Photolysis and Photoinduced Isomerization of Cis-Trans Diethylbis(tertiary phosphine)palladium(II)[†]

Fumiyuki Ozawa and Akio Yamamoto*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Yokohama 227, Japan

Takao Ikariya and Robert H. Grubbs*

Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125

Received June 2, 1982

The photolysis of dialkylpalladium phosphine complexes has been investigated. In contrast to the thermal chemistry, the photolysis products of the diethyl complex are independent of the starting stereochemistry and the metallacyclopentane yielded the C–C bond cleavage product ethylene rather than 1-butene, the thermal product. The dimethyl complex showed a facile photoinduced cis–trans isomerization. Structures for the photointermediate are proposed.

Introduction

Photochemistry of organotransition-metal complexes is attracting growing attention.[1] There are reports of fundamental and extreme differences between the thermal and photochemistry of some group 8 metallacycles[2,3] and suggestions of homolytic cleavage of metal–alkyl bonds on irradiation of simple alkyl systems.[4] However, mechanistic studies comparing thermal and photochemical reactions of isolated alkyl transition-metal complexes are still scarce. To complement our other studies, we have examined the photochemistry of dialkylpalladium complexes whose thermal chemistry is well established.[5-7] *cis*- and *trans*-diethylbis(tertiary phosphine)palladium represent intriguing examples of complexes which are thermolyzed through totally different routes depending on the stereochemical configurations of the diethyl complexes.

We now report the photochemical properties of these complexes together with a palladium metallacycle focusing on the similarities and differences of the thermal and photochemical reactions.

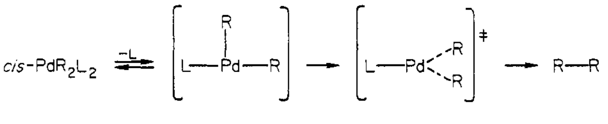
Before describing the results of the photochemical studies, a brief summary of the thermal reactions of the *cis*- and *trans*-dialkylpalladium complexes is given for comparison.

trans-$PdEt_2L_2$ (where L = monodentate tertiary phosphines) are thermally decomposed in toluene with liberation of a 1:1 mixture of ethylene and ethane (eq 1). The

$$trans\text{-}PdEt_2L_2 \xrightarrow[\text{toluene}]{} C_2H_4 + C_2H_6 \qquad (1)$$

thermolysis is only weakly hindered by added tertiary phosphine, indicating that the major thermolysis pathway does not involve the partial dissociation of the coordinated tertiary phosphine ligands. Thermolysis of *trans*-$Pd(CH_2CD_3)_2L_2$ cleanly liberated $CH_2{=}CD_2$ and CH_2DCD_3, indicating a β-hydrogen elimination pathway.

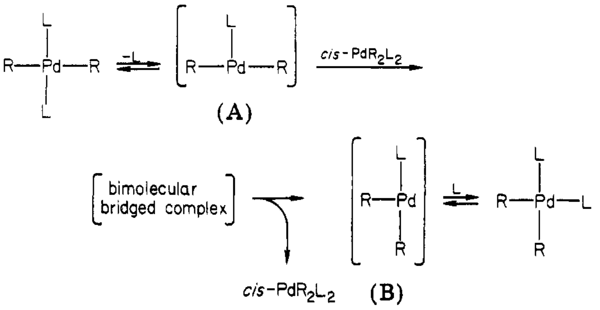
In contrast to the behavior of *trans*-$PdEt_2L_2$, the cis isomers afforded reductive elimination products exclusively (ethane from *cis*-$PdMe_2L_2$ and butane from *cis*-$PdEt_2L_2$) by a process involving the rate-determining dissociation of a tertiary phosphine ligand (eq 2).[6,7]



(2)

Again, no H–D scrambling was observed in the thermolysis of *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$ which cleanly liberated $CD_3CH_2CH_2CD_3$.

Cis-trans isomerization also proceeded via a pathway involving ligand dissociation (eq 3). The presence of an



(3)

energy barrier between the T-shaped "*trans*"-dialkylpalladium species (A) and the T-shaped "*cis*"-dialkylpalladium species (B) was indicated by the kinetic study[6,7] and supported by MO theoretical calculations.[8]

Results

Photolysis of *cis*- and *trans*-$PdEt_2L_2$. Toluene solutions (2×10^{-2}–0.1 mol L^{-1} of *cis*- and *trans*-diethylpalladium complexes coordinated with various tertiary phosphine ligands were irradiated in quartz Schlenk tubes at 2 °C and −10 °C, and the evolved gases were collected and analyzed (Table I). Under these conditions, other decomposition modes are slow. For displacing the coordinated ethylene and trapping the Pd(0) species formed on photolysis, we added diphenylacetylene to the system. It was confirmed that the addition of diphenylacetylene had little effect on the course of reaction.

[†] Contribution No. 6658.

(1) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(2) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. *J. Am. Chem. Soc.* **1977**, *99*, 3863.

(3) Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1980**, *191*, 481.

(4) (a) Bamford, C. H.; Puddephatt, R. J.; Slaten, D. M. *J. Organomet. Chem.* **1978**, *159*, C31. (b) Hackelberg, O.; Wojcicki, A. *Inorg. Chim. Acta* **1980**, *44*, L63. (c) van Leeuwen, P. W. N. M.; Roobeck, C. F.; Huis, R. *J. Organomet. Chem.* **1977**, *142*, 233.

(5) Ozawa, F.; Ito, T., Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 6457.

(6) Ozawa, F.; Ito, T.; Nakamura, Y., Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1968.

(7) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

(8) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857.

0276-7333/82/2301-1481$01.25/0

Table I. Gases Evolved on Photolysis of $PdEt_2L_2$[a]

run	complex (mol/L)	additive (mol/L)	time, h	evolved gas ratio[b]: C_2H_4 + C_2H_6	C_4H_{10}	total,[c] %
1	*cis*-$PdEt_2(PMe_2Ph)_2$ (0.10)	PhC≡CPh (0.14)	5.5	0.79	0.21	100
2	*cis*-$PdEt_2(PMe_2Ph)_2$ (0.10)	PhC≡CPh (0.14) PMe_2Ph (0.17)	6.0	0.90	0.10	64
3	*cis*-$PdEt_2(PMe_2Ph)_2$	PhC≡CPh PMe_2Ph (excess)	1.5	0.98	0.02	e
4	*trans*-$PdEt_2(PMe_2Ph)_2$ (0.11)	PhC≡CPh (0.14)	5.5	0.82	0.18	92
5	*trans*-$PdEt_2(PEt_3)_2$ (0.14)	PhC≡CPh (0.28)	7.5	0.80	0.20	100
6	*trans*-$PdEt_2(PEt_2Ph)_2$ (0.14)	PhC≡CPh (0.28)	7.5	0.82	0.18	99

[a] At 2 °C in toluene, 400-W high-pressure Hg lamp was used. [b] $[C_2H_4]/[C_2H_6] \simeq 1$. [c] $100\,\{^1/_2([C_2H_4] + [C_2H_6]) + [C_4H_{10}]\}/[\text{complex}]$. [d] −10 °C, in toluene, quartz Schlenk tube. [e] Photolysis incomplete.

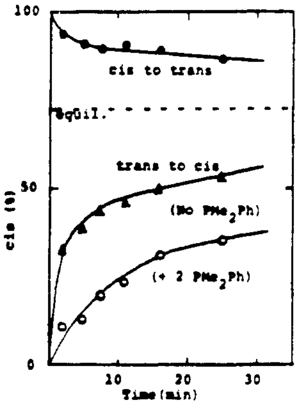
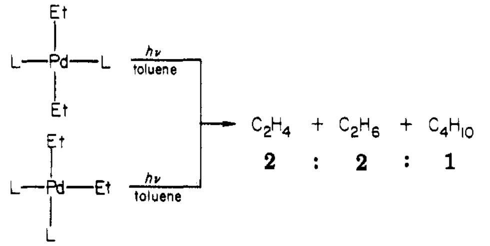


Figure 1. Time course of the photoisomerizations. A 100-W high-pressure Hg lamp was used.

When the photolysis was carried out in the absence of added tertiary phosphine, the *cis*- and *trans*-$PdEt_2L_2$ liberated ethylene, ethane, and butane in a 2:2:1 ratio irrespective of the configuration of the starting diethyl complexes (eq 4; runs 1 and 4–6 in Table I).



(4)

These results stand in a sharp contrast with the thermolysis results in which the configuration of the starting complex dictates the thermolysis products (eq 1 and 2). Photolysis of the cis isomer in a toluene-d_8 solution gave a 1:1 mixture of ethylene and ethane together with butane without deuterium incorporation.

$$cis\text{-}Pd(C_2H_5)_2(PMe_2Ph)_2 + C_7D_8 \xrightarrow{h\nu} CH_2{=}CH_2 + CH_3CH_3 + C_4H_{10}$$

In the photolysis of *cis*-$PdEt_2(PMe_2Ph)_2$ addition of PMe_2Ph to the system markedly slowed the photolysis rate and changed the distribution of the photolysis products. It was observed that addition of the ligand hindered the formation of butane more severely than the formation of ethylene and ethane (runs 2 and 3).

Photolysis of *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$ in toluene cleanly liberated $CD_2{=}CH_2$, CH_2DCD_3, and $CD_3CH_2CH_2CD_3$, indicating the absence of H–D scrambling.

$$cis\text{-}Pd(CH_2CD_3)_2(PMe_2Ph)_2 \xrightarrow{h\nu} CD_2{=}CH_2 + CH_2DCD_3 + CD_3CH_2CH_2CD_3 \quad (5)$$

During the photolysis, cis–trans isomerization took place concurrently as observed by $^{31}P\{^1H\}$ NMR spectroscopy. *cis*-$PdEt_2(PMe_2Ph)_2$ in toluene at −20 °C shows a $^{31}P\{^1H\}$ chemical shift at −5.5 ppm (referred to PPh_3, downfield positive), whereas *trans*-$PdEt_2(PMe_2Ph)_2$ at 8.1 ppm and a photolysis product (presumably $Pd(PMe_2Ph)_2(PhCCPh)_x$) at −3.8 ppm. The photoisomerization occurs more rapidly than the thermal isomerization.

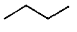
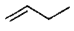
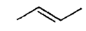
$$\underset{}{cis\text{-}PdEt_2(PMe_2Ph)_2} \xrightarrow[2\ ^\circ C,\ 1\ h,\ PhC\equiv CPh]{h\nu,\ toluene} \underset{45\%}{cis\text{-}PdEt_2(PMe_2Ph)_2} + \underset{2\%}{trans\text{-}PdEt_2(PMe_2Ph)_2} + \underset{53\%}{\text{decomp products}}$$

$$trans\text{-}PdEt_2(PMe_2Ph)_2 \xrightarrow[2\ ^\circ C,\ 1\ h,\ PhC\equiv CPh]{h\nu,\ toluene} \underset{11\%}{cis\text{-}PdEt_2(PMe_2Ph)_2} + \underset{34\%}{trans\text{-}PdEt_2(PMe_2Ph)_2} + \underset{55\%}{\text{decomp products}}$$

Photoisomerization of *cis*- and *trans*-$PdMe_2(PMe_2Ph)_2$. In order to get more information on the photoinduced cis–trans isomerization, thermally stable *cis*- and *trans*-$PdMe_2(PMe_2Ph)_2$ in acetone-d_6 sealed in Pyrex NMR tubes were irradiated at 6 °C with a 400-W high-pressure mercury lamp and the course of isomerization was followed by ^1H NMR spectroscopy. Under these conditions, thermolysis was slow.

The photoinduced isomerization took place much more rapidly than the thermal reaction. *trans*-$PdMe_2(PMe_2Ph)_2$ of initial concentrations of 0.12 and 0.064 mol/L was transformed into its cis isomer in 8 min with conversions of 64 and 66%, respectively. When the acetone-d_6 solution of the same initial concentration (0.12 mol/L) containing 0.23 mol/L of added PMe_2Ph was similarly irradiated by the 400 W Hg lamp at 6 °C for 8 min, 37% of the trans isomer was photoisomerized to the cis isomer. Thus, the photoisomerization is inhibited by added phosphine. The time evolution of the photochemical reactions is illustrated in Figure 1. These results indicated that the rate of photoisomerization was independent of the initial concentration of the *trans*-$PdEt_2L_2$; i.e. reaction may be first order in the concentration of the complex as judged from the time–conversion curve. A detailed kinetic study was not attempted, since the photoisomerization was accompanied by photodecomposition to ethane. About 5% of the dimethylpalladium was photolyzed in these experiments. The equilibrium of *trans*- and *cis*-$PdMe_2(PMe_2Ph)_2$ lay on the side of the cis isomer. The photoisomerization from the cis to trans isomer can also be followed spectrophotometrically, although the change is less marked than in the trans → cis isomerization (Figure 1). The system approached an equilibrium at cis/trans

Table II. Gases Evolved on Thermolysis and Photolysis of $\overline{Pd(CH_2CH_2CH_2CH_2})(PMe_2Ph)_2$

			evolved gas ratio					
run	conditns	additive	C_2H_4					
1	*a*		0	0	2	98	0	0
2	*b*		76	0	3	21	0	0
3	*b*	PhC≡CPh	75	0	3	22	0	0
4	*b*	PhC≡CPh PMe_2Ph (excess)	80	1	2	17	0	0

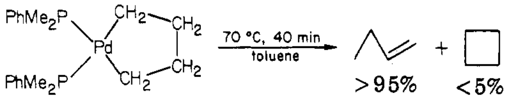
[a] Thermolysis, at 70 °C in toluene. [b] Photolysis, at −15 °C in toluene, a 450-W medium-pressure Hg lamp was used.

ratio of 7:3 after irradiation of 1 h. This reaction almost certainly involves nonradical intermediates.

To complement the study of photodecomposition and thermal decomposition of diethylpalladium complexes, photodecomposition and thermal decomposition behavior of the corresponding palladacyclopentane was examined.

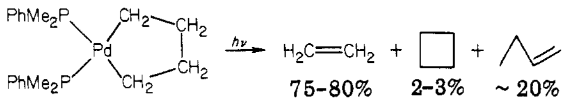
Bis(dimethylphenylphosphine)palladacyclopentane was prepared from $PdCl_2(PMe_2Ph)_2$ and 1,4-dilithiobutane in ether at room temperature as colorless crystals. Table II summarizes the thermolysis and photolysis results of the palladacyclopentane.

Thermolysis of the palladacyclopentane in toluene at 70 °C for 40 min liberated 1-butene as the major product accompanied by a minor amount of cyclobutane (eq 6). No ethylene, butane, or 2-butene was detected.



(6)

The decomposition course is dramatically altered on photolysis. Ethylene is formed as the predominant photolysis product with minor amounts of 1-butene and cyclobutane (eq 7).



(7)

The addition of the tertiary phosphine changed the photoreaction only slightly.

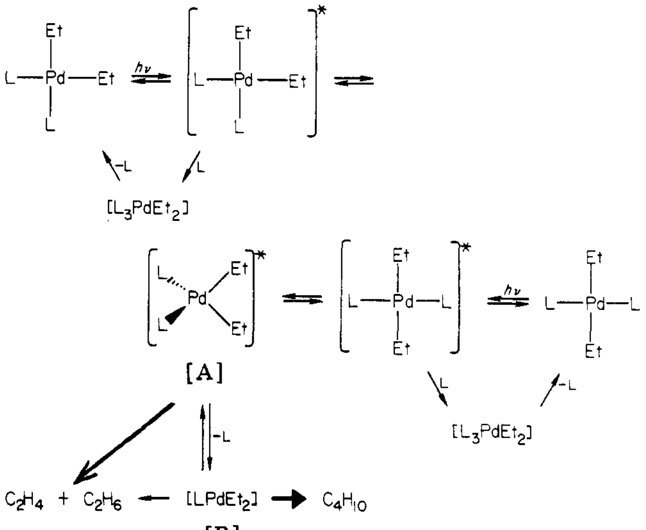
Similar change of the decomposition pathways in thermal and photochemical decompositions was observed in the reactions of trimethylphosphine-coordinated nickellacyclopentanes.[9] The results will be reported separately.

Discussion

Unlike the thermal reactions, the products of the photolysis of diethylpalladium complexes are independent of the starting isomer. This suggests that both isomers are photolyzed through a common intermediate or intermediates that rapidly equilibrate with each other. On first sight, it might appear that this could be explained by a photoinduced homolytic cleavage of the metal–alkyl bond. However, the lack of deuterium incorporation into the products when the reaction was carried out in deuterated solvents, the 1:1 ratio of C_2H_4/C_2H_6, and the changes in rates and products when the phosphine ligands were added to the system, as well as no H–D scrambling in photolysis of *cis*- and *trans*-$Pd(CH_2CD_3)_2L_2$, exclude the radical pathways.

As a possible mechanism to account for the results of the photochemical reactions of the ethylpalladium complexes, Scheme I is proposed. In this scheme a photoactivated tetrahedral species, [A], is assumed as a common intermediate that may be produced through photoactivated square-planar species formed from *cis*- and *trans*-$PdEt_2L_2$. Ethylene and ethane may result from [A] as is observed in thermolysis of *trans*-$PdEt_2L_2$. This thermal reaction has been proposed to proceed through a distorted pseudotetrahedral species promoted by the steric influence of the phosphine ligands.[5] Butane may be formed in a reductive elimination process directly from [A] or more likely through the three-coordinate intermediate [B] formed by partial dissociation of the phosphine ligand from [A]. The inhibitory effect of the addition of the phosphine may be accounted for as quenching of the photoactivated species. Addition of the phosphine suppresses the formation of butane, presumably by blocking the reductive elimination pathway from [B]. The photoinduced isomerization between the cis and trans isomers is also accommodated in this scheme by assuming the common tetrahedral intermediate [A]. Photoinduced trans–cis isomerization of $Pd(PR_3)_2Cl_2$-type complexes is known, and the isomerization was explained by a mechanism proceeding through a tetrahedral intermediate.[10]

Scheme I



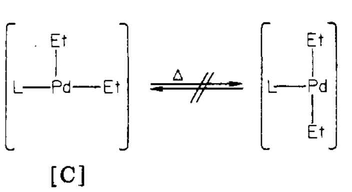
[B]

As an alternate to Scheme I, a mechanism without involvement of the tetrahedral species is also conceivable. In this case, the photoisomerization may proceed by interconversion of planar three-coordinated T-shaped species $PdEt_2L$ formed by dissociation of L from $PdEt_2L_2$. The intramolecular polytopal isomerization between the "trans" and "cis" T-shaped species shown in eq 8 did not proceed

---

(9) Ikariya, T.; Grubbs, R. H., unpublished data.

(10) (a) Alcock, N. W.; Kemp, T. J.; Wimmer, F. J. *J. Chem. Soc., Dalton Trans.* **1981**, 635. (b) Haake, P.; Hylton, T. A. *J. Am. Chem. Soc.* **1962**, *84*, 3374. (c) Mastin, S. H.; Haake, P. *J. Chem. Soc., Chem. Commun.* **1980**, 202. (d) Cusumano, M.; Gugliemo, G.; Ricevuto, V.; Traverse, O.; Kemp, T. J. *J. Chem. Soc., Dalton Trans.* **1981**, 302.



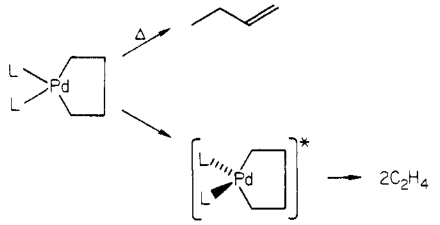
(8)

[C]

as shown by the kinetic studies,[6,7] and the MO calculation indicates that the Y-shaped intermediate for the isomerization has a high energy.[8] This process through a Y-shaped transition state may occur rapidly under the influence of light. The formation of ethylene and ethane as well as of butane may be explained as in thermal reactions (eq 1 and 2). Suppression of butane formation by addition of the phosphine can be also accommodated in this scheme as blocking the formation of the three-coordinate species. A possible mechanism is presented in Scheme II.

The presently available data without information on the nature of the photoexcited species do not allow us to decide which mechanism is operative. The results with metallacyclopentanes, however, provide us complementary information that is more consistent with the mechanism through the tetrahedral intermediate.

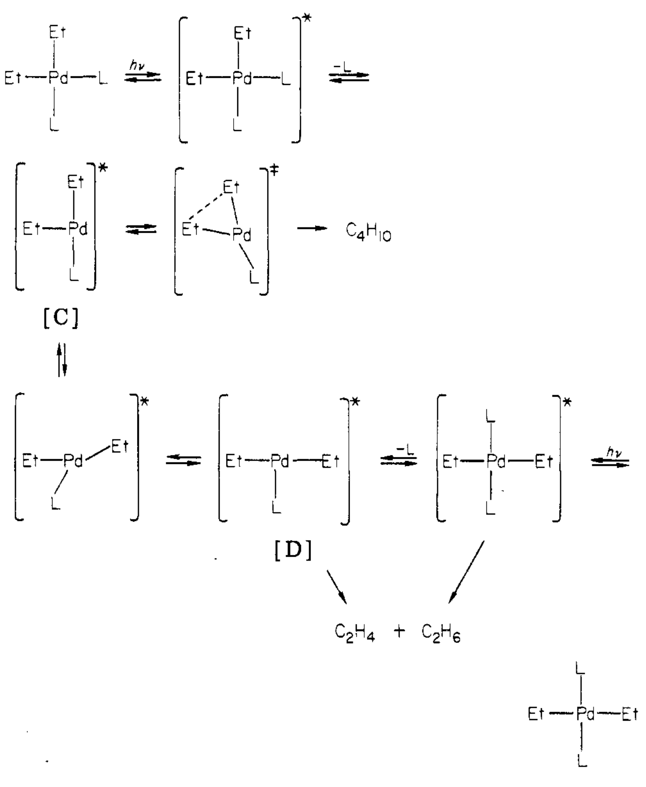
Photolysis of the palladacyclopentane liberates ethylene as a major product while thermolysis of the same complex releases no ethylene and affords only 1-butene. The result is more consistent with assumption of the photoactivated tetrahedral intermediate.



If we assume that the photo-activation leads to a three-coordinated species $[LPd(CH_2)_4]^*$ as in with Scheme II, it seems more likely that the photolysis would produce cyclobutane or 1-butene since the three-coordinated species seems to be favorable for reductive elimination as in thermolysis of *cis*-$PdEt_2L_2$ or of the palladacyclopentane. It has also been demonstrated that the corresponding platinum metallacyclopentanes decompose to 1-butene through three-coordinate intermediates on thermolysis.[11] The tetrahedral configuration may be more suitable for including rupture of the metallacyclopentane to form ethylene. This assumption is supported by MO calculations by Hoffmann and his co-workers.[12] According to their results, the process producing ethylene from a metallacyclopentane is thermally disallowed and photochemically allowed. The clear-cut difference between the photochemical and thermal decomposition behavior of the palladacyclopentane may be taken as the indication of the occurrence of the completely different pathways in the thermal and photochemical reactions.

Obviously, more work is needed concerning the nature of the photoactivated species of the organopalladium complexes. Nevertheless, the striking change of the decomposition pathways from thermal to photochemical reactions of these organopalladium complexes is noteworthy. The control of the reaction course by means of light may have some potentiality in designing palladium-promoted organic reactions.

Scheme II



Experimental Section

All manipulations were carried out under an atmosphere of nitrogen or argon or in vacuo. Solvents were dried in the usual manner, distilled, and stored under an atmosphere of nitrogen.

Infrared spectra were recorded on a Hitachi 295 spectrometer. ^1H NMR spectra were measured on JEOL PS-100 and FX90Q spectrometers. Analysis of the gases evolved by the reactions were carried out by gas chromatography (Shimadzu GC-3BT or Varian 1400GC, Porapak Q column) after the gases were collected by using a Toepler pump, by which the volumes of gases were also measured. Analysis of the gases dissolved in solution was also carried out by gas chromatography using propane as an internal standard after the volatile matters were collected in the reaction solution by a trap-to-trap distillation. Mass spectra were measured on a Hitachi M-80 GC-MS spectrometer.

A series of *cis*- and *trans*-$PdEt_2L_2$, and *cis*- and *trans*-$PdMe_2(PMe_2Ph)_2$ complexes were prepared according to the method described previously.[5,6]

Photolysis was performed with 400- or 100-W high-pressure Hg lamps contained in a quartz well submerged in a bath thermostated at low temperatures (−30 to +6 °C).

Photolysis of *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$. *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$ was prepared according to the method described previously.[5] It was confirmed by mass spectrometry and IR spectroscopy[6] that ethylene and ethane evolved on photolysis of *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$ at 2 °C in toluene containing $PhC{\equiv}CPh$ were only $CD_2{=}CH_2$ (*m/e* 30) and $C_2D_4H_2$ (*m/e* 34), respectively; IR ($CD_2{=}CH_2$) 943 and 750 cm^{-1}.

Preparation of Bis(dimethylphenylphosphine)palladacyclopentane. To an orange heterogeneous mixture of $PdCl_2(PMe_2Ph)_2$ (1.9 g, 4.2 mmol) and Et_2O (10 mL) was added an Et_2O solution (20 mL) of $Li(CH_2)_4Li$ (5.9 mmol) at −50 °C. The system was stirred at room temperature to give a heterogeneous pale yellow mixture containing a white precipitate of LiCl. Stirring was continued for 4 h. After hydrolysis at 0 °C, evaporation of the ether phase by pumping afforded a crude product of $Pd(CH_2CH_2CH_2CH_2)(PMe_2Ph)_2$. The crude product was recrystallized from Et_2O–acetone to yield colorless prisms of $Pd(CH_2CH_2CH_2CH_2)$ $(PMe_2Ph)_2$ (0.93 g, 46%): ^1H NMR [δ (ppm) at

---

[11] Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.

[12] McKinney, R. J.; Thorn, D. L.; Hoffmann, R.; Stockis, A.; *J. Am. Chem. Soc.* **1981**, *103*, 2595.

31 °C, $CDCl_3$] 1.5–2.0 (br, $\overline{PdCH_2CH_2CH_2CH_2}$, 8 H), 1.32 (d, $^2J_{P-H}$ = 6 Hz, PCH_3, 12 H), 7.23 (m, PPh, 10 H). Anal. Calcd for $C_{20}H_{30}P_2Pd$: C, 54.7; H, 6.9. Found: C, 54.9; H, 6.9.

Acknowledgment. This work was partly supported by U.S.–Japan Cooperative Science Program jointly sponsored by the National Science Foundation and the Japan Society for the Promotion of Science and by the National Science Foundation (Grant CHE-79-04814).

Registry No. *cis*-$PdEt_2(PMe_2Ph)_2$, 77881-06-2; *trans*-$PdEt_2(PMe_2Ph)_2$, 75108-70-2; *trans*-$PdEt_2(PEt_3)_2$, 60885-31-6; *trans*-$PdEt_2(PEt_2Ph)_2$, 75108-73-5; $\overline{Pd(CH_2CH_2CH_2CH_2})(PMe_2Ph)_2$, 82871-37-2; *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$, 79075-56-2; $PdCl_2(PMe_2Ph)_2$, 15616-85-0; $Li(CH_2)_4Li$, 2123-72-0; *cis*-$PdMe_2(PMe_2Ph)_2$, 82871-38-3; *trans*-$PdMe_2(PMe_2Ph)_2$, 82916-00-5.

Organometallic Chemistry. 19. Correlation of ^{29}Si to ^{13}C NMR Chemical Shifts in Analogous Compounds. Application in Attempted Preparation of Silicenium Ions[1]

George A. Olah* and Leslie D. Field

Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089

Received April 27, 1982

Although the parallel between ^{29}Si NMR chemical shifts in silicon compounds and ^{13}C NMR chemical shifts in the analogous carbon compounds has been recognized, no systematic study was made to explore the relationship. We have carried out such a study extending the relationship from tetraalkyl-substituted silanes to polarized trimethylsilyl halides in search for still elusive stable silicenium ions. Due to the high affinity of silicon for oxygen and fluoride (or chloride), methods used for the preparation of stable carbocations were not applicable. Using bromosilanes and aluminum tribromide, in methylene bromide solution, strongly polarized donor–acceptor complexes of $Me_3Si^{\delta+}Br \rightarrow {}^{\delta-}AlBr_3$ were observed but no free silicenium ions.

Although many long-lived carbenium ions (trivalent carbocations) have been prepared and studied as stable entities in solution,[2] the analogous silicenium ions (trivalent sila cations, R_3Si^+) have never been directly observed in solution or in the solid state. Silicenium ions are well-known in the gas phase as high abundance fragments in the mass spectra of organosilicon compounds.[3] In solution, silicenium ions have been proposed as reaction intermediates in many organosilicon reactions,[4] but attempts directed toward the preparation of stable silicenium ions have been so far unsuccessful.[5] Even under conditions developed for the preparation and study of stable carbocations[2] (low-nucleophilicity systems, low temperatures), the extreme affinity of silicon for oxygen, fluorine, and chlorine usually results in the reaction of solvents (even SO_2, SO_2ClF) and/or reagents (Lewis acid halides, superacidic systems) with the developing electrophilic silicon center (i.e., to yield silyl fluorides, fluorosulfates, trifluoromethyl sulfates, etc.).

The most valuable analytical tool employed to study stable carbocations has been ^{13}C NMR spectroscopy since this permits direct observation of the cationic center. The sensitivity of ^{13}C chemical shifts[6] and coupling constants to changes in hybridization, geometry, and charge density provides specific information concerning the nature of the carbocation. Our interest in the possible preparation of silicenium ions and the need for techniques to characterize such compounds has prompted us to examine the parallels between ^{29}Si chemical shifts in silicon compounds and ^{13}C chemical shifts in the analogous carbon compounds. Close analogies of silicon chemical shifts with carbon chemical shifts have earlier been realized in the case of methyl-substituted silanes.[7]

The Correlation of ^{13}C Chemical Shifts to ^{29}Si Chemical Shifts

Several theoretical treatments of nuclear screening and chemical shift have been developed, but, as yet, no approach provides generally satisfactory values for chemical shifts. The present understanding of chemical shift is based principally on Ramsey's formulation,[8] which disects nuclear screening into diamagnetic and paramagnetic contributions. The paramagnetic term reflects the influence of other atoms (and their electrons) in the molecule on the local magnetic environment of a nucleus; for the lighter nuclei such "substituent effects" are the dominant contributions to chemical shifts. Roberts et al.[9] found that the ^{15}N chemical shifts in amines and related compounds correlate linearly to the ^{13}C chemical shifts of structurally identical hydrocarbons, i.e., $\delta(^{15}N)$ in $R_1R_2R_3N$ and $\delta(^{13}C)$ in $R_1R_2R_3CH$. This implies that the same structural fac-

---

(1) Part 18 see: Olah, G. A.; Garcia-Luna, A. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5036–5039.

(2) For comprehensive reviews see: Olah, G. A. *Top. Curr. Chem.* **1979**, *80*, 19–88.

(3) Weber, W. P.; Felix, R. A.; Willare, A. K. *Tetrahedron Lett.* **1970**, 907–910 and references therein.

(4) (a) Flowers, M. S.; Gusel'nikov, L. E. *J. Chem. Soc. B* **1968**, 419–423. (b) West, R. *Int. Symp. Organosilicon Chem., Sci. Commun.* **1965**, 1–13. (c) Sommer, L. H.; Evans, F., *J. Am. Chem. Soc.* **1954**, *76*, 1186–1187. (d) Sommer, L. H.; Bailey, D. L.; Coulf, J. R.; Whitmore, F. C. *Ibid.* **1954**, *76*, 801–803.

(5) (a) Olah, G. A.; O'Brien, D. H.; Lin, C. Y. *J. Am. Chem. Soc.* **1969**, *91*, 701–706. (b) Brook, A. G.; Pannell, A. K. *Can. J. Chem.* **1970**, *48*, 3679–3693. (c) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 4942–4943. (d) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *Ibid.* **1980**, *102*, 624–628.

(6) See for instance: "NMR and the Periodic Table", Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978.

(7) Kintzinger, J. P. In "NMR—Basic Principles and Progress"; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1981; Vol. 17.

(8) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699–703.

(9) (a) Lichter, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 2495–2500. (b) Duthaler, R. O.; Williamson, K. L.; Giannini, D. D.; Bearden, W. H.; Roberts, J. D. *Ibid.* **1977**, *99*, 8406–8412. (c) Duthaler, R. O.; Roberts, J. D. *Ibid.* **1978**, *100*, 3889–3895. (d) *Ibid.* **1978**, *100*, 3882–3889.

0276-7333/82/2301-1485$01.25/0