

downfield shift for Zn^{2+} is less than expected from the predicted pK_a and that a similar pattern is observed for the experimental pK_a in Figure 3A.

General Conclusions

(1) The results presented in this paper seem to confirm the suggestion⁵ (see above) that highly concentrated solutions of certain metal salts must be regarded as strong protonic acids.

(2) For highly concentrated aqueous solutions of metal salts the protonating power increases rapidly, and results such as those shown in Figure 2 indicate that when the metal aquo complex is rid of outer-sphere water molecules, it becomes a very powerful acid. Thus the pK_a values determined for metal ions in aqueous solution (i.e., the "experimental" values in Table I) do not represent the true acidity of the metal aquo complexes. On the other hand, the pK_a values predicted from optical-basidity theory seem much more informative. Furthermore, the previously obtained 1H NMR data for concentrated aqueous solutions of metal salts⁵ are explicable in terms of the predicted pK_a values but not with the experimental ones. The difference of 10–12 pK units between experimental and predicted values must reflect the enormous neutralizing effect of outer-sphere water molecules which severely attenuates the acidity of the metal aquo complexes.

(3) To avoid possible misunderstanding, it is worth pointing out that in comparing the acidity of a metal aquo complex, e.g., $[Zn(H_2O)_4]^{2+}$, with that of a conventional mineral acid, e.g., H_3PO_4 , a comparison is *not* being made directly between the acidity of zinc(II) and phosphorus(V). To make such a comparison, it would be necessary to consider $[Zn(H_2O)_4]^{2+}$ alongside the (hypothetical) $[P(H_2O)_4]^{5+}$ species. The latter species would instantly lose five protons to yield H_3PO_4 , and from this point of view, our present comparison is between the first dissociation of $[Zn(H_2O)_4]^{2+}$ and the *sixth* dissociation of $[P(H_2O)_4]^{5+}$.

(4) An important question arising from the present work is why solvation has such an enormously attenuating effect upon the acidity of the metal aquo complex. Bearing in mind that in terms of the pK–optical basicity argument, strong acids

are those giving rise to conjugate bases with low λ values, it is necessary to consider how solvation affects the optical basicity of the conjugate base. Conjugate bases bearing a negative charge (i.e., those derived from oxyacids) will be solvated by the positive ends of the water dipoles, and thus the overall basicity will be reduced. On the other hand, conjugate bases bearing a positive charge (i.e., those derived from metal aquo complexes $[M(H_2O)_x]^{n+}$ and having the formula $[M(H_2O)_{x-1}(OH)]^{(n-1)+}$) will be solvated by the negative ends of the water dipoles. This can be viewed in terms of hydrogen bonding between the oxygen atoms of the outer-sphere H_2O molecules and the hydrogen atoms on the surface of the inner coordination sphere. In other words the basicity-moderating effect of these hydrogen atoms (expressed by γ_H) is no longer focused within the aquo complex but is dissipated throughout the solvent. This results in the basicity of the OH^- group in the coordination sphere being enhanced, and thus the original aquo complex behaves as a weaker acid.

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Registry No. $Ca(H_2O)_6^{2+}$, 17787-72-3; $Mg(H_2O)_6^{2+}$, 19592-06-4; $Zn(H_2O)_6^{2+}$, 15906-01-1; $Al(H_2O)_6^{3+}$, 15453-67-5; Li, 7439-93-2; Na, 7440-23-5; $ZnCl_2$, 7646-85-7.

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Reactions of Monomeric Silicon Difluoride and Silylene with Conjugated Pentadienes

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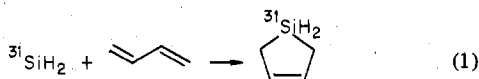
Monomeric $^{31}SiF_2$ formed in a nuclear recoil system reacts with 1,3-butadiene, *trans*-pentadiene, *cis*-pentadiene, and 2-methyl-1,3-butadiene to give equivalent amounts of difluorosilacyclopent-3-ene- ^{31}Si and its methyl derivatives. The singlet to triplet $^{31}SiF_2$ ratios evaluated from these systems are all around 1:3. Similar equivalence in product yields is also observed for $^{31}SiH_2$ reactions with 1,3-butadiene and the pentadienes, and the evaluated singlet to triplet ratio from the pentadienes is about 1:6. For each of these two silylenes, the relative reactivities of the various dienes toward them have been measured. Minor steric hindrance exists in most cases to account for the smaller reactivities of the pentadienes. However, a large steric effect has been observed between *trans*- and *cis*-pentadienes for their reactivities toward a triplet $^{31}SiF_2$ -donor, indicating a possible direct 1,4-addition process for such $^{31}SiF_2$ -donor complexes.

Following the maturity of carbene chemistry, studies of silylene, silicon difluoride, and other substituted silylenes have drawn much interest during the past decade.¹⁻⁵ Silylenes are generally formed through the following three methods: (i) decomposition or reaction of silicon-containing compounds through pyrolysis or photolysis;⁶⁻¹¹ (ii) the reactions of silicon species formed by the thermal vaporization method;^{4,5,12-16} and (iii) the reactions of silicon atoms formed by the nuclear recoil

technique.¹⁷⁻²⁸ The last method has been proven to be very useful in studying the reactions of SiH_2 and monomeric SiF_2 .

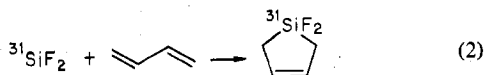
Gaspar and co-workers have employed the nuclear transmutation, $^{31}P(n,p)^{31}Si$, to produce ^{31}Si atoms which subsequently abstract H atoms to give $^{31}SiH_2$.^{17,18} They have demonstrated that the $^{31}SiH_2$ being formed can insert into the Si-H bond of SiH_4 to give $^{31}SH_3-SiH_3$.¹⁸ Later, we have shown in our laboratory that the $^{31}SiH_2$ thus formed can add

to 1,3-butadiene to give silacyclopent-3-ene-³¹Si (SCP*) (eq. 1).^{22,23} Studies using nitric oxides as a scavenger demonstrate

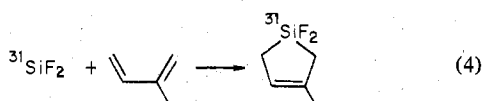
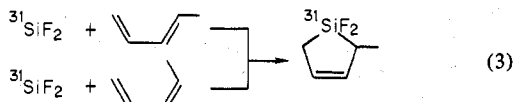


that the reacting silylene is present as 80% triplet and 20% singlet, while studies using neon as a moderator proved that the ground electronic state of silylene is a singlet.²⁵

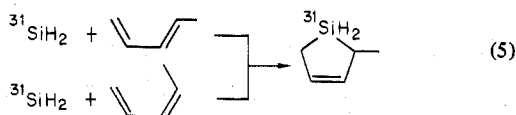
The ground electronic state of SiF₂ has been spectroscopically established by Margrave and co-workers as a singlet.¹⁵ Chemically it is extraordinarily stable, having a half-life at 0.1 Torr of 150 s. They have demonstrated that when SiF₂ is formed in high concentrations by the thermal vaporization method, the SiF₂ species dimerize very readily upon condensation to give (SiF₂)₂ and undergo further interactions in this dimer form.^{4,5} With the nuclear recoil technique, we have formed ³¹SiF₂ by irradiating PF₃ with fast neutrons.²² We have estimated that in such a nuclear recoil system the singlet to triplet ³¹SiF₂ ratio being formed is 1.0:3.3. Singlet ³¹SiF₂ reacted with 1,3-butadiene to give difluoro-silacyclopent-3-ene-³¹Si (DFSCP*), but triplet ³¹SiF₂ only gave this product in the presence of paramagnetic molecules such as NO, NO₂, or O₂.²⁶⁻²⁸



In the present work we have extended the reactions of monomeric ³¹SiF₂ to conjugated pentadienes. The reactions of ³¹SiF₂ with *trans*- and *cis*-1,3-pentadiene will both give 2-methyl-1,1-difluorosilacyclopent-3-ene-³¹Si (2MDFSCP*) as a product, while the reactions of ³¹SiF₂ with 2-methyl-1,3-butadiene (isoprene) will give the 3-methyl isomer (3MDFSCP*) of the above product.²⁸



The purpose of the present study is threefold: (i) to compare the characteristics of ³¹SiF₂ reactions of pentadienes with those of butadiene; (ii) to evaluate the relative reactivities of various conjugated dienes toward ³¹SiF₂; and (iii) to search for the mechanistic reasons such as steric considerations to account for the differences in reactivity of *trans*- and *cis*-pentadienes toward ³¹SiF₂. The corresponding studies of ³¹SiH₂ with *trans*- and *cis*-pentadienes to give 2-methylsilacyclopent-3-ene-³¹Si (2MSCP*) are also included for comparison.



Experimental Section

General Procedure. The general procedure used in this study was essentially identical with those described in our earlier publications.^{25,27} Phosphorus trifluoride (or phosphine) and the conjugated dienes along with other desired additives were sealed in Pyrex bulbs using high-vacuum techniques. Sample analyses were performed using standard radio-gas chromatography.²⁹

In order to minimize the undesired chemical interactions possibly taking place among the reactants during long periods of storage, the samples were usually prepared 1–2 h prior to irradiation. This precaution is definitely required for the nitric oxide containing samples since it has been observed before that NO can be chemically removed

by phosphorus compounds such as PH₃ during standing.²⁵ A small number of the samples without NO as an additive were prepared 2–10 h prior to irradiation, but they were usually stored at 0 °C in darkness.

In most of the experiments the ³¹Si atoms from the ³¹P(n,p)³¹Si nuclear transmutation were formed using fast neutrons from a Triga nuclear reactor at the Texas A&M Nuclear Science Center. The samples were irradiated for 10 min in an internal cadmium-lined boron rotisserie at an external thermal neutron flux of approximately 2 × 10¹¹ neutrons/(cm² s). In some of the experiments, irradiation was carried out at the Texas A&M University cyclotron with fast neutrons produced from a 16-MeV deuteron beam with a 50-μA intensity impinging on a beryllium target.

Sample Analysis. Four gas chromatography columns were used for the analysis of the substituted silacyclopent-3-ene products: (i) a 7-ft 35% dimethylsulfolane (DMS) column operated at 25 °C; (ii) a 30-ft 20% silicone fluid (SF-96) column operated at 80 °C; (iii) a 25-ft 10% silicone oil (D.C. 550) column operated at 25 °C; (iv) a 9-ft 10% tri-*o*-tolyl phosphate (TTP) column operated at 55 °C. The DMS column was used for the routine analysis of ³¹SiF₂ reaction products, while the SF-96 column was used for that of ³¹SiH₂ reaction products. Since reproducible results in recoil ³¹Si experiments can only be obtained with well-conditioned columns, the above four columns were all initially conditioned with PH₃ and SiH₄ and were again conditioned prior to the analysis of every set of samples. In the latter case, two to four portions of SiH₄ were first injected, followed by the injection of carrier compounds such as SCP or DFSCP until reproducible specific mass peak responses were obtained.

Products from recoil ³¹Si reactions were confirmed by coinjection of authentic samples of SCP, DFSCP, 2MSCP, and 2MDFSCP with irradiated samples on various columns. In order to ensure that there were no minor components overlapping with the above major products, the ³¹Si-labeled products from irradiated samples were trapped from one column and injected into other columns of different separation characteristics. In some cases there were no minor peaks observed, but in one case the correction factor for overlapping peaks amounts to as much as 14%. However, the majority of the correction factors fall in the range of 3–5%.

In every one of the pentadiene systems, there is always another major ³¹Si-labeled product observed besides the expected silacyclopent-3-ene. Presumably, it is a methyl-substituted silacyclopentadiene product, formed in a fashion similar to that of silacyclopentadiene from the butadiene system as invoked by Gaspar and co-workers.²⁴ However, since they are not derived from silylene and since no similar carrier molecules are available to quantitatively preserve their yields, we are not going to consider the implications of these products in this silylene-oriented paper.

Chemicals. PF₃ (97–99%) was obtained from PCR, Inc. PH₃ (>99%), 1,3-butadiene (>99.5%), and NO (>99%) were obtained from Matheson. *cis*-Pentadiene (>99%), *trans*-pentadiene (>99%), and 2-methyl-1,3-butadiene (>99.9%) were obtained from Chemical Samples Co. Most of these gases were used without further purification except for several cycles of degassing. However, NO and 2-methyl-1,3-butadiene were occasionally purified by bulb-to-bulb distillation in the vacuum line. Both SCP and DFSCP were prepared using the method described by Chao et al.³⁰

In the synthesis of 2MDFSCP, 2-methyl-1,1-dichlorosilacyclopent-3-ene was first synthesized by pyrolyzing a mixture of hexachlorodisilane (Chemical Samples Co., 98% pure) and *cis*- or *trans*-1,3-pentadiene (Chemical Samples Co., 98% purity) at 550 °C.³¹ The pyrolysis tube was constructed of 22 mm o.d. Vycor tubing placed into a vertical Lindemann oven. The heating zone was approximately 6 cm in length and was filled with Vycor glass chips to increase reaction surface area. The pentadiene and hexachlorodisilane in an approximate ratio of 3:1 were introduced into the pyrolysis tube using a one-pass flow process, with dried helium as carrier. Products were "trapped out" using a dry ice-acetone bath. The resulting 2-methyl-1,1-dichlorosilacyclopent-3-ene was identified by infrared spectroscopy. 2MDFSCP was then prepared from this dichloro compound through a fluorination process using antimony trifluoride in a dried *m*-xylene solvent. Products were separated by fractional distillation; the fraction boiling between 60 and 80 °C was observed to contain 2MDFSCP. Again, infrared spectroscopy was used for identification. 3MDFSCP was similarly prepared and identified.

2MSCP was synthesized by pyrolyzing a mixture of disilane and 1,3-pentadiene at 350 °C. The pyrolysis tube was constructed of 7 mm o.d. Vycor tubing with a heating zone of 6-cm length. Disilane

Table I. Equivalence of Product Yields Derived from Silylenes in the Systems of 1,3-Butadiene and Pentadienes

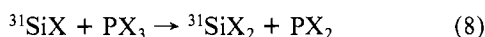
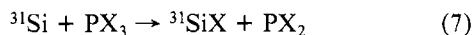
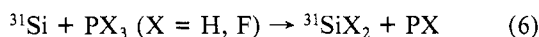
data set	P_{PF_3} , Torr	P_{PH_3} , Torr	$P(\text{diene})$, Torr	pentadienes		specific activities		normalized specific activities ^a	
				type	P , Torr	SCP* or DFSCP*	MSCP* or MDFSCP*	SCP* or DFSCP*	MSCP* or MDFSCP*
1	60.9			trans	19.9				
1	64.5		19.7			591	606	(1.00)	1.02
2	69.8			cis	20.0				
2	71.5		20.0			1075	1146	(1.00)	1.07
3	66.2			isoprene	20.1				
3	61.1		20.2			1039	1382	(1.00)	1.33
4		67.1		trans	20.0				
4		67.8	19.9			972	1007	(1.00)	1.04
5		70.9		cis	20.2				
5		73.1	16.2			475	496	(1.00)	0.99

^a The mean NSA values of MSCP* or MDFSCP* derived from the pentadienes are shown below together with the standard deviations and the number of samples in parentheses: 1.0 ± 0.2 (6) for *trans*-pentadiene (PF₃); 1.0 ± 0.2 (7) for *cis*-pentadiene (PF₃); 1.2 ± 0.1 (3) for isoprene (PF₃); 1.1 ± 0.1 (8) for *trans*-pentadiene (PH₃); and 0.96 ± 0.05 (4) for *cis*-pentadiene (PH₃).

was prepared by reducing hexachlorodisilane over LiAlH₄ in a dried *n*-butyl ether solvent and was purified by bulb-to-bulb distillation. Prior to pyrolysis, the entire pyrolysis apparatus was evacuated. The diene and disilane were mixed in a 2-L vessel at a 3:1 ratio and then passed through the pyrolysis tube by cryogenic pumping to cold traps downstream. The products were "trapped out" using a CCl₄ slush, a CH₃OH slush, and a liquid N₂ trap in sequence. Infrared spectroscopy was again used for the product identification.

Results and Discussion

Equivalence of Product Yields Derived from Silylenes in the Systems of Butadiene and Pentadienes. ³¹Si-labeled silylene is presumably formed in the present systems through the following abstractive processes by either a single-step or a two-step mechanism as shown in (6)–(8). Although these two



mechanisms of silylene formation remain indistinguishable at the present stage, the silylenes, once formed, are likely to add to the dienes very efficiently to give the silacyclopentenes as shown in eq 1–5.

When ³¹Si is formed in the systems of either phosphine–butadiene (1:1) or phosphorus trifluoride–butadiene (1:1), the absolute yield of SCP* or DFSCP* is only in the range of 5%.^{24,25,27} This means that the majority of the recoil silicon-31 species have undergone nonabstractive reactions either as ³¹Si atoms or as other silylene precursors such as ³¹SiH or ³¹SiF. Only 1 out of every 20 ³¹Si atoms can successfully abstract two H or F atoms to give silylenes without being removed by butadiene or the phosphorus compounds in some nonabstractive process prior to the silylene formation. The implication included in the above statement that silylene addition to dienes is a very efficient process can find support in the phosphine–butadiene and phosphorus trifluoride–butadiene composition studies.^{24,25,27} Previous work from our laboratory²⁷ has shown that in the phosphorus trifluoride–butadiene system, in going from 2 to 75% butadiene, there is at most a 10% variation in the DFSCP* specific yield, while that of Gaspar, Hwang, and Eckelman²⁴ has shown that in the phosphine–butadiene system, the SCP* specific yield increases sharply to a maximum with the addition of 2% butadiene and then declines gradually with further additional amounts of butadiene. Both of these results indicate that as little as 2% butadiene is required to capture all the silylenes formed in the system. The eventual gradual decline of the SCP* yield in the latter system reflects the decrease in the amount of ³¹SiH₂ formed when the percentage of butadiene increases, presumably through the removal of its precursors. In conclusion,

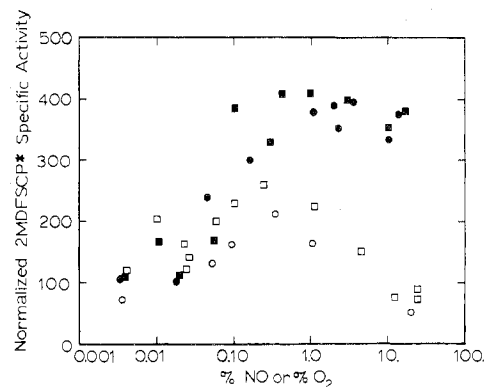


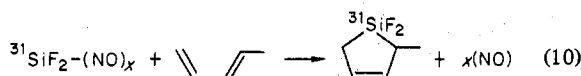
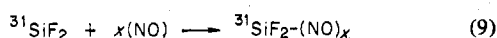
Figure 1. Concentration effects of NO and O₂ on the normalized 2MDFSCP* specific activity produced from ³¹SiF₂ reactions with *cis*-pentadiene in the presence of NO (●) or O₂ (○) and with *trans*-pentadiene in the presence of NO (■) or O₂ (□).

reactions 1 and 2 are so efficient that essentially all silylenes formed in the recoil ³¹Si systems should be captured by butadiene if the diene is present in amounts of 2% or more.

In Table I, the amounts of silylene captured by various pentadienes under various conditions are compared with those captured by butadiene under equivalent conditions. In this and the following tables, specific activity refers to the observed activity of the product per unit PV of phosphorus precursor where PV is expressed in Torr-milliliter. The arbitrary standard used in normalizing the specific activities to give the normalized specific activity (NSA) values was a sample containing 75% PH₃ (or PF₃) and 25% butadiene. In Table I, every pair of samples consists of such a standard and an equivalent pentadiene sample. The NSA value chosen for the standard was 100. It is obvious from the results of this table that equivalent amounts of ³¹SiH₂ or ³¹SiF₂ were always captured by either butadiene or any one of the pentadienes. This fact coupled with the discussion presented in the previous paragraph leads to the conclusion that the reactions between silylenes and each of the pentadienes are efficient and that essentially all of the silylenes being formed are captured by each of the pentadienes when they are present in the amount employed in these experiments, namely, about 25%. In practice, about five sets of samples for each of the equivalent pairs as shown in Table I have been analyzed. The data presented in the table are those with NSA values that were closest to the average NSA values of the various sets of experiments which have been performed.

Effect of NO and O₂ on the 2MDFSCP* Specific Activity. In Figure 1, the effects of NO and O₂ on the NSA values of 2MDFSCP* derived from ³¹SiF₂ reactions with *trans*- and

cis-pentadienes are shown. In this figure, the specific activity of 2MDFSCP* from a pure system without NO is normalized as 100. For both conjugated diene systems, the addition of as little as 0.1% of NO increases the 2MDFSCP* yield by fourfold, and the yield stays approximately constant with further increase in NO concentration. For *trans*-pentadiene, the initial portion of the plateau region where the moderating condition remains unaltered has a value 4.1 times higher than that from standard samples containing no NO. The corresponding plateau value for *cis*-pentadiene is about 3.8. This increase in yield is essentially the same as that observed in the butadiene system.²⁷ By using similar reasoning, the present result implies that singlet ³¹SiF₂ reacts with conjugated dienes directly to give silacyclopentenes, but triplet ³¹SiF₂ only undergoes such addition reactions in the presence of paramagnetic molecules such as NO. In the latter case a ³¹SiF₂-donor complex in the form of ³¹SiF₂-(NO)_x is probably formed³² which reacts with conjugated dienes to give the corresponding silacyclopentenes (see eq 9 and 10). Therefore



the present study with pentadienes again confirms the previous finding that the reacting ³¹SiF₂ in the recoil ³¹Si systems with PF₃ and conjugated dienes consists of approximately 25% singlet and 75% triplet.²⁷

In Figure 1 the variation of 2MDFSCP* specific activities from both *trans*- and *cis*-pentadiene systems increases sharply with the addition of trace amounts of O₂, reaches a maximum (at 0.3% O₂) which is about 3 times the yield of a standard sample without O₂, and declines back to the level of the standard samples when approximately 10% O₂ has been added. This observation is again similar to that which has been observed in the butadiene system.²⁷ It can be explained by the supposition that the ³¹SiF₂-O₂ complex being formed by triplet ³¹SiF₂ undergoes further reaction very favorably with O₂ molecules to give unobservable products. As a result, as the concentration of O₂ increases in the system, it competes with the conjugated dienes for the ³¹SiF₂-O₂ complex, and finally when the concentration of O₂ is high enough, it eliminates essentially all of the complexes from reaction with the conjugated dienes.

An alternate mechanism involving collisional quenching has been considered in our earlier work.²⁷ It is possible that paramagnetic molecules would effect a spin-conversion process changing triplet ³¹SiF₂ into its singlet form which then could add to the dienes to give the observed products. However, it is very difficult for this mechanism to account for the detailed variations in the O₂ systems.

Effects of NO on the 2MSCP* Specific Activity. In Figure 2 the effect of NO on the NSA values of 2MSCP* derived from the reactions of ³¹SiH₂ with *trans*- and *cis*-pentadiene is shown. In this figure the specific activity of 2MSCP* from a pure system without NO is normalized as 100. With the addition of 5% NO, the yield drops very sharply to the 15% level and stays nearly constant with further addition of the scavenger. The variation here is very similar to that observed in the butadiene system,²⁵ and thus a similar mechanistic implication applies. This means that the reacting ³¹SiH₂ consists of about 15% singlet and 85% triplet. These percentages are actually slightly different from those observed in the previous butadiene system which shows 20% singlet and 80% triplet. Since the electronic state distribution of ³¹SiH₂ found in both nuclear recoil systems should be similar regardless of the reacting diene, the present set of data seems more reliable than the previous one. As mentioned in the

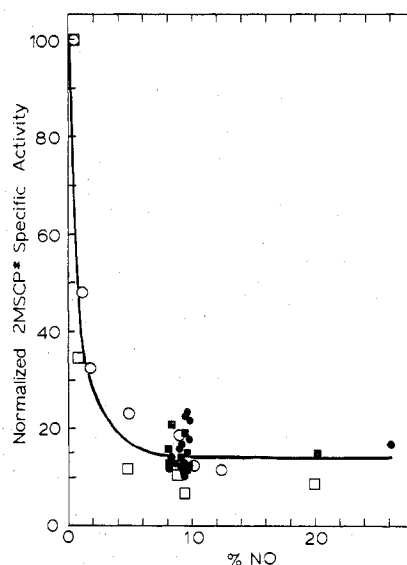


Figure 2. Effects of NO on the normalized 2MSCP* specific activity produced from ³¹SiH₂ reactions with *cis*-pentadiene (○) and with *trans*-pentadiene (□). Also included are the effects of NO on the total normalized specific activities of SCP* and 2MSCP* from samples with equal amounts of 1,3-butadiene and *cis*-pentadiene (●) or with 1,3-butadiene and *trans*-pentadiene (■).

Experimental Section, the NO-addition samples of the PH₃ system must be prepared fresh in order to get meaningful results. In the present experiments, in comparison with the previous ones, more attention has been placed on this precaution.

Specific Activity Ratios (SAR) for ³¹SiF₂ and ³¹SiH₂ Reactions with Various Pentadienes in Comparison with 1,3-Butadiene. The major type of experiments performed in this work was to mix approximately equal amounts of 1,3-butadiene and one of the pentadienes such that they would compete for the available ³¹SiF₂ or ³¹SiH₂ in the reaction system. The specific activity ratios (SAR) of the pentadienes in comparison with those of butadiene could then be evaluated through the observed specific activities of the various ³¹Si-labeled silacyclopentenes and the relative amounts of the two dienes employed. In Table II the evaluation of the SAR values of ³¹SiH₂ reactions with *cis*-pentadiene and 1,3-butadiene is shown. In this table the specific activities of both SCP* and 2MSCP* in the competition samples are all normalized to the standard phosphine-1,3-butadiene sample by assigning its SCP* specific activity as 100. The sums of the two silacyclopentene yields are also listed. It is obvious from the data that there is a complementary relationship between the two individual specific yields when the pentadiene is added to the butadiene system.

In Table II the SAR values for 2MSCP* are calculated as follows.

$$\text{SAR}(2\text{MSCP}^*) = \frac{\text{specific activity of } 2\text{MSCP}^* / P_{\text{cis-pentadiene}}}{\text{specific activity of SCP}^* / P_{1,3\text{-butadiene}}}$$





The SAR values evaluated from the seven competition experiments were averaged to give a value of 0.79 ± 0.11 , where the quoted error represents the standard deviation. Similar experiments have been performed for both ³¹SiF₂ and ³¹SiH₂ with other pentadienes in either the presence or absence of NO, and the average SAR values are summarized in Table III. In this table the number in parentheses after the averages represents the number of samples employed in averaging, and

Table II. Specific Activity Ratio of $^{31}\text{SiH}_2$ Reactions with *cis*-Pentadiene and 1,3-Butadiene

P_{PH_3} , Torr	$P(1,3\text{-butadiene})$, Torr	$P(\text{cis-pentadiene})$, Torr	normalized specific activities ^a			specific activity ratio (SAR)
			$^{31}\text{SiH}_2$ (1,3-butadiene)	$^{31}\text{SiH}_2$ (<i>cis</i> -pentadiene)	total	
69	20		(100)		(100)	
66.9	10.0	10.2	60.9	52.1	113	0.84
69.4	10.1	10.0	43.6	43.1	87	1.01
66.9	11.7	10.0	59.2	40.2	99	0.79
68.4	10.2	10.1	52.6	34.9	87	0.89
68.7	9.9	10.1	51.5	37.0	89	0.70
70.0	9.8	10.3	51.5	44.1	96	0.82
67.0	9.6	10.0	64.5	50.3	115	0.75
						Av 0.79 ± 0.11

^a Normalized to SCP* activity of 1,3-butadiene standard samples as 100.

Table III. Summary of Average Specific Activity Ratios (SAR) for $^{31}\text{SiF}_2$ and $^{31}\text{SiH}_2$ Reactions with Various Pentadienes in Comparison with 1,3-Butadiene

reacting dienes	average specific activity ratios (SAR) for silylenes ^a			
	$^{31}\text{SiF}_2$		$^{31}\text{SiH}_2$	
	without NO ^b	with NO ^c	without NO ^d	with NO ^e
	(1.00)	(1.00)	(1.00)	(1.00)
 (trans)	0.92 ± 0.09 (9) ^f	0.84 ± 0.09 (5)	0.91 ± 0.09 (9)	1.31 ± 0.15 (10)
 (cis)	0.88 ± 0.08 (7)	0.63 ± 0.05 (5)	0.79 ± 0.11 (7)	1.07 ± 0.11 (14)
	1.07 ± 0.08 (12)	0.92 ± 0.02 (4)		





^a Based on 1,3-butadiene as a comparison standard. ^b Typical sample composition: PF_3 (650 Torr); pentadiene (100 Torr); 1,3-butadiene (100 Torr). ^c Typical sample composition: same as *b*, with NO (49 Torr). ^d Typical sample composition: PH_3 (650 Torr); pentadiene (100 Torr); 1,3-butadiene (100 Torr). ^e Typical sample composition: same as *d*, with NO (80 Torr). ^f The number in parentheses represents the number of samples employed in averaging. The standard deviation is quoted after the average.

again the standard deviation is quoted in every case. It is obvious that a majority of the average SAR values are around unity.

Relative Reactivities of Conjugated Dienes toward Singlet and Triplet $^{31}\text{SiF}_2$ and $^{31}\text{SiH}_2$. The SAR values listed in Table III can be converted to show the relative reactivities of the dienes by taking into account the following points. (i) In the absence of NO the SAR values for $^{31}\text{SiF}_2$ reactions involve only the singlet species, while in the presence of NO the SAR values represent the total reactivity of both singlet and triplet $^{31}\text{SiF}_2$. (ii) Triplet $^{31}\text{SiF}_2$ is 3 times more abundant than its singlet counterpart. (iii) In the absence of NO the SAR values for $^{31}\text{SiH}_2$ reactions involve both singlet and triplet forms of the species, while in the presence of NO the SAR values represent only the reactivity of singlet $^{31}\text{SiH}_2$. (iv) Triplet $^{31}\text{SiH}_2$ is about 6 times more abundant than its singlet counterpart. After these points are taken into consideration, the relative reactivities of various conjugated dienes toward singlet and triplet $^{31}\text{SiF}_2$ and $^{31}\text{SiH}_2$ are resolved and summarized in Table IV. The overall picture of the relative reactivities for these four types of conjugated dienes toward silylenes is that all of them are similar within a factor of 2.

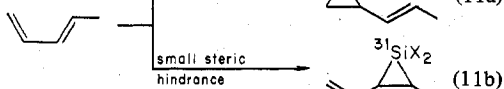
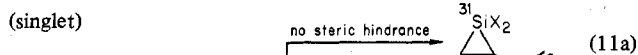
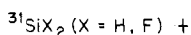
Singlet Silylene Addition Processes. Values in Table IV indicate the following observations for the reactivities of the dienes toward the *singlet* silylenes. (i) Toward singlet $^{31}\text{SiF}_2$, the order of the relative reactivities is isoprene > 1,3-butadiene > *trans*-pentadiene > *cis*-pentadiene. (ii) Toward singlet $^{31}\text{SiH}_2$, the order of the relative reactivities is *trans*-pentadiene > *cis*-pentadiene > 1,3-butadiene. (iii) Quantitatively, the reactivities of the pentadienes toward $^{31}\text{SiF}_2$ are, on the av-

Table IV. Relative Reactivities of Various Conjugated Dienes toward Singlet and Triplet Silylenes

type of silylene	relative reactivities				(cis-pentadiene/trans-pentadiene) reactivity ratio
					
singlet $^{31}\text{SiF}_2$	(1.00)	0.92	0.88	1.07	0.96
triplet $^{31}\text{SiF}_2$	(1.00)	0.81	0.54	0.86	0.67
singlet $^{31}\text{SiH}_2$	(1.00)	1.31	1.07		0.82
triplet $^{31}\text{SiH}_2$	(1.00)	0.84	0.74		0.88

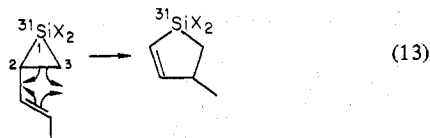
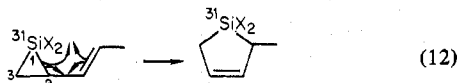
erage, about the same as that of butadiene, while in the case of $^{31}\text{SiH}_2$, the pentadienes are about 20% more reactive. (iv) *trans*-Pentadiene is always somewhat more reactive than its *cis* counterpart. In order to explain the above observations it must be first recognized that there are two possible factors operating in opposite directions which may influence the reactivities of the dienes. (i) The silylenes should be electrophilic in nature, and the addition of electrophiles to dienes should be enhanced by the presence of alkyl substituents.³³ (ii) The physical existence of the methyl groups may sterically hinder the addition process of the silylenes to the dienes.³³ The various observations are consistent with the situation that for singlet silylenes the relative reactivities of the dienes are primarily regulated by the electrophilic nature of the reactants

and are slightly modified by the steric factors. Although the very existence of the steric factor can only be detected in the smaller reactivities of *cis*-pentadiene in comparison with that of *trans*-pentadiene, such a negative modifying factor should exist for the methyl substitution in every one of the pentadienes. This means that in the absence of such a steric factor, the reactivities of the pentadienes toward singlet silylenes should be always higher than that of butadiene. Since singlet ³¹SiF₂ and ³¹SiH₂ are likely to add to the dienes via a 1,2-addition process to a π bond followed by isomerization to give DFSCP* and SCP*, there are two possible stages where steric factors may affect the reactivity. The first possibility may exist in the actual addition step of the silylenes. Although the

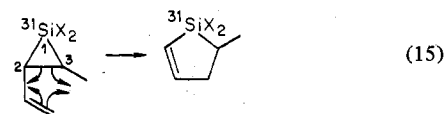
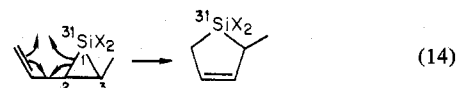


efficiency of singlet silylene 1,2-addition to pentadiene as shown in (11a) should be similar to that of 1,3-butadiene, the corresponding 3,4-addition as shown in (11b) may be slightly hindered by the presence of the methyl group. After addition, the silacyclopropane ring will immediately collapse due to the high ring strain and undergo isomerization.³⁴ The second stage where the methyl group may impose a steric effect is to hinder the achievement of certain transition-state configurations for the isomerization step.³³ However, it should be emphasized that although some steric hindrance exists, it is likely to be small in such singlet silylene addition processes. Nevertheless, in the case of *trans*- and *cis*-pentadiene reactions with ³¹SiF₂, the steric hindrance is actually significant enough to make their reactivities lower than that of 1,3-butadiene. From the observed fact that isoprene is more reactive than both *trans*- and *cis*-pentadienes, another minor conclusion can also be drawn that methyl substituents at the terminal carbon atoms hinder the yield slightly more than when they are attached to the middle carbon atoms.

The present pentadiene results also shed some light on the steps involved in the isomerization of the silacyclopropanes if the silylene addition is really a one-double-bond addition process. The isomerization may proceed via either a concerted or a biradical mechanism. First let us consider the four possible cases of concerted isomerization which are geometrically favorable. As shown in (12) and (13), the prop-

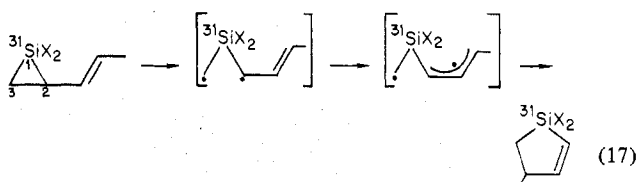
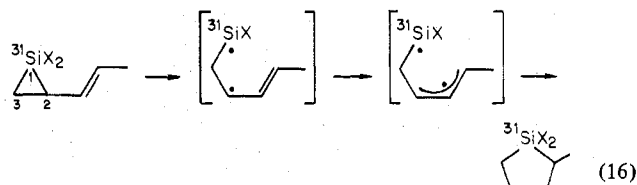


nylsilacyclopropane molecules formed in (11a) may isomerize by coupling the remaining C=C double bond with either the Si-C bond at the 1,2-position or with the C-C bond at the 2,3-position. 2MSCP* and 2MDFSCP* are the expected products for the former case as shown in (12), while 4-methylsilacyclopent-2-ene should be formed in the latter case as shown in (13). On the other hand, for the 2-vinyl-3-methylsilacyclopropane molecules formed in (11b), reaction at the S-C bond at the 1,2-position again yields 2MSCP* or 2MDFSCP* as products as shown in equation 14, while reaction at the C-C bond at the 2,3-position will give 5-methylsilacyclopent-2-ene.



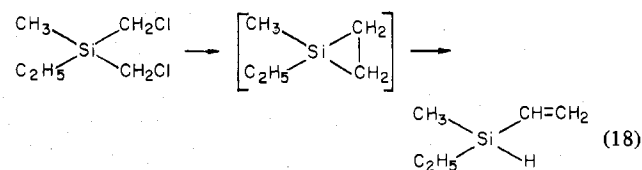
In summary, although isomerization by coupling the remaining C=C double bond with the Si-C bond will always give products with double bonds at the 3-position and methyl groups at the 2-position such as 2MSCP* or 2MDFSCP*, the isomerization involving the C-C bond at the 2,3-positions in silacyclopropanes will give other isomers with methyl groups and/or double bonds at other positions. The fact that only 2MSCP* and 2MDFSCP* are actually observed as products but not their other isomers means that for the concerted isomerization of a silacyclopropane ring such as the two cases considered here, it is always the Si-C bond at the 1,2-position which is involved in the bond-breaking, bond-forming process.

Similar conclusions can be drawn if the isomerization proceeds through biradical intermediates. In the case of propenylsilacyclopropane formed in (11a), the silacyclopropane ring can cleave in three different ways, namely, by a 1,2-, 2,3-, or 1,3-cleavage. Among the three, the 1,3-cleavage should be the least likely one because it lacks the resonance stabilization of the electrons after cleavage. Although the 1,2-cleavage will give rise to the 2-methyl derivative of silacyclopentene as shown in eq 16, the 2,3-cleavage will, on the other hand, lead to the formation of 4-methylsilacyclopent-2-ene as shown in eq 17.



Through a similar process it can be shown that only 1,2-cleavage of the Si-C bond in 2-vinyl-3-methylsilacyclopropane will lead to 2MSCP* and 2MDFSCP*. Then with similar reasoning as that shown above for the concerted mechanism, it can be concluded that even if the isomerization proceeds via a biradical mechanism, it is always the SiC bond at the 1,2-position which cleaves to initiate the isomerization.

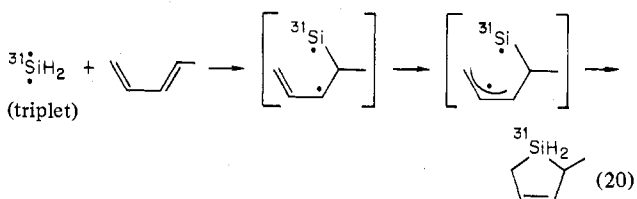
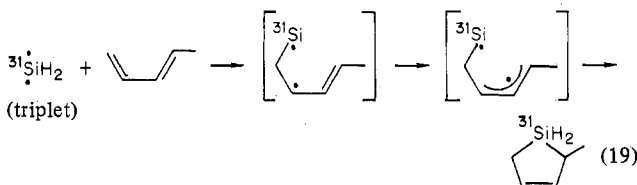
The present conclusion that it is the Si-C and not the C-C bond which cleaves in a silacyclopropane ring is consistent with Skell and Goldstein's earlier findings as shown in (18).³⁴ In their case, the observed product can only be formed via a Si-C cleavage mechanism.



Coming back to the singlet silylene addition mechanism, it is also conceivable that one or both of these two silylenes may add to the conjugated dienes through a 1,4-addition process instead of the 1,2-addition process to a singlet π-bond

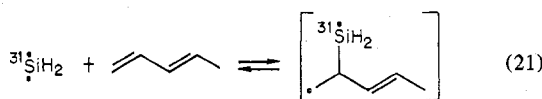
as discussed above. The large size of the silicon atoms and the conjugation of the two double bonds makes a 1,4-addition process both geometrically and electronically feasible. Such a mechanism can not be ruled out without further experimental evidence.

Triplet $^{31}\text{SiH}_2$ Addition Process. For the reactions of conjugated dienes with triplet $^{31}\text{SiH}_2$, the order of relative reactivities is 1,3-butadiene > *trans*-pentadiene > *cis*-pentadiene. The existence of a steric hindrance by methyl groups is again obvious from these results. However, mechanistically the triplet $^{31}\text{SiH}_2$ addition to conjugated dienes is likely to proceed via a 1,4-addition process. This is based on the knowledge of reactions of other triplet species, such as CH_2 , with conjugated systems.³⁵ The steps involved in such a 1,4-addition are illustrated in eq 19 and 20 with *trans*-



pentadiene to give 2MSCP*. The illustrations are for triplet $^{31}\text{SiH}_2$ addition at a terminal π -bonded carbon at the 1-position, as in reaction 19, or at the 4-position, as in reaction 20. In either case, only 2MSCP* is obtained.

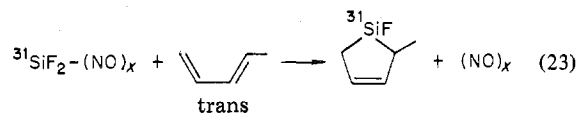
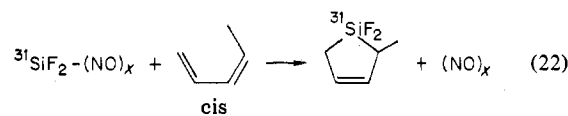
The addition of triplet $^{31}\text{SiH}_2$ to one of the "inner" carbons of the conjugated double bonds as at the 2- or 3-position in *trans*-pentadiene as shown in (21) should be energetically



much less favored. In this case the resonance is completely destroyed by the triplet addition, while for the addition processes shown in (19) and (20) the resonance is only partially hindered. If this mode of addition does take place, it is likely that the resulting adduct will either decompose to regenerate $^{31}\text{SiH}_2$ or further react with bath molecules to yield undetected products. The reverse reaction of (21) is proposed where Si-C bond cleavage predominates over a C-C bond cleavage process. This is due to the fact that a Si=C double bond is difficult to form and that the illustrated decomposition route will regain all the resonance energy of the conjugated diene. If, however, the adduct reacts further to abstract H from PH_3 , it would most likely yield products that are undetectable by the present analytical system. Although the PH_3 molecule is a source of labile hydrogens, it may interact somehow with silicon-containing species in certain nonabstractive processes to give some undetectable products. This becomes evident in the pure PH_3 system where only a 2% yield of $^{31}\text{SiH}_4$ is observed as a result of H-abstraction from PH_3 .¹⁸ Nevertheless, since reaction 21 is expected to be much less important than reactions 19 and 20 and since a major fraction of the adduct formed in (21) will decompose to regenerate $^{31}\text{SiH}_2$, only a relatively insignificant fraction of triplet $^{31}\text{SiH}_2$ is expected to be removed as undetectables. This means that the observed 6:1 triplet to singlet ratio for $^{31}\text{SiH}_2$, although theoretically a lower-limit value, should be a reasonably good approximation in practice.

Reactions of the Triplet $^{31}\text{SiF}_2$ -Donor. The reactivities of the conjugated dienes toward the triplet $^{31}\text{SiF}_2$ -donor follow the following order: 1,3-butadiene > isoprene > *trans*-pentadiene > *cis*-pentadiene. Little is actually known about the nature of this $^{31}\text{SiF}_2-(\text{NO})_x$ complex: it may or may not behave as an electrophile; it may contain one or more NO molecules in the complex.³² However, from the observed relative reactivities of the dienes toward this complex as shown above, it would seem to be certain that it is a very bulky species and can be easily hindered.

Actually, the most surprising observation here is that *trans*-pentadiene is about 50% more reactive than its *cis* counterpart. Such a difference has been noted before in methylene reactions with certain cyclic molecules of very special steric arrangements.³⁶ In the present case, a steric effect of such a magnitude can be best explained by the possible operation of a concerted 1,4-addition process of the $^{31}\text{SiF}_2$ -donor to the conjugated double bonds. Such a concerted addition is likely to have the geometric requirement that both double bonds are oriented on the same side of the molecule. With this in mind, it is obvious that the methyl group in the *cis* compound will introduce considerable hindrance to the approach of the reactants as illustrated in eq 22, while in the *trans* compound such additional hindrance is absent as seen in eq 23.



However, it is also conceivable that the triplet $^{31}\text{SiF}_2$ -donor may undergo a normal 1,4-addition process through a biradical intermediate similar to reactions 19 and 20 shown for triplet $^{31}\text{SiH}_2$ additions. In this case, the unusually large steric hindrance introduced by the CH_3 group of *cis*-pentadiene may be attributed to the very bulky size of the $^{31}\text{SiF}_2-(\text{NO})_x$ complex.

Finally, an important question remains basically unanswered, that is, why triplet $^{31}\text{SiF}_2$ reacts with dienes apparently only as a complex of the paramagnetic NO or O_2 molecules, while triplet $^{31}\text{SiH}_2$ reacts directly with them. This may be due to the stabilization effect of the nonbonded electrons by F atoms to render triplet $^{31}\text{SiF}_2$ as a much less reactive species than triplet $^{31}\text{SiH}_2$ toward dienes. In the presence of NO or O_2 , the adducts being formed by $^{31}\text{SiH}_2$ with these paramagnetic molecules may possess stronger Si-O or Si-N linkages such that they would not be acting as $^{31}\text{SiH}_2$ -donors in any possible subsequent reactions.

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Registry No. $^{31}\text{SiF}_2$, 37520-92-6; $^{31}\text{SiH}_2$, 53971-28-1; 1,3-butadiene, 106-99-0; *trans*-1,3-pentadiene, 2004-70-8; *cis*-1,3-pentadiene, 1574-41-0; isoprene, 78-79-5; DFSCP*, 37520-97-1; 2MDFSCP*, 67194-78-9; 3MDFSCP*, 67194-79-0; SCP*, 53473-31-7; 2MSCP*, 67226-38-4.

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Substituent Effects upon Dissociation and Migration Reactions of Five-Coordinate Platinum(II) Carbonyl Complexes

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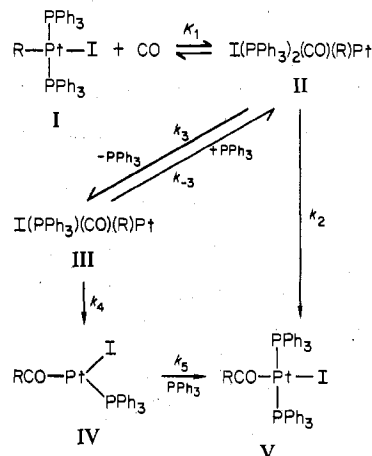
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A series of five iodobis(triphenylphosphine)arylplatinum(II) complexes was prepared and rates of carbonylation in the presence and absence of excess triphenylphosphine were measured. Four related palladium(II) complexes were compared with the platinum complexes. The results are interpreted in terms of a five-coordinated carbonyl intermediate which forms the acylmetal product by two reaction paths—a migratory route and a dissociative route. The migratory reaction is much more sensitive to changes in the electronic character of the migrating group than the dissociative reaction is. The results show that carbon monoxide insertion is not rate limiting in the catalytic carbonylation of aryl halides.

The carbon monoxide insertion reaction is one of the basic reactions of organo-transition-metal compounds. Knowledge of the mechanism of this reaction would be useful in understanding how different ligands affect the reaction course. This information ultimately could lead to new catalysts with optimum activity for various carbonylation reactions.

We undertook a study of the reaction of halobis(triorganophosphine)organoplatinum, -palladium, and -nickel complexes with carbon monoxide with the above goal in mind.¹ With the platinum complexes the reaction was shown to involve a preequilibrium step forming a fluxional five-coordinate carbonyl complex, II, which then reacted by two paths to form the acylplatinum product V. One of the two paths involved a direct migration of the organic group from platinum to the carbon monoxide ligand and the other a dissociation of one of the triorganophosphine groups. In the second process fluxional intermediate III was believed to be formed which then underwent a migration to three-coordinate species IV. A final reassociation of a phosphine ligand gives the observed product. Numerous metal complexes were studied and

Scheme I



considerable knowledge of ligand effects in this reaction was acquired. We now report additional data bearing on how various aryl substituents influence the relative preference of the five-coordinated intermediate for the two reaction paths

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