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Silylium Ion-Catalyzed Challenging Diels–Alder Reactions: The Danger of Hidden Proton Catalysis with Strong Lewis Acids

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S *Supporting Information*

ABSTRACT: The pronounced Lewis acidity of tricoordinate silicon cations brings about unusual reactivity in Lewis acid catalysis. The downside of catalysis with strong Lewis acids is, though, that these do have the potential to mediate the formation of protons by various mechanisms, and the thus released Brønsted acid might even outcompete the Lewis acid as the true catalyst. That is an often ignored point. One way of eliminating a hidden proton-catalyzed pathway is to add a proton scavenger. The low-temperature Diels–Alder reactions catalyzed by our ferrocene-stabilized silicon cation are such a case where the possibility of proton catalysis must be meticulously examined. Addition of the common hindered base 2,6-di-*tert*-butylpyridine resulted, however, in slow decomposition along with formation of the corresponding pyridinium ion. Quantitative deprotonation of the silicon cation was observed with more basic $(Mes)_3P$ to yield the phosphonium ion. A deuterium-labeling experiment verified that the proton is abstracted from the ferrocene backbone. A reasonable mechanism of the proton formation is proposed on the basis of quantum-chemical calculations. This is, admittedly, a particular case but suggests that the use of proton scavengers must be carefully scrutinized, as proton formation might be provoked rather than prevented. Proton-catalyzed Diels–Alder reactions are not well-documented in the literature, and a representative survey employing TfOH is included here. The outcome of these catalyses is compared with our silylium ion-catalyzed Diels–Alder reactions, thereby clearly corroborating that hidden Brønsted acid catalysis is not operating with our Lewis acid. Several simple-looking but challenging Diels–Alder reactions with exceptionally rare dienophile/enophile combinations are reported. Another indication is obtained from the chemoselectivity of the catalyses. The silylium ion-catalyzed Diels–Alder reaction is general with regard to the oxidation level of the α,β-unsaturated dienophile (carbonyl and carboxyl), whereas proton catalysis is limited to carbonyl compounds.

■ INTRODUCTION

Silylium ions, tricoordinated silicon cations, are extremely strong Lewis acids due to the electron sextet at the silicon atom.[1] Serious efforts had been invested into the isolation of a "naked" three-coordinate silicon cation until a combination of steric shielding of the empty orbital at the silicon atom and the use of weakly coordinating anions finally allowed for the crystallographic characterization[2] of Lambert's "free" Mes_3Si^+ cation[3] with Reed's $[HCB_{11}Me_5Br_6]^-$ anion.[4] During this long quest and thereafter, many inter- and intramolecularly donor-stabilized silylium ions were discovered; π basic solvents[5] and groups,[6] weakly σ coordinating counteranions[7] and halogen atoms,[8] as well as Si–H bonds[9,10] were accidently found or deliberately utilized to lend stabilization to the cationic silicon atom.

Despite the progress in isolation and characterization of silicon cations, it was only realized recently that these electron-deficient compounds are promising reagents in catalysis.[11] There are now several processes where the reactive silicon cation is consumed in a bond formation but another molecule of the silicon cation is then regenerated from a suitable precursor in a subsequent step (self-regeneration,[12] not self-healing or self-repair[13]). That is found in alkene[14] and carbonyl[12,15] hydrosilylation as well as in aliphatic C–F bond dehydrofluorination,[9b,16] and it also includes silicon cation-promoted polymerization reactions with diverse initiation strategies.[13,17] The use of silicon cations in transformations where these are released unchanged after the catalytic event is particularly attractive, as it holds significant potential in the broad area of Lewis acid catalysis. While tetracoordinate silicon Lewis acids, e.g., Me_3SiOTf (**4**) and Me_3SiNTf_2 (**5**), are widely applied in synthetic chemistry,[18] these are either not able to catalyze, e.g., "challenging" Diels–Alder reactions, or require high loadings. A remarkable counteranion-dependent reactivity difference between Me_3SiOTf (**4**) and Me_3SiNTf_2 (**5**) was demonstrated by Ghosez in the cycloaddition of cyclohexa-1,3-diene (**1**) and methyl acrylate (**2**) (Scheme 1).[19] To identify a more reactive silicon Lewis acid, Sawamura[20] introduced the solvent-stabilized silicon cation $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$ (**6**)[5] to the above Diels–Alder reaction (Scheme 1). Recently, our research group established the ferrocene-stabilized silylium ion **7**[21] as an even more effective catalyst for difficult Diels–

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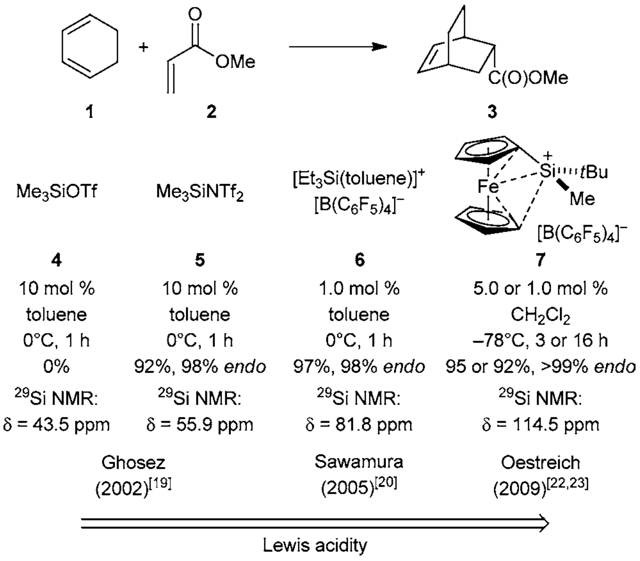
Scheme 1. Comparison of Different Silicon Lewis Acids 4−7 as Catalysts in the Diels−Alder Reaction of Cyclohexa-1,3-diene (1) and Methyl Acrylate (2)

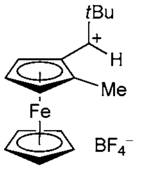


Alder reactions, and excellent yields and *endo*/*exo* selectivities were obtained at low temperatures.[22−24]

When dealing with Lewis acid catalysis, the possibility of competing Brønsted acid catalysis (in part or as a whole) must always be considered. It is, however, an issue that is rarely alluded to, except for the actively explored current areas of metal-catalyzed hydroamination and related transformations[25−29] as well as transition metal-catalyzed carbophilic activation.[30−33] It is particularly the former catalyses where proton-catalyzed pathways are now experimentally verified.[26−28] Conversely, the role of protons in gold-catalyzed reactions is not generally clarified.[30] A recent quantum-chemical comparison of gold- and proton-catalyzed alkene hydroamination resulted in different (stepwise and concerted) mechanisms;[31] gold and proton catalysts might even produce different constitutional isomers.[32] It was also demonstrated for a platinum-catalyzed skeletal rearrangement that the same enyne metathesis is catalyzed by a Brønsted acid.[33] There are other individual investigations uncovering proton instead of Lewis acid catalysis.[34]

With regard to Diels−Alder reactions, proton catalysis was infrequently suspected to be operating.[35] In fact, very little is known about the use of achiral (inorganic) Brønsted acids as promoters in simple Diels−Alder reactions,[36] and that is particularly noteworthy in view of the recent success in asymmetric Brønsted acid catalysis.[37] An early report by Wassermann[38] qualitatively showed the catalytic activity of several Brønsted acids in Diels−Alder reactions of cyclopentadiene with quinones. Six decades later (!), Yamamoto observed a reversal of chemoselectivity in Diels−Alder reactions with *α*,*β*-unsaturated aldehydes and ketones depending on the choice of catalyst.[39] When an equimolar mixture of acrolein and ethyl vinyl ketone was reacted with cyclopentadiene, bulky Lewis acids selected the aldehyde whereas Brønsted acids preferentially activated the more basic ketone.

Although Sawamura had ruled out proton catalysis in the case of $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$ as the silylium ion catalyst,[20] a forgotten investigation by Sammakia[40] attracted our attention. The planar chiral ferrocene-based carbenium ion 8 (Figure 1), prepared from the corresponding alcohol by protonation followed by dehydration, was tested as a chiral Lewis acid catalyst in Diels−Alder reactions. As only racemic material was obtained and the addition of the proton-scavenger 2,6-di-*tert*-butylpyridine inhibited the reaction, it was concluded that it must be protons to promote the reaction.

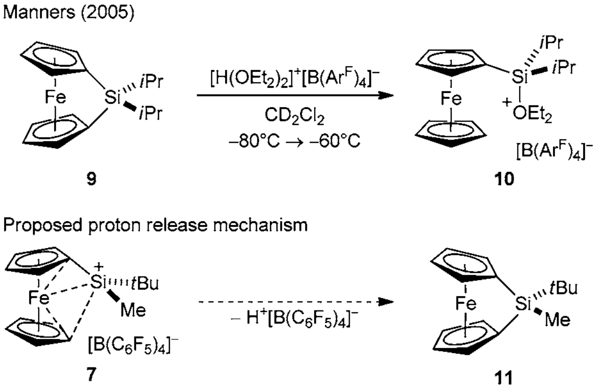


8

Figure 1. Planar chiral ferrocene-stabilized carbenium ion **8** used by Sammakia.

Aware of these findings, we wished to secure that our ferrocene-based silylium ion 7 indeed acts as a Lewis acid catalyst in those unusual Diels−Alder reactions[22] rather than a proton source. Our concern was further fueled by the known ring-opening protonolysis of sila[1]ferrocenophane 9, providing access to ether-stabilized analogue 10 of our silicon cation 7 (Scheme 2, upper).[41] We, therefore, anticipated the reverse reaction to be a conceivable origin of protons in our catalysis (Scheme 2, lower). In this full account, we report a spectroscopic and theoretical analysis of this hypothesis and we also present a systematic comparison of silylium ion- and Brønsted acid-catalyzed Diels−Alder reactions of simple-looking but unusually difficult dienophile/enophile combinations.

Scheme 2. Ring-Opening Protonolysis of Sila[1]ferrocenophane 9 (top) and Proposed Origin of Protons Generated from Silylium Ion 7 (bottom) [Ar^F = 3,5-Bis(trifluoromethyl)phenyl]

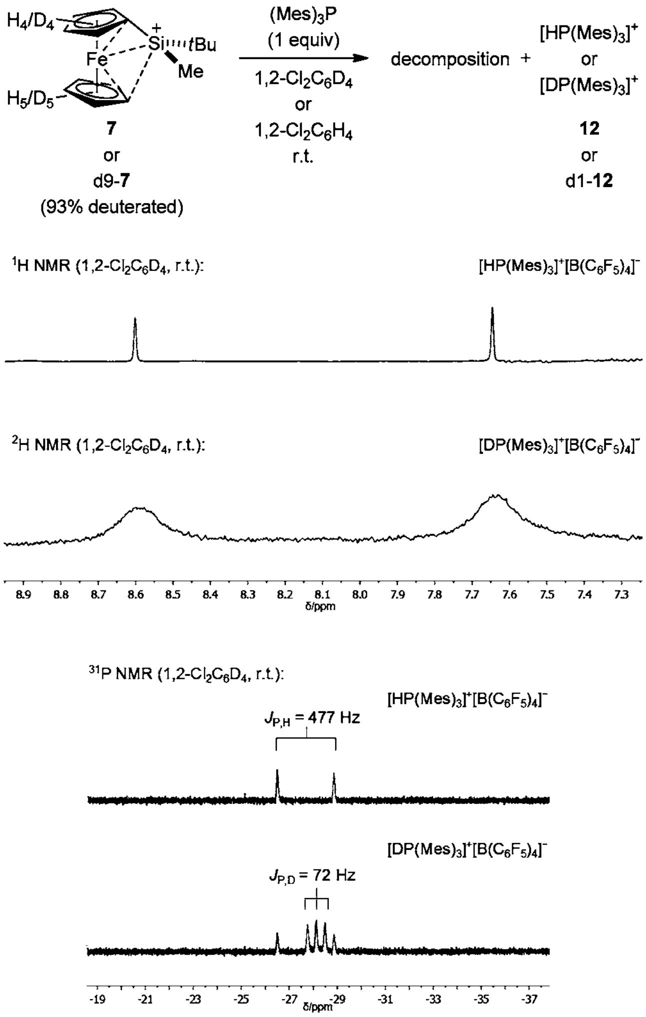


■ RESULTS AND DISCUSSION

Proton Release Mechanism or Provoking Proton Abstraction: NMR Experiments. As an initial experiment, we spectroscopically examined an equimolar mixture of our silylium ion 7 and the proton-scavenger 2,6-di-*tert*-butylpyridine.[42] This hindered nitrogen donor was expected to not form a Lewis pair with the electrophilic silicon atom but act as a base instead. A small amount of the protonated pyridine was observed in the ^1H NMR spectrum immediately recorded after mixing both compounds in $1,2\text{-}Cl_2C_6D_4$ at room temperature (cf. the Supporting Information). Its quantity increased upon prolonged reaction time while the disappearance of the signals corresponding to 7 indicated decomposition.

To further elucidate the origin of the proton(s), we decided to employ $(Mes)_3P$, a stronger and also hindered phosphorus base (Scheme 3, upper). That would also allow for monitoring the reaction by ^{31}P NMR spectroscopy. An equimolar mixture of 7 and $(Mes)_3P$ immediately showed quantitative formation of the phosphonium salt **12** (= protonated phosphine), as indicated by a doublet in both the ^1H NMR and ^{31}P NMR spectra with a $^1J_{P,H}$ coupling constant of 477 Hz (Scheme 3). The very broad ferrocene signals in the ^1H NMR spectrum (cf. the Supporting Information for the full ^1H NMR spectrum) suggested decomposition of 7. To prove the ferrocene backbone's involvement in this, we repeated this NMR experiment with silylium ion d_9-7 containing a deuterated ferrocenyl substituent (93% deuteration grade). As expected, a doublet in the ^2H NMR spectrum and a triplet with a $^1J_{P,D}$ coupling constant of 72 Hz in the ^{31}P NMR spectrum were observed (Scheme 3), thereby providing unambiguous evidence for the proton to originate from the ferrocene group.[43]

Scheme 3. Reaction of Silylium Ions 7 and d_9-7 with $(Mes)_3P$ (top^a) and ^1H and ^2H NMR Spectra (middle) and ^{31}P NMR Spectra (bottom) of the Resulting Phosphonium Salts 12 and d_1-12



^{a}Mes = mesityl (2,4,6-trimethylphenyl); counteranion $[B(C_6F_5)_4]^-$ is omitted for the sake of clarity.

Proton Release Mechanism or Provoking Proton Abstraction: DFT Calculations. The deprotonation of silylium ion 7 to the sila[1]ferrocenophane **11** using $(Mes)_3P$ and 2,6-di-*tert*-butylpyridine as bases was modeled with DFT calculations (TPSS-D3/dev2-TZVPP,[44−46] cf. the Supporting Information for details). We investigated the reaction in a solvent, 1,2-dichlorobenzene, using a continuum solvation model (COSMO).[47]

The large dip angle of 7 (Figure 2, left) and the partly covalent character of the Si−C'_{ipso} bond[21] are a first indication that the abstraction of the proton at the C'_{ipso} atom might be facile; **11** (Figure 2, right) is indeed a stable energetic minimum. Attempts to locate a C'_{ipso}-protonated intermediate ("σ-complex") with a short Si−C'_{ipso} bond yielded the silicon cation 7 in all cases, indicating that its deprotonation is a one-step process.

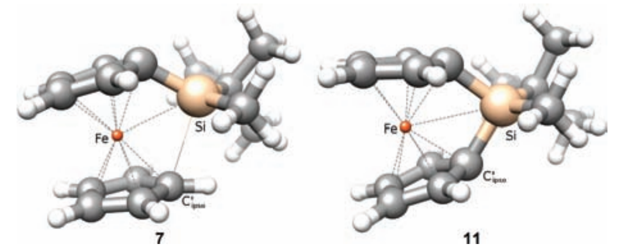


Figure 2. Silylium ion 7 and sila[1]ferrocenophane **11** (TPSS-D3/def2-TZVPP + COSMO). Selected bond lengths (Å): 7: Si−Fe, 2.440; Fe−C'_{ipso}, 2.063; Si−C'_{ipso}, 2.621. **11**: Si−Fe, 2.700; Fe−C'_{ipso}, 2.007; Si−C'_{ipso}, 1.900.

Location of transition structures (TSs) was achieved with both $(Mes)_3P$ and 2,6-di-*tert*-butylpyridine as proton scavengers. Geometries and selected atom distances are given in Figure 3. It is immediately notable from the shortened Si−C'_{ipso} distances that the structure of the silicon fragment is significantly changed compared to that of the cation, largely resembling that of the product. Si−C bond formation is therefore the main structural change during the initial phase of the deprotonation. The C'_{ipso}−H distance in the TS is slightly longer in **TS−P** (1.399 Å) than in **TS−N** (1.372 Å), but this is a consequence of the larger H−base distance in the former.

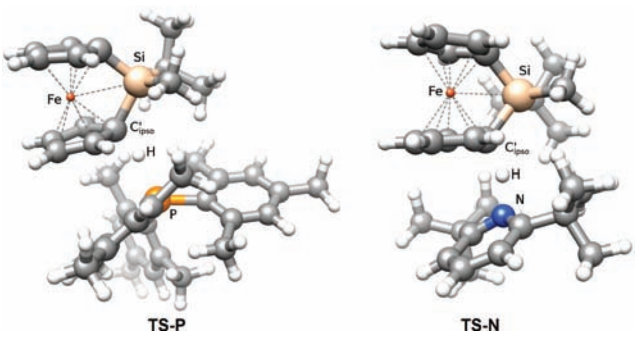


Figure 3. Transition structures of the deprotonation of silylium ion 7 with $(Mes)_3P$ (**TS−P**, left) and di-*tert*-butylpyridine (**TS−N**, right) (TPSS-D3/def2-TZVPP + COSMO). Selected atom distances (Å): **TS−P**: C'_{ipso}−H, 1.399; H−P, 1.841; Si−C'_{ipso}, 2.023. **TS−N**: C'_{ipso}−H, 1.372; H−N, 1.409; Si−C'_{ipso}, 2.035.

The deprotonation is exothermic with both bases (Table 1); reaction with $(Mes)_3P$ is more favorable by 3.9 kcal·mol^{-1}.

Table 1. Energies and Barriers for the Deprotonation of Ferrocene-Stabilized Silicon Cation 7 by $(Mes)_3P$ and 2,6-Di-*tert*-butylpyridine[a]

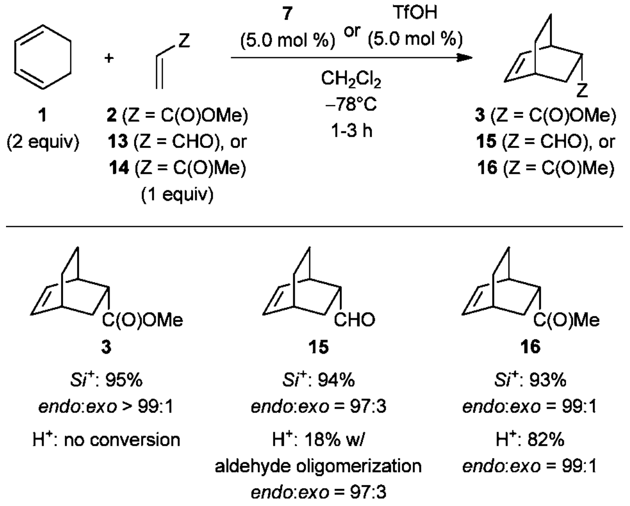
		energies and barriers (kcal·mol^{-1})	
base	medium	ΔE	$\Delta E^{\ddagger}$
$(Mes)_3P$	1,2-$Cl_2C_6H_4$	−6.7	+13.4
di-*tert*-butylpyridine	1,2-$Cl_2C_6H_4$	−2.8	+18.6

[a] TPSS-D3/def2-TZVPP+COSMO.

Both reaction barriers are in a range suitable for reaction at ambient temperatures. Proton abstraction is, however, expected to be significantly slower with the hindered pyridine than that with the phosphine, as the energy difference of the transition states is 5.2 kcal·mol^{-1}. Assuming similar activation entropies, this difference should result in rate constants differing by a factor of 1.5×10^{-4}. This agrees nicely with the different rates observed in the NMR experiments.

Survey of Silylium Ion- and Proton-Catalyzed Diels–Alder Reactions. To compare our silicon Lewis acid 7 and the Brønsted acid TfOH (generated from Tf_2O and H_2O) as catalysts in low-temperature Diels–Alder reactions (Scheme 4),[48] we tested representative dienophiles at various oxidation levels (**2**, **13**, and **14**) in the cycloaddition with cylohexa-1,3-diene (**1**). Reaction rates for the 5.0 mol % of Brønsted acid employed here are likely to be much higher than that potentially released from 5.0 mol % of our silicon cation, but reaction rates with a more realistic amount of 0.50 mol % TfOH were significantly slower; essentially the same results were obtained.

Scheme 4. Comparison of Lewis and Brønsted Acid-Catalyzed Diels–Alder Reactions of Cyclohexa-1,3-diene (1) and Representative Dienophiles 2, 13, and 14 (*Si* = *tert*-Butylferrocenylmethylsilyl)



As to least reactive *α*,*β*-unsaturated carboxyl compound **2** (Z = C(O)OMe), the outcome of the silicon cation and Brønsted acid catalyses was dramatically different. Our previously reported silylium ion-catalyzed procedure yielded adduct **3** almost quantitatively whereas no reaction occurred with TfOH under otherwise identical reaction conditions.[49] The use of the stronger Brønsted acid Tf_2NH[50] as the proton source also had no effect. The situation with the most reactive carbonyl compound **13** (Z = CHO) was similar. It had also performed well in the Lewis acid-catalyzed reaction while the protic media appeared to primarily promote oligomerization of aldehyde **13**, and isolation of the desired adduct **15** proved difficult. We were, however, pleased to note that **14** (Z = C(O)Me) reacted smoothly to afford **16** in both the silylium ion and the proton catalysis; the isolated yield was lower in the latter though. It must be noted that addition of $(Mes)_3P$ (1.1 equiv based on **7**) to silicon cation **7** completely thwarted the same low-temperature Diels–Alder reaction, thereby indicating that catalysis is not promoted by the phosphonium ion. Conversely, less basic 2,6-di-*tert*-butylpyridine reacts only slowly with the silicon cation (even at room temperature), and this silylium ion-catalyzed Diels–Alder reaction proceeded nicely in its presence. The outcome of this pair of catalyses is evidence against hidden proton catalysis.

As expected, on the basis of the chemoselectivity reported by the Yamamoto group,[39] we found *α*,*β*-unsaturated ketones to be the preferred dienophiles for the Brønsted acid-catalyzed Diels–Alder reaction. We therefore decided to investigate the application of both our silicon cation **7** and TfOH as catalysts in Diels–Alder reactions in more detail.

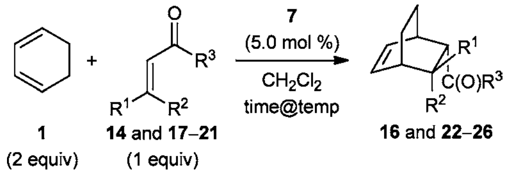
Silylium Ion-Catalyzed Diels–Alder Reactions of *α*,*β*-Unsaturated Ketones. We began exploring the scope of our silylium ion catalysis in the reaction of relatively unreactive cyclohexa-1,3-diene (**1**) [approximately 500 times less reactive than cyclopentadiene (**34**)] with a challenging selection of acyclic and cyclic dienophiles **14** and **17**–**21** (Table 2). We note here that there are hardly any examples reported for the seemingly simple Diels–Alder reaction of **1** and **18**–**21**.

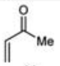
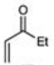
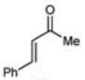
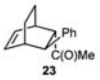
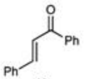
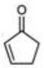
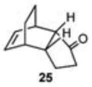
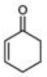
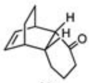
As methyl vinyl ketone (**14**) had undergone the reaction in high yield (Scheme 4 and Table 2, entry 1), we also examined commonly employed ethyl vinyl ketone (**17**) with success (Table 2, entry 2). We next turned our attention to the *β*-aryl-substituted dienophiles 4-phenyl-butenone (**18**) and chalcone (**19**) with *E* configuration (Table 2, entries 3 and 4). To the best of our knowledge, only two reports of their Diels–Alder reactions with cyclohexa-1,3-diene (**1**) exist, requiring either high pressure[51a] or microwave heating.[51b] We were therefore delighted to find that, with 5.0 mol % of **7** at a reaction temperature of −40 °C, we obtained both adducts **23** and **24** in good yield and with superb *endo*/*exo* selectivity. As reported before,[22] cyclic ketones **20** and **21**, which are equally delicate dienophiles in Diels–Alder reactions, reacted particularly well, and adducts **25** and **26** were formed with excellent *endo*/*exo* ratios (Table 2, entries 5 and 6).

We also examined the same series of dienophiles **14** and **17**–**21** in the silylium ion-catalyzed Diels–Alder reaction with slightly more reactive 2,3-dimethyl-1,3-butadiene (**27**) [approximately 250 times less reactive than cyclopentadiene (**34**)] (Table 3).

Alkyl-substituted acyclic **14** and **17** again performed well, yielding the desired adducts **28** and **29** in good yields after just 1 h at −78 °C (Table 3, entries 1 and 2). The uncommon *β*-aryl-substituted dienophiles **18** and **19** reacted at slightly elevated temperature of −40 °C, affording adducts **30** and **31** in good yields (Table 3, entries 3 and 4). For cyclic **20**, we detected full conversion to **32** (GC-MS analysis) after only minutes, but we were not able to isolate the product **32** in pure form, assuming decomposition upon workup. In turn, cyclic **21**

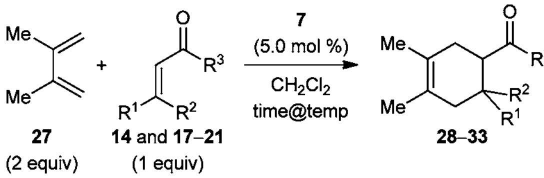
Table 2. Silylium Ion-Catalyzed Diels−Alder Reactions of α,β-Unsaturated Ketones 14 and 17−21 with Cyclohexa-1,3-diene (1)[a]

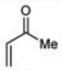
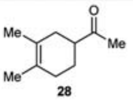
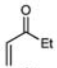
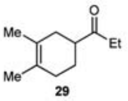
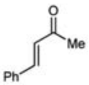
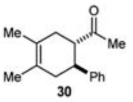
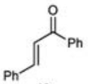
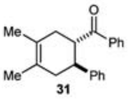
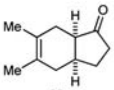
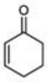
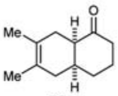


en-try	dieno-phile	adduct	time (h)	temp (°C)	*endo*:*exo*[b] (d.r.[c])	yield[d] (%)
1	 14	 16	3	−78	99:1	93
2	 17	 22	1	−78	99:1	73
3	 18	 23	12	−40	> 99:1 (99:1)	65
4	 19	 24	12	−40	99:1 (99:1)	71
5	 20	 25	12	−40	96:4	85
6	 21	 26	24	−40	96:4	80

[a]All reactions were performed according to General Procedure 2 (GP 2 in the Supporting Information) at a concentration of 0.5 M of the dienophile. [b]Determined by GLC analysis of the reaction mixture prior to purification. [c]*trans*/*cis* ratio. [d]Analytically pure product after flash column chromatography on silica gel.

Table 3. Silylium Ion-Catalyzed Diels−Alder Reactions of α,β-Unsaturated Ketones 14 and 17−21 with 2,3-Dimethyl-1,3-butadiene (27)[a]



en-try	dieno-phile	adduct	time (h)	temp (°C)	d.r.[b]	yield (%)[c]
1	 14	 28	1	−78	–	62
2	 17	 29	1	−78	–	64
3	 18	 30	9	−40	99:1	72
4	 19	 31	12	−40	99:1	71
5	 20	 32	1	−40	99:1	–[d]
6	 21	 33	20	−40	99:1	45

[a]All reactions were performed according to General Procedure 2 (GP 2 in the Supporting Information) at a concentration of 0.5 M of the dienophile. [b]*trans*/*cis* ratio. [c]Analytically pure product after flash column chromatography on silica gel. [d]Full conversion; decomposition upon isolation.

yielded analytically pure **33** in moderate isolated yield (Table 3, entries 5 and 6).

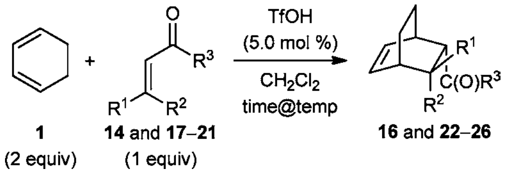
Proton-Catalyzed Diels−Alder Reactions of α,β-Unsaturated Ketones. We next turned our attention to Brønsted acid-catalyzed Diels−Alder reactions, applying our straightforward protocol to the previous selection of α,β-unsaturated ketones as dienophiles and three representative dienes (Tables 4−6).

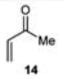
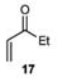
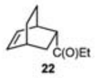
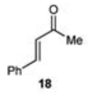
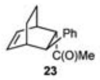
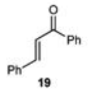
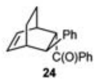
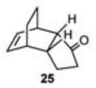
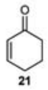
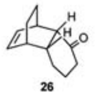
As shown in our comparative survey (Scheme 4), methyl vinyl ketone (**14**) reacted with cyclohexa-1,3-diene (**1**) in high yield (Table 4, entry 1). We also examined ethyl vinyl ketone (**17**) and found that after only half an hour full conversion had occurred, and **22** was isolated in moderate yield (Table 4, entry 2). Challenging substrate **18** underwent the Diels−Alder reaction with **1** to form **23** in decent yield (Table 4, entry 3); even at a reaction temperature of 0 °C, full conversion was not reached though. Not surprisingly, more challenging chalcone (**19**) was not sufficiently reactive in the Brønsted acid catalysis (Table 4, entry 4). No conversion of the dienophile was seen at ambient temperature and after prolonged reaction times. Cyclic **20** and **21** were equally unreactive, but the former decomposed after three days at room temperature (Table 4, entries 5 and 6).

Similar results were obtained in the TfOH-catalyzed Diels−Alder reaction with 2,3-dimethyl-1,3-butadiene (**27**). The reactions of alkyl vinyl ketones **14** and **17** proceeded rapidly at −78 °C to form adducts **28** and **29**, respectively, in decent yields (Table 5, entries 1 and 2). Again, β-aryl-substituted **18** performed well to yield **30** (Table 5, entry 3). We next examined the reaction of chalcone (**19**) with **27**. There had been only one previous example of a catalytic Diels−Alder reaction of these reaction partners reported,[52] and we were therefore delighted to find that our TfOH catalysis yielded significant amounts of **31** (Table 5, entry 4). Conversely, cyclic **20** and **21** were still too unreactive in the proton catalysis (Table 5, entries 5 and 6), and only decomposed material was detected with 10 mol % TfOH after several days at 0 °C or room temperature.

We decided to also investigate the Brønsted acid-catalyzed Diels−Alder reaction of cyclopentadiene (**34**), arguably the most commonly used diene. Alkyl-substituted **14** and **17** again reacted smoothly at low temperature to form **35** and **36** in good yields and with excellent *endo*/*exo* selectivities (Table 6, entries 1 and 2). **18** with an aryl substituent in the β-position afforded **37** at −40 °C in good yield (Table 6, entry 3). Remarkably, the scarcely reported[53,54] Diels−Alder reaction of chalcone (**19**) also proceeded cleanly to yield **38** with high *endo*/*exo* selectivity (Table 6, entry 4). With diene **34**, cyclic **20**

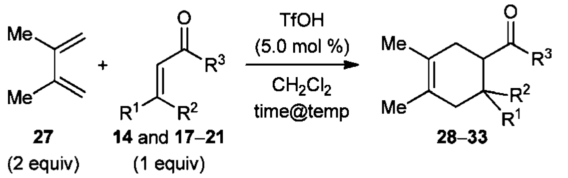
Table 4. Proton-Catalyzed Diels–Alder Reactions of *α*,*β*-Unsaturated Ketones 14 and 17–21 with Cyclohexa-1,3-diene (1)[a]

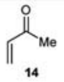
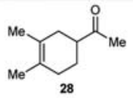
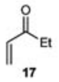
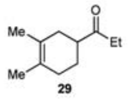
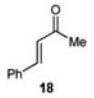
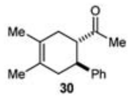
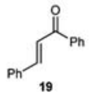
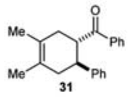
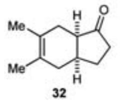
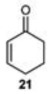
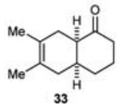


entry	dienophile	adduct	time (h)	temp (°C)	*endo*:*exo*[b] (d.r.[c])	yield[d] (%)
1	 14	 16	3	−78	99:1	82
2	 17	 22	0.5	−78	99:1	45
3	 18	 23	16	0	>99:1 (99:1)	44[e]
4	 19	 24	72	0 → 25	–	–[f]
5	 20	 25	72	25	n.d.	–[g]
6	 21	 26	72	−30 → 25	–	–[f]

[a]All reactions were performed according to General Procedure 3 (GP 3 in the Supporting Information) at a concentration of 0.5 M of the dienophile. [b]Determined by GLC analysis of the reaction mixture prior to purification. [c]*trans*/*cis* ratio. [d]Analytically pure product after flash column chromatography on silica gel. [e]68% conversion. [f]No conversion. [g]Traces due to decomposition under reaction conditions. n.d. = not determined.

Table 5. Proton-Catalyzed Diels–Alder Reactions of *α*,*β*-Unsaturated Ketones 14 and 17–21 with 2,3-Dimethyl-1,3-butadiene (27)[a]



entry	dienophile	adduct	time (h)	temp (°C)	d.r.[b]	yield[c] (%)
1	 14	 28	1.5	−78	–	45
2	 17	 29	0.5	−78	–	62
3	 18	 30	5	0	99:1	57
4	 19	 31	5	0	99:1	44
5[d]	 20	 32	48	−30 → 25	–	–[e]
6[d]	 21	 33	96	0	–	–[e]

[a]All reactions were performed according to General Procedure 3 (GP 3 in the Supporting Information) at a concentration of 0.5 M of the dienophile. [b]*trans*/*cis* ratio. [c]Analytically pure product after flash column chromatography on silica gel. [d]5.0 and 10 mol % of TfOH. [e]Decomposition under reaction conditions.

and **21** reacted well under proton catalysis; **39** and **40** were isolated in decent yields (Table 6, entries 5 and 6).

■ CONCLUSION

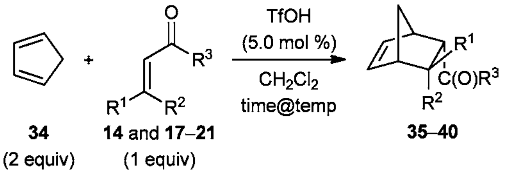
Doubts about whether the unique reactivities seen in our silylium ion-catalyzed Diels–Alder reactions are due to protons rather than the ferrocene-stabilized silicon cation **7** marked the beginning of the present investigation. The experimental observation that 2,6-di-*tert*-butylpyridine is slowly protonated under the above reaction setup further increased these doubts. Proton catalysis is a serious but often ignored twist with strong Lewis acids.

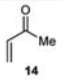
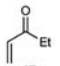
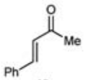
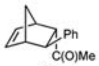
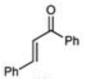
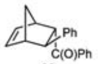
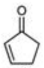
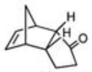
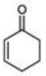
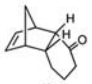
As verified by deuterium-labeling of the ferrocene backbone of silicon cation **7** (= d_9-**7**), hindered bases that will not form a Lewis pair with the electrophilic silicon atom do abstract a proton from the lower Cp ring with concomitant (assumed) ring closure to yield the correponding sila[1]ferrocenophane **11**; the reverse reaction, the ring-opening protonolysis with $[H(OEt_2)_2]^+[B(ArF)_4]^-$, is well-documented.[41] The ring-opening and, likewise, ring-closing events were found to be one-step processes by quantum-chemical calculations. The deprotonation was examined spectroscopically and theoretically with 2,6-di-*tert*-butylpyridine and with $(Mes)_3P$, and the data are in excellent qualitative agreement. Proton abstraction is kinetically ($\Delta\Delta E^\ddagger$ = 5.2 kcal·mol^{-1}) and thermodynamically ($\Delta\Delta E$ = 3.9 kcal·mol^{-1}) favored for the hindered phosphine.

That indirect evidence for protons (through pyridinium and phosphonium ions when adding proton scavengers) in the silylium ion-catalyzed Diels–Alder reactions called for a systematic comparison of these with the same set of reactions potentially catalyzed by protons using TfOH and Tf_2NH. One immediate difference between silyium ion and proton catalysis is its chemoselectivity in the reaction with *α*,*β*-unsaturated dienophiles; catalysis with **7** is equally efficient with any oxidation level whereas the Brønsted acids cannot promote the reaction of *α*,*β*-unsaturated esters, and *α*,*β*-unsaturated aldehydes are even oligomerized. Moreover, the silicon cation **7** catalyzes several simple-looking but delicate Diels–Alder reactions with exceptionally rare dienophile/enophile combinations at low temperature. Conversely, proton catalysis fails in almost all of these cases.

All experimental data clearly support silylium ion catalysis not blurred by proton catalysis, but in turn, it also suggests that the use of proton scavengers must be carefully scrutinized, as proton formation might be provoked rather than prevented.

Table 6. Proton-Catalyzed Diels−Alder Reactions of α,β-Unsaturated Ketones 14 and 17−21 with Cyclopentadiene (34)[a]



entry	dienophile	adduct	time (h)	temp (°C)	*endo*:*exo*[b] (d.r.[c])	yield[d] (%)
1	 14	 35	1	−78	99:1	62
2	 17	 36	1	−78	99:1	76
3	 18	 37	3	−40	>95:5[e] (99:1)	77
4	 19	 38	3	−40	>95:5[e] (99:1)	73
5	 20	 39	4	−40	95:5	68
6	 21	 40	5.5	−40	95:5	68

[a] All reactions were performed according to General Procedure 3 (GP 3 in the Supporting Information) at a concentration of 0.5 M of the dienophile. [b] Determined by GLC analysis of the reaction mixture prior to purification. [c] *trans*/*cis* ratio. [d] Analytically pure product after flash column chromatography on silica gel. [e] Determined from the ^{1}H NMR spectrum of the crude product.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, characterization data, as well as ^{1}H, ^{2}H, ^{11}B, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR spectra and quantum-chemical calculation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(7) Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science* **1993**, *262*, 402−404.

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(10) Intermolecular stabilization by 3c2e [Si···H···Si] bonds: Hoffmann, S. P.; Kato, T.; Tham, F. S.; Reed, C. A. *Chem. Commun.* **2006**, 767−769.

(11) Klare, H. F. T.; Oestreich, M. *Dalton Trans.* **2010**, *39*, 9176−9184.

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