

Communication

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Diaryl-λ³-chloranes: Versatile Synthesis and Unique Reactivity as Aryl Cation Equivalent

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Supporting Information Placeholder

ABSTRACT: We have developed a versatile, high-yield synthesis of diarylchloroniums/ λ^3 -chloranes through the reaction of various chloroarenes with readily prepared mesityldiazonium tetrakis(pentafluorophenyl)borate under mild conditions. The scope of the reaction is broad, including ArCl, ArBr, and ArI. The diarylchloroniums/ λ^3 -chloranes prepared here show unique reactivity in various respects, enabling intermolecular electrophilic arylation reaction of weak nucleophiles, and chlorane-halogane exchange reaction.

Hypervalent halogen compounds are currently attracting widespread interest in academia and industry as unique electrophiles/oxidants in organic synthesis.¹ For example, diaryl- λ^3 -iodanes 1 are used as an aryl cation equivalent.² However, their application has generally been limited to potent nucleophiles such as metal enolates, amides, halides.¹⁻³ first Nesmeyanov synthesized and diaryl- λ^3 -bromane derivatives **2**,⁴ which enabled electrophilic arylation of a range of weak nucleophiles such as pyridine⁵ due to their high electron-withdrawing ability⁶ and nucleofugality⁷ arising from the large ionization potential of the bromine atom (Figure 1a). Therefore, the Cl(III)-analogue 3 should be highly attractive species as a potent electrophilic arylating reagent and a unique synthetic tool (Figure 1a).⁸ However, in fact diaryl- λ^3 -chlorane chemistry remains largely unexplored, mainly due to the lack of efficient preparation methods. The first synthesis of **3** was achieved in 1955 by Nesmeyanov,^{8b} who found that thermal solvolysis of aryldiazonium 4-BF4 in chloroarenes afforded a mixture containing **3**, though in only 6% yield (Figure 1b). Much later, in 1978, Olah reported an improved method, in which 4-PF₆ or 4-CF₃CO₂ is used instead of 4-BF₄ in the presence of trifluoroacetic acid.^{8c} However, all these methods suffer from significant limitations, such as extremely low yield $(\leq 17\%)$, various side-reactions including the Balz-Schiemann reaction (fluorination),⁹ other decomposition reactions with counter ions, and so on.



Figure 1. a) Physicochemical properties of diaryl- λ^3 -haloganes 1– **3.** b) The first synthesis of diarylchloronium/ λ^3 -chlorane by Nesmeyanov. c) Olah's improved protocol.

Herein we report a versatile synthesis, isolation and full structural characterization of diaryl- λ^3 -chloranes. We further demonstrate the unique reactivity of these chloranes for unprecedented electrophilic arylation reactions. A key to the present achievement is the use of a chemically inert and nucleophilic weakly counter-ion, tetrakis(pentafluorophenyl)borate¹⁰ (denoted here as $[B(C_6F_5)_4]^-$ or $[BAr_{f4}]^-$). Another key feature of the synthetic strategy is the use of the mesityl (2,4,6-trimethylphenyl, denoted here as Mes) group to provide steric bulk around the aryl cationic center, together with the electronic stabilization. Overall, this strategy enables efficient preparation of various diaryl- λ^3 -haloganes (1–3) in high yield under ambient conditions for the first time.

For the synthesis of diaryl- λ^3 -chlorane **3**, mesityldiazonium salts were subjected to solvolysis in the presence of an excess of chlorobenzene at room temperature. We firstly focused on screening of counter anions of the putative mesityl cation intermediate. We previously reported the first isolation of a diarylborinium ion Ar₂B⁺, in which boron bears only four valence electrons, by utilizing chemically inert and weakly nucleophilic counter-ion such as

 $[CHB_{11}Cl_{11}]^{-}$ or $[B(C_6F_5)_4]^{-.11}$ Gratifyingly, exposure to mesityldiazonium tetrakis(pentafluorophenyl)borate $[MesN_2^+ (C_6F_5)_4B^-]$ **4a**-BAr_{f4} in chlorobenzene at room temperature afforded 3aa-BAr_{f4} in high yield (Table 1, entries 1 and 2). Note that the mesityl moiety was crucial for smooth aryl transfer, and the use of phenyldiazonium salt **4b**-BAr_{f4} decreased the yield of **3ba**-BAr_{f4} (57%), accompanied with the formation of a considerable amount of chlorobiphenyls (Friedel-Crafts by-products) (entry 3). On the other hand, the chemical yield of the desired **3aa**-BF₄ formation was drastically decreased (1%) with the use of tetrafluoroborate salt $(4a-BF_4)$ (entry 4), and the Balz-Schiemann by-product was mainly obtained instead. We then demonstrated that the 3aa-BAr_{f4} could be obtained from **4a**-BF₄ via sequential (anion exchange/aryl transfer) reactions in one pot. Exposure of 4a-BF4 to chlorobenzene (6 eq) in the presence of NaBAr_{f4} (1 eq) at room temperature under dry air afforded **3aa**-BArf4 selectively in 69% yield on a 1 mmol scale (entry 5). Rapid precipitation of NaBF₄ from the reaction mixture is probably responsible for the suppression of the Balz-Schiemann reaction and other side reactions. We would like here to emphasize that the use of a readily available anion such as $[B(C_6F_5)_4]^-$ greatly enhances the synthetic accessibility of the diaryl- λ^3 -chloranes. On the other hand, all attempts to use carborane anion [CB₁₁H₁₂]⁻ as a counter anion of mesityldiazonium salts failed (entry 6), partly because of poor solubility of **4a**-CB₁₁H₁₂ and low chemical stability of $[CB_{11}H_{12}]^{-.12}$

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3aa-BAr_{f4} thus obtained showed remarkably high stability both in the solid state and in solution. It is non-explosive under friction or impact, and can be stored indefinitely on the bench-top; no decomposition was detected under ambient conditions (under air at room temperature) without shielding light for at least 1 year. It also exhibits high thermal stability in solution. When a solution of **3aa**-BAr_{f4} in CDCl₃ or CD₃OD was stored at ambient temperature, no sign of decomposition was observed after 2 months. This is in sharp contrast to the tetrafluoroborate salt **3aa**-BF₄, which gradually decomposed in CDCl₃ solution *via* the Balz-Schiemann reaction to give fluoroarene with a half-life time ($t_{1/2}$) of 7 days.

Table 1. Diaryl- λ^3 -chlorane synthesis with diazonium salt **4a**.^{*a*}



^{*a*} Reactions were carried out in the concentration range of 0.3–1.7 M. ^{*b*} Isolated yields. Numbers in parentheses are ¹H NMR yield. ^{*c*} Ph₂ClBAr_{f4}. ^{*d*} 1 mmol scale. ^{*c*} NaBAr_{f4} (1 eq) was added. ^{*f*} Complex mixture. ^{*g*} **4a**-BAr_{f4} (1.0 g, 1.2 mmol) was used.

Examination of co-solvents showed that fluorinated solvents such as fluoroarenes and fluoroalkanes were the most effective, allowing a reduction of the necessary amount of chlorobenzene and a gram-scale reaction (entries 7–10). On the other hand, fluorine-free (polar/non-polar/aromatic) co-solvents did not promote, or scarcely promoted, this aryl transfer reaction (Table S1 in Supporting Information). Finally, the set of conditions shown in entry 2 (small scale) or 10 (large scale) was found to be optimal.

With the optimal conditions in hand, we next investigated the scope of the present chlorane formation reaction (Table 2). A range of chlorobenzenes and their analogues could be employed: 1) electron-donating substituents (Me and OMe) at the para-position of the aryl ring were efficiently converted to the corresponding chloranes in excellent yields without formation of undesirable side-products such as biphenyls and/or oxonium salts, 2) a para-fluoro group was not deleterious to the reaction, and **3ad**-BArf4 was obtained in 90% yield, 3) the use of inert co-solvent C₆F₅H allowed the arylation of the solid substrate *p*-dichlorobenzene (mp 53.5 °C) without any reduction in yield (3ae-BArf4, 87%), 4) strongly electron-withdrawing substituents (CF₃ and OTf) significantly slowed down the reaction, 13 5) sterically hindered chloroarenes with ortho-substituents needed extended reaction times to afford the desired products in moderate yields, and 6) bromobenzene and iodobenzene, were both good substrates, affording the corresponding λ^3 -haloganes **1aa**-BAr_{f4} and **2aa**-BAr_{f4} in high yield.

Table 2. Chlorine-selective arylation of ArCl with 4a-BAr_{f4}.^{*a,b*}



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^{*a*} Conditions: **4a**-BAr_{f4} (0.01–0.06 mmol), ArCl (6 eq). ^{*b*} Isolated yields. ^{*c*} *p*-Dichlorobenzene (10 eq) was used in C_6F_5H . ^{*d*} 30 °C. ^{*c*} PhBr (6 eq) was used. ^{*f*} PhI (10 eq) was used.



Figure 2. X-ray structure of 3aa-BArf4.

The ¹³C NMR signals due to the phenyl ring of **3aa**-BAr_{f4} at 25 °C in CDCl₃ appear at 136.9 (C_{ipso}), 124.2 (Cortho), 133.8 (Cmeta) and 134.1 (Cpara) ppm, significantly downfield than those reported for chlorobenzene (134.2 (C_{ipso}), 128.6 (C_{ortho}), 129.7 (C_{meta}) and 126.4 (C_{para}) ppm), reflecting exceptional electron deficiency at the chlorine center. Interestingly, the X-ray structural analysis of **3aa**-BAr_{f4} (Figure 2) reveals an intermediate (hybrid) nature between hypervalent and onium structures.¹⁴ The shortest distance between the chlorine center and a fluorine atom of $[(C_6F_5)_4B]^-$ (3.0187(12) Å) is within the sum of the van der Waals radii (3.22 Å), as expected for hypervalent bonding. However, the angle between the mesityl and phenyl rings is 107.30(9)°, reflecting partial breakdown of three-center-four-electron (3c-4e) hypervalent bonding interactions (T-shaped structure, see also Figure S1 in Supporting Information). The phenyl C_{ipso}-Cl bond length (1.811(2) Å) is slightly longer than that in chlorobenzene (1.74 Å), but similar to that in $[Me_2Cl^+][CHB_{11}Cl_{11}^-]$ salt (1.81 Å).¹⁵

Diarylchloronium **3aa**-BAr_{f4} thus prepared turned out to serve as a phenyl cation equivalent through C_{sp2} -Cl bond activation (Scheme 1). For instance, **3aa**-BAr_{f4}, was treated under cross-coupling conditions (Suzuki-Miyaura and Heck reactions) to give the desired coupling product **6** in high yields. **3aa**-BAr_{f4} also underwent Pd-catalyzed quaternary phosphonium formation to give **8** in 82% yield. Furthermore, a peculiar phenylation of sodium enolate **9** with **3aa**-BAr_{f4} proceeded smoothly at ambient temperature to afford **10** in moderate yield.¹⁶ Thus, chloronium/chlorane formation can be regarded as an activation reaction of chlorobenzene derivatives.



During this study, we unexpectedly found that a change of nucleophiles switched the phenyl/mesityl transfer aptitude of diarylchloronium 3aa-BArf4 (Scheme 2).¹⁷ Use of less-reactive heteroatom nucleophiles gave the mesitylated product exclusively. The unprecedented direct N-mesitylation of pyridine with 3aa-BArf4 proceeded conditions smoothly under ambient to afford N-mesitylpyridinium salt 11 in 98% yield, but in contrast, the use of iodane 1aa-BArf4, bromane 2aa-BArf4, or tetrafluoroborate salt **3aa**-BF₄ did not give satisfactory results.^{18,19} This unique mesitylation is not limited to pyridine, and less reactive diazines such as pyridazine, pyrimidine, and pyrazine afforded the desired N-mesitylated products in high yield.²⁰ The mesitylation of five-membered 1-phenylimidazole provided a useful synthetic method for unsymmetrical 1,3-diarylimidazolium salt. Not only heteroaromatic sp²-nitrogens, but also other less-reactive nucleophiles such as diphenyl sulfide, MeCN, and even unactivated benzene, also efficiently underwent this peculiar mesitylation in high yield, in marked contrast to hypervalent iodine/bromine chemistry. Indeed, arylation with 1aa/2aa-BAr_{f4} was unsuccessful (Scheme S4 in Supporting Information).



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Conditions: **3aa**-BAr₆₄ (0.01–0.2 mmol): a) pyridine (1.1 eq), CH₂Cl₂, rt, 48 h; b) pyridazine (1.5 eq), CH₂Cl₂, rt, 24 h; c) pyrimidine (1.5 eq), CH₂Cl₂, 50 °C, 72 h; d) pyrazine (1.5 eq), CH₂Cl₂, 50 °C, 72 h; e) 1-phenylimidazole (2 eq), CH₂Cl₂, rt, 24 h; f) Ph₂S (solv.), 30 °C, 4 d; g) 2,6-di-*tert*-butylpyridine (1 eq), MeCN (solv.), 50 °C, 24 h; h) benzene (solv.), 80 °C, 14 h.

Scheme 2. Selective mesitylation of weak nucleophiles

The unique arylating ability of **3**, featuring strong nucleofugality of the chlorine(III) hyper-leaving group, enables easy λ^3 -halogane formation reaction of chloro/bromo/iodoarenes (Scheme 3).²¹ Heating of **3aa**-BAr_{f4} in the haloarenes at 50 °C resulted in chemoselective mesitylation and afforded the corresponding chloroniums/ λ^3 -chloranes **3ab**-**c**-BAr_{f4}, bromane **2aa**-BAr_{f4}, and iodanes **1aa**-**1ad**-BAr_{f4} in high yield. On the other hand, fluorobenzene did not react at all.²² Further, iodanes **1ab**-**1ad**-BAr_{f4} were selectively obtained in high yield when *o*-, *m*-, *and p*-chloroiodobenzenes were used, in contrast to the non-selective arylation of diazonium salt **4a**-BAr_{f4} (Scheme S1 and Table S2 in Supporting Information).



Scheme 3. Mesitylation of haloarenes with 3aa-BArf4.

We also applied the present chemoselective λ^3 -iodane formation to an *in situ* vinylic S_N2 reaction (Scheme 4). Iodane **20** formation reaction of (*E*)-vinyl iodide **19** with **3aa**-BAr_{f4} followed by treatment with thioamide **21** in CH₂Cl₂, selectively produced (*Z*)-vinylthioimidonium salt **22** in good yield.²³ This reactivity is unique, as the use of **1aa/2aa**-BAr_{f4} instead of **3aa**-BAr_{f4} in this *in situ* vinylic S_N2 reaction was unsuccessful (Scheme S4 in Supporting Information). **22** serves as a useful precursor of Ag/Au (*Z*)-enethiolate.²⁴



Scheme 4. Stereoinversive substitution of vinyl iodide 19.

In summary, we have developed the first efficient and method for practical preparation diarylchloroniums/ λ^3 -chloranes. With this ready synthetic accessibility, relative ease of handling, and potent arylation ability. the electrophilic diaryl chloroniums/ λ^3 -chloranes should provide a novel platform for hypervalent and super-electrophile chemistry, and should prove to be a powerful tool for exploring new chemical transformations.^{8h}

ASSOCIATED CONTENT

Supporting Information

Experimental details and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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- diaryl- λ^3 -iodanes, see references 1 and 2.
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