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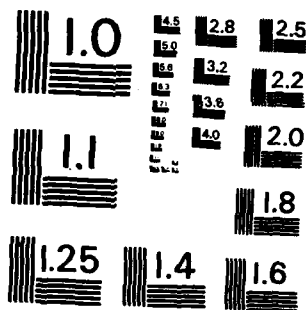
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21. ABSTRACT (Continue on reverse side if necessary and identify by block number) Using nutation NMR spectroscopy the distance between adjacent ¹³ C labels was measured in samples of polyacetylene prepared by polymerizing a dilute solution of double ¹³ C-labelled acetylene in ¹³ C-acetylene using titanium tetra-n-butoxide plus triethylaluminum as a catalyst. The experiments accord with expectation if the polymerization proceeds by a four-center insertion mechanism rather than by a metallacycle mechanism involving metal-carbenes.		

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TECHNICAL REPORT NO. 7

The Mechanism of Ziegler-Natta Polymerization of Acetylene:

A Nutation NMR Study

by

T.C. Clarke and C.S. Yannoni

IBM Research Laboratory
5600 Cottle Road
San Jose, California 95193

and

T.J. Katz
Department of Chemistry
Columbia University
New York, New York

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In spite of the widespread commercial application of Ziegler-Natta catalysis in olefin polymerization, the mechanism of the fundamental carbon-carbon bond forming reaction in this process is not well understood.¹ Currently available data do not distinguish between the more traditional four-center olefin insertion mechanism of Cossee and Arlman² and the recent metallacycle proposal of Green and co-workers.³

A similar dichotomy exists in the related question of acetylene polymerization, where comparable mechanisms have been proposed. The direct four-center acetylene insertion mechanism is illustrated in Scheme 1,⁴ while the metallacycle mechanism suggested by Katz is shown in Scheme 2.⁵ In contrast to the olefin case, however, a clear-cut distinction can be drawn between these two mechanisms. Scheme 1 predicts that the two carbons of a given monomer unit will end up doubly bonded to one another in the resulting polymer; according to Scheme 2 these carbons will be connected by a single bond. We present here the results of an experiment designed to test this difference and demonstrate that, at least in the case of acetylene polymerization by the particular Ziegler-Natta catalyst system employed, the predictions of Scheme 1 are observed.

The keys to this experiment are the use of doubly ^{13}C labelled acetylene monomer and the use of nutation NMR spectroscopy to measure the bond distance between these labelled carbons in the resulting polymer. We have previously shown that the nutation technique can be used to determine bond lengths in amorphous or polycrystalline solids to an accuracy of $\sim 1\%$.⁶ Essentially, this procedure relies on the fact that the dipole-dipole splitting of two bonded magnetic nuclei (in this case ^{13}C) varies inversely as the third power of the internuclear separation. The nutation technique is used to eliminate the effects of chemical shift anisotropy which mask this information in the conventional

^{13}C spectrum of a non-ordered solid material. To avoid interference from longer range dipole-dipole splittings, the bonded nuclei must be relatively isolated from other ^{13}C nuclei. We have achieved this situation in polyacetylene by polymerizing a mixture of 4% doubly ^{13}C enriched acetylene (MSD Isotopes - ≥ 99 atom % ^{13}C) in doubly depleted acetylene (MSD Isotopes - 99.9 atom % ^{12}C). This dilution also assures that each of the bonded ^{13}C pairs in the resulting polymer arises from a doubly labelled acetylene monomer, allowing us to test the above two mechanisms by determining the bond length between these atoms.

The acetylene mixture was polymerized by the method of Ito *et al.* using a titanium tetra-n-butoxide/triethylaluminum catalyst mixture in toluene.⁷ The polymerization was carried out at 196K to provide the *cis-transoid* isomer of polyacetylene. The polymer films were washed free of catalyst residue and packed into sample tubes under dry box conditions before being sealed under vacuum. The samples were stored at 77K before use to avoid isomerization to the *trans-transoid* isomer.⁸⁻¹⁰ A detailed description of the nutation technique has been published previously.⁶

The proton-decoupled ^{13}C nutation spectrum of a *cis*-polyacetylene sample prepared in this manner is shown in Figure 1. The relatively sharp peak in the center arises from isolated ^{13}C nuclei in the sample. The symmetrically disposed satellites and shoulders are the expected features of the doublet pattern arising from the dipole-dipole splitting of the adjacent ^{13}C nuclei in a powder sample.⁶ This spectrum can be fit using a comprehensive simulation program, with the desired carbon-carbon bond distance as the only adjustable parameter. The best fit to the observed spectrum (shown as the dotted curve in Figure 1) corresponds to a bond length of 1.37 Å, a value clearly indicative of a carbon-carbon double bond and not a single bond.¹¹ These

results require that in the polymerization process the carbons of a given monomer unit end up doubly bonded, in agreement with the predictions of Scheme 1.

Thus, these data indicate that, at least for this particular Ziegler-Natta catalyst system, the metallacycle mechanism is not operative. The extent to which these results can be generalized to other types of catalysts and to olefin polymerization mechanisms is currently under investigation.¹²✕

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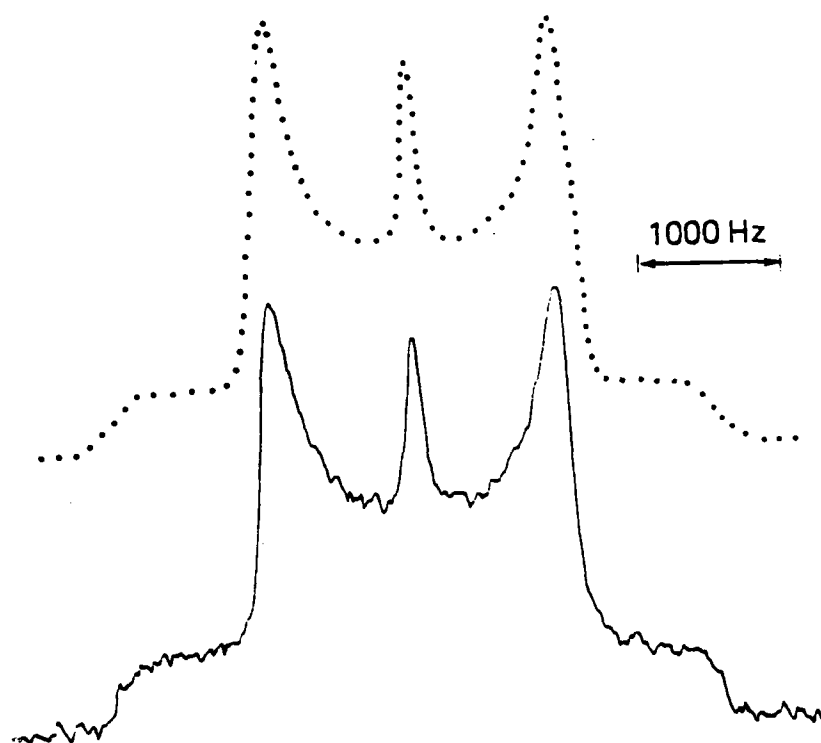
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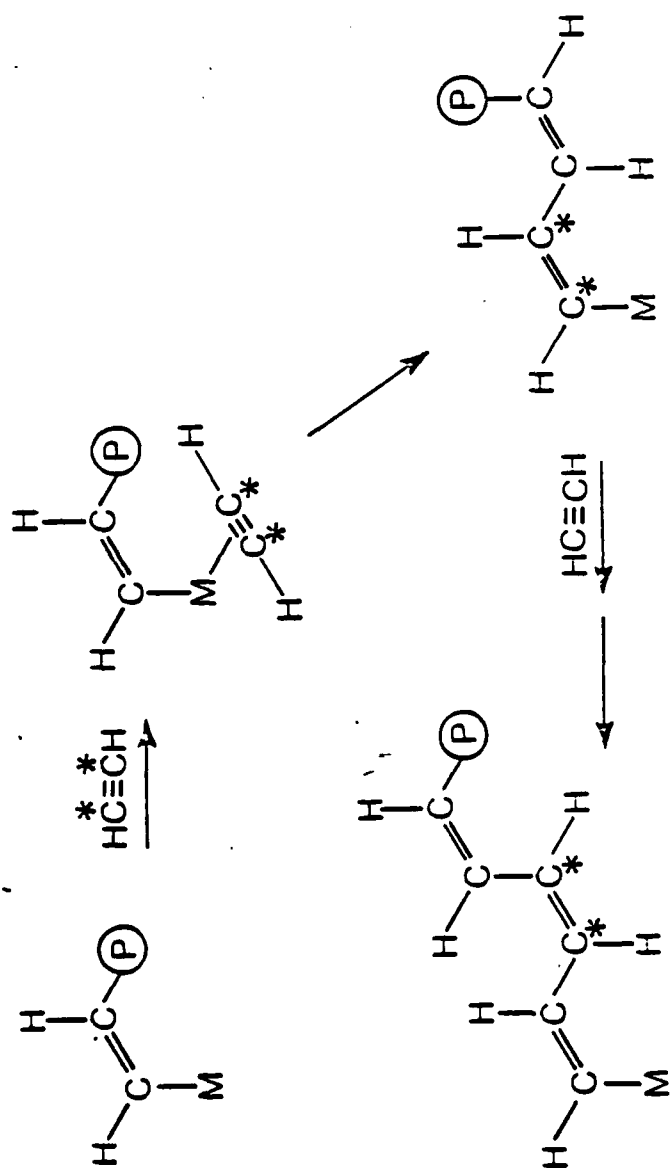
implications for the proposed soliton theories of defect formation and electronic transport in polyacetylene¹⁰ see Yannoni, C. S.; Clarke, T. C. *Phys. Rev. Lett.* submitted for publication.

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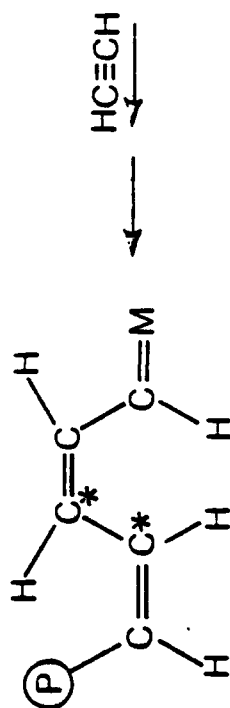
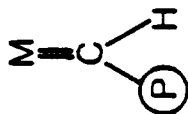
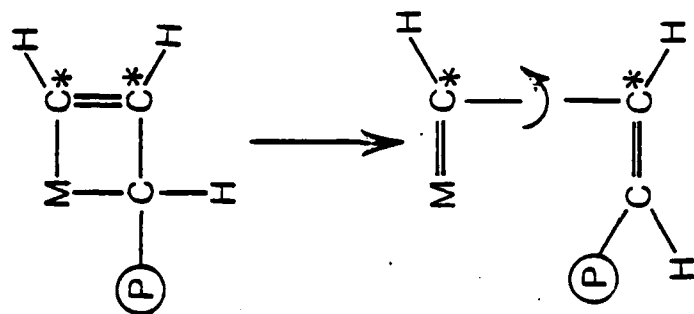
FIGURE CAPTIONS

Figure 1. Proton decoupled ^{13}C nutation NMR spectrum at 77K of doubly labelled cis-(CH)_x (solid line). Simulation of nutation spectrum of cis-(CH)_x using a $1.37\text{\AA}$ C-C bond length (dotted line). The peak in the middle is due to isolated ^{13}C nuclei.





1
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Scheme 2

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