

formed by rapid ( $10^{-11}$  s)  $S_1 \rightarrow S_0$  internal conversion.<sup>13</sup> These energized  $S_0^*$  molecules, which interconvert freely between trans and cis forms, dissociate fully in less than 2 ns through a process believed to involve a short-lived but real diazenyl intermediate.<sup>2d,10,14,15</sup> This view may be confirmed by a quantitative theoretical interpretation of the product state distribution or by further experimental studies of the methyl energetics and of related azoalkanes.

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**Registry No.** Azomethane, 503-28-6.

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## Mechanisms of Phenylacetylene Polymerization by Molybdenum and Titanium Initiators

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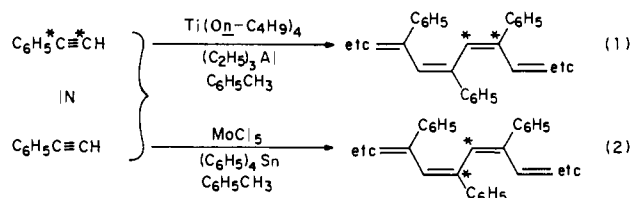
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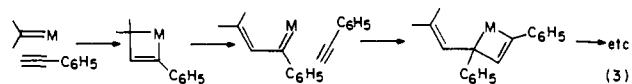
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We are reporting that while phenylacetylene, a few of whose molecules are doubly labeled by  $^{13}\text{C}$ 's on the triple bond, is polymerized by some catalysts including titanium tetrabutoxide plus triethylaluminum to give poly(phenylacetylene) in which the labels are separated by a double bond (eq 1), when the initiator is molybdenum pentachloride plus tetraphenyltin, the labels are separated by a single bond (eq 2). This tallies with the idea that



derivatives of molybdenum are effective initiators of both olefin metatheses<sup>1,2</sup> and acetylene polymerizations,<sup>3,4</sup> not by coincidence, but because the acetylene polymerizations they induce *are* olefin metatheses (eq 3).<sup>5,6</sup> In contrast, the titanium-initiated acetylene

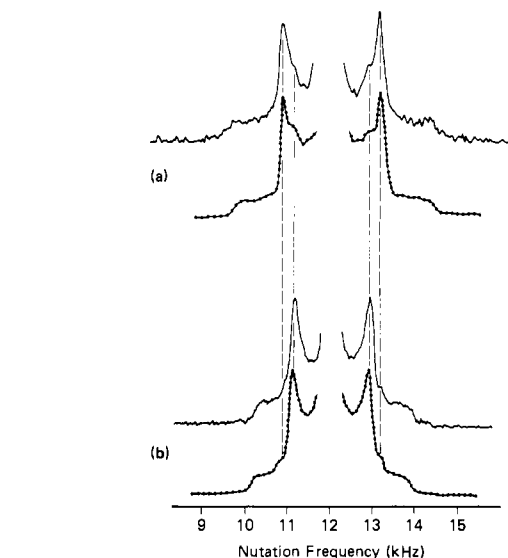


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**Figure 1.**  $^{13}\text{C}$  NMR nutation spectra of poly(phenylacetylene) at 77 K. (a) Sample prepared according to eq 1. The cross-polarization time was 0.5 ms and the recycle time 1 s. The number of scans was 144 000. (b) Sample prepared according to eq 2. The cross-polarization time was 1.0 ms and the recycle time 0.5 s. The number of scans was 115 200. The dotted curves are simulated spectra, calculated as described in the text. The center peaks, due to isolated  $^{13}\text{C}$  nuclei, have been cropped for clarity. The inner and outer pairs of dashed lines mark, respectively, the peaks of curves arising from  $^{13}\text{C}$ 's separated by single and double bonds.

polymerizations—both the one reported here and one reported earlier, in which titanium tetrabutoxide plus triethylaluminum polymerized unsubstituted acetylene<sup>7</sup>—seem to follow an insertion mechanism like that believed to apply to the titanium-catalyzed polymerization of ethylene.<sup>8</sup>

Whether the labeled carbons are separated in the polymers by single or by double bonds was analyzed by nutation NMR spectroscopy.<sup>7,9</sup> Thus the spectra displayed in Figure 1 exhibit Pake doublets, produced by the dipole-dipole interaction of adjacent  $^{13}\text{C}$  nuclei, that are coincidence, by 2196 Hz in a sample prepared with the titanium catalyst and by 1765 Hz in one prepared with the molybdenum catalyst. The best theoretical simulations, also displayed in the figure, correspond in the first sample to 91% of the carbons being separated by 1.36 Å and 9% by 1.48 Å. In the second sample (made with the molybdenum catalyst), the analysis is optimized if 88% of the carbons are separated by 1.48 Å and 12% by 1.36 Å. The only parameters in the theoretical simulations are the two bond lengths, the fraction of the bonds having these lengths, and a natural width (75 Hz) for lines assumed to be Lorentzian.<sup>9</sup> The accuracy of the nutation method and fitting procedure is demonstrated by the measured C-C length for acetic acid agreeing with X-ray diffraction measurements within 0.7%,<sup>9</sup> by the C=C length in phenylacetylene agreeing with microwave measurements within 1.8%,<sup>10</sup> and by the single- and double-bond lengths analyzed above agreeing with those (averaging  $1.47 \pm 0.01$  and  $1.35 \pm 0.01$  Å) determined for a variety of polyenes.<sup>11</sup>

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The nutation experiments were carried out as described previously.<sup>7,9</sup> The <sup>13</sup>C magnetization (at 15 MHz) was generated by an <sup>1</sup>H-<sup>13</sup>C cross-polarization sequence using a 40-kHz Hartmann-Hahn match,<sup>12</sup> and proton broadening was then removed during data acquisition by a strong (2.5 mT) 60-MHz decoupling field. The nutation excitation sequence was the same for both samples: an 8- $\mu$ s carbon transmitter pulse (3.6-mT rotating component), followed by a 9.9- $\mu$ s delay and a 7- $\mu$ s receiver window. The carbon carrier frequency was kept close to the center of the spectrum in the laboratory frame. The temperature of the samples was 77 K.

The phenylacetylene (93% <sup>13</sup>C<sub>0</sub>, 4% <sup>13</sup>C<sub>2</sub>)<sup>13</sup> was polymerized by combining it in toluene either at -20 °C for 3 h with MoCl<sub>5</sub> plus (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Sn (1/100 equiv of each, previously incubated for 10 min at room temperature)<sup>14,15</sup> or at 0 °C for 4.5 h with titanium tetrabutoxide and triethylaluminum (1/50 and 4/50 equiv, previously incubated for 20 min at room temperature).<sup>16</sup> The polymers were purified by repeatedly dissolving them in cold chloroform and precipitating them with methanol, and they were then dried at -35 °C for 12 h. The yields were 28% and 4%, respectively, and the <sup>1</sup>H NMR spectra were characteristic of 97% and 75% "cis" (E) materials.<sup>17,18</sup>

For the experiments to succeed with the catalysts containing molybdenum pentachloride, the poly(phenylacetylene) samples had to be prepared, purified, and maintained below 0 °C. When they were prepared at room temperature, the spectra exhibited prominent peaks characteristic of <sup>13</sup>C's separated both by single and by double bonds, implying that the positions of the double bonds, which remain fixed in the cold samples, move on warming.<sup>7b,17,19</sup> When WCl<sub>6</sub> was substituted for MoCl<sub>5</sub>,<sup>14</sup> it was impossible, even with samples prepared at -20 °C,<sup>20</sup> to distinguish whether eq 1 or 2 applied, for the intensities of the two kinds of peaks were similar.

When the Casey metal-carbene [pentacarbonyl(diphenylmethylene)tungsten]<sup>6a,21</sup> or the Fischer metal-carbyne [*trans*-bromotetracarbonyl(phenylmethylidyne)tungsten]<sup>18,22</sup> was used

as the initiator, the experiments did distinguish the alternatives, but the results were unexpected and are at present unexplained. The composition of the polymers was essentially the same as when the titanium-containing mixture was the initiator.<sup>23</sup>

However, that the titanium- and molybdenum-initiated reactions seemingly follow different paths agrees with the observation that compounds of titanium, unlike those of molybdenum, are only marginally effective in bringing about olefin metatheses.<sup>24</sup> It might also account for another distinction, in selectivity, that the literature seems to reveal: that titanium-containing initiators are more effective than those containing molybdenum in polymerizing unsubstituted acetylene,<sup>27</sup> whereas the reverse is true for substituted acetylenes.<sup>5b,28</sup>

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**Registry No.** MoCl<sub>5</sub>, 10241-05-1; Ti(O-*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, 5593-70-4; (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al, 97-93-8; (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Sn, 595-90-4; C<sub>6</sub>H<sub>5</sub>C≡CH, 536-74-3.

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(24) Titanium catalysts do not metathesize common olefins appreciably.<sup>1</sup> Titanium tetrachloride plus triethylaluminum (or related materials) metathesizes strained olefins,<sup>25</sup> and the Tebbe reagent exchanges isotopically labeled terminal methylenes.<sup>26</sup>

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(20) 47% yield after 2 h, 39% E. The greater structural inhomogeneity of samples of poly(phenylacetylene) prepared with WCl<sub>6</sub> rather than MoCl<sub>5</sub> has been analyzed by Percec.<sup>17a,e,18</sup>

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## Novel Photoinduced Carbon-Carbon Bond Formation in Purines<sup>1</sup>

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Recently much attention has been focused on C-alkylated purines.<sup>2-8</sup> The reported antitumor activity of these compounds and the limited synthetic methodology available to attain them prompted us to consider alternate synthetic approaches to this class of compounds. This paper reports on the successful development of a new synthetically useful method of carbon-carbon bond formation in purines through a photochemical S<sub>RN</sub>1 reaction

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