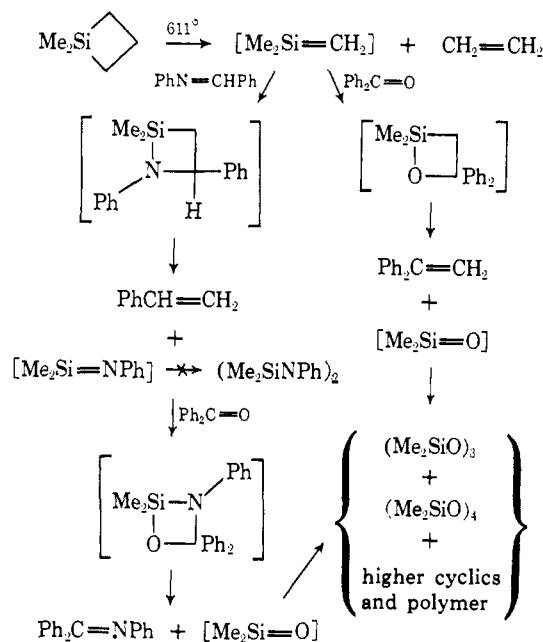


**Table I.** Pyrolysis of Silacyclobutane-Imine Solutions at 611°

Silacyclobutane (mmol)	Imine (mmol)	Benzene (mmol)	Products (% yield) <sup>a</sup>	
(CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>2</sub> (21.2)	PhCH=NPh (14.5)	(59)	(Me <sub>2</sub> SiNPh) <sub>2</sub> (41)	PhCH=CH <sub>2</sub> (32)
(CH <sub>2</sub> ) <sub>3</sub> SiMe <sub>2</sub> (13.2)	Ph <sub>2</sub> C=NPh (5.20)	(55)	(Me <sub>2</sub> SiNPh) <sub>2</sub> (30)	Ph <sub>2</sub> C=CH <sub>2</sub> (36)
(CH <sub>2</sub> ) <sub>3</sub> SiPh <sub>2</sub> (6.33)	Ph <sub>2</sub> C=NPh (3.03)	(62)	(Ph <sub>2</sub> SiNPh) <sub>2</sub> (25) <sup>b,c</sup>	Ph <sub>2</sub> C=CH <sub>2</sub> (33) <sup>b</sup>

<sup>a</sup> These are based on the amounts of material actually isolated (either by preparative glpc or crystallization) and are probably 10–20% lower than the quantities actually present. All reaction products are known compounds and, except as noted, were completely characterized by their ir and nmr spectra and, where applicable, melting points. <sup>b</sup> Calculated after correction for a 24% recovery of limiting reagent. <sup>c</sup> Material was impure (mp 335–343°, lit.<sup>8</sup> mp 355.5°). Further recrystallization did not afford a purer sample.

benzophenone (4.73 mmol), and benzene (66.7 mmol) afforded a homogeneous, yellow pyrolysate which, after resolution by preparative glpc afforded benzophenone phenylimine (0.79 mmol), styrene (0.78 mmol), 1,1-diphenylethylene (1.95 mmol), octamethylcyclotetra-siloxane (0.04 mmol), hexamethylcyclotrisiloxane (trace), benzophenone (1.74 mmol), and *N*-phenylbenzaldimine (12.7 mmol). Glpc analysis of the pyrolysate did not detect any 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane, (Me<sub>2</sub>SiNPh)<sub>2</sub>. Isolation of benzophenone phenylimine provides definitive evidence for the formation of Me<sub>2</sub>Si=NPh and its reaction with benzophenone since pyrolysis of equimolar quantities of either benzophenone and *N*-phenylbenzaldimine or benzophenone and (Me<sub>2</sub>SiNPh)<sub>2</sub> did not produce detectable quantities of this material. An explanation which accommodates all of these observations is outlined in Scheme II. Assuming quantitative formation

**Scheme II**

of Me<sub>2</sub>Si=CH<sub>2</sub> and correcting, on the basis of the isolated yield of 1,1-diphenylethylene, for the fact that 38.5% of the Me<sub>2</sub>Si=CH<sub>2</sub> produced reacted with benzophenone, then the 0.79 mmol of benzophenone phenylimine isolated represents a 25.4% yield of trapped Me<sub>2</sub>Si=NPh. This is a minimum value since isolated yields were used and factors such as decomposition of the trapping reagents and products and other side reactions were ignored. The absence of significant side reactions and the relatively high yield of benzophenone phenylimine indicate that reaction schemes more complex than II are unlikely.

The absence of (Me<sub>2</sub>SiNPh)<sub>2</sub> and the comparable quantities of styrene and benzophenone phenylimine observed indicate that benzophenone is a very efficient trapping reagent for silicon-nitrogen doubly bonded intermediates. This is in accord with our observation<sup>16</sup> that benzophenone is an excellent trapping reagent for intermediates containing silicon-carbon double bonds.

**Acknowledgment.** We thank the National Science Foundation for support of this work.

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Received September 20, 1973

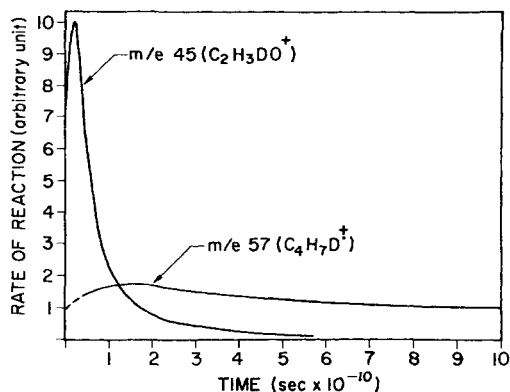
### Mechanisms of Unimolecular Gas-Phase $\gamma$ -Hydrogen Rearrangements of Radical Cations. The Influence of Entropy as Opposed to Energy

Sir:

Those  $\gamma$ -hydrogen rearrangements commonly referred to as McLafferty-type rearrangements have probably attracted more attention than any other rearrangement encountered in mass spectrometry;<sup>1</sup> yet there is still considerable contention as to whether these ubiquitous rearrangements occur in a concerted or a stepwise manner.<sup>2–6</sup> We have sought to elucidate this persistent question by applying the powerful capabilities of field ionization kinetics (FIK)<sup>7–9</sup> to a study of two complementary  $\gamma$ -hydrogen rearrangements in hexanal.<sup>10,11</sup> The FIK technique<sup>7–9</sup> allows rates of unimolecular gas-phase reactions of (radical-) cations to be measured over a time range extending from 10<sup>-12</sup> or 10<sup>-11</sup> sec to 10<sup>-6</sup> or 10<sup>-5</sup> sec.

The rates of formation of *m/e* 45 (C<sub>2</sub>H<sub>3</sub>DO) and *m/e* 57

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**Figure 1.** The dependence on time of the rates of formation of  $m/e$  45 ( $C_2H_3DO^+$ ) and  $m/e$  57 ( $C_4H_7D^+$ ) from hexanal-4,4- $d_2$  within the time range  $10^{-11}$ – $10^{-9}$  sec following FI. The rate of formation of  $m/e$  57 ( $C_4H_7D^+$ ) at the very shortest times can only be estimated due to the simultaneous formation of  $m/e$  57 ( $C_3H_5O^+$ ) by field dissociation.

( $C_4H_7D$ ) from hexanal-4,4- $d_2$  following field ionization (FI) are shown in Figure 1 as functions of time over the range  $10^{-11}$ – $10^{-9}$  sec. The means by which these curves were obtained have been described.<sup>9,12,13</sup> The formation both of  $m/e$  45 ( $C_2H_3DO$ ) and of  $m/e$  57 ( $C_4H_7D$ ) involves  $\gamma$ -D rearrangement and  $\beta$  cleavage. The hexanal-4,4- $d_2$  species was studied so as to distinguish between  $\gamma$  transfer and transfer from other sites.<sup>14</sup> There is no H/D randomization prior to fragmentation at  $10^{-11}$ – $10^{-9}$  sec (ref 14). It is evident from Figure 1 that the relative rates of these two reactions are sensitive functions of time. At times of a few  $\times 10^{-11}$  sec the rate of formation of  $m/e$  45 ( $C_2H_3DO$ ) exceeds the rate of formation of  $m/e$  57 ( $C_4H_7D$ ) by almost 1 order of magnitude. At times of the order of  $10^{-10}$  sec, however, the formation of  $m/e$  57 ( $C_4H_7D$ ) is the faster reaction. The trend for the formation of  $m/e$  57 ( $C_4H_7D$ ) to be faster at longer times is supported by measurements<sup>15</sup> of the metastable transitions in the first field free region (corresponding to reaction at  $\sim 10^{-6}$  sec after ionization). The transition  $C_6H_{10}D_2O^+ \rightarrow C_4H_7D^+$  is at least 2 orders of magnitude more intense than  $C_6H_{10}D_2O^+ \rightarrow C_2H_3DO^+$  (which cannot be detected at all).

We assume that the formation of  $m/e$  45 ( $C_2H_3DO$ ) and the formation of  $m/e$  57 ( $C_4H_7D$ ) are competing reactions of the ground electronic state. The average internal excitation energy available through FI is probably of the order of tenths of an eV.<sup>16</sup> The photoelectron spectrum of hexanal suggests that the ground electronic state may be an isolated state approximately 1.5 eV below the first excited state.<sup>17</sup> Reactions at the shortest times can be assumed to involve the most energetic reactant ions, and reactions at longer times the less energetic. Thus with the most energetic

reactant ions, the rate of formation of  $m/e$  45 ( $C_2H_3DO$ ) exceeds the rate of formation of  $m/e$  57 ( $C_4H_7D$ ). It is at the lowest energies that energy considerations will be most influential in directing the competition between the reactions. The results suggest, therefore, that the formation of  $m/e$  57 ( $C_4H_7D$ ) is energetically more favorable than the formation of  $m/e$  45 ( $C_2H_3DO$ ). This is consistent with the observation in electron impact (EI) studies<sup>10</sup> that on lowering the electron energy the intensity of  $m/e$  57 ( $C_4H_7D$ ) increases relative to the intensity of  $m/e$  45 ( $C_2H_3DO$ ). The higher rate of formation of  $m/e$  45 ( $C_2H_3DO$ ) at the highest energies, however, is not readily explicable on energetic grounds. We suggest that the explanation lies in the realm of entropy. We suggest that the formation of  $m/e$  45 ( $C_2H_3DO$ ), although discriminated against by the energy factors, is favored by the entropy factors and that it is the entropy factors which direct the competition between the reactions at the shortest times ( $\sim 10^{-11}$  sec).<sup>18</sup> In terms of transition-state theory, we are suggesting that the formation of  $m/e$  57 ( $C_4H_7D$ ) has the lower activation energy but that the formation of  $m/e$  45 ( $C_2H_3DO$ ) has the more favorable (*i.e.*, the less negative) activation entropy.

The kinetic results pose considerable mechanistic difficulties. For the present let us consider that both reactions are initiated by a common  $\gamma$ -D transfer step. This interpretation is consistent with recent trends.<sup>5,6,11</sup> Simple  $\beta$  cleavage at times of the order of  $10^{-11}$  sec could form the enol fragment  $m/e$  45 ( $C_2H_3DO$ ); at longer times  $\beta$  cleavage together with rearrangement within the hydrocarbon chain could form  $m/e$  57 ( $C_4H_7D$ ) with the 2-butene structure. These mechanisms satisfy our energy and entropy criteria. The formation of  $m/e$  57 ( $C_4H_7D$ ) should be favored by energy considerations,<sup>19</sup> as the ionization potential (IP) of vinyl alcohol has been estimated as 9.5 eV<sup>20</sup> and that of 2-butene has been measured as 9.1 eV.<sup>21</sup> There is, however, an objection to these mechanisms. Simple  $\beta$  cleavage subsequent to  $\gamma$ -hydrogen transfer at times of the order of  $10^{-11}$  sec would be expected to form both  $m/e$  45 ( $C_2H_3DO$ ) and  $m/e$  57 ( $C_4H_7D$ ) with the 1-butene structure) at comparable rates. This is not what is observed (Figure 1). The IP of 1-butene has been measured as 9.6 eV.<sup>21</sup> The situation would be that of charge competition as discussed by Meyerson, *et al.*<sup>11</sup> The analogous reactions in heptanal induced by FI have the same kinetic characteristics as the reactions in hexanal.<sup>22</sup> Here the IP of the 1-pentene molecule competing for the charge is 9.5 eV.

Alternatively the natures of the cyclic transition states involved in the two initial  $\gamma$ -D transfers could differ. An attractive possibility is that the observed reactions correspond to stepwise and concerted mechanisms discussed so extensively in the literature.<sup>2-6,11</sup> Chemical intuition demands that the concerted mechanism

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represent the faster process leading to *m/e* 45 (C<sub>2</sub>H<sub>3</sub>DO). The slower process *via* an intermediate would lead to *m/e* 57 (C<sub>4</sub>H<sub>7</sub>D) presumably with the 2-butene structure. Calculations by Boer, Shannon, and McLafferty<sup>2</sup> indicate that the transition state in the stepwise mechanism is energetically preferable to that in a concerted mechanism. These mechanisms would demand that the transition state for the concerted mechanism be "looser" than that in the stepwise.<sup>2,3</sup> This would probably mean that the transition state in the concerted mechanism does not need to be exactly planar. The weakly bonding and extended  $\beta$  bond in the concerted transition state might result in the internal rotations of the reactant being less constrained than they would be in the stepwise transition state. This could give the concerted transition state a higher entropy.<sup>24</sup>

The kinetic results leave little doubt that there are two distinct processes in hexanal involving  $\gamma$ -hydrogen transfer and  $\beta$  cleavage. It does not seem useful to refer to two mechanistically distinct reactions by the same name. We would suggest that it is time to give a more precise and therefore more meaningful definition to the term "McLafferty rearrangement."

**Acknowledgment.** Financial support for this work was provided by the National Aeronautics and Space Administration (Grant NGL 05-003-003) and the National Science Foundation (Grant NSF GP-38389X).

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Received July 5, 1973

### Platinum(0) Complexes of Heterocyclic Acetylenes. Synthesis of a Stable Metallacycle: Bis(triphenylphosphine)[di(2-pyridyl)acetylene]- platinumdichlorocobalt(II)<sup>1</sup>

Sir:

Since the initial report of Pt(Ar<sub>3</sub>P)<sub>2</sub>(diphenylacetylene) complexes,<sup>2</sup> a wide variety of substituted acetylene transition metal complexes have been described.<sup>3</sup> In view of the substantial attention devoted specifically to acetylene platinum complexes, we sought to extend this work by exploring the unique coordinating properties of several 2-pyridylacetylenes.

We wish to report the preparation of several new complexes of the type Pt(Ar<sub>3</sub>P)<sub>2</sub>(2-Pyr-C<sub>2</sub>Ar) and an

(1) Part 14 in a series on the Chemistry of Heterocyclic Compounds; presented in part at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 29, 1973, Abstract ORGN-90.

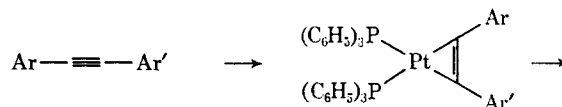
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especially novel heterodinuclear complex, Pt(Ar<sub>3</sub>P)<sub>2</sub>[(2-Pyr)<sub>2</sub>C<sub>2</sub>]CoCl<sub>2</sub> (**9**), which exploited the dual functionality of the 2-pyridylacetylene: (1) platinum-acetylene coordination, and (2) N complexation. Formation of this metallacycle (**9**) capitalized on the 2-pyridyl groups in the imposed Z orientation, which was caused by deviation (*ca.* 40°)<sup>4</sup> from linearity of the acetylene bond in the initial Pt acetylene complex.

Treatment of di(2-pyridyl)acetylene (**3**)<sup>5</sup> with tetrakis(triphenylphosphine)platinum(0)<sup>6</sup> in anhydrous benzene at 26° (Scheme I) afforded the yellow crystalline

Scheme I



1, Ar = Ar' = C<sub>6</sub>H<sub>5</sub>

2, Ar = C<sub>6</sub>H<sub>5</sub>; Ar' = 2-Pyr

3, Ar = Ar' = 2-Pyr

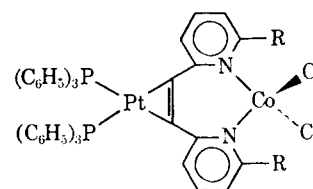
4, Ar = Ar' = 2-(6-CH<sub>3</sub>-Pyr)

5, Ar = Ar' = C<sub>6</sub>H<sub>5</sub>

6, Ar = C<sub>6</sub>H<sub>5</sub>; Ar' = 2-Pyr

7, Ar = Ar' = 2-Pyr

8, Ar = Ar' = 2-(6-CH<sub>3</sub>-Pyr)



9, R = H

10, R = CH<sub>3</sub>

platinacyclopentadiene (**7**):<sup>7,8</sup> mp 192–193° (ethanol, sealed tube),  $\nu_{\max}$  (KBr) 1728 (>C=C<), 1583 (Pyr) cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  8.5 (d, 6-Pyr-H, 2 H), and 7–8 (m, Arom and Pyr-H, 36 H). Reaction of **2**<sup>9</sup> and **4**<sup>4</sup> under identical conditions gave the crystalline complexes **6**<sup>7</sup> (mp 170–175°;  $\nu_{\max}$  (KBr) 1747 (>C=C<), 1580 (Pyr) cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  8.45 (d, 6-Pyr-H, 1 H) and a complex aromatic region) and **8**<sup>7</sup> (mp 189–195° (sealed tube);  $\nu_{\max}$  (KBr) 1747 (>C=C<), 1580 (Pyr) cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  2.16 (s, 6-Pyr-CH<sub>3</sub>), respectively. From a survey of the infrared data (Table I) for com-

Table I. Selected Infrared Data for Substituted Platinacyclopentadienes

Ligand	$\nu_{\max}$ , cm <sup>-1</sup>	Platinacyclopentadiene	$\nu_{\max}$
1	2222 <sup>a</sup>	5	1768, 1740 <sup>b</sup>
2	2227	6	1747
3	2220 <sup>a</sup>	7	1764
4	2215 <sup>a</sup>	8	1754

<sup>a</sup> Raman data. <sup>b</sup> E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Can. J. Chem.*, **46**, 3879 (1968).

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