Steric and Electronic Effects of the Tertiary Phosphine Ligand on the Dissociative Reductive Elimination from *cis*-Aryldimethyl(triarylphosphine)gold(III)

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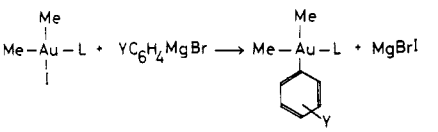
A series of *cis*-aryldimethyl(triarylphosphine)gold(III) complexes, *cis*-Au(C_6H_4Y)Me_2($P(C_6H_4X)_3$) (X = *p*-OMe, *p*-Me, H, *p*-F, *o*-Me; Y = *p*-OMe, *p*-Me, H, *p*-F, *o*-OMe, *o*-Me) and $AuPhMe_2(P(C_6H_4\text{-}o\text{-}Me)_nPh_{3-n})$ (n = 0–2), has been prepared by the alkylation of *cis*-$AuMe_2IL$ by the corresponding Grignard reagents. Electron withdrawal from and the steric bulk of the triarylphosphine ligand as well as electron donation by the aryl ligand enhances phosphine dissociation, leading to a facile and selective reductive elimination of aryl Me.

Introduction

Reductive elimination from transition metal complexes resulting in carbon–carbon bond formation is regarded as one of the key steps in various transition-metal-catalyzed organic reactions.[1] Isolation of alkyl transition-metal complexes has been made possible by employing suitable auxiliary ligands such as tertiary phosphines and 2,2′-bipyridine[2] and recent investigations of the thermolysis of four-coordinate d^8 transition-metal di- or trialkyl complexes have shed light on the mechanisms of reductive elimination.[3] A dissociative pathway for the reductive elimination seems to be the most common thermolysis mechanism of the organotransition-metal complexes, whereas associative and direct reductive elimination pathways are also known. However, the ease of ligand dissociation which lead to a facile reductive elimination has not been kinetically well understood,[4] although the importance of steric bulkiness of tertiary phosphine ligands in the ligand dissociation equilibria has been widely accepted.[5] We wish to report the preparation and kinetic aspect for the thermolysis of a series of *cis*-aryldimethylgold(III) complexes having a triarylphosphine ligand. The importance of the steric and electronic effects of both the tertiary phosphine and the aryl ligands on the phosphine ligand dissociation, followed by reductive elimination is described.

Results and Discussion

Preparation of *cis*-Aryldimethylgold(III) Complexes with Triarylphosphine Ligand. A series of *cis*-aryldimethyl(triarylphosphine)gold(III) complexes, **1**, was prepared by the reaction of *cis*-dimethyliodo(triarylphosphine)gold(III) with the corresponding aryl Grignard reagents.[6] Complexes **1**, which were purified by recrystallization, after workup are air and thermally stable. Tables I–III summarize yields, decomposition points, elemental analyses, and ^1H and ^{13}C NMR spectra, respectively. The two doublets for the Au–Me groups cis and



(1)

1a–f, 2–7

1a, L = PPh_3; Y = *p*-OMe
b, L = PPh_3; Y = *p*-Me
c, L = PPh_3; Y = H
d, L = PPh_3; Y = *p*-F
e, L = PPh_3; Y = *o*-OMe
f, L = PPh_3; Y = *o*-Me
2, L = $P(C_6H_4\text{-}p\text{-}OMe)_3$; Y = H
3, L = $P(C_6H_4\text{-}p\text{-}Me)_3$; Y = H
4, L = $P(C_6H_4\text{-}p\text{-}F)_3$; Y = H
5, L = $P(C_6H_4\text{-}o\text{-}Me)_3$; Y = H
6, L = $PPh(C_6H_4\text{-}o\text{-}Me)_2$; Y = H
7, L = $PPh_2(C_6H_4\text{-}o\text{-}Me)$; Y = H

trans with respect to the phosphine ligand in the ^1H NMR spectra of complexes **1** indicate the square-planar cis configuration. A large C–P coupling constant for trans methyl–Au (15.08 ppm (117.2 Hz)) compared with that for cis methyl–Au (7.08 ppm (7.3 Hz)) in the ^{13}C NMR spectrum for **1c** reflects the strong trans influence of the phosphorus atom on the C–P coupling constant. A large influence of substituents of the aryl groups on the ^1H and ^{13}C NMR spectra was not observed.

Reductive Elimination of Methylarene from *cis*-Aryldimethylgold(III) Complexes. Thermolysis of complexes **1** in benzene afforded cleanly and selectively the intramolecular reductive elimination product (methylarene) as noted by Puddephatt.[7] The resulting gold complexes were Au^IMeL as confirmed by their ^1H NMR spectra. The rates of the thermolysis in benzene-d_6 were

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Table I. Yield, Decomposition Point (dp), and Elemental Analyses of Complexes 1-7

compound	yield,[a] %	dp, °C	anal. found (calcd) C	H
1a, $AuMe_2(C_6H_4$-*p*-OMe$)(PPh_3)$	58	99	53.97 (54.37)	4.62 (4.73)
1b, $AuMe_2(C_6H_4$-*p*-Me$)(PPh_3)$	65	105	55.58 (55.87)	4.79 (4.86)
1c, $AuMe_2(C_6H_5)(PPh_3)$	55	101	54.25 (55.13)	4.60 (4.63)
1d, $AuMe_2(C_6H_4$-*p*-F$)(PPh_3)$	73	111	53.37 (53.43)	4.29 (4.31)
1e, $AuMe_2(C_6H_4$-*o*-OMe$)(PPh_3)$	53	109	54.02 (54.37)	4.73 (4.73)
1f, $AuMe_2(C_6H_4$-*o*-Me$)(PPh_3)$	64	101	55.29 (55.87)	4.62 (4.86)
2, $AuMe_2(C_6H_5)[P(C_6H_4$-*p*-OMe$)_3]$	32	113	53.36 (53.06)	4.98 (4.91)
3, $AuMe_2(C_6H_5)[P(C_6H_4$-*p*-Me$)_3]$	37	131	56.95 (57.24)	5.25 (5.30)
4, $AuMe_2(C_6H_5)[P(C_6H_4$-*p*-F$)_3]$	66	115	50.42 (50.34)	3.83 (3.74)
5, $AuMe_2(C_6H_5)[P(C_6H_4$-*o*-Me$)_3]$	60	95	59.02 (57.24)	5.56 (5.30)
6, $AuMe_2(C_6H_5)[PPh(C_6H_4$-*o*-Me$)_2]$	51	104	56.90 (56.57)	5.32 (5.09)
7, $AuMe_2(C_6H_5)[PPh_2(C_6H_4$-*o*-Me$)]$	54	117	56.91 (55.87)	4.88 (4.86)

[a] After recrystallization.

Table II. ^1H NMR Spectra of Complexes 1-7[a]

compound	Au-Me cis to P	Au-Me trans to P	Au-Ar H_o	Au-Ar H_m	Au-Ar H_p	others	PR_3
1a, $AuMe_2(C_6H_4$-*p*-OMe$)(PPh_3)$	0.18 (d, 7.3, 3 H)	1.17 (d, 9.0, 3 H)	6.89 (d, 7.8, 2 H)	6.53 (d, 8.6, 2 H)		OMe 3.68 (s, 3 H)	7.1-7.5 (m, 15 H)
1b, $AuMe_2(C_6H_4$-*p*-Me$)(PPh_3)$	0.16 (d, 7.1, 3 H)	1.18 (d, 8.8, 3 H)	6.88 (d, 7.6, 2 H)	6.72 (d, 7.6, 2 H)		Me 2.13 (s, 3 H)	7.2-7.6 (m, 15 H)
1c, $AuMe_2(C_6H_5)(PPh_3)$	0.18 (d, 7.3, 3 H)	1.18 (d, 9.0, 3 H)	7.01 (t, 7.3, 2 H)	6.87 (t, 7.3, 2 H)	6.76 (t, 7.3, 1 H)		7.2-7.5 (m, 15 H)
1d, $AuMe_2(C_6H_4$-*p*-F$)(PPh_3)$	0.21 (d, 7.3, 3 H)	1.14 (d, 9.0, 3 H)	6.93 (ddd) (1.0, 6.8, 8.5, 2 H)	6.62 (dd, 8.5, 10.5, 2 H)			7.2-7.5 (m, 15 H)
1e, $AuMe_2(C_6H_4$-*o*-OMe$)(PPh_3)$	0.21 (d, 7.3, 3 H)	1.16 (d, 9.0, 3 H)		6.1-6.9 (m, 4 H)		OMe 3.12 (s, 3 H)	7.2-7.5 (m, 15 H)
1f, $AuMe_2(C_6H_4$-*o*-Me$)(PPh_3)$	0.18 (d, 7.3, 3 H)	1.11 (d, 9.0, 3 H)		6.7-7.2 (m, 4 H)		Me 1.94 (s, 3 H)	7.2-7.6 (m, 15 H)
2, $AuMe_2(C_6H_5)P(C_6H_4$-*p*-OMe$)_3$	0.17 (d, 7.3, 3 H)	1.12 (d, 8.8, 3 H)	7.09 (d, 7.8, 2 H)	7.00 (t, 7.8, 2 H)	6.89 (t, 7.8, 1 H)		6.7-7.2 (m, 12 H), OMe 3.80 (s, 9 H)
3, $AuMe_2(C_6H_5)P(C_6H_4$-*p*-Me$)_3$	0.16 (d, 7.1, 3 H)	1.13 (d, 9.0, 3 H)	7.00 (d, 7.3, 2 H)	6.87 (t, 7.3, 2 H)	6.77 (t, 7.3, 1 H)		7.1-7.2 (m, 12 H), Me 2.36 (s, 9 H)
4, $AuMe_2(C_6H_5)P(C_6H_4$-*p*-F$)_3$	0.17 (d, 7.6, 3 H)	1.19 (d, 9.0, 3 H)		6.7-7.0 (br, 5 H)			7.0-7.3 (m, 12 H)
5, $AuMe_2(C_6H_5)P(C_6H_4$-*o*-Me$)_3$	-0.05 (d, 7.6, 3 H)	1.19 (d, 8.8, 3 H)		6.7-7.0 (br, 5 H)			7.1-7.4 (m, 13 H), Me 1.95 (s, 9 H)
6, $AuMe_2(C_6H_5)PPh(C_6H_4$-*o*-Me$)_2$	0.01 (d, 7.8, 3 H)	1.19 (d, 8.8, 3 H)	6.98 (d, 7.8, 2 H)	6.87 (t, 7.8, 2 H)	6.83 (t, 7.8, 1 H)		7.1-7.4 (m, 13 H), Me 2.15 (s, 6 H)
7, $AuMe_2(C_6H_5)PPh_2(C_6H_4$-*o*-Me$)$	0.04 (d, 7.8, 3 H)	1.18 (d, 9.0, 3 H)	7.10 (d, 7.9, 2 H)	6.95 (t, 7.9, 2 H)	6.84 (t, 7.9, 1 H)		7.1-7.4 (m, 14 H), Me 2.40 (s, 3 H)

[a] Parts per million in $CDCl_3$ at room temperature. Chemical shifts are referred to internal Me_4Si, and the numbers in parentheses indicate coupling constants in hertz. Abbreviations: s, singlet; d, doublet; t, triplet; dd, double doublet; ddd, double double doublet; m, multiplet; br, broad.

Table III. $^{13}C\{^1H\}$ NMR Spectra of Complexes 1-7[a]

compound	Au-Me cis to P	Au-Me trans to P	PR_3 and Au-Ar
1a, $AuMe_2(C_6H_4$-*p*-OMe)(PPh_3)	7.40 (d, 7.3)	15.29 (d, 118.7)	114-159, OMe 55.10
1b, $AuMe_2(C_6H_4$-*p*-Me)(PPh_3)	7.39 (d, 5.9)	15.17 (d, 118.7)	126-165, Me 20.85
1c, $AuMe_2(C_6H_5)(PPh_3)$	7.08 (d, 7.3)	15.08 (d, 117.2)	122-169
1d, $AuMe_2(C_6H_4$-*p*-F)(PPh_3)	7.04 (d, 5.9)	15.20 (d, 98.7)	114-164
1e, $AuMe_2(C_6H_4$-*o*-OMe)(PPh_3)	6.86 (d, 5.9)	13.13 (d, 118.7)	123-169, OMe 53.93
1f, $AuMe_2(C_6H_4$-*o*-Me)(PPh_3)	7.81 (d, 7.3)	12.37 (d, 115.8)	122-169, Me 24.53
2, $AuMe_2(C_6H_5)P(C_6H_4$-*p*-$OMe)_3$	7.18 (d, 5.9)	14.95 (d, 115.8)	113-162, OMe 55.19
3, $AuMe_2(C_6H_5)P(C_6H_4$-*p*-$Me)_3$	7.20 (d, 7.3)	14.78 (d, 120.2)	122-169, Me 22.66
4, $AuMe_2(C_6H_5)P(C_6H_4$-*p*-$F)_3$	7.04 (d, 5.9)	15.20 (d, 118.9)	115-169
5, $AuMe_2(C_6H_5)P(C_6H_4$-*o*-$Me)_3$	6.95 (d, 5.9)	15.19 (d, 115.8)	123-168, Me 22.75 (d, 11.7)
6, $AuMe_2(C_6H_5)PPh(C_6H_4$-*o*-$Me)_2$	7.36 (d, 5.9)	15.78 (d, 115.8)	123-169, Me 22.76 (d, 7.3)
7, $AuMe_2(C_6H_5)PPh_2(C_6H_4$-*o*-Me)	7.88 (br)	16.25 (d, 115.8)	115-169, Me 22.60 (d, 5.6)

[a] Parts per million in $CDCl_3$ at room temperature. Chemical shifts are referred to internal Me_4Si and the numbers in parentheses indicate coupling constants with phosphorus nucleus in hertz. Abbreviations: d, doublet; br, broad.

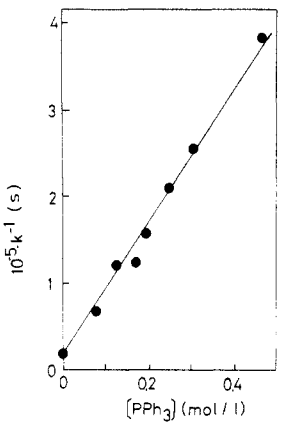
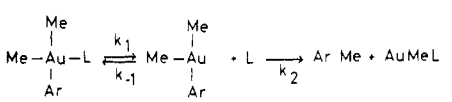


Figure 1. Relation of the reciprocal of k_1 with the concentration of the triphenylphosphine ligand for **1c** in C_6D_6 at 70 °C.

followed by ^1H NMR and found to be the first order in the concentration of 1.

$$-d/dt[1] = k_{obsd}[1] \quad (2)$$

The rate of the thermolysis of 1 was strongly suppressed by the addition of free tertiary phosphine. The reciprocal plot of the pseudo-first-order rate constant, k_{obsd}, vs. the concentration of added phosphine gives a straight line as shown in Figure 1. From these kinetic results, the following dissociative mechanism has been proposed (eq 3).



(3)

Complex 1 dissociates L to give an unstable T-shaped intermediate, from which facile cis reductive elimination of methyl and aryl ligands in adjacent positions takes place. As we previously demonstrated in the reductive elimination of trialkylgold(III) complexes,[1a] the following rate equation for the thermolysis of 1 has been derived by assuming the steady-state approximation of the coordinatively unsaturated intermediate $AuArMe_2$.

$$-\frac{d[1]}{dt} = \frac{k_1k_2[1]}{k_2 + k_{-1}[L]} = k_{obsd}[1] \quad (4)$$

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}[L] \quad (5)$$

Thus, the intercept and slope in Figure 1 correspond to $1/k_1$ and k_{-1}/k_1k_2, respectively.

The estimated phosphine dissociation rate constants, k_1, for complexes 1–7 are listed in Table IV. An electron-withdrawing para substituent such as fluorine on the aryl ligand as well as electron-donating para substituents such as OMe and Me on the aromatic ring in the PAr_3 ligand considerably reduce the rate of phosphine dissociation. The trend is compatible with the coordination of the tertiary phosphine ligand to Au(III) mainly through electron donation from the ligand rather than through π-back-donation as usually considered in soft organotransition-metal complexes.

Table IV. Phosphine Dissociation Rate Constants k_1 for Aryldimethylgold(III) Complexes in C_6D_6

compd	temp, °C	10^5k_1, s^{-1}
1a	70	10.3
1b	70	15.7
1c	70	5.5
	60	4.1
1d	70	2.2
1e	70	1.2
1f	70	2.6
2	70	3.7
3	70	2.4
4	70	12.5
5	60	78.2
6	60	8.5
7	60	5.0

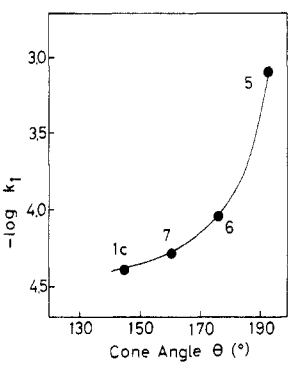


Figure 2. Correlation of dissociation rate constant k_1 for aryldimethyl(triarylphosphine)gold(III) complexes with the cone angle θ of the triarylphosphine ligand in C_6D_6 at 60 °C.

On the other hand, the steric effect of the tertiary phosphine ligand was examined by substituting the phenyl rings of PPh_3 with *o*-tolyl groups. Figure 2 demonstrates the relationship between k_1 and cone angle of $P(C_6H_4$-*o*-$Me)_nPh_{3-n}$. Thus, k_1 dramatically increases with increasing the steric bulkiness of tertiary phosphine ligand, in spite of the increase in the electron-donating property of L by substituting an ortho hydrogen with a methyl group (vide supra). Complex **5**, having the most bulky triarylphosphine ligand employed in this study, liberated the reductive elimination product instantaneously in benzene

at 70 °C. Consequently, both electronic and steric factors of the tertiary phosphine ligand in trialkylgold(III) complexes play an important role in the ligand dissociation step, followed by reductive elimination from an unstable T-shaped intermediate. The contradicting tendency of the electron-donating ortho substituent on the aryl ligand to suppress the k_1 value is controversial.[8]

It is of interest to note the relationship between kinetic and thermodynamic aspects for the ligand dissociation from aryldimethyl(triarylphosphine)gold(III). Since the rate of the reductive elimination from the T-shaped intermediate, k_2, for the series of $AuPhMe_2L$ (**1c**, **2–7**) should be constant, relative values of both the equilibrium constant K ($= k_1/k_{-1}$) for the ligand dissociation and ligand association rate constant k_{-1} can be evaluated from the slope in Figure 1. The values of slope are found to be proportional to k_1^{-1}, so that the value of k_{-1}/k_2 (ca. 60 mol/L at 60 °C and 36 mol/L at 70 °C) becomes constant for these compounds. Therefore, the k_{-1} value is considered to be invariable without regard to the type of triarylphosphine ligand employed. Namely, only the ligand dissociation process (k_1), but not the ligand association process (k_{-1}), is affected by the apparent change of both steric and electronic properties of the tertiary phosphine ligand. Thus, the kinetic ease of phosphine dissociation (k_1) is considered to reflect on the ligand dissociation equilibrium constant K. Stabilization of the square-planar trialkylgold(III) complexes having a tertiary phosphine ligand probably originated from the thermodynamic stability of **1** itself, giving rise to the high activation energy for the phosphine dissociation process.[9]

Experimental Section

Materials and Measurements. Solvents dried by usual methods, distilled, and stored under nitrogen before use. Aryl Grignard reagents were prepared from the corresponding aryl halides and Mg in ether under nitrogen. *cis*-Dimethyliodo(triarylphosphine)gold(III) complexes were synthesized by the following two methods. One is the iodinolysis of $AuMe_3L$ (L = PPh_3, $P(C_6H_4\text{-}p\text{-}Me)_3$),[10] and another is the reaction of $(Me_2AuI)_2$[11] with 2 mol of triarylphosphine[12] (L = $P(C_6H_4\text{-}p\text{-}OMe)_3$, $P(C_6H_4\text{-}p\text{-}F)_3$, $P(C_6H_4\text{-}o\text{-}Me)_3$, $PPh(C_6H_4\text{-}o\text{-}Me)_2$, $PPh_2(C_6H_4\text{-}o\text{-}Me)$). These complexes were purified by recrystallization from suitable solvents.

Elemental analyses were performed by using Yanagimoto CHN autocorder type MT-2. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on JEOL FX-200 and MH-60 spectrometers.

Preparation of *cis*-Aryldimethyl(triarylphosphine)gold(III). A typical procedure of the preparation for **1a** is shown below. Yields, decomposition points, analytical data, and ^1H and ^{13}C NMR spectra of these complexes are summarized in Tables I–III.

An etheral suspension of $Me_2IAu(PPh_3)$ (549 mg, 0.890 mmol) was treated with an excess of $(C_6H_4\text{-}p\text{-}OMe)MgBr$ (2 mL of 1.1 M solution) at 0 °C. After the mixture had been stirred for 3 h at room temperature, it was slowly hydrolyzed with deoxygenated water at 0 °C. The ether layer and benzene extracts were collected, and solvents were removed by evaporation. The resulting colorless solid was recrystallized from a benzene–pentane mixture; yield 308 mg (58%).

Kinetics of the Thermal Reductive Elimination. Requisite amounts of the *cis*-aryldimethyl(triarylphosphine)gold(III) complex and the triarylphosphine in an NMR tube were dissolved in 0.50 mL of benzene-d_6. The sealed NMR tube was placed in a thermostated oil bath (±1 °C) and removed periodically for NMR analysis. The amounts of *cis*-aryldimethylgold(III) complex and products were determined by measuring the peak areas of the resonances relative to the 1,4-dioxane added as an internal standard.

Registry No. **1a**, 94859-24-2; **1b**, 66485-01-6; **1c**, 42029-61-8; **1d**, 94859-25-3; **1e**, 94859-26-4; **1f**, 94889-67-5; **2**, 94859-27-5; **3**, 94859-28-6; **4**, 94859-29-7; **5**, 94859-30-0; **6**, 94859-31-1; **7**, 94859-32-2; $Au^IMe(PPh_3)$, 23108-72-7; $Me_2IAu(PPh_3)$, 34275-48-4; $Me_2IAu(P(C_6H_4\text{-}p\text{-}OMe)_3)$, 94859-33-3; $Me_2IAu(P(C_6H_4\text{-}p\text{-}Me)_3)$, 94859-34-4; $Me_2IAu(P(C_6H_4\text{-}p\text{-}F)_3)$, 94859-35-5; $Me_2IAu(P(C_6H_4\text{-}o\text{-}Me)_3)$, 94859-36-6; $Me_2IAu(PPh(C_6H_4\text{-}o\text{-}Me)_2)$, 94859-37-7; $Me_2IAu(PPh_2(C_6H_4\text{-}o\text{-}Me)_2)$, 94859-38-8; $MeC_6H_4\text{-}p\text{-}OMe$, 104-93-8; $MeC_6H_4\text{-}p\text{-}Me$, 106-42-3; C_6H_5Me, 108-88-3; $MeC_6H_4\text{-}p\text{-}F$, 352-32-9; $MeC_6H_4\text{-}o\text{-}OMe$, 578-58-5; $MeC_6H_4\text{-}o\text{-}Me$, 95-47-6; $p\text{-}OMeC_6H_4MgBr$, 13139-86-1; $p\text{-}MeC_6H_4MgBr$, 4294-57-9; C_6H_5MgBr, 100-58-3; $p\text{-}FC_6H_4MgBr$, 352-13-6; $o\text{-}OMeC_6H_4MgBr$, 36282-40-3; $o\text{-}MeC_6H_4MgBr$, 932-31-0; PPh_3, 603-35-0; $P(C_6H_4\text{-}p\text{-}OMe)_3$, 855-38-9; $P(C_6H_4\text{-}p\text{-}Me)_3$, 1038-95-5; $P(C_6H_4\text{-}p\text{-}F)_3$, 18437-78-0; $P(C_6H_4\text{-}o\text{-}Me)_3$, 6163-58-2; $PPh(C_6H_4\text{-}o\text{-}Me)_2$, 18803-08-2; $PPh_2(C_6H_4\text{-}o\text{-}Me)$, 7579-70-6.

(8) Interaction of the ortho substituent in the aryl ligand with the square-planar Au(III) metal to fix the aryl group perpendicular to the coordinating plane might reduce the steric hinderance when the phosphine ligand coordinates. Further detailed study is required in order to clarify this point.

(9) The positive value of activation entropy estimated for the dissociation of L from **4** ($\Delta S^* = 167$ J/K·mol) is consistent with the proposed dissociative mechanism.

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