7 and Figure 2, are listed in Table II. Using these values of ϕ_{CT} and eq 8, values of $\phi(E)$ as a function of dopant concentration are obtained. These are listed in Table II also. The increase of $\phi(E)$ with increasing dopant level indicates that the dopant aids not only geminate ion pair formation but also ion-pair dissociation into free charge carriers. This is perhaps not surprising since TNF is known to be an electron transporting molecule.

In summary, the aforementioned results show that electron donors and acceptors strongly quench the fluorescence of solid metal-free phthalocyanine. The fluorescence quenching is attributed to the formation of exciplexes at the surface. The probability of exciplex formation with TNF at a monolayer coverage was found to be high, approaching 0.87. Photoconductivity and fluorescence measurements indicate that the exciplexes decay to regenerate the singlet ground state and in the presence of a field to form free charge carriers. The carrier photogeneration efficiency of X-H_2Pc increased by as much as a factor of 3 in the presence of TNF. Perhaps the principal mechanism of charge carrier photogeneration in X-H_2Pc is extrinsic, involving exciplexes with electron acceptors such as oxygen.

α-Lithiosilanes. 4. Silaethylene Cycloadditions with Conjugated Dienes

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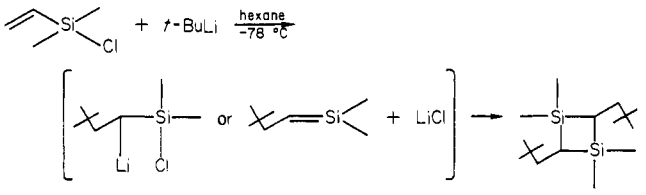
Contribution from the Department of Chemistry, North Texas State University, Denton, Texas 76203. *Received January 22, 1980*

Abstract: The reaction of vinyldimethylchlorosilane with *tert*-butyllithium was investigated in the presence of several conjugated dienes. With 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene, and anthracene, cycloadducts of the silaethylene intermediate are obtained in hydrocarbon solvents. The presence of tetrahydrofuran in the reaction mixture suppresses the formation of cycloadducts in favor of 1,3-disilacyclobutane formation. No cycloadduct is obtained with 2,5-dimethylfuran. It is concluded that lithium chloride elimination to give silaethylene intermediates occurs in hydrocarbon solvents, while in THF or in the presence of strong Lewis bases the addition reaction to give α-lithiosilanes occurs and products arising from their coupling reactions are obtained.

Introduction

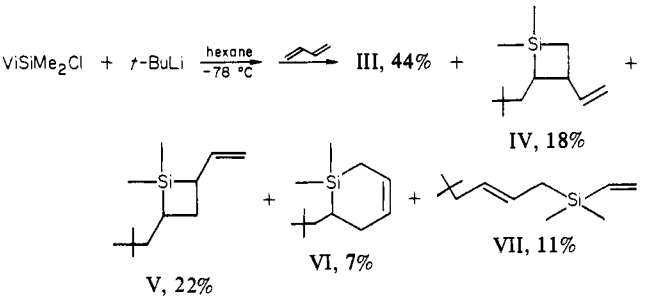
Recently, we reported the production of 1,3-disilacyclobutanes from vinyldimethylchlorosilane and *tert*-butyllithium in hydrocarbon solvent.[1] At that time, we proposed that the reaction went through an α-lithiochlorosilane (I) which eliminated LiCl to give the silaethylene II, which then dimerized to give the products.



Other reports have also indicated that species such as I may be important low-temperature silaethylene precursors.[2-4] In as much as silaethylenes produced by high-temperature thermolysis have been trapped with conjugated dienes,[5,6] we were led to investigate similar reactions involving our low-temperature silaethylene. We report the results of our investigation here.

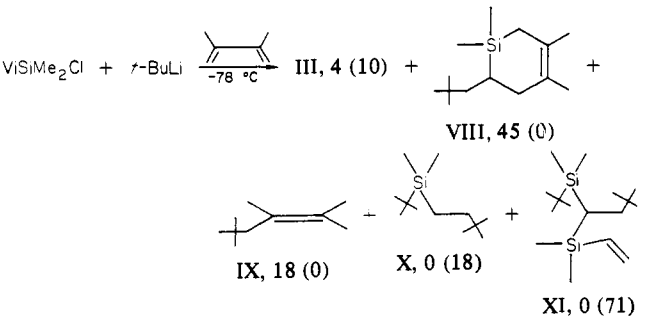
Results

When 1,3-butadiene was used as the trapping reagent, the products and percent yields obtained are shown below.



As we have noted elsewhere,[1] the ratio of [2 + 2] products IV and V to the [2 + 4] product VI is consistent with the cycloaddition of the highly reactive silaethylene II to the predominant s-trans conformer of butadiene. Product VII presumably arises from addition of *tert*-butyllithium to butadiene followed by coupling with vinyldimethylchlorosilane.

When 2,3-dimethyl-1,3-butadiene was used as the trapping reagent in hexane, the [2 + 4] cycloadduct was obtained. The products and yields shown below were obtained. The numbers in parentheses represent yields where THF was used as the solvent.



(% yield in THF)

It is of interest to note that only the [2 + 4] cycloadduct VIII

(1) P. R. Jones and T. F. O. Lim, *J. Am. Chem. Soc.*, 99, 2013 (1977); 99, 8447 (1977).
(2) D. Seyferth and T. L. Lefferts, *J. Am. Chem. Soc.*, **96**, 6237 (1974); *J. Organomet. Chem.*, **116**, 257 (1976).
(3) N. Wiberg and G. Preiner, *Angew. Chem., Int. Ed. Engl.*, **16**, 328 (1977).
(4) T. J. Barton and D. Banasiak, *J. Am. Chem. Soc.*, 99, 5199 (1977).
(5) N. S. Nametkin, L. E. Gusel'nikov, R. L. Ushakova, and V. M. Vdovin, *Dokl. Akad. Nauk SSSR*, **201**, 1365 (1971); W. J. Bailey and M. S. Kaufman, 157th National Meeting of the American Chemical Society, Minneapolis, MN, April 1969, Abstr. ORGN-55.
(6) E. A. Kline, Ph.D. dissertation, Iowa State University, 1973; *Diss. Abstr. Int. B*, **34**, 5904 (1974).

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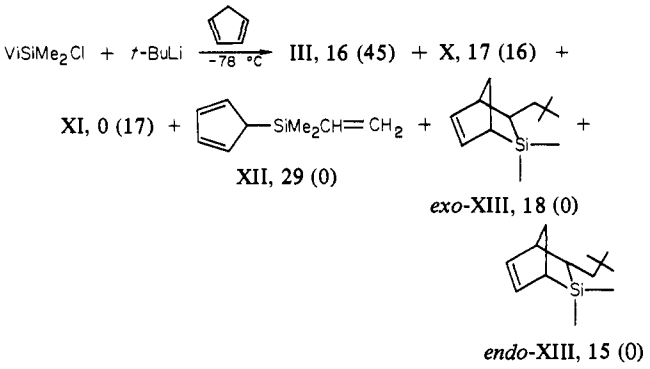
was detected, and then only in hydrocarbon solvent. In THF, the major products, X and XI, arise from addition of *tert*-butyllithium to vinyldimethylchlorosilane, substitution at silicon, and then hydrolysis (X) or coupling (XI) of the α-lithiosilane, I.

Cyclopentadiene, when used as a trapping reagent, gave results similar to those with 2,3-dimethyl-1,3-butadiene. Again, the [2 + 4] cycloadducts were only obtained in hexane; in this case, both the exo and endo isomers of the silanorbornene isomers XIII were obtained in a 55:45 ratio. These isomers were distinguished by 100-MHz ^{1}H NMR studies in which the methyl groups on silicon and the allylic proton, H-4, provided the clues to the identities.



(% yield in THF)

In *exo*-XIII, the *endo*-methyl on silicon is shielded by the rear lobe of the π bond, and the *exo*-methyl is shielded by the neopentyl group adjacent to it. These absorptions occur at 0.17 and 0.02 ppm, respectively. However, in *endo*-XIII, the shielding of the two methyl groups on silicon differs more than in the exo isomer. The *exo*-methyl is no longer shielded by the neopentyl group, but the *endo*-methyl is shielded by both the neopentyl group and the rear lobe of the π bond. The respective absorptions in this case are 0.24 and −0.03 ppm. Further, the allylic proton, H-4, also helped differentiate between the two isomers. In *exo*-XIII, H-4, shielded by the neopentyl group, is found at 2.60 ppm. In *endo*-XIII, in which the neopentyl group is away from H-4, the absorption is at 2.83 ppm. These data are consistent with assignments made by Davis and VanAuken in a similar case.[7]

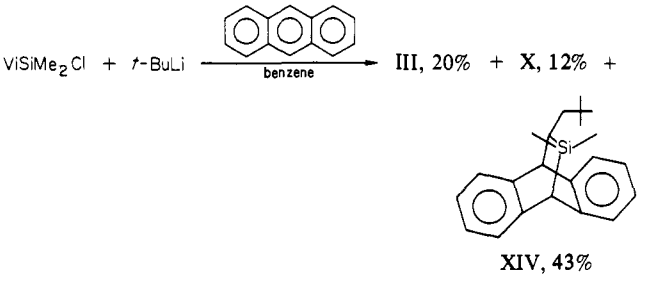
Product XII, obtained in 29% yield, was probably produced by metalation of cyclopentadiene by *tert*-butyllithium and coupling with vinyldimethylchlorosilane. It seems unlikely that cyclopentadiene was metalated by the α-lithiochlorosilane I, as no other products resulting from that reaction were found. Further, in THF, a solvent which is known to promote the addition of alkyllithium reagents to olefins,[8] products arising from the α-lithiosilane, e.g., III, X, and XI, are obtained while cyclopentadienyl-substituted silanes were not detected. These considerations suggest that in hydrocarbon solvents there is a competition between cyclopentadiene and the vinylsilane for the *tert*-butyllithium. Support for this conclusion was obtained from an experiment in which 1 equiv of *tert*-butyllithium at 0 °C was added dropwise to a solution of 5 equiv of vinyldimethylchlorosilane and 1 equiv of cyclopentadiene in hexane at 0 °C. The ratio of products arising from reaction of the *tert*-butyllithium reagent with vinylsilanes to XII increased from 2.3 to 5.3.

The effect of THF on the reaction with cyclopentadiene is similar to that observed with 2,3-dimethyl-1,3-butadiene. In THF, neither the cycloadducts nor the metalation product of cyclopentadiene, XII, is observed. Indeed, the presence of as little as *1* equiv of THF in the reaction mixture completely suppresses the formation of XII and XIII.

A slightly different system had to be designed in order to trap II with anthracene. The insolubility of anthracene in hexane or THF forced the use of benzene as the solvent. In this system, *tert*-butyllithium was added dropwise to a heterogeneous mixture of vinyldimethylchlorosilane and anthracene in benzene at room temperature to give the following results.

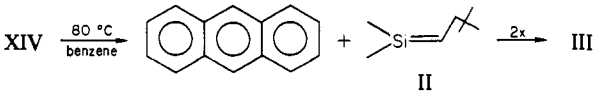
Table I. Analytical Data for VIII–XIV

compound	% C calcd	% C found	% H calcd	% H found	mass spectra calcd	mass spectra *m/e*, M$^+$
VIII	74.91	72.11	12.57	12.33	224	224
IX	85.63	85.44	14.37	14.31	140	140
X	71.89	71.60	14.09	14.00	200	200
XI	67.52	67.41	12.75	12.70	284	284
XII	71.91	71.60	9.40	9.10	150	150
XIII	74.91	74.90	11.62	11.55	208	208
XIV	82.43	82.68	8.80	8.57	320	320



When the reaction was carried out in sufficient benzene to dissolve all of the anthracene, the yield of XIV increased to 70%, and the formation of the disilacyclobutane (III) was suppressed. The [2 + 4] cycloadduct XIV was identified by its ^{1}H NMR spectrum which closely agreed with the spectrum of a similar compound recently reported by Sakurai.[9]

Interestingly, when the reaction was carried out in refluxing benzene, none of the cycloadduct XIV was obtained. The disilacyclobutanes (III) were the only isolated product. Presumably,



this was caused by the facile retro-Diels–Alder reaction at 80 °C of XIV to give anthracene and the silaethylene II which then dimerized to give III. Experiments are currently being conducted in our laboratory to determine the feasibility of this reaction as a convenient silaethylene generator.

When attempts were made to trap the silaethylene from the *tert*-butyllithium/vinyldimethylchlorosilane reaction by using 2,5-dimethylfuran or quadricyclane,[10] no cycloadducts were obtained. In both cases, the 1,3-disilacyclobutanes (III) were obtained in the usual 70–80% yields.

Discussion

One of the most significant observations reported above is the complete suppression of cycloadducts to 2,3-dimethyl-2,3-butadiene or cyclopentadiene when THF is present in the system. In the only other detailed study of the reactions of silaethylenes produced from α-lithiosilanes with dienes, Preiner and Wiberg observed 20–78% yields of the [2 + 4] cycloadduct of the silaethylene XVI with 2,3-dimethyl-1,3-butadiene in ether solvent.[11] They also observed complete suppression of the cycloadduct XVII in favor of the dimer XVIII when the reaction was carried out in THF. Further, it was shown that THF did *not* prevent the [2 + 4] cycloaddition of XVI from a thermal source with dimethylbutadiene.[11] Brook and co-workers also have observed the cy-

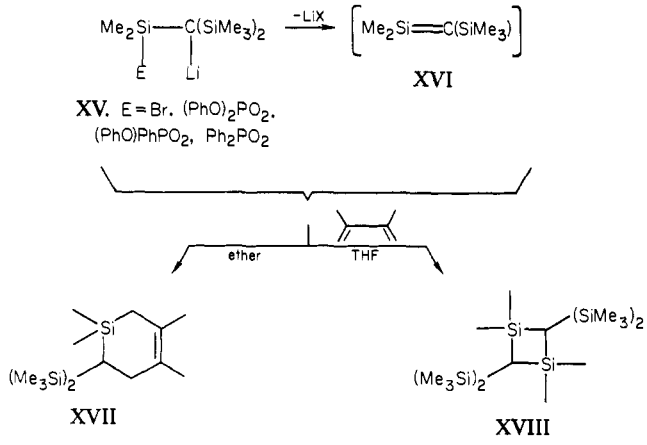
(7) J. C. Davis, Jr., and T. V. VanAuken, *J. Am. Chem. Soc.*, **87**, 3900 (1965).

(8) P. D. Bartlett, S. J. Tauber, and W. P. Weber, *J. Am. Chem. Soc.*, **91**, 6362 (1969).

(9) Y. Nakadaira, T. Kobayashi, T. Otsuka, and H. Sakurai, *J. Am. Chem. Soc.*, **101**, 486 (1979).

(10) We thank Professor Michael Landis, Southern Illinois University at Edwardsville, for providing us with a sample of quadricyclane, tetracyclo-[3.2.0.0^{2,7}.0^{4,6}]heptane.

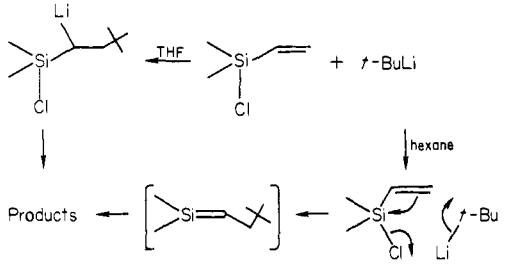
(11) G. Preiner, Doctoral dissertation, University of Munich, 1979. We thank Professor N. Wiberg for sending us a copy of this dissertation.



cloaddition of a silaethylene produced by thermolysis with dimethylbutadiene in THF.[12]

We indicated previously that the disilacyclobutane III might be produced by condensation of the α-lithiosilane I in THF. The results presented here support that suggestion. We further note that in THF derivatives of the α-lithiosilane, X and XI, are obtained. Our earlier attempts to trap the α-lithiosilane with trimethylchlorosilane were only successful in THF.[1] To date, we have been unable to obtain any evidence for the presence of the α-lithiosilane in hexane. Indeed, when the reaction of *tert*-butyllithium with vinyldimethylchlorosilane in hexane is monitored by NMR, no peaks attributable to the α-lithio compound are observed. There is no change in the spectrum until the temperature reaches about −20 °C, at which time peaks due to the starting materials decrease concomitantly with the appearance of peaks due to the disilacyclobutane III.

Based on these observations, we believe that silaethylene formation only occurs in hydrocarbon solvents, perhaps by a concerted addition–elimination process similar to that illustrated below. The



presence of THF or other strong Lewis bases (e.g., 2,5-dimethylfuran) in the system promotes the addition reaction to give the α-lithiosilane. Silaethylene formation is suppressed in favor of coupling reactions of the α-lithiosilanes. This may well be due to enhanced solvation of the lithium reagents by THF. In the absence of appropriate traps, both pathways lead to the formation of high yields of the "apparent silaethylene" dimers, 1,3-disilacyclobutanes.

Our findings support the conclusion of Seyferth and Lefferts that the disilacyclobutane XVIII formed from XV, E = Br, in a dimethyl ether/THF solvent system was produced by sequential coupling rather than by silaethylene dimerization.[2] An implication of our findings is that the formation of [2 + 4] cycloadducts with appropriate dienes may well provide definitive evidence for silaethylene intermediates.

Finally, our results may have some bearing on the reported generation of silabenzene by the dehydrochlorination of 1-chloro-1-methyl-1-silacyclohexadiene by using lithium bis(trimethylsilyl)amide.[4] As Barton and co-workers noted in a subsequent report of an unambiguous generation of silabenzene by a retro-ene reaction, the apparent adduct of silabenzene with perfluoro-2-butyne obtained could have been produced by addition of an initially formed pentadienyl anion to the alkyne followed by an intramolecular displacement of chloride.[13] The lack of any well-characterized product from the reaction of silabenzene with 1,3-butadiene and the presence of the Lewis base hexamethyldisilazane in their system[4] coupled with our findings seem to add some weight to that possibility.

Experimental Section

The solvents were dried by distillation from lithium aluminum hydride and sodium–potassium alloy, respectively. All glassware was dried prior to use by flaming the assembled apparatus while flushing with dry nitrogen or argon. Solutions of *tert*-butyllithium were obtained from Lithium Corp. of America and were standardized by using the method of Kofron.[14] Vinyldimethylchlorosilane was obtained from Petrarch Systems or synthesized by using the method of Okawara and Sakiyama.[15] For the GLC preparative work, a 20 ft × $^3/_8$ in. stainless-steel column containing 10% OV-17 on 80–100 mesh Supelcoport in a Varian Series 1800 gas chromatograph with thermal conductivity detectors was used. All yields were determined by GLC with *n*-butyl ether as the internal standard. For this work, a 6 ft × $^1/_8$ in. stainless-steel column containing 3% OV-17 on 100–120 mesh Supelcoport or a 6 ft × $^1/_8$ in. stainless-steel column containing 3% SP-2250 on 100–120 mesh Supelcoport was used in a Perkin-Elmer Sigma-3 gas chromatograph with flame ionization detector. NMR spectra were obtained on a R24B 60-MHz spectrometer or a Jeol MH-100 100-MHz spectrometer by using tetramethylsilane or chloroform as internal standard and carbon tetrachloride as solvent. Chemical shifts are given in parts per million downfield from tetramethylsilane. Mass spectra were obtained by using a Hitachi Perkin-Elmer RMU-6E spectrometer, and elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

General Procedure for the Trapping Experiments. A solution of 0.02 mol of vinyldimethylchlorosilane with 0.02 mol of *tert*-butyllithium in 50 mL of hexane or THF at −78 °C was stirred for 3 h, and then 0.02 mol of the diene was added.[16] The reaction mixture was allowed to warm to room temperature and was stirred overnight. The white precipitate which had formed when hexane was the solvent dissolved when the reaction was quenched with 10 mL of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer extracted three times with hexane. When THF was used as the solvent, the aqueous layer was saturated with potassium carbonate prior to extraction. After the combined organic layers were dried with magnesium sulfate, the solvent was removed by using a rotary evaporator. GLC analysis was carried out on the residue.

1,3-Butadiene as the Trapping Reagent. This reaction and the characterization of the products III–VII have been described previously.[1]

2,3-Dimethyl-1,3-butadiene as the Trapping Reagent. Analysis of this reaction mixture with hexane as the solvent gave III, VIII, and IX in 4, 45, and 18% yields, respectively. The reaction in THF gave III, X, and XI in 4, 18, and 71% yields, respectively.

NMR data for the purified compounds are as follows. 1,1,3,4-Tetramethyl-6-neopentylsilacyclohex-3-ene (VIII): 0.06 (s, 3 H), 0.10 (s, 3 H), 0.99 (s, 9 H), 1.26 (m, 3 H), 1.74 (m, 6 H), 1.35–2.35 (m, 4 H). 2,3,5,5-Tetramethyl-2-hexene (IX):[17] 1.02 (s, 9 H), 1.75 (s, 9 H), 2.08 (s, 2 H). 2,2,3,3,6,6-Hexamethyl-3-silaheptane (X): −0.03 (s, 6 H), 0.31–0.63 (m, 2 H), 0.89 (s, 9 H), 0.90 (s, 9 H), 1.08–1.38 (m, 2 H). 3,3,5,5,6,6-Hexamethyl-4-neopentyl-3,5-disilahept-1-ene (XI): 0.16 (s, 6 H), 0.25 (s, 6 H), 0.36–0.81 (m, 1 H), 0.98 (s, 9 H), 1.03 (s, 9 H), 1.57 (m, 2 H), 5.96 (m, 3 H).

Cyclopentadiene as the Trapping Reagent. This reaction was run under the same conditions as those above. From the hexane reaction, five products, III, X, XII, *exo*-XIII, and *endo*-XIII, were obtained in 16, 17,

(12) A. G. Brook and J. W. Harris, *J. Am. Chem. Soc.*, **98**, 3381 (1976).
(13) T. J. Barton and G. T. Burns, *J. Am. Chem. Soc.*, **100**, 5246 (1978).
(14) W. G. Kofron and L. M. Baclawski, *J. Org. Chem.*, **41**, 1879 (1976).
(15) R. Okawara and M. Sakiyama, *Nippon Kagaku Zasshi*, **58**, 805 (1955).
(16) It should be noted that this 3-h stirring time was used to maintain experimental conditions comparable to the first work with butadiene as the trap (ref 1). The trap may be added before or immediately after the addition of *tert*-butyllithium, and similar results are obtained. However, in these cases, the ratio of addition product to the diene, VII or IX, or metalation product, XII, to silaethylene products increases. One might speculate that the stirring for a period at low temperature promotes an association of the alkyllithium reagent with vinyldimethylchlorosilane and favors the lithium chloride elimination on warming.
(17) D. Grosjeau, G. Mouvier, and J. Dubois, *J. Org. Chem.*, **41**, 3872 (1976).

29, 18, and 15% yields, respectively.

A reaction was run under the same conditions as above but with THF as the solvent. Three products were isolated, III, X, and XI, in 45, 16, and 17% yields, respectively. When the same reaction was run in hexane with a fivefold excess of vinyldimethylchlorosilane, III, X, XII, and XIII were obtained in 11, 3, 10, and 19% yields, respectively. A reaction with a 20% mixture of THF in hexane as the solvent gave only III, X, and XI in yields of 48, 19, and 23%, respectively.

The NMR data for the new products are as follows. Cyclopentadienyldimethylvinylsilane (XII): 0.04 (s, 6 H), 3.11 (m, 1 H), 5.60–6.40 (m, 3 H), 6.64 (m, 4 H). *exo*-2,2-Dimethyl-3-neopentyl-2-silanorborn-5-ene (*exo*-XIII): 0.02 (s, 3 H), 0.17 (s, 3 H), 0.46 (m, 1 H), 0.95 (s, 9 H), 1.05–1.24 (m, 2 H), 1.60 (m, 2 H), 1.96 (m, 1 H), 2.60 (m, 1 H), 5.85 (m, 2 H). *endo*-2,2-Dimethyl-3-neopentyl-2-silanorborn-5-ene (*endo*-XIII): −0.03 (s, 3 H), 0.24 (s, 3 H), 0.80–0.95 (m, 1 H), 0.96 (s, 9 H), 1.18 (m, 2 H), 1.53 (m, 2 H), 2.05 (m, 1 H), 2.83 (m, 1 H), 5.85 (m, 2 H).

Anthracene as the Trapping Reagent in Benzene Solvent. To a mixture of 0.05 mol of vinyldimethylchlorosilane with 0.01 mol of anthracene in 250 mL of benzene was added 0.01 mol of *tert*-butyllithium at room temperature. Analysis after the usual hydrolytic workup gave three products, III, X, and XIV, in 20, 12, and 43% yields, respectively. When the reaction was run with sufficient benzene to dissolve all the anthracene, ~600 mL, a 70% yield of XIV was obtained. However, when this reaction was run at 80 °C, only III was obtained in 75% yield.

NMR data for the new compound are as follows. 2,2-Dimethyl-3-neopentyl-5,6,7,8-dibenzo-2-sila-bicyclo[2.2.2]octane (XIV): −0.03 (s, 3 H), 0.07 (s, 3 H), 0.19–0.59 (m, 1 H), 0.99–1.39 (m, 2 H), 1.14 (s, 9 H), 3.87 (s, 1 H), 4.17 (d, 1 H, J = 2.4 Hz), 7.10 (s, 8 H). Analytical data for the new compounds are given in Table I.

Acknowledgments. The authors gratefully acknowledge the Robert A. Welch Foundation and the North Texas State Faculty Research Fund for their support of this work.

Palladium-Assisted Alkylation of Olefins

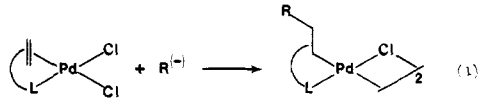
Louis S. Hegedus,* Robert E. Williams, Michael A. McGuire, and Tamio Hayashi

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. *Received September 6, 1979*

Abstract: Stabilized carbanions (pK_a = 10–17) react with olefin–palladium(II) complexes to result in alkylation of the olefin predominantly at the 2 position after a reductive or β-elimination isolation procedure. Two equivalents of triethylamine is optimum for this alkylation reaction, and the key step is thought to involve external (trans) attack of the complexed olefin. With the addition of HMPA to the above system, anions with pK_as up to ~30 reacted well. With propene exclusive attack at the 2 position was observed, while with 1-hexene attack at the 1 position was almost exclusive. With the addition of HMPA, internal disubstituted olefins as well as terminal olefins reacted in reasonable yield.

Introduction

The ability to directly alkylate simple olefins with carbanions would be of significant use in organic synthesis. While unactivated olefins are generally inert toward nucleophiles, complexation to appropriate transition metals can promote reaction in some cases. Chelated olefin complexes of palladium(II), such as those of dicyclopentadiene[1] and other diolefins, and of allylic and homoallylic amines[2] and sulfides[2,3] readily undergo reaction with stabilized carbanions of acetylacetone, ethyl acetoacetate, and diethyl malonate to form isolable σ-alkylpalladium(II) complexes stabilized by chelation (eq 1). (Carbanions with pK_as in excess of



L = C≡C, −NR$_2^1$, −SR^1

15 result in reduction of the metal rather than alkylation of the olefin.) This "carbopalladation" of *N,N*-dimethylallylamine was the key step in an elegant synthesis of the prostaglandins.[4]

The alkylation of simple olefins *not* held into coordination with a metal by chelation is a much less general process. Cationic olefin complexes of η^5-cyclopentadienyliron dicarbonyl undergo facile alkylation of the coordinated olefin by a wide range of carbanions, from malonates through organocuprates, to produce very stable σ-alkyliron complexes from which removal of the metal is difficult. The regiospecificity of this process with unsymmetrical olefins is low. Grignard and organolithium reagents result in olefin displacement and reduction of the organometallic complex, rather than alkylation.[5] Ethylene and methyl acrylate complexes of iron tetracarbonyl also react with malonate ester anions to give moderate yields of alkene alkylation products after oxidative removal of the iron from the product.[6] Finally, styrene reacts with methyllithium in the presence of palladium(II) acetylacetonate to give *trans*-β-methylstyrene in 90% yield. In contrast to the above reactions, this is thought to proceed by insertion of the olefin into a "Pd–CH_3" complex, rather than by external attack of the carbanion on the palladium-coordinated styrene.[7,8] Recently we reported the palladium(II)-assisted alkylation of olefins by stabilized carbanions (pK_a = 10–17).[9] Herein we report the full details of that study as well as the successful extension of this alkylation reaction to much less stabilized carbanions.

Results and Discussion

While in principle nucleophilic attack on palladium-complexed olefins is a very general process, in practice competing side reactions, particularly olefin displacement and/or reduction of the metal by the nucleophile, often seriously limit the synthetic utility of this type of reaction. Previous studies directed toward palladium-assisted amination of olefins[9,10] indicated that these side reactions could be suppressed by carrying out the reaction at low temperatures. The observation that 2 equiv of amine *in excess* of the one acting as the nucleophile was required for reasonable yields suggested either that the step involving amination of the

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