

# Low-Temperature Reactions of Copper(I) Triflate Complexes of *cis*- and *trans*-Cyclooctene and *cis*- and *trans*-Cycloheptene with Trimethyl Phosphite. Spectroscopic Evidence for Free *trans*-Cycloheptene

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The reactions of *cis*- and *trans*-cyclooctene and *cis*- and *trans*-cycloheptene complexes of copper(I) triflate (CuOTf) with trimethyl phosphite at  $-80\text{ }^\circ\text{C}$  were followed by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR. The *cis*-olefins are readily displaced at a 1:1 ratio of  $\text{P}(\text{OMe})_3$  to the complex. The complexes of the *trans*-olefins are unreactive at this concentration of ligand. At higher phosphite-to-complex ratios they yield intermediate olefin-CuOTf-P(OMe)<sub>3</sub> species. At ratios in excess of 4:1 the complex of *trans*-cyclooctene (*t*-C<sub>8</sub>H<sub>14</sub>·CuOTf) is converted to the free *trans*-olefin. Under identical conditions *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf liberates a species characterized by its  $^{13}\text{C}$  NMR spectrum and tentatively identified as *trans*-cycloheptene. Under the conditions of the experiment, this species is converted into *cis*-cycloheptene at  $-80\text{ }^\circ\text{C}$  over a period of several hours. *trans*-Cyclooctene is stable under these conditions. However, at temperatures above  $-45\text{ }^\circ\text{C}$  it is converted into *cis*-cyclooctene. A mechanism accounting for the formation and isomerization of the *trans*-cycloolefins is proposed.

The smallest *trans*-cycloalkene that has been isolated and characterized is *trans*-cyclooctene (*t*-C<sub>8</sub>H<sub>14</sub>).<sup>1</sup> Although there is indirect evidence for the existence of *trans*-cycloheptene (*t*-C<sub>7</sub>H<sub>12</sub>),<sup>2,3</sup> no spectroscopic data on this olefin appear to have been published so far, although it is presumably stable at  $-78\text{ }^\circ\text{C}$ .<sup>3</sup> It has been shown recently<sup>4</sup> that the copper(I) triflate complex of *trans*-cycloheptene (*t*-C<sub>7</sub>H<sub>12</sub>·CuOTf) can be prepared by UV irradiation of the corresponding complex of the *cis*-olefin (*c*-C<sub>7</sub>H<sub>12</sub>·CuOTf). We now report the results of our efforts to generate free *t*-C<sub>7</sub>H<sub>12</sub> from this complex by removing the copper ion in a ligand displacement reaction.

Early in our investigations a dynamic process was detected in *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf by  $^{13}\text{C}$  NMR and ascribed to a conformational automerization of the *trans*-cycloheptene ring.<sup>5</sup> Based on the  $^{13}\text{C}$  DNMR data for the complex and on semiempirical and molecular mechanics calculations for the free olefin it was concluded that in the *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf complex the *trans*-cycloheptene ring adopts an unsymmetrical chair conformation and undergoes a pseudorotation which is rapid on the  $^{13}\text{C}$  NMR time scale at room temperature. Furthermore, on the basis of similar studies of *t*-C<sub>8</sub>H<sub>14</sub>·CuOTf and *t*-C<sub>8</sub>H<sub>14</sub>, we proposed that the free *t*-C<sub>7</sub>H<sub>12</sub> will also adopt the unsymmetrical conformation of the *t*-C<sub>7</sub>H<sub>12</sub> ring found in the complex.

Since the Cu(I) ion is very strongly bound to this strained olefin and since it was necessary to work at a low temperature, finding a reagent suitable for the liberation of *t*-C<sub>7</sub>H<sub>12</sub> presented a considerable challenge. After screening a number of different reagents (Table I) it was observed that  $\text{P}(\text{OMe})_3$  decomposed *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf at  $-80\text{ }^\circ\text{C}$  and generated a transient species which subsequently yielded *cis*-cycloheptene. The  $^{13}\text{C}$  spectrum of the transient can be rationalized in terms of the unsymmetrical chair conformation for *t*-C<sub>7</sub>H<sub>12</sub> proposed previously.<sup>5</sup> In order to understand both the reaction that liberates the

Table I. Attempts To Decompose *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf at  $-80\text{ }^\circ\text{C}$ <sup>a</sup>

Unreactive Reagents			
PCl <sub>3</sub>	P(OPh) <sub>3</sub>	O <sub>2</sub>	Fe(ClO <sub>4</sub> ) <sub>3</sub> <sup>b</sup>
PF <sub>3</sub>	PClPh <sub>2</sub>	NaI <sup>b</sup>	( <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> N <sup>+</sup> ·SbCl <sub>6</sub> <sup>-</sup>
PPh <sub>3</sub>	CO	NaCN <sup>b</sup>	(NC) <sub>2</sub> C=C(CN) <sub>2</sub>
P( <i>n</i> -Bu) <sub>3</sub>	NH <sub>3</sub>	Ce(NH <sub>4</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> <sup>b</sup>	[(CH <sub>3</sub> ) <sub>2</sub> N] <sub>2</sub> C=C[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>
	(CH <sub>3</sub> ) <sub>3</sub> COLi	NH <sub>4</sub> SH <sup>b</sup>	
Reactive Reagents Generating <i>c</i> -C <sub>7</sub> H <sub>12</sub> or Other Products			
PCl(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	N(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub>	Zn(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	
Na <sup>+</sup> C <sub>10</sub> H <sub>5</sub> <sup>-</sup>	LiAlH <sub>4</sub>	CH <sub>3</sub> Li	
	(CH <sub>3</sub> ) <sub>3</sub> CLi		

<sup>a</sup> Solvent was diethyl ether or acetone unless stated otherwise.  
<sup>b</sup> Liquid NH<sub>3</sub> solvent.

free olefin and the reaction that causes its subsequent isomerization, the reactions of  $\text{P}(\text{OMe})_3$  with *c*-C<sub>8</sub>H<sub>14</sub>·CuOTf and *t*-C<sub>8</sub>H<sub>14</sub>·CuOTf were also investigated.

## Results

Since the complete separation of pure *trans* complexes from the irradiated *cis*-*trans* mixtures is laborious and involves considerable losses of material, mixtures of the *cis* and *trans* complexes of cycloheptene and cyclooctene were employed in the reactions with  $\text{P}(\text{OMe})_3$  unless stated otherwise. The reactions were performed inside precooled NMR tubes which were then transferred to the variable-temperature probe of the spectrometer.

**Cycloheptene Complexes.** Titration of a 1:2 mixture of *c*-C<sub>7</sub>H<sub>12</sub>·CuOTf and *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf (*c/t*-C<sub>7</sub>H<sub>12</sub>·CuOTf) in acetone-*d*<sub>6</sub> at  $-80\text{ }^\circ\text{C}$  with trimethyl phosphite results in the disappearance of the complexes as shown by  $^{13}\text{C}$  NMR (Figure 1). Spectrum 1A was taken before the addition of any phosphite ligand; *c*-C<sub>7</sub>H<sub>12</sub>·CuOTf displays a single olefinic resonance at 109 ppm, while *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf shows two  $^{13}\text{C}$  signals at 96.8 and 99.6 ppm due to the unsymmetrical chair conformation of the *trans*-cycloheptene ring in which the two unsaturated carbon atoms are inequivalent. The aliphatic region of the spectrum is largely obscured by the intense poorly resolved acetone peak. Upon addition of the first aliquot of  $\text{P}(\text{OMe})_3$  the signal from *c*-C<sub>7</sub>H<sub>12</sub>·CuOTf disappears and a broad new resonance appears at 128 ppm (Figure 1B). Upon subsequent additions of  $\text{P}(\text{OMe})_3$  this broad signal sharpens and moves downfield until it is at 131 ppm in Spectrum 1D, nearly the position of free *c*-C<sub>7</sub>H<sub>12</sub>. Control experiments

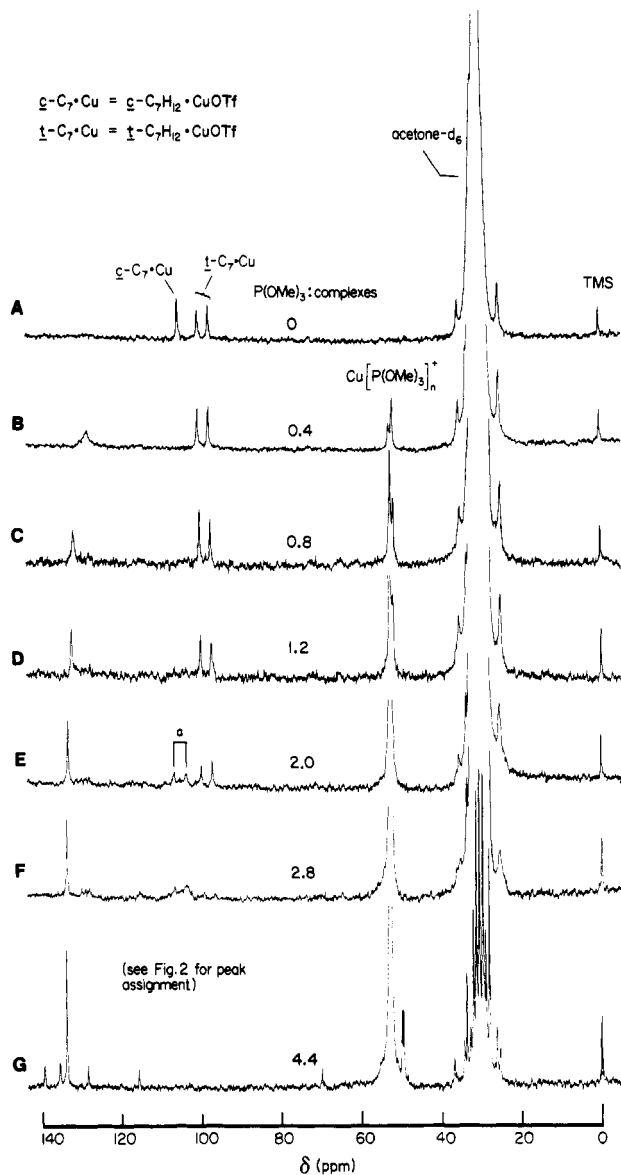
(1) Ziegler, K.; Wilms, H. *Ann.* 1950, 567, 1.

(2) Corey, E. J.; Carey, F. A.; Winter, R. A. E. *J. Am. Chem. Soc.* 1965, 87, 934.

(3) Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* 1981, 1031. Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* 1983, 983. Inoue, Y.; Ueoka, T.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* 1984, 2053.

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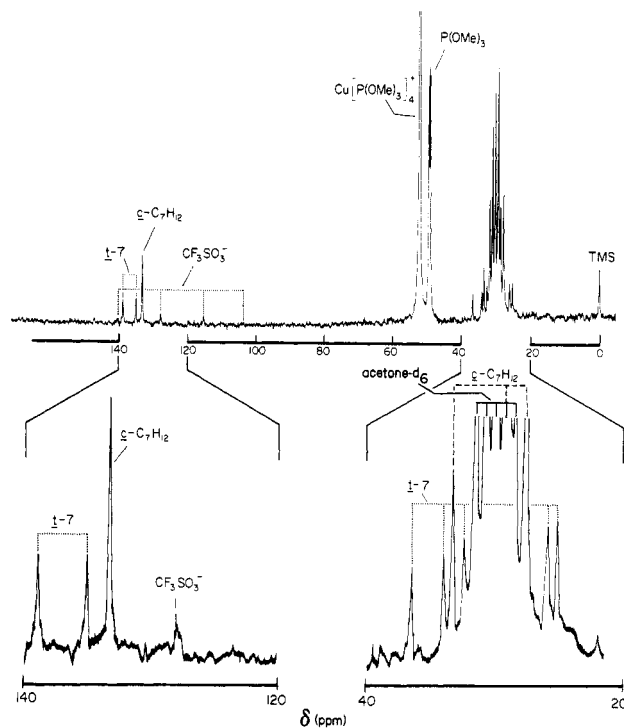
(5) Wallraff, G. M.; Boyd, R. H.; Michl, J. *J. Am. Chem. Soc.* 1983, 105, 4550.



**Figure 1.** Titration of a mixture of *c*-C<sub>7</sub>H<sub>12</sub>CuOTf and *t*-C<sub>7</sub>H<sub>12</sub>CuOTf (*c/t*-C<sub>7</sub>H<sub>12</sub>CuOTf) in acetone-*d*<sub>6</sub> with P(OMe)<sub>3</sub> at -80 °C monitored by <sup>13</sup>C NMR.

on solutions of pure *c*-C<sub>7</sub>H<sub>12</sub>CuOTf showed that this behavior is not affected by the presence of *t*-C<sub>7</sub>H<sub>12</sub>CuOTf. At higher ratios of phosphite to complex, the *t*-C<sub>7</sub>H<sub>12</sub>CuOTf begins to react and the signals of a new species, still containing two different olefinic carbon signals, appear at 103 and 106 ppm (labeled a in Figure 1E). At this point there are at least three species present in the cold solution: free *c*-C<sub>7</sub>H<sub>12</sub>, *t*-C<sub>7</sub>H<sub>12</sub>CuOTf, and the compound a containing *t*-C<sub>7</sub>H<sub>12</sub>CuOTf apparently coordinated to P(OMe)<sub>3</sub>. If the solution is warmed up at this point (not shown in Figure 1) the two doublets coalesce into two singlets.

Addition of more P(OMe)<sub>3</sub> (Spectrum 1F) results in the conversion of all of the *t*-C<sub>7</sub>H<sub>12</sub>CuOTf complex into the new species labeled a which now has a much broader line shape and a slightly different chemical shift from that found in spectrum 1E. Subsequent attempts at better characterization of this intermediate (not shown) showed that the broad resonance will broaden further and disappear into the base line upon addition of a little more P(OMe)<sub>3</sub>. At a P(OMe)<sub>3</sub>:complex mixture ratio in excess of 4:1 (Figure 1G) the broad peaks a present in Figure 1E,F disappear. Two sharp new peaks are then observed at 139.7 and 135.7 ppm downfield from the olefinic resonance of free *c*-C<sub>7</sub>H<sub>12</sub>. The species responsible for these downfield



**Figure 2.** <sup>13</sup>C NMR spectrum of *c/t*-C<sub>7</sub>H<sub>12</sub>CuOTf after addition of excess P(OMe)<sub>3</sub> at -80 °C.

peaks will be labeled *t*-7. The overall resolution of Spectrum 1G is much improved over that of the preceding spectra<sup>6</sup> and consequently a number of other peaks can be distinguished in the aliphatic region. Five of these belong to *t*-7. Figure 2 shows another spectrum of *c/t*-C<sub>7</sub>H<sub>12</sub>CuOTf (with a lower ratio of *c/t* complexes) in the presence of excess P(OMe)<sub>3</sub>, with all of the resonances labeled. In addition to the signals of *t*-7, those from acetone-*d*<sub>6</sub> and *c*-C<sub>7</sub>H<sub>12</sub>, the resonances for P(OMe)<sub>3</sub>, both free and complexed to copper, and the center two peaks of the CF<sub>3</sub> quartet of the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> (triflate) anion can be seen clearly. It should be noted (Figure 1) that the ratio of *t*-7 to *c*-C<sub>7</sub>H<sub>12</sub> is much smaller than the starting ratio of the *t*-C<sub>7</sub>H<sub>12</sub>CuOTf to the *c*-C<sub>7</sub>H<sub>12</sub>CuOTf originally present.

The single species responsible for the seven signals labeled *t*-7 in Figure 2 converts into *c*-C<sub>7</sub>H<sub>12</sub> over a period of several hours at -80 °C and much more rapidly at higher temperatures. It can be rapidly transformed into *c*-C<sub>7</sub>H<sub>12</sub> already at -80 °C by addition of additional Cu(I) in the form of C<sub>6</sub>H<sub>6</sub>(CuOTf)<sub>2</sub>. The decay of *t*-7 is relatively independent of the concentration of P(OMe)<sub>3</sub>, but attempts to measure the decay rate quantitatively as a function of P(OMe)<sub>3</sub> concentration were inconclusive since it was too fast on the time scale needed for FT-NMR measurements. It was also observed that cooling the sample down to the solvent freezing point (-94 °C) made no apparent difference in the ratio of *c*-C<sub>7</sub>H<sub>12</sub> to *t*-7 initially observed in the reaction with excess P(OMe)<sub>3</sub>. The <sup>13</sup>C chemical shift values and <sup>1</sup>H-<sup>13</sup>C coupling constants (olefinic carbons) for *t*-7 and *c*-C<sub>7</sub>H<sub>12</sub> are listed in Table II along with the corresponding values for the CuOTf complexes. The <sup>13</sup>C NMR signals of *t*-7 were also generated in methylene chloride and methanol solvents, albeit in much lower yield.

Several methods for isolating *t*-7 were attempted, none of which were successful. In all cases, *c*-C<sub>7</sub>H<sub>12</sub> was obtained instead. These were (i) filtration at -78 °C, with diethyl

(6) High concentrations of P(OMe)<sub>3</sub> result in the reduction of trace amounts of paramagnetic Cu(II) present in the solution and consequently produce better spectral resolution.

Table II. NMR Parameters for Free and Copper-Complexed Cycloheptenes and Cyclooctenes

compd	$^{13}\text{C}$ NMR <sup>a</sup>		$^{13}\text{C}$ - $^1\text{H}$ olefinic coupling constant, Hz
	olefinic	aliphatic	
<i>cis</i> -cycloheptene <sup>b</sup>	133.0	27.8, 29.8, 33.0	155
<i>c</i> - $\text{C}_7\text{H}_{12}$ ·CuOTf <sup>c</sup>	109.0	30.0, 31.4, 32.4	154
<i>trans</i> -cycloheptene <sup>d,e</sup>	139.7, 135.7	25.4, 26.2, 32.7, 34.3, 36.9	158 <sup>f</sup>
<i>t</i> - $\text{C}_7\text{H}_{12}$ ·CuOTf <sup>e,c</sup>	96.8, 99.6	23.6, 34.0, 24.4, 30.8, 31.2	150
<i>cis</i> -cyclooctene <sup>b</sup>	131.0	25.5, 26.2, 29.2	155
<i>c</i> - $\text{C}_8\text{H}_{14}$ ·CuOTf <sup>c</sup>	106.4	26.8, 27.2, 30.4	156
<i>trans</i> -cyclooctene <sup>b,g</sup>	134.8	35.7, 29.2	152
<i>t</i> - $\text{C}_8\text{H}_{14}$ ·CuOTf <sup>c</sup>	106.0	28.2, 35.2, 35.8	154

<sup>a</sup>In ppm, downfield from  $\text{Me}_4\text{Si}$ . <sup>b</sup>Acetone- $d_6$  solvent. <sup>c</sup>Diethyl ether solvent. <sup>d</sup>-80 °C. <sup>e</sup>-85 °C. <sup>f</sup>Only the coupling constant for the 139.7 ppm peak was measured at -80 °C. The other doublet was partially obscured by the resonance from *cis*-cycloheptene. <sup>g</sup>Two of the aliphatic resonances are accidentally equivalent under these conditions.

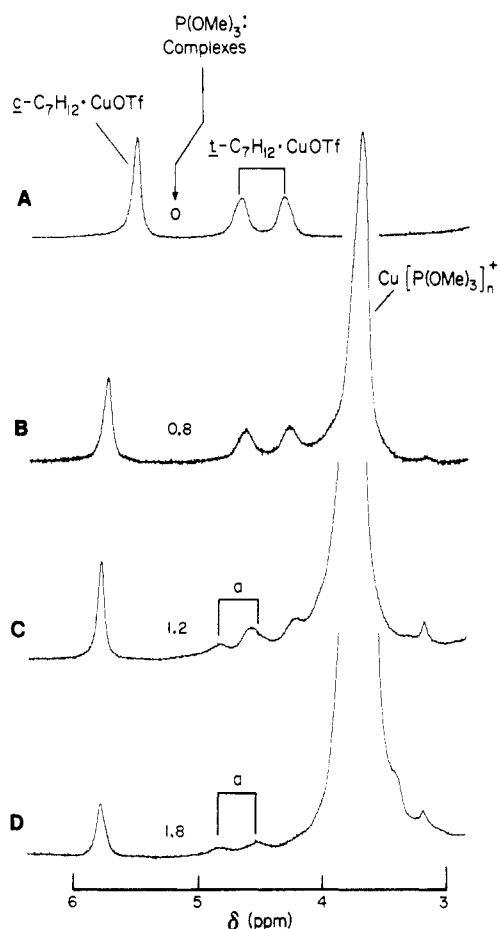


Figure 3. Titration of *c/t*- $\text{C}_7\text{H}_{12}$ ·CuOTf in acetone- $d_6$  with  $\text{P}(\text{OMe})_3$  at -80 °C monitored by  $^1\text{H}$  NMR.

ether as solvent ( $\text{Cu}[\text{P}(\text{OMe})_3]_4^+\text{OTf}^-$  is not soluble in this solvent), (ii) bulb-to-bulb distillation of the reaction mixture at  $10^{-5}$  torr with tri-*n*-butyl phosphite substituted for  $\text{P}(\text{OMe})_3$  and the entire apparatus cooled to -45 °C, and (iii) chromatography on neutral alumina at -90 °C with liquid propane as the eluent.<sup>7</sup>

Figure 3 shows a set of  $^1\text{H}$  NMR spectra obtained in a similar series of titrations. The poorly resolved resonances of the olefinic proton signals in Figure 3A are due to traces of the paramagnetic Cu(II) ion. The first addition of  $\text{P}(\text{OMe})_3$  shifts the vinylic proton resonances of *c*- $\text{C}_7\text{H}_{12}$ ·CuOTf from 5.6 ppm downfield to the position expected for free *c*- $\text{C}_7\text{H}_{12}$ , while the positions of the *t*-

(7) Attempts to trap *t-7* in situ using acidified methanol or 1,5-diphenylisobenzofuran were not successful. In the former case this is presumably due to the fact that the rate of isomerization is faster than the rate of the trapping reaction. In the latter case the enophile rapidly reacts with the copper complexes present in solution.

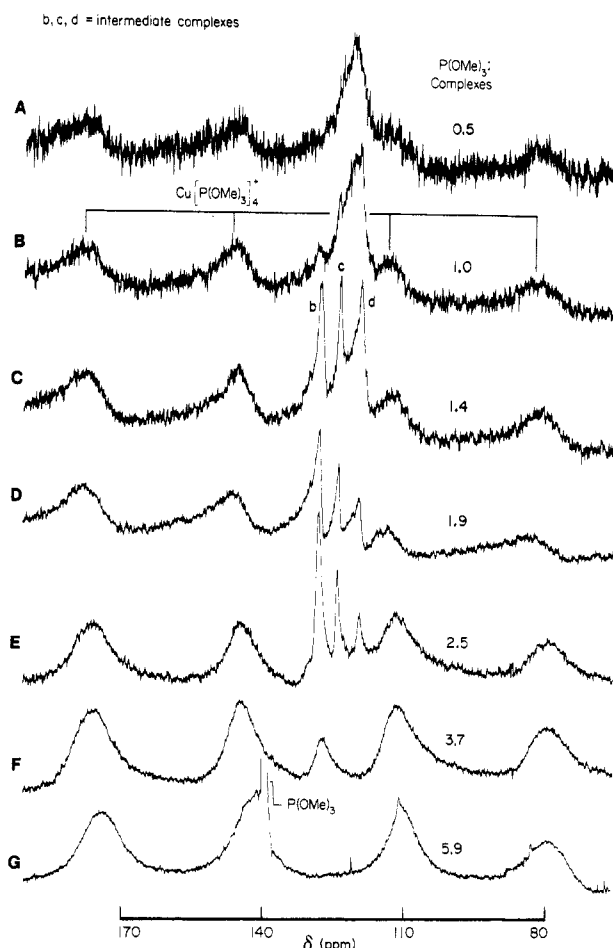
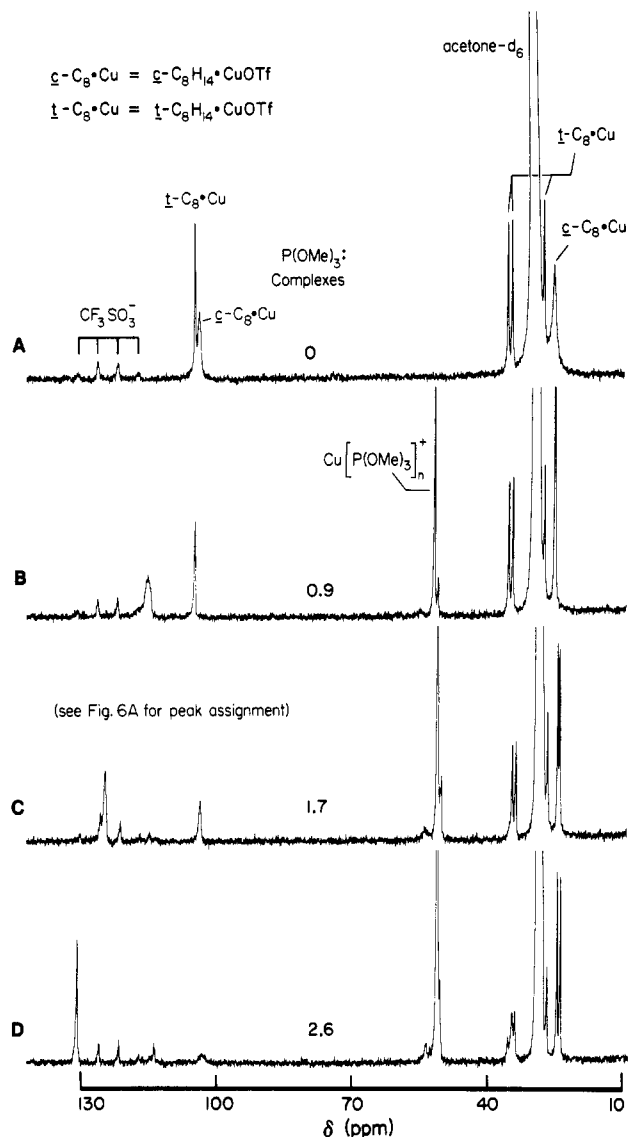


Figure 4. Titration of *c/t*- $\text{C}_7\text{H}_{12}$ ·CuOTf in acetone- $d_6$  with  $\text{P}(\text{OMe})_3$  at -80 °C monitored by  $^{31}\text{P}$  NMR.

$\text{C}_7\text{H}_{12}$ ·CuOTf peaks remain unchanged at 4.6 and 4.3 ppm. Addition of the next aliquot of  $\text{P}(\text{OMe})_3$  results in the formation of a new species with resonances at 4.8 and 4.5 ppm downfield from that of *t*- $\text{C}_7\text{H}_{12}$ ·CuOTf (Figure 3C). At a  $\text{P}(\text{OMe})_3$  to complex *t-7* mixture ratio of 1.8:1 (Figure 3D) only the peaks of a single species containing *t*- $\text{C}_7\text{H}_{12}$  present in low concentrations can be detected. Subsequent experiments failed to identify any signals other than those mentioned above. No signals which could be unambiguously ascribed to *t-7* could be observed at higher  $\text{P}(\text{OMe})_3$ :complex mixture ratios. This was presumably due to the low concentration of *t-7* and the expected similarity of the chemical shift of the olefinic protons of *t*- $\text{C}_7\text{H}_{12}$  to those of *c*- $\text{C}_7\text{H}_{12}$ .

Figure 4 shows the titration of the *c/t*- $\text{C}_7\text{H}_{12}$ ·CuOTf mixture monitored by  $^{31}\text{P}$  NMR. Addition of the first aliquot of  $\text{P}(\text{OMe})_3$  gave a broad signal upfield from that of free phosphite (141 ppm) as well as generating a broad



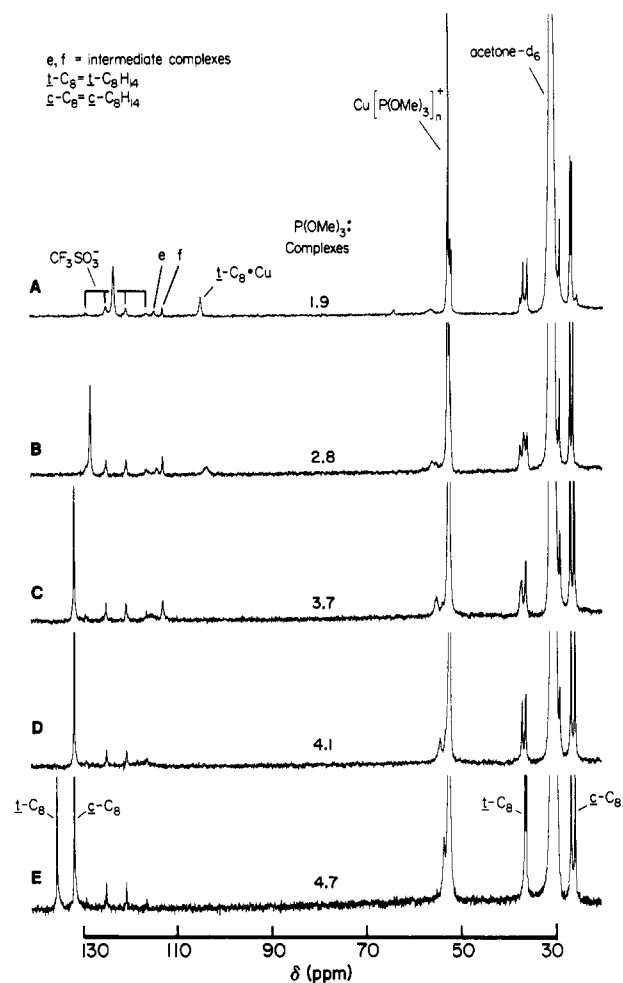
**Figure 5.** Titration of a mixture of  $c\text{-C}_8\text{H}_{14}\text{CuOTf}$  and  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$  ( $c/t\text{-C}_8\text{H}_{14}\text{CuOTf}$ ) in acetone- $d_6$  monitored by  $^{13}\text{C}$  NMR at  $-80^\circ\text{C}$ . Low concentrations of  $\text{P}(\text{OMe})_3$ .

quartet due to  $\text{Cu}[\text{P}(\text{OMe})_3]_4^+$ . By the time the ratio of  $\text{P}(\text{OMe})_3$  to the complexes is 1.4:1 (Figure 4C) the broad signal seen in Figure 4A has been replaced by three sharper signals (b-d). Throughout the rest of the titration the relative intensities of the three sharp signals change, until in the presence of a high ratio of  $\text{P}(\text{OMe})_3$  to the complexes the only signals present are the quartet and a sharp signal whose chemical shift is the same as that of a  $\text{P}(\text{OMe})_3$  standard (Figure 4G).

In addition to monitoring these titration reactions by  $^{13}\text{C}$ ,  $^1\text{H}$ , and  $^{31}\text{P}$  NMR an attempt to probe this reaction with  $^{63}\text{Cu}$  NMR was made. This was unsuccessful due to the very broad resonances of the unsymmetrically substituted copper species.<sup>8</sup>

**Cyclooctene Complexes.** A mixture of  $c\text{-C}_8\text{H}_{14}\text{CuOTf}$  and  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$  was titrated in a fashion identical with that described above.

Figures 5 and 6 show the  $^{13}\text{C}$  spectra for two titration experiments, done at low and high  $\text{P}(\text{OMe})_3$  to complex mixture ratios, respectively. Spectrum 5A shows the  $c/t$  mixture in the absence of  $\text{P}(\text{OMe})_3$ . Note the broad signals from  $c\text{-C}_8\text{H}_{14}\text{CuOTf}$  in the olefinic and aliphatic regions



**Figure 6.** Titration of  $c/t\text{-C}_8\text{H}_{14}\text{CuOTf}$  in acetone- $d_6$  monitored by  $^{13}\text{C}$  NMR at  $-80^\circ\text{C}$ . High concentrations of  $\text{P}(\text{OMe})_3$ .

as well as the sharp peaks from the  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$ . It is already known<sup>5</sup> that  $c\text{-C}_8\text{H}_{14}\text{CuOTf}$  undergoes a dynamic process observable by  $^{13}\text{C}$  NMR while  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$  does not.

Addition of the first aliquot of  $\text{P}(\text{OMe})_3$  shifted the olefinic signal of  $c\text{-C}_8\text{H}_{14}\text{CuOTf}$  downfield to 110 ppm (Figure 5B). Spectrum 5C shows this signal sharpening and moving further downfield to 126 ppm; at the same time the peak from  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$  begins to broaden. Note also that in the aliphatic region the  $c\text{-C}_8\text{H}_{14}\text{CuOTf}$  resonances have split while the  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$  peaks remained unchanged. Addition of more  $\text{P}(\text{OMe})_3$  causes the olefinic signal from  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$  to broaden further with the appearance of new signals downfield (at 120 and 122 ppm) and in the aliphatic region (Figure 5D).

Spectrum 6A (Figure 6) is of a different sample with a slightly lower concentration of  $\text{P}(\text{OMe})_3$  than in Figure 5C. It shows the olefinic signals of  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$  and resonances from two additional species (the same two signals as in Figure 5C,D) containing the  $t\text{-C}_8\text{H}_{14}$  ligand (e,f). Both Spectra 6A and 6B show changes in the aliphatic region as well, with two new lines appearing near the peaks of  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$ . Throughout the remainder of the titration the changes are obvious with the two new olefinic signals, e,f broadening until they either coalesce or independently disappear into the base line in Spectrum 6D. In the final Spectrum 6E the signal of free  $t\text{-C}_8\text{H}_{14}$  has appeared. In the aliphatic region the changes in the peaks of  $c\text{-C}_8\text{H}_{14}\text{CuOTf}$  parallel the changes in the position of the olefinic peak of  $c\text{-C}_8\text{H}_{14}\text{CuOTf}$ . The  $t\text{-C}_8\text{H}_{14}\text{CuOTf}$  peaks are converted into signals from a single species in Spectrum

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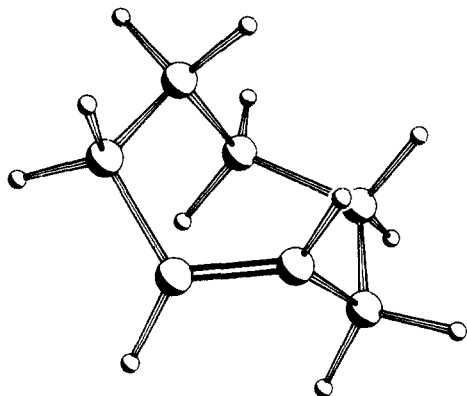


Figure 7. Calculated<sup>5</sup> equilibrium geometry of *trans*-cycloheptene.

6D and then change into the different signals of free *t*-C<sub>8</sub>H<sub>14</sub> in Spectrum 6E.

In the case of the cyclooctene complexes the *cis*-*trans* ratio of the liberated free olefins is identical with the *cis*-*trans* ratio of the original complexes. This was not true for the cycloheptene complexes where the relative concentration of *t*-7 is much smaller than that of the original *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf. Moreover, it is observed that *t*-C<sub>8</sub>H<sub>14</sub>, unlike *t*-7, is stable at -80 °C in the reaction mixture. However, when the temperature of the reaction mixture is raised to -45 °C, *t*-C<sub>8</sub>H<sub>14</sub> slowly isomerizes to *c*-C<sub>8</sub>H<sub>14</sub>. The addition of excess Cu(I) results in the rapid isomerization of the *trans*-olefin while excess P(OMe)<sub>3</sub> has little effect. These results are identical with those observed for *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf.

Experiments with authentic pure *t*-C<sub>8</sub>H<sub>14</sub><sup>9</sup> showed that it is stable in the presence of P(OMe)<sub>3</sub> as long as Cu(I) is absent. If Cu(I) is added to the mixture of *t*-C<sub>8</sub>H<sub>14</sub> and P(OMe)<sub>3</sub> at room temperature, *t*-C<sub>8</sub>H<sub>14</sub> is rapidly and quantitatively converted into *c*-C<sub>8</sub>H<sub>14</sub>.

The <sup>13</sup>C chemical shifts and the <sup>1</sup>H-<sup>13</sup>C coupling constants of *cis*- and *trans*-cyclooctene and their CuOTf complexes are also listed in Table II.

The <sup>31</sup>P NMR experiments were repeated with *c/t*-C<sub>8</sub>H<sub>14</sub>·CuOTf. The result of this titration was essentially identical with that observed for *c/t*-C<sub>7</sub>H<sub>12</sub>·CuOTf with one notable exception. Only two sharp signals are observed in addition to the quartet; the signal corresponding to the signal b was absent.

## Discussion

**Evidence for the Formation of Free *trans*-Cycloheptene (*t*-C<sub>7</sub>H<sub>12</sub>).** The identification of the short-lived species *t*-7 as *trans*-cycloheptene is based on the following:

(i) *t*-7 is generated in the reaction of P(OMe)<sub>3</sub> with *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf but not in the analogous reaction with *c*-C<sub>7</sub>H<sub>12</sub>·CuOTf.

(ii) *t*-7 converts into *c*-C<sub>7</sub>H<sub>12</sub> (slowly at -80 °C or more rapidly at higher temperatures). *c*-C<sub>7</sub>H<sub>12</sub> is the only product derived from the copper coordinated cycloheptene moieties.

(iii) The seven <sup>13</sup>C resonances observed for *t*-7 (Figure 2) are consistent with the unsymmetrical chair conformation (Figure 7) proposed for *t*-C<sub>7</sub>H<sub>12</sub> based on the results of our previous NMR study of *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf.<sup>5</sup> The only significant difference between the spectra of *t*-7 and *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf is in the chemical shifts of their olefinic carbon atoms. This "coordination shift" is similar to that

observed for other cycloalkenes and their CuOTf complexes (Table II).

(iv) Two of the <sup>13</sup>C resonances in *t*-7 are downfield from the olefinic carbon peak of *cis*-cycloheptene. The olefinic carbons of *trans*-cyclooctene are downfield from this *cis*-cyclooctene resonances.

(v) The *t*-7 <sup>13</sup>C resonances at 139.7 and 135.7 ppm each show coupling to only a single hydrogen with a <sup>13</sup>C-H coupling constant consistent with sp<sup>2</sup> hybridization.<sup>10</sup>

(vi) The <sup>13</sup>C chemical shift data (Table II) and the absence of resonances from copper-phosphite complexes other than Cu[P(OMe)<sub>3</sub>]<sub>4</sub><sup>+</sup> in the <sup>31</sup>P NMR (Figure 4G) argue against the identification of *t*-7 as a Cu<sup>+</sup>-olefin-P(OMe)<sub>3</sub> intermediate.

(vii) The reaction of *t*-7 with excess copper(I) in the presence of Cu[P(OMe)<sub>3</sub>]<sub>n</sub><sup>+</sup> and P(OMe)<sub>3</sub> results in the conversion of *t*-7 to *c*-C<sub>7</sub>H<sub>12</sub> and not the conversion of *t*-7 back into the original *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf complex. The latter would be expected if *t*-7 were a *t*-C<sub>7</sub>H<sub>12</sub>·Cu[P(OMe)<sub>3</sub>]<sub>n</sub> complex. This isomerization is discussed in detail later.

(viii) The <sup>13</sup>C NMR data for the reaction between *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf and varying concentrations of P(OMe)<sub>3</sub> are very similar to that obtained in the analogous reaction for *t*-C<sub>8</sub>H<sub>14</sub>·CuOTf in which *trans*-cyclooctene is produced. In the titrations of the *c/t* complex mixtures shown in Figures 1, 5, and 6, first the *cis*-olefin complexes react, followed by the appearance of new complexes due to reaction with the *trans*-olefin. As the concentration of P(OMe)<sub>3</sub> increases the <sup>13</sup>C resonances of these intermediate complexes broaden until they disappear into the base line. Finally it is observed that *t*-7 appears at the same P(OMe)<sub>3</sub>:complexes ratio that the signals for *trans*-cyclooctene also appear.

(ix) The short lifetime of *t*-7 in the presence of Cu(I) and P(OMe)<sub>3</sub> is in accord with the behavior of *t*-C<sub>8</sub>H<sub>14</sub> under similar conditions. *t*-7 has a lifetime of several hours at -80 °C. While *t*-C<sub>8</sub>H<sub>14</sub> is unreactive at this temperature, it too isomerizes into the *cis*-olefin at temperatures above -45 °C. This isomerization of the less strained *t*-C<sub>8</sub>H<sub>14</sub> argues that the instability of *t*-7 is due to the reaction conditions used in its generation. Pure *trans*-cycloheptene may well have the far higher thermal stability suggested by the results of other studies.<sup>3</sup>

Based on the above considerations we feel justified in suggesting that *t*-7 most likely is the long sought *trans*-cycloheptene.

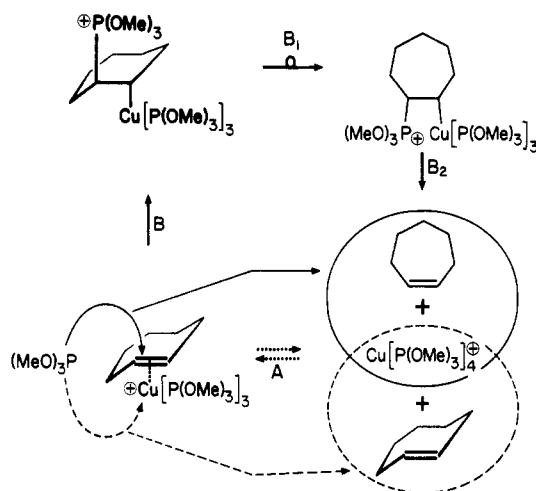
**Formation and Isomerization of *trans*-Cycloheptene.** It is proposed that a copper-phosphite-olefin complex (*t*-C<sub>7</sub>H<sub>12</sub>·Cu[P(OMe)<sub>3</sub>]<sub>3</sub><sup>+</sup>) is the precursor for both the *t*-C<sub>7</sub>H<sub>12</sub> and *c*-C<sub>7</sub>H<sub>12</sub> formed in the reaction between *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf and P(OMe)<sub>3</sub>, as shown in Scheme I. The site of attack by a fourth molecule of P(OMe)<sub>3</sub> on this complex determines which of the two isomeric olefins is obtained, path A giving *t*-C<sub>7</sub>H<sub>12</sub> and path B resulting in the formation of *c*-C<sub>7</sub>H<sub>12</sub>. A similar mechanism is proposed for the reaction of *t*-C<sub>8</sub>H<sub>14</sub>·CuOTf with trimethyl phosphite. A discussion of the details of the mechanism proposed in Scheme I follows.

**Path A.** (i) Intermediate *trans*-olefin·Cu[P(OMe)<sub>3</sub>]<sub>n</sub> complexes are observed by <sup>31</sup>C, <sup>1</sup>H, and <sup>31</sup>P NMR. Figures 1, 5, and 6 show new olefinic resonances at P(OMe)<sub>3</sub> to complex ratios of 2:1 for the *t*-C<sub>7</sub>H<sub>12</sub> and *t*-C<sub>8</sub>H<sub>14</sub> complexes. At this concentration of P(OMe)<sub>3</sub> a single new species a is observed for the former while two new species

(9) Vedejs, E.; Snoble, K. A. J.; Fuchs, P. L. *J. Org. Chem.* 1973, 38, 1178.

(10) The size of this coupling constant is of interest in view of predicted changes in the hybridization of the olefinic carbons due to twisting about the double bond (Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* 1972, 94, 5734).

**Scheme I. The Proposed Mechanism for the Formation of *cis*- (Path B) and *trans*-Cycloheptene (Path A) from  $t\text{-C}_7\text{H}_{12}\cdot\text{Cu}[\text{P}(\text{OMe})_3]_3^{\oplus a}$**



<sup>a</sup> The long unlabeled arrows point out the relationship to the final products. The reverse of step A need not be a single step process.

(e,f) were detected for  $t\text{-C}_8\text{H}_{14}\cdot\text{CuOTf}$ .<sup>11</sup> In the case of  $t\text{-C}_7\text{H}_{12}\cdot\text{CuOTf}$  the species a has also been detected by <sup>1</sup>H NMR (Figure 3). Furthermore <sup>31</sup>P NMR shows the presence of sharp singlets in addition to the quartet from the tetrahedral  $\text{Cu}[\text{P}(\text{OMe})_3]_4^{\oplus}$  (Figure 4). In this case the absence of <sup>31</sup>P–Cu coupling, the changes in peak intensity with increasing concentration of  $\text{P}(\text{OMe})_3$  and the similarity in chemical shift to the analogous  $\text{Ag}[\text{P}(\text{OMe})_3]_n$ <sup>12</sup> complexes suggest that the resonances labeled b–d) in Figure 4 are intermediate  $\text{Cu}[\text{P}(\text{OMe})_3]_n$ -olefin complexes. Based on similar experiments with  $t\text{-C}_8\text{H}_{14}\cdot\text{CuOTf}$  and  $\text{C}_6\text{H}_6(\text{CuOTf})_2$  it was observed that the <sup>31</sup>P chemical shift of these intermediate resonances does not depend on the coordinated hydrocarbon. Thus it was not possible to correlate the <sup>31</sup>P to the <sup>1</sup>H and <sup>13</sup>C NMR data in order to satisfactorily establish the structures of these intermediate complexes.

Another factor complicating the interpretation of the <sup>13</sup>C and <sup>31</sup>P NMR data is the presence of line broadening, apparently due to olefin and/or  $\text{P}(\text{OMe})_3$  exchange processes, observed for both the *cis*- and *trans*-olefin complexes. This exchange is readily seen in the spectra of the weakly bound *cis*-olefin complexes at low concentrations of  $\text{P}(\text{OMe})_3$  in which only a single olefinic resonance is observed (Figures 1 and 5). This is in marked contrast to the situation for the *trans*-olefin complexes where intermediate complexes can be observed which do not begin to undergo similar, albeit slower, exchange until the  $\text{P}(\text{OMe})_3$  to complexes ratio exceeds 3:1 (Figure 1, 5, and 6). At this point in the titration the <sup>13</sup>C resonances have broadened into the base line for both the  $t\text{-C}_7\text{H}_{12}$  and  $t\text{-C}_8\text{H}_{14}$  complexes and based on the concentration of  $\text{P}(\text{OMe})_3$  the predominant olefin complex in solution should be *trans*-olefin- $\text{Cu}[\text{P}(\text{OMe})_3]_3$  as shown in Scheme I.

(ii) No *trans*-olefins are observed until the concentration of  $\text{P}(\text{OMe})_3$  is high. This argues in favor of a highly ligated complex as being the immediate precursor of  $t\text{-C}_7\text{H}_{12}$  and  $t\text{-C}_8\text{H}_{14}$ . That all of the other coordination sites on copper

are filled before the coordinated olefin is displaced is reasonable for a complex in which the *trans*-olefin is so strongly bound.

(iii) At a high  $\text{P}(\text{OMe})_3$  to complexes ratio, just before the point at which *trans*-cycloheptene is detected, the only <sup>31</sup>P resonance present in addition to the quartet due to  $\text{Cu}[\text{P}(\text{OMe})_3]_4^{\oplus}$  is that of the intermediate b as seen in Figure 4F. The downfield position of this peak is consistent with its designation as the most ligated of the intermediate complexes and this agrees with similar observations for  $\text{Ag}^+$ -phosphite complexes.<sup>12</sup>

(iv) The reversibility of step A accounts for the eventual disappearance of all of the *trans*-olefins, via the reformation of the *trans*-olefin- $\text{Cu}[\text{P}(\text{OMe})_3]_3^{\oplus}$  complex from the free olefin and  $\text{Cu}[\text{P}(\text{OMe})_3]_4^{\oplus}$ . This equilibrium could involve either a dissociative or an associative mechanism. It is not possible to distinguish between these two possibilities from the data at hand. This exchange process involving coordinated and free olefin is slow on the <sup>13</sup>C NMR time scale as evidenced by the sharp peaks of  $t\text{-C}_7\text{H}_{12}$ . This is consistent with reports of slow exchange of  $\text{P}(\text{OMe})_3$  with  $\text{Cu}[\text{P}(\text{OMe})_3]_4^{\oplus}$  on <sup>31</sup>P NMR time scale, given that  $\text{P}(\text{OMe})_3$  and the *trans*-olefin appear to have comparable affinities for Cu(I).

**Path B.** (i) Isomerization requires the presence of both Cu(I) and  $\text{P}(\text{OMe})_3$ . This argues strongly in favor of a mechanism involving nucleophilic attack on the coordinated olefin. Reactions of nucleophiles with coordinated olefins are well documented.<sup>13</sup>

(ii) The production of  $c\text{-C}_7\text{H}_{12}$  in excess of that coming from the decomposition of  $c\text{-C}_7\text{H}_{12}\cdot\text{CuOTf}$  does not occur until the concentration of  $\text{P}(\text{OMe})_3$  is high (Figure 1G). Both  $t\text{-C}_7\text{H}_{12}$  and the excess  $c\text{-C}_7\text{H}_{12}$  appear at the same point in the titration, suggesting that they come from the same intermediate.

(iii) The mechanism is consistent with the observed reactions of additional Cu(I) and  $\text{P}(\text{OMe})_3$  with the complexes. The increased rate of isomerization observed for  $t\text{-C}_7\text{H}_{12}$  and  $t\text{-C}_8\text{H}_{14}$  upon addition of Cu(I) in the presence of uncomplexed  $\text{P}(\text{OMe})_3$  should result from a shift in the equilibrium between free and complexed *trans*-olefin to favor the complexed olefins including *trans*-olefin- $\text{Cu}[\text{P}(\text{OMe})_3]_3^{\oplus}$ . This in turn can react with the free  $\text{P}(\text{OMe})_3$  still present to form the *cis* olefins.

Excess  $\text{P}(\text{OMe})_3$  appears to have little effect on the amount of  $t\text{-C}_7\text{H}_{12}$  originally produced in the reaction or on its lifetime in solution. This is consistent with steps A and B both being first order in  $\text{P}(\text{OMe})_3$ .

(iv) Phosphonium ions similar to that shown in Scheme I have been reported for the nucleophilic attack on other metal coordinated hydrocarbons.<sup>14</sup> Depending on the particular system either the phosphonium ion or a phosphonate adduct is isolated. To our knowledge there are no reports of similar adducts of copper-olefin complexes. In the proposed mechanism this intermediate ion is unstable with respect to rearrangement (Step B<sub>1</sub>, Scheme 1) followed by elimination of  $\text{Cu}[\text{P}(\text{OMe})_3]_4^{\oplus}$  to form the *cis*-olefin.

(v) The apparent activation of the *trans*-olefins by the coordination of three  $\text{P}(\text{OMe})_3$  ligands to copper ion is consistent with the results of calculations for nucleophilic attack on other metal-olefin complexes.<sup>13a</sup> These studies indicate that while d<sup>10</sup> metals such as nickel are generally

(11) Since both species appear at the same point in the titration it may be that they represent geometric isomers with the formula  $t\text{-C}_8\text{H}_{14}\cdot\text{Cu}[\text{P}(\text{OMe})_3]_2$ . One isomer would have the double bond in the P–Cu–P plane while in the other complex the double bond would be perpendicular to this plane.

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poor at activating olefins toward nucleophilic attack the reactivity of these complexes should increase if the metal is also complexed to  $\pi$  acceptor ligands such as carbon monoxide. Since  $\text{P}(\text{OMe})_3$  is also a  $\pi$  acceptor in addition to being a  $\sigma$  donor, it should have a similar effect, particularly in view of the fact that the  $\pi$  back-bonding of the phosphites should increase at the expense of  $\sigma$  donation as the number of coordinated ligands increases.<sup>15</sup>

(vi) The attack on the strained double bond is depicted in Scheme I as occurring in the direction opposite to the coordinated face of the olefin. Trans attack on coordinated double bonds is in general much more common than that involving syn addition to the double bond.<sup>16</sup> In the present case we have no experimental data permitting us to distinguish between these two possibilities. However, the proposed trans attack is attractive for two reasons. First, the bond rotation (step B<sub>1</sub>, Scheme 1) involved in the rearrangement will put the phosphonium ion in the proper geometry for the facile elimination of  $\text{Cu}[\text{P}(\text{OMe})_3]_4^+$  (step B<sub>2</sub>). Second, a mechanism involving a backside attack may account for the difference in reactivity of *t*-C<sub>8</sub>H<sub>14</sub> and *t*-C<sub>7</sub>H<sub>12</sub>. Due to its C<sub>2</sub> symmetry conformation, *t*-C<sub>8</sub>H<sub>14</sub> has one face of the double bond shielded from attack, as is known from studies involving electrophilic addition to the uncomplexed olefin.<sup>17</sup> The shielded face of the double bond, in the case of the complex, is opposite to the coordinated copper ion. On the other hand, due to its unsymmetrical chair conformation, *trans*-cycloheptene does not suffer from this steric hindrance and has one of its olefinic carbons exposed to nucleophilic attack. The reduced reactivity of *t*-C<sub>8</sub>H<sub>14</sub>·CuOTf is compatible with this steric effect. Of course, the greater strain energy present in the smaller cycloheptene ring most likely also contributes to the observed reactivity difference.

### Conclusion

The addition of trimethyl phosphite to *cis*- and *trans*-cycloheptene and *cis*- and *trans*-cyclooctene complexed to copper(I) triflate results in the liberation of the free olefins at low temperatures in reactions in which intermediate

olefin-copper-phosphite complexes participate. A transient species for which we propose the structure of *trans*-cycloheptene is liberated at -80 °C from *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf. Under the reaction conditions, it isomerizes to *cis*-cycloheptene in a matter of hours at this temperature. This transient could not be isolated under the reaction conditions employed. Under similar conditions, *t*-C<sub>8</sub>H<sub>14</sub>·CuOTf liberates the free *trans*-cyclooctene which is also unstable with respect to isomerization to the *cis*-olefin, albeit only at a somewhat higher temperature. It is proposed that the isomerization is a consequence of nucleophilic attack on the coordinated trans olefin by  $\text{P}(\text{OMe})_3$  to give a phosphonium ion which rearranges to give  $\text{Cu}[\text{P}(\text{OMe})_3]_4^+$  and the *cis*-olefin.

### Experimental Section

**General.** The complexes were prepared as previously described<sup>5</sup> by using standard Schlenk techniques. Acetone-*d*<sub>6</sub> was dried over 4-Å molecular sieves and degassed by an argon purge prior to use. Trimethyl phosphite was purchased from Aldrich Chemical Co. (Gold Label grade) and purified by stirring over sodium followed by distillation. The purified phosphite was stored in the dark under argon. The other reagents and solvents used were obtained from the usual commercial sources and purified by using standard techniques. *trans*-Cyclooctene was prepared by using the method of Vedejs.<sup>9</sup>

**NMR Experiments.** The <sup>13</sup>C and <sup>1</sup>H spectra were run on a Varian SC-300 or a Varian XL-100 spectrometer fitted with a variable-temperature probe as described earlier. Screw cap NMR tubes (5 or 10 mm) fitted with Teflon septa were employed, and  $\text{P}(\text{OMe})_3$  was added via a gas-tight syringe. Adding  $\text{P}(\text{OMe})_3$  to a frozen solution of the complexes in acetone (77 K) followed by warm-up to -80 °C did not result in an improved yield over that of the above procedure, where  $\text{P}(\text{OMe})_3$  at room temperature was added to the -80 °C solution. The <sup>31</sup>P NMR data were obtained on a Varian XL-100 spectrometer and the <sup>63</sup>Cu spectra were run on a Bruker CXP-200 spectrometer.

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**Registry No.** *t*-7, 45509-99-7; *c*-C<sub>7</sub>H<sub>12</sub>·CuOTf, 69515-66-8; *t*-C<sub>7</sub>H<sub>12</sub>·CuOTf, 69496-00-0; *c*-C<sub>8</sub>H<sub>14</sub>·CuOTf, 85761-20-2; *t*-C<sub>8</sub>H<sub>14</sub>·CuOTf, 51826-48-3; *c*-C<sub>7</sub>H<sub>12</sub>, 628-92-2; *c*-C<sub>8</sub>H<sub>14</sub>, 931-87-3; *t*-C<sub>8</sub>H<sub>14</sub>, 931-89-5;  $\text{P}(\text{OMe})_3$ , 121-45-9.

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