of implications, including the use of lanthanide cryptates as cationic tracers in biological systems,[8a] as T_1 relaxation[38] and chemical-shift reagents in NMR spectroscopy,[7] and as redox reagents in studies of electron-transfer kinetics.[10] The large differences in formal potential of the cryptate couples compared with the corresponding aquo couples, arising from the sensitivity of the complexation thermodynamics to the metal oxidation state, suggest that it should be possible to design macrobicyclic ligands that selectivity stabilize given oxidation states and therefore yield large yet controllable changes in the redox thermodynamics. Experiments to explore these possibilities further are currently in progress in our laboratory.

Acknowledgments. We are indebted to Drs. Brian Cox and H. Schneider for generously supplying kinetic data for the substitution kinetics of alkali and alkaline-earth cryptates prior to publication. One of the authors (E.L.Y.) was partially supported by a fellowship from the General Electric Corp. The support of this work by the Air Force Office of Scientific Research (Grant AFOSR 77-3408) and initially by the Research Corporation (M.J.W.), and by the National Science Foundation (Grant CHE-78-1024) (O.A.G.) is gratefully acknowledged.

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(16) It should be noted that the time taken to attain true equilibrium will be determined by the ligand exchange rate (i.e., the first-order rate constant for dissociation of the complex) irrespective of whether the complex is allowed to aquate spontaneously or the free metal ion is allowed to complex with added ligand.
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(35) These partial molal entropies have been converted to the "absolute" scale which assumes the most probable value of $\bar{S}°_{H^+} = -5.5$ eu, rather than the "conventional" scale where it is assumed that $\bar{S}°_{H^+} = 0$.[10,37]
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Formation of 1-Silacyclopenta-2,4-diene through Recoil Silicon Atom Reactions

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Abstract: $[^{31}Si]$-1-Silacyclopenta-2,4-diene was prepared through the reactions of recoil silicon-31 atoms with butadiene. Its identification was verified by the fact that it was catalytically hydrogenated to $[^{31}Si]$-1-silacyclopent-3-ene. $[^{31}Si]$-1-Silacyclopenta-2,4-diene is sensitive to γ-ray irradiation. It is also thermally unstable at a temperature higher than 100 °C. Possible mechanisms for its formation are considered.

The synthesis of silacyclopentadienes has been a long-term challenge to chemists during the past 2 decades. The successful preparation and characterization of such compounds were reported as early as 1961 and labeled as the first example of an aromatic system containing the silicon atom.[1-4] However, some reinvestigation in the same laboratory found that such syntheses cannot be experimentally duplicated.[5] Over the years, attempts to prepare this type of compound have been

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continued. Very recently Barton and co-workers have reported the successful synthesis of phenyl-substituted silacyclopentadienes (silole),[6] but an attempt to prepare a silole with all the ring carbons unsubstituted still cannot be achieved with the ordinary synthetic means.[7] In the present work, we would like to confirm the successful preparation of 1-silacyclopenta-2,4-diene (SCPD) through the use of recoil silicon atom reactions.

During the reactions of recoil silicon atoms formed via the ^{31}P(n,p,)^{31}Si nuclear transmutation with 1,3-butadiene, an unknown product was observed besides the identified products arising from silylene reactions.[8-10] The same unknown compound was obtained when either PH_3 or PF_3 was used as a ^{31}Si precursor. Gaspar and co-workers had suggested that this unknown compound is probably SCPD based on the following reasons.[9,10] (1) The product contains C, H, and Si but no phosphorus because the same compound was obtained when ^{30}Si, instead of ^{31}P, was used as the ^{31}Si source. (2) The chromatographic behavior of this product suggests that it contains four carbon atoms. (3) Its yield increases monotonically with 1,3-butadiene mole fraction. (4) It was obtained in nearly identical (20 ± 3%) yields from 1:1 PH_3-butadiene and 1:1 PF_3-butadiene mixtures. In the present work we have obtained more direct proof that this compound is actually SCPD. We have also observed certain properties of this species.

The study of recoil ^{31}Si reactions has furnished various valuable information about silicon chemistry during the past decade.[8-15] However, most of the information obtained concerns the reactions of silylenes[16] which are formed through abstractive interactions by ^{31}Si atoms. Such studies have provided a vast amount of useful knowledge about the reactions of $^{31}SiH_2$ and monomeric $^{31}SiF_2$. The work described here, on the other hand, presents a study of the direct interaction of ^{31}Si atoms with a substrate to give a final product without involving the abstractive steps.

Experimental Section

General Procedure. The general procedure used in this study was mostly the same as that employed in our previous studies,[8,14,15] with certain minor modifications. Samples were usually prepared 1-2 h prior to irradiation. PH_3 or PF_3 and 1,3-butadiene, along with other additives, were sealed in Pyrex bulbs with high-vacuum techniques. Silicon-31 from the ^{31}P(n,p)^{31}Si nuclear transformation was formed using fast neutrons from a Triga nuclear reactor at the Texas A&M Nuclear Science Center. Sample analysis was performed with standard radio-gas chromatography.[17] For the PH_3-containing samples, a 30-ft 20% silicone fluid (SF-96) column operated at 55 °C was used for product analysis. With this column, SCPD eluted much faster than silacyclopent-3-ene or silacyclopentane. For the PF_3-containing samples, a 7-ft, 35% dimethylsulfolane (DMS) column operated at 25 °C was used for the analysis. With this column, SCPD eluted far in advance of 1,1-difluorosilacyclopent-3-ene.

Sample Injection Device. One of the major modifications in the present experiments was the use of a stainless steel sample injection device to ensure the preservation of the products. Irradiated samples were directly crushed in the helium stream of a gas chromatographic flow system. Carriers such as silacyclopentane and silacyclopent-3-ene were added to the sample-crushing chamber beforehand in order to enhance the preservation. The whole gas chromatographic system was usually conditioned with compounds such as SiH_4 before the analysis of each series of samples.

Hydrogenation Experiments. The silicon-31 labeled products used for hydrogenation were first trapped from the helium stream with liquid nitrogen. The trapping periods were predetermined with similar samples. After helium was slowly pumped off from the trap, hydrogen gas and appropriate carrier molecules were added to the trapped compound. The mixture was injected through a catalyst tube containing Pd supported on active carbon maintained at a fixed temperature. Helium was again used as a carrier gas, although in one experiment hydrogen was employed directly as the eluent gas. The hydrogenation products were trapped from the outlet of the catalyst tube and were analyzed with radio-gas chromatography. Both the SF-96 and the DMS columns were used for the identification and separation of the hydrogenation products.

Radiation Dose Effect. The samples were irradiated in an internal cadmium-lined boron rotisserie at the Texas A&M Nuclear Science Center reactor. The external thermal neutron flux was approximately 2×10^{11} neutrons/(cm^2 s) when the reactor was operating at a power level of 1 MW. During the radiation dose effect studies, various irradiation times and power levels were used. They ranged from 6 min at 4 kW to 10 min at 300 kW.

γ-Ray Irradiation Experiments. The γ-ray irradiation experiments were performed with the cobalt-60 source of the Nuclear Engineering Department at Texas A&M University. The intensity of the γ-ray source was 0.572 Mrad/h. A reaction system containing 70% PF_3 and 30% 1,3-butadiene was chosen for these experiments. A set of four samples of the above composition was irradiated with fast neutrons from the nuclear reactor for ^{31}Si formation. One of these four was analyzed immediately as a comparison standard. The other three were further irradiated with γ rays for time periods of 30, 60, and 120 min, respectively. Sample analysis was performed with the 7-ft DMS column at 25 °C as previously described.

Thermal Stability Experiments. A reaction system containing 70% PH_3 and 30% 1,3-butadiene was chosen for these experiments. Samples of the above composition were irradiated in sets of four for each series of the thermal stability studies. The irradiation temperature was around 25 °C. One of these four samples was used as a standard and was analyzed immediately after irradiation. Each of the other three samples was heated separately at a specific temperature for 30 min using a ceramic tube with heating elements. The temperature employed for such thermal stability studies ranged from 50 to 300 °C. All of these samples were analyzed with radio-gas chromatography through the 30-ft SF-96 column at 55 °C as previously described.

Chemicals. Phosphine (>99.999%), 1,3-butadiene (>99.5%), silane (>99.99%), and nitric oxide (>99.0%) were all obtained from Matheson. PF_3 (97-99%) was obtained from PCR, Inc. Each gas was used without further purification except for several cycles of degassing. The catalyst, Pd supported on active carbon, was obtained from Matheson Coleman and Bell.

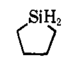
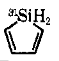
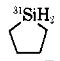
Results and Discussion

Composition Studies on Recoil ^{31}Si Reactions with 1,3-Butadiene. In the work published by Gaspar and co-workers[9,10] where a tentative identification of [^{31}Si]-1-silacyclopenta-2,4-diene (SCPD*) was described, they have studied product yields as a function of sample composition. As the mole fraction of 1,3-butadiene in the PH_3-butadiene mixture increases, the yield of SCPD* increases linearly while that of [^{31}Si]-silacyclopent-3-ene (SCP*) goes through a maximum. We have repeated the same experiments and have confirmed their results quantitatively. However, strictly speaking, the product SCPD* is still not positively identified, and a more direct verification for its identity is definitely necessary.

Identification of [^{31}Si]-1-Silacyclopenta-2,4-diene through Catalytic Hydrogenation. A check on the trapping efficiency of the tentatively identified SCPD* was performed before the catalytic hydrogenation of this compound for identification. Five experiments were performed for this purpose. In each experiment, SCPD* was condensed out from the helium stream of a GC system and was injected immediately through a radio-gas chromatographic system for counting. Approximately half of the expected amount of this compound was usually detected. However, similar experiments performed with SCP* indicate that the trapping was quantitative. This means that certain amounts of this compound were removed during either the trapping or the reinjection processes. One of the possible removal mechanisms might be due to hydrolysis of this silicon-containing compound with trace amounts of H_2O or other components in the transferring and analytical devices. Whatever the removal process is, SCPD* is *not* converted into one of its potential hydrogenation products such as SCP* and [^{31}Si]silacyclopentane, as none of them was observed during the reinjection runs.

Seven hydrogenation experiments have been performed and

Table I. Hydrogenation of ^{31}Si-Labeled Silacyclopenta-2,4-diene and Silacyclopent-3-ene over Pd/C Catalyst

trapped compd for hydrogenation	hydrogenation conditions			obsd product yields[a]		
	temp, °C	H_2 added, Torr	 added, Torr			
SCPD*	100	123	32	0.70	10.70	0
	100	240	36	3.46	2.13	0
	100	H_2 stream	67	1.14	8.44	0
	103	120	38	0.85	2.65	0
	130	115	31	4.30	17.40	0
	145	239	41	5.60	7.44	0
	200	240	38	4.48	13.44	0
SCP*	100	240	16	0	279.91	0.28
	120	240	18	0	381.45	0.11
	144	240	18	0	413.30	0.28

[a] Observed product yields are expressed in the unit of observed ^{31}Si radioactivity per Torr mL of ^{31}Si precursor.

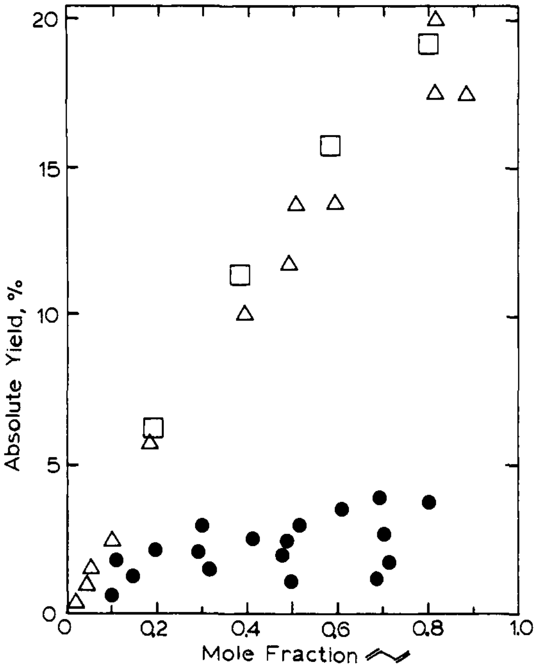


Figure 1. Radiation dose effect on the absolute yield of [^{31}Si]-1-silacyclopenta-2,4-diene from PH_3-butadiene systems: 3.0 × 10^3 (●); 6.0 × 10^2 (▵); 1.8 × 10^2 kW min (□).

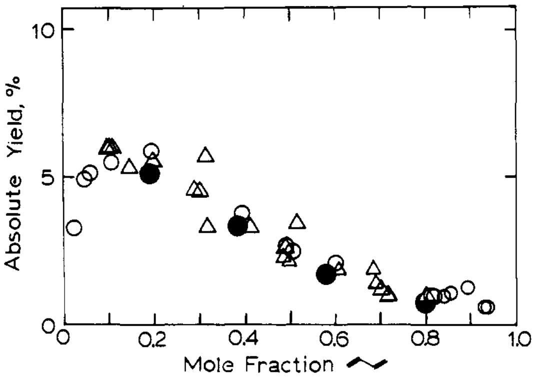
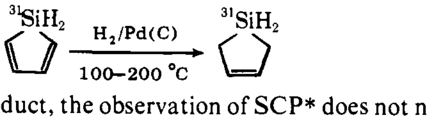


Figure 2. Radiation dose effect on the absolute yield of [^{31}Si]-silacyclopent-3-ene from PH_3-butadiene systems: 3.0 × 10^3 (▵); 6.0 × 10^2 (○); 1.8 × 10^2 kW min (●).

the results are summarized in Table I. Under a variety of conditions such as different temperatures and different amounts of additives, SCP* is always the only hydrogenation product observed from SCPD*. Since it is a flow system with relatively short residence time in the catalyst bed, there is always some unreacted SCPD* left. No [^{31}Si]silacyclopentane was observed as a product, although its unlabeled counterpart was always added as a carrier. The fact that SCP* was observed as a hydrogenation product from this trapped compound provides the strongest chemical evidence that this trapped compound is indeed SCPD*. The reaction must proceed as shown in eq 1. Although no [^{31}Si]silacyclopent-2-ene was



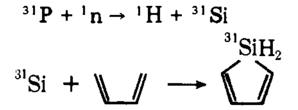
(1)

observed as a product, the observation of SCP* does not necessarily imply that the catalytic hydrogenation proceeds definitely or solely via a direct 1,4-addition mechanism. A 1,2-addition followed by catalytic isomerization to effect an apparent 1,4-addition is also possible. On the other hand, the absence of [^{31}Si]silacyclopentane indicates that further hydrogenation of SCP* is unlikely under the experimental conditions. This was verified by three experiments as shown in the bottom part of Table I where SCP* was trapped and hydrogenated under similar conditions. Less than one part per thousand of SCP* was converted to [^{31}Si]silacyclopentane at a temperature range of 100–144 °C.

The relative yields of SCPD* and SCP* included in Table I have no quantitative significance because the conditioning of the catalyst was not well controlled when these experiments were performed. In addition, various amounts of SCPD* may have been lost during various steps of the experimental procedure. A significant amount of ^{31}Si radioactivity was detected on the catalyst's surface after such a hydrogenation experiment.

Radiation Dose Effect on SCPD*. The fact that SCPD* was observed during recoil ^{31}Si reactions with 1,3-butadiene when either PH_3 or PF_3 was employed as the ^{31}Si precursor indicates that the following sequence of reactions proceeds (eq 2 and 3).

$$^{31}P + {}^{1}n \rightarrow {}^{1}H + {}^{31}Si \qquad (2)$$



(3)

In Figure 1, the yields of SCPD* as a function of butadiene mole fraction in a PH_3-butadiene system were plotted for three different radiation dose levels. It is obvious that, with low radiation doses such as 6.0 × 10^2 kW min or below, the original SCPD* yield was preserved. However, at higher dose levels such as 3.0 × 10^3 kW min, a significant fraction of the SCPD* produced was removed through radiation damage. In Figure 2, it is observed that the corresponding SCP* yields from similar samples do not show such a radiation dose dependence.

In Figure 3, the yields of SCPD* as a function of butadiene mole fraction in a PF_3-butadiene system were plotted. At a

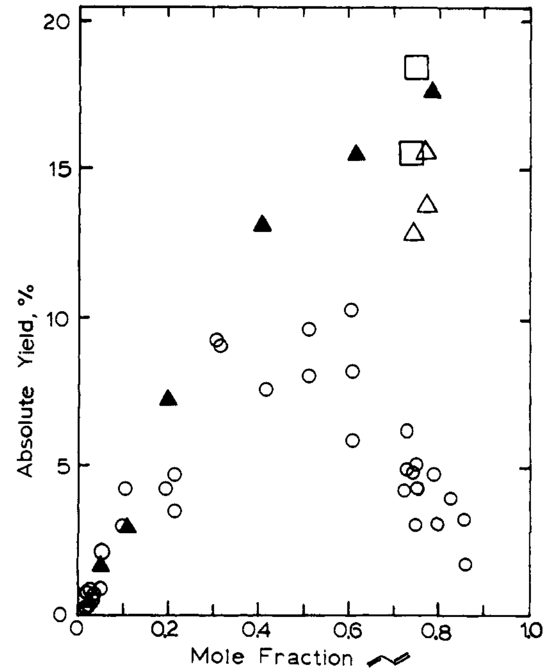


Figure 3. Radiation dose effect on the absolute yield of [^{31}Si]-1-silacyclopenta-2,4-diene from PF_3-butadiene systems: 6.0 × 10^2 (○); 1.8 × 10^2 (△); 2.4 × 10^1 (□); 6.0 × 10^2 kW min with nitric oxide (▲).

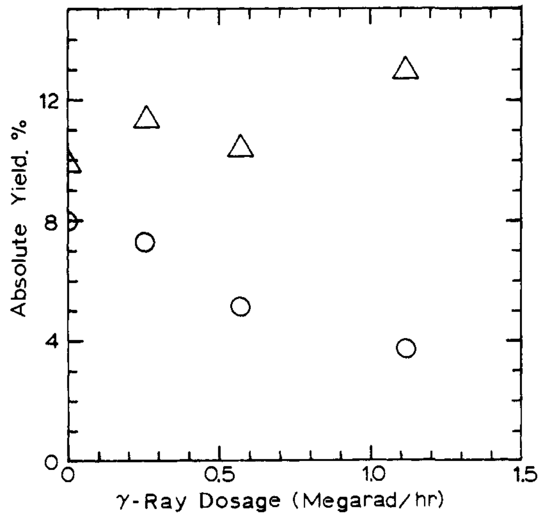


Figure 4. Effect of γ-ray doses on the absolute yields of SCPD* and DFSCP* from PF_3-butadiene systems: SCPD* (○); DFSCP* (△).

radiation dose of 6.0 × 10^2 kW min, the SCPD* yield increases with butadiene mole fraction with a similar slope as the corresponding results of the PH_3-butadiene system until a butadiene mole fraction of 0.3 is reached. Beyond this butadiene concentration, radiation damage becomes serious and the SCPD* yield drops sharply. For samples of 0.75 mole fraction of butadiene, the yield of SCPD* mostly recovered when the radiation dose was lowered down to 1.2 × 10^2 kW min, and essentially returned to the slope of a linear increase at a dose of 2.4 × 10^1 kW min. It seems that the SCPD* yield formed in the PF_3-butadiene mixture is more seriously subjected to radiation damage than those formed in the PH_3-butadiene mixture.

The supposition that SCPD* is formed in its original amount and is partially removed by species derived from radiation damage finds support in the nitric oxide scavenged results which are also included in Figure 3. With the addition of 5% NO, but with an extremely high radiation dose of 3.0 × 10^3 kW min, the SCPD* yield from the PF_3-butadiene system increases linearly with butadiene mole fraction with a slope characteristic of systems which are free from radiation damage. The mechanism of SCPD* removal is, therefore, likely due to the high reaction efficiency between free radicals, derived from radiation damage, and the conjugated π-bond systems of SCPD*.

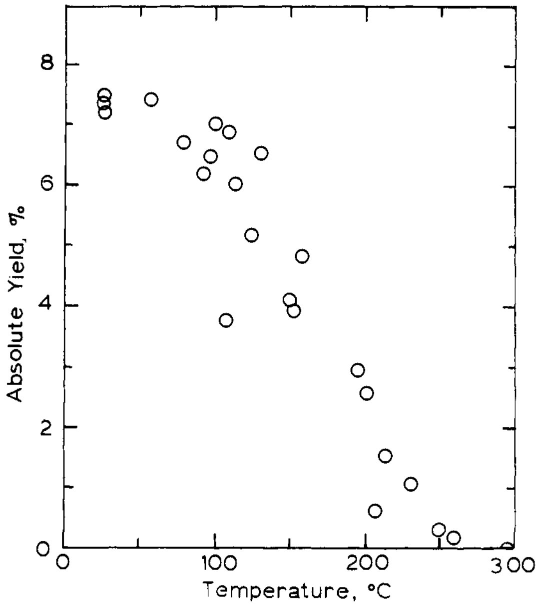


Figure 5. Thermal stability of SCPD* as a function of temperature.

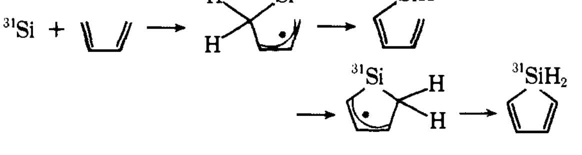
The most concrete support for the above supposition comes from the γ-ray irradiation studies of such ^{31}Si samples. After the completion of neutron irradiation and the hot atom reactions, the samples were exposed to γ-ray dosages which were equivalent to the γ-ray dosage in a nuclear reactor. For a 10-min neutron irradiation at a 300-kW power level in the nuclear reactor, the total accompanied γ-ray dosage was around 1.3 Mrad. As seen in Figure 4, the yield of SCPD* decreased sharply when the dosage of the additional γ-irradiation from the cobalt-60 source increased. This proved that SCPD* was removed with a mechanism involving species derived from γ-radiation. It is also seen in Figure 4 that the [^{31}Si]-1,1-difluorosilacyclopent-3-ene (DFSCP*) yield was not sensitive to additional γ-radiation.

Thermal Stability of SCPD*. SCPD* seems to be thermally stable at room temperature for about 12 h. After decay corrections, quadruplicate samples analyzed over the span of 1 day showed essentialy the same SCPD* yields.

A more detailed SCPD* thermal stability study has been performed and the results are show in Figure 5. It is seen that SCPD* starts to decompose around 100 °C. At a temperature of 200 °C or above, essentially all of the SCPD* decomposes during the time period of 30 min. The thermal instability of this compound at slightly elevated temperatures may be partially responsible for the failure of its synthesis by the conventional methods during the earlier studies.[1-5]

On the other hand, a similar thermal stability study for SCP* indicates that it is stable up to 300 °C.

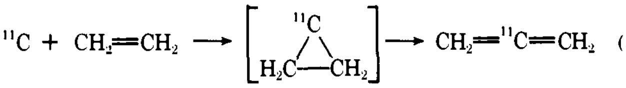
Mechanism for the Formation of SCPD*. Hwang and Gaspar[10] have proposed the following mechanism for the formation of SCPD* from the reactions of ^{31}Si atoms with butadiene (eq 4). The mechanism seems to suggest that the



(4)

reacting ^{31}Si atoms were in their triplet ground state. The cyclization process involved a two-stage addition of the unpaired electrons in the triplet ^{31}Si atoms to the conjugated π-bond systems of butadiene, each followed by a C-to-Si shift of H atoms. This is definitely a probable mechanism, and it should be responsible for the formation of the major portion of the observed SCPD* yields. However, other plausible mechanisms also may contribute to the SCPD* formation.

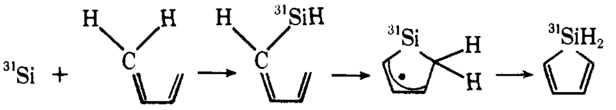
Let us turn to the recoil ^{11}C systems. For the reactions of ^{11}C atoms with alkenes, although π-bond interaction is always the predominant one, C-H insertion also contributes significantly to the product spectrum. In the case of C_2H_4, π-bond interaction with ^{11}C atoms will produce center-labeled propadiene, as shown in (5), while C-H insertion by ^{11}C atoms will form end-labeled propadiene, as illustrated in (6).



$$^{11}C + CH_2{=}CH_2 \longrightarrow \left[\begin{matrix} ^{11}C \\ H_2C{-}CH_2 \end{matrix}\right] \longrightarrow CH_2{=}{}^{11}C{=}CH_2 \quad (5)$$

$$^{11}C + CH_2 = CH_2 \rightarrow [^{11}CHCH{=}CH_2] \rightarrow {}^{11}CH_2{=}C{=}CH_2 \quad (6)$$

Degradation of the ^{11}C-labeled propadiene demonstrated that about two-thirds of the propadiene was center labeled, but the other one-third had ^{11}C atoms on the end.[18,19] Judging from this, and the expectation that there should be certain similarities in the reactions of C and Si atoms, it is likely that part of the SCPD* yields are also formed via a C-H insertion mechanism. As illustrated in eq 7, the C-H insertion by ^{31}Si atoms in butadiene may be followed by an intramolecular π-bond addition process to give SCPD*. The formation of SCPD* via two consecutive C-H insertion steps is probably less likely than the related mechanism as shown in (7).



(7)

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Specific Sequestering Agents for the Actinides. 3. Polycatecholate Ligands Derived from 2,3-Dihydroxy-5-sulfobenzoyl Conjugates of Diaza- and Tetraazaalkanes[1]

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Abstract: As part of a program to develop specific sequestering agents for the actinides, we have reported the synthesis of *N,N′,N″,N‴*-tetra(2,3-dihydroxybenzoyl)tetraazacycloalkanes. These tetra(DHB) amides are potentially octadentate ligands via coordination of the catechol oxygen atoms. We now report the synthesis of the DHB amides of linear tetraaza- and diazaalkanes. Furthermore, sulfonation of these compounds in 20–30% SO_3–H_2SO_4 yields exclusively their tetra(5-sulfo-DHB) analogues (**2, 7, 10, 13**). The sulfonated derivatives have several properties which make them superior to their precursors with respect to actinide coordination; these properties include increased water solubility, enhanced phenolic acidity, and improved oxidative stability near neutral pH. In vivo tests with mice have shown that tetrameric (5-sulfo-DHB) compounds (**15, 18, 21**) are generally acutely nontoxic, efficient sequestering agents for the actinides which promote rapid urinary excretion of ^{238}Pu. Compound **21**, the tetra(5-sulfo-DHB) derivative of spermine, is more effective than any other plutonium sequestering agent yet tested.

Introduction

The biological hazard presented by plutonium is a combination of its radioactivity and chemical properties.[2-5] Plutonium is a potent carcinogen whose long-term retention in mammals is due to the immobility of Pu(IV) in vivo. We are pursuing a biomimetic design concept to prepare new sequestering agents which will expedite plutonium removal and isolation.[6] This approach is based on the observation that there are many chemical and biological similarities of Pu(IV) and

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