Reaction between Hydridotetracarbonyl(trichlorosilyl)iron, $HFe(CO)_4SiCl_3$, and Conjugated Dienes. Evidence for a Free Radical Mechanism

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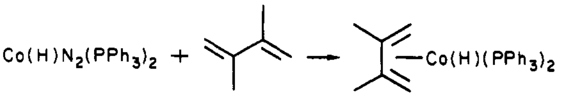
The reaction between $HFe(CO)_4SiCl_3$ and several conjugated dienes has been investigated. Chemical kinetics data, diene reactivity patterns, and the observation of the CIDNP effect are consistent with a hydrogen atom transfer free radical type mechanism in all cases. In most cases the reaction was cleanly first order in each reagent. Second-order rate constants (× 10^4 $L{\cdot}mol^{-1}{\cdot}s^{-1}$) in toluene at 20 °C are 3.9 (1,3 butadiene), 39 (isoprene), 88 (2,3-dimethyl-1,3-butadiene), 1.7 (*trans*-1,3-pentadiene), 0.9 (*cis*-1,3-pentadiene), and 0 (*trans,trans*-2,4-hexadiene). In the case of isoprene the rate constant is insensitive to solvent polarity and to the presence of CO. With $DFe(CO)_4SiCl_3$ an inverse isotope effect (k_D/k_H = 1.4) was observed.

Introduction

The addition of the transition-metal hydride functional group to conjugated dienes, enones, etc. is an important step in transition-metal moderated elaboration of dienes.[1] In many cases the first step of the reaction between the transition-metal hydride and the diene involves complexation of the diene. This would be the case where the metal hydride is coordinatively unsaturated or contains a labile ligand.[2,3] Equation 1 exemplifies one of the few cases

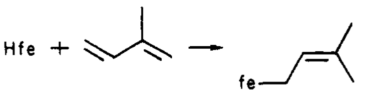


(1)

where the (diene)metal hydride complex was isolated prior to conversion to an η^3-allyl complex.[4] There are other cases in which non labile coordinatively saturated transition-metal hydrides add to conjugated dienes (eq 2) and in such cases the mechanistic picture is less clear.[5,6]

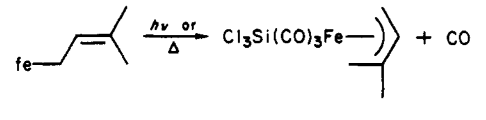
(2)

Previously we reported that hydrido(trichlorosilyl)tetracarbonyliron, Hfe (the symbol fe will be used to represent the $Fe(CO)_4SiCl_3$ group in this paper), adds to conjugated dienes as shown in eq 3. The 1,4 adduct de-



(3)

picted in eq 3 was observed spectroscopically, but the isolated product was the η^3-allyl species (eq 4).[7] In the case of dienes that were substituted on either or both ends, such as 1,3-pentadiene or cyclohexadiene, we found that the diene was converted to the olefin (eq 5).



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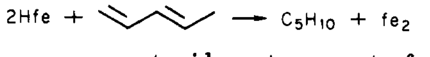


(5)

Table I. Kinetics for the Reaction Hfe + diene ⟶ Products (20 °C, Touluene Solvent; Rate = k_2(diene)(Hfe))

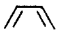
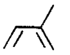
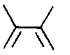
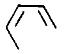
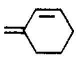
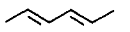
diene	10^4k_2, $L{\cdot}mol^{-1}{\cdot}s^{-1}$ (±20%)	reaction
	3.9	1,4 addition
	39	1,4 addition
	88	1,4 addition
	1.7	hydrogenation
	0.9	hydrogenation
	not cleanly second order	hydrogenation
	rearranges to internal diene	
	0	none

Table II. Effect of Solvent Dielectric Constant vs. Rate Constant for Hfe + isoprene ⟶ $feCH_2CH{=}C(CH_3)_2$

solvent	ε	10^3k,[a] $L{\cdot}mol^{-1}{\cdot}s^{-1}$
toluene	2.38	2.3
chlorobenzene	5.71	2.1
methylene chloride	9.08	2.9

[a] Unthermostated.

In this paper we report evidence to support a free radical mechanism for the reaction between Hfe and several different conjugated dienes with the product of the reaction being determined by the relative rates of various radical combination reactions.

Results

Kinetics parameters were obtained for the reaction between Hfe and several different dienes under pseudo-first-order conditions as described in the Experimental Section. The second-order rate constants are listed in Table I.

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(1) Collman, J. P.; and Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; Chapter 7.

(2) Roundhill, M. D. *Adv. Organomet. Chem.* **1975**, *13*, 274.

(3) Lobach, M. I.; Kormer, V. A. *Russ. Chem. Rev.* (*Engl. Transl.*) **1979**, *48*, 758.

(4) Rinze, P. V. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 336.

(5) McClellan, R. W.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L. Holuk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601.

(6) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, 189.

(7) Connolly, J. W.; Hoff, C. D. *J. Organomet. Chem.* **1978**, *160*, 467.

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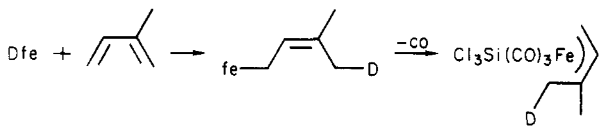
The most detailed kinetics study was done on the reaction between Hfe and isoprene. In this case it was found that the second-order rate constant was quantitatively the same when the reaction was done under 1 atm of carbon monoxide or under an atmosphere of nitrogen. Similarly the presence of trichlorosilane up to 0.3 M had no effect on the rate constant. Table II shows that solvents of different dielectric constant have little effect on the second-order rate constant for this reaction. The choice of solvents is necessarily limited because Hfe protonates nitriles, ethers, and other nucleophilic solvents, and the resulting solutions are not thermally stable. With use of Dfe of approximately 70% isotopic purity, an inverse isotope effect ($k_D/k_H = 1.4$) was observed.

In a variable-temperature study using toluene as the solvent, it was found that at 20, 30, and 40 °C the second-order rate constants were 3.94×10^{-3}, 8.45×10^{-3} and 1.22×10^{-2} mol·L^{-1}·s^{-1}, respectively. These data yield the activation parameters $\Delta H^{\ddagger} = 11.0$ kcal/mol and $\Delta S^{\ddagger} = -31.6$ eu.

Using Dfe, it was possible to examine the stereochemistry of reaction 6. The ^{1}H NMR resonances in the η^1 adduct are (in ppm) 5.5 (vinyl), 2.6 (α-CH$_2$), and 1.6 (methyls).[7] The integral values for the product solution in reaction 6 indicated that all the deuterium ended up in the allyl methyl groups. The ^{1}H NMR resources for the η^3-allyl product are (in ppm) 0.8 (anti methyl), 0.5 (syn methyl and anti methylene proton), 1.5 (syn methylene protons), and 4.1 (methyne proton).[7] Relative signal sizes here indicate that the deuterium selectively ends up on the anti methyl group as indicated in eq 6.

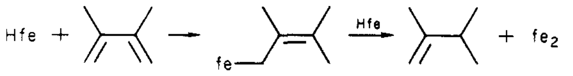


(6)

We were not able to obtain parent ion peaks in the mass spectrum of Hfe or Dfe so the isotopic purity of Dfe was estimated by using ^{1}H NMR. Selected relative ion intensities in the mass spectrum of the deuterated η^3-allyl product were consistent with complete transfer of the deuterium from Dfe to the organometallic product even though the reaction was done in a large excess of isoprene.

Useful information about reactive intermediates was obtained by examining the ^{1}H NMR spectra of reaction mixtures both in the case of 1,3-cyclohexadiene and in the case of 2,3-dimethyl-1,3-butadiene. Figure 1 shows NMR spectra of a Hfe–cyclohexadiene reaction mixture recorded at 2-min intervals. The only NMR signals present are those due to starting material and cyclohexene. Initially the 1.8 ppm signal due to the nonallylic protons in cyclohexene appeared as an emission indicating the CIDNP effect. This was the only reaction in the study in which the CIDNP effect was observed.

In the reaction between Hfe and 2,3-dimethyl-1,3-butadiene, as the resonances due to the starting diene disappeared, new resonances at 2.6 and 1.4 ppm appeared. These latter resonances disappeared and were replaced by the resonances of the final product 2,3-dimethyl-1-butene. We interpret the transitory resonances to be due to the α-CH$_2$ and the alkylmethyl groups (three types, not resolved) of the intermediate 1,4 adduct shown in eq 7.



(7)

Conjugated exo methylene dienes react with Hfe as shown in eq 8a and 8b. The diene equilibration is catalyzed by Hfe, but Hfe is consumed only in the reduction step. Due to the complexity of the system our rate information is qualitative but the first step is faster than the second step.

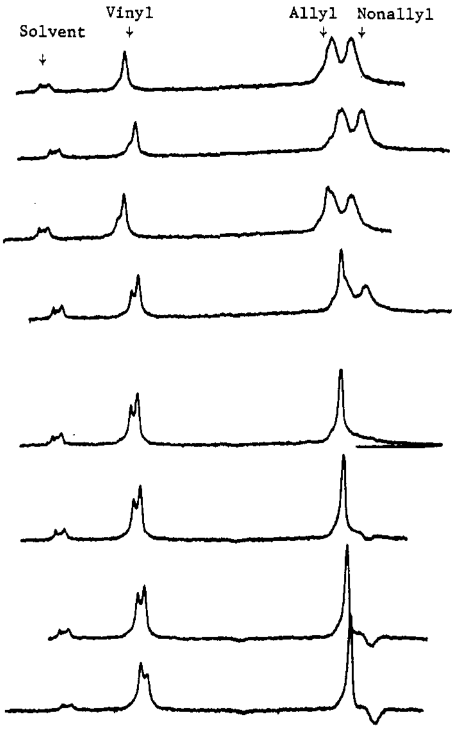
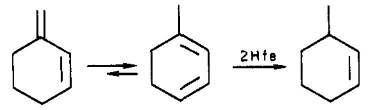
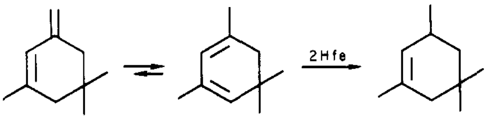


Figure 1. ^{1}H NMR spectrum of Hfe–1,3-cyclohexadiene reaction mixture run at approximately 2-min intervals.



(8a)



(8b)

Discussion

There are several plausible mechanisms by which Hfe could react with conjugated dienes. It is a strong acid[8] so there is the possibility of a proton-transfer reaction. It is a metal carbonyl so there is the possibility of prior CO loss followed by coordination of the diene and then intramolecular hydrogen atom transfer. While it is as yet unprecedented, there is the possibility of a concerted (six-center) reaction between the H–Fe group and the termini of the diene. There is also the possibility of a free radical reaction.

Since proton transfer would involve a polar transition state, the fact that solvents of different dielectric constant do not affect the rate constant argues against this mechanism. The fact that the reaction rate is not affected by CO pressure suggests that CO loss or ligand migration is not involved in a preequilibrium step (the rate of reaction of HFe(CO)$_4^-$ with acrylate esters is retarded more than 100-fold by 1 atm of CO[9]).

We are assuming that all the dienes studied here react with Hfe by the same mechanism. Given that assumption our results fit best with a free radical mechanism. There have been several recent reports of free radical hydro-

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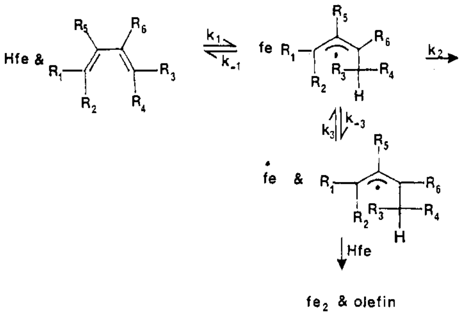
[8] Jetz, W.; Graham, W. A. G. *Inorg. Chem.* **1971**, *10*, 1647.

[9] Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahreu, R.; Komoto, R. G.; Brauman, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 1119.

Scheme I

$$\text{m−H} + \text{substrate} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{radical pair}] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{substrate radical} + \text{metal radical} \longrightarrow\!\!\longrightarrow \text{products}$$

Scheme II

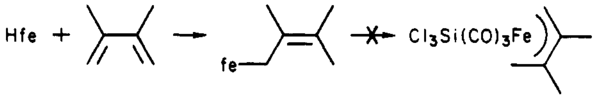


genation of aromatic and unsaturated hydrocarbons by transition-metal hydrides.[10-19] In general these reactions exhibit second-order kinetics with negative activation entropies and inverse kinetic isotope effects. (The origin of the inverse isotope effect lies in the fact that the C–H bond being formed is stronger than the M–H bond being broken. See ref 16 for a more complete explanation.) In some cases the CIDNP effect has been observed as well. The mechanism for the reactions may be summarized as in Scheme I. Orchin and Roth[11] found rapid deuterium loss to the substrate pool in the reaction between $DCo(CO)_4$ and 1,1-diphenylethylene. However, Ungvary and Marko[19] observed quantitative deuterium transfer to substrate in the reaction between $DCo(CO)_4$ and styrene. Apparently in the former case k_{-1} is significant compared to k_1 while in the latter case it is not.

Our results can be explained in terms of a similar mechanism shown in Scheme II. The radical pair formed by initial H atom transfer can collapse to an alkenyliron product (k_2 path), or the radical pair can separate to give ultimately an olefin and fe_2 (k_3 path). The relative rates of the k_2 and k_3 paths are apparently governed by steric factors. Hydrogen atom transfer from metal hydrides to substituted styrenes and fluorenes is very sensitive to steric effects. (The relative reactivities of styrene, α-methylstyrene, and β-methylstyrene with $HCo(CO)_4$ are 1.0, 2.1, and 0, respectively.[15]) Therefore when one end of the diene in Scheme II is substituted (R_1 = alkyl; R_{2-4} = H), H atom transfer would occur at the other end, resulting in an allyl radical that is substituted on both ends. The k_2 pathway here would require the bulky fe· radical to couple with a substituted carbon-centered radical. Such coupling has not been observed in the studies reported in ref 10–19. We observed the k_2 path only when both ends of the diene are unsubstituted (R_{1-4} = H). In this case the fe· radical can couple with an unsubstituted carbon-centered radical. If both ends of the diene are substituted (R_1, R_3 = alkyl), no reaction is observed at room temperature (k_1 is small) since both ends of the diene are inaccessible to H atom transfer. However 1,3-cyclohexadiene does react at room temperature, which suggests a reduction in steric hindrance and/or an increase in stain of the cyclic diene.

A combination of diene reactivity patterns, observation of the CIDNP effect, and an inverse isotope effect make it apparent that Scheme II is a useful description of the reaction between Hfe and conjugated dienes. To wit, Hfe hydrogenates both *cis*- and *trans*-1,3-pentadiene at similar rates. It is known that these two 1,3-pentadiene isomers react with organosulfur radicals with comparable rates[20] while they undergo Diels–Alder reactions at very different rates.[21] Wrighton observed that the trans isomer underwent chromium-catalyzed hydrogenation exclusively in the presence of the cis isomer.[22] Subsequently it was observed that this hydrogenation involves prior coordination of the diene in the s-cis conformation.[23] Observation of the CIDNP effect is good evidence for a free radical mechanism in the Hfe–1,3-cyclohexadiene reaction. We did not observe the CIDNP effect in the other reactions reported here. It is possible that the polarizations were too small to be observed, but it should be noted that no deuterium exchange occurred in the Hfe–isoprene reaction. That is consistent with a small k_{-1} valve that also would rule out the CIDNP effect. Finally, the inverse isotope effect seen in the Hfe–isoprene reaction strongly suggests that this too is a free radical reaction.

We reported earlier[7] that we had IR evidence for the presence of the 1,4 adduct in the reaction between Hfe and 2,3-dimethyl-1,3-butadiene, but that we were not able to isolate the π-allyl product (eq 9). In the Results above



(9)

we described ^1H NMR evidence for the transitory presence of the 1,4 adduct followed by further reaction with Hfe to product 2,3-dimethyl-1-butene (eq 6). In the corresponding Hfe–isoprene reaction (eq 3 and 4), the reaction between Hfe and $feCH_2CH{=}C(CH_3)_2$ is slow enough that the reaction can be cleanly stopped at the first step even when equimolar quantities of Hfe and isoprene are used. In the case of reaction 9 the 1,4 adduct has only transitory existence unless a large excess of 2,3-dimethyl-1,3-butadiene is used. Apparently the 1,4 adduct in reaction 9 reacts much more rapidly with Hfe than in reaction 3, but we have no explanation for the difference.

Our efforts to obtain kinetics data for the hydrogenation of exo methylene compounds were frustrated by the fact that these compounds rapidly equilibrate to the isomeric internal diene in the presence of Hfe (eq 8a,b). Kinetics data obtained by following the disappearance of Hfe indicates that overall hydrogenation is about 10 times as fast in (8a) as in (8b) at 20 °C, which is consistent with the greater steric hindrance in (8b).

In addition to being regiospecific, which can be explained on steric grounds, the reaction between Hfe and isoprene is stereospecific. While we cannot directly observe the stereochemistry of the addition reaction, a correlation is possible based on the stereochemistry of the overall reaction. Rosenblum has shown that the reaction shown in

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(10) Sweany, R.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8335.

(11) Roth, J.; Orchin, M. *J. Organomet. Chem.* **1979**, *182*, 299.

(12) Nalesnik, T.; Orchin, M. *J. Organomet. Chem.* **1980**, *199*, 265.

(13) Nalesnik, T. E.; Orchin, M. *J. Organomet. Chem.* **1981**, *222*, C5.

(14) Nalesnik, T. E.; Freudenberger, J.; Orchin, M. *J. Organomet. Chem.* **1981**, *221*, 193.

(15) Roth, J.; Wiseman, P. *J. Organomet. Chem.* **1981**, *217*, 231.

(16) Sweany, R.; Comberrel, D. S.; Dombourian, M. F.; Peters, N. A. *J. Organomet. Chem.* **1981**, *216*, 57.

(17) Sweany, R.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487.

(18) Nalesnik, T. E.; Orchin, M. *Organometallics* **1982**, *1*, 222.

(19) Ungvary, F.; Marko, L. *Organometallics* **1982**, *1*, 1120.

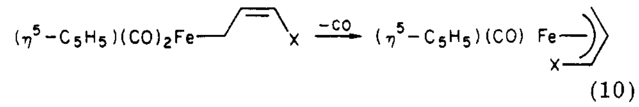
(20) Thaler, W. A.; Oswald, A. A.; Hudson, B. E. *J. Am. Chem. Soc.* **1965**, *87*, 311.

(21) Craig, D.; Shipman, J. J.; Fowler, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 2825.

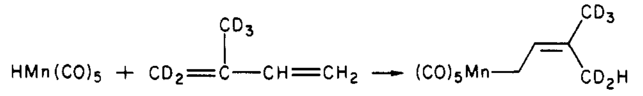
(22) Schroeder, M. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1974**, *96*, 6225.

(23) Geoffrey, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1900; pp 173–180.

eq 10 occurs with retention of stereochemistry at the double bond[24] and we presume the same retention of configuration in the analogous second step of reaction 6. This leads us to the conclusion that the D–Fe addition step must be a 1,4 cis addition to the s-cis rotamer of isoprene. We would expect the allyl radical formed in Scheme II to be rigid[20] so the stereoselectivity in this reaction must occur before the radical pair formation. The observed stereoselectivity, which has also been reported in the reaction shown in eq 11,[26] cannot be a result of random collision between Hfe and isoprene molecules since the s-trans rotamer is the stable form of isoprene at room temperature.[21] We can confidently rule out prior coordination of the diene to the metal since, in cases where that occurs,[2,26,28] π-allyl products are formed directly. The π-allyl product cannot be an intermediate in reaction 6 since we have shown in a separate experiment that the $\sigma \rightarrow \pi$ reaction is not reversible (eq 12).



(10)



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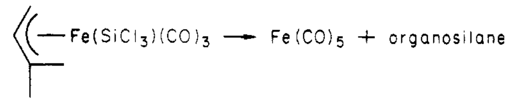

(12)

Any suggestion we would make regarding the nature of the stereoselective step in Scheme II would be purely speculative at present. Experiments are planned to investigate this question further.

Experimental Section

The hydrocarbons used here were distilled from calcium hydride and deaerated with dried HP nitrogen or argon. Methylene chloride and chlorobenzene were distilled from phosphorous pentoxide and similarly deaerated. The solutions used in the kinetics runs were made by using syringe-transfer techniques.

The Hfe used here was prepared by the literature method.[28] It was isolated by short-path vacuum distillation (bp 85 °C (10 mm)) and was stored at −20 °C prior to use. The exo methylene compounds used here were prepared by literature methods;[29,30] the other dienes were available from the Aldrich Chemical Co. or Wiley Organics, Inc.

In order to prepare Dfe, Hfe was converted to the anion in methylene chloride.[8] To this solution was added D_2SO_4 (99% deuterated, Aldrich) in increments while the solution was vigorously stirred under nitrogen until the anion was completely converted to Dfe. The IR spectrum of the solution was monitored to determine when the conversion was complete. It normally required about a threefold excess of D_2SO_4 to complete the conversion. If the addition of D_2SO_4 was too fast, the reaction mixture frothed badly causing considerable reduction in yield. If too large an excess of D_2SO_4 was used, the degree of deuteration was reduced, presumably due to an isotope effect in the protonation/deuteration step. Attempted protonation of the anion with trifluoroacetic acid gave $H_2Fe(CO)_4$.

Table III. Deuterium Atom Transfer in Dfe + Isoprene Reaction

deuterium atoms in Dfe	0.7
deuterium atoms in feC_5H_8D	0.6
deuterium atoms in (η^3-C_5H_8D)Fe(CO)$_3$SiCl$_3$	0.64
deuterium atoms in anti methyl group	0.54

The Dfe used in the kinetics studies was isolated. We were unable to obtain its mass spectrum, but ^{1}H NMR comparison with internal Me_4Si indicated that it was approximately 70% deuterated.

Reaction of Dfe with Isoprene. One milliliter (10 mmol) of degassed isoprene was placed in a serum stopper capped vial under nitrogen. To this was added 0.2 mL (1.1 mmol) of Dfe. When the IR spectrum of the mixture indicated that the addition reaction was complete, 1 mL of toluene-d_8 was added and the isoprene was pumped off. The resulting solution was then filtered into an NMR tube (under nitrogen) that was then sealed off. An identical experiment was done using Hfe in place of Dfe. In the Hfe reaction mixture the α-CH_2–vinyl CH–alkyl CH_3 ^{1}H NMR resonances were in the ratio 2:1:6, respectively, while in the Dfe solution the ratio was 2:1:5.5, indicating that all the deuterium was in the methyl groups. The η^1-alkenyl product converted to the η^3-allyl product when the NMR tube was allowed to stand at room temperature for 18 h. The NMR spectra of the resulting solutions (A higher yield of cleaner product can be obtained by 20 °C or lower photolysis of the reaction mixture. Essentially the same stereochemical results are obtained either way.) indicated the presence of some impurities but a comparison of the ratios of the syn methyl/anti methyl peaks for the Hfe reaction mixture to that for the Dfe reaction mixture indicated that the anti methyl group in the latter case contained 2.44 protons. If 100% of the deuterium from the 70% isotopically pure Dfe transferred to the anti methyl group, it would contain 2.30 protons.

The product from the Dfe reaction mixture was recrystallized from heptane at −78 °C, and its mass spectrum was obtained. Isotopic purity was determined by 259/258 ($Cl_3SiFeC_5H_8D$/$Cl_3SiFeC_5H_9$) and 161/160 ($ClFeC_5H_8D$/$ClFeC_5H_9$) peak height ratios. (These ratios are both zero for $Cl_3SiFe(CO)_3C_5H_9$.) These results indicate the presence of 0.64 deuterium atom in the product.

A summary of these results is given in Table III. Given the uncertainty involved in these measurements, it appears that the deuterium atom is selectively transferred to the anti methyl group.

^{1}H NMR Measurements. The spectrometer used was a Perkin-Elmer R20B with a magnet temperature of 33 °C. One reagent was transferred into the serum stopper capped NMR tube under nitrogen, and the other reagent was syringed in immediately prior to the first measurement. Deuterated aromatic solvents were used; concentrations were typically less than 2 M in each reagent.

In the reaction between 1-methylene-3-cyclohexene (1 M) and Hfe (0.05 M) the exo methylene resonance (4.8 ppm) was gone within 2 min. The vinyl signals continued to change for an additional 30 min. In the reaction of 1,5,5-trimethyl-3-methylenecyclohexene and Hfe the exo methylene (4.5 ppm) and vinyl (5.6 ppm) resonances were replaced by the vinyl resonances (4.9 and 5.3 ppm) of 1,3,5,5-tetramethylcyclohexadiene.[31]

In the reaction between 1,3-cyclohexadiene (0.6 M) and Hfe (2 M) emission was observed for approximately 5 min; hydrogenation was complete in approximately 60 min. With 0.7 M Hfe and 0.6 M 2,3-dimethyl-1,3-butadiene reaction was complete in approximately 15 min.

Kinetics Measurements. Procedure a. Rate data were obtained (Perkin-Elmer 621 or 1320 spectrophotometer) by following the disappearance of the 2128 cm^{-1} band of Hfe continuously while the reaction solution was being pumped through a 1-mm IR cell. In a separate experiment it was demonstrated that Hfe solutions in toluene obey Beer's law in the (1–10) × 10^{-3} M concentration range. Diene solutions were in the 1–4 M concentration range while Hfe concentrations were approximately 1 × 10^{-3} M. First-order rate constants were obtained from the

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slope of ln *a* vs. *t* plots. Reactions were typically first order for several half lives, and the correlation coefficients were 0.995 or better. Second-order rate constants were obtained from the slope of the pseudo-first-order rate constant vs. the diene concentration. Three diene concentrations were used to obtain each second-order rate constant. The second-order rate constants were obtained in triplicate.

In a typical experiment 10 mL of diene solution was placed in a rubber capped reaction flask containing a stirring bar. The flask was put in a thermostated bath and stirred for 30–60 min. At the same time the bath water was circulated through a jacket especially designed to house the IR cell (Precision Cells, Inc., part no. 20710). The reaction flask was connected to the IR cell by Teflon tubing. With the IR instrument set at 2128 cm^{-1} and in the time drive mode about 0.1 mL of approximately 1 M Hfe in the reaction solvent was injected into the reaction flask. The reaction mixture was then forced through the IR cell by inert-gas pressure supplied by a nitrogen or argon tank while the absorbance vs. time data was obtained. Rate data was obtained for 60–300 s. Kinetics data were obtained at 20, 30, and 40 °C for activation energy studies. Carbon monoxide was used in place of the inert gas in each step of the experiment to test its retarding effect on the rate. Similarly rates were measured by using a solvent that was successively 0.1, 0.2, and 0.3 M in trichlorosilane.

Procedure b. For the slower reactions, reaction mixtures were made up in a constant temperature bath and aliquots were periodically transferred to the IR cell.

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Registry No. Hfe, 33361-70-5; Dfe, 91002-46-9; 1,3-butadiene, 106-99-0; 2-methyl-1,3-butadiene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; *trans*-1,3-pentadiene, 2004-70-8; *cis*-1,3-pentadiene, 504-60-9; 1,3-cyclohexadiene, 592-57-4; 3-methylenecyclohexene, 1888-90-0; (*E,E*)-2,4-hexadiene, 5194-51-4; deuterium, 7782-39-0.

Organometallic Chemistry. 21. Silyl Trifluoromethanesulfonate (Triflate)–Boron Trichloride (Tribromide) Complexes[1]

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Trimethyl- and triethylsilyl triflate form with BCl_3 and BBr_3 strongly polarized donor–acceptor complexes. The deshielding of the ^{29}Si NMR shifts [$\Delta\delta_{^{29}Si}$ (BCl_3) 28.81 and 32.26, respectively] and shielding of ^{11}B NMR shifts characteristic for tetracoordinated boron are consistent with the development of partial positive charge at silicon involving *O*-coordination of boron halide with the triflates. Data also show that no ionization to silicenium ions takes place. Similarly, dimethylisopropyl- and tri-*n*-butylsilyl triflate gave donor–acceptor complexes on reaction with BCl_3 [$\Delta\delta_{^{29}Si}$ 30.51 and 25.18, respectively]. In general BCl_3 was found to interact more strongly than BBr_3. The reaction of a number of other alkylarylsilyl triflates or dialkylsilyl ditriflates with BX_3 was also investigated. The deshielding of ^{29}Si NMR shifts diminished when the steric bulkiness of the alkyl ligands on silicon was increased, such as in the case of $(i\text{-}Pr)_3SiOTf$ or $Me_2(t\text{-}Bu)SiOTf$. Ligand exchange of the triflates with BX_3 is a competing process in the reactions, the rate of which increases significantly by increasing the temperature or reaction time. The reaction of tris(alkylthio)silyl triflate with BCl_3 at low temperature led only to ligand exchange. The reaction of Me_3SiOR (R = Me, Et, Ph) with BBr_3 (−30 °C) or with BCl_3 (−75 °C) gave Me_3SiBr, Me_3SiCl, and the corresponding $ROSiX_2$ indicative of initial complexation followed by rapid Si–O cleavage. The initial complexation, however, could not be observed by NMR. The reaction of $AlCl_3$ and $AlBr_3$ with silyl triflates resulted only in ligand exchange. Attempts to utilize the R_3SiOTf–BX_3 systems as electrophilic trialkylsilylating agents for aromatics were unsuccessful.

Introduction

We have previously shown that trimethylsilyl halides form donor–acceptor complexes with Lewis acid halides such as $AlBr_3$, $AlCl_3$, and BI_3 in solvents such as CS_2, CH_2Cl_2, and CH_2Br_2.[2] Spectroscopic evidence for the formation of these polarized complexes is based on the observed deshielding of the ^{29}Si NMR shifts and a considerable sharpening of ^{27}Al NMR resonances, indicating a pseudotetrahedral environment around the aluminum atoms. However, the Si–halogen bonds are not ionized and no trivalent silicenium ions were formed in these systems (eq 1).

$$Me_3Si^{\delta+}Br \rightarrow {}^{\delta-}AlBr_3 \qquad (1)$$

Recently, the generation of a stable silicenium ion was reported by Lambert by hydride abstraction from tris(isopropylthio)silane with trityl perchlorate in CH_2Cl_2 at room temperature. The poorly resolved ^{29}Si NMR signal was deshielded by only 17 ppm as compared to the silane precursor. This was attributed to "polymer formation", and it was suggested that the ^{29}Si NMR signal of the ion has a very slow relaxation time.[3] We feel this evidence is inadequate, and further studies are needed to substantiate whether a truly electron-deficient silicenium ion was obtained. The formation of silicenium ylides and their

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