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The Synthesis, X-ray Crystal Structure, and Molecular Structure of Rhenium Tetracarbonylbromidetrimethylamineisocyanoborane[†]

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Introduction

Although carbon monoxide has been the mainstay of donor ligands to transition metals, isocyanides $R-N^{+}\equiv^{-}C{:}$[1,2,3−5] have enjoyed a novel revival because the donor features on the isocyano group can be easily modified by changing the R groups.[6] Thus, both organic and inorganic functions can be used to modulate the electron density on the isocyano donor carbon atom.[7] Even multidentate isocyanides can be generated because the functionality of the R group is so easily changed.[8−10]

Isocyanoboranes[11−14] represent one class of functional isocyanides that have received little attention. In 1976,[15−18] Vidal and Ryschkewitsch reported the interaction of the boron isocyanide Me_3N-BH_2NC with manganese pentacarbonyl bromide. The low-temperature facile substitution of carbon monoxide by this nucleophile reportedly generated σ- and/or π-complexed intermediates and a possible fast exchange between coordinated and uncoordinated compounds. In an attempt to clarify the reaction chemistry of this unusual isocyanide, we have studied its reaction with the more thermally stable rhenium pentacarbonyl bromide. This paper describes the first X-ray molecular structure characterization of trimethylamine isocyanoborane and its coordination adduct with $[Re(CO)_4Br]_2$.

Table 1. Summary of Crystallographic Data for **1** and **2**

crystal	**1**	**2**
formula	$C_4H_{11}BN_2$	$ReC_8H_{11}BBrN_2O_4$
fw	97.96	476.11
space group	$P1$	$C2/c$ (No. 15)
a, Å	5.579(1)	23.9353(2)
b, Å	13.918(1)	5.887 90(10)
c, Å	18.737(2)	20.613 80(10)
α, deg	111.41(1)	90
β, deg	96.55(1)	90.2910(10)
γ, deg	91.12(1)	90
V, Å^3	1342.7(3)	2905.04(6)
Z	8	8
λ, Å	0.71073	0.71073
ρ_{calc}, g/mL	0.97	2.177
T, °C	−90	20
μ, cm^{-1}	0.59	111.19
$R_w(F^2)$	0.190[b]	7.90%[c]
$R(F)$	0.0940[a]	4.77%[d]

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|)^4\}^{1/2}$ where w is defined as $w = 1/\{\sigma^2(|F_o|^2 + (0.0322P)^2\}$; $P = [{}^1/_3 \max(0 \text{ or } |F_o|^2) + {}^2/_3|F_c|^2]$. [c] $R(F)^2 = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$, with $F_o > 4.0\sigma(F)$. $w = 1/[\sigma(F_o^2) + (0.0547P)^2$, where $P = (F_o^2 + 2F_c^2)/3$. [d] $R(F) = \sum||F_o| - |F_c||)/\sum|F_o|$, with $F_o > 4.0\sigma(F)$.

Experimental Section

General Data. Infrared spectra were taken on a Bio-Rad Digilab FTS-60 FTIR spectrometer as powders between AgCl plates. Mass spectra were taken on an AutoSpec Instrument at UCLA. The ^{1}H NMR spectra were obtained on Bruker DRX 250 (250.13 MHz), General Electric GN-500 (500.12 MHz), and Nicolet NT 300 (300.16 MHz) instruments. ^{13}C NMR spectra were obtained on the same instruments at 63.9, 125.76, and 75.4 MHz, respectively. The ^{1}H and ^{13}C chemical shifts are reported relative to Me_4Si referenced with respect to residual protonated material in the solvent. ^{11}B NMR spectra were referenced with respect to boric acid. The compounds $[Re(CO)_4Br]_2$,[19] $[Mn(CO)_4Br]_2$,[20,21] and Me_3N-BH_2-NC[11,14] were synthesized according to published procedures. The isocyanide had the correct mp and was further characterized by ^{1}H and ^{13}C NMR spectroscopy. Deuterated NMR solvents were distilled from $LiAlH_4$, degassed, and stored in a Vacuum Atmospheres drybox. All reactions and handling of products were done under argon according to previously described procedures.[22]

X-ray Structure Determination of 1. Crystals of $C_4H_{11}BN_2$ were grown as thin colorless plates by sublimation in a thermal gradient sublimator. The data crystal was a triangular prism of approximate dimensions 0.08 × 0.40 × 0.40 mm. The data were collected at −90 °C on a Siemens P4 diffractometer, equipped with a Nicolet LT-2 low-temperature device and using a graphite monochromator with Mo Kα radiation (λ = 0.710 73 Å). Details of crystal data, data collection, and structure refinement are listed in Tables 1 and 2. Four reflections (0,−4,2; −1,−1,4; −1,1,2; 1,1,0) were remeasured every 96 reflections to monitor instrument and crystal stability. A smoothed curve of the intensities of these check reflections was used to scale the data. The

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[†] Dedicated to Professor H. Werner on the occasion of his 65th birthday.

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Table 2. Averaged Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $C_4H_{11}BN_2$ (**1**)

1	*2*	*3*	*1−2*	*1−2−3*
N2	B1	N1	1.534(14)	108.1(4)
N1	B1		1.595(5)	
C4	N2	B1	1.146(6)	177.7(4)
C[a]	N1	C[a]	1.494(18)	108.5(9)
C[a]	N1C	B1C		110(2)[b]

[a] C refers to averages involving all the methyl carbon atoms. [b] There is a bimodal distribution in the C−N−B1 bond angles. Angles involving C1 of the four unique molecules average 107.5(5)°, while all other C−N1−B1 angles average 111.7(6)°.

scaling factor ranged from 0.982 to 1.00. The data were corrected for Lp effects but not for absorption. Data reduction, decay correction, structure solution, and refinement were performed using the SHELXTL/PC software package.[23] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms. The hydrogen atoms were observed in a ΔF map and refined to reasonable positions with isotropic displacement parameters. There are four crystallographically independent molecules of $C_4H_{11}BN_2$ per asymmetric unit. All exist as the isocyanide adduct. The molecules differ slightly in conformation as seen by the N−B−N−C torsion angles (Supporting Information, Table 7). The different molecules are labeled A, B, C, and D, respectively (Supporting Information, Figures 1−4). Columns of like molecules stack along the **a** direction in the unit cell (Supporting Information, Figure 5). The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = 1/[F(\sigma(F_o))^2 + (0.0322P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. The data were corrected for secondary extinction effects. Neutral atom scattering factors and the values used to calculate the linear absorption coefficient are from the *International Tables for X-ray Crystallography* (1992).[24] Other computer programs used in this work are listed elsewhere.[25] All figures were generated using SHELXTL/PC. Tables of positional and thermal parameters, bond lengths, angles and torsion angles, and figures are located in the Supporting Information.

X-ray Structure Determination of 2. A crystal was mounted on a thin glass fiber with 5-min epoxy glue. The crystal was then mounted on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo K radiation = 0.710 73 Å) operating at 50 kW and 40 mA. About 1.3 hemisphere of intensity data were collected in 1321 frames with scans (width of 0.30 and exposure times of 10 s per frame). Unit cell dimensions were determined by a least-squares fit of reflections with $I > 10\sigma(I)$ and $1.7 < 2\theta < 28.16$. Empirical absorption corrections based on ψ scans[26] were applied. The structure was solved by direct methods followed by successful difference Fourier methods. All calculations were done using SHELXTL running on a Silicon Graphics Indy 5000. Final full-matrix refinements were against F^2 with all reflections and include anisotropic thermal parameters for all non-hydrogen atoms. Parameter shifts in the final least-squares cycle were smaller than 0.03. The crystallographic results are summarized in Table 1 while the selected bond distances are listed in Table 3.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for **2**

Re1−Br1	2.6448(10)	C5−N1−B1	178.7(9)
Re1−C1	2.016(10)	Re1−C5−N1	177.4(8)
Re1−C2	1.992(10)	N1−B1−N2	105.3 (7)
Re1−C3	1.997 (9)	C4−Re1−C5	177.1 (3)
Re1−C4	1.984 (9)	Br1−Re1−C1	89.7 (3)
Re1−C5	2.102(9)	C1−Re1−C2	91.3 (4)
N1−C5	1.155(10)	C1−Re1−C4	91.1(4)
N1−B1	1.590(12)	C1−Re1−C3	174.9 (4)
N2−B1	1.594(13)		
C4−O4	1.131(10)		

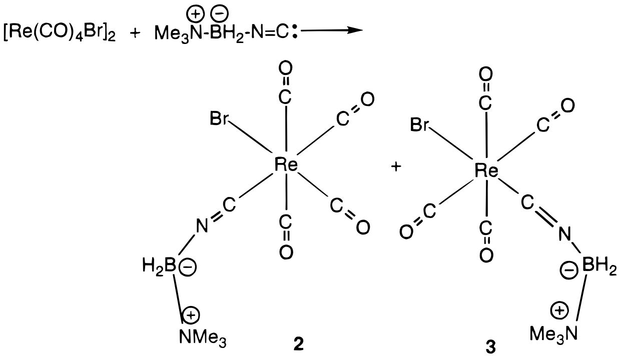
Table 4. Ab Initio/GIAO Chemical Shift Predictions Run at the B3LYP/6-311G** Level on B3LYP/6-31G*-Optimized Geometries

	^{13}C (CH_4)	^{11}B ($BF_3{\cdot}Et_2O$)
H_3BH_2CN	138.6	−26.8
H_3BH_2NC	206.1	−20.0
Me_3BH_2NC	203.4	−12.6

Preparation of the Compounds. $Me_3N{-}BH_2{-}NC$ (0.047 g, 0.480 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a suspension of 0.182 g (0.241 mmol) of $[Re(CO)_4Br]_2$ in ice-cold CH_2Cl_2 for 1 h. The mixture became homogeneous after it was allowed to warm to room temperature for 24 h. The solid obtained after vacuum removal of the CH_2Cl_2 was recrystallized from CH_2Cl_2−pentane to give white crystals: yield of **2** 0.210 g (91.7%); mp 118−120 °C; ^1H NMR (δ 500 MHz, CD_2Cl_2) 2.71 (s, 9H, CH_3, **2**), 2.70 (s, 9H, CH_3, **3**); ^{13}C (δ 125.76 MHz, CD_2Cl_2) 51.05 (s, 3C, CH_3, **2**), 50.93 (s, 3C, CH_3, **3**), 181.74 (s, 1C, CO trans to NC, **2**), 182.71 (s, 2C trans to CO, **2**), 184.50 (s, 1C, C═O, trans to Br), 189.33 (s, 4C, CO, **2**), 139.71, (s, 1C, N═C, **2**), 146.11 (s, 1C, NC, **3**); ^{11}B (δ 66 MHz, C_7D_8) δ −27.1 (1:1:1, $J_{BH} = 108.25$ Hz, BH_2); IR spectrum (AgCl plates) ν(N═C) 2200, 2109 (s) cm^{-1}; ν(C═O) 2021 (s), 2004 (s), 1967 (s), 1942 (s) cm^{-1}; CI (NH_3) mass spectrum (*m*/*z*) calcd for $C_8H_{11}N_2O_4BBrRe$ 476.10987, found 475.955288. Anal. Calcd for $C_8H_{11}N_2O_4BBrRe$: C, 20.65; H, 2.38; N, 6.02. Found: C, 20.51; H, 2.22; N, 5.85. These data are described for compound **2** since it is the major species in the reaction mixture. Compound **2** crystallized from the reaction mixture. Compound **3** could not be isolated from the mixture. An area analysis of the ^1H and ^{13}C NMR spectra (*cis*- and *trans*-carbonyl groups) showed that compounds **2** and **3** are in a ratio of 15:1.

Results

Equation 1 describes the treatment of $[Re(CO)_4Br]_2$ with $Me_3N{-}BH_2{-}NC$ in methylene chloride in a 1:2 molar ratio to give white crystals that are an apparent mixture of adducts **2** and **3**.



(1)

Adduct **2** was characterized by ^1H, $^{13}C\{^1H\}$, and ^{11}B NMR spectroscopy. The ^1H NMR spectrum of the reaction product in CD_2Cl_2 displays a major single resonance for the Me_3N hydrogen atoms at δ 2.71 (**2**) and a minor peak as a shoulder at δ 2.70 (**3**). This is almost unchanged from the free ligand resonance at δ 2.70. The hydrogen atoms on the boron are too broad to clearly discern because of quadrupolar broadening. A dramatic solvent shift occurs for the Me_3N hydrogen atoms in toluene-d_8 with a major peak at δ 1.72 (**2**) and a minor peak as a shoulder at δ 1.78 (**3**). In a variable-temperature study from −70 to +40 °C in toluene-d_8 there is no change in the character of these peaks except for some broadening at low temperature. The ^{11}B NMR shows a broadened triplet at δ −27.1.

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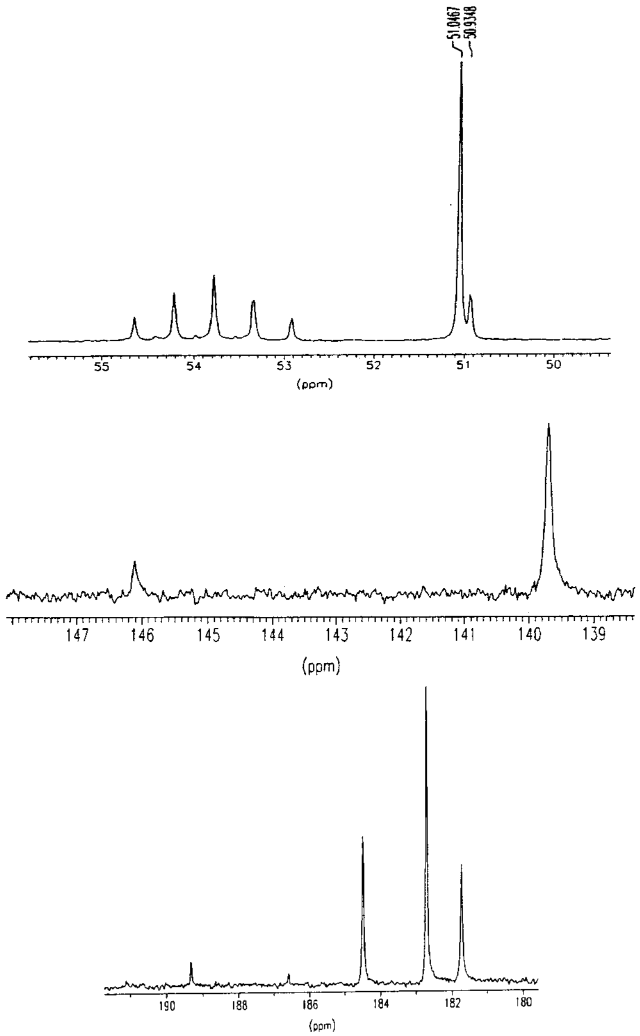

Figure 1. ^{13}C NMR spectrum of **2** and **3** in CD_2Cl_2.

The $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2 (Figure 1) was more informative at room temperature with a major resonance at δ 51.05 and a minor resonance at δ 50.93 for the carbon atoms of the trimethylamine group of **2** and **3**, respectively. The free ligand has a resonance at δ 50.7 that is not affected at all by complexation to the metal. This is consistent with the ^1H NMR findings. In addition, there are isocyano carbon resonances at δ 139.71 for **2** and δ 146.11 for **3**, the major and minor products, respectively. Both of these resonance positions reflect deshielding of the isocyano carbon by complexation to the rhenium atom. The free ligand shows a higher field resonance position at δ 115.3. The carbonyl region of the spectrum further illustrates the difference between **2** and **3**. There is a major resonance at δ 182.7 for the set of *trans*-carbonyl groups, δ 184.5 for the carbonyl group trans to the bromo group, and δ 181.74 for the carbonyl group trans to the isocyano group in **2**. Another resonance at δ 189.33 represents the equivalent *trans*-carbonyl groups in substituted product **3** (Figure 1).

A single crystal from the crystallized mixture of **2** and **3** was taken for analysis. An X-ray crystal determination showed the crystal to be that of **2**. This is consistent with the NMR data of **2**. The structure (Figure 2) shows an octahedrally coordinated rhenium complex with cis-coordinated bromide and trimethylamineisocyanoboron. The carbon−metal bond distance of 2.10 Å is very similar to the equatorial substituted $Re_2(CO)_9(CN^tBu)$ where the Re−C distance is 2.05 Å[27] and to $[Re(CO)(CNC_6H_3Me_2\text{-}2,6)_4Br]$ where the Re−C distance is 2.033 Å.

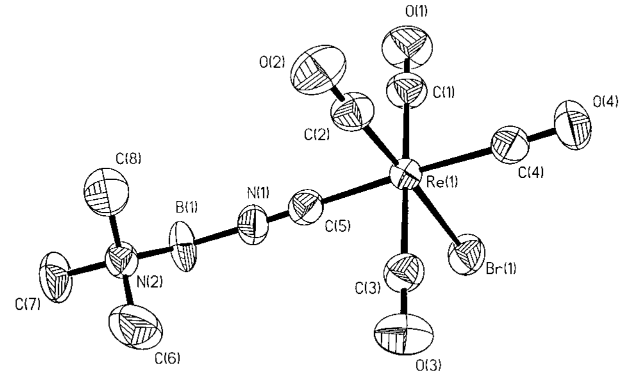

Figure 2. Ortep plot of rhenium tetracarbonylbromidetrimethylamineisocyanoboron with the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level.

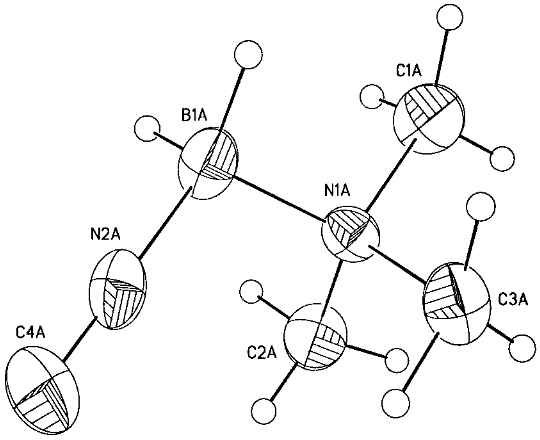

Figure 3. Ortep plot of trimethylamineisocyanoboron with the atom labeling scheme. Thermal ellipsoids are scaled to the 50% probability level.

Tripodal isocyanides generally have metal−carbon bond lengths of 2.13−2.10 Å.[8] The CN bond length is 1.17 Å in the free ligand vs 1.14 Å in the complex. The CN bond lengths are usually a little longer in the uncoordinated material because of π back-bonding in the metal complexes. The Re−C− N bond angle is very close to being linear at 178.5°. The N−B−N bond angle is 106° in the complex and 108° in the metal-free material (Figure 3). The smaller angle may reflect lower nonbonded repulsions in the complex compared to the metal free molecule.

Discussion

The most convenient procedure to obtain pure $[M(CO)_4LX]$ (M = Mn, Re) compounds is to treat the metal dimer $[M(CO)_4Br]_2$ with L under mild conditions.[28,29] This normally gives the cis product. We report here that trimethylamine−isocyanoborane most likely interacts with $[Re(CO)_4Br]_2$ by direct cleavage of the bridging halide to give a *cis*-tetracarbonyl complex as the major product with a minor trans product. Variable temperature NMR measurements show that there is no change in the concentrations of either **2** or **3** upon long standing once they are formed. No further peaks appear over the temperature range studied. Thus, the trimethylamine−boryl group must convey a certain stability to the trans product so that it does not isomerize to the more thermodynamically stable cis complex.[30]

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In addition, the ^{13}C spectra of the carbonyl region shows the expected one signal for all equivalent carbonyl groups of the trans-substituted product and a single resonance for the isocyano carbon of **3**. Another possibility is that the minor product is a rhenium complex of the rearranged Me_3N-BH_2-CN ligand.[31] We prepared the trimethylaminecyanoborane and its rhenium complex. The ^{13}C NMR spectrum shows a typical pattern for a cis-substituted carbonyl complex with peaks at δ 187.0, 184.4, and 183.0 for the carbonyl carbon atoms and δ 53.2 for the trimethylamino carbon atoms. There was no conclusive evidence for the presence of another isomer. The ^{13}C resonance for the cyano carbon bound to boron could not be observed in the adduct or the pure ligand. This is most likely due to the relaxtion of the boron-bound carbon.[32] Hence, calculated values are shown in Table 4.[33]

In contrast to the isocyano complex, the ^{1}H NMR of the cyano complex with Re showed only one resonance for the trimethylamino group at δ 2.70.

Treatment of **1** with $[Mn(CO)_4Br]_2$ gives a product whose ^{1}H NMR in CD_2Cl_2 shows a single resonance for the trimethylamino group at δ 2.71 (200 and 500 MHz). However, the ^{13}C NMR in CD_2Cl_2 shows two resonances at δ 51.1 and 51.2 at 500 MHz. There are also two isocyano resonances at δ 115.4 and 112.5. The carbonyl groups on the manganese were not observed. In benzene-d_6 there are two resonances at δ 1.72 and 1.83 for the trimethylamino group, again indicating the strong effect of the polar trimethylamine−boryl group on the chemical shift. These resonances do not disappear upon long standing.

Although there is some controversy about the electronic effects of the trimethylamine−boryl group,[13,34] there is strong chemical evidence that it is strongly electron releasing. This could make **1** an even better σ donor than an organic substituted isocyanide. If this is the case, then cleavage of the halide bridge bonds in the metal dimer could generate a transition state for a small amount of trans-coordinated product. The amount of this material could of course vary with the polarity of the solvent.

The evidence we have presented suggests that there is no need to postulate the formation of a dynamic $\pi-\sigma$ coordinated complex of **1** with $[Mn(CO)_4Br]_2$ as suggested by Vidal[16] or dynamic exchange between free and metal-coordinated complexes in the rhenium or manganese carbonyl complexes of trimethylamineisocyanoborane.

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Supporting Information Available: Tables with full crystallographic details for complex **2** and an X-ray crystallographic CIF file for the structure determination of complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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