# Molybdenum Tricarbonyl Complexes of 1-Substituted Borepins

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The reaction of 1-substituted borepins $C_6H_6BX$, where X = Me, Ph, and Cl, with $Py_3Mo(CO)_3$ and $BF_3{\cdot}OEt_2$ affords the corresponding borepin molybdenum tricarbonyl complexes. Similar reaction of 1-methoxyborepin affords $(C_6H_6BF)Mo(CO)_3$. The reaction of $(C_6H_6BCl)Mo(CO)_3$ with appropriate nucleophiles affords the boron-substituted complexes $(C_6H_6BX)Mo(CO)_3$, where X = H, $OCH_3$, OH, $O_{1/2}$, $N(iPr)_2$, $N(CH_2)_5$, $N(c\text{-}C_6H_{11})_2$, and NBnMe. All complexes $(C_6H_6BX)Mo(CO)_3$ have been compared using $^1H$ NMR, $^{11}B$ NMR, and $^{13}C$ NMR spectroscopies. The X-ray structure of $(C_6H_6BN(iPr)_2)Mo(CO)_3$ shows that Mo is $\eta^6$-coordinated to the ring carbon atoms but not to B. Rates of rotation about the B−N bonds of $(C_6H_6BN(iPr)_2)Mo(CO)_3$ and $(C_6H_6BNBnMe)Mo(CO)_3$ have been measured using variable-temperature NMR spectroscopy.



## Introduction

Fully unsaturated boron heterocycles (**1, 2, 3** Chart 1) are versatile ligands toward transition metals.[2] The ligand properties of the five-membered ring borole (**1**)[2,3] and the six-membered ring boratabenzene (**2**)[2,4−8] have been extensively investigated. Typical complexes are illustrated by structures **4c**[9] and **5c**.[10] For both ring systems, exocyclic $\pi$-donor substituents can interact strongly with boron in a manner which can change the properties of the ligand. For example, the X-ray structure of **4c**[9] shows that the phenylborole ring is $\eta^5$-coordination to the metal. However, when the borole ring bears a strong $\pi$-donor as in complexes **7** and **8**, the ring is only $\eta^4$-coordinated to the metal.[11] In the same manner, B−Mn bonding is much stronger in **5c**[10] than that in **5l**.[7a]

The recent availability of the seven-membered ring borepins (**3**)[12] has allowed exploration of their ligand properties. We have previously reported on $Cr(CO)_3$ complexes of ring-fused borepins **9**[13] and **10**[14] and have made preliminary reports on $Mo(CO)_3$ complexes of 1-substituted borepins **6a**,[15] **6c**,[15] and **6d**.[16] We now report in detail on $Mo(CO)_3$ complexes of a larger series of 1-substituted borepins, **6a**−**l** and on the structure of **6i**.

## Results and Discussion

**Syntheses.** 1-Substituted borepins **3b**−**d** are easily prepared by the exchange reaction of 1,1-dibutylstannepin (**11**)[17] with the appropriate boron halide.[12] Alternatively, the reaction of 1-chloroborepin (**3d**) with nucleophiles affords 1-substituted borepins **3a**,[15] **3e**−**l**.[12] Thus, borepins with a large variety of substituents are available for study.

1-Alkyl- and 1-arylborepins are conveniently converted to their $Mo(CO)_3$ complexes by reaction with tricarbonyltris(pyridine)molybdenum and boron trifluoride etherate, Scheme 1. In this manner, we have obtained (1-methylborepin)$Mo(CO)_3$, **6b**, as a red air-sensitive oil and the phenyl derivative **6c** as red crystals which are only modestly air sensitive. In the case of **6c**, it is interesting that the $Mo(CO)_3$ group is coordinated to the borepin rather than the phenyl ring.[15] Similar metal coordination to the borepin as opposed to the benzocyclic ring has been observed for **9**.[13] These data suggest that the borepin moieties of **9** and **6c** are

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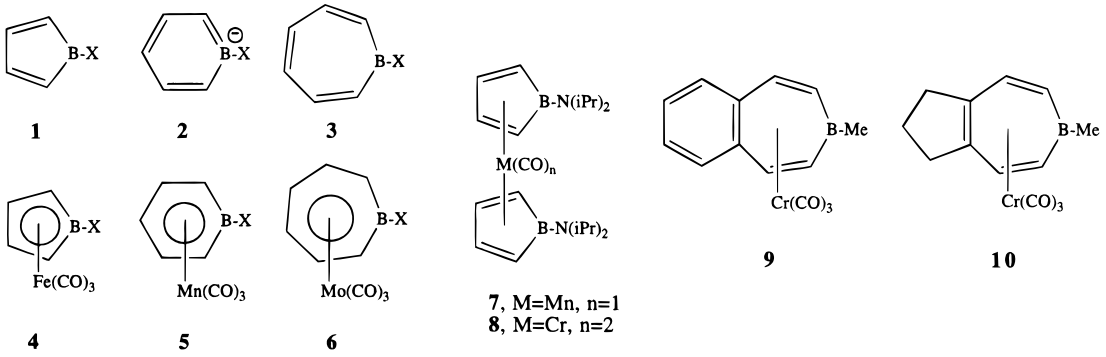
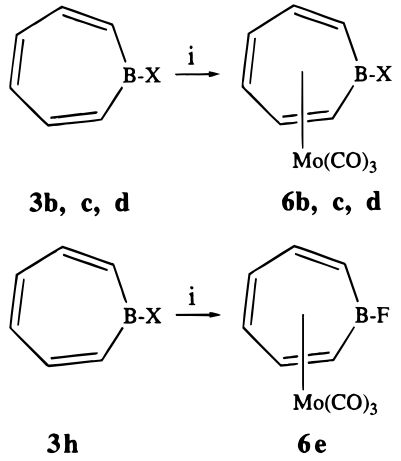
**Chart 1**



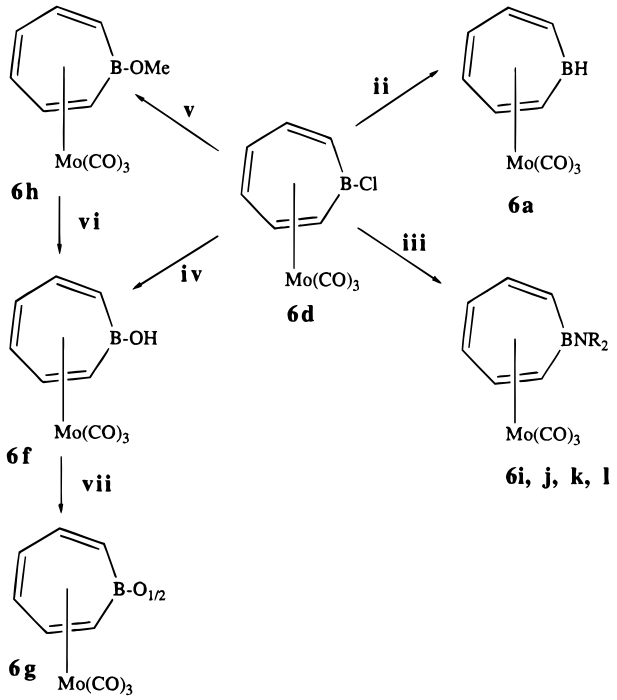

**a**, X=H; **b**, X=Me; **c**, X=Ph; **d**, X=Cl; **e**, X=F; **f**, X=OH; **g**, X=$O_{1/2}$; **h**, X=OMe; **i**, X=$N(iPr)_2$; **j**, X=$N(CH_2)_5$; **k**, X=$N(c\text{-}C_6H_{11})_2$; **l**, X=NBnMe.

**Scheme 1**[a]




[a] Key: (i) $Py_3Mo(CO)_3/BF_3{\cdot}OEt_2$.

**Scheme 2**[a]




[a] Key: (ii) $LiAlEt_3H$; (iii) $2HNR_2$; (iv) $H_2O$; (v) $HOCH_3$; (vi) $Al_2O_3$; (vii) $MgSO_4$.

the better ligands toward the group 6 metal tricarbonyl groups.

Borepins bearing Lewis acid sensitive substituents cannot be converted directly to their $Mo(CO)_3$ complexes by using the $BF_3{\cdot}OEt_2$-mediated ligand transfer. The reaction of 1-methoxyborepin (**3h**) with $Py_3Mo(CO)_3/BF_3{\cdot}OEt_3$ gives **6e** rather than **6h**. A similar reaction of (1-diisopropylamino)borepin (**3i**) leads to largely intractable products, although small quantities of **6e** were detected using $^1$H NMR spectroscopy.

The reaction of 1-chloroborepin (**3d**) with $Py_3Mo(CO)_3/BF_3{\cdot}OEt_2$ afforded 64% of the corresponding $Mo(CO)_3$ adduct **6d**. **6d** is quite moisture sensitive. Unless all manipulations involving **6d** are performed in glassware which has been silylated with hexamethyldisilazane and subsequently flame-dried in vacuum, the products are contaminated with hydrolysis products **6f** and **6g**. The chloride **6d** is a useful precursor to a variety of 1-substituted borepin $Mo(CO)_3$ complexes. The reaction of **6d** with methanol in ether gives the methoxy complex **6h** in 87% yield. Treating **6h** with alumina affords the crystalline hydroxy complex **6f**, which on drying over anhydrous $MgSO_4$ was converted to the bis(oxide) **6g**.

The reaction of **6d** with secondary amines gives good yields of corresponding aminoborepin complexes. In this manner we have obtained complexes as crystalline solids **6i**−**l**, Scheme 2. Finally, the reaction of **6d** with $Li(AlEt_3H)$ in THF affords 1-*H*-borepin(tricarbonyl)-molybdenum (**6a**) as a stable crystalline product. This complex cannot be prepared directly from the very labile free 1-*H*-borepin **3a**.

The above syntheses have provided us with a series of borepin $Mo(CO)_3$ complexes with a range of substituents. It is now appropriate to compare their properties.

**NMR Spectra.** The borepin−$Mo(CO)_3$ complexes display characteristic NMR spectra. The $^1$H NMR spectra in $C_6D_6$ are summarized in Table 1.[18] The signals for the six ring protons form an [AA′BB′CC′] pattern. For all derivatives, the signals for the $\beta$-protons occur at lowest field ($\delta$ 4.84−5.20) as a broad multiplet, while the relative positions of the α-proton doublet ($\delta$ 3.75−4.85) and $\gamma$-proton multiplet ($\delta$ 4.26−4.85) are more variable. Analysis of the spectra by computer simulation (RACCOON) shows that the $^3J_{H_\alpha-H_\beta}$ (12.0−11.4 Hz) and $^3J_{H_\beta-H_\gamma}$ (7.8−7.5) vary little in the series. Comparison of the signals of **6** with those of **3**

(18) The $^1$H NMR spectra are subject to rather large solvent shifts. See refs 12 and 14.

**Table 1. $^1$H NMR Parameters of $(C_6H_6BX)Mo(CO)_3$ (6)[a]**

| X (compd) | $\delta(H_\alpha, \Delta)$ | $\delta(H_\beta, \Delta)$ | $\delta(H_\gamma, \Delta)$ | $^3J_{H_\alpha-H_\beta}$ | $^3J_{H_\beta-H_\gamma}$ | $\delta$(X) |
|---|---|---|---|---|---|---|
| H (**6a**) | 4.62 (dd, 3.47)[b] | 5.15 (br, 2.45)[c] | 4.52 (m, 2.37) | 11.4 | 7.8 | n.o.[c] |
| $CH_3$ (**6b**) | 4.31 (d, 3.33) | 5.07 (br, 2.35) | 4.52 (m, 2.27) | 11.5 | 7.8 | 1.08 |
| Ph (**6c**) | 4.86 (d, 3.24) | 5.33 (br, 2.29) | 4.64 (m, 2.21) | 11.6 | 7.8 | 7.32−7.46 (m), 7.84 (d) |
| Cl (**6d**) | 4.45 (d, 3.15) | 4.84 (br, 2.41) | 4.26 (m, 2.31) | 11.4 | 7.8 | |
| F (**6e**) | 4.14 (dd, 2.91)[d] | 4.96 (br, 2.36) | 4.34 (m, 2.24) | 11.4 | 7.7 | |
| OH (**6f**) | 3.84 (d, 3.02) | 5.05 (br, 2.18) | 4.48 (m, 2.02) | 11.5 | 7.7 | 3.07 |
| $O_{1/2}$ (**6g**) | 4.37 (d, 2.73) | 5.16 (br, 2.17) | 4.53 (m, 2.08) | 11.5 | 7.5 | |
| OMe (**6h**) | 4.08 (d, 2.91) | 5.15 (br, 2.15) | 4.53 (m, 2.03) | 11.7 | 7.8 | 3.42 |
| $N(iPr)_2$(**6i**) | 3.99 (d, 2.78) | 5.14 (br, 1.92) | 4.77 (m, 1.72) | 12.0 | 7.8 | 3.72 (sept, $J$ = 7 Hz)<br>1.25, 1.23 (d, $J$ = 7 Hz) |
| $N(CH_2)_5$ (**6j**) | 3.75 (d, 2.95) | 5.15 (m, 1.93) | 4.77 (m, 1.70) | 12.0 | 7.8 | 3.27 (d), 2.71 (t), 1.6−1.2 (m) |
| $N(c\text{-}C_6H_{11})_2$ (**6k**) | 4.20 (d)[e] | 5.20 (m) | 4.85 (m) | | | 2.55 (m), 1.8 (m), 1.7−1.5 (m),<br>1.2−1.0 (m) |
| NBnMe (**6l**) | 3.85 (m, 2.86) | 5.16 (m, 1.94) | 4.76 (m, 1.73) | | | 7.3−7.1 (m), 4.10 (d, $J$ = 16.2 Hz)<br>3.89 (d, $J$ = 16.2 Hz), 2.44 (s) |

[a] All $\delta(C_6D_6)$ values in ppm; $\Delta = \delta(C_6H_6BX) - \delta(C_6H_6BXMo(CO)_3)$. $^3J_{H_\alpha H_\beta}$ and $^3J_{H_\beta H_\gamma}$ in Hz. [b] $^3J_{CH-BH}$ = 6.0 Hz. [c] Br = broad; n.o. = not observed. [d] $^3J_{CH-BF}$ = 3.2 Hz. [e] Free ligand unknown.

**Table 2. $^{13}$C NMR Chemical Shift Values ($\delta$) for $(C_6H_6BX)Mo(CO)_3$ (6) and the Changes on Complexation ($\Delta$)[a]**

| X (compd) | $\delta(C_\alpha, \Delta)$ | $\delta(C_\beta, \Delta)$ | $\delta(C_\gamma, \Delta)$ | $\delta$(CO) | $\delta$(X) |
|---|---|---|---|---|---|
| H (**6a**)[b] | n.o.[c] | 112.8 (36.4) | 97.4 (39) | 214.0 | |
| $CH_3$ (**6b**)[b] | 98.8 (br, 51.2)[c] | 112.0 (34.3) | 101 (33.7) | 215.5 | 6.0 (br) |
| Ph (**6c**)[b] | 98.1 (br, 51.4) | 112.1 (36.1) | 96.8 (38.6) | 214.3 | 127.7(m), 129.0(p), 133.4(o), $C_{ipso}$ n.o. |
| Cl (**6d**)[b] | 92 (br, 58) | 109.4 (38.9) | 95.9 (39.5) | 213.9 | |
| F (**6e**)[b] | 88 (br, 61) | 110.7 (d, 38.8)[e] | 95.9 (38.1) | 214.0 | |
| OH (**6f**)[b] | n.o. | 111.3 (35.0) | 95.5 (37.1) | 214.0 | |
| $O_{1/2}$ (**6g**)[b] | n.o. | 111.4 (35.6) | 95.8 (37.5) | 215.0 | |
| OMe (**6h**)[b] | 88 (br, 52) | 111.5 (34.7) | 95.7 (37.0) | 214.0 | 53.4 |
| $N(iPr)_2$ (**6i**)[d] | 84 (br, 54) | 109.8 (28.9) | 96.2 (34.7) | 218.4 | 46.6(NCH), 22.61, 22.95(Me) |
| $N(CH_2)_5$ (**6j**)[d] | 83 (br, 55) | 110.0 (31.2) | 96.0 (35.5) | 218.3 | 48.1($NCH_2$), 27.7, 25.6 ($CH_2$) |
| $N(c\text{-}C_6H_{11})_2$ (**6k**)[d] | 85 (br)[f] | 109.8 | 96.2 | 218.5 | 53.2(NCH), 33.4, 32.8, 26.5, 25.9, 25.4 ($CH_2$) |
| NBnMe(**6l**)[b] | 83 (br, 56) | 111.53, 111.18 (30.6) | 96.28, 96.16 (35.4) | 218.2 | 55.4($NCH_2$), 36.7(Me) |

[a] All $\delta$ values in ppm; $\Delta = \delta(C_6H_6BX) - \delta((C_6H_6BX)Mo(CO)_3)$. [b] Solvent, $C_6D_6$. [c] n.o. = not observed, br = broad. [d] Solvent, $CDCl_3$. [e] $^3J_{CH-BF}$ = 17.0 Hz. [f] Free ligand unknown.

show that the upfield shifts on complexation are in the usual range.[19] The complexation shifts are similar to those between cycloheptatriene and $(C_7H_8)Mo(CO)_3$.[20]

The $^{13}$C NMR chemical shifts of the borepin−$Mo(CO)_3$ complexes **6a**−**l** are collected in Table 2. In all cases, the signals due to the α-carbon atoms are broad due to $^{11}$B coupling, while the other signals are sharp. The $\beta$-carbon signals are invariably at lowest field and occur over a very narrow range ($\delta$ 109−112). The range of the $\gamma$-carbon signals is also small ($\delta$ 96−101), while the α-carbon signals are most variable ($\delta$ 83−99). Relative to the corresponding free borepins, the α-carbon signals experience the largest complexation shift (52−61 ppm). The complexation shifts of the $\beta$- and $\gamma$-carbons are in the range of 39−29 ppm. In this respect also the borepin−$Mo(CO)_3$ complexes resemble cycloheptatriene−$Mo(CO)_3$.[21]

The $^{11}$B NMR chemical shift values of **6** and the shifts on complexation are collected in Table 3. The complexes **6b**−**l** display $^{11}$B chemical shift values over a very narrow range ($\delta$ 27.0−31.7), while the parent borepin complex **6a** has a significantly higher field shift ($\delta$ 23.1). This is the usual effect since the complexes of BH-derivatives of boratabenzenes,[22] 1,2,5-thiadiborolenes,[23] and boroles[24] also show high-field $^{11}$B signals.

The borepins with poor $\pi$-donor substituents (H, Me, Ph,Cl) show an upfield shift of about 20 ppm on complexation. However, the aminoborepins show only modest (5.6−7.0 ppm) shifts on complexation, while the oxygen- and fluorine-substituted borepins show intermediate shifts on complexation (10.3−11.6 ppm). This complexation shift suggests that borepins with $\pi$-donor substituents are more weakly coordinated to the $Mo(CO)_3$ moiety.[25] However, the chemical shift values of the complexes themselves do not seem to be sensitive to the strength of complexation.

**Table 3. $^{11}$B NMR Chemical Shift Values ($\delta$) of Complexes $(C_6H_6BX)Mo(CO)_3$ with the Change on Complexation ($\Delta$)[a,b]**

| X (compd) | $\delta$ ($\Delta$) | X (compd) | $\delta$ ($\Delta$) |
|---|---|---|---|
| H (**6a**) | 23.1 (d, $J$ = 94 Hz, 24.9) | $O_{1/2}$ (**6g**) | 29.7 (10.6) |
| $CH_3$ (**6b**) | 31.7 (23.1) | OMe (**6h**) | 29.7 (10.3) |
| Ph (**6c**) | 28.1 (20.7) | $N(iPr)_2$ (**6i**) | 27.0 (7.0) |
| Cl (**6d**) | 30.5 (17.4) | $N(CH_2)_5$ (**6j**) | 28.4 (5.6) |
| F (**6e**) | 30.5 (11.6) | $N(c\text{-}C_6H_{11})$ (**6k**) | 28.7[c] |
| OH (**6f**) | 29.9 (10.4) | NBnMe (**6l**) | 29.0 (6.5) |

[a] Solvent, $C_6D_6$. [b] $\Delta = \delta(C_6H_6BX) - \delta((C_6H_6BX)Mo(CO)_3)$. [c] Free ligand unknown.

**Structures.** The molecular structures of **6c**[15] and **6d**[16] are illustrated in parts a and b of Figure 1, respectively, while selected bond distances are listed in Table 4. These structures have been discussed in

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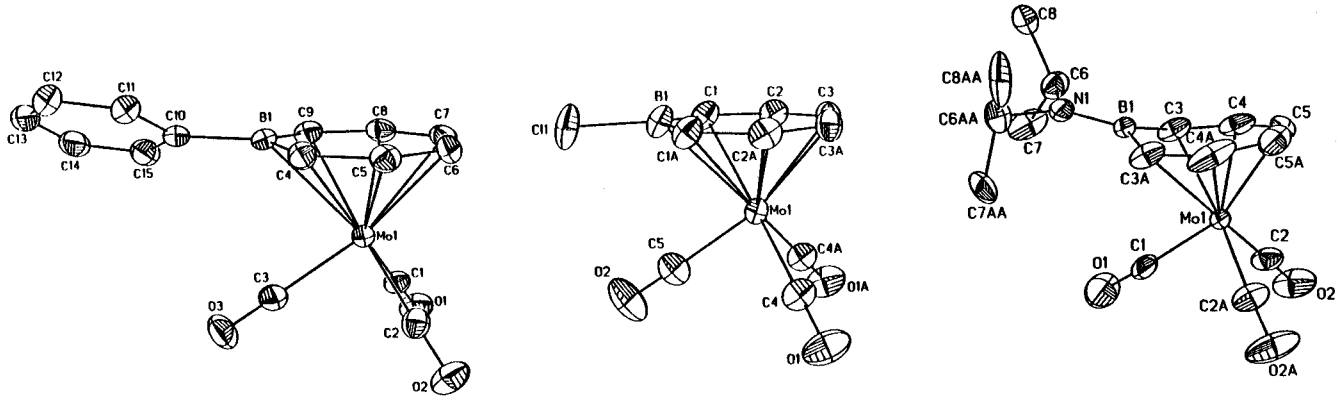
(25) Similiar trends have been found for the 1,2,5-triaborolene−$Fe(CO)_3$ complexes. See ref 23.




(a) **6c** (b) **6d** (c) **6i**

**Figure 1.** Comparison of the molecular structures of (a) **6c**, (b) **6d**, and (c) **6i**.

**Table 4. Selected Bond Distances (Å) of $(C_6H_6BX)Mo(CO)_3$ for X = Cl, Ph, and $N(iPr)_2$ (6d, 6c, and 6i)**

| bond | **6d** (X = Cl) | **6c** (X = Ph) | **6i** (X = $N(iPr)_2$) |
|---|---|---|---|
| B−$C_\alpha$ | 1.514(3) | 1.529(4)[a] | 1.549(5) |
| $C_\alpha$−$C_\beta$ | 1.398(3) | 1.391(4)[a] | 1.368(6) |
| $C_\beta$−$C_\gamma$ | 1.421(3) | 1.422(4)[a] | 1.432(6) |
| $C_\gamma$−$C_{\gamma'}$ | 1.411(3) | 1.408(5) | 1.363(13) |
| B−X | 1.802(2) | 1.578(4) | 1.394(7) |
| B−Mo | 2.486(4) | 2.523(3) | 2.769(5) |
| $C_\alpha$−Mo | 2.417(2) | 2.408(8)[a] | 2.424(4) |
| $C_\beta$−Mo | 2.362(2) | 2.363(34)[a] | 2.336(4) |
| $C_\gamma$−Mo | 2.325(2) | 2.337(11)[a] | 2.320(4) |

[a] Average value.

preliminary communications, however, it is necessary to recall their salient features in order to compare them with **6i**. The structures of **6c** and **6d**, which are very similar, show nearly planar borepin rings which are $\eta^7$-bound to the $Mo(CO)_3$ unit. The B−Mo distances (2.523(3) Å for **6c** and 2.486(4) Å for **6d**) are slightly longer than the C−Mo distances (2.33−2.42 Å), and the boron atom is slightly displaced above the ring plane (0.04−0.05 Å). This conforms to the pattern shown by the transition metal complexes of most boron heterocycles and is consistent with the the larger size of boron. The small range of C−C bond distances (1.39−1.42 Å) shows that the $\pi$-bonds are highly delocalized, while the short intraring B−C distances (1.529(4) Å for **6c** and 1.514(3) Å for **6d**) indicate significant $\pi$-bonding. These data clearly show that 1-phenyl and 1-chloroborepins behave as aromatic ligands.

For comparison, it was of considerable interest to obtain a crystal structure of a $Mo(CO)_3$ complex of a borepin bearing a strong donor substituent. A crystal of **6i** suitable for X-ray diffraction was obtained by recrystallization from pentane. An ORTEP diagram of the molecular structure of **6i**, which shows the numbering scheme used in the refinement, is illustrated in Figure 1c. In contrast to the structures of **6c** and **6d**, the $Mo(CO)_3$ group of **6i** is only $\eta^6$-coordinated to the six carbon atoms of the boracycloheptatriene ring. The B−Mo distance of 2.769(5) Å of **6i** is about $^1/_4$ Å longer than that of **6c** and **6d** and must be too long for significant metal−boron bonding. There is a strong resemblance of **6i** to cycloheptatrienemolybdenum tricarbonyl (**12**).[26] In both **6i** and **12**, the six-coordinated carbon atoms are close to coplanar while the uncoordinated ring atoms lie above this plane away from the $Mo(CO)_3$ unit (0.37 Å for **6i** and 0.73 Å for **12**). The C−C bond distances of **6i** show a clear distinction between single and double bonds (1.35−1.46 Å), which is typical of cycloheptatriene metal complexes. The B−C bonds of **6i** (1.55 Å) are longer than those of **6c** and **6d**, indicating weak B−C $\pi$-bonding, while the exocyclic B−N bond (1.39 Å) is quite short, indicating strong B−N $\pi$-bonding.

These changes are readily explained. The $\pi$-donation of the nitrogen lone pair of **6i** saturates the boron, attenuating its ability to $\pi$-bond to the ring carbon atoms. Since these additional electrons would make the B−Mo interaction antibonding, the B−Mo distance lengthens. The net effect of changing the exocyclic substituent is to change the ligand character of the borepin. For poor $\pi$-donor substituents (Cl, Ph, and presumably H and $CH_3$), the borepin is an $\eta^7$-aromatic ligand. For good donors ($NR_2$), the borepin becomes an $\eta^6$-trienyl ligand.

Computational studies, (HF/6-31G*)[16,28] and MP2/6-31G*),[29] on the uncomplexed aminoborepin have indicated that the molecule adopts a boat conformation similar to that of cycloheptatriene.[30] A boat conformation is also suggested from indirect experimental evidence based on analysis of the $^1$H NMR spectrum of **3i**.[14] On complexation of **3i**, as in cycloheptatriene,[26b] the major change is a flattening of the bow of the boat, presumably to effect better overlap with the metal orbitals in **6i** and **12**. As in other metal−cycloheptatriene complexes, the alternating single−double bond pattern is altered little in complexation.[26,27]

In contrast, X-ray structural data on **3d**[16] and computational data on **3a**,[21] **3b**,[21,22] and **3d**[16] indicate that these borepins are planar aromatic rings with a sub-

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stantial delocalization of the $\pi$-electrons. The major structural charge on complexation is to reduce the C−C bond alternation from ±0.058 Å in **3d** to ±0.023 Å in **6d**. Thus, delocalization of the $\pi$-bonding is enhanced on complexation.

**B−N Rotation Barriers.** The strong B−N $\pi$-bonding in $Mo(CO)_3$ complexes of aminoborepins is indicated by the large rotational barriers about the B−N bonds. The $^{13}C$ NMR spectrum of **6i** in $C_6D_6$ at 25 °C shows signals at $\delta$ 22.61 and 22.95 for the pairs of diastereotopic iPr methyl groups. The methyl groups are nonequivalent due to the slow rotation about the B−N bond. On heating **6i** to 54 °C the signals coalesce, indicating a barrier height of 16.5 ± 0.5 kcal/mol.

An analogous process involving a slow B−N rotation can be detected from examining the NMR spectra of **6l**. At ambient temperature, the $^1H$ NMR spectrum shows two signals for the nonequivalent benzyl protons. The $^{13}C$ NMR spectrum of $C_6D_6$ solutions of **6l** shows two signals each for $C_\beta$ and $C_\gamma$, but the signals for $C_\alpha$ are too broad to detect the presumed nonequivalence. On heating to 62 °C, the signals at $\delta$ 96.253 and 96.133 due to the nonequivalent $\gamma$ carbon atoms coalesce, indicating a barrier height of 17.6 ± 0.5 kcal/mol.

The measured barriers to rotation about the B−N bonds of **6i** and **6l** are nearly identical. Thus, there are no significant energetic differences between the rotation of the NBnMe and $N(iPr)_2$ groups past the $Mo(CO)_3$ unit. A similar conclusion had been drawn previously in the boratabenzene series. The barrier to B−N rotation in **6l** is identical to that found for **3l** (18.0 ± 0.5 kcal/mol).[31] Thus, complexation has no effect on the barrier and presumably the B−N $\pi$-bond strength. We argue that the B−N groups are electronically isolated from the six ring carbon atoms in both aminoborepins and their $Mo(CO)_3$ complexes.

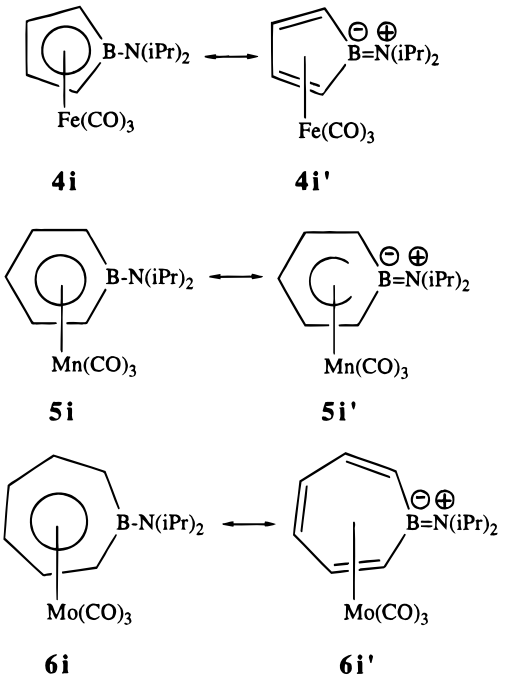
The B−N rotational barriers of analogous tricarbonyl metal complexes **4i**,[32] **5i**,[7a] and **6i** have been found to be 17.9, 16.5, and 17.5 kcal/mol, respectively. Since the barriers are similar, the B−N $\pi$-bond strengths must be similar. In each case, the pendant nitrogen is strongly $\pi$-bonded to boron while the $\pi$-bonding between boron and the ring carbon atoms must be weak. Electronically these compounds are better represented by structures **4i′**, **5i′**, and **6i′** rather than **4i**, **5i**, and **6i**, respectively.



## Experimental Section

**General Remarks.** All reactions were carried out under an atmosphere of nitrogen or argon. Solvents were dried using standard procedures. The mass spectra were determined by using a VG-70-S spectrometer, while the NMR spectra were obtained by using either a Bruker WH-360 or WH-300 spectrometer on solutions in $CHCl_3$, $C_6D_6$, or $CD_2Cl_2$ as noted. The $^1H$ NMR and $^{13}C$ NMR spectra were calibrated using signals from the solvents referenced to $Me_4Si$, while external $BF_3{\cdot}OEt_2$ and $CCl_3F$ were used to calibrate the $^{11}B$ NMR and $^{19}F$ NMR spectra, respectively. The IR spectra were obtained using a Nicolet 5DXB FT-IR instrument. Experimental procedures have previously been reported for **6a**,[15] **6c**,[15] and **6d**.[16]

**Tricarbonyl(1-methylborepin)molybdenum (6b).** A solution of 1-methylborepin (50 mg, 0.48 mmol) in 10 mL of THF was added to a suspension of tris(pyridine)molybdenum tricarbonyl (0.5 g, 1.2 mmol) in 10 mL of THF. Boron trifluoride etherate (0.5 mL, 4.1 mmol) was added, and the reaction mixture was allowed to stir at 25 °C for 1 h. The solvent was then removed in vacuo leaving a brown residue, which was extracted with pentane. Removal of pentane left 30 mg (22%) of a red air-sensitive oil. High-resolution EI-MS: calcd for $C_{10}H_9{}^{11}B^{98}MoO_3$, 285.9699; found, 285.9688. IR ($CDCl_3$, $\nu$(CO)): 2003, 1947, 1919 $cm^{-1}$.




**Tricarbonyl(1-fluoroborepin)molybdenum (6e).** A solution of 1-methoxyborepin (400 mg, 3.25 mmol) in 2 mL of methylene chloride was added slowly to a suspension of tris(pyridine)molybdenum tricarbonyl (1.36 g, 3.25 mmol) in 20 mL of ether. Then boron trifluoride etherate (1.9 mL, 15.6 mmol) was added dropwise with stirring. After 4 h at 25 °C, the solvent was removed under vaccum and the residue was extracted with pentane. The orange-red filtrate was cooled to −78 °C, and $BF_3$ gas was bubbled through the solution for 3 min. The reaction mixture was warmed to 25 °C and filtered. The filtrate was evaporated to dryness under vacuum leaving an orange-red oil (650 mg, 69%), which on cooling to −15 °C formed long red-orange needles, mp 53 °C. This compound is extremely moisture sensitive. $^{19}F$ NMR ($C_6D_6$): $\delta$ −136.9. EI-MS *m/z* (relative intensity): 290 (49, $M^+$ for $C_9H_6{}^{11}BF^{98}MoO_3$, 206 (100, $M^+ - 3CO$). High-resolution EI-MS: calcd for $C_9H_6{}^{11}BF^{98}MoO_3$, 289.9448; found, 289.9460. IR ($CDCl_3$, $\nu$(CO)): 2010, 1948, 1924 $cm^{-1}$.

**Tricarbonyl(1-hydroxyborepin)molybdenum (6f) and 1,1′-Bis(tricarbonyl(borepin)molybdenum) Oxide (6g).** Tricarbonyl(1-methoxyborepin)molybdenum (250 mg, 1 mmol) was dissolved in 20 mL of ether and added to a chromotography column ($Al_2O_3$). Nonpolar impurities were eluted with pentane, while the product was eluted with ether. Slow evaporation of the solvent left the hydroxy compound as orange-yellow clusters, mp 123−126°. EI-MS *m/z* (relative intensity): 288 (21, $M^+$ for $C_9H_7{}^{11}B^{98}MoO_4$), 204 (70, $M^+ - 3CO$), 98 (100, Mo). IR ($CDCl_3$, $\nu$(CO)): 2007, 1946, 1917 $cm^{-1}$.

The crude hydroxy compound from above was dissolved in 20 mL of ether, and 2 g of anhydrous $MgSO_4$ was added. After the mixture was allowed to stand for 20 h, the solvent was removed under vacuum and the product was extracted with pentane. Crystallization at −78 °C afforded 200 mg (80%) of yellow needles, mp 170−172°. EI-MS *m/z* (relative intensity): 554 (38, $M^+$ for $C_{18}H_{12}{}^{11}B_2{}^{98}Mo_2O_7$). High-resolution EI-MS: calcd for $C_{18}H_{12}{}^{11}B_2{}^{98}Mo_2O_7$, 553.8863; found, 553.8899. IR ($CDCl_3$, $\nu$(CO)): 2006, 1944, 1917 $cm^{-1}$.

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**Tricarbonyl(1-methoxyborepin)molybdenum (6h).** Tricarbonyl(1-chloroborepin)molybdenum (245 mg, 0.8 mmol) was stirred for 15 h in 0.5 mL of methanol with 1 g of anhydrous $MgSO_4$. The liquid phase was decanted, and the solvent was removed under vacuum. The residue was extracted with pentane. On cooling to −78 °C, the solution gave 210 mg (87%) of orange-red air- and moisture-sensitive crystals, mp 110−115 °C. Prolonged manipulation of this compound led to product contamination by the corresponding hydroxy borepin complex. EI-MS *m*/*z* (relative intensity): 302 (40, $M^+$ for $C_{10}H_9{}^{11}B^{98}MoO_4$), 218 (100, M − 3CO). High-resolution EI-MS: calcd for $C_{10}H_9{}^{11}B^{98}MoO_4$, 301.9648; found, 301.9665. IR ($CDCl_3$, $\nu$(CO)): 2005, 1945, 1915 $cm^{-1}$.

**Tricarbonyl(1-(diisopropylamino)borepin)molybdenum (6i).** Diisopropylamine (72 mg, 0.7 mmol) was added dropwise with stirring to a solution of tricarbonyl(1-chloroborepin)molybdenum (100 mg, 0.33 mmol) in 15 mL of hexane at 25 °C. A white precipitate formed immediately. After 10 min, the mixture was filtered and the clear filtrate was concentrated under vacuum. Crystallization at −20 °C afforded 70 mg (63%) of orange crystals, mp 152 °C (dec). EI-MS *m*/*z* (relative intensity): 371 (35, $M^+$ for $C_{15}H_{20}{}^{11}B^{98}MoNO_3$), 285 (100, $M^+$ − 3CO). High-resolution EI-MS: calcd for $C_{15}H_{20}{}^{11}B^{98}MoNO_3$, 371.0590; found, 371.0588. IR (hexane) ($\nu$(CO)): 1996, 1937, 1911 $cm^{-1}$. $^{13}C$ NMR (90.5 MHz, Tc=54 °C): $\delta$ 22.61, 22.95 (iPr $CH_3$)

**Tricarbonyl(piperidinoborepin)molybdenum (6j).** Piperidine (43 mg, 0.5 mmol) was added dropwise with stirring to a solution of tricarbonyl(1-chloroborepin)molybdenum (60 mg, 0.2 mmol) in 15 mL of hexane. A precipitate formed immediately. The reaction mixture was filtered after 10 min, affording a clear solution, which was concentrated under vacuum. Crystallization at −20 °C gave 30 mg (42%) of orange crystals, mp 87 °C (dec). EI-MS *m*/*z* (relative intensity): 355 (35, $M^+$ for $C_{14}H_{16}{}^{11}B^{98}MoNO_3$), 271 (80, $M^+$ − 3CO), 84 (100). High-resolution EI-MS: calcd for $C_{14}H_{16}{}^{11}B^{98}MoNO_3$, 355.0277; found, 355.0273. IR (pentane, $\nu$(CO)): 1997, 1937, 1913 $cm^{-1}$.

**Tricarbonyl(1-(dicyclohexylamino)borepin)molybdenum (6k).** Dicyclohexylamine (127 mg, 0.72 mmol) was added dropwise with stirring to a solution of tricarbonyl(1-chloroborepin)molybdenum (110 mg, 0.36 mmol) in 15 mL of pentane at 25 °C. A white precipitate formed after 5 min. After 1 h at 25 °C, the mixture was filtered and the filtrate was concentrated under vacuum. Crystallization at −20 °C gave 60 mg (37%) of red crystals, mp 151 °C (dec). EI-MS *m*/*z* (relative intensity): 451 (4, $M^+$ for $C_{21}H_{28}{}^{11}B^{98}MoNO_3$), 363 (13, $M^+$ − 3CO), 138 (100). High-resolution EI-MS: calcd for $C_{21}H_{28}{}^{11}B^{98}MoNO_3$, 451.1216; found, 451.1218. IR ($C_6D_6$, $\nu$(CO)): 1988, 1925, 1892 $cm^{-1}$.

**Tricarbonyl(1-(*N*-benzyl-*N*-methylamino)borepin)molybdenum (6l).** A solution of *N*-benzyl-*N*-methylamine (95 mg, 0.79 mmol) in 0.5 mL of dry benzene was added dropwise with stirring to a solution of tricarbonyl(1-chloroborepin)-molybdenum (120 mg, 0.39 mmol) in 1.0 mL of dry benzene at 25 °C. A white precipitate formed immediately, and the color changed to red. After 1 h, 5 mL of pentane was added and the resulting suspension was filtered, affording a clear filtrate. On cooling to −20 °C, 90 mg (60%) of product was isolated as red crystals, mp 152 °C (dec). EI-MS *m*/*z* (relative intensity): 391 (39, $M^+$ for $C_{17}H_{16}{}^{11}B^{98}MoNO_3$), 307 (100, $M^+$ − 3CO). High-resolution EI-MS: calcd for $C_{17}H_{16}{}^{11}B^{98}MoNO_3$, 391.0277; found, 391.0284. $^{13}C$ NMR (90.5 MHz, 25 °C, $C_6D_6$, $T_c$ = 61 °C): $\delta$ 96.28, 96.16 ($C_\gamma$).

**Table 5. Crystal Data and Structure Refinement for 6i[a]**

| | |
|---|---|
| empirical formula | $C_{15}H_{20}BMoNO_3$ |
| fw | 369.07 |
| temperature | 178(2) K |
| wavelength | 0.710 73 Å |
| cryst syst | orthorhombic |
| space group | *Pnma* (No. 62) |
| unit cell dimensions | a = 19.360(6) Å<br>b = 12.551(3) Å<br>c = 6.723(2) Å |
| volume, Z | 1633.6(8) $Å^3$, 4 |
| density (calcd) | 1.501 $Mg/m^3$ |
| abs coeff | 0.810 $mm^{-1}$ |
| *F*(000) | 752 |
| cryst size | 0.50 × 0.24 × 0.14 mm |
| $\theta$ range for data collection | 2.66−28.67 deg |
| limiting indices | $-26 \le h \le 26$, $0 \le k \le 17$, $0 \le l \le 9$ |
| no. reflns collected | 9277 |
| no. independent reflns | 2183 ($R$(int) = 0.0504) |
| abs corr | XEMP |
| max and min transmission | 0.605 and 0.497 |
| refinement method | full-matrix least-squares on $F^2$ |
| data/restraints/parameters | 2178/0/136 |
| goodness-of-fit on $F^2$ | 1.386 |
| final $R$ indices ($I > 2\sigma(I)$) | R1 = 0.0430, wR2 = 0.0951 |
| $R$ indices (all data) | R1 = 0.0531, wR2 = 0.1066 |
| largest diff. peak and hole | 0.909 and −1.050 e·$Å^{-3}$ |

[a] The molecule occupies a mirror plane in the crystal lattice. The iPr group is disordered across this plane in two orientations, each at 50% occupancy. Refinement in the lower symmetry space group *Pna*2(1) results in ordered iPr groups; however, the remainder of the structure then exhibits problems typically associated with refinement in an incorrect space group. Since the majority of the X-ray scattering reveals a centrosymmetric structure, we have opted for the disordered model.

**X-ray Structure Determination.** Crystals of **6i** were obtained by recrystallization from pentane. Crystallographic data are collected in Table 5. An ORTEP diagram of the molecular structure of **6i** showing the numbering scheme used in refinement is illustrated in Figure 1c. Table 4 gives the more important distances for non-hydrogen atoms. A list of observed and calculated structural factors is available from A.J.A. on request.

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**Supporting Information Available:** Tables of bond distances and angles, positional values, anisotropic thermal parameters of non-hydrogen atoms, and positional parameters of hydrogen atoms of **6i** (3 pages). Ordering information is given on any current masthead page.

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