by use of difference electron density maps. In the course of refinement all cage C and B atoms were initially assigned scattering factors for boron. After refinement, carboranyl carbon atom positions could be distinguished by their anomalously low temperature factors and by shorter interatomic distances. Reported R and R_w values are defined as $R = [\sum(|F_o| - |F_c|)/\sum|F_o|]$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$, and "goodness of fit" is defined by $[\sum w(|F_o| - |F_c|)^2/(N_{\mathrm{observns}} - N_{\mathrm{variables}})]^{1/2}$. Scattering factors for hydrogen were obtained from Stewart et al.,[22] and those for other atoms were taken from ref 23. Details of the individual data collections are given in Table IV.

***commo*-3,3′-Si(3,1,2-SiC$_2$B$_9$H$_{11}$)$_2$ (1).** A colorless crystal was affixed to a fiber. Systematic absences were found for reflections $0k0$ ($k = 2n + 1$) and for $h0l$ ($h + l = 2n + 1$). Unit cell parameters were determined from a least-squares fit of 13 accurately centered reflections (13.9° < 2θ < 16.2°). Three intense reflections (2,1,–5, 210, 1,3,–1) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca ±3%, with decay less than 2% during the course of the experiment (71.4-h exposure). Anisotropic thermal parameters were refined for all non-hydrogen atoms. All carboranyl H atoms were kept in located positions with assigned B values of 4 Å^2. Anomalous dispersion terms were applied to the scattering of Si. A final difference electron density map was essentially featureless; maximum and minimum peaks were ca. 0.4 e Å^{-3}. Positional parameters for 1 are given in the supplementary material (Table 2s).

(C$_5$H$_5$N)$_2$Si(C$_2$B$_9$H$_{11}$)$_2$ (4). A colorless parallelepiped was sealed in an argon-filled capillary. Systematic absences were found for reflections $0k0$ ($k = 2n + 1$) and for $h0l$ ($l = 2n + 1$). Unit cell parameters were determined from a least-squares fit of 34 accurately centered reflections (9.6° < 2θ < 25.9°). Three intense reflections (108, 433, 053) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca. ±4.5%, during the course of the experiment (89.9-h exposure). Anisotropic thermal parameters were refined for all non-hydrogen atoms. All carboranyl H atoms except H(12) were kept in located positions; all carboranyl H atoms were assigned B values of 2 Å^2. Positional parameters were refined for H(12). All other hydrogen atoms were kept in calculated positions and were assigned B values of 3 Å^2. Anomalous dispersion terms were applied to the scattering of Si. A final difference electron density map was essentially featureless; maximum and minimum peaks were ca. 0.8 e Å^{-3}, near Si. Positional parameters for 4 are given in the supplementary material (Table 5s).

[(Me$_3$P)$_2$BH](C$_2$B$_8$H$_{10}$)Si(C$_2$B$_9$H$_{11}$) (5). A colorless crystal was sealed in an argon-filled capillary. Systematic absences were found for reflections $0k0$ ($k = 2n + 1$) and for $h0l$ ($h + l = 2n + 1$). Unit cell parameters were determined from a least-squares fit of 29 accurately centered reflections (7.6° < 2θ < 20.2°). Three intense reflections (014, 1,–2,1, 1,2,–1) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca. ±4%, during the course of the experiment (91.8-h exposure). Anisotropic thermal parameters were refined for Si and P. All carboranyl H atoms were refined (positions) with assigned U values of 0.03 Å^2. All other hydrogen atoms were kept in calculated positions with assigned U values of 0.05 Å^2 (CH$_3$). Anomalous dispersion terms were applied to the scattering of Si and P. A final difference electron density map was essentially featureless; maximum and minimum peaks were ca. 0.2 e Å^{-3}. Positional parameters for 5 are given in the supplementary material (Table 8s).

Acknowledgment. This work was funded by a grant from the National Science Foundation (Grant No. CHE-88-06179). We also thank Andrea Owyeung for the illustrations.

Supplementary Material Available: Tables of positional and thermal parameters and complete interatomic distances and angles for 1, 4, and 5 (23 pages); listings of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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Synthesis and Molecular and Crystal Structures of (3-Methyl-3-benzoborepin)chromium Tricarbonyl

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(3-Methyl-3-benzoborepin)chromium tricarbonyl was obtained by treating the free ligand with tris(acetonitrile)chromium tricarbonyl in refluxing tetrahydrofuran. Red crystals of the complex C$_{14}$H$_{11}$BCrO$_3$ form in the $P2_1/n$ space group with $Z = 4$, a = 9.421 (2) Å, b = 14.046 (3) Å, c = 9.949 (2) Å, and β = 98.63 (1)°. The full structure has been determined and indicates that chromium is η^7-coordinated to the borepin rather than the benzo ring.

Introduction

Unsaturated boron–carbon heterocycles can serve as versatile π-ligands toward transition metals.[1-3] Thus, the five-membered rings borole 1 and 1,3-diborolyl 2 form η^5-complexes 6[4] and 7.[5] Similarly, the six-membered ring heterocycles boratabenzene 3 and 1,4-diboracyclohexadiene 4 are known to form η^6-complexes 8[6] and 9,[7] respectively. On the other hand, the chemistry of the seven-membered ring borepin 5 has been less well explored,[8-12] and only a

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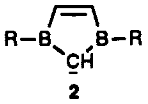

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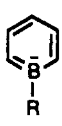

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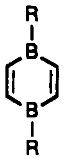

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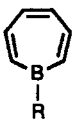

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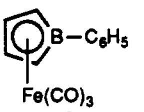

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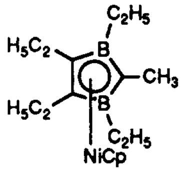

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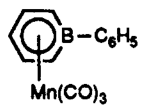

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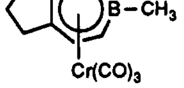


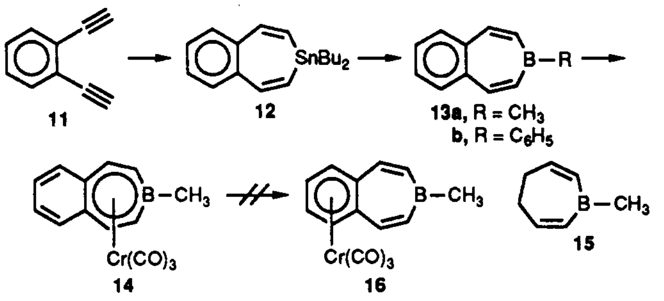
10

single complex **10** has been reported.[11a] No prior structural data are available for borepins.

We report here on the preparation of (3-methyl-3-benzoborepin)chromium tricarbonyl (**14**) and on structural data that show that borepin serves as a η^7-ligand.

Results and Discussion

3-Methyl-3-benzoborepin (**13a**) was prepared by an adaptation of the method used by van der Kerk et al. to prepare the corresponding phenyl derivative **13b**.[9] Hydrostannation of *o*-diethynylbenzene (**11**) by dibutyltin dihydride using powdered KOH/18-crown-6 ether in benzene gave a 51% yield of 3,3-dibutyl-3-benzostannepin (**12**). This base-catalyzed reaction gives the product in higher yield and in better purity than the thermal hydrostannation.[13] The reaction of the stannepin with methylboron dibromide in toluene afforded 67% of the desired 3-methyl-3-benzoborepin (**13a**) as an air-sensitive, low-melting solid. The ^{1}H, ^{11}B, and ^{13}C NMR chemical shift values of **13a** are summarized in Figure 1.



As had previously been noted for compound **13b** and other borepins, the ^{1}H NMR chemical shift values of the borepin ring protons occur at rather low field.[9,11,12,14] Thus, both boron ring proton signals of **13a** are shifted ca. 1 ppm downfield relative to the nonaromatic model compound 1-methyl-4,5-dihydroborepin (**15**).[15] This effect seems consistent with the presence of an aromatic ring current and/or substantial π-electron donation from carbon to boron.[16] The small upfield shift in the ^{11}B NMR spectrum of **13a** relative to **15** is also consistent with an increased electron density at boron.[17] However, the similarities of the ^{13}C NMR chemical shifts for the corresponding signals of the α- and β-carbon atoms of **13a** and **15** suggest that there are only modest differences in the C-electron density between the two compounds.

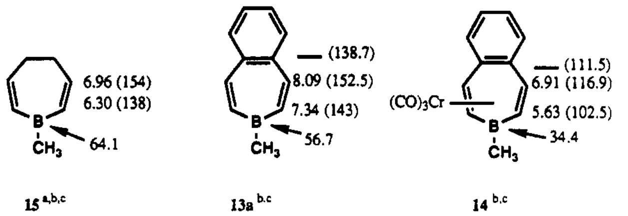


Figure 1. Comparison of the ^{1}H NMR, ^{11}B NMR (with arrows), and ^{13}C NMR (in parentheses) chemical shift values of 3-methyl-3-benzoborepin (**13a**) with **14** and **15**. (a) Reference 15. (b) The ^{1}H NMR spectra were run in $CDCl_3$. (c) The ^{13}C NMR spectra of **13a** and **15** were run in $CDCl_3$, while **14** was run in C_6D_6. Carbon spectra of **13a** show negligible solvent shifts.

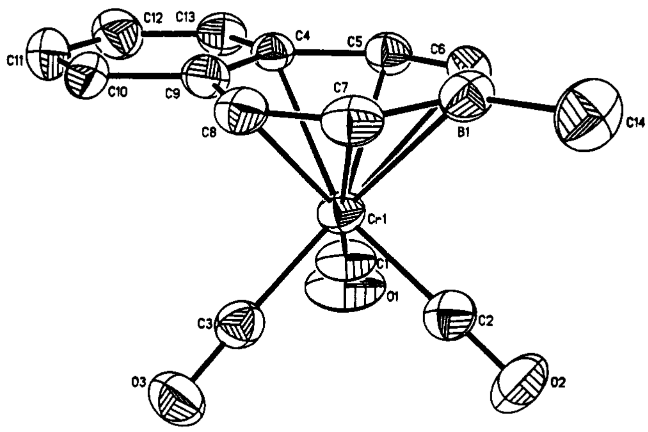


Figure 2. ORTEP drawing of the solid-state structure of (3-methyl-3-benzoborepin)chromium tricarbonyl (**14**), with thermal ellipsoids at the 50% probability level.

The reaction of **13a** with tris(acetonitrile)chromium tricarbonyl in refluxing tetrahydrofuran afforded adduct **14** as red crystals. The ^{1}H, ^{11}B, and ^{13}C NMR chemical shifts of **14** are also summarized in Figure 1. A numbering scheme used in crystallographic work (Figure 2) has been used.

The ^{13}C NMR signals for the borepin ring carbon atoms $C_6(C_7)$, $C_5(C_8)$, and $C_4(C_9)$ are shifted upfield by 27–40 ppm in comparison to those of the free ligand. Since the benzocyclic signals $C_{10}(C_{13})$ and $C_{11}(C_{12})$ are relatively unaffected on complexation, these data suggest that the borepin rather than the benzocyclic ring is coordinated to Cr. Similar shifts are observed in the ^{1}H NMR spectra in which $H_5(H_8)$ and $H_6(H_7)$ are shifted upfield by an average value of 1.5 ppm while the benzocyclic ring proton shifts are relatively unchanged. Lastly, the ^{11}B NMR signal for **14** is 22 ppm upfield from that of **13a**.[18] As had previously

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Table I. Summary of Crystallographic Data for 14

Crystal Data	
emp formula	$C_{14}H_{11}BO_3Cr$
fw, amu	290.04_9
cryst color and habit	pale red, irregular
cryst dimens, mm	0.10 × 0.08 × 0.16
cryst system	monoclinic
space group	$P2_1/n$
Z	4
unit cell dimens from 25 reflns ($20.1° \le 2\theta \le 27.1°$)	
a, Å	9.421 (2)
b, Å	14.046 (3)
c, Å	9.949 (2)
β, deg	98.63 (1)
vol, $Å^3$	1301.7 (3)
density (calc), g cm^{-3}	1.48_0
$F(000)$, e	592
linear abs coeff (μ), cm^{-1}	8.53
Data Collection	
diffractometer	Siemens R3m/v
radiation type	Mo $K\bar{\alpha}$, $\lambda = 0.71073$ Å, Lp corrected, graphite monochromator
temp	ambient
scan type	$\theta/2\theta$ scan
2θ scan range, deg	5–45
octants used	$+h,+k,\pm l$ (h, 0/11; k, 0/16; l, $\overline{11}/11$)
scan rate, deg/min	1.5–4.0, variable
scan width, deg	0.7 below $K\alpha_1$ to 0.7 above $K\alpha_2$
background/scan ratio	0.5
std reflns	3 measd every 100 rflns, max dev <3%
no. of data collected	1998
no. of unique rflns	1695, $R_{int.} = 0.0056$
obsd rflns with $F_o \ge 3.0\sigma(F)$	1215
abs corrn	none applied
Solution and Refinement	
system used	Siemens SHELXTL PLUS, VAXStation 3500
solution	Patterson
refinement method	full-matrix least squares
function minimized	$\Sigma w(F_o - F_c)^2$
hydrogen atoms	Riding model, $d_{C\text{-}H} = 0.96$ Å, isotropic U(H) refined to 0.097(8)
no. of parameters refined	173
obsd/parameter ratio	7.0
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert)$	0.0554
$R_w = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F\rvert^2]^{1/2}$	0.0510
$w^{-1} = \sigma^2(F_o) + 0.000438F_o^2$	
GOF	1.25
mean shift/error	0.000
max shift/error	<0.001
secondary extinction	no correction applied
residual electron density, e/$Å^3$	0.30, 1.15 Å away from Cr
coordinates (x, y, z)	0.1439, 0.1432, 0.2874

been found for **10**,[11a] these data show that the borepin ring of **14** is π-coordinated to Cr as a η^7-ligand. Thus, is was of interest to obtain a crystal structure for **14**.

A crystal of **14** suitable for X-ray diffraction was obtained by recrystallization from a pentane solution. Crystal data and data collection and refinement parameters are summarized in Table I. An ORTEP plot of the molecular structure of **14** which shows the numbering used in the refinement is illustrated in Figure 2. Table II gives the positional values, while Tables III and IV give the more important distances and the bond angles for the non-hydrogen atoms. Table VI, a list of observed and calculated structure factors, is available in the supplementary data.

Table II. Positional Parameters and Isotropic Equivalent Thermal Parameters for 14[a]

atom	x	y	z	u(eq)
Cr1	0.2109 (1)	0.07776 (7)	0.2684 (1)	0.0423 (3)
C1	0.1291 (8)	−0.0179 (5)	0.1566 (7)	0.060 (3)
O1	0.0820 (6)	−0.0786 (4)	0.0845 (5)	0.094 (2)
C2	0.0304 (7)	0.1257 (5)	0.2722 (6)	0.055 (3)
O2	−0.0847 (5)	0.1554 (4)	0.2714 (5)	0.080 (2)
C3	0.2164 (7)	0.1508 (5)	0.1159 (7)	0.051 (3)
O3	0.2152 (5)	0.1973 (3)	0.0192 (5)	0.073 (2)
C4	0.4032 (6)	−0.0246 (4)	0.3286 (6)	0.041 (2)
C5	0.2884 (7)	−0.0449 (4)	0.4065 (6)	0.044 (2)
C6	0.2146 (7)	0.0129 (4)	0.4834 (6)	0.049 (2)
B1	0.2226 (8)	0.1188 (6)	0.5095 (8)	0.055 (3)
C7	0.3155 (7)	0.1804 (5)	0.4359 (7)	0.056 (3)
C8	0.4146 (7)	0.1575 (5)	0.3512 (7)	0.051 (3)
C9	0.4595 (6)	0.0672 (5)	0.3048 (6)	0.050 (2)
C10	0.5692 (7)	0.0706 (6)	0.2166 (7)	0.063 (3)
C11	0.6159 (8)	−0.0068 (6)	0.1586 (7)	0.071 (3)
C12	0.5575 (8)	−0.0953 (6)	0.1810 (7)	0.070 (3)
C13	0.4547 (7)	−0.1044 (4)	0.2607 (6)	0.049 (2)
C14	0.1176 (8)	0.1651 (5)	0.6024 (8)	0.088 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter, U(eq), defined as one-third of the trace of the orthogonalized U_{ij} tensor: $U(\text{eq}) = {}^1/_3 \cdot \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Table III. Selected Bond Distances (Å) for 14

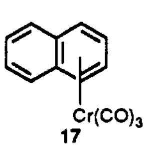
Cr1–C1	1.838 (7)	Cr1–C9	2.320 (6)	B1–C7	1.50 (1)
Cr1–C2	1.834 (7)	C1–O1	1.159 (8)	B1–C14	1.59 (1)
Cr1–C3	1.839 (6)	C2–O2	1.161 (8)	C7–C8	1.386 (9)
Cr1–C4	2.319 (6)	C3–O3	1.161 (8)	C8–C9	1.434 (9)
Cr1–C5	2.256 (6)	C4–C5	1.450 (8)	C9–C10	1.454 (8)
Cr1–C6	2.321 (5)	C4–C9	1.427 (9)	C10–C11	1.33 (1)
Cr1–B1	2.453 (7)	C4–C13	1.429 (8)	C11–C12	1.39 (1)
Cr1–C7	2.309 (6)	C5–C6	1.374 (8)	C12–C13	1.346 (9)
Cr1–C8	2.267 (6)	C6–B1	1.51 (1)		

Table IV. Selected Bond Angles (deg) for 14

C4–C5–C6	131.4 (6)	B1–C7–C8	131.3 (6)
C4–C9–C8	127.6 (5)	C7–B1–C14	120.5 (7)
C4–C9–C10	116.4 (6)	C7–C8–C9	131.2 (6)
C4–C13–C12	122.0 (6)	C8–C9–C10	115.9 (6)
C5–C4–C9	126.3 (5)	C9–C4–C13	117.9 (5)
C5–C4–C13	115.6 (5)	C9–C10–C11	123.1 (7)
C5–C6–B1	131.4 (6)	C10–C11–C12	119.6 (6)
C6–B1–C7	120.2 (6)	C11–C12–C13	121.0 (7)
C6–B1–C14	118.9 (6)		

The structure of **14** consists of a near planar 3-methyl-3-benzoborepin ligand that is monofacially bound to a $Cr(CO)_3$ unit. The $Cr(CO)_3$ fragment is centered above the borepin ring, while the benzo ring is uncoordinated. The juxtaposition of the borepin ring of **14** relative to the metal tricarbonyl fragment resembles those of the borole ring of **6**[4] and boratabenzene ring of **8**.[6] Indeed, structures **6** and **8** serve as useful overall comparisons for **14**.

The intra-ring C–C bond distances of **14** range from 1.37 to 1.45 Å with the formal single bonds (1.45, 1.43 Å) being somewhat longer than the formal double bonds (1.37, 1.39 Å). This range is larger than is found for **6** and **8** (1.40–1.42 Å). However, since naphthalenechromium tricarbonyl (**17**) shows an identical variation in C–C bond lengths (1.37–1.45 Å),[19] it is tempting to ascribe the major portion of variation



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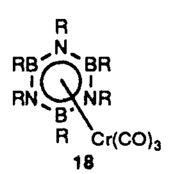

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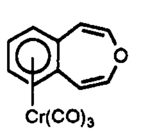

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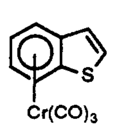

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in bond lengths to the perturbing effect of the benzo-fused ring rather than to the inherent properties of the borepin ligand.

The intra-ring B–C bond lengths (1.51, 1.50 Å) of **14** are significantly shorter than the exo cyclic $B-CH_3$ distance of 1.59 Å. This compares with the endo/exo cyclic B–C distances of 1.54/1.56 Å for **6** and 1.52/1.58 Å for **8**. In all cases, the shorter intra-ring B–C distance indicates B–C π-bonding.

As had been noted for **6** and **8**, the boron ring of **14** shows small deviations from planarity. Thus, the B atom and C4C9 are displaced away from the Cr from the approximate plane defined by C5C6C7C8 (see Table V in the supplementary material). The folding along lines C6C7 and C5C8 is 5.1° and 4.1°, respectively. Indeed, structures **6–9**[1-7] show analogous displacements of the boron atom away from the transition metals.

The B–Cr distance of **14** (2.45 Å) is somewhat larger than the π-coordinated C–Cr distances of 2.26–2.32 Å. This conforms to the patterns shown by **6** and **8** and suggests that the coordination to carbon is stronger than that to boron. In this context, it is interesting to note that one of the CO groups eclipses the ring boron atom in all three structures. A similar situation has been found for (hexaethylborazine)chromium tricarbonyl (**18**) in which all three CO groups eclipse ring boron atoms.[20] Thus, there is a strong preference for CO eclipsing of the more positive weaker coordinated atoms. The conformational preferences of polyene–$M(CO)_3$ complexes in general[21] and compound **8**,[22] in particular, have been treated by molecular orbital (MO) studies, which can probably be extended to included **14**.

The structure found for **14** is somewhat unusual in that metal complexes of most benzo-fused heterocycles, e.g., **19**[23] and **20**,[24] show coordination to the benzocyclic rather than the heterocyclic ring. Heating **14** in benzene to 134 °C served only to decomplex the ligand rather than effect haptotropic[25] isomerization to **15**. Although we cannot exclude the possibility that **15** may be thermodynamically more stable, the thermal robustness of **14** and particularly the structural data indicate that borepin is a good π-ligand.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen or argon. Solvents were dried by using standard procedures and distilled prior to use. The mass spectra were determined by using a VG-70-S spectrometer, while the IR spectrum was recorded on a Nicolet 5DX spectrometer.

NMR Spectra. All NMR spectra were obtained by using either a Brucker WH-360 or AM-300 spectrometer on solutions in $CDCl_3$ or C_6D_6 as noted. The ^1H and ^{13}C NMR spectra were calibrated by using signals from the solvents referenced to Me_4Si, while external boron trifluoride etherate was used to calibrate the ^{11}B NMR spectra.

Where possible, the ^1H NMR spectral assignments were made by considering the multiplicity of the signals. The relative assignment of the olefinic signals of **13a** and **14** could be made since the protons trans to boron show signals broadened by coupling to ^{11}B, while the geminal protons do not.[26] The relative assignment of the olefinic protons of **12** was made from the ^{119}Sn satellite signals. The protons trans to tin are more strongly coupled than the geminal protons.[27]

In the ^{13}C NMR spectra of **13a** and **14**, the assignment of signals α to boron could be made since their signals are broadened by ^{11}B quadrupole relaxation,[28] while the assignment of signals for carbons α to Sn was based on the large value of $^1J(^{119}Sn^{13}C)$.[27] Other assignments were made by analogy to related compounds.

3,3-Dibutyl-3-benzostannepin (12). Powdered potassium hydroxide (0.1 g) was added to a solution of *o*-diethynylbenzene (0.50 g, 4 mmol) and dibutyltin dihydride (1.05 g, 4.4 mmol) in 20 mL of benzene. With stirring, 0.05 g of 18-crown-6 ether was added. The mixture turned red, and the temperature rose to 50 °C. After stirring at 25 °C for 2.5 h, the solution was washed with excess water and dried over anhydrous magnesium sulfate. Removal of the solvent left an oil that was distilled (bp 150 °C, 0.1 Torr) to give 0.76 g (51% yield) of 3,3-dibutyl-3-benzostannepin as a pale yellow oil. The mass and ^1H NMR spectra were identical with those of the product obtained by the thermal hydrostannation reaction. ^1H NMR ($CDCl_3$): δ 7.67 (d, J = 13.8, $J(^{119}SnH)$ = 156 Hz, 2 H); 7.32 (m, 2 H); 7.22 (m, 2 H); 6.51 (d, J = 13.8, $J(^{119}SnH)$ = 78 Hz, 2 H); 1.44 (m, 4 H); 1.28 (m, 4 H), 0.96 (t, J = 7.8 Hz, 4 H); 0.86 (t, J = 7.4 Hz, 6 H). ^1H NMR (C_6D_6): δ 7.65 (d, J = 13.8, $J(^{119}SnH)$ = 159 Hz, 2 H); 7.19 (m, 2 H), 6.98 (m, 2 H); 6.48 (d, J = 13.8, $J(^{119}SnH)$ = 79 Hz, 2 H); 1.37 (m, 4 H); 1.19 (m, 4 H); 0.85 (t, J = 7.8 Hz, 4 H); 0.79 (t, J = 7.3 Hz, 6 H). ^{13}C NMR (C_6D_6): δ 147.1 (C^β); 140.2(C^γ); 137.2 ($J(^{119}SnC)$ = 375 Hz, C^α), 132.9, 126.2 (C_6H_4), 29.3, 27.3, 13.7, 10.2 (C_4H_9).

3-Methyl-3-benzoborepin (13a). A solution of methylboron dibromide (0.67 g, 3.6 mmol) in 2.5 mL of toluene was added dropwise with stirring to a solution of 3,3-dibutyl-3-benzostannepin (1.3 g, 3.6 mml) in 10 mL of toluene at −30 °C. The reaction mixture was allowed to warm to 25 °C slowly and was stirred for 1 h. Removal of solvent under reduced pressure left a brown residue that was purified by distillation (60 °C/0.01 Torr) to yield 370 mg (67%) of 3-methyl-3-benzoborepin as a colorless solid, mp 37 °C. The product turned yellow on exposure to air. The H NMR spectrum indicated traces of dibutyltin dibromide, which did not interfere with subsequent complex formation. ^1H NMR ($CDCl_3$): δ 8.09 (br d, J = 13.5 Hz, 2 H); 7.84 (m, 2 H), 7.58 (m, 2 H), 7.34 (d, J = 13.5 Hz, 2 H), 1.10 (br s, 3 H). ^1H NMR (C_6D_6): δ 7.85 (br d, J = 13.8 Hz, 2 H), 7.44 (m, 2 H), 7.17 (m, 2 H); 7.30 (d, J = 13.8 Hz, 2 H), 1.13 (br s, 3 H). C NMR (C_6D_6): δ 152.5 (C^β), 143 (br, C^α), 138.7 (C^γ), 135.4, 128.7 (C_6H_4), 11.9 (br, CH_3). B NMR (C_6D_6): δ 56.7. MS exact mass (EI): Calcd for $C_{11}H_{11}{}^{11}B$, 154.0954; Found, 154.0952.

(3-Methyl-3-benzoborepin)tricarbonylchromium (14). A solution of 3-methyl-3-benzoborepin (340 mg, 2.2 mmol) and tris(acetonitrile)chromium tricarbonyl (600 mg, 2.3 mmol) in 20 mL of tetrahydrofuran was heated to 65 °C for 10 h. A large green precipitate formed. The solution was filtered through Celite to give a dark red filtrate. After removal of solvent under reduced pressure, the byproduct (acetonitrile)chromium pentacarbonyl was sublimed off (40 °C/0.01 Torr), leaving a greenish red residue which was extracted with 100 mL of 1:1 methylene chloride/pentane. Subsequent filtration of the solution over celite followed by removal of solvent in vacuo to a volume of 30 mL and storage at −20 °C gave burgundy red crystals (380 mg, 60%), mp 134 °C. A suitable crystal for X-ray diffraction was obtained by recrystallization from a pentane solution at −20 °C. ^1H NMR ($CDCl_3$): δ 7.89 (m, 2 H), 7.70 (m, 2 H), 6.91 (d, J = 12.7 Hz, 2 H); 5.03 (d, J = 12.7 Hz, 2 H); 1.04 (s, 3 H). ^1H NMR (C_6D_6): δ 7.07 (m, 2 H); 6.88 (m, 2 H), 6.24 (d, J = 12.7 Hz, 2 H), 4.71 (d, J = 12.7 Hz), 1.26 (s, 3 H). ^{13}C NMR (C_6D_6): δ 227.3 (CO); 135.0, 130.0 (C_6H_4); 116.9 (C^β); 111.5 (C^γ); 102.5 (br, C^α); 10.5 (br, CH_3). ^{11}B NMR (C_6D_6): δ 34.4. IR ($CDCl_3$): ν 1981, 1895 cm^{-1}. MS exact mass (EI): calcd for $C_{14}H_{11}{}^{11}BCrO_3$, 290.0206; found, 290.0213.

Thermolysis of (3-Methyl-3-benzoborepin)chromium Tricarbonyl. A sample of 10 mg of **14** in 500 μL of benzene-d_6 was sealed in an NMR tube. The tube was heated to 94, 104, and 124 °C, after which the ^1H NMR spectrum was monitored. No change was noted. Finally, after heating to 134 °C for 10 h, the

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spectrum showed 10% of the free ligand in addition to the complex. No other products were noted.

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Supplementary Material Available: Table V, listing equations of planes, Table VII, listing hydrogen positional parameters for 14, and Table VIII, listing anisotropic thermal parameters for 14 (3 pages); a table of calculated and observed structure factors for 14 (6 pages). Ordering information is given on any current masthead page.

Chemistry of Iridium(I) and Rhodium(I) Compounds Containing Pyridylmethyl Ligation

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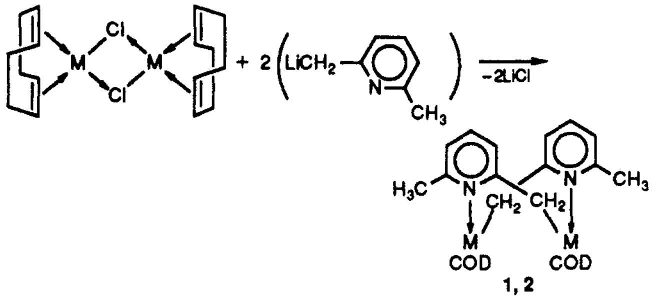
Treatment of the chloro-bridged dimers $[(COD)M(\mu\text{-}Cl)]_2$ (M = Rh, Ir; COD = 1,5-cyclooctadiene) with [(6-methyl-2-pyridyl)methyl]lithium ($Li\text{-}CH_2\text{-}py\text{-}6Me$) leads to the formation of the dinuclear compounds $[(COD)M(\mu\text{-}CH_2\text{-}py\text{-}6Me\text{-}C,N)]_2$ (M = Rh, **1**; Ir, **2**) in high yields. The solid-state structures of orange **1** and red **2** show the compounds to possess an "open book" type structure consisting of two square planes held together by the pyridylmethyl bridges similar to the known hydroxypyridinato analogues. A long metal–metal distance of 3.6806 (3) Å for **1** and 3.5889 (3) Å for **2** indicates little interaction between adjacent square planes. Treatment of iridium compound **2** with $EtPPh_2$ did not lead to displacement of the COD ligand. Instead formation of the mononuclear compound $(COD)Ir(EtPPh_2)_2(CH_2\text{-}py\text{-}6Me)$ (**3**) takes place. A solid-state structural analysis of **3** confirmed the stoichiometry and showed the pyridylmethyl group to be only carbon bound with a five-coordinate (18-electron) iridium metal center. Attempts to form new binuclear species by reaction of **1** and **2** with dppm ($Ph_2PCH_2PPh_2$) led instead to new compounds of formula [(dppm)M(dppm-H)] (M = Rh, **4**; Ir, **5**). In this reaction, the pyridylmethyl group has acted as an intramolecular base, leading to deprotonation of the methylene group of one of the dppm ligands and formation of 2,6-dimethylpyridine. A single-crystal X-ray diffraction study of rhodium complex **4** showed a square-planar rhodium(I) center chelated through the phosphorus atoms of both dppm and its deprotonated, methanide form. Crystal data for $Rh_2N_2C_{30}H_{40}$ (**1**) at 20 °C are $a = 7.529$ (1) Å, $b = 10.667$ (1) Å, $c = 16.573$ (2) Å, $\alpha = 83.620$ (9)°, $\beta = 80.93$ (1)°, $\gamma = 84.86$ (1)°, $Z = 2$, $d_{calcd} = 1.617$ g cm^{-3} in space group $P\bar{1}$; for $Ir_2N_2C_{30}H_{40}$ (**2**) at 20 °C are $a = 7.5369$ (8) Å, $b = 10.6727$ (6) Å $c = 16.482$ (2) Å, $\alpha = 85.020$ (6)°, $Z = 2$, $d_{calcd} = 2.082$ g cm^{-3} in space group $P\bar{1}$; for $IrP_2NC_{43}H_{50}$ (**3**) at 20 °C are $a = 11.236$ (2) Å, $b = 13.663$ (50) Å, $c = 13.809$ (3) Å, $\alpha = 64.40$ (2)°, $\beta = 78.33$ (2)°, $\gamma = 80.68$ (2)°, $Z = 2$, $d_{calcd} = 1.486$ g cm^{-3} in space group $P\bar{1}$; and for $RhP_4C_{62}H_{55}\cdot 2C_6H_6$ (**4**) at -43 °C are $a = 29.793$ (5) Å, $b = 10.055$ (3) Å, $c = 18.666$ (3) Å, $\beta = 114.00$ (2)°, $Z = 4$, $d_{calcd} = 1.335$ g cm^{-3} in space group *Cc*.

Introduction

One of the most interesting developments in transition-metal chemistry over the last 15 years has been in the area of dinuclear systems.[1] Pivotal to this exploration has been the use of binuleating ligation, which has the correct geometry to hold the two metal centers close to each other.[2,3] In an attempt at the rational synthesis of mixed-metal binuclear compounds containing early and late d-block metals, we have isolated a series of group 4 metal compounds containing pyridylmethyl ligation; e.g., $(ArO)_2M(CH_2\text{-}py\text{-}6Me)_2$ and $Cp_2M(CH_2\text{-}py\text{-}6Me)_2$ (M = Zr, Hf; CH_2-py-6Me = (6-methyl-2-pyridyl)methyl).[4,5]

Scheme I



Attempts to incorporate either rhodium(I) or iridium(I) into these systems by coordination through the pyridyl

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