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Synthesis of the sterically hindered complexes $[M(CO)_5(CNBR_2)]$ [$R = CH(SiMe_3)_2$; M = Cr, Mo, or W]. Crystal structure of $[Cr(CO)_5(CNBR_2)]$ *

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Abstract

The reaction of the dialkylchloroborane $BClR_2$ [$R = CH(SiMe_3)_2$] with a Group 6 pentacarbonyl(cyano)metallate(0) $[NEt_4][M(CN)(CO)_5]$ in CH_2Cl_2 or PhMe gives the thermally stable complexes $[M(CO)_5(CNBR_2)]$ [M = Cr (**2a**), Mo (**2b**), or W (**2c**)]. Crystalline **2a** has a linear Cr–C–N–B skeleton with long Cr–C and B–N bonds and a short C–N bond, consistent (as are the IR, Raman and NMR spectra) with its formulation as $[(OC)_5\bar{C}r\text{–}C{\equiv}\overset{+}{N}\text{–}BR_2]$.

Key words: Group 6; Boron; Silicon; Crystal structure; Isocyanide; Carbonyl

1. Introduction

In connection with our studies on the reactivity of sterically hindered dialkylboranes [1], we were interested in exploring various substitution reactions involving the BR_2X [$R = CH(SiMe_3)_2$] system. The starting material that we employed was bis{bis(trimethylsilyl)methyl}chloroborane, $BClR_2$ (**1**). This compound had previously been prepared and some of its reactions studied [2]. In this paper we report on the reactions of **1** with the weak organometallic nucleophiles $[M(CN)(CO)_5]^-$ (M = Cr, Mo, or W). Reactions of the latter with other electrophiles have recently been reviewed [3].

2. Results and discussion

2.1. Synthesis and stability of the complexes $[M(CO)_5(CNBR_2)]$ [$R = CH(SiMe_3)_2$ and M = Cr (2a), Mo (2b), or W (2c)]

Reaction of $BClR_2$ [$R = CH(SiMe_3)_2$] (**1**) in toluene or dichloromethane with the appropriate tetraethylammonium pentacarbonyl(cyano)metallate(0) led to the corresponding Cr, Mo, or W (boryl isocyanide)penta(carbonyl)metal(0) complex **2**, eqn. (1).

$$\underset{(\mathbf{1})}{BClR_2} + [NEt_4][M(CN)(CO)_5] \xrightarrow[R=CH(SiMe_3)_2]{} [M(CO)_5(CNBR_2)] + [NEt_4]Cl \quad (1)$$

M = Cr (**2a**)
M = Mo (**2b**)
M = W (**2c**)

In contrast to the known highly reactive isocyanoborane complexes containing a three-coordinate boron atom [4], these yellow crystalline compounds are relatively stable, towards both heat and aerial oxidation. Thus, when the chromium complex **2a** was treated with an excess of triphenylphosphine in light petroleum (b.p. 100–120°C) and the mixture heated for 20 h under reflux, there was no noticeable reaction as indicated by infrared spectral monitoring. Use of ^{31}P NMR spectroscopy revealed that only a very small amount of $[Cr(CO)_5(PPh_3)]$ (δ −58) and *trans*-$[Cr(CO)_4(PPh_3)_2]$ (δ −75) had been formed. Complex **2a** was similarly

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* Dedicated to Professor Heinrich Nöth to mark his 65th birthday. We, and especially M.F.L. (who has enjoyed his friendship for more than three decades), pay tribute to his many contributions to chemistry and education in both a national and the international sphere.

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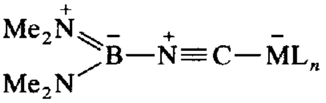
unreactive towards acetonitrile or pyridine. These observations demonstrate that the complexes **2** are kinetically stable despite having the skeletal arrangement MCNB. This is attributed to steric effects.

Similar stability has not previously been observed for related (boryl isocyanide)metal complexes, although electronic effects have been shown to confer an alternative mode of stabilization. Thus, Höfler and Löwenich [4a] showed that for the series of compounds $[Cr(CO)_5(CNBX_2)]$ (X = Et, OMe, or NMe_2) only the dimethylamido derivative (X = NMe_2) was sufficiently stable to be stored at ambient temperature in an inert atmosphere. Nöth and Geltinger [4b] found that the iron(0) and nickel(0) complexes $[M(CO)_n(L)]$ [L = $B(CN)(NMe_2)_2$ and M = Fe with $n = 4$, or M = Ni with $n = 3$] were unstable, but IR spectroscopy showed them to be isocyanoborane complexes rather than the cyanoborane isomers.

In compounds such as $[Cr(CO)_5\{CNB(NMe_2)_2\}]$, the effect of the $\bar{N}Me_2$ ligand at boron is thus in part (a) to reduce the electrophilicity at boron by a π-bonding mechanism, this effect being conjugatively transmitted to the metal centre, as in the canonical form **A**; and (b)



(A)

to shield the boron atom sterically. Such a strategy has been widely used, especially by Nöth *et al.* [5], to stabilize otherwise kinetically labile boron compounds, at the steric extreme using the 2,6-dimethylpiperidinato ligand, as in $^tBuN{=}B[NCMe_2(CH_2)_3CMe_2]$.

2.2. Spectroscopic characterization

If the $[M(CO)_5(CNR')]$ system is assumed to have C_{4v} skeletal symmetry, then three IR-active carbonyl stretching modes ($2A_1$ and E) are to be expected in the same region of the spectrum as the isocyanide band (A_1). On the other hand, in the Raman spectrum the expectation is for four ν(CO) ($2A_1$, B_1, and E) and one ν(NC) (A_1) bands. Our experimental data for the vibrational spectra are shown in Table 1. It will be apparent that for complexes **2** in solution these expectations were realized, certainly for the chromium **2a** and molybdenum **2b** compounds, although an extra band was observed for the tungsten complex **2c**. Nevertheless, the precise assignment of the individual bands remains uncertain. The two highest energy bands in, for example, the chromium complex **2a** (at 2113 and 2028 cm^{-1}) appear to be somewhat low in energy when compared with the corresponding bands in $[Cr(CO)_5(CNBX_2)]$ (X = Et, OMe, or NMe_2) (*e.g.* 2140 and 2060 cm^{-1} for X = Et), which also were rather insensitive to the nature of X (± 10 cm^{-1}) [4a]. To resolve some of the uncertainty, we undertook the synthesis and subsequent spectroscopic characterization of the ^{13}C-labelled complex $[W(CO)_5(^{13}CNBR_2)]$ (**3**). For the synthesis of **3**, we used $K^{13}CN$ (99% in ^{13}C); its ^{13}C isotopic content was verified by examination of its mass spectrum.

The IR spectrum in n-hexane of complex **3** revealed seven bands in the CO/CN stretching region. In addition to those found in the unlabelled isotopomer **2c**, there were two new bands at 2001vs and 2105vw cm^{-1}. We cannot account for the large number of bands in the 2000 cm^{-1} region in complex **3** in terms of its contamination by the isotopomer **2c**. Hence, we con-

TABLE 1. IR and Raman spectral data (CO and CN stretching modes, cm^{-1}) for $[M(CO)_5(CNBR_2)]$ [M = Cr (**2a**), Mo (**2b**), or W (**2c**)] and $[W(CO)_5(^{13}CNBR_2)]$ (**3**) [R = $CH(SiMe_3)_2$]

Complex	IR/Raman	ν(CN) + ν(CO)	Solvent or solid
2a	IR	2113w, 2028s, 1965vs, 1934w	n-Hexane
	Raman	2116m, 2033vs, 1995s, 1965vw, 1947w	Solid
2b	IR	2121m, 2031m, 1968vs, 1936w,	n-Pentane
	Raman	2119m, 2035vs, 1995vs, 1965vw, 1947m	Solid
2c	IR	2119w, 2026m, 1986vw, 1962vs, 1930w	n-Hexane
	IR	2121w, 2037m, 2026m, 1988w, 1955vs	Solid [a]
	Raman	2122m, 2032vs, 1985m, 1959vw, 1941w	Solid
	Raman	2121m(p), 2034vs(p), 1994w(dp), 1950vw(?)	CH_2Cl_2
3	IR	2118vw, 2105vw, 2025w, 2001m, 1986vw, 1961vs, 1929w	n-Hexane
	IR	2122vw, 2105w, 2036m, 2016s, 1988m, 1945vs, 1918vw(?)	Solid [b]
	IR	2122vw, 2105w, 2037m, 2015m, 1990m, 1957vs, 1945sh, 1918s	Solid [a]
	Raman	2121vw, 2106m, 2035w, 2013vs, 1995m, 1951vw	CH_2Cl_2
	Raman	2124w, 2106w, 2037w, 2011vs, 1990m, 1961vw(?), 1941w, 1921vw(?)	Solid

[a] Nujol mull. [b] KBr disc.

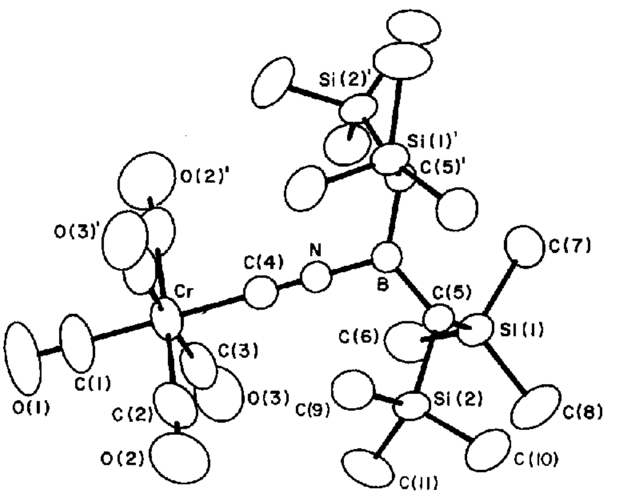


Fig. 1. The molecular structure of $[Cr(CO)_5(CNBR_2)]$ $[R = CH(SiMe_3)_2]$ (**2a**).

clude that presence of the sterically demanding ligand $\bar{C}H(SiMe_3)_2$ on boron renders the C_{4v} point group assignment untenable; alternatively, **2c** may comprise a mixture of conformers that give different IR spectra.

The NMR spectral data are listed in Table 2; there were no significant variations in the ^1H NMR spectra in $CDCl_3$ when these were measured at 305 K or 265 K. The main noteworthy feature was the position of the ^{13}C signal attributable to the isocyanide moiety. For the chromium complex **2a** this appeared at δ 197.8, a value comparable with those found for $[Cr(CO)_5(CNCCl_3)]$ (δ 200.7) [6], $[Cr(CO)_5(CNCN)]$ (δ 200.0) [7], and $[Cr(CO)_5(CNCPh_2)][BF_4]$ (δ 200.4) [8]. Nevertheless, these signals are well outside the normal range (δ 105–175) expected for most isocyanide–metal complexes [9]. In the complex $[Cr(CO)_5\{CNB(NMe_2)_2\}]$, δ(CN) has been assigned to the signal at 184.4 ppm [4a]. The fact that the $\delta[^{13}CN]$ signal in the complexes **2** was found at relatively high frequency, as well as the magnitude of $^1J(^{185}W-^{13}CN)$ (115.5 Hz), confirms that they are properly formulated as isocyanide–metal complexes, rather than the cyanide isomers. Complex **3** was used to establish the magnitude of the $^{185}W-^{13}C$ coupling constant.

The isocyanide formulation is consistent with (i) the fact that the starting materials for complexes **2** and **3** already have the M–CN skeleton, and (ii) previous experiments on the reactions between a cyanoborane and a transition metal complex, which invariably led to (boryl isocyanide)metal complexes [4]. A further analogy relates to the mode of coordination of cyanides of Si^{IV} [10] or Sn^{IV} [11].

Further features of the structure, and conclusions relating to bonding, are most readily accessible by consideration of the molecular structure of the crystalline complex **2a**, Section 2.3.

2.3. X-Ray structure of $[Cr(CO)_5(CNBR_2)]$ $[R = CH(SiMe_3)_2]$ (2a)

The molecular structure of complex **2a**, together with the atom numbering scheme, is shown in Fig. 1. Important intramolecular bond distances and angles are given in Table 3 and atom coordinates in Table 4.

Because the molecule has a two-fold rotation axis it is inevitable that the Cr–C–N–B skeleton is linear. The $Cr-CNBR_2$ distance, Cr–C(4), is 1.971(4) Å. This is significantly longer than the Cr–CN bond length of 1.942(12) in $[Cr(CO)_5(CNCF{=}CF_2)]$ [12a] or 1.883(3) Å in $[Cr(CO)_5(CNCN)]$ [7]; only electron-rich pentacarbonyl(isocyanide)chromium(0) complexes have longer Cr–CN distances: 2.031(3) Å in $[Cr(CO)_5(CNNPPh_3)]$, and 2.000(3) Å in $[Cr(CO)_5(CNNH_2)]$ [12b]. On comparing *cis*- and *trans*-Cr–CO distances, it is noteworthy that the former [1.887(5) Å] are somewhat longer than the latter [1.873(5) Å]. We conclude that the coordinated borylisocyanide ligand is a weaker π-acceptor than a coordinated carbonyl group.

The B–N bond length in **2a** is 1.475(6) Å. This may be compared with the values proposed for a B–N single and double bond of 1.58 and 1.41 Å, respectively [13]; the latter value, however, was taken from compounds containing both the nitrogen and boron atoms

TABLE 2. ^1H, ^{13}C, and ^{11}B NMR spectral chemical shift (δ) and coupling constant (Hz) data for complexes **2** and **3** in $CDCl_3$ at *ca.* 305 K

Complex	^1H	^{11}B	^{13}C
2a	0.99 (CH, s, 2H) 0.19 (Me, s, 36H)	55.6	216.6 (CO_{tr}); 214.2 (CO_{cis}); 197.8 (CN); 32.4 (CH); 2.3 (Me)
2b	1.00 (CH, s, 2H), 0.20 (Me, s, 36H)	58.0	206.2 (CO_{tr}); 203.3 (CO_{cis}); 189.3 (CN); 32.5 (CH); 2.3 (Me)
2c, **3**	0.99 (CH, s, 2H), 0.20 (Me, s, 36H)	56.4	196.2 [CO_{tr}, J(wc) = 129.6 Hz]; 193.6 [CO_{cis}, J(wc) = 125.6 Hz]; 177.6 [CN, J(wc) = 115.5 Hz]; 32.7 (CH); 2.3 [Me, J(SiC) = −51.4 Hz] [a]

[a] *Cf.* J(SiC) = 52.0 Hz in $SiMe_4$ [20].

TABLE 3. Selected intramolecular bond distances (Å) and angles (°) in **2a** with estimated standard deviations in parentheses [a]

Cr–C(1)	1.873(5)	Cr–C(2)	1.882(4)
Cr–C(3)	1.891(4)	Cr–C(4)	1.971(4)
Si(1)–C(5)	1.902(3)	Si(1)–C(6)	1.864(4)
Si(1)–C(7)	1.860(4)	Si(1)–C(8)	1.864(4)
Si(2)–C(5)	1.894(3)	Si(2)–C(9)	1.864(4)
Si(2)–C(10)	1.858(4)	Si(2)–C(11)	1.857(4)
O(1)–C(1)	1.138(6)	O(2)–C(2)	1.132(5)
O(3)–C(3)	1.137(5)	N–C(4)	1.159(5)
N–B	1.475(6)	C(5)–B	1.535(4)
C(1)–Cr–C(2)	89.2(1)	C(1)–Cr–C(3)	91.7(1)
C(1)–Cr–C(4)	180	C(2)–Cr–C(2)′	178.4(2)
C(2)–Cr–C(3)	90.4(2)	C(2)–Cr–C(3)′	89.7(2)
C(3)–Cr–C(3)′	176.6(1)	C(3)–Cr–C(4)	88.3(1)
C(2)–Cr–C(4)	90.8(1)	C(5)–Si(1)–C(6)	112.6(1)
C(5)–Si(1)–C(7)	107.6(1)	C(5)–Si(1)–C(8)	111.2(1)
C(6)–Si(1)–C(7)	108.9(2)	C(6)–Si(1)–C(8)	109.3(2)
C(7)–Si(1)–C(8)	107.1(2)	C(5)–Si(2)–C(9)	111.9(1)
C(5)–Si(2)–C(10)	108.6(2)	C(5)–Si(2)–C(11)	112.9(1)
C(9)–Si(2)–C(10)	106.7(2)	C(9)–Si(2)–C(11)	106.4(2)
C(10)–Si(2)–C(11)	110.1(2)	C(4)–N–B	180
Cr–C(1)–O(1)	180	Cr–C(2)–O(2)	178.5(4)
Cr–C(3)–O(3)	179.0(3)	Cr–C(4)–N	180
Si(1)–C(5)–Si(2)	114.7(2)	Si(1)–C(5)–B	110.6(1)
Si(2)–C(5)–B	116.2(2)	C(5)–B–C(5)′	127.0(3)
N–B–C(5)	116.5(2)		

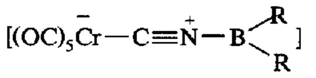
[a] Symmetry element ′ is $-x$, y, $0.5-z$.

in a three-coordinate environment. Because in complex **2a** the nitrogen atom is two-coordinate, it is appropriate to take note of available B–N bond length data in which the nitrogen is likewise two-coordinate, *viz.* [$Mes_2B{=}N{=}BMes_2$]$^-$, 1.343(5) and 1.348(5) Å [14]; [$Me_2N{=}B{=}NC_9H_{18}$]$^+$, 1.30(4) and 1.42(4) Å [15]; and $Mes_2B{-}N{=}CPh_2$, 1.38(2) Å [16] (Mes = $C_6H_2Me_3$-2,4,6; $NC_9H_{18} = NC_5H_6Me_4$-2,2,6,6). These distances are significantly shorter than that found in complex **2a**. We conclude therefore that in **2a** the B–N bond multiplicity is very close to unity, with little evidence for any B=N double-bond character.

TABLE 4. Fractional atomic coordinates ($\times 10^4$) for complex **2a**

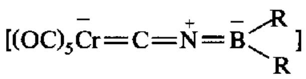
Atom	*x*	*y*	*z*
Cr	0	1232.3(3)	2500
Si(1)	1955.3(7)	3950.8(4)	1918.5(7)
Si(2)	1.5(7)	3464.3(5)	127.3(7)
O(1)	0	−238(2)	2500
O(2)	−621(3)	1198(2)	33(3)
O(3)	−2345(2)	1286(1)	2788(3)
N	0	2762(2)	2500
C(1)	0	317(2)	2500
C(2)	−394(3)	1219(2)	960(3)
C(3)	−1466(3)	1260(2)	2678(3)
C(4)	0	2195(2)	2500
C(5)	447(2)	3817(1)	1549(2)
C(6)	2696(3)	3183(2)	2353(3)
C(7)	2175(3)	4545(2)	3076(3)
C(8)	2525(3)	4322(2)	749(3)
C(9)	−1376(3)	3107(2)	−13(3)
C(10)	−59(3)	4136(2)	−898(3)
C(11)	899(3)	2803(2)	−225(3)
B	0	3482(2)	2500

As a consequence of the relatively long Cr–$CNBR_2$, Cr–C(4), and B–N distances in complex **2a** and the short C(4)–N bond length of 1.159(5) Å (appropriate for a C≡N triple bond), it follows that **2a** is best described in terms of the $BR_2(CN)$ ligand behaving in a boryl isocyanide (**B**) rather than an azametalla-allenium (**C**) fashion. This conclusion is further supported by comparing the Cr–CN and C–N distances in **2a** with those determined for the cationic complex [$Cr(CO)_5\{CNC(C_{12}H_8O)\}$]$^+$ [8] ($C_{13}H_8O$ = **D**). The latter has a short Cr–CN bond, 1.899(6) Å, a long CrC–N bond, 1.182(3) Å, and a short CrCN–CR'_2 bond, 1.345(8) Å. The analogy which we make between the boryl isocyanide complex **2a** and this skeletally isoelectronic cationic complex draws attention to the lower π-acceptor capacity of a three-coordinate boron atom compared with that of an isoelectronic carbenium ion.



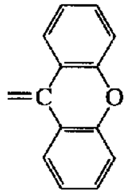
$$[(OC)_5\overset{-}{Cr}{-}C{\equiv}\overset{+}{N}{-}BR_2]$$

(**B**)



$$[(OC)_5\overset{-}{Cr}{=}C{=}\overset{+}{N}{=}\overset{-}{B}R_2]$$

(**C**)



(**D**)

X-Ray diffraction data are also available for the radical [$Cr(CO)_5(CNCMes_2)$] having Cr–CN 1.982(4), C–N 1.157(5), and N–$CMes_2$ 1.429(6) Å [17]. These values are close to those of the corresponding distances in complex **2a**.

The sp^2-hybridization at the boron atom requires that the bond angles around boron approximate to 120°. However, the angle subtended by the bulky bis(trimethylsilyl)methyl groups R are somewhat widened: C(5)–B–C(5)′ = 127.0(7)°. The interplanar angle between BC(5)C(5)′ and NC(4)CrC(2)O(2) is 141°.

3. Experimental section

All experiments were carried out under argon by use of standard Schlenk techniques. Solvents were of reagent grade and were rigorously freed from oxygen gas or moisture by standard methods and were freshly distilled under nitrogen gas and freeze-degassed prior to use. Glassware was successively oven-dried, flame-dried *in vacuo*, and cooled under argon. IR, NMR, and mass spectra were obtained on a Perkin-Elmer 597, Bruker WM360, and a Kratos M3902 instrument, respectively. The Raman spectra were obtained using the Ramalog SPEX instrument, using the double monochromator 1403 and a Spectra Physics krypton laser. Microanalytical data were provided by the University of Sussex Analytical Department.

3.1. Preparation of starting materials

The dialkylchloroborane **1** [2] was made in 75% yield from $BCl_3 + 2LiR$ [$R = CH(SiMe_3)_2$] in n-hexane. A derivative, $BR_2(OMe)$, m.p. 37–38°C was made. ^1H NMR ($CDCl_3$): δ 3.67 (OMe), 0.19 (CH), 0.08 (Me). ^{13}C ($CDCl_3$): δ 55.1 (OMe), 21.7 (CH), 2.8 (Me). ^{11}B ($CDCl_3$): δ 52.0. Anal. Found: C, 49.1; H, 11.1. Calc.: C, 50.0; H, 11.1%.

The complexes [NEt_4][$M(CN)(CO)_5$] (M = Cr or W) were prepared by published procedures [18].

3.2. Synthesis of pentacarbonyl[bis{bis(trimethylsilyl)-methyl}isocyanoborane]chromium(0) (2a)

Bis{bis(trimethylsilyl)methyl}chloroborane (**1**) (1.53 g, 4.19 mmol) was added to a solution of [NEt_4][$Cr(CN)(CO)_5$] (1.46 g, 4.88 mmol) in CH_2Cl_2 (30 ml) at room temperature. After 16 h the solvent was removed *in vacuo*. The residue was extracted with n-hexane and the extract was concentrated, filtered, and cooled to −20°C to yield pale yellow crystals of **2a** (2.02 g, 88%), m.p. 154–155°C. Anal. Found: C, 43.5; H, 6.80; N, 2.63. $C_{20}H_{38}BCrNO_5Si_4$ calc.: C, 43.9; H, 6.99; N, 2.56%.

3.3. Synthesis of pentacarbonyl[bis{bis(trimethylsilyl)-methyl}isocyanoborane]molybdenum(0) (2b)

Similarly, the borane **1** (470 mg, 1.29 mmol) in toluene (15 ml) was added to a suspension of [NEt_4][$Mo(CN)(CO)_5$] (510 mg, 1.30 mmol) in toluene (15 ml). The mixture was stirred at 50°C for 2 h, during which time the initially colourless solution became yellow. The solvent was removed *in vacuo* and the residue was extracted with n-pentane. The pale yellow compound **2b** (590 mg, 77%), m.p. 155–156°C, was crystallized from the extract as described for **2a**. Anal. Found: C, 40.8; H, 6.68; N, 2.55. $C_{20}H_{38}BMoNO_5Si_4$ calc.: C, 40.6; H, 6.47; N, 2.37%.

3.4. Synthesis of pentacarbonyl[bis{bis(trimethylsilyl)-methyl}isocyanoborane]tungsten(0) (2c)

From **1** (480 mg, 1.31 mmol) and [NEt_4][$W(CN)(CO)_5$] (630 mg, 1.31 mmol), by the procedure described for **2b**, pale yellow crystals of **2a** (570 mg, 64%), m.p. 158°C were obtained. Anal. Found: C, 35.5; H, 5.67; N, 2.10. $C_{20}H_{38}BNO_5Si_4W$ calc.: C, 35.4; H, 5.64; N, 2.06%.

3.5. Pentacarbonyl[bis{bis(trimethylsilyl)methyl}{^{13}C-isocyano}borane]tungsten(0) (3)

Complex **3** (310 mg, 70%) was obtained from [NPr_4][$W(^{13}CN)(CO)_5$] [19] (350 mg, 0.65 mmol), by the procedure described for **2a**; it had m.p. 158–160°C. Anal. Found: C, 35.1; H, 5.73; N, 2.29. $C_{19}{}^{13}CH_{38}BCrNO_5Si_4$ calc.: C, 35.4; H, 5.58; N, 2.06%.

3.6. X-Ray structure determination of [$Cr(CO)_5$-$(CNBR_2)$] [$R = CH(SiMe_3)_2$] (2a)

$C_{20}H_{38}BCrNO_5Si_4$, $M = 547.7$, monoclinic, space group $C2/c$, $a = 12.582(2)$, $b = 20.468(4)$, $c = 12.294(3)$ Å, $\beta = 98.88(1)°$, $U = 3128.2$ Å^3, $Z = 4$, $D_c = 1.16$ g cm^{-3}, $F(000) = 1160$. Monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 5.3$ cm^{-1}.

Data were collected at *ca.* 295 K, using a crystal of dimensions *ca.* $0.4 \times 0.3 \times 0.2$ mm^3, sealed in a capillary under argon, on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with $\theta = (0.8 + 0.35 \tan \theta)°$ and a maximum scan time of 1 min. A total of 2837 unique reflections was measured for $2 < \theta < 25°$ and $+h$, $+k$, $\pm l$, and 1801 reflections with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{\frac{1}{2}}/Lp$. There was no crystal decay and no absorption correction was applied.

The structure was solved by routine heavy atom methods and refined by full-matrix least-squares with non-hydrogen atoms anisotropic. Hydrogen atoms were held fixed at calculated positions with a common B_{iso} of 6.0 Å^2. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residuals were $R = 0.040$, $R' = 0.048$. A final difference map was featureless. Programs from the Enraf-Nonius SDP-PLUS package were run on a MicroVax computer.

The atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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