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NMR Evidence for a Planar Arene Intermediate in the
Electron-Transfer Induced η^6 to η^4 Hapticity Change of a
Rhodium Arene Complex

by

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NMR EVIDENCE FOR A PLANAR ARENE INTERMEDIATE IN THE
ELECTRON-TRANSFER INDUCED η^6 TO η^4 HAPTICITY CHANGE
OF A RHODIUM ARENE COMPLEX[&]

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ABSTRACT

¹H NMR spectra have been obtained for the Rh(II) complex $[(\eta\text{-C}_6\text{Me}_6)\text{RhCp}^*]^+$, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, at 200 MHz, 250 MHz, and 470 MHz. A single resonance was observed for the arene CH₃ protons between 298 K and 183 K in CD₂Cl₂. The temperature dependence of the resonance was consistent with a doublet state formulation of the Rh(II) complex. At 298 K, the CH₃ chemical shifts were 56 ppm for the arene substituents and 123 ppm for the cyclopentadienyl substituents. The magnetic equivalence of the methyl arene resonances is consistent with a planar arene structure in the complex. It is shown that a structural formulation including a highly fluxional bent arene is unlikely. The results demonstrate that when a metal complex undergoes a 2 electron-transfer induced change from $\eta^6\text{-}$ to $\eta^4\text{-}$ arene hapticity, the one-electron intermediate can retain the planar arene structure, even if this results in a 19 e⁻ metal.

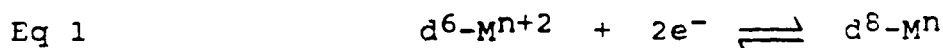
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INTRODUCTION

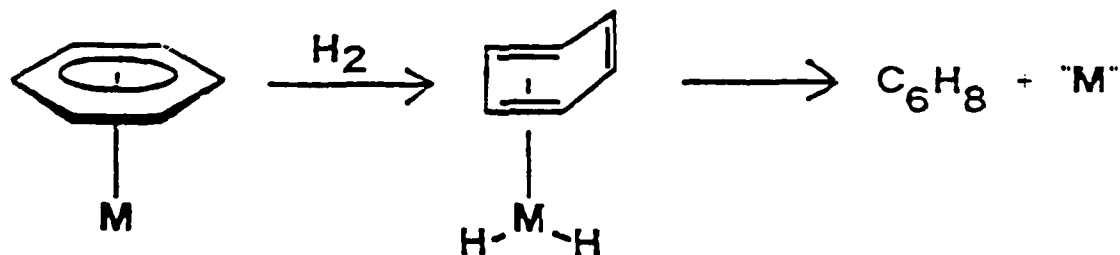
Ligands with a variable hapticity may be important in the action of metal-based catalytic systems, since their electronic ambivalence allows low-energy associative and dissociative pathways¹. The importance of this property has been identified in connection with both 16/18 electron diamagnetic systems² and with 17/19 electron radical systems³.

Muetterties and Bleeke pointed out that most catalyst precursors for arene hydrogenation have an accessible formal two-electron couple involving the d^6 and d^8 electronic configurations (Eq 1)⁴:



They and others suggested⁵⁻⁷ that the arene bends into a tetrahapto-bonding mode to accommodate the two electrons gained in coordination of dihydrogen prior to transfer of 2H to the arene (Scheme I):

SCHEME I



A key factor in this process was identified as the effect of the d^x electronic configuration on the energy of both the η^6 and η^4 arene complexes⁴. It is logical to address

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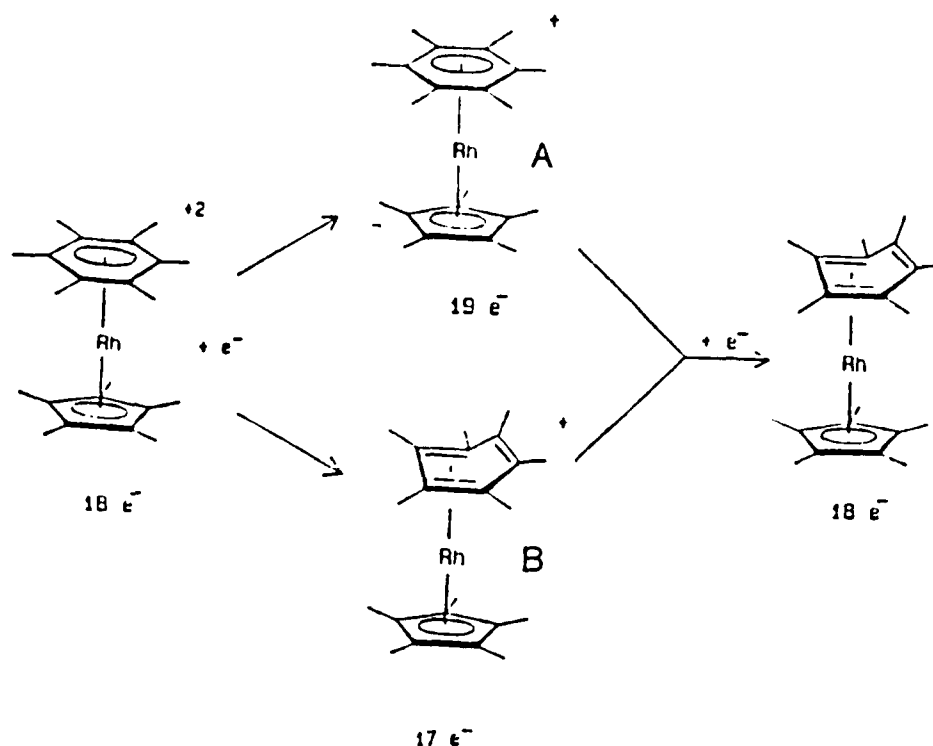
this problem by studies of model metal-arene complexes in which the $d^6 \rightleftharpoons d^8$ change occurs by transfer of two electrons rather than by transfer of H_2 ⁸⁻¹¹.

Two redox systems have so far been reported which display the hexahapto/tetrahapto arene transformation upon receipt of two electrons by the metal, $[(\eta^n\text{-arene})Ru(\eta^6\text{-arene})]^{2+/0}$ ¹⁰⁻¹² and $[(\eta^n\text{-arene})MCp^*]^{2+/0}$, $M = Rh$ or Ir , $Cp^* = \eta^5\text{-C}_5\text{Me}_5$ ^{8,9}. Crucial to these studies is knowledge of the arene hapticity in the odd-electron intermediate. Arguments have been made, based on the influence of arene substituents on the d^6/d^7 and d^7/d^8 formal potentials of a $Rh(III)/Rh(II)/Rh(I)$ sequence^{13a}, and utilizing kinetic data for electron exchange^{13b}, that arene bending occurs in the second electron transfer. However, no direct spectroscopic or crystallographic evidence has been presented.

We now report ¹H NMR data consistent with the assertion that the $Rh(II)$ species in that series has a planar or nearly planar arene. The d^7 intermediate is shown to prefer a 19-electron configuration (structure A, Scheme II) to a 17-electron configuration (structure B, Scheme II), at least when the metal is rhodium.

Besides being of fundamental importance in understanding the $\eta^6 \rightleftharpoons \eta^4$ hapticity change, the geometry of the arene in the d^7 intermediate is also relevant to the mechanism of arene hydrogenation catalysis, since d^7 monohydrides must be considered as potential intermediates or transition states in the process, and some d^7 metals are known as hydrogenation catalysts¹⁴.

SCHEME II



EXPERIMENTAL

Chemicals. $[(\eta^6\text{-C}_6\text{Me}_6)\text{RhCp}^*]^{2+}$ was prepared as the bis-hexafluorophosphate salt by a literature method ¹⁵. The neutral complex $(\eta^4\text{-C}_6\text{Me}_6)\text{RhCp}^*$ was prepared by reduction of the dication with two moles of cobaltocene, as in a recently described procedure ^{13a}. CD_2Cl_2 (Aldrich) was distilled from P_2O_5 and stored under argon prior to use.

NMR Spectroscopy. Data at the University of Vermont were obtained on a Bruker 250 MHz instrument. Spectra at Purdue University were obtained using Nicolet NT 200 and NT 470 instruments. Data acquisition utilized a single-pulse technique with a 5-9 μsec pulse width, acquired in a 32 K block size; 100 scans were usually sufficient. The temperature

(± 1 degree) was controlled with a nitrogen gas-flow device and was measured with a substitution technique using methanol and ethylene glycol standard samples¹⁶.

RESULTS AND DISCUSSION

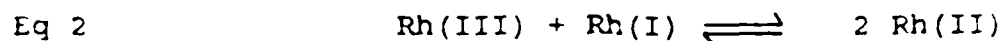
Assignment of the Resonances.

The complexes $[(\eta\text{-C}_6\text{Me}_6)\text{RhCp}^*]^{n+}$, where $n = 2, 1,$ and $0,$ are stable or persistent in all three oxidation states. Bowyer showed that acetone or dichloromethane solutions of $[(\eta\text{-C}_6\text{Me}_6)\text{-RhCp}^*]^+$ did not decompose under dinitrogen for several hours⁸. However, the deep blue Rh(II) solutions were ESR silent down to 77 K¹⁷, implying a very fast electronic relaxation process, and suggesting the possibility that narrow-line resonances might be observed in an NMR experiment¹⁸.

If the arene is planar (η^6) in the Rh(II) complex, a single resonance should be observed for the protons in the arene Me groups. A bent arene (η^4) should show three arene Me resonances, as observed for the neutral complex $(\eta^4\text{-C}_6\text{Me}_6)\text{RhCp}^*$ ⁸. It is also possible that a bent arene complex could give a single ^1H resonance for the Me groups if the complex is fluxional in such a way that the motion averages the environments of all the Me groups within the NMR time scale (vide infra).

In collecting spectra, care was taken to assure that only the Rh(II) monocation was present in solution, since the presence of either the dication or the neutral complex could lead to electron exchange, giving shifted and/or broadened peaks. This condition was realized by adding a slightly substoichiometric amount of Cp_2Ce reductant to a slurry of $[(\eta^6\text{-C}_6\text{Me}_6)\text{RhCp}^*][\text{PF}_6]_2$ in CD_2Cl_2 , since the dication is poorly soluble in this solution and its concentration could be neglected. Alternatively, equimolar amounts of the dicationic and neutral

complexes when mixed in CD₂Cl₂ gave the monocation through the comproportionation reaction¹⁹ (Eq 2):



Essentially identical results were obtained by the two methods. Data at 200 MHz are discussed as representative (Table I). Two resonances were observed (Fig 1, 298K), one at 56 ± 1 ppm (w_{1/2} = 81 Hz) and one at 123 ± 1 ppm (w_{1/2} = 305 Hz). w_{1/2} is the peak width at half-height. Integration of these peaks enabled assignment of the signal at 56 ppm to the C₆Me₆ group and that at 123 ppm to the C₅Me₅ group. Identical results were obtained when the monocation was prepared by comproportionation in acetone, so that the solvent appears to have no major effect on the chemical shifts.

Spectra at lower temperatures showed that the chemical shifts of both the C₆Me₆ and the C₅Me₅ peaks increased linearly with 1/T over the range T = 183-298 K (Figure 2). The 1/T dependence of the chemical shift is consistent with a Curie law dependence of the spin susceptibility²⁰, and infers that one state is responsible for the observed paramagnetism. Put in other terms, the magnetic susceptibility apparently arises from a doublet spin state, with no evidence of a singlet/triplet equilibrium being involved. The line widths of the resonances increased with decreasing temperatures, but not excessively so, and the effect appears to be due merely to decreasing electronic relaxation times at lower temperatures.

An experiment performed using a 470 MHz instrument resulted

in a decrease in line widths for both the arene and cyclopentadienyl Me resonances. Since a linewidth limited by exchange (i.e., fluxionality in the present case) should increase with increased magnetic field^{21,22}, this indicates that little if any of the observed linewidth is due to such site exchange effects.

Significance of the Single Arene Resonance.

As mentioned above, there are two possible interpretations for the observed equivalence of the arene methyl resonances. One is that the arene is planar in the Rh(II) monocation. The second is that the arene Me groups are magnetically equivalent owing to rapid fluxionality of the metal-arene bond. Although the latter behavior is known for bent metal-arene complexes, the structures are usually non-fluxional at or slightly below room temperature²³⁻²⁵. We now show that fluxionality cannot account for the behavior of the present Rh(II) system.

In order for a fluxional system to be in the fast exchange limit of the NMR time scale, the rate constant for exchange, k_{ex} , needs to be much greater than $2\pi\delta$, where δ is the difference in chemical shifts (in Hz) between the exchanging sites²². In order to calculate the minimum rate of fluxionality needed to average the NMR environments of the arene resonances, we need to estimate the differences in chemical shifts expected for the distinguishable pairs of Me groups in a bent arene paramagnetic complex.

It may be expected that the Rh(II) complex, like other paramagnetic sandwich complexes, has a metal-ligand spin delocaliz-

ation mechanism dominated by the Fermi contact interaction, rather than by a dipolar interaction²⁶. The downfield shift of the Me resonances supports this assumption, as does the small g-value anisotropy in the closely related Co sandwich complex, $[(\eta^6\text{-C}_6\text{Me}_6)\text{CoCp}^*]^+$ ²⁷. We can therefore expect that the chemical shifts will reflect primarily the spin densities on the ligands.

There appears to be only one measurement of ligand chemical shifts or hyperfine splittings for a paramagnetic tetrahapto arene complex. Elschenbroich and co-workers²⁸ observed large differences in coupling constants for the protons of the bent benzene ring in the ESR spectrum of $[(\eta^4\text{-C}_6\text{H}_6)\text{Cr}(\eta^6\text{-C}_6\text{H}_6)]^-$. Values of a_{H} , the isotropic proton hyperfine splitting, are 7.75 G, 1.57 G, and 1.00 G. Since spin transmission from a carbon $p\pi$ orbital to CH_3 groups and to H atoms is about equally effective²⁹, we could expect similar differences in methyl proton hyperfine splittings if the Rh(II) complex had a bent arene. At room temperature in fluid media, a difference of over 6 G in a_{H} corresponds to a difference of over 4000 ppm³⁰ in ^1H chemical shifts. Being more conservative, if we assume a difference in hyperfine splittings of only 1 G, a chemical shift difference of about 75 ppm is predicted at 298 K. The inferred difference in chemical shifts is well over 100 ppm at 183 K, a temperature at which we clearly observe a single arene resonance.

Assuming even this minimum chemical shift difference, the rate constant for fluxionality needed to average the magnetic environments on the basis of the above relations is well in excess of 10^5 sec^{-1} , even at 183 K. For the sake of comparison,

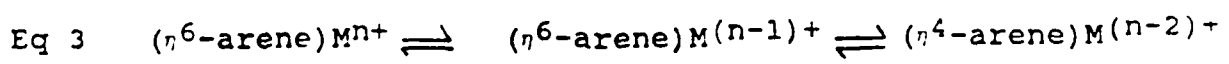
the rate of 1,2-shifts of the neutral

fluxional tetrahapto complex $[\eta^4\text{-C}_6(\text{CO}_2\text{Me})_6\text{RhCp}^*]$ is only 2 sec^{-1} at the considerably higher temperature of 356 K. An activation barrier of over 20 kcal/mol was reported for the fluxionality of the neutral Rh(I) complex²³. In contrast, the ΔG^\ddagger for fluxionality in the Rh(II) system would have to be less than 5 kcal/mole to explain the singlet arene resonance at low temperatures. This activation energy is of the order of magnitude seen for the barrier to rotation of planar pi-bonded ligands like $\eta^5\text{-Cp}$ and $\eta^6\text{-arene}$ ³¹, and far from that expected for a 1,2-shift mechanism for a bent arene. We can therefore deduce with confidence that the Rh(II) intermediate must have a planar or nearly planar arene ring.

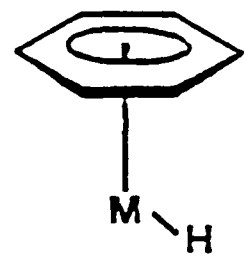
The present findings are also consistent with the results of a recent investigation of the self-exchange and electrochemical exchange kinetics for $[(\eta^5\text{-C}_6\text{Me}_6)\text{RhCp}^*]^{2+}/+ / 0$ in relation to the congeneric Co system^{13b}. In contrast to the cobalt redox steps, for which no hapticity change occurs, the second (+/0) electron-transfer step for rhodium exhibits markedly (up to 10^4 fold) slower exchange kinetics than for the 2+/+ step. The substantial additional intrinsic barrier for the addition of a second electron is consistent with the hapticity change being coupled primarily with this step. The examination of solvent-dependent kinetic data also suggests that this coupling of the hapticity change with the second electron transfer is partly concerted in nature^{13b}.

Comparisons to Other Metal-Arene Systems.

Two classes of compounds have been structurally confirmed as undergoing a η^6 to η^4 hapticity transformation induced by two-electron addition: $[(\eta\text{-C}_6\text{Me}_6)\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)]^{2+/0}$ 10,11,31 and $[(\eta\text{-C}_6\text{Me}_6)\text{MCp}^*]^{2+/0}$ $\text{M} = \text{Rh}, \text{Ir}$ 8,9,13. In other cases, the hapticity change has been postulated, but its confirmation has been frustrated by the instability of either the fully reduced ³² or fully oxidized ²⁴ member of the electron-transfer series. In each study, it has been recognized that the key to understanding the mechanism of the structural change is knowledge of the hapticity of the one-electron intermediate^{8,11,32a,24}. The present results demonstrate that this process can occur through an η^6 -arene intermediate (Eq 3). There is also an implication that 19-



electron intermediates or transition states such as



M = 12-electron moiety

may be important in some arene hydrogenation reactions.

A number of 19-electron metal-arene species are now known. With the exception of $[(\text{C}_6\text{H}_6)_2\text{Cr}]^-$ ²⁸, which is exceptional in being an early transition metal complex, the complexes previously structurally characterized have a planar or nearly planar arene ring^{27,33,34}. However, this may be due to the fact that all of these complexes were with first-row metals, which exhibit reluctance in forming tetrahapto complexes ^{6,8,24,25}. The present

work appears to provide the first information concerning metal-arene hapticities in second or third row odd-electron complexes.

Distribution of the Unpaired Electron.

It is generally believed that the half-filled orbital in d⁷ sandwich compounds has e₁^{*} symmetry, and is an admixture of the metal d_{x²-y²} (or d_{y²-x²}) orbital and the pi^{*} orbitals of the two polyolefins³⁶. Physical studies on the isoelectronic and isostructural mixed sandwich complex (η⁶-arene)FeCp indicate that the spin is about 60-70% metal-centered³³. The ligand contribution is predominantly on the Cp ring rather than on the arene³³, in contrast to theoretical predictions³⁷. A similar situation is found in the Co analogs, [(η⁶-arene)CoCp]⁺²⁷, for which a 60% metal contribution to the e₁^{*} orbital is estimated, the remaining spin density being 3-4 times larger on the five-membered ring than on the six-membered ring.

The contact shifts for [(η⁶-C₆Me₆)CoCp^{*}]⁺ in CD₂Cl₂ are 21.4 and 48.5 ppm for the C₆Me₆ and C₅Me₅ groups, respectively^{27,38}, so that the analogous contact shifts for the Rh complex (56 and 123 ppm) are about 2.5 times larger than those reported for the Co congener. If it is assumed that the g-values of the Rh complex are also not highly anisotropic, then the larger observed contact shifts are due to significantly larger electron density on the rings of the Rh complex. Since the Rh 4d orbitals are more spatially diffuse than are the Co 3d orbitals, the greater delocalization may be due to more effective overlap of the metal orbital with the carbon p_z orbitals of the aromatic ligands. A similar effect has been noted for the two

19-electron radicals $[(\eta^5\text{-C}_5\text{Ph}_5)\text{M}(\text{CO})_2]^-$ $\text{M} = \text{Co}, \text{Rh}^{39}$, in which the metal contribution to the half-filled orbital was calculated to be about 20% lower for $\text{M} = \text{Rh}$ than for $\text{M} = \text{Co}$.

SUMMARY

NMR studies of the Rh(II) complex $[\eta^6\text{-C}_6\text{Me}_6)\text{RhCp}^*]^+$ show that the arene Me groups are magnetically equivalent. This fact does not support a bent arene structural formulation for the complex in this oxidation state. Rather, a planar or near-planar arene geometry is favored. This result answers the question, at least for this system, of whether an arene bends in the first or second electron transfer step when going from a hexahapto to tetrahapto complex through Eq 1. It is clearly implied that the major arene structural change occurs roughly concomitantly with the second, rather than the first, electron transfer. Odd-electron metal hydride structures may exhibit similar behavior, so that 19-electron intermediates in metal arene hydrogenation reactions, having planar arene rings, must be viewed as plausible.

By analogy with the present system, it is likely that $[(\text{arene})_2\text{Ru}]^+$, an intermediate in the reduction of $[(\eta^6\text{-C}_6\text{R}_6)_2\text{Ru}]^{2+}$ to $(\eta^4\text{-C}_6\text{R}_6)\text{Ru}(\eta^6\text{-C}_6\text{R}_6)$ ^{10,11,31}, has two planar arenes, the metal therefore having a 19-electron count. This would be consistent with the hypothesis of Finke, *et al.*, that the Ru(I) intermediate has a structure closer to that of the Ru(II) complex $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}]^{2+}$ than that of the Ru(0) complex $(\eta^4\text{-C}_6\text{Me}_6)\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)$ ¹¹.

One other study of relevance to this discussion is that of

the reduction of (arene)Cr(CO)₃ complexes^{32,40,41}. First, Rieke and co-workers^{32,40}, and then Leong and Cooper⁴¹, have shown that this class of compounds undergoes a two-electron reduction to a reactive dianion which apparently has η^5 - type bonding between the ring and the metal. The metal-ring slippage has been postulated to occur after the first electron transfer^{40c}, in contrast with our results on the Rh system. Taken together with the ESR characterization by Elschenbroich, et al., of the bent arene 19-electron complex $[(\eta^4\text{-C}_6\text{H}_6)\text{Cr}(\text{C}_6\text{H}_6)]^-$ ²⁸, it must be considered that bent arene structures are more likely for electron-rich early transition metals than for their later transition metal counterparts.

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38. The contact shift is the difference in shift between the paramagnetic complex and an analogous diamagnetic complex. The diamagnetic complexes used for these calculations were $[(C_6Me_6)CoCp^*][PF_6]_2$ ($C_6Me_6 = 2.32$ ppm, $C_5Me_5 = 1.68$ ppm) and the analogous Rh dication ($C_6Me_6 = 2.29$ ppm, $C_5Me_5 = 1.84$ ppm), in acetonitrile- d_3 .
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FIGURE CAPTIONS

Figure 1. 270 MHz 1H NMR spectrum of $[(\eta-C_6Me_6)RhCp^*][PF_6]$ in acetone- d_6 at 298 K. Chemical shift in δ vs. TMS.

Figure 2. Shift of CH_3 proton resonances of $[(\eta-C_6Me_6)RhCp^*]^+$ in acetone- d_6 as function of $1/T$. The circles refer to the methyl arene resonance, the diamonds to the methyl cyclopentadienyl resonance.

Table I. ^1H NMR Data for 0.010 M $[(\eta\text{-C}_6\text{Me}_6)\text{RhCp}^*][\text{PF}_6]$ in CD_2Cl_2 at 200 MHz.

| T(K) | C_6Me_6 | | C_5Me_5 | |
|------|-------------------------|------------------------|-------------------------|------------------------|
| | $w_{1/2}(\text{Hz})^a$ | $\delta(\text{ppm})^b$ | $w_{1/2}(\text{Hz})^a$ | $\delta(\text{ppm})^b$ |
| 233 | 124 | 70.60 | 526 | 154.51 |
| 243 | 121 | 68.09 | 486 | 148.57 |
| 253 | 108 | 65.78 | 444 | 143.09 |
| 298 | 81 | 56.28 | 305 | 123.10 |
| 298 | 68 ^c | 56.42 ^c | 218 ^c | 123.26 ^c |
| 298 | 94 ^d | 57.71 ^d | 313 ^d | 122.0 ^d |

^a Peak full width at half height.

^b Chemical shift with respect to tetramethylsilane .

^c The frequency was 469.58 MHz.

^d in acetone- d_6 ; the frequency was 250 MHz.

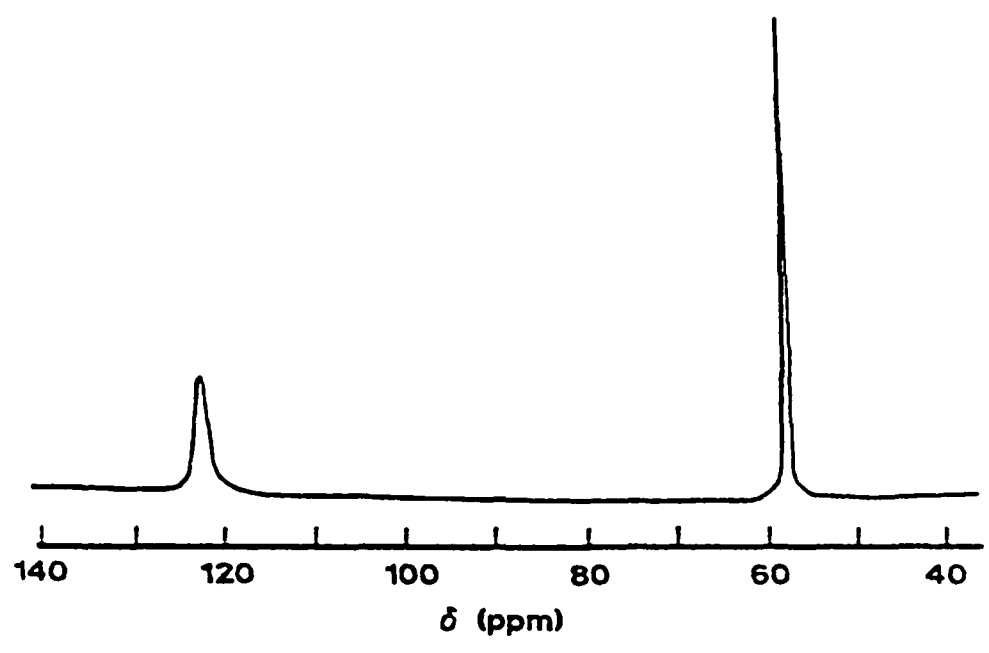
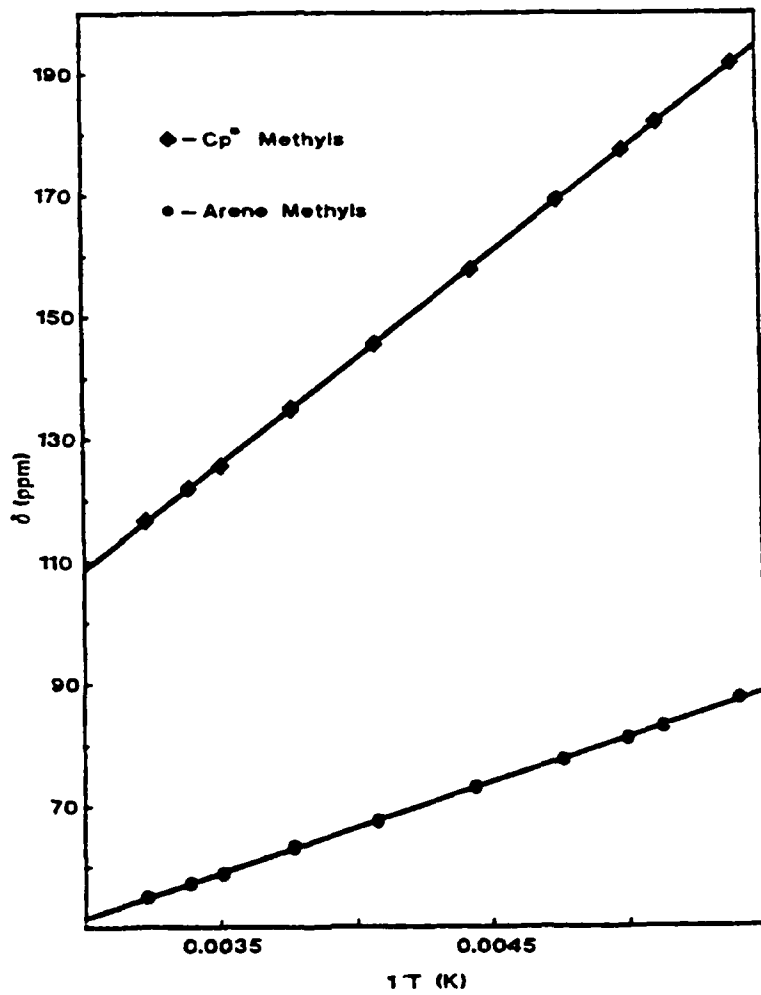


FIG 1
Merkel et al. . . .



F. E. 2
M. S. 1955