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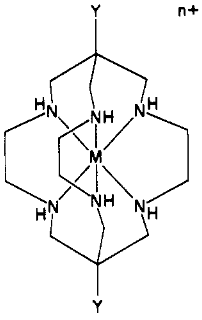
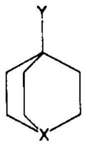
Vicinal Heteroatom-^{13}C Spin-Spin Coupling Constants in the Apical Positions of Cage Complexes: Inorganic Analogues of Heteroatomic Bicyclo[2.2.2]octane Molecules

Sir:

Comparatively large vicinal $^{103}Rh-^{13}C$ and $^{195}Pt-^{13}C$ spin-spin coupling constants were observed for the apical carbon in comparison to other carbons in the ^1H-decoupled ^{13}C NMR spectra of platinum and rhodium sar[1] cage complexes (I).[2-4] These results are in concert with those obtained from heterobicyclo[2.2.2]octanes (II),[5-8] which indicate that direct through-space overlap of the heteroatom orbitals with the orbitals of the apical carbons (IV, V) has a minimal contribution to the coupling. They are also in accord with theoretical analyses which show that direct overlap of such orbitals is minimal.[9]



I



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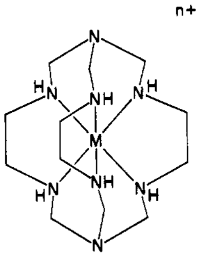
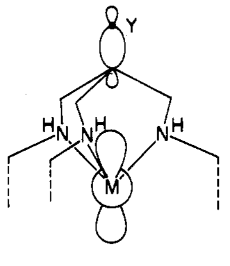


III

There has been much interest in the relatively rigid bicyclo-[2.2.2]octane compounds in order to determine both the extent of direct coupling of the orbitals of the bridgehead atoms and whether or not a Karplus relationship exists for coupling constants between heteroatoms and ^{13}C atoms.[5-8] We recently reported the syntheses and properties of the cage complexes I and III of Pt(IV)[2,3] and Rh(III),[4] which contain analogous ring systems, and we noted surprisingly large $^3J_{^{13}C-M}$ coupling constants for the apical carbons in the ^1H-decoupled ^{13}C NMR spectra of sar complexes I (Table I). These coupling constants were more than an order of magnitude greater than either the $^2J_{M-^{13}C}$ (cap) or $^{2/3}J_{M-^{13}C}$ (1,2-ethanediamine) coupling constants.[2-4] Furthermore, the magnitudes of the coupling constants were strongly dependent on the magnetogyric ratios, where $^3J \sim 40-50$ Hz for ^{195}Pt and $^3J \sim 3-4$ Hz for ^{103}Rh, but the reduced coupling constants,[10] $K_{M-^{13}C}$, were similar (Table II). Such observations were consistent with the coupling constants of the type II molecules (Table I), where the strengths of the ^3J coupling constants are dependent on the magnetogyric ratio of the heteroatom (Table II). Again, the reduced coupling constants only varied by a factor of 3 for the range of compounds, even though the actual coupling constants varied by a factor of 20. No well-resolved M-^{13}C coupling was observed in the ^1H-decoupled ^{13}C NMR spectra of cage complexes of either Co(III)[11-13] or Ir(III).[4,11] However, in both cases, the apical carbon resonances were considerably broadened in comparison to the methylene carbon resonances of both the cap and the 1,2-ethanediamine moieties. The ratio of the broadening for the various carbon resonances was consistent with the ratio of coupling constants for the other cage complexes. The lack of well-defined octets for ^{59}Co and quartets for ^{191}Ir and for ^{193}Ir couplings to the apical carbons is no doubt due to quadrupolar broadening. Normally, vicinal coupling decreases with increasing electron-withdrawing power of substituents,[14] and a similar trend was noted in the ^{13}C NMR spectra of the cobalt cage complex-



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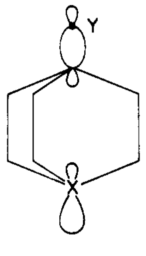

V

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(1) sar = sarcophagine = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane; sep = sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane; diAMsar = 1,8-diaminosar; diAMsarH_2 = 1,8-diammoniosar; diHAsar = 1,8-bis(hydroxylamino)sar; diNOsar = 1,8-dinitrosar; diNOsar-H = 1,8-dinitrosarato-N^3; en = 1,2-ethanediamine.

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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	$^{3}J^{a}$	$^{2}J^{a}$	$^{1}J^{a}$	$^{2/3}J^{a,b}$	$^{3}J/^{2}J$	ref
I	Rh(III)	$^{+}NH_3$	4.15	$\lesssim 0.3^{e}$		<0.3	~10	4
I	Rh(III)	NH_2	3.42	$\lesssim 0.3^{e}$		<0.3	~10	4
I	Rh(III)	NO_2	3.36	$\lesssim 0.3^{e}$		<0.3	~10	4
III	Rh(III)			$\lesssim 0.3^{e}$		<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		$\lesssim 2$	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 ^{3}J Coupling Constants (Hz) and Magnetic Properties[10] of Heteroatoms in Bicyclo[2.2.2]octane Ring Systems

heteroatom	^{3}J	$10^{-20}K^{a}$	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 ^{3}J:^{2}J 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 ^{3}J:^{2}J 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 $^{3}K_{M-^{13}C}$ and $^{3}K_{X-^{13}C}$ 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 ^{3}J 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 ^{2}J coupling constants (cap) probably arise from cancellation of ^{2}J and ^{3}J pathways (of opposite sign), while the ^{2}J and ^{4}J 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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