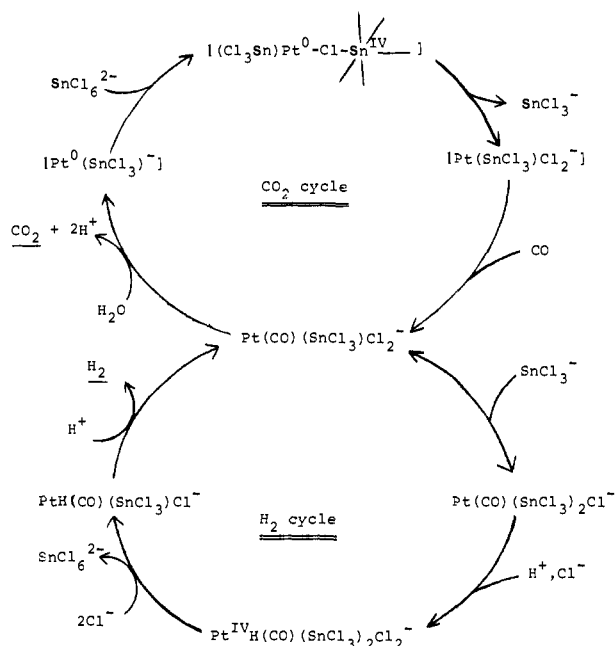
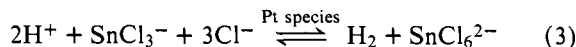
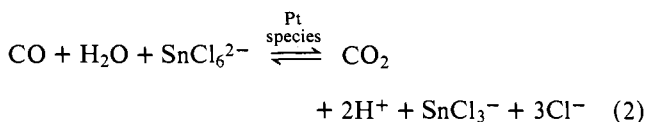


Scheme I



sample of the bis complex $[\text{PtCl}(\text{CO})(\text{SnCl}_3)_2]^-$ was heated in the HOAc/HCl/H₂O catalyst "solution" under N₂, hydrogen evolution was observed with little CO₂ being evolved. The mono complex $[\text{PtCl}_2(\text{CO})(\text{SnCl}_3)]^-$ was isolated from this solution. In a separate experiment, dissolution of the mono complex in the catalyst "solution", followed by heating under CO, led within 10 min to CO₂ evolution corresponding to ~0.6 mol of CO₂ per Pt complex with only a trace of H₂ observed. In acetonitrile, $[\text{PtCl}_2(\text{CO})(\text{SnCl}_3)]^-$ in the presence of SnCl₄·5H₂O under CO reacted readily to form the bis complex. We conclude from these experiments that $[\text{PtCl}(\text{CO})(\text{SnCl}_3)_2]^-$ is most likely responsible in the catalysis for H₂ formation, that $[\text{PtCl}_2(\text{CO})(\text{SnCl}_3)]^-$ is most likely responsible for CO₂ formation, and that the two complexes are related by either a stoichiometric reaction or a simple ligand substitution.

It is evident from the foregoing studies that the Sn(II)/Sn(IV) redox couple ($\text{SnCl}_6^{2-} + 2e \rightleftharpoons \text{SnCl}_3^- + 3\text{Cl}^-$) is actively involved in the observed reaction chemistry, and hence in the mode of catalysis by this system. Through the intermediacy of the Sn(II)/Sn(IV) couple, the water gas shift reaction can be separated into two component reactions



and a mechanism based on this separation can be proposed. This mechanism, which we describe as "coupled cycles", is shown in Scheme I. In the H₂-forming part of the catalysis, Sn(II) is oxidized to Sn(IV), while, in the oxidation of CO to CO₂, Sn(IV) is reduced back to Sn(II). The Sn(II)/Sn(IV) couple thus serves to shuttle electrons from CO to H⁺ in this catalysis, each step of which occurs via the intermediacy of a platinum complex species.¹⁵ The facts that at least one common platinum species exists for the two component reactions and that the tin product of one is a reactant for the other leads to a coupling of the component reactions such that, once the proper Sn(II):Sn(IV) ratio is attained, the stoichiometry of the shift reaction is followed in the observed catalysis.

With regard to the intimate formation of the product gases, it is probable that CO₂ forms via aqueous attack on a Pt(II)-coordinated carbonyl and that H₂ is produced via a platinum hydride species and its reaction with H⁺.

Acknowledgments. We thank the National Science Foundation (Grant CHE77-12519) for support of this research and Matthey Bishop, Inc., for a generous loan of platinum salts.

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- (a) This [Sn(II)]:[Sn(IV)] ratio is not invariant throughout the catalysis, but changes as the partial pressures of CO, H₂, and CO₂ change in the course of each run. (b) A reviewer has suggested that significant solubility of CO₂ in the catalyst solution may alter the conclusions drawn from Figure 1. However, we find that CO₂ is not soluble to a significant extent in the reaction medium. Dissolution of small amounts of K₂CO₃ (1-3 mmol) into the catalyst preparation used for run A leads to quantitative evolution of CO₂, detected gas chromatographically.
- (a) The complex $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ can be isolated from these runs and in separate experiments has been shown to serve as a catalyst precursor for the present system. (b) In this experiment, the [Sn]:[Pt] ratio was 15:1. After heating for 7 h, 12.3 mol of H₂/mol of Pt had been released with no CO₂ formed. Removal of the H₂ and CO gases from above the solution, replacement by N₂, and further heating for 1 h led to an additional 3.2 mol of H₂/mol of Pt and a color change of the active catalyst solution from orange to pale yellow. Precipitation by the addition of Et₄N⁺Cl⁻ gave a colorless product which decomposed at 310 °C and showed E_{1/2} at -1.57 V vs. Ag/AgNO₃ using differential pulse polarography and cyclic voltammetry. These values agree well with those from an independent preparation of the compound (I. Wharf and D. F. Shriver, *Inorg. Chem.*, **8**, 914 (1969)) and differ significantly from those for (Et₄N)[SnCl₃] reported by Parshall (G. W. Parshall, *J. Am. Chem. Soc.*, **94**, 8716 (1972)). (c) In addition to the isolation experiments discussed below in the text, we have observed by visible-ultraviolet spectroscopy $[\text{Pt}(\text{SnCl}_3)_2\text{Cl}_2]^{2-}$ after the removal of CO from catalyst preparations based solely on Sn(IV).
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- The complex $[\text{PtCl}_2(\text{CO})(\text{SnCl}_3)]^-$ exhibits two ν_{CO} values at 2095 and 2065 cm⁻¹ which may be due to different geometric isomers. The 2095-cm⁻¹ band is much more intense in the initially prepared sample, but, if a solution of the complex is allowed to stand, the 2065-cm⁻¹ band becomes stronger at the expense of the higher energy ν_{CO}.
- The exact nature of the Pt species at each point in Scheme I is unknown, but it is highly probable that the intermediates are trichlorostannyl species. Except where indicated, the Pt oxidation state is assumed to be 2+. However, the active involvement of the Sn(II)/Sn(IV) couple via the platinum species requires at least transitory formation of Pt(0) and Pt(IV) species.

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Metalloenes: First Models for Nuclear Magnetic Resonance Isotope Shifts in Paramagnetic Molecules¹

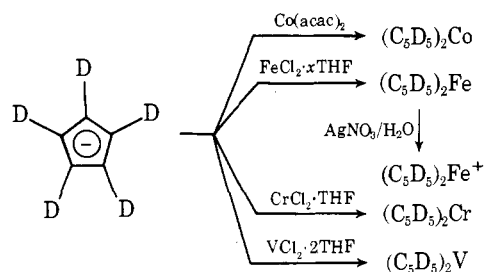
Sir:

The effect of isotopic substitution on NMR spectra of diamagnetic molecules has been widely studied² and this has led to numerous applications for the elucidation of structural and bonding parameters. It was an open question of general in-

Table I. ^{13}C NMR Data on Paramagnetic Metallocenes at 298 K

compd	solvent	expt shift, $\delta(^{13}\text{C})$	isotope shift		dipolar shift, $\delta(^{13}\text{C})^{\text{dip}}$
			$\Delta\delta(^{13}\text{C})$	% ^a	
$(\text{C}_5\text{H}_5)_2\text{Co}$	dioxane- <i>d</i> ₈	-541.2 ± 1.5^b			9.1
$(\text{C}_5\text{D}_5)_2\text{Co}$	dioxane- <i>d</i> ₈	-534.8 ± 1.5^b	+7.4	1.4	
$(\text{C}_5\text{H}_5)_2\text{Fe}^+$	D_2O	-254.0 ± 0.3			-107.7
$(\text{C}_5\text{D}_5)_2\text{Fe}^+$	D_2O	-256.0 ± 0.3	-2.0	0.8	
$(\text{C}_5\text{H}_5)_2\text{Cr}$	toluene- <i>d</i> ₈	$+318.6 \pm 0.5$			-7.9
$(\text{C}_5\text{D}_5)_2\text{Cr}$	toluene- <i>d</i> ₈	$+314.3 \pm 0.5$	-4.3	1.3	
$(\text{C}_5\text{H}_5)_2\text{V}$	toluene- <i>d</i> ₈	$+576.4 \pm 0.5$			0.4
$(\text{C}_5\text{D}_5)_2\text{V}$	toluene- <i>d</i> ₈	$+583.7 \pm 0.5$	+7.3	1.3	
$(\text{C}_5\text{H}_5)_2\text{Fe}^c$	C_6D_6	68.25 ± 0.02			
$(\text{C}_5\text{D}_5)_2\text{Fe}^{c,d}$	C_6D_6	67.85 ± 0.02	-0.40		

^a Percent of shift for $(\text{C}_5\text{H}_5)_2\text{M}$. ^b Exceeds digital resolution (0.11 or 0.27 ppm/point) due to line width. ^c Diamagnetic standards. ^d $^1J(^{13}\text{C}-^2\text{H}) = 26.8$ Hz.

Scheme I

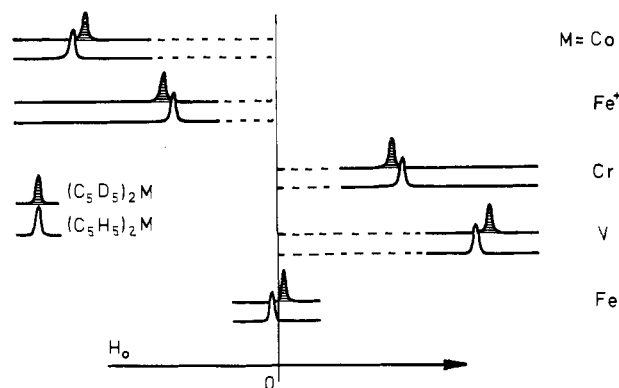
terest, however, whether an isotope effect could be detected in the NMR of paramagnetic compounds.

A particularly suitable model system to answer this question is the series of metallocene radicals because a possible effect may be studied depending on the number of unpaired electrons and different central metals. As we have shown earlier,³ ^{13}C NMR spectra may easily be obtained for these molecules. So, after replacement of the metallocene five-ring hydrogens by deuterium, the ^{13}C signal should show an isotopic displacement which was expected to vary with the central metal.

We have synthesized the perdeuterated metallocenes as shown in Scheme I. Experimental details for the preparation of $(\text{C}_5\text{D}_5)_2\text{Cr}$ and $(\text{C}_5\text{D}_5)_2\text{V}$ are given in a previous paper.⁴ $(\text{C}_5\text{D}_5)_2\text{Fe}$ was needed as a reference compound for paramagnetic shifts and as starting material for $(\text{C}_5\text{D}_5)_2\text{Fe}^+$; its synthesis was based on Wilkinson's method⁵ while a different route was used by Fritz who first described it.⁶ The content of deuterium as determined by mass spectroscopy was $>92\%$ ($(\text{C}_5\text{D}_5)_2\text{Co}$, $92 \pm 2\%$; $(\text{C}_5\text{D}_5)_2\text{V}$, $95 \pm 2\%$).

The ^{13}C NMR spectra were obtained from saturated solutions in 10-mm sample tubes equipped with ground-glass joints and stoppers to assure long term exclusion of oxygen. A Bruker HX 90 spectrometer with BST 700 temperature unit was used; temperatures were measured before and after each experiment with a Lauda R 42 resistance thermometer. Shifts were taken relative to solvent peaks (dioxane-*d*₈, δ 65.4;⁷ toluene-*d*₈, $\delta(\text{C}-\alpha)$ 19.27) or $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{SO}_3\text{Na}$ in D_2O with $\delta(\text{SiCH}_3) -1.6$; they were calculated relative to the corresponding ferrocene and transformed to 298 K using the Curie equation (for all metallocenes $\delta(^{13}\text{C})$ vs. $1/T$ is linear between 250 and 390 K^{3,8}). Results are given in Table I.

While for diamagnetic ferrocene the isotope shift $\Delta\delta(^{13}\text{C}) = 0.4$ and $^1J(^{13}\text{C}-^2\text{H}) = 26.8$ Hz fall in the usual range for organic compounds⁷ in paramagnetic metallocenes, the carbon deuterium coupling is not resolved and the isotope shifts are much greater than has been observed before. All diamagnetic molecules show an upfield shift of the NMR signal when the observed nucleus is substituted with heavier isotopes. We now find that $\Delta\delta(^{13}\text{C})$ can also be shifted to lower fields; this is illustrated in Figure 1. It should be noted that—contrary to

**Figure 1.** Scheme of relative ^{13}C signal positions of metallocenes.

NMR on diamagnetic molecules—shifts to low field were negative for NMR of radicals. Since all shifts are referenced to the corresponding ferrocene, the usual isotope shift in diamagnetic molecules has been eliminated. Thus the paramagnetic $\Delta\delta(^{13}\text{C})$ must be due to different interaction of the unpaired electrons with the five-ring carbons. One contribution to the $\delta(^{13}\text{C})$ may arise from the metal-centered dipolar shift which can be calculated from the expressions of Kurland and McGarvey.⁹ We obtained these $\delta(^{13}\text{C})^{\text{dip}}$ values with a mean geometric factor of 0.087 \AA^{-3} derived from Haaland's electron diffraction work on the metallocenes¹⁰ and the g factors given in ref 11. The results in Table I indicate that an important dipolar shift is observed only in ferricenium ion. This is reflected in $\Delta\delta(^{13}\text{C})$ where $(\text{C}_5\text{D}_5)_2\text{Fe}^+$ has an isotope shift of only 0.8%. In all other metallocenes, the paramagnetic $\delta(^{13}\text{C})$ and $\Delta\delta(^{13}\text{C})$ values are largely dominated by Fermi contact shifts. Consequently, the isotope shift increases not only with the number of unpaired spins (one for cobaltocene and ferricenium ion, two for chromocene and three for vanadocene) but also with the efficiency of electron delocalization, whereas the percent isotope shift remains constant. As for the signs of $\Delta\delta(^{13}\text{C})$, we cannot exclude the possibility that dipolar shifts are responsible for all changes because nothing is known about bond lengths in $(\text{C}_5\text{D}_5)_2\text{M}$. However, it has been shown by the ESR spectra of ^{199}HgH and ^{199}HgD that isotopic substitution leads to different electron spin densities on the metal arising from Fermi contact interaction.¹² For the metallocenes, this would mean that the isotope shifts are produced by different spin delocalization mechanisms; this is consistent with earlier findings.³

We expect that these NMR isotope shifts may be observed in numerous radical complexes, thus facilitating spectral assignment and illuminating electron distribution within molecules. A similar effect of $\sim 1.5\%$ should also be detectable in the ^{13}C hyperfine splittings of aromatic hydrocarbon radicals by ESR.

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Structures and Energetics of Planar and Tetrahedral Dilithiomethane. A Near Degeneracy of Singlet and Triplet Electronic States

Sir:

In a very important recent paper,¹ Collins, Dill, Jemmis, Apeloig, Schleyer, Seeger, and Pople (CDJASSP) have shed new light on the stabilization of planar tetracoordinate carbon. Pople and Schleyer predict¹ that because of their π -acceptor and σ -donor character, electropositive substituents, especially lithium, are particularly effective in stabilizing the planar arrangements selectively. Perhaps the simplest viable candidate for planar carbon is CH_2Li_2 , dilithiomethane, for which the predictions of Pople and Schleyer are summarized in Table I. Although not particularly emphasized by CDJASSP, we were particularly struck by their prediction that both planar and tetrahedral CH_2Li_2 have triplet electronic ground states. CDJASSP explicitly note that the triplet states are artificially favored in their work, since the single determinant Hartree-Fock approximation does not treat singlet and triplet states of this type on an equal footing.² They conclude that "it is difficult to assign the ground state configuration of CH_2Li_2 but the two states should be close in energy". The purpose of the present research is to provide state-of-the-art theoretical predictions, including the effects of electron correlation,^{2,3} of the relative energies of planar and tetrahedral CH_2Li_2 in its lowest singlet and triplet electronic states.

The basis set used in the present research was of double ζ plus polarization (DZ + P) quality⁴ and may be precisely designated C(9s 5p 1d/4s 2p 1d), Li(9s 4p/4s 2p), H(4s 1p/2s 1p). Experience with systems such as methylene⁵ suggest that, in conjunction with large-scale configuration interaction (CI) techniques⁶ and many body theory corrections⁷ for unlinked clusters, predictions of singlet-triplet separations reliable to within 3 kcal may be achieved. With the above specified basis set, self-consistent-field (SCF) theory was used to predict the equilibrium geometrical structures, shown in Figure 1, of the

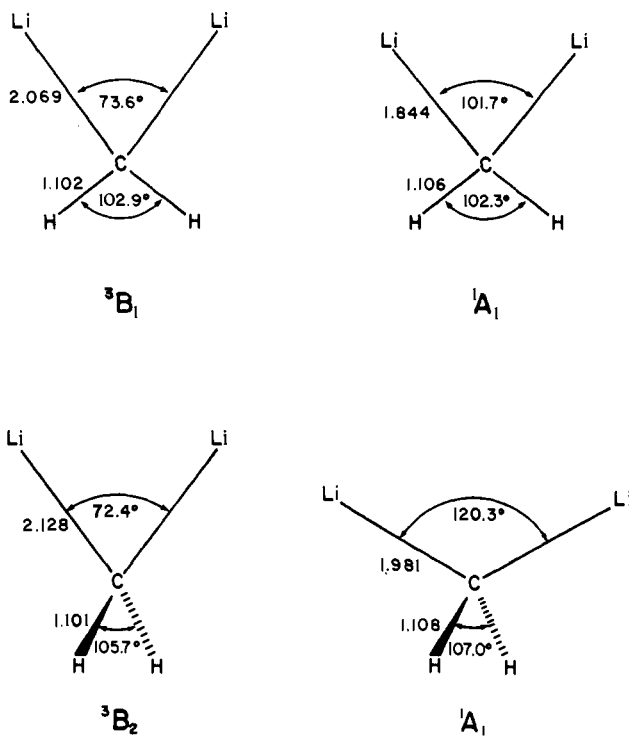


Figure 1. Predicted geometries of planar (upper) and tetrahedral (lower) CH_2Li_2 in its lowest singlet and triplet electronic states. Bond distances are in ångstroms.

Table I. Summary of the Self-Consistent-Field Predictions of Collins, Dill, Jemmis, Apeloig, Schleyer, Seeger, and Pople (CDJASSP)¹ Concerning the Relative Energies of CH_2Li_2

species	minimum basis	double ζ basis
tetrahedral singlet	0	0
tetrahedral triplet	-12	-16
planar cis singlet	17	10
planar cis triplet	-2	-13
planar trans singlet	54	48

four species in question. Our structures are in qualitative agreement with the minimum basis predictions of CDJASSP, although a few quantitative differences may be cited. The present C-Li distances are all longer, by from 0.058 to 0.100 Å, and the Li-Cl-Li bond angles are from 0.2 to 4.7° (planar triplet) larger than those of CDJASSP. However, the most important conclusion of CDJASSP, that the singlet Li-Cl-Li bond angles are much greater than the comparable triplet angles, is given strong support here.

At the predicted SCF equilibrium geometries, CI wave functions including all single and double excitations were determined variationally using the BERKELEY system⁸ of mini-computer-based programs. The numbers of space- and spin-adapted configurations actually included were 7075, 9241, 6724, and 8814. The original Davidson correction⁷ was also applied to these results, which are summarized in Table II. Before going on to the energetic results, we note the remarkable dipole moment predictions also seen in Table II. The planar and tetrahedral singlets have very large dipole moments, with polarity C^-Li^+ , while the triplet μ values are much smaller, and, quite surprisingly, of C^+Li^- polarity.

As suggested by Pople and Schleyer,¹ electron correlation preferentially lowers the singlet states, and in a dramatic fashion. From lying 16.6 kcal above the tetrahedral triplet at the SCF level of theory, the cluster corrected CI eliminates this gap and actually predicts the tetrahedral singlet to lie 2.1 kcal lower. However, the planar triplet lies only 1.8 kcal above the