

$\pi^*$ (bipy) transitions at  $\lambda_{\max}$  480–490 nm. Qualitative observations indicate that the bands have the expected solvent dependence. However, reliable estimates for band half-widths and molar extinction coefficients cannot be easily made because of distortions in the band shapes caused by the  $d \rightarrow \pi^*$  bands.

The IT transitions are at higher energies for the larger 4,4'-bipy and BPE ligands. This can be predicted from the Hush model since the intersection region between the potential surfaces for the Ru(II)–Ru(III) and Ru(III)–Ru(II) states (and therefore the energy of the IT transition) is a function of the distance separating the metal centers.

The energies of the IT transitions for the  $[(\text{NH}_3)_5\text{Ru}^{(II)}(\text{pyz})\text{Ru}^{(III)}\text{X}(\text{bipy})_2]^{4+}$  complexes are at higher energies than the transition for the pentaammine Creutz and Taube ion, as expected, because of the energetically unsymmetrical nature of the light-induced electron transfer process (eq 1). However, the IT band for the unsymmetrical complex (X = Cl) shows the band width and solvent dependence predicted by Hush, which is in contrast to the Creutz and Taube ion. The oscillator strength of the IT transition for  $[(\text{NH}_3)_5\text{Ru}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{4+}$  is lower by a factor of  $\sim 2$  than the value found for the Creutz and Taube ion indicating less metal–metal interaction.<sup>2,6</sup> The appearance of a moderately intense IT band for the unsymmetrical dimer is in marked contrast to the  $[(\text{bipy})_2\text{ClRu}(\text{pyz})\text{RuCl}(\text{bipy})_2]^{3+}$  ion where if an IT band exists in the region 700–2500 nm,  $\epsilon$  must be less than  $5 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>11</sup> It is interesting to note that although the intervalence transfer properties of the symmetrical pentaammine and 2,2'-bipyridine mixed-valence ions are unusual, the properties of the IT bands for the unsymmetrical mixed-valence ions are in good agreement with the Hush theory.

A noteworthy feature of the data in Table I is that the properties of the IT transitions are dependent upon both bridging and nonbridging ligand effects. From the treatment given by Hush for the properties of IT transitions, it follows that the extent of metal–metal interaction and rates of thermal electron transfer between the metal centers in the mixed-valence ions can be controlled in a systematic way by varying these molecular features.

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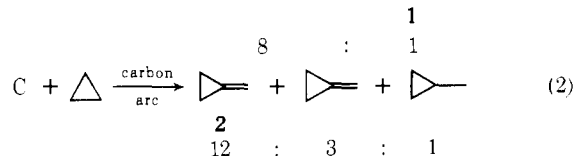
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## Reaction of Chemically Generated $^{14}\text{C}$ Atoms with Cyclopropane

Sir:

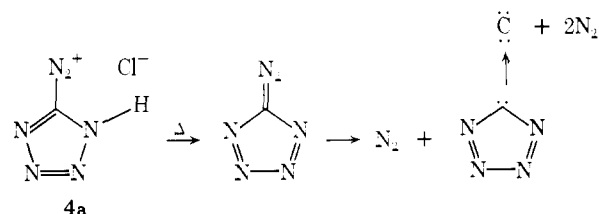
One of the most intriguing aspects of carbon atom chemistry is the reaction of atomic carbon with cyclopropane. Nucleogenic carbon-11 reacts with cyclopropane to produce acetylene- $^{11}\text{C}$  along with smaller amounts of 1,3-butadiene (**1**) (eq 1).<sup>1,2</sup> In contrast, the major product formed when arc generated carbon atoms are allowed to react with cyclopropane is methylenecyclopropane (**2**) (eq 2).<sup>3,4</sup>



The formation of acetylene and **1** in the  $^{11}\text{C}$  reaction is consistent with a mechanism involving an initial C–H insertion to generate cyclopropyl carbene, **3**. This carbene is known to fragment to ethylene and acetylene, as well as rearrange to cyclobutene and subsequently to **1**.<sup>5–7</sup> It should be noted that in the  $^{11}\text{C}$  system acetylene is also generated by an intermolecular reaction, the mechanism of which has not been resolved.<sup>8</sup>

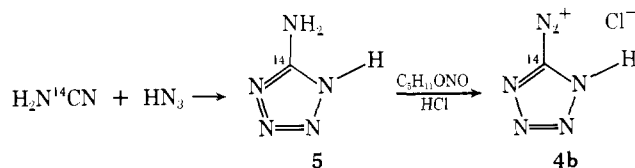
Inasmuch as **3** is not known to rearrange to **2**, the formation of this product in the reaction of carbon with cyclopropane is surprising. It may be that **2** results from a spectroscopic state of carbon (or intermediate carbene) that is not produced in the nucleogenic reaction. Alternately, the higher energy of the nuclear system may preclude the isolation of labile products such as **2** in the reactions of  $^{11}\text{C}$ .

We have recently shown that atomic carbon can be conveniently generated by the thermal decomposition of 5-tetrazoyldiazonium chloride (**4a**).<sup>9,10</sup> These chemically generated carbon atoms, which possess little excess kinetic energy, are ideally suited for a study of the reaction of carbon with cyclopropane. We now report the results of such a study.






These studies are carried out by coating **4** on the walls of a flask, as described previously,<sup>9</sup> and thermally ( $120^\circ$ ) decomposing it in the presence of gaseous cyclopropane. Low product yields presented an initial problem in this reaction. These low yields are due to competing processes such as reaction of atomic carbon with starting material on the walls of the flask and dimerization of the carbon atoms. In order to circumvent the problem of low yields and increase the sensitivity of product analysis, we have employed  $^{14}\text{C}$  atoms in this study.

The  $^{14}\text{C}$  atoms were generated by the thermolysis of 5-tetrazoyldiazonium- $^{14}\text{C}$  chloride (**4b**). This radioactive car-



**Table I.** Radioactivity Yields from the Reaction of  $^{14}\text{C}$  Atoms with Cyclopropane

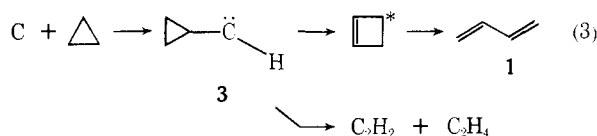
Reactants	Dpm in products ( $\times 10^{-3}$ )				
	$\text{C}_2\text{H}_2^a$	$\text{C}_2\text{H}_4$			
200 mm $\Delta$	$39.7 \pm 2.2$	$4.1 \pm 0.3$	0.25	0.28	$6.1 \pm 0.3$
200 mm $\Delta$ + 200 mm Ar	40.7	<i>b</i>	0.27	0.13	2.3
200 mm $\Delta$ + 5% $\text{O}_2$	38.2	<i>b</i>	0.15	5.7 <sup>c</sup>	
$\Delta$ at $-196^\circ$	<i>b</i>	<i>b</i>	0.05	0.7	0.3

<sup>a</sup> Large variations in  $\text{C}_2\text{H}_2$  yields are invariably observed. The manner in which **4** is coated on the walls of the reactor effects  $\text{C}_2\text{H}_2$  yields but not those of other products. <sup>b</sup> These products were not determined in these runs. <sup>c</sup> This number represents total dpm in cyclobutene and butadiene.

bon atom precursor was conveniently synthesized by the reaction of cyanamide- $^{14}\text{C}$  with hydrazoic acid<sup>11</sup> to yield 5-aminotetrazole- $^{14}\text{C}$  (**5**), which was diazotized to form **4b**.

The products of the reaction of  $^{14}\text{C}$  atoms with cyclopropane were analyzed for acetylene, ethylene, methylenecyclopropane, 1,3-butadiene, cyclobutene (**6**), methylcyclopropane, and isobutylene. Analyses were carried out by adding each of the above unlabeled hydrocarbons to the reaction vessel after pyrolysis of **4b** in the presence of cyclopropane. Each hydrocarbon was then separated by gas chromatography, trapped, and counted. Of the  $\text{C}_4$  products analyzed, only **1** contained appreciable activity when  $^{14}\text{C}$  atoms were allowed to react with gaseous cyclopropane. Table I shows the radioactivity yields for acetylene, ethylene, **1**, **2**, and **6**.

The reaction of chemically generated carbon atoms with cyclopropane to produce **1** can be formulated as shown in eq 3. The formation of 1,3-butadiene rather than cyclobutene



parallels the chemistry of  $^{11}\text{C}$  and is undoubtedly a result of the exothermicity of the reaction which effects ring opening of the initially formed cyclobutene.

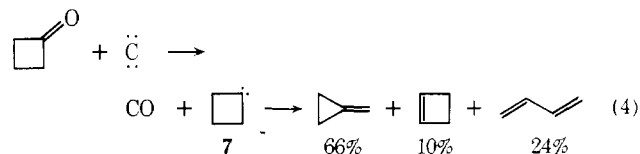
The chemical yield of acetylene, determined by gas chromatography, was  $3.4 \times 10^{-3}$  mmol while that of ethylene was  $5.0 \times 10^{-3}$  mmol. A calculation of the chemical yield of **1** from the specific molar activity of **5** gives  $2.5 \times 10^{-4}$  mmol. Assuming that 3 mol of nitrogen is produced per mole of atomic carbon, the yield of hydrocarbon products from this reaction is 3%. It should be noted that this is a lower limit for the hydrocarbon yield as nitrogen may be produced in processes which do not result in the formation of carbon atoms. The ratio of total activity in acetylene to that in **1** (6.5:1) is in reasonable agreement with the 8:1 ratio observed in the  $^{11}\text{C}$  + cyclopropane system.<sup>1</sup> However, the acetylene produced contains only about half the specific molar activity of **5**. We are currently investigating the origin of this reduced activity in the acetylene.

An important point is the absence of methylenecyclopropane in this reaction. Table I shows that the addition of argon reduces the yield of **1** but does not increase that of **2**. This decrease in yield is attributed to a degradation of the carbon atoms to their  $^3\text{P}$  ground state which is relatively unreactive toward cyclopropane. Since the yield of **2** does not increase with pressure, we conclude that  $^3\text{P}$  carbon is not a precursor of **2**. The  $\text{C}_4$  hydrocarbon yield is little effected by added oxygen (Table I), a scavenger of  $^3\text{P}$  car-

bon,<sup>12</sup> indicating again that these products do not result from ground state carbon.

The reactions of arc generated carbon take place in the condensed phase at  $-196^\circ$ , while the present studies are carried out in the gas phase. This difference in reaction conditions may be significant in that the condensed phase could effect stabilization of **2** or allow degradation of **3** to the triplet state. In order to assess this factor, we have carried out the decomposition of **4b** in an apparatus allowing reaction with cyclopropane at  $-196^\circ$ . The cyclopropane is coated on two cold fingers at  $-196^\circ$ , and **4b** is thermally decomposed on the walls of the flask below the cold fingers. In this way, some carbon atoms impinge upon the cold fingers and react with the cyclopropane in the condensed phase. While these reaction conditions do not increase the yield of **2**, a dramatic change in the ratio of cyclobutene to butadiene is observed (Table I). The large increase in this ratio is due to a stabilization of the excited cyclobutene in the condensed phase which prevents ring opening. The lower overall product yields under these conditions are the result of fewer carbon atoms reaching the cyclopropane than in the gas phase reaction. These experiments establish that **2** is not a product when chemically generated carbon atoms react with cyclopropane at  $-196^\circ$ .

In order to test the possibility that **2** is labile under our reaction conditions, we have treated chemically generated carbon atoms with cyclobutanone. Since carbonyl compounds are deoxygenated by atomic carbon to yield a carbene and carbon monoxide,<sup>13</sup> this reaction should produce cyclobutylidene (**7**) which is known to rearrange to **2**.<sup>5</sup> Equation 4 shows that this reaction does take place when



5-tetrazoyldiazonium chloride is pyrolyzed in the presence of cyclobutanone. Although  $^{14}\text{C}$  labeled  $\text{C}-4$  products cannot result from this reaction, the yields are high enough to permit separation of the products by gas chromatography and identification by ir spectroscopy. The three products in eq 4 are obtained in a 3.8% overall yield based on nitrogen produced in the decomposition of **4a**. Since **2** produced by the sequence in eq 4 survives the reaction conditions, we feel that it would be detected if formed in the reaction with cyclopropane.

Although **2** is a major product in the reaction of arc generated carbon with cyclopropane, it is not found in the present study or in the reactions of  $^{11}\text{C}$ . We believe the most plausible pathway to **2** in the arc system to be a C-C insertion producing **7** which rearranges to **2**. The reactions of arc generated carbon are thought to involve  $^1\text{S}$  carbon,<sup>14</sup> and it may be that this species, in the condensed phase, effects a C-C insertion. In theory it is possible to use labeled carbon atoms to distinguish between **2** which arises from **7** via a C-C insertion and **2** arising from **3** via a C-H insertion. Since **2** was not formed in our experiments, we could not carry out this interesting labeling experiment. The reaction of chemically generated carbon with cyclopropane is similar to that of  $^{11}\text{C}$  and appears to proceed via an initial C-H insertion to yield **3**.

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## Mechanistic Studies of Oxidative Addition to Low Valent Metal Complexes. IV. Observation of CIDNP Effects in Platinum(0) and Palladium(0) Reactions

Sir:

In a previous communication<sup>1</sup> we offered evidence that the reactions of many alkyl (and related) bromides with  $M(\text{PEt}_3)_3$  (**1**) ( $M = \text{Pt}$ , **1a**;<sup>2</sup>  $M = \text{Pd}$ , **1b**<sup>3</sup>) involve radical chain processes. In the scheme presented, the adduct *trans*- $\text{MRBr}(\text{PEt}_3)_2$  (**2**) and *trans*- $\text{MHBr}(\text{PEt}_3)_2$  (**3**) are both formed early in the reaction sequence, whereas *trans*- $\text{MBr}_2(\text{PEt}_3)_2$  (**4**) is produced in a slower, subsequent step involving **3** as an intermediate. We find, however, that several very reactive halides (e.g.,  $\alpha$ -bromoesters, benzyl bromide, secondary alkyl iodides) when allowed to react with **1** produce **4** too rapidly for the previously described chain process to be operative in these cases.<sup>4</sup> The results presented here on the investigation of such reactions show other paths are indeed available and also provide the first definitive<sup>5</sup> evidence that one-electron processes can be involved in these reactions.

When **1a** (1 mol) and isopropyl iodide (2.5 mol) are allowed to react in benzene- $d_6$  and/or toluene- $d_8$  at ambient temperatures, the reaction is complete within a few minutes, and analysis<sup>8</sup> of the products shows *trans*- $\text{PtHI}(\text{PEt}_3)_2$  (0.45 mol), *trans*- $\text{PtI}_2(\text{PEt}_3)_2$  (0.55 mol), *trans*- $\text{Pt}(i\text{Pr})\text{I}(\text{PEt}_3)_2$  (trace), propene (0.75 mol), propane (0.30 mol), and 2,3-dimethylbutane (0.25 mol). When this reaction is followed by <sup>1</sup>H nmr spectroscopy, pronounced CIDNP enhancements (multiplet effects) are observed in the resonances of propene and isopropyl iodide.<sup>9</sup> Identical observations were made for the reaction of isopropyl iodide

Scheme I

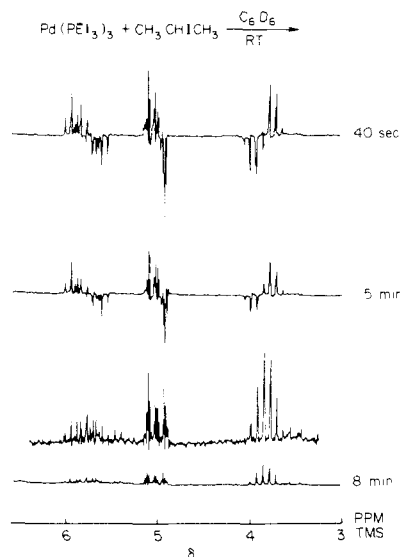
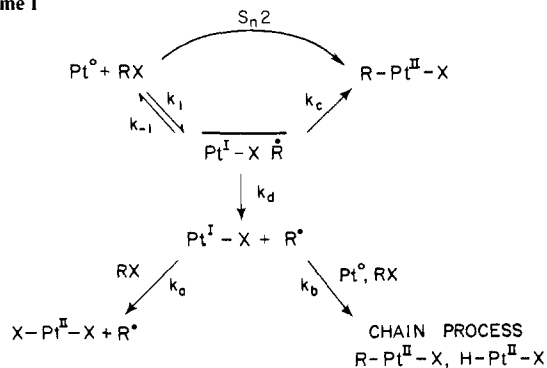


Figure 1. <sup>1</sup>H nmr spectra recorded at 100 MHz during the ambient temperature reaction of isopropyl iodide and  $\text{Pd}(\text{PEt}_3)_3$  in benzene- $d_6$ .

with **1b** (Figure 1). These observations clearly indicate that at least a component of the reaction involves a radical (one-electron) process. The phase of the multiplet effects<sup>10</sup> indicates that the predominant path for enhancement in both propene and isopropyl iodide involves the diffusive encounter of isopropyl radicals. Further evidence that this is a significant reaction path is provided by product analysis. When correction is made for propene produced by the competitive radical chain process (which is equal to the moles of *trans*- $\text{PtHI}(\text{PEt}_3)_2$  produced), the mole ratios of propene:propane:2,3-dimethylbutane (i.e., 0.30:0.30:0.25) are consistent with that expected for a disproportionation-combination reaction of isopropyl radical pairs.<sup>11</sup>

The reaction of benzyl bromide (2.5 mol) and **1a** (1 mol) yields **2a** (0.2 mol), **4a** (0.8 mol), and bibenzyl (0.8 mol), the rate of addition and the product ratios being unaffected by the addition of 5 mol % duroquinone. During the reaction, CIDNP (multiplet) effects are observed in the aromatic resonances (<sup>1</sup>H nmr), and, although the origin of these effects has yet to be determined, benzyl radicals are clearly implicated. However, in the reaction of **1a** with  $\alpha$ -bromoethylbenzene, the AE multiplet effects observed in the nonaromatic resonances (<sup>1</sup>H nmr) of the disproportionation products, ethylbenzene and styrene, characterize this process as one involving the diffusive encounter of  $\alpha$ -methylbenzyl radicals.

It must be noted that we have observed CIDNP effects only when *trans*- $\text{MX}_2(\text{PEt}_3)_2$  ( $X = \text{Br}, \text{I}$ ) is produced rapidly in the initial stages of the reaction, but, as yet, not in cases when only the regular addition and hydrido complexes, *trans*- $\text{MRX}(\text{PEt}_3)_2$  and *trans*- $\text{MHX}(\text{PEt}_3)_2$ , are formed.<sup>12</sup> For example, benzyl chloride reacts cleanly with **1a** to yield the regular adduct, *trans*- $\text{Pt}(\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{PEt}_3)_2$ , in quantitative yield. No CIDNP effects are observed, in contrast to the corresponding reaction with benzyl bromide.

We have written a generalized scheme for alkyl halide reactions with **1**, drawing together these and other results (Scheme I). Platinum(0) may react initially with an organic halide by two paths.<sup>13</sup> (i) One path is the  $\text{S}_{\text{N}}2$  displacement on carbon to give an incipient cationic complex (possibly strongly ion paired) followed by reentry of the anion to give the regular oxidative addition adduct. Recent work by Stille<sup>7,14</sup> strongly substantiates the feasibility of this route. (ii) The other path is halide abstraction (possibly preceded