Table I. M–^{13}C and X–^{13}C Spin–Spin Coupling Constants in Cage Complexes and Heterobicyclo[2.2.2]octanes

type	M or X	Y	$^3J^a$	$^2J^a$	$^1J^a$	$^{2/3}J^{a,b}$	$^3J/^2J$	ref
I	Rh(III)	$^+NH_3$	4.15	$\lesssim0.3^e$		<0.3	~10	4
I	Rh(III)	NH_2	3.42	$\lesssim0.3^e$		<0.3	~10	4
I	Rh(III)	NO_2	3.36	$\lesssim0.3^e$		<0.3	~10	4
III	Rh(III)			$\lesssim0.3^e$		<0.3		4
	$[Rh(en)_3]^{3+}$					<0.3		4
I	Pt(IV)	NO_2^c	52	7		3	7.4	2
I	Pt(IV)	NHOH	40	7		$\lesssim2$	5.7	2
III	Pt(IV)			8		2.5		2
	$[Pt(en)_3]^{4+}$					<2		2
II	$^{14}N^+$–CH_3	variable^d	4.5 ± 1	<2	3 ± 0.5		n.o.^{f}	5
II	$^{14}N^+$–CH_3	H	4.8	~0	3.1		n.o.^{f}	6
II	$^{15}N^+$–H	H	6.7	<0.2	4.8		n.o.^{f}	7
II	^{15}N	H	2.8	<0.2	2.1		n.o.^{f}	7
II	P=O	H	47	5	63		9.4	8

^{a}Coupling constants in Hz. ^{b}Coupling constants in the 1,2-ethanediamine moieties of the cage complexes. ^{c}Monodeprotonated at a coordinated amine. ^{d}For a large range of substituents. ^{e}Obtained by line widths. ^{f}Not observed.

Table II. ^{13}C ^3J Coupling Constants (Hz) and Magnetic Properties[10] of Heteroatoms in Bicyclo[2.2.2]octane Ring Systems

heteroatom	^3J	$10^{-20}K^a$	μ^b	I	γ^c	Q^d
^{14}N	~5	~23	0.5706	1	1.9324	1.6×10^{-2}
^{15}N	~7	~23	−0.4901	$^1/_2$	−2.7107	
^{31}P	~50	~41	1.9581	$^1/_2$	10.829	
^{59}Co			5.2344	$^7/_2$	6.3171	0.40
^{103}Rh	3–4	~37	−0.1522	$^1/_2$	−0.8420	
^{191}Ir			0.1440	$^3/_2$		1.5^e
^{193}Ir			0.1568	$^3/_2$		1.5^e
^{195}Pt	~40	~62	1.0398	$^1/_2$	5.7505	

^{a}Reduced coupling constant, N A^{-2} m^{-3}. ^{b}Magnetic moment, μ_N. ^{c}Magnetogyric ratio, 10^7 rad T^{-1} s^{-1}. ^{d}Quadrupole moment, 10^{-28} m^2. ^{e}Reference 10b.

es,[11,13] where the apical carbon resonance was very broad for $[Co(sar)]^{3+}$ (Y = H) but much narrower with electron-withdrawing substituents such as $-NO_2$.[11-13]

A further feature observed was that the ratio ^3J:^2J for all the heterobicycles remained approximately constant (Table I). Clearly, this would not be expected if direct overlap of orbitals (IV, V) was the reason for the large apical coupling constants, since the degree of orbital overlap would change dramatically for the heteroatoms ^{14}N, ^{15}N, ^{31}P, ^{103}Rh, and ^{195}Pt, and hence the ratio ^3J:^2J would also alter. We could expect, for example, that the radial extension of the d orbitals of the metal ions of the second- and third-row transition elements would be considerably greater than those of N and P. Furthermore, the similar values of $^3K_{M-^{13}C}$ and $^3K_{X-^{13}C}$ would not be expected if the degree of direct orbital overlap was drastically affected by changing the heteroatom. All these factors show conclusively that the large ^3J coupling constants result from the relatively fixed dihedral angle of ~0° between the heteroatom and the apical carbon and that direct through-space coupling can be ruled out. The lower $^{3/2}J$ coupling constants (1,2-ethanediamine) as opposed to ^2J coupling constants (cap) probably arise from cancellation of ^2J and ^3J pathways (of opposite sign), while the ^2J and ^4J couplings are of the same sign and, hence, are basically additive.[15]

In summary, the large M–^{13}C coupling constants observed in the apical positions of cage complexes result from a Karplus type relationship, which is consistent with mounting evidence on ^{13}C coupling constants.[6,8,15-18] The coupling results also imply that direct coupling of the heteroatom with the apical carbon in bicyclo[2.2.2]octane ring type systems can be ruled out. These conclusions are consistent with theoretical calculations[9] and deductions from the effects of various substituents on the properties of cobalt cage complexes.[11,19]

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Carbon-to-Boron Bridged *o*-Carboranes[1]

Sir:

Although many *o*-carboranes in which the two carbons are attached through carbon (or other) bridges are known,[2] the literature contains no examples of molecules in which the framework borons and carbons are attached through a simple carbon bridge.[3] We have developed an easy synthesis of such compounds and describe it here.

We recently reported the reaction of carbomethoxycarbene with the B–H bonds of *o*-carborane[4] to form the products of formal B–H insertion and noted that the C–H bonds were ignored by the carbene. We have used an intramolecular version of this

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(1) Support by the National Science Foundation through Grant CHE 83-18345 is gratefully acknowledged. We thank the Department of the Army for a generous supply of decaborane.

(2) *Boron Compounds, Gmellin Handbook of Inorganic Chemistry*; Springer-Verlag: West Berlin, 1981; 1st Supplement, Vol. 3 and earlier volumes. Grimes, R. N. *Carboranes*; Academic: New York, 1970.

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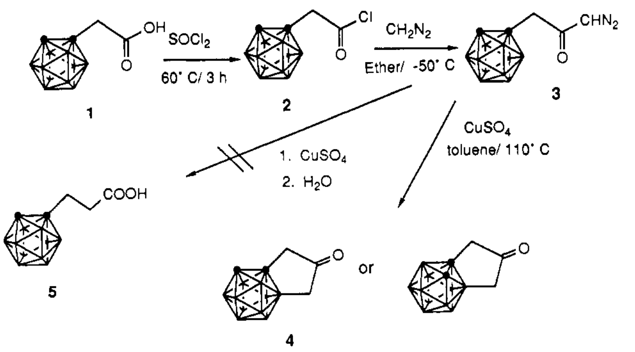
Scheme I



Scheme II

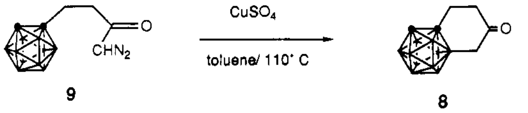
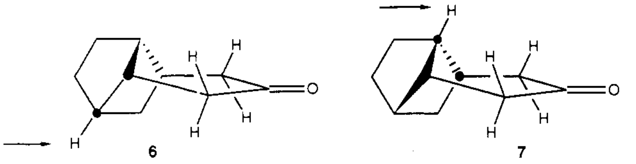
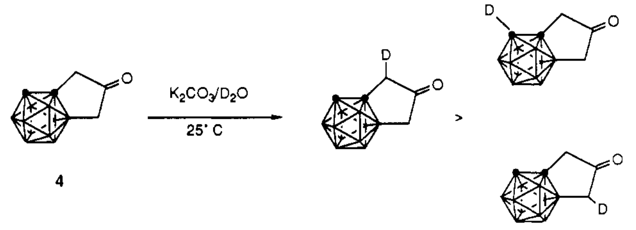


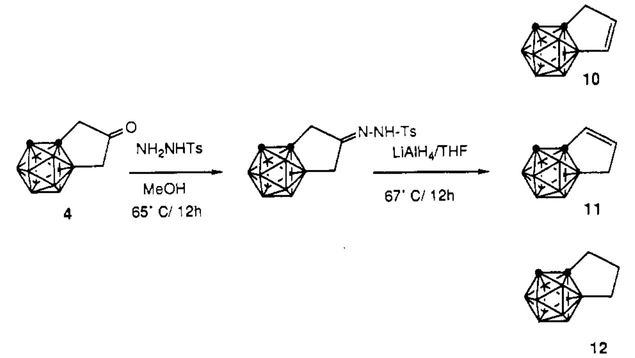
Chart I



Scheme III



Scheme IV



reaction, whose mechanism remains unknown, to produce the first carbon-to-boron bridged *o*-carboranes. *o*-Carboranylacetic acid **1** was converted to its acid chloride **2** and then to the diazo ketone **3** by treatment with excess diazomethane below −40 °C (Scheme I). Above this temperature an *o*-carborane acts as a catalyst for the decomposition of diazo compounds, as we have noted before.[5] In this case polymethylene is the result of the relatively high temperature attempt to make **3**. Diazo ketone **3** can be decomposed by copper sulfate in toluene at 110 °C to give a single major product (**4**, mp 177–179 °C) in 90% yield as determined gas chromatographically. The reaction mixture was washed with KOH/H_2O directly after the cessation of nitrogen evolution and the product of Wolff rearrangement (**5**) sought but not found. Precise mass spectrometry revealed the molecular formula of **4** to be $C_5B_{10}H_{14}O$.[6] The infrared spectrum showed the presence of a C–H (3050, 3100 cm^{-1}) and a ketone (1750 cm^{-1}). The ^1H NMR spectrum confirmed that a single hydrogen remained attached to carbon ($\delta = 3.90$), and the coupled and decoupled ^{11}B NMR spectra showed that one boron had been substituted.[7] As the ^1H NMR spectrum also showed two methylene groups as AB quartets centered at $\delta = 2.94$, $J = 18.3$ Hz, and $\delta = 2.24$, $J = 19.7$ Hz, the only remaining question concerned the point of attachment of the five membered ring. Two B–H bonds, at the 4,5,7,11 and 3,6-positions were within reach, and in principle either could have been attacked by the carbenoid reagent. A nuclear Overhauser experiment (NOE) showed that substitution was at the 4,5,7,11-position.[7] Irradiation at the position of the remaining framework C–H ($\delta = 3.90$) resulted in an Overhauser effect at only one of the protons of the lower field AB quartet and showed no effect at all on the higher field AB quartet. Partial structures **6** (attack at 4,5,7,11) and **7** (attack at 3,6) (Chart I) show that were the structure of the cyclized product to be **7**, two protons, one in each AB quartet, would have to be affected as they are at almost exactly the same distance from the C–H irradiated. Thus intramolecular addition occurs most easily at the 4,5,7,11-position, as is the case in the intermolecular version of this reaction.[4]

The analogous six membered ring **8** (mp 124-126 °C) can be made in a similar way from diazo ketone **9**, albeit in lower yield (Scheme II). In addition, **8** is accompanied by 20–40% of an adduct of the carbene with solvent (benzene or toluene). Once more it appears that the 4,5,7,11-position is the one attacked, as judged by the similarity of the coupled and decoupled ^{11}B NMR spectra of **4** and **8**.[7] With ketone **4** in hand the way is open to synthesize a variety of bridged *o*-carboranes and to use such compounds to compare the effects of neighboring carbon and boron on the chemistry of the α-positions. We can mention a few details here. Thus **4** exchanges H for D faster at the methylene group adjacent to carbon than at the other methylene, adjacent to boron, or at the cage position (Scheme III).

Ketone **4** can be converted to a tosyl hydrazone and then reduced with $LiAlH_4$[8] to give two cyclopentenes in 61% (**10**) and 18% (**11**) relative yield.[7] These two carborane versions of indene are accompanied by ca. 8% of the fully reduced cyclopentane, **12** (Scheme IV). The major product is assigned the structure **10** and the minor product **11** because these compounds have signals very similar to the downfield and upfield AB quartets of **4** respectively. An NOE experiment on **10** in which the framework C–H was irradiated showed an Overhauser effect on only one proton of the AB quartet centered at $\delta = 2.97$, just as was the case for **4**. Compounds **10** and **11** complement the already known[9] carbon–carbon-bridged version of indene. It remains to be seen if their chemistries are similar.

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(7) ^{11}B NMR spectra were recorded at 80 MHz in $CDCl_3$ and signals referenced to boron trifluoride etherate. Chemical shifts were measured on decoupled spectra and multiplicities on coupled spectra: **4**, δ −2.9 (d, 1 B), −4.9 (s, 1 B), −7.0 (d, 1 B), −10.5 (br d, 4 B), −14.1 (d, 2 B), −16.0 (d, 1 B); **8**, δ −2.4 (d, 1 B), −5.3 (s, 1 B), −7.7 (d, 1 B), −10.0 (d, 2 B), −12.7 (d, 2 B), −13.7 (d, 2 B), −17.1 (d, 1 B); **10**, δ −0.1 (s, 1 B), −4.2 (d, 1 B), −7.9 (d, 2 B), −9.7 (d, 2 B), −11.9 (d, 1 B), −13.0 (d, 2 B), −17.6 (d, 1 B). ^1H NMR spectra were recorded at 250 MHz in $CDCl_3$ and signals referenced to Me_4Si: **10**, δ 6.16 (br s, 2 H), 3.83 (br s, 1 H), 3.10 (d, 1 H, $J = 18.3$ Hz), 2.85, (d, 1 H, $J = 18.3$ Hz); **11**, δ 6.28 (br s, 1 H), 6.04 (br s, 1 H), 3.82 (br s, 1 H), 1.99 (br s, 2 H). We thank Mary W. Baum for her usual expert help with the NMR spectroscopy.

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