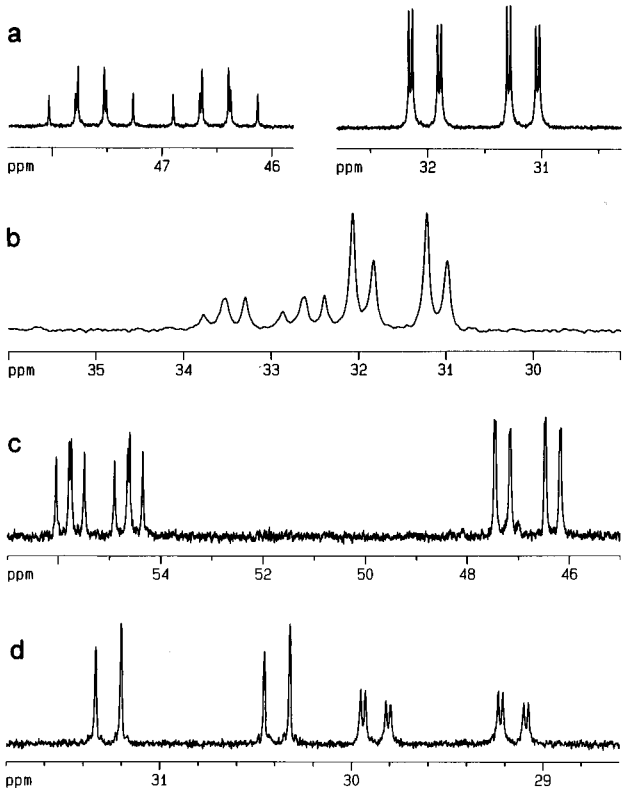
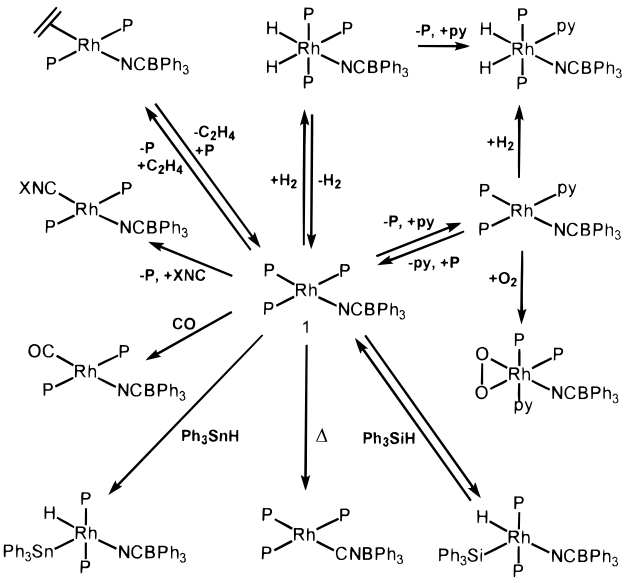


Figure 2. $^{31}P\{^1H\}$ NMR spectra (161.98 MHz). (a) $[Rh(^{15}NCBPh_3)(PPh_3)_3]$ (chloroform, 27 °C). (b) $[Rh(CNBPh_3)(PPh_3)_3]$ (toluene, 27 °C). (c) *cis*-$[Rh(^{15}NCBPh_3)(PPh_3)_2(py)]$ (10% pyridine/toluene, −25 °C). (d) *cis*-$[Rh(^{15}NCBPh_3)(O_2)(PPh_3)_2(py)]$ (0.02 M) stabilized with PPh_3 (0.3 M) in 5% pyridine/toluene, −25 °C.

Both C- and N-bonded isomers undergo a number of ligand exchange and oxidative addition reactions (Schemes 1 and 2). Many of the products could not be isolated and were studied *in situ*.

Ligand Exchange Reactions. With pyridine (0.2 M), **1** gives *cis*-$[Rh(NCBPh_3)(PPh_3)_2(py)]$, with the *cis* geometry confirmed by the nonequivalence of the two phosphines, each phosphine

Scheme 1. P = PPh_3



giving rise to a doublet of doublets (coupling between the phosphines and to rhodium) in the $^{31}P\{^1H\}$ NMR spectrum. The SC_6F_5 analogue of this compound is known.[12] In the $^{31}P\{^1H\}$ NMR spectrum of the ^{15}N-enriched form, these lines are further split by coupling to ^{15}N (Figure 2c). With higher concentrations of pyridine, the signals are broadened as a result of increased exchange of free and coordinated pyridine and resolution is restored by lowering the temperature. The $^{15}N\{^1H\}$ NMR spectrum (Figure 1b) shows a doublet of doublets of doublets, $J(^{31}P-^{15}N$*trans*$)$ having a magnitude approximately 10 times that of $J(^{31}P-^{15}N$*cis*$)$ (Table 1). The second signal shown in Figure 1b is from the pyridine-containing complex derived from $[Rh(C^{15}NBPh_3)(PPh_3)_3]$.

Carbon monoxide and 2,6-xylyl isocyanide (XNC) react with **1** to give the crystalline products *trans*-$[Rh(NCBPh_3)(PPh_3)_2$-

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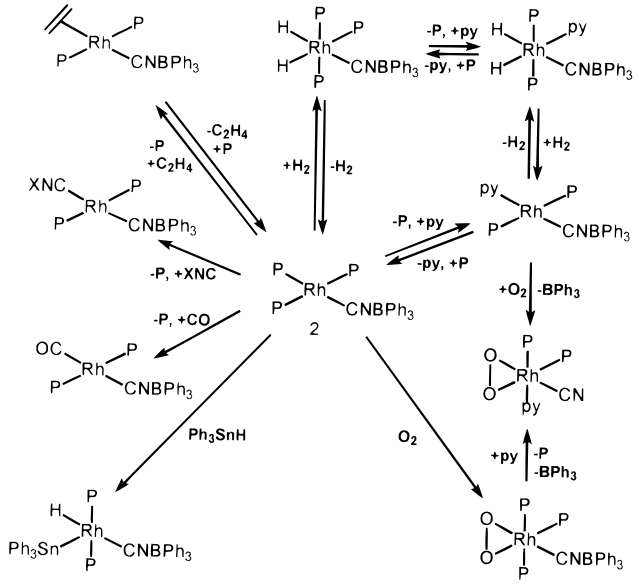
Scheme 2. P = PPh_3



(L)] (L = CO, XNC). The carbonyl complex obtained from this reaction contains a trace of free PPh_3 which causes broadening of the ^{31}P NMR signal to the point where it is difficult to detect at room temperature; only at reduced temperatures (−50 °C) is a $^{31}P\{^1H\}$ signal (a broadened doublet) observed while the $^{15}N\{^1H\}$ NMR spectrum recorded at room temperature consists of a well-resolved doublet (coupling of ^{15}N to ^{103}Rh) with no detectable coupling to phosphorus. To a lesser extent, the broadening of spectral lines also occurs with the isocyanide complex. After the product is recrystallized, satisfactory ^{15}N and ^{31}P NMR spectra are obtained. When [Rh(NCBPh$_3$)(PPh$_3$)$_2$(CO)] is allowed to stand in solution at room temperature, another effect becomes noticeable: a slow conversion occurs to the C-bonded isomer [Rh(CNBPh$_3$)(PPh$_3$)$_2$(CO)], a process which is accelerated at higher temperatures. A solution of the N-bonded complex in chloroform, upon standing at room temperature for 4 days, undergoes a *ca*. 10% conversion to the C-bonded form. In chlorobenzene at 75 °C, conversion is *ca* 10% after 10 min. This rearrangement occurs at temperatures where **1** is considered to be reasonably stable (i.e. the exchange of a phosphine for a carbonyl in the position *trans* to NCBPh$_3$ favors the isomerization process, presumably by limiting the electron density available for the formation of the C−B bond). The CO-stretching frequency for [Rh(CNBPh$_3$)(PPh$_3$)$_2$(CO)] (measured both in the solid state and in solution) is approximately 10 wavenumbers higher than that of the N-bonded isomer. Although this would seem to imply a lower electron density on rhodium for the C-bonded form (chemical evidence described below strongly suggests that the opposite is true), it is possible that the vibrational interaction between the carbonyl and cyanoborate ligands is a contributing factor.

A solution of **1** (0.002 M) in toluene when treated with ethylene at room temperature and atmospheric pressure shows some 60% conversion to *trans*-[Rh(NCBPh$_3$)(PPh$_3$)$_2$(C$_2$H$_4$)]; this product is reconverted to **1** by purging the solution with argon. At higher concentrations of **1**, competition with PPh_3 (liberated in the reaction) inhibits the binding of ethylene and the conversion percentage drops significantly. ^{31}P NMR data for the ethylene complex are very similar to those reported for the chloro analogue.[13]

The ^{31}P NMR spectrum obtained from a solution of **2** in chloroform or toluene containing *ca*. 5% pyridine shows a doublet, consistent with the presence of *trans*-[Rh(CNBPh$_3$)(PPh$_3$)$_2$(py)] where the geometry is dictated by the strong *trans* effect of the Ph_3BNC^- ligand (in effect a modified cyanide ion). This formulation is confirmed by the identity of the product obtained on binding hydrogen. With carbon monoxide, 2,6-xylyl isocyanide, and ethylene, **2** reacts to give *trans*-[Rh(CNBPh$_3$)(PPh$_3$)$_2$(L)], the products being crystalline (L = CO, XNC) and the (reversible) binding of ethylene occurring to an extent of only *ca*. 5% at room temperature and atmospheric pressure.

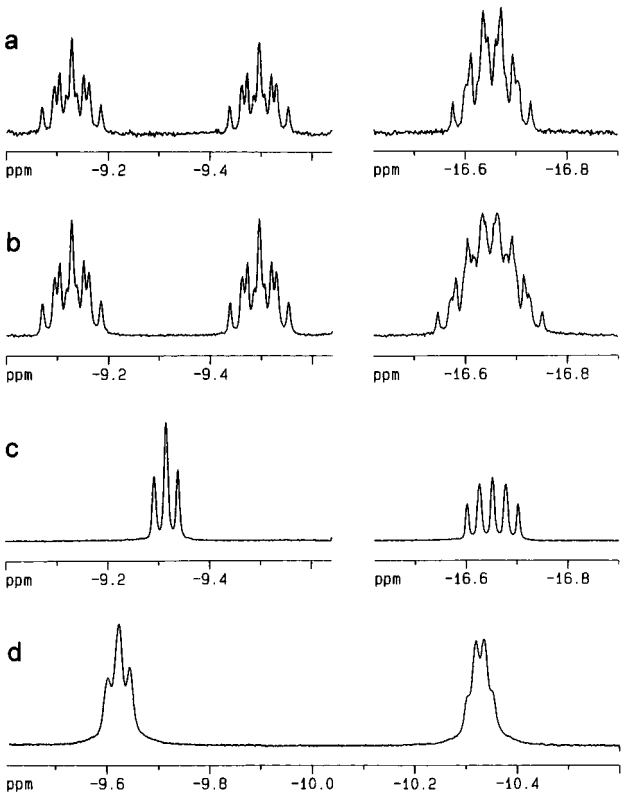


Figure 3. ^1H NMR spectra (400.13 MHz). (a) [Rh(NCBPh$_3$)(H)$_2$(PPh$_3$)$_3$] (22 °C). (b) [Rh(^{15}NCBPh$_3$)(H)$_2$(PPh$_3$)$_3$] (22 °C). $^1H\{^{31}P\}$ NMR spectra. (c) [Rh(^{15}NCBPh$_3$)(H)$_2$(PPh$_3$)$_3$] (22 °C). [Rh(C^{15}NBPh$_3$)(H)$_2$(PPh$_3$)$_3$] (−25 °C). The solvent is toluene.

Reactions with Hydrogen. Hydrogen combines reversibly with both **1** and **2** to form [Rh(NCBPh$_3$)(H)$_2$(PPh$_3$)$_3$] and [Rh(CNBPh$_3$)(H)$_2$(PPh$_3$)$_3$], respectively, at room temperature and atmospheric pressure. The ^1H and ^{31}P NMR signals of the latter are broadened, and the ^1H NMR spectrum shows significant detail only at reduced temperatures. Hydrogen is more readily displaced from the CNBPh$_3$ complex by purging a solution in toluene at room temperature with argon for 2−3 min than from the N-bonded isomer, which releases its hydrogen only upon warming to *ca*. 70 °C. In the ^1H NMR spectra of the ^{15}N-enriched H_2 adducts (Figure 3), one hydrogen shows spin coupling to ^{15}N: for the NCBPh$_3$ complex $^2J(^{15}N-^1H\textit{trans}) = 20.7$ Hz and for the CNBPh$_3$ isomer $^3J(^{15}N-H\textit{trans}) = 6.3$ Hz (an unusually high value for N−H coupling over three bonds). Coupling between nitrogen and the hydride in the *cis* position is not observed for either complex. The $^{15}N\{^1H\}$ NMR spectrum of [Rh(^{15}NCBPh$_3$)(H)$_2$(PPh$_3$)$_3$] consists of a doublet of quartets, showing that coupling of ^{15}N to the phosphines is relatively insensitive to the differences in the two phosphine environments (Figure 1c).

The complexes *cis*-[Rh(NCBPh$_3$)(PPh$_3$)$_2$(L)] (L = pyridine (py), 4-(dimethylamino)pyridine (4-Me$_2$Npy), and 4-cyanopyridine (4-CNpy)) and *trans*-[Rh(CNBPh$_3$)(PPh$_3$)$_2$(py)] (prepared *in situ* from **1** or **2** and an excess of L) also bind hydrogen; the

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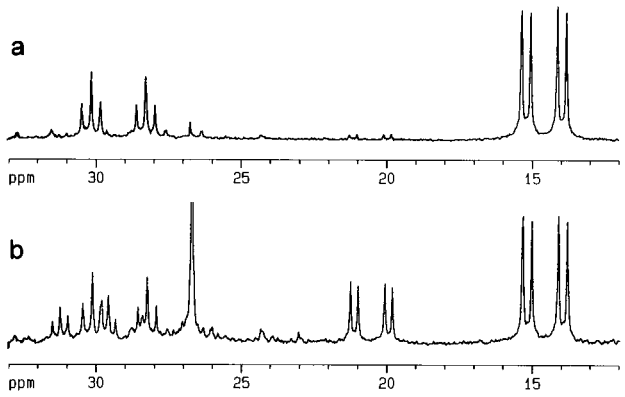
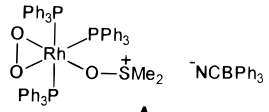


Figure 4. $^{31}P\{^1H\}$ NMR spectra (81.03 MHz). [$Rh(NCBPh_3)(PPh_3)_3$] (0.02 M) PPh_3 (0.02 M) in DMSO/oxygen at 22 °C (a) on mixing and (b) after 24 h. The signal at 26.7 ppm is from Ph_3PO.

rate of binding (monitored by ^{31}P NMR) is much slower than that of **1** or **2**, which bind H_2 rapidly even in the presence of free PPh_3. While hydrogen can be displaced from [$Rh(CNBPh_3)(H)_2(PPh_3)_2(py)$] by purging solutions in toluene at room temperature with argon for 2−3 min, it remains firmly bound in [$Rh(NCBPh_3)(H)_2(PPh_3)_2(py)$]. The complex remains unaffected by heating for 5 min at 100 °C with continuous bubbling of Ar and is also unchanged in the presence of oxygen at atmospheric pressure and room temperature, decomposition amounting to no more than *ca*. 20% after 1 week. Reasons for these differences in stability are likely to be as follows. Dissociation of a σ-donor ligand (here the pyridine) has been shown to be a prerequisite of the reductive elimination of H_2 in a number of cases.[14,15] The $NCBPh_3$ ligand would appear to be more effective in inhibiting dissociation (by virtue of its electron-withdrawing properties) thus preventing the formation of a five-coordinate species from which loss of H_2 can occur. The six-coordinate dihydro complex is intrinsically more stable,[15,16] and loss of H_2 from this, without prior dissociation of a neutral ligand, will require more forcing conditions than those used here. Evidence supporting this interpretation is found by treating solutions of [$Rh(NCBPh_3)(H)_2(PPh_3)_2(py)$] and [$Rh(CNBPh_3)(H)_2(PPh_3)_2(py)$] with triphenylphosphine: only with the latter is there conversion to the tris(phosphine) complex.

Reactions with Oxygen. The low solubility of **1** in toluene led to the use of chloroform for the study of several reactions, but with O_2 there is extensive decomposition in this solvent and further studies were performed in DMSO. Although **1** also has low solubility in DMSO, after O_2 is bubbled for 5 min through a mixture of **1** and a 10-fold excess of PPh_3 (the stability in solution of dioxygen complexes [$RhX(O_2)(PPh_3)_3$] (*e.g.*, X = Cl) is greatly enhanced by the presence of free PPh_3) in DMSO at room temperature, a brown solution is formed which gives a $^{31}P\{^1H\}$ NMR spectrum {δ 29.10 (dt, 1P, J(Rh−P) = 152.2 Hz, J(P−P) = 25.7 Hz), 14.59 (dd, 2P, J(Rh−P) = 99.3 Hz, J(P−P) = 25.7 Hz)} (Figure 4a) similar to that which might be expected for a tris(triphenylphosphine)(dioxygen)rhodium triphenylcyanoborate complex. However, the $^{15}N\{^1H\}$ NMR spectrum consists of a single sharp line (δ − 113 ppm), indicating that nitrogen is no longer directly bound to rhodium. In view of the ready formation of transition metal complexes of DMSO[17] (those in which binding is *via* oxygen, showing a substantial decrease in the S−O bond order from 2.0 to *ca*. 1.5) and the relative ease with which sulfoxides can be converted into sulfonium salts (by protonation or by treatment with Me_3I^+, $(EtO)_2CH^+$, alkyl halides, tosylates, and sulfates)[18] a possible explanation for these findings may be the presence of a salt of the type shown (**A**).



A

In the formation of this complex, the high electrophilicity of Rh (which has O_2 and $NCBPh_3$ as ligands) is envisaged as causing polarization of the S−O bond of a coordinated DMSO such that a full positive charge resides on sulfur; Ph_3BCN^- is released, providing the counterion to the newly formed sulfonium ion. Although DMSO has been shown to undergo oxidation (to dimethyl sulfone) in the presence of dioxygen complexes,[19] the complex [$Co(salen)(DMSO)_2$] is known to bind O_2 without oxidation of DMSO.[20]

Further evidence for the loss of the Ph_3BCN^- ligand is found on repeating the above experiment (**1**/PPh_3/DMSO/O_2) with analogues of **1** containing azide and dicyanamide[21] ligands in place of cyanoborate. $^{31}P\{^1H\}$ NMR spectra are obtained showing signals indistinguishable from those in Figure 4a. With [$RhCl(PPh_3)_3$] the only product is the complex [$RhCl(O_2)(PPh_3)_3$],[22] suggesting that the dissociation of the anionic ligand may be related to the opportunities for charge delocalization.

Changes occur in the $^{31}P\{^1H\}$ NMR spectrum of the mixture **1**/PPh_3/DMSO/O_2 over a period of hours: the initial signals (Figure 4a) diminish and new signals (again a doublet of triplets and doublet of doublets, Figure 4b) appear which closely match those obtained from a solution (in $CDCl_3$) containing [$Rh(CN)(PPh_3)_3$], PPh_3, and O_2 {*i.e.*, the dioxygen complex [$Rh(CN)(O_2)(PPh_3)_3$], ^{31}P NMR δ 31.20 (dt, 1P, J(Rh−P) = 133.5 Hz, J(P−P) = 21.0 Hz) 20.91 (dd, 2P, J(Rh−P) = 96.2 Hz, J(P−P) = 21.0 Hz)}. The conversion of Ph_3BCN^- into CN^- can be accounted for by the following equilibrium

$$Ph_3BCN^- + PPh_3 \rightleftarrows Ph_3BPPh_3 + CN^-$$

in which small amounts of Ph_3BPPh_3[23] and CN^- are formed from Ph_3BCN^- in the presence of the large excess of PPh_3 in solution. The strongly coordinating CN^- ion can then displace DMSO from complex **A** to give the cyano complex. Complex

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Table 2. ^{31}P NMR Spectral Data

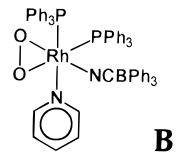
complex[a]	signal[b]	δ[c]	$J(^{103}Rh-^{31}P)$[d]	$J(^{31}P-^{31}P)$
$[Rh(NCBPh_3)(PPh_3)_3]$[e]	dt	47.13	176.6	40.9
	dd	31.60	139.1	40.9
cis-$[Rh(NCBPh_3)(PPh_3)_2(py)]$[f]	dd[g]	55.36	185.7	48.2
	dd	46.71	160.3	48.2
cis-$[Rh(NCBPh_3)(PPh_3)_2(4\text{-}Me_2Npy)]$[f]	dd[g]	55.99	186.6	47.6
	dd	47.09	157.7	47.6
cis-$[Rh(NCBPh_3)(PPh_3)_2(4\text{-}CNpy)]$[f]	dd[g]	54.48	183.8	49.1
	dd	45.91	161.8	49.1
trans-$[Rh(NCBPh_3)(PPh_3)_2(CO)]$[e]	d	29.32	122.8	
trans-$[Rh(NCBPh_3)(PPh_3)_2(XNC)]$[e]	d	30.46	131.3	
trans-$[Rh(NCBPh_3)(PPh_3)_2(C_2H_4)]$	d	35.45	124.1	
$[Rh(NCBPh_3)(H)_2(PPh_3)_3]$	dd	33.74	112.3	18.7
	dt	23.91	92.6	18.7
$[Rh(NCBPh_3)(H)_2(PPh_3)_2(py)]$[f]	d	47.20	115.7	
$[Rh(NCBPh_3)(H)_2(PPh_3)_2(4\text{-}Me_2Npy)]$[f]	d	46.84	116.2	
$[Rh(NCBPh_3)(H)_2(PPh_3)_2(4\text{-}CNpy)]$[f]	d	47.11	115.0	
cis-$[Rh(NCBPh_3)(O_2)(PPh_3)_2(py)]$[f,i]	dd	30.77	142.6	21.5
	dd	29.49	116.3	21.5
cis-$[Rh(NCBPh_3)(O_2)(PPh_3)_2(4\text{-}Me_2Npy)]$[f,i]	dd	31.77	143.6	21.0
	dd	28.65	114.3	21.0
cis-$[Rh(NCBPh_3)(O_2)(PPh_3)_2(4\text{-}CNpy)]$[f,i,j]	dd	29.94	118.2	22.2
	dd	29.51	140.8	22.2
$[Rh(NCBPh_3)(H)(SiPh_3)(PPh_3)_2]$[e]	d	33.95	121.9	
$[Rh(NCBPh_3)(H)(SnPh_3)(PPh_3)_2]$[e]	d[k]	36.72	111.8	
$[Rh(CNBPh_3)(PPh_3)_3]$[e]	dt	33.08	146.3	38.4
	dd	31.53	137.1	38.4
trans-$[Rh(CNBPh_3)(PPh_3)_2(py)]$	d	34.68	146.1	
trans-$[Rh(CNBPh_3)(PPh_3)_2(CO)]$[e]	d	30.42	121.0	
trans-$[Rh(CNBPh_3)(PPh_3)_2(XNC)]$[e]	d	32.56	128.3	
trans-$[Rh(CNBPh_3)(PPh_3)_2(C_2H_4)]$[e]	d	36.51	123.2	
$[Rh(CNBPh_3)(H)_2(PPh_3)_3]$[e,j]	dd	41.24	108.1	18.5
	dt	28.74	91.5	18.5
$[Rh(CNBPh_3)(O_2)(PPh_3)_3]$	dd	31.63	90.1	19.2
	dt	28.26	130.1	19.2
$[Rh(CNBPh_3)(H)_2(PPh_3)_2(py)]$	d	50.62	110.3	
$[Rh(CNBPh_3)(H)(SnPh_3)(PPh_3)_2]$[e]	d[l]	40.37	107.5	

[a] Solution in toluene (*ca*. 0.02 M); temperature 27 °C unless otherwise specified. [b] Signal from unenriched complexes. $J(^{31}P-^{15}N)$ given in Table 1. [c] Chemical shifts in ppm from 85% H_3PO_4. [d] Coupling constants (absolute magnitude) in hertz. [e] Solution in chloroform. [f] Solution in ≤0.3 M pyridine (or substituted pyridine)/toluene. [g] Signal from phosphine *trans* to cyanoborate. [i] Stabilized with PPh_3 (0.06 M). [j] Recorded at −25 °C. [k] $J(^{119}Sn-^{31}P) \approx J(^{117}Sn - {}^{31}P) = 102$ Hz. [l] $J(^{119}Sn-^{31}P) \approx J(^{117}Sn-^{31}P) = 95$ Hz.

2 reacts with O_2 in DMSO in the presence of PPh_3 to give only $[Rh(CN)(O_2)(PPh_3)_3]$.

When oxygen is bubbled through a solution of **2** and PPh_3 (0.06 M) in toluene at room temperature, ^{31}P NMR signals are observed that are consistent with the formation of $[Rh(CNBPh_3)(O_2)(PPh_3)_3]$. With **1** there is no evidence for the formation of such a product, since **1** is stable for 1−2 days in dichloromethane in the presence of oxygen and triphenylphosphine. In the absence of PPh_3 decomposition occurs over a period of hours. The reason for this surprising lack of reactivity toward O_2 must lie in the electronic properties of the Ph_3BCN^- ligand, giving rise to a lower electron density at the metal than in the case of Ph_3BNC^-, since steric properties are considered to be virtually identical to those of Ph_3BNC^-. Such inertness is shown by many Rh(I) complexes with strongly electron-withdrawing π-acid ligands (*e.g.*, *trans*-$[RhCl(PPh_3)_2(CO)]$). The lack of affinity for O_2 is unlikely to be related to the inhibition of dissociation by a phosphine (loss of PPh_3 has been shown to be a prerequisite of the binding of H_2 to $[RhCl(PPh_3)_3]$[24]), since the H_2 complex is formed even in the presence of 0.2 M PPh_3. When the electron density of Rh is increased by the exchange of a phosphine for pyridine, an O_2 adduct is readily formed.

A solution of *cis*-$[Rh(NCBPh_3)(PPh_3)_2(py)]$, prepared from **1** and an excess of both pyridine (0.3 M) and PPh_3 (0.1 M) in toluene, when treated with O_2 (bubbled through the solution for 2 min at room temperature) gives ^{31}P and ^{15}N NMR spectra indicating the presence of the O_2 complex *cis*-$[Rh(NCBPh_3)(O_2)(PPh_3)_2(py)]$ (not isolated) which is stable for several hours at −25 °C. The $^{31}P\{^1H\}$ NMR spectrum (Figure 2d) of the ^{15}N-enriched complex contains two signals, each from a single phosphine, which show coupling between the phosphines and to the Rh. This indicates a *cis* geometry, with only one signal showing further coupling to nitrogen; the $^{15}N\{^1H\}$ NMR spectrum consists of a doublet of doublets (coupling to Rh and one of the phosphines). The phosphorus−nitrogen coupling has a magnitude of 4.1 Hz (Table 1); therefore, both phosphines must also be positioned *cis* to cyanoborate since a coupling $J(^{31}P-^{15}N$*trans*) of *ca*. 40 Hz would otherwise be expected.[11] Only one coordination geometry (**B**) is consistent with these data.



B

The $^{31}P\{^1H\}$ NMR spectrum of the unenriched complex is very similar to that obtained from a solution of $[RhCl(O_2)(PPh_3)_3]$ following treatment with pyridine. Analogous products are formed using 4-(dimethylamino)pyridine and 4-cyanopyridine (Tables 1 and 2). The latter complex displays very similar ^{31}P NMR chemical shifts for its phosphines, giving a second-order ^{31}P NMR spectrum at room temperature and no detectable

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Table 3. ^{1}H NMR Spectral Data for the Hydride Complexes.

complex[a]	signal[b]	δ[c]	$J(^{103}Rh-^1H)$[d]	$J(^{31}P-^1Htrans)$	$J(^{31}P-^1Hcis)$	$J(^1H-^1H)$	$J(^{15}N-^1Htrans)$[e]
$[Rh(NCBPh_3)(H)_2(PPh_3)_3]$	dddt	−9.31	9.5	147.1	13.5	9.3	
	dddt	−16.65	10.4		13.6	9.3	20.7
$[Rh(NCBPh_3)(H)_2(PPh_3)_2(py)]$[f]	ddt	−16.62	15.1		13.8	10.8	
	ddt	−16.86	15.7		14.7	10.8	21.7
$[Rh(NCBPh_3)(H)_2(PPh_3)_2(4\text{-}Me_2Npy)]$[f]	ddt	−16.41	14.3		14.3	10.7	
	ddt	−16.80	15.6		15.0	10.7	21.7
$[Rh(NCBPh_3)(H)_2(PPh_3)_2(4\text{-}CNpy)]$[f]	ddt	−16.74	15.8		12.6	10.8	
	ddt	−16.99	15.8		14.5	10.8	21.7
$[Rh(NCBPh_3)(H)(SiPh_3)(PPh_3)_2]$[g,h]	dt[i]	−14.29	15.5		15.2		15.7
$[Rh(NCBPh_3)(H)(SnPh_3)(PPh_3)_2]$[g]	dt[j]	−15.55	9.9		15.9		16.0
$[Rh(CNBPh_3)(H)_2(PPh_3)_3]$[g,k]	dddt	−9.62	∼8.0	143.1	12.0	∼8.0	
	dddt	−10.33	∼8.0		14.3	∼8.0	6.3
$[Rh(CNBPh_3)(H)_2(PPh_3)_2(py)]$[f,k]	ddt	−10.16	∼9.5		9.8	∼9.5	
	ddt	−16.53	14.9		12.6	∼9.5	
$[Rh(CNBPh_3)(H)(SnPh_3)(PPh_3)_2]$[g]	dt[i]	−9.14	7.0		15.9		5.2

[a] Solution in toluene (*ca*. 0.02 M); temperature 27 °C unless otherwise specified. [b] Signal from unenriched complexes. [c] Chemical shift in ppm from TMS. [d] Coupling constants (absolute magnitude) in hertz. [e] Measured from spectra of 99% ^{15}N-enriched compounds. [f] Solution in 0.3 M pyridine (substituted pyridine)/toluene. [g] Solution in $CDCl_3$. [h] Solution containing Ph_3SiH (0.1 M). [i] Satellites not observed. [j] $J(^{119}Sn-^1H) \approx J(^{117}Sn-^1H) = 29$ Hz. [k] Recorded at −25 °C.

^{15}N signal. At −25 °C, satisfactory ^{31}P and ^{15}N NMR spectra are obtained.

On treatment of a solution containing a mixture of $[Rh(CNBPh_3)(O_2)(PPh_3)_3]$, PPh_3, and unreacted **2** with pyridine or of a solution of *trans*-$[Rh(CNBPh_3)(PPh_3)_2(py)]$, excess pyridine, and PPh_3 with oxygen, the ^{31}P NMR signals of these complexes disappear and are replaced by signals from $[Rh(CN)(O_2)(PPh_3)_3]$ and *cis*-$[Rh(CN)(O_2)(PPh_3)_2(py)]$ {^{31}P NMR δ 34.35 (dd, 1P, J(Rh−P) = 120.2 Hz, J(P−P) = 18.8 Hz) 33.83 (dd, 1P, J(Rh−P) = 128.0 Hz, J(P−P) = 18.8 Hz)}, formed in a process involving breaking of the N−B bond. It would appear that in both of these complexes the electron density on rhodium, and hence *via* bonds to carbon, on nitrogen, is sufficiently low that the CN−BPh_3 interaction (which is perhaps best viewed as an equilibrium between free and bound forms) is discouraged to the point where the formation of a BPh_3−pyridine adduct becomes a viable alternative.

Reactions with Ph_3SiH and Ph_3SnH. Triphenylsilane combines reversibly with **1** in deuteriochloroform at room temperature to give $[Rh(NCBPh_3)(H)(SiPh_3)(PPh_3)_2]$: in the presence of 0.064 M Ph_3SiH, the conversion of **1** (0.007 M) is 12% (measured from the ^{31}P{^{1}H} NMR spectrum), while with 0.64 M Ph_3SiH this increases to 23%. Dilution of the latter solution by a factor of 2 (using 0.007 M **1**) results in a decrease in the concentration of the triphenylsilane adduct to 19% of the total. Spectroscopic data are consistent with a five-coordinate geometry of the type reported for $[Rh(Cl)(H)(SiCl_3)(PPh_3)_2]$:[25] the phosphine environments are equivalent, shown by a doublet in the ^{31}P{^{1}H} NMR spectrum, and the hydride signal (δ −14.29 ppm) recorded from the ^{15}N-enriched compound has $J(^{15}N-^1H) = 15.7$ Hz indicating that N and H are positioned mutually *trans*. Complex **2** shows no evidence of a reaction with Ph_3SiH in deuteriochloroform at room temperature after 1 h, but after several hours, complex **2** is slowly converted into $[Rh(CNBPh_3)(H)_2(PPh_3)_2]$, the hydrides presumably originating from Ph_3SiH. Under the same conditions, a mixture of **1** and Ph_3SiH produces $[Rh(NCBPh_3)(H)_2(PPh_3)_3]$ as the major product after 16 h.

Triphenyltin hydride combines with **1** and **2** in toluene at room temperature to form the stable crystalline products $[Rh(NCBPh_3)(H)(SnPH_3)(PPh_3)_2]$ and $[Rh(CNBPh_3)(H)(SnPh_3)(PPh_3)_2]$. The structure of the former and an NMR study (focusing on the nature of the bonding between rhodium, hydrogen, and tin) of a series of derivatives will be reported in another paper. The ^{1}H NMR spectrum of the $NCBPh_3$ complex contains a signal at δ −15.55 ppm; this, together with the magnitude of $J(^{15}N-^1H)$ (16.0 Hz), indicates that N and H are positioned mutually *trans*.[11] The $CNBPh_3$ complex gives a ^{1}H NMR signal with $\delta = -9.14$ ppm (consistent with H *trans* to carbon) and $^3J(^{15}N-^1Htrans) = 5.2$ Hz. In each case, the ^{1}H spin-coupling pattern (doublet of triplets for the unenriched complexes) and the ^{31}P{^{1}H} NMR spectrum (doublet) show the phosphines to be equivalent. ^{1}H NMR spectral data are given in Table 3.

Comparison of Properties of the Ph_3BCN^- and Ph_3BNC^- Ligands. A comparison of the reactions undergone by **1** and **2** (Schemes 1 and 2) shows that although the properties of the two are broadly similar, **1** is the more electrophilic (*i.e*., the N-bonded cyanoborate ligand is more strongly electron-withdrawing than the C-bonded form). This is seen in the chemistry of **1** and its derivatives in the ability of **1** to combine with Ph_3SiH, the lack of reactivity (of **1**) toward oxygen, and the apparent inability of pyridine to dissociate from the complex $[Rh(NCBPh_3)(H)_2(PPh_3)_2(py)]$. The N−B bond of the $CNBPh_3$ ligand is significantly more labile than the C−B bond of $NCBPh_3$, the N−B bond in **2** being labilized in the presence of O_2 and pyridine at room temperature to the point where loss of BPh_3 and complete conversion (of **2**) to a mixture of $[Rh(CN)(O_2)(PPh_3)_3]$ and *cis*-$[Rh(CN)(O_2)(PPh_3)_2(py)]$ is observed. In the case of **1**, the only product formed in significant quantity is *cis*-$[Rh(NCBPh_3)(O_2)(PPh_3)_2(py)]$ and the cyano complex cannot be detected. Dissociation (presumably heterolytic) of the C−B bond of **1** is favored only at elevated temperatures (100−120 °C), since under these conditions rearrangement to **2** takes place. The complex *trans*-$[Rh(NCBPh_3)(PPh_3)_2(CO)]$, with a lower electron density on the metal than **1**, undergoes slow rearrangement to the C-bonded isomer in solution at room temperature.

Trends in ^{15}N Chemical Shifts. The replacement of a phosphine of **1** by ligands (L = pyridine, carbon monoxide, 2,6-xylyl isocyanide, and ethylene) causes changes in the chemical shift of the cyanoborate nitrogen that are related to the σ-donor and π-acceptor properties of L. A scale devised by Chatt, Leigh, Pickett, and co-workers,[26] based on electrochemical measurements on a series of complexes $[Cr(CO)_5L]$, quantifies σ-donor and π-acceptor effects, ordering a series of approximately 20 ligands with respect to a parameter (the change in oxidation potential) that correlates with the energy of the

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highest occupied molecular orbital and reflects the extent to which electron density is transferred from the ligand to the metal. On this scale, in increasing order of σ-donor ability, the sequence CO < PPh_3, CNPh < pyridine is found, which correlates with a *decrease* in ^{15}N shielding for the corresponding complexes [Rh($^{15}NCBPh_3$)(PPh_3)$_2$(L)] in Table 1. Similarly, on replacing a phosphine of [Rh($^{15}NCBPh_3$)(H)$_2$(PPh_3)$_3$] by pyridine, the cyanoborate nitrogen is deshielded to an extent of 13.6 ppm; with O_2 in place of the hydrides {to give [Rh($^{15}NCBPh_3$)(O_2)(PPh_3)$_2$(py)]}, an increase in shielding of 24.3 ppm is observed. By varying the substituent in the 4-position (in order to minimize steric effects), the nucleophilicity of the pyridine, and hence the electron density on the metal, can be varied while other factors remain constant. The groups Me_2N and CN occupy positions at opposite ends of the Hammett scale[27] of electron-withdrawing and -releasing properties, providing close to the maximum range that can be achieved by replacement of a single substituent. The ^{15}N chemical shifts for the three series of the complexes *cis*-[Rh($^{15}NCBPh_3$)(PPh_3)$_2$(L)], [Rh($^{15}NCBPh_3$)(H)$_2$(PPh_3)$_2$(L)], and [Rh($^{15}NCBPh_3$)(O_2)(PPh_3)$_2$(L)] (L = py, 4-Me_2Npy, 4-CNpy) show a decrease in shielding as the nucleophilicity of the pyridine is increased. The accuracy of the chemical shifts is estimated to be within 0.2 ppm (based on a few repeated measurements), while the changes in ^{15}N chemical shift are larger than this by factors of *ca.* 2−10.

These findings are in accordance with those obtained from complexes of the triply bonded, linearly bound ligands CO, CN^-, and N_2, where the ^{13}C and/or ^{15}N shielding decreases as the electron density on the metal is increased. Numerous studies have shown moderate to excellent correlations to exist between ^{13}C and/or ^{15}N shieldings and other parameters as follows: for CO complexes, the C−O stretching frequency[28] and the metal−carbon bond length[28b] (a decrease in shielding is associated with a decrease in ν_{CO} and in M−C bond length); for CN^- complexes of Co and Fe, the energy of the first d−d transition[29] and the Mössbauer isomer shift[29b] (a decrease in shielding accompanies a decrease in the energy of the d−d transition and a decrease in ligand field strength at Fe); for N_2 complexes the N−N stretching frequency and the oxidation potential[30] (a decrease in shielding accompanies a decrease in ν_{N-N} and an increase in negative $E_{1/2}^{ox}$). Chatt *et al.* have further correlated their electrochemical scale of ligand properties with ν_{C-O} and ν_{N-N} for complexes [Mo(L)(dppe)$_2$(X)] (L = CO, N_2)[31] (an increase in σ-donor ability is related to a decrease in ν_{C-O} and ν_{N-N}). An increase in the electron density on the metal leads to an increase in metal to ligand (here CO, CN^-, N_2) π back donation, which is responsible for a decrease in the separation between the electronic ground state and the lowest lying excited states.[28] This energy difference is identified with ΔE, the excitation energy in the paramagnetic shielding term (σp) in the treatment of Karplus and Pople,[32] and is considered to be the major contributor to changes in the chemical shift. A full account of theory related to nitrogen NMR is given by Mason.[33]

Spin Coupling to ^{15}N. The $^{103}Rh-^{15}N$ coupling constants show no correlation with the formal oxidation state of rhodium or the electron density on the metal as seen for *cis*-[Rh($^{15}NCBPh_3$)(PPh_3)$_2$(py)] (17.8 Hz), [Rh($^{15}NCBPh_3$)(H)$_2$(PPh_3)$_2$(py)] (11.5 Hz), and [Rh($^{15}NCBPh_3$)(O_2)(PPh_3)$_2$(py)] (20.2 Hz). These findings do little to confirm the apparent trend emerging from earlier studies {$^1J(^{103}Rh-^{15}N)$/Hz in parentheses} of [Rh(H)$_2$(picolinate)(PPh_3)$_2$] (9.7),[11a] [Rh(H)$_2$(SC_6F_5)(PPh_3)$_2$(py)] (8.4),[11b] [Rh(en)$_3$]Cl_3 (14.6),[34a] [Rh(Cl)(P^iPr_3)$_2$(C_6H_5NSO)] (15.5),[34b] *trans*-[Rh(Cl)(N_2)(PCy_3)$_2$] (30),[34c] *trans*-[Rh(Cl)(CO)(NO)(P^iPr_3)$_2$][ClO_4] (4.5),[34d] [Rh(NH_3)$_6$][ClO_4]$_3$ (14.2),[34e] [{(PMe_2Ph)$_3$(Cl)$_2$Rh}$_2$CN][ClO_4] (9),[34f] [Rh(Cl)(N_2Ph)($PMePh_2$)$_3$][PF_6] (15),[34g] *cis*-[Rh(Cl)(py)(PPh_3)$_2$] (15), and *cis*-[Rh(py)$_2$(PPh_3)$_2$]Cl (28),[34h] namely that the highest values of $^1J(^{103}Rh-^{15}N)$ are observed for Rh(I) complexes with electron-donating ligands and the lowest for Rh(III) complexes with electron-withdrawing ligands. Clearly, the electronic properties of the individual ligands and the nature of their interaction with the metal are of greater significance in determining the magnitude of $^1J(^{103}Rh-^{15}N)$ than the more generalized parameters such as electron density on the metal. Factors influencing coupling constants and the processes underlying nuclear spin−spin coupling have been analyzed in some detail.[35]

The values measured for $^2J(^{31}P-^{15}N)$ show *trans* coupling in the range of 37.8−41.9 Hz and *cis* coupling to be smaller than this by approximately 1 order of magnitude. Unlike $^{31}P-^{31}P$ *cis* coupling, which in complexes of rhodium is a useful indicator of oxidation state, $J(^{31}P-^{15}N$*cis*) conveys little information. For the dihydro complexes, $^2J(^{15}N-^1H$*trans*) lies in the range of 20.7−21.7 Hz, while the *cis* coupling is too small to be detected. The P−N and N−H coupling constants closely resemble those found in similar compounds where the nitrogen is present in the form of a pyridine derivative[11b] and appear to be largely uninfluenced by the difference in electronic configuration of N. $^2J(^{15}N-^1H$*trans*), used to optimize delay times in the INEPT polarization transfer pulse sequence, is readily obtained by comparison of the ^{31}P-decoupled proton NMR spectra of enriched (Figure 3c) and unenriched compounds.

Acknowledgment. We thank the University of the Witwatersrand and the FRD for financial support.

IC9601293

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