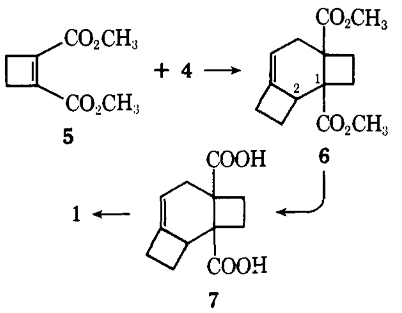
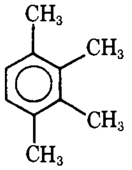
Table I. Melting Point (°C) and Ultraviolet (nm) Absorption Data

Compound	mp	$\lambda_{max}^{95\%EtOH}$ (ϵ)		
1	36	266 (1360)	269 (1370)	275 (1540)
8	−6	267 (301)	272 (244)	276 (235)
2[1]	101	276 (4570)	280 (5125)	286 (3890)
9	79	268 (712)	273 (654)	278 (727)



Utilizing 2 equiv of lead tetraacetate in a manner previously described,[4] the bis decarboxylation of 1.11 g of **7** and subsequent aromatization were achieved in a single reaction. Chromatography of the crude product on silica gel, eluting with 20% ether–hexane, provided 70 mg of material which was 50% of a single component by VPC. A pure sample of **1**, mp 36°,[5] was obtained by preparative gas chromatography on a Carbowax 20M column.

A high resolution mass spectrum of the purified product showed a parent peak at 130.0782 (calcd for $C_{10}H_{10}$ 130.0783) as well as significant peaks at *m/e* 115 (rel intensity 90, loss of $\cdot CH_3$) and *m/e* 102 (rel intensity 12, loss of $CH_2{=}CH_2$). In the infrared spectrum, the only noteworthy absorption below 1200 cm^{-1} was a sharp, strong band at 821 cm^{-1} which corresponds to the characteristic out-of-plane bending for a 1,2,3,4-substituted benzene.[6] The 100-MHz NMR spectrum of **1** showed a two proton singlet at δ 6.74 and an eight proton singlet at δ 3.08, again indicating a tetrasubstituted benzene ring. The uv data recorded in Table I further support the existence of a benzene nucleus and differentiate clearly between structures **1** and **2**. The only structure for **1** which is completely consistent with all the above spectroscopic evidence is benzo[1,2:3,4]dicyclobutene.



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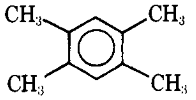

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The upfield singlet in the NMR spectrum of **1** must be explained by the two nonequivalent benzylic methylenes having coincidental chemical shifts.[7] In the open-chain analogue, **8**, the nonequivalent methyl groups exhibit a 5 Hz difference in chemical shifts. Even more surprising is the aromatic signal whose chemical shift is identical with that of prehnitene. By comparison, the ortho ring protons of benzocyclobutene show a chemical shift of δ 6.91[8] which is 0.19 ppm upfield from the value reported for *o*-xylene.[9]

An examination of the uv data recorded in Table I reveals an interesting difference between isomers **1** and **2**. Cava points out that the distortion due to the strain caused by two fused four-membered rings gives rise to a substantial bathochromic shift on going from durene, **9**, to **2**.[1] When the two rings are fused meta, however, a slight hypsochromic shift is observed by comparison of **1** with prehnitene, **8**. A comparable increase in the intensity of absorption is observed for both strained systems. Since the strain inherent in **1** and **2** should be nearly equal, the position at which the second four-membered ring is fused to the benzene nucleus must be of importance in determining the electronic characteristics of the molecule. Investigations into the properties of meta and para bis-annelated benzene systems are currently being carried out.

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^{59}Co Nuclear Quadrupole Resonance Spectra and Low Temperature ^{13}C Magnetic Resonance Spectra of $X_3SnCo(CO)_4$ Compounds[1]

Sir:

As the initial stage in an investigation of intramolecular rearrangements in five-coordinate molecules using ^{13}C and ^{31}P magnetic resonance, we have studied the ^{13}C NMR spectra of several compounds of the form $X_3SnCo(CO)_4$. All these compounds possess idealized trigonal symmetry at cobalt, with two distinct chemical environments for the CO groups, axial and radial, in the ratio 1:3.

Observation of the ^{13}C NMR spectra associated with the CO groups in metal carbonyl compounds of manganese and cobalt often proves to be rather difficult. The ^{13}C NMR absorptions may be very broad at room temperature because of relaxation of the ^{13}C spin system due to scalar relaxation of the second kind.[2,3] The salutary effect of lower temperatures on the relaxation behavior of spin $1/2$ systems scalar-coupled to spin systems with $I > 1/2$ has been noted for ^1H in boranes and carboranes,[4] and for carbonyl compounds of Co, Mn, and Re.[5]

Tribenzyltintetracarbonylcobalt (I) exhibits solid-state nuclear quadrupole transitions (27 °C) at 21.51 and 14.24 MHz. By analogy with other similar compounds[6,7] these are assigned to ν_3 and ν_2, respectively, corresponding to a quadrupole coupling constant of 100.4 MHz, and an asymmetry parameter η of 0.15. These may be compared with values of 96.8 MHz and $\eta = 0.03$ for trimethyltintetracarbonylcobalt,[6] and 104.1 MHz and $\eta = 0.05$ for triphenyltintetracarbonylcobalt.[7]

The ^{13}C NMR spectrum of I at room temperature consists of a single very broad line centered at about 198.6 ppm relative to Me_4Si.[8] As the temperature is lowered this line sharpens, and appears as a single line of about 10 Hz half-width at −60 °C.

Table I. $X_3SnCo(CO)_4$ ^{13}C NMR

X	Av chem shift[a,b]	T_c, °C	Axial chem shift[b]	Radial chem shift[b]	$\Delta G^‡$, kcal/mol	e^2qQ/h, MHz
$C_6H_5CH_2$	198.8	−111	205.3	196.6	7.1	100.4
n-C_4H_9	200.6	−110	206.1	198.7	7.2	–
C_6H_5	199.0	−110	204.9	197.1	7.2	104.1[7]
CH_3	200.4	−119	205.8	198.6	6.8	96.8[6]
Cl	191.1	<−155	–	–	–	163.4[7]

[a] Fast exchange value. [b] All shifts are ±0.1 ppm, downfield from Me_4Si with $HFCCl_2$ as secondary standard (−94.2 ppm).

Below −90 °C the line broadens, and below −120 °C a pair of lines of intensity ratio 1:3 emerges.

In the slow exchange region, the lines corresponding to the axial and radial CO groups exhibit chemical shifts of −205.3 and −196.6 ppm downfield, respectively, relative to Me_4Si. The coalesence temperature for the intramolecular exchange of axial and radial CO groups is −111 °C. A preliminary analysis of line shapes at various temperatures yields values of $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$ for the exchange of 7.1 kcal/mol, 8.2 kcal/mol, and 7.1 cal/°K, respectively. (In making this analysis we have assumed that the scalar interaction with ^{59}Co makes no contribution to the line shape in the temperature region in which spectra were analyzed, i.e., below about −100 °C. This seems a reasonable assumption, since the line width remains 10 Hz from −60 to −80 °C.)

These results are, so far as we are aware, the first reported example of a stopped exchange in any compound of the form $XM(CO)_4{}^n$. possessing idealized axial symmetry at the metal. Low temperature ^{13}C NMR spectra of several compounds of this general formula, e.g., $C_5H_5NFe(CO)_4$,[9] $PF_3Fe(CO)_4$,[10] $(C_6H_5)_3PFe(CO)_4$,[11] and (olefin)$Fe(CO)_4$,[12] have been reported. With the exception of the olefin compounds, in which the olefin occupies an equatorial site, none of these systems has shown evidence of slow exchange at the lowest temperature studied. The origin of the barrier to the intramolecular rearrangement in the olefin systems is thought to lie in the necessity for the olefin group to rotate in the course of the rearrangement.[12] One previously studied system which bears some resemblance to those reported here is $CF_3Co(CO)_3PF_3$, in which cis and trans isomers have been observed.[13] The exchange between the isomeric forms, as observed in the ^{19}F NMR spectra, is slowed at −70 °C.

The barrier to intramolecular rearrangement in $Fe(CO)_5$ is thought to be very low.[10,14] On the other hand, the barriers in $ML_5{}^n$ compounds (M = Co, Rh, Ir, Ni, Pd, Pt), where L is a phosphine or phosphite, are sufficiently high so that the stopped exchange region for intramolecular exchange can be observed in the ^{31}P NMR spectra.[15]

It is well known that the detailed pathway by which an $XM(CO)_4$ species undergoes axial-radial exchange cannot be determined by observation of the ^{13}C NMR spectra of any of the possible variously labeled molecules.[16-18] However, a related matter of possibly more significance, the dependence of the kinetics of axial-radial interchange on the nature of X, can be determined by systematic studies. Table I shows preliminary ^{13}C NMR data for several $X_3SnCo(CO)_4$ compounds at low temperatures. The slow exchange region is reached for all except $Cl_3SnCo(CO)_4$. The relationship of the ^{13}C NMR results to ^{59}Co quadrupole coupling constants is interesting. The four organotin compounds all possess considerably lower quadrupole coupling constants than $Cl_3SnCo(CO)_4$, which in turn possesses a quadrupole coupling constant very near the value of 156 MHz predicted[19] for the as yet unknown $Co(CO)_5{}^+$. By analogy with the results for isoelectronic $Fe(CO)_5$, one might expect the intramolecular exchange rate in $Co(CO)_5{}^+$ to be very rapid. Barring the possibility that the chemical shift difference between axial and radial CO groups in $Cl_3SnCo(CO)_4$ is small, these preliminary results suggest that the ability of the X group in $XCo(CO)_4$ compounds to act as a π-acceptor is an important factor in determining the barrier to axial-radial interchange. Detailed line shape analyses and studies of other $XCo(CO)_4$ compounds are underway.

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New Synthetic Reactions. Catalytic vs. Stoichiometric Allylic Alkylation. Stereocontrolled Approach to Steroid Side Chain

Sir:

Control of stereochemistry in acyclic systems remains a formidable problem in synthetic organic chemistry. A classic example is creation of stereochemistry at C-20 of steroids.[1-3] Absorption of the substrate on a transition metal to enforce conformational rigidity and thus stereochemical control is a possible approach to the problem. In this paper, we wish to report that either stereochemistry at the C-20 position of a steroid can be obtained via π-allylpalladium complexes[4-6] from the same olefin substrate. In particular, the results demonstrate a contrast between the catalytic and stoichiometric approaches to allylic alkylation utilizing organopalladium chemistry and offer insight into the mechanism of the catalytic process.[7] Furthermore, the catalytic palladium reaction allows an overall SN2 displacement with a net retention of configuration at the carbon undergoing displacement.