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Shelf-Stable (*E*)- and (*Z*)-Vinyl-λ^3-chlorane: A Stereospecific Hyper-vinylating Agent

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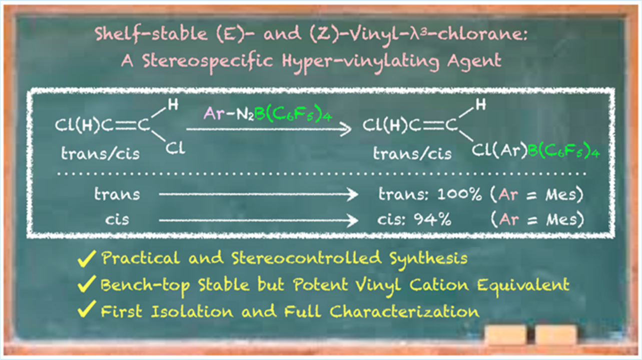
ABSTRACT: We report the first stereoselective synthesis of stable (*E*)- and (*Z*)-*β*-chlorovinyl-λ^3-chlorane via direct mesitylation of 1,2-dichloroethylene with mesityldiazonium tetrakis(pentafluorophenyl)borate under mild reaction conditions. The structure of the (*E*)-vinyl-λ^3-chlorane was established by single-crystal X-ray analysis. Because of the enormously high leaving group ability of the aryl-λ^3-chloranyl group, vinyl-λ^3-chloranes undergo not only $S_NV\sigma$-type reaction with extremely weak nucleophiles such as perfluoroalkanesulfonate, iodobenzene, and aromatic hydrocarbons but also coupling with phenylcopper(I) species.



The concerted bimolecular nucleophilic substitution (S_N) reaction at sp^3 carbon is one of the best-understood mechanisms in organic chemistry.[1] In contrast, nucleophilic substitution at sp^2 carbon with inversion of stereochemistry ($S_NV\sigma$) has been shown to proceed only in specific cases.[2,3] For example, vinyl chloride/bromide-containing nucleophilic functionalities tethered with a suitable alkyl chain undergo *intra*molecular $S_NV\sigma$ reaction to form a variety of carbo/heterocycles (Figure 1a).[3a−d] Metal vinylcarbenoid also serves as a good substrate, partly because of the metal-assisted elimination of leaving groups (Figure 1b).[3e−m] However, these substrates rarely undergo *inter*molecular transformations. In marked contrast, hypervalent vinyl-λ^3-iodane **1** undergoes *inter*molecular $S_NV\sigma$ reaction with a variety of Group 15−17 heteroatom nucleophiles under mild reaction conditions (Figure 1c).[4] This *inter*molecular $S_NV\sigma$ reaction was first demonstrated with the λ^3-iodanyl group ($-I(Ph)FBF_3$), a so-called hyper-leaving group that is ca. 10^6 times more effective than triflate ($-OSO_2CF_3$),[5] enabling it to drive this extremely difficult type of transformation. It occurred to us that the introduction of an even more potent leaving group, the λ^3-chloranyl group ($-Cl(Ar)X$),[6,7] might greatly expand the range of applicable nucleophiles. We report herein the first stereoselective synthesis of shelf-stable (*E*)- and (*Z*)-*β*-chlorovinyl-λ^3-chlorane **2** that functions as a stereospecific electrophilic vinylating agent not only toward common heteroatom nucleophiles but also toward simple aromatic hydrocarbons under mild conditions (Figure 1d).

There has been only one report of a synthesis of vinyl(alkyl)-λ^3-chlorane **3**, which involved a direct methylation of ethylene chloride with Me/EtF−SbF$_5$.[8] However, unfortunately the λ^3-chloranes **3** were too unstable to be isolated and were characterized only at −90 °C. Other attempted electrophilic attacks on vinyl chloride (e.g., transylidations with *N*-triflylimino-λ^3-bromane/bromonium ylide,[9,10] phenylation with phenyldiazonium tetrafluoroborate, and oxidation with chlorine trifluoride) were all unsuccessful and resulted in degradation/polymerization of the starting materials. Gratifyingly, the use of mesityldiazonium tetrakis(pentafluorophenyl)borate $[B(C_6F_5)_4^-]$ (**4**) proved to be a game-changer. Recently, we reported that the thermal decomposition of **4** in chloroarenes selectively afforded diaryl-λ^3-chloranes.[7] The direct mesitylation protocol tolerates *π*-electrons of vinyl chloride, and undesired polymerized products are not formed. Thus, exposure of **4** to *trans*-1,2-dichloroethylene (**5**) (30 equiv) at room temperature under air resulted in a slow but chlorine-selective mesitylation and afforded the corresponding (*E*)-vinyl-λ^3-chlorane **2** almost quantitatively (Scheme 1). Use of pentafluorobenzene accelerated the reaction without decreasing the yield.[11] This transformation could be operated on a gram scale with comparable yield: (*E*)-**2** was obtained in 86% yield (0.48 g). The *Z*-isomer (*Z*)-**2** was also obtained in

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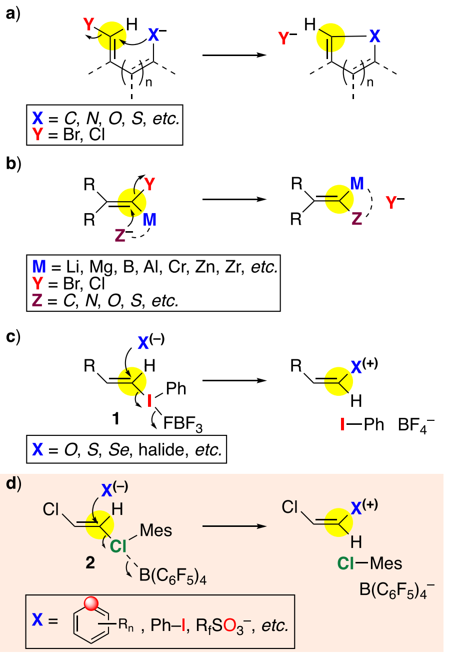
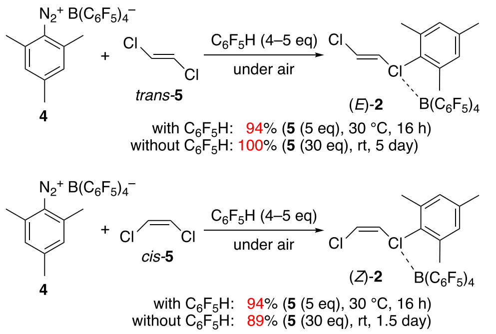


Figure 1. Vinylic S_N2 ($S_NV\sigma$) reaction of (a) vinyl halide (intramolecular), (b) metal carbenoid (intra/intermolecular), (c) vinyl-λ^3-iodane (intermolecular), and (d) vinyl-λ^3-chlorane (intermolecular, this work).

Scheme 1. Stereoselective Synthesis of (*E*)- and (*Z*)-*β*-Chlorovinyl-λ^3-chloranes 2



with C_6F_5H: 94% (**5** (5 eq), 30 °C, 16 h)
without C_6F_5H: 100% (**5** (30 eq), rt, 5 day)

with C_6F_5H: 94% (**5** (5 eq), 30 °C, 16 h)
without C_6F_5H: 89% (**5** (30 eq), rt, 1.5 day)

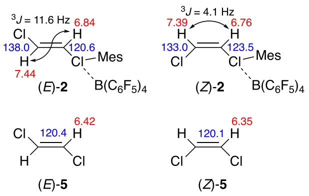


Figure 2. ^{1}H NMR and ^{13}C NMR chemical shifts of vinylic protons/carbons: δ values in ppm in $CDCl_3$.

high yield under similar conditions without formation of the *E*-isomer (Scheme S1).

The (*E*)/(*Z*)-vinyl-λ^3-chloranes **2** are colorless crystalline compounds, which show surprising thermal and moisture stability: no decomposition was detected under air without shielding from light for at least 1 year at room temperature for (*E*)-**2** and for 1 week at room temperature (months in a refrigerator at 4 °C) in the case of (*Z*)-**2**. In solution, however, both compounds are rather unstable and gradually decompose at ambient temperature. For example, in $CDCl_3$ at 23 °C, the half-life times ($t_{1/2}$) of 40 h for (*E*)-**2** and 22 h for (*Z*)-**2** were observed. The compounds are much less stable in more polar solvents, especially the (*Z*)-isomer: (*E*)-**2** is about 5 times more stable than (*Z*)-**2** in CD_3CN ($t_{1/2}$ of 8 h for (*E*)-**2**; 1.6 h for (*Z*)-**2** at 23 °C) and ≥24 times more stable in acetic acid-d_4 ($t_{1/2}$ of 4 h for (*E*)-**2**; <10 min for (*Z*)-**2** at 23 °C). In the ^{1}H NMR and ^{13}C NMR spectra of **2** (Figure 2), the vinylic α and β protons and vinylic β carbon of (*E*)/(*Z*)-**2** are significantly deshielded compared to those of the parent 1,2-dichloroethylene **5**, probably reflecting the potent electron-withdrawing ability of the λ^3-chloranyl group (Hammett σ_I for $-Cl(Ph)BF_4$: 1.72).[12] This consideration is in good agreement with the smaller coupling constants between vicinal vinylic protons (J_{trans} 11.6 Hz; J_{cis} 4.1 Hz) compared to dihaloethylene such as 2-chloro-1-iodoethene (J_{trans} 13.5 Hz; J_{cis} 5.8 Hz)[13] and (*E*)/(*Z*)-vinyl-λ^3-iodanes and λ^3-bromanes.[14,15] On the other hand, a negligibly small chemical shift change of the α carbon in **2** was observed, presumably due, at least in part, to the negligible spin−orbit effect (heavy atom effect) of the chlorine atom.[16]

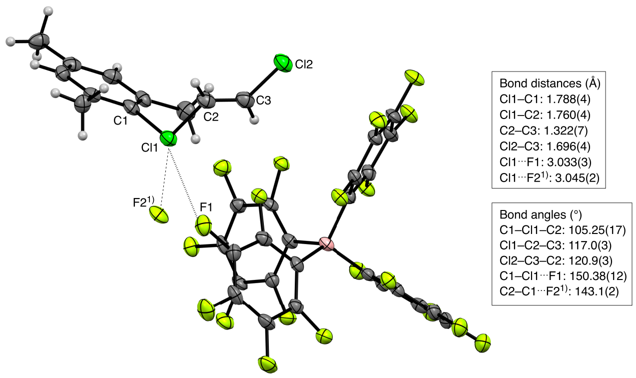
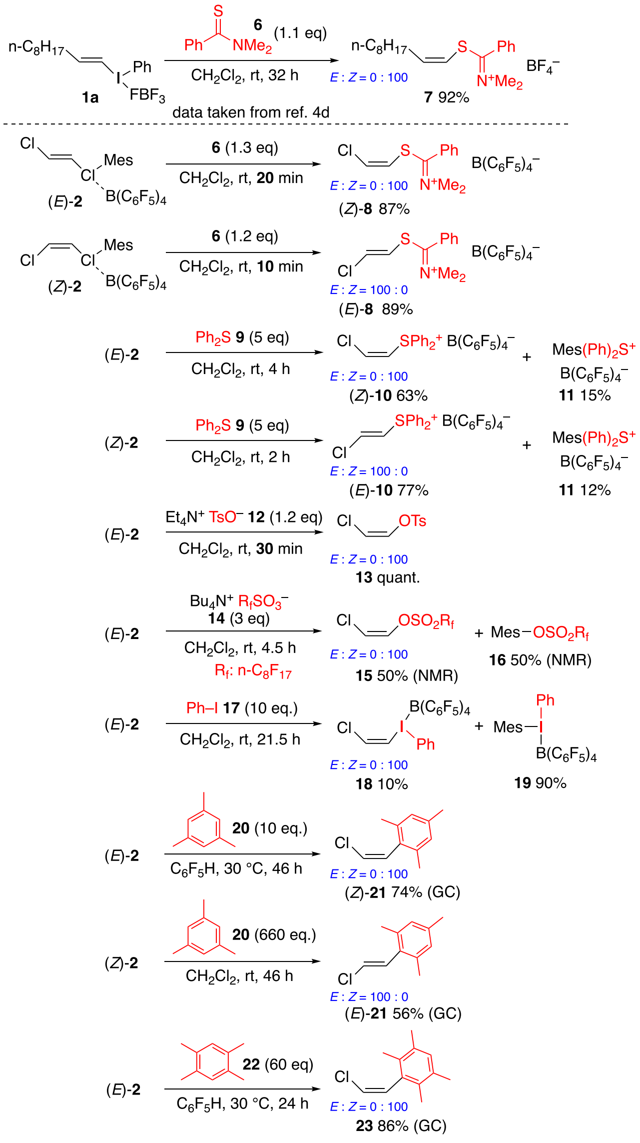


Figure 3. ORTEP drawing of (*E*)-**2** with thermal ellipsoids at 50% probability. The BAr_{f4}^- anion containing F2$^{1)}$ was omitted for clarity. For symmetry operation: 1) *X*, −*Y* + 1, *Z* + 1.

Recrystallization from CH_2Cl_2−hexane at −20 °C afforded single crystals of (*E*)-isomer **2** that were suitable for X-ray crystallography. Figure 3 shows the structure of the (*E*)-2-chlorovinyl(mesityl)chloronium unit stabilized by the fluorine atoms of $B(C_6F_5)_4^-$ anions. While the large C1−Cl1−C2 bond angle (105.25°) suggests onium-like character of the Cl(III) center,[7,17] the close contacts Cl1···F1 (3.033 Å) and Cl1···F2$^{1)}$ (3.045 Å) probably constitute a part of a distorted three-center four-electron (3c-4e) hypervalent bonding, due to the large bond angles of C1−Cl1···F1 and C2−Cl1···F2^{1}) (150.4° and 143.1°). In the vinyl unit, the vinylic C2−C3 bond length is comparable to the reported value of common $C_{sp2}{=}C_{sp2}$ bonds (1.31−1.32 Å).[18] On the other hand, the Cl1−C1 bond length (1.788 Å) is considerably longer than that of the Cl2−C3 bond (1.696 Å) or the bonds in 1,2-dichloroethylene **5** (1.71 Å), but it is close to that of the Cl(III)−C_{sp2} bond of diaryl-λ^3-chloranes.[7] The smaller angle of Cl1−C2−C3 (117.0°) compared to the common sp^2 angle of 120° probably reflects the carbocationic character of the C2 center.[19] 2-Chlorovinyl-λ^3-chlorane (*E*)-**2** thus synthesized serves as a tremendously active electrophile toward a variety of nucleophiles (Schemes 2 and S2). The $S_NV\sigma$ reaction of vinyl-λ^3-iodane **1a** with thiobenzamide **6** yielding (*Z*)-vinylthioimidonium salt **7** takes place, but the reaction is very sluggish at room temperature and requires a prolonged

Scheme 2. Reaction of (*E*)-*β*-Chlorovinyl-λ^3-chlorane (*E*)-2



reaction time.[4d] In contrast, (*E*)-**2** reacts instantaneously with **6** at room temperature to afford the completely inverted (*Z*)-vinylthioimidonium salt **8** in high yield, indicating the enhanced nucleofugality of the λ^3-chloranyl group. Similarly, sterically hindered diphenyl sulfide (**9**) smoothly underwent $S_NV\sigma$ reaction with both (*E*)- and (*Z*)-2 in high yields. The hyper-vinylating agent (*E*)-**2** undergoes $S_NV\sigma$ reaction with the much more weakly nucleophilic *p*-toluenesulfonate ion **12** at room temperature. This, to our knowledge, is the only example of the synthesis of (*Z*)-*β*-chlorovinyl tosylate **13** with complete stereoselectivity. Under these reaction conditions, possible undesired side reactions such as elimination of vinylic *α*/*β*-proton, ligand coupling, and mesitylation of nucleophile were not observed at all. In marked contrast, under these conditions, (*Z*)-**2** did not produce the corresponding (*E*)-vinyl tosylate, probably because of the stereoelectronically favored anti-*β*-elimination process. The superacid counterion $n\text{-}C_7F_{15}SO_3^-$ **14** (the conjugate acid's H_0 is lower than −12)[20] also functions as a potent nucleophile toward (*E*)-**2**, though this reaction is accompanied by formation of the *O*-mesitylated product **16**. The direct vinylation of iodobenzene (**17**) with **2** proceeded to afford inverted (*Z*)-*β*-chlorovinyl-λ^3-iodane **18** stereoselectively. This is the first example of the stereoinvertive vinylation of iodobenzene. Although the precise reason for the low vinylic $S_N2\sigma$ selectivity is unclear, vinylic $S_N2\sigma/S_NAr$ selectivity is known to be affected by stereoelectronic factors, solvent polarity, temperature, etc.[2b,4,21]

During the vinylation of haloarenes, we unexpectedly found that simple aromatic hydrocarbons also served as efficient nucleophiles. Thus, treatment of (*E*)-**2** with mesitylene (**20**) at 30 °C stereoselectively afforded 1-[(*Z*)-2-chlorovinyl]- 2,4,6-trimethylbenzene (**21**) in high yield (Scheme 2). (*Z*)-**2** also serves as stereospecific electrophile. These reactions were, however, sensitive to the *π*-electron density. For example, vinylation of durene (**22**) smoothly proceeded in 86% yield, while benzene with **2** did not give any vinylation product at all, but instead only mesitylation reaction took place (Table S2 in the Supporting Information). Given the features of the unusual vinylation of arene, i.e., (1) it follows second-order kinetics, (2) (*Z*)-**2** reacts faster than (*E*)-**2**,[14] and (3) there is a small and positive activation entropy $\Delta S^\ddagger$ (1.4 cal mol^{-1} K^{-1}), the reaction probably proceeds via an $S_NV\sigma$-type mechanism (Scheme S3, Figures S1 and S2, in the Supporting Information).

To gain mechanistic insights of this untraversed reaction, we performed DFT calculations using model compounds: (*E*)-*β*-chlorovinyl(mesityl)chloronium ion and mesitylene (Figure 4).

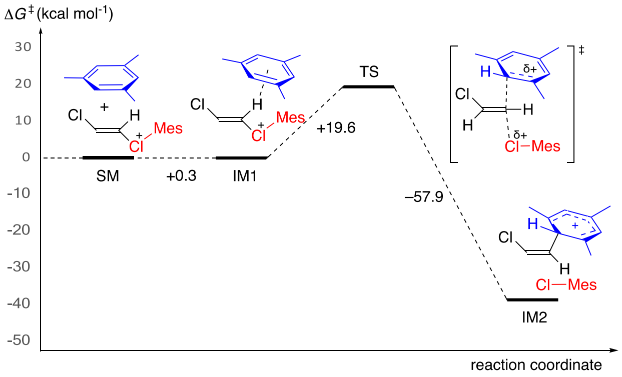
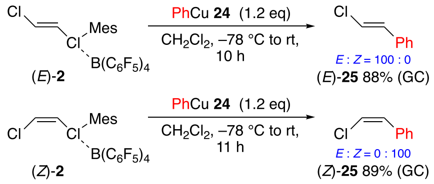


Figure 4. DFT calculation (M06-2*X*/6-31+G**).

The vinylation step is computed to be a concerted process of C−Cl(III) bond cleavage and $C_{Ar}-C_{vinyl}$ bond formation with an activation barrier of 19.6 kcal mol^{-1} leading to the *σ*-complex (IM2). In the TS, the vinylic *α*-carbon takes a nearly sp-hybridized configuration, which is comparable to the reported TS of $S_NV\sigma$ reactions.[22,2a] The transient IM2 would lead to barrierless deprotonation (rearomatization) to give the stable product (*Z*)-*β*-chlorovinylmesitylene (*Z*)-**21**.

Organometallics are widely utilized in C−C bond-forming reactions, but they generally do not work well with hypervalent vinyl-λ^3-iodanes due to their high basicity, which favors deprotonation reaction over bond-forming reaction.[15,23,24] Preliminary work has shown that organocopper reagents offer unique reactivity and chemo-/stereoselectivity with vinyl-λ^3-chloranes **2** (Scheme 3).[25] Exposure of (*E*)-**2** to phenylcopper(I) **24** in dichloromethane at −78 °C to room temperature resulted in the formation of the coupling product (*E*)-*β*-chlorostyrene (*E*)-(**25**) in 88% yield with full retention of configuration, while the reaction of (*Z*)-**2** proceeded smoothly to give exclusively (*Z*)-**25** in 89% yield. Further

Scheme 3. Stereoselective Phenylation of Vinyl-λ^3-chlorane 2 with Phenylcopper(I) 24



work to examine the scope of the reaction and to elucidate the reaction pathway with the help of theoretical and spectroscopic studies is in progress.

In conclusion, we present the first synthesis and characterization of (*E*)- and (*Z*)-vinyl-λ^3-chlorane **2**, which serves as a potent $S_NV\sigma$ type vinylating agent. These reagents enable direct, metal-free C_{Ar}–C_{vinyl} bond formation via $S_NV\sigma$ reaction of **2** with simple aromatic hydrocarbons. Further work on hypervalent λ^3-chlorine reagents and their applications is under way.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00924.

Experimental procedures, characterization data, theoretical data, and NMR spectra (PDF)

Accession Codes

CCDC 1983270 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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