emission spectrum is observed even when *cis*-stilbene is excited by 212.8 nm light to the second absorption maximum $\sim$18 000 cm^{-1} above the red limit of *cis*-stilbene fluorescence excitation spectrum.

These spectroscopic observations are explained by the following mechanism: (i) in a free *cis*-stilbene molecule, fluorescence is quenched by isomerization because the Franck-Condon excitation is much above the barrier to isomerization; (ii) in inert gas clusters, intramolecular vibrational relaxation and interactions with the solvent distribute the initial excitation energy among *cis*-stilbene degrees of freedom; (iii) the energy in low-frequency vibrations such as phenyl torsion[10] efficiently transfers to cluster van der Waals modes; (iv) the cluster evaporatively cools; and (v) the cooling process traps some *cis*-stilbene molecules into a potential minimum from where the molecule emits.

This mechanism is tested by exciting *trans*-stilbene above the barrier of isomerization; emission spectral profile changes with stagnation pressure provide evidence for cluster formation and vibrational relaxation. Below 300 Torr Ar, the spectrum is structureless due to the intramolecular vibrational redistribution, but at higher pressures (Figure 2, insert) it develops typical vibrational structure of *trans*-stilbene solution spectra.[5] High-pressure spectra are from *trans*-stilbene S_1 origin ($\sim$310 nm)[11] independent of excess excitation energy indicating that vibrational relaxation occurs within 2.7 ns, the emission lifetime of *trans*-stilbene.[2] The emission quantum yield of clusters is found to be higher than for the free molecule because *trans*-stilbene vibrationally cools, in competition with temperature-activated isomerization. The increase in emission intensity with mass of the noble gas correlates well with clustering efficiency; however, other factors such as vibrational relaxation rates should be important. A detailed investigation of these interesting new observations on *cis*-stilbene isomerization dynamics is in progress.

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Reaction of Dimesitylsilylene in a Cryogenic Oxygen Matrix: IR Spectroscopic Observation of a Silylene-Oxygen Adduct

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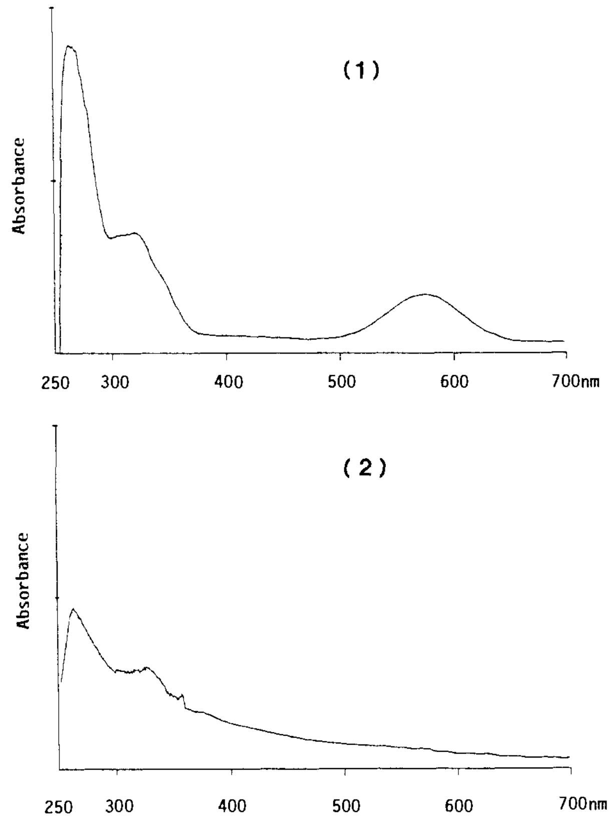
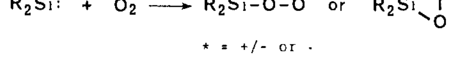


Figure 1. Difference UV spectra, (1) and (2), obtained upon photolysis of trisilane **2** isolated in argon and oxygen matrices at 16 K, respectively.

The chemistry of silylenes has been the subject of considerable interest in recent years.[2] The isolation of silylenes in an argon or hydrocarbon matrix has contributed greatly to the knowledge of these reactive species.[2c,3] Silylenes are known to react very rapidly with oxygen[2d,4] affording the adducts for which silanone *O*-oxide (**1a**) or siladioxirane (**1b**) structures have been suggested,[2d]



$$R_2Si: + O_2 \longrightarrow R_2\overset{*}{Si}{-}O{-}\overset{*}{O} \text{ or } R_2Si\langle O_2 \rangle$$

* = +/- or ·

	1a	1b
R = mesityl ;	3a	3b
R = H ;	4a	4b

similar to the case of reaction of carbenes with oxygen giving the corresponding carbonyl oxides and dioxiranes.[5] However, no spectroscopic evidence for such silylene-oxygen adducts has been reported.[2d] Our interest in the reactivities of initially formed peroxidic intermediates in the oxygenation mechanism of divalent atoms, such as carbenes[5a] and sulfides,[6] has led us to initiate low-temperature photolysis studies of silylene precursors.[7] Here, we report the results of recent investigations of silylenes in a cryogenic oxygen matrix, leading to the first spectroscopic observation of a silylene-oxygen adduct. A theoretical study of the

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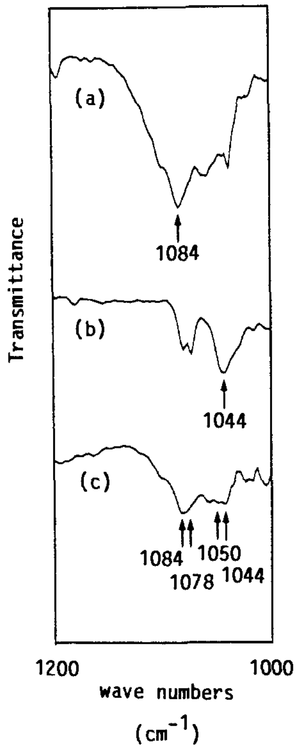

Figure 2. Difference IR spectra obtained upon photolysis of trisilane **2** isolated in oxygen matrices at 16 K. The following isotopic mixtures were used: (a) $^{16}O_2$, (b) $^{18}O_2$, and (c) $^{16}O_2$, $^{18}O_2$, and $^{16}O-^{18}O$.

adduct has also been carried out.

In our experiments 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**2**) was first photolyzed to give the corresponding silylene in an argon matrix at 16 K,[8] since **2** was known previously as an effective precursor of silylene by photochemical route in solution.[9] An absorption band due to dimesitylsilylene was observed at 577 nm similar to that reported by West et al.,[7a] as shown in Figure 1.1. When a similar photolysis of trisilane **2** was carried out in an oxygen matrix at 16 K, quite different results were obtained as shown in Figure 1.2. The band associated with dimesitylsilylene was not observed at all, suggesting that the generated silylene was smoothly trapped with oxygen.

The reaction intermediates resulting from UV irradiation of trisilane **2** were studied by FT-IR spectroscopy.[6] Irradiation of trisilane **2** isolated in an oxygen matrix at 16 K gave new species with an intense IR band at 1084 cm^{-1}.[10-12] The product behaves as a single chemical entity (i.e., the IR bands appear and disappear simultaneously at the initial stage of irradiation). Upon subsequent annealing[13] of the matrix (at temperatures up to 40 K) no change was observed in the IR absorption bands.[14] This intense band may result from the characteristic O–O stretching mode in the structure of **3a** or **3b** and is consistent with the calculated value (1083 cm^{-1}) for dihydrosilylene-oxygen adduct as mentioned below. In an experimental attempt to assign absorption peaks, information on the isotopic frequency shifts is often useful. Isotopic labeling experiments show that the IR band for **3** shifts by 40 cm^{-1} to a lower wave number with $^{18}O_2$ (95% doubly labeled). Moreover, to show which of the intermediates **3a** and **3b** participates in the oxidation,[15] the silylene-oxygen adduct in matrices with $^{16}O-^{18}O$[6] was generated. Figure 2 shows the IR spectra in the region 1200–1000 cm^{-1} from three experiments in which different isotopic mixtures of O_2 were used. In the $^{16}O-^{18}O$ adduct, the stretching vibration band was split into two additional absorption bands. Such splitting for the mixed isotope indicates that two oxygen atoms are not equivalent in the intermediate and therefore rules out the siladioxirane structure **3b** and the corresponding silanone. The IR results also rule out an alternative intermediate such as dimer structures (which should show more complicated isotopic shifts).

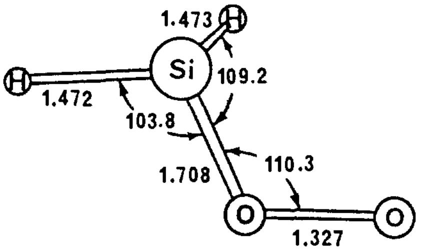

Figure 3. HF/6-31G* optimized geometry of **4a**.

Parallel theoretical studies of products of reaction of dihydrosilylene with oxygen offer a basis for the possible structure of the adduct **4**.[16] The optimized structure of the adduct **4a** in the triplet state at the HF/6-31G* level[17] is shown in Figure 3.[18-20] The O–O bond length of the adduct **4a** is calculated to be 0.159 Å longer than that of triplet oxygen (1.168 Å) at the HF/6-31G* level. Because of a considerable bonding between dihydrosilylene and oxygen,[18] the intramolecular Si–O bond distance is as short as 1.708 Å. A calculation of harmonic vibrational frequencies predicts that the O–O stretching mode is actually expected to be observed near 1083 cm^{-1} ($\nu_{calcd}/1.126$[21]). Upon ^{18}O substitution the O–O stretching frequency was calculated to shift in the following way: 1022 cm^{-1} for $H_2Si^{18}O_2$, 1054 cm^{-1} for $H_2Si^{16}O^{18}O$, and 1052 cm^{-1} for $H_2Si^{18}O^{16}O$. These agree reasonably with the isotopic shifts observed for the adduct **3a**. We may therefore conclude that the labile intermediate formed in dimesitylsilylene oxygenation is a silanone *O*-oxide **3a**.

Acknowledgment. Calculations were carried out at the Computer Center of the Institute of Molecular Science. This work

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(8) The cryogenic apparatus has been described previously.[6] UV irradiation was carried out by means of a 10-W low-pressure mercury lamp (Riko UVL10). A sharp-cut optical filter (Toshiba UV-D33S) was used at all times to select exciting wavelengths ($240 < \lambda < 400$ nm and $\lambda > 680$ nm).

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(10) Other characteristic absorption bands appeared at 655, 724, 758, 848, 1196, 1418, 1586, and 1617 cm^{-1}.

(11) No absorption band assigned to ozone was observed at 1034 cm^{-1}: Hashimoto, S.; Akimoto, H. *J. Phys. Chem.* **1986**, *40*, 529.

(12) At the initial stage of photolysis in an argon matrix containing a small amount of oxygen, both silylene-oxygen adduct and silylene were observed.

(13) Td, mp, and bp of oxygen are 26, 54, and 90 K, respectively: *Cryochemistry*; Moskovits, M., Ozin, G. A., Ed.; Wiley: New York, 1976; p 24.

(14) At temperature higher than 40 K, the intense bands at around 1080 cm^{-1} disappeared, and the oxygen matrix became cloudy. Product analysis at room temperature showed the formation of polymeric products containing Si–O bonds.

(15) For a discussion of isotopic labeling experiments in the related structural problem of a carbonyl oxide, dioxirane, and their sulfur analogues, see: ref 5b, d, and j and 6.

(16) The program used in GAUSSIAN 82 developed by Binkley et al.: Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Rahgavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fludre, E. M.; Pople, J. A. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA.

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(18) No significant minimum corresponding to **4a** was located on the singlet potential energy surface: open structures like **4a** collapsed almost without a barrier to a cyclic minimum C_{2v} structure **4b**, unlike the singlet case of carbonyl oxide, H_2COO. For the case of carbonyl oxide, see: (a) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1978**, *100*, 7180. (b) Martinez, R. I.; Huie, R. E.; Herron, J. T. *J. Chem. Phys.* **1981**, *75*, 5975. (c) Cremer, D.; Schmidt, T.; Gauss, J.; Krishnan, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 427.

(19) The addition of singlet dihydrosilylene to triplet oxygen was 22.7 kcal/mol exothermic at the MP4SDTQ/6-31G*//HF/6-31G* level. The triplet adduct **4a** was 61.5 kcal/mol less stable than the singlet siladioxirane **4b**.

(20) No ESR signal in the photolysis products of trisilane **2** at 77 K in oxygen-saturated 3-methylpentane has been observed.

(21) For the details of the scale factor, see: Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833. For comparison with experiment, see: Withnall, R.; Andrews, L. *J. Am. Chem. Soc.* **1985**, *107*, 2567; *J. Phys. Chem.* **1985**, *89*, 3261.

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Supplementary Material Available: Table of HF/6-31G* vibrational frequencies of dihydrosilylene–oxygen adduct and its isotopomers in the triplet state (1 page). Ordering information is given on any current masthead page.

An Unusually Lower Barrier to Reductive Elimination of an 18-Electron η^3-Allyl(organo)nickel(II) Complex Than Those of a 16-Electron η^3-Allyl Counterpart and a 16-Electron η^1-Allyl Isomer

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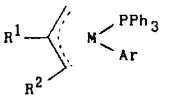
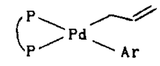
In spite of a versatile role played by reductive elimination of η^3-allylmetal complexes in organic transformations,[1-3] little has been known concerning the mechanistic details of this step. We wish to report a novel finding that the coupling of allyl and aryl groups on Ni is much more facile in an η^3-allyl form with 18-electron configuration than in both a 16-electron η^3-allyl counterpart and a 16-electron η^1-allyl isomer. This trend, not observed in the η^3-allylpalladium chemistry,[4] seems of particular relevance to the origin of some unique ligand and metal effects upon reactivity and selectivity in catalyses.[1,5] Acceleration of reductive elimination upon change of electron count on Ni from 16 to 18 has precedence in alkylnickel chemistry,[6] but none has revealed such a remarkable rate enhancement, in a quantitative manner, as is disclosed here.

Spontaneous reductive elimination of η^3-allyl(aryl)nickel(II) complexes **1**[7] in toluene proceeded smoothly to afford high yields (>85%) of allylbenzene derivatives (eq 1). The first-order rate constant (k_1)[8] of eq 1 for **1a** and **1b** was found independent of the amount of excess PPh_3 (up to 5 equiv) added,[9] as in eq 1 for the palladium analogue **2**.[4] The ratio of k_1 for **1a** versus that[4] for **2** at 0 °C ($k_1[Ni]/k_1[Pd] = 26$) provides the first direct comparison of the reactivity, between organonickel and palladium complexes with the identical composition, for the reductive elimination proceeding through a common mechanism.[10]



1 or 2



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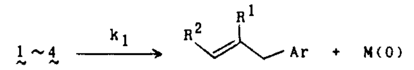
	M	R^1	R^2	Ar
1a	Ni	H	H	$C_6H_3Cl_2$-2,5
1b	Ni	Me	H	C_6F_5
1c	Ni	H	Me	C_6F_6
2	Pd	H	H	$C_6H_3Cl_2$-2,6

	Ar	diphos
3a	$C_6H_3Cl_2$-2,6	dppe
3b	$C_6H_3Cl_2$-2,6	dppen
3c	C_6F_6	dppen



(1)

Particularly noteworthy are the contrasting behaviors of **1** and **2** with respect to both structure and reactivity when chelating diphosphine ($Ph_2PCH_2CH_2PPh_2$ dppe; Z-$Ph_2PCH{=}CHPPh_2$ dppen) was added to these complexes. Thus, **2** and its C_6F_5 analogue reacted with the diphosphines quite rapidly to give η^1-allylpalladium complexes **3**[4,7b,11] which are *less reactive*[12] as compared to the reductive elimination of the parent η^3-allyl complexes. On the other hand, addition of the diphosphines to **1** dramatically *enhanced* the reductive elimination rate, which is attributed to formation of quite reactive, 18-electron η^3-allyl complexes **4**, as discussed below.

Attempts to isolate **4** from the solution containing any of **1** and the diphosphines even at temperatures below 0 °C were unsuccessful. Nor could we obtain any spectral clue to an intermediate in the rapid reductive elimination caused by adding dppe or dppen (1–2 equiv) to **1a** at -50 °C (half-life ≤ 0.5 h). However, NMR (^1H, ^{13}C, ^{31}P) spectra[13] and the color (reddish-orange)[14] of a solution obtained by mixing **1b** or **1c** with dppen (1 equiv) below -20 °C were sufficiently informative. Thus, the ^{31}P spectra showed complete dissociation of PPh_3 from Ni and coordination of both phosphorus atoms of dppen, and the ^{13}C chemical shifts of newly

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[5] For example, nickel catalysts are generally more effective than palladium catalysts in cyclooligomerization of dienes.[3b] Also, chelating diphosphine/nickel systems are unique catalysts for regio- and enantioselective allylic alkylations as compared to the analogous palladium systems.[2a,c,e-g,3c]

[6] (a) McKinney, R. J.; Roe, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 5167–5173. (b) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *Ibid.* **1984**, *106*, 8181–8188. (c) Komiya, S.; Abe, Y.; Yamamoto, A.; Yamamoto, T. *Organometallics* **1983**, *2*, 1466–1468.

[7] (a) Prepared in a manner similar to that[4] for the palladium analogue. (b) All new complexes isolated gave satisfactory analytical and spectral results.

[8] (a) Rates were followed by observing the coupling products by GLC and ^1H NMR (see ref 4). The initial concentrations of the complexes were 0.1 M (^1H NMR) and 0.02 M (GLC). The decomposition of **1a** was run in the presence of excess $PhC{\equiv}CPh$ in order for the clean kinetics to be attained, with the role of $PhC{\equiv}CPh$ being attributed possibly to stabilization of the Ni(0) species formed (cf. ref 8b,c for the palladium case). k_1 (h^{-1}) in toluene is as follows: **1a** 0.077 (0 °C); **1b** 0.382 (101 °C), 1.34 (116 °C), 5.15 (127 °C). (b) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868–1880. (c) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933–4941.

[9] Excess of free PPh_3 caused no change at all in ^1H NMR spectra of **1a** and **1b**.

[10] Theoretical prediction: Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867.

[11] Kurosawa, H.; Urabe, A.; Miki, K.; Kasai, N. *Organometallics* **1986**, *5*, 2002–2008.

[12] For example, k_1 (h^{-1}) in toluene at 40 °C are as follows: **2**, 0.693; **3a**, 0.0578; **3b**, 0.0866.

[13] (a) **4b**: ^1H NMR (toluene-d_8, -20 °C), δ 1.59 (t, $J_P = 3$ Hz, CH_3), 2.15 (br t, $J_P = 4.5$ Hz, -CH_2); ^{13}C NMR (CD_2Cl_2, -80 °C) δ 22.2 (CH_3), 58.4 and 61.1 (allyl terminal), 109.1 (allyl center); ^{31}P NMR (CD_2Cl_2, -80 °C) δ (external H_3PO_4) 21.3 and 39.5, $J_{P-P} = 150$ Hz. **4c**: ^1H NMR (toluene-d_8, -20 °C) δ 0.68 (dt, $J_H = 6$, $J_P = 4.5$ Hz, CH_3), 1.23 (q, $J_H = J_P = 9$ Hz, -CH_2), 3.32 (br, -C*H*Me), 5.21 (dt, $J_H = 9$, 10 Hz, -CH-); ^{13}C NMR (CD_2Cl_2, -50 °C) δ 19.7 (CH_3), 48.2 (-*C*H_2), 78.0 (-*C*HMe), 96.1 (allyl center); ^{31}P NMR (CD_2Cl_2, -80 °C) δ 23.0 and 38.5 (very br, J_{P-P} not resolved). (b) Lowering the temperature down to -90 °C resulted in only broadening of the ^1H NMR spectra. (c) Nonequivalent signals of two allyl terminal carbons in **4b** as well as those of two phosphorus nuclei of dppen in **4b** and **4c** coalesced to one signal (δ 59.6, 29.9, 30.0, respectively) at above -50 °C.

[14] The 16-electron complexes of the type Ni(η^3-allyl)(Ar)(PR_3) and Ni(CH_3)(Ar)(PR_3)$_2$ are all yellow colored.

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