Willgerodt-Type Dichloro(aryl)-λ^3-Iodanes: A Structural Study

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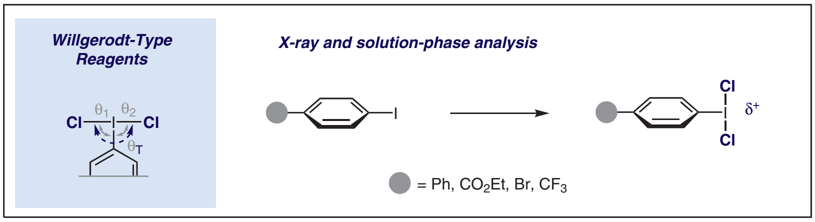

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Abstract Crystallographic structural analysis of four electronically diverse Willgerodt-type reagents is disclosed together with a solution-phase NMR analysis. These data reveal a plethora of intermolecular non-covalent interactions and confirm the expected T-shape geometry of the reagents. In all cases the I–Cl bonds are orthogonal to the plane of the aryl ring. This study provides important structural insights into this venerable class of dichlorination reagent and has implications for crystal engineering.

Key words chlorination, hypervalency, iodine(III), X-ray crystallography

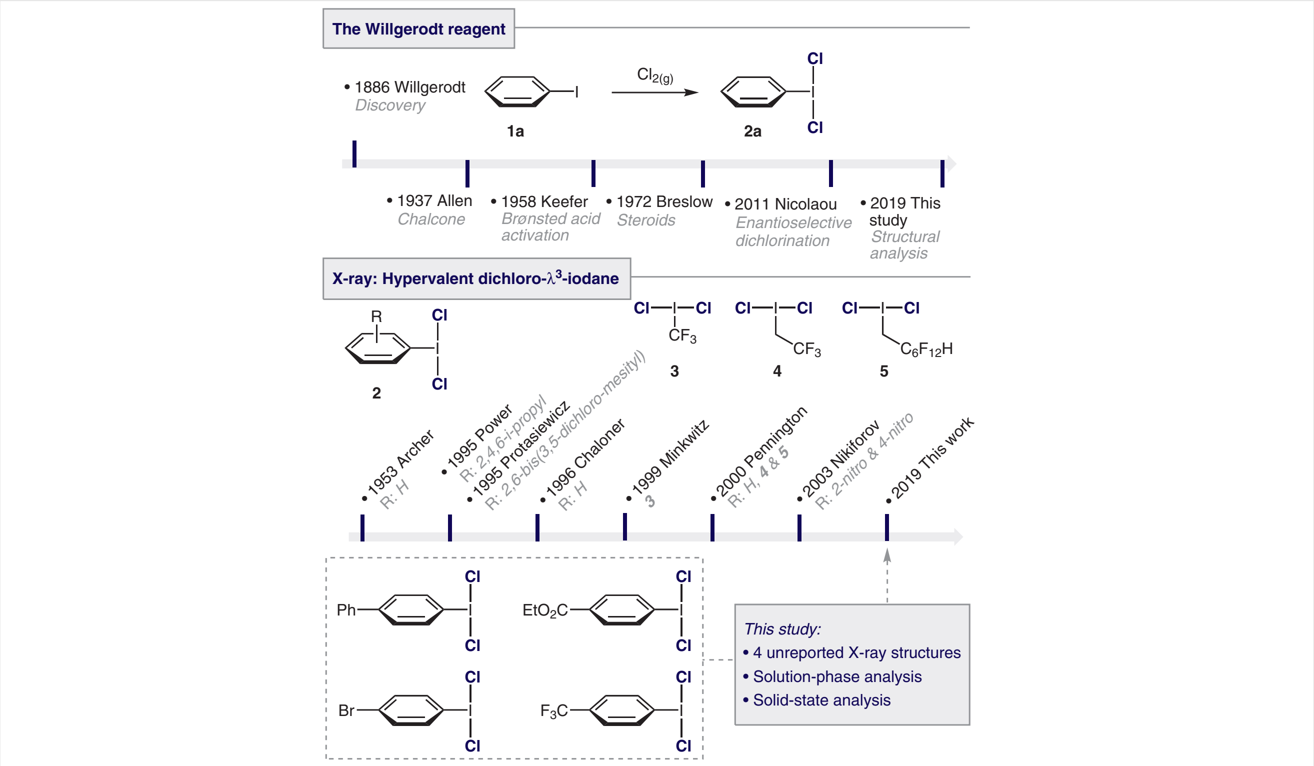
Willgerodt's synthesis of dichloro(phenyl)-λ^3-iodane in 1886 remains a defining innovation in main group structural chemistry, and the genesis of hypervalent iodine.[1] Generated by exposing iodobenzene to $Cl_{2(g)}$, the product was named '*Phenyljodidchlorid*' (**1a** → **2a**) and attributed the molecular formula PhI(III)Cl$_2$ (Scheme 1). Historically, it is pertinent to note that Kekule's papers on the structure of benzene were published only 20 years earlier.[2] Over a century of interest and sustained innovation exploring the reactivity of the Willgerodt reagent has resulted in a powerful legacy.[3] This is a consequence of the reagent's versatility in serving as both a nucleophilic and electrophilic chlorine source. Its synthetic value was demonstrated as early as 1937 in the vicinal dichlorination of chalcone, where the practical advantages of **2a** versus $Cl_{2(g)}$ were highlighted.[4] Brønsted acid activation was later demonstrated through kinetic interrogation leading to a putative mechanism to account for the formation of the *anti*-adducts.[5] This latter development continues to inform and inspire the design of catalytic paradigms to generate ArX$_2$ species in situ via I(I)/I(III) catalysis.[6] The polar reactivity of **2a** is complemented by its ability to engage in radical processes, as is evident from the dichlorinate rubber induced by thermal decomposition.[7] This free-radical character was elegantly harnessed by Breslow and co-workers to achieve the site-selective C(sp^3)–H chlorination in steroids triggered by light irradiation.[8]

The Willgerodt reagent and derivatives thereof continue to enjoy widespread appeal as both oxidants and chlorination agents.[9] A prominent, contemporary application includes the vicinal difunctionalisation of π-bonds. Employing the *para*-substituted analogue (*p*-PhC$_6$H$_4$ICl$_2$), Nicolaou and co-workers developed an enantioselective dichlorination of cinnamyl alcohols (Scheme 1, top).[10]

Despite their venerable history, Willgerodt's original report cautions that a principal weakness of dichloro(aryl)-λ^3-iodanes is their lack of stability.[1] This has led to the development of innovative strategies to mitigate degradation. Approaches including recycling strategies[11] or in situ generation from iodosobenzene[12] have been reported to address this intrinsic limitation.

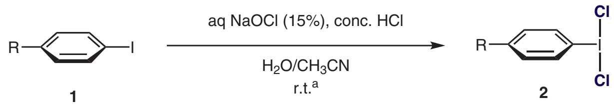
The reactivity of dichloro(aryl)-λ^3-iodanes is a consequence of the linear three-centre, four-electron Cl–I–Cl bond intrinsic to these reagents. The distorted T-shape geometry expected for these RICl$_2$ species has been confirmed by X-ray analysis on a number of derivatives.[13,14] However, despite their prominence as chlorination/oxidation reagents, structural studies of *para*-substituted ArICl$_2$ species in the solid state are underrepresented. Herein, a solid-state analysis of selected *para*-substituted ArICl$_2$ systems is disclosed to contribute to the current renaissance of hypervalent iodine mediated halogenation (Figure 1, bottom).

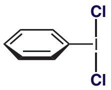
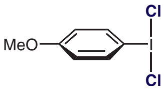
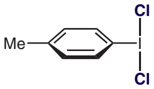
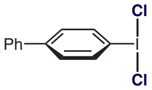
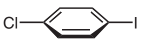
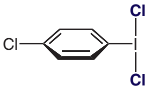
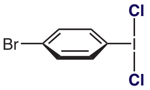
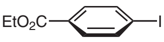
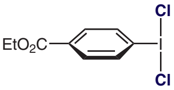
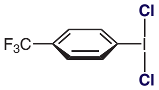
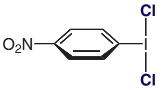
Initially, a series of electronically diverse Willgerodt-type reagents was prepared according to a modified procedure reported by Zhang and Zhao (Table 1).[15]



Scheme 1 Conceptual framework of this study

Table 1 Synthesis of Dichloroaryl-λ^3-iodanes **2a–i**



Entry	Iodoarene	Product		Time (h)	Yield (%)
1			**2a**	0.5	85
2[b]			**2b**	–	94
3			**2c**	0.5	83
4			**2d**	0.5	88
5[c]			**2e**	0.5	83
6[c,d]			**2f**	0.5	94
7[d]			**2g**	0.5	97
8[c]			**2h**	2	93
9[c]			**2i**	2	92

[a] According to a modified procedure reported by Zhang and Zhao:[15] iodoarene (1 mmol), aq NaOCl (15%, 2 mL), conc. HCl (2 mL), H_2O/MeCN (8 mL, 1:1 v/v).
[b] At 0 °C, filtered directly after addition of conc. HCl.
[c] Iodoarene (4 mmol scale).
[d] H_2O/MeCN (2:1 v/v). All yields refer to isolated yields.

Gratifyingly, all nine aryl iodides were successfully converted into the corresponding hypervalent dichloro(aryl)-λ^3-iodanes in high yields (up to 97%). The synthesis of the electron-rich *p*-methoxy-substituted analogue **2b** was performed at 0 °C and was filtered instantly after the addition of concentrated HCl (Table 1, entry 2). Electron-deficient substrates such as *p*-trifluoromethyl- and *p*-nitro-derivatives required extended reaction times (Table 1, entries 8 and 9). Gratifyingly, several examples could be scaled-up to 4 mmol scale with no erosion of the yield (Table 1, entries 5, 6, 8 and 9).

The structural evaluation began with a solution-phase NMR analysis of this electronically diverse pool of $ArICl_2$ species. Consistent with the findings reported by Wu and Shafir with $ArI(OAc)_2$,[16] the ^1H NMR spectrum of the Willgerodt reagent **2a** shows consistent deshielding of all protons on the aromatic ring compared to iodobenzene. This downfield shift is more pronounced for the *ortho*-proton H2 ($\Delta\delta_H$ 0.48) than for the *meta*-H3 and *para*-H4 signals ($\Delta\delta_H$ 0.37 and 0.26, respectively) (Figure 1, a).

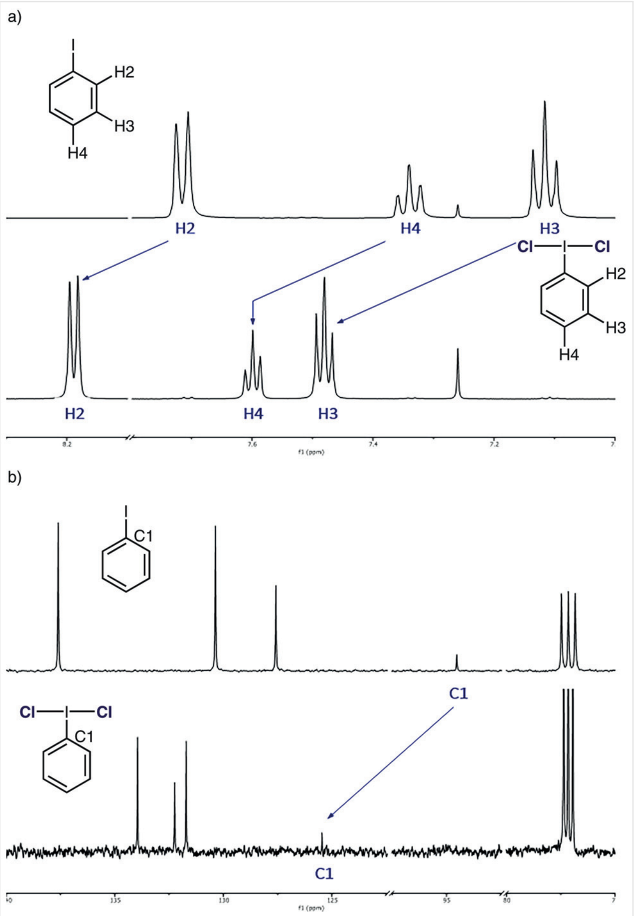


Figure 1 (a) ^1H NMR stack plot of iodobenzene (top, 400 MHz, $CDCl_3$, 296 K) and **2a** (bottom, 599 MHz, $CDCl_3$, 299 K). (b) ^{13}C NMR stack plot of iodobenzene (top, 101 MHz, $CDCl_3$, 296 K) and **2a** (bottom, 151 MHz, $CDCl_3$, 299 K).

In the ^{13}C NMR spectra, the *ipso*-carbon (C1) of iodobenzene shows a characteristic upfield signal at $\delta = 94.5$ due to normal halogen dependence (NHD).[17] After oxidation to the hypervalent species **2a**, this signal is drastically shifted to the downfield region at $\delta = 125.5$, corresponding to a Δppm of 31.0 and illustrating once more the expected, strong electron-withdrawing character of ICl_2 (Figure 1, b).[18]

These observations are persistent throughout the series, from the most electron-rich *p*-methoxy-substrate **2b** to the most electron-poor *p*-nitro **2i** (see the experimental section). The average deviation of the *ipso*-carbon C1 between ArI and $ArICl_2$ is 29.9 ppm and a linear shift correlation between the starting material and the product is observed (Figure 2, a).

Consistent with the observation from the ^1H NMR spectra of the Willgerodt reagent and of iodobenzene, the I(I)/I(III) oxidation results in a downfield shift of the *ortho*- and *meta*-protons, regardless of the *para*-substituent. This difference remains a constant 0.49 ppm for H2 and 0.35 ppm for H3. Again, a linear correlation between the corresponding proton signals from the starting materials and the products can be observed (Figure 2, b).

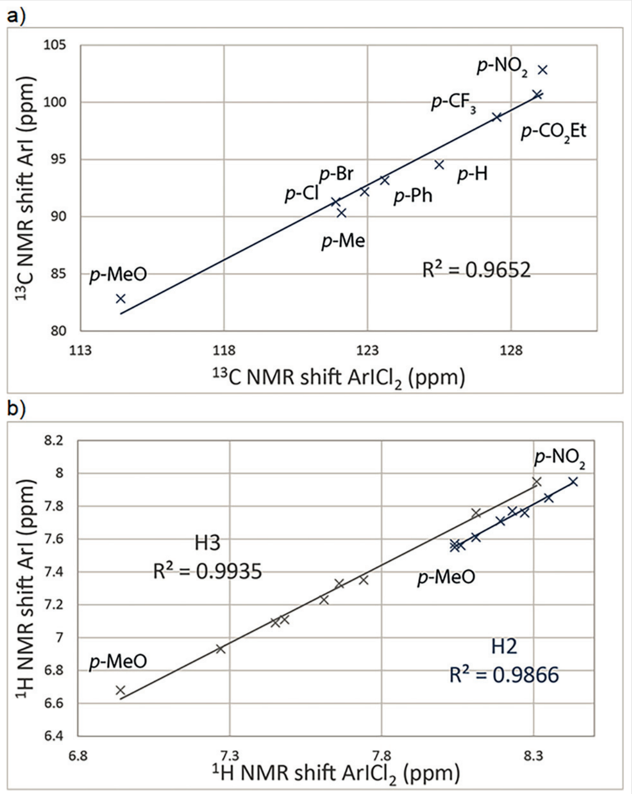
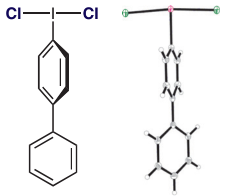
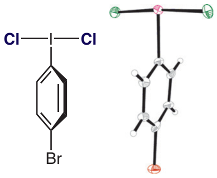
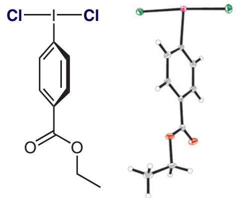
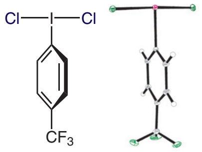


Figure 2 (a) Correlation between the ^{13}C NMR signals of C1 for ArI and $ArICl_2$. (b) Correlation between the ^1H NMR signals of H2 and H3 for ArI and $ArICl_2$

From the test set, it was possible to isolate crystals of four dichloro-λ^3-iodanes that were suitable for X-ray analysis (Table 2). The first of this quartet, p-$PhC_6H_4ICl_2$ (**2d**) (CCDC 1918404), was employed by Nicolaou and co-workers in combination with catalytic $(DHQ)_2PHAL$ for the enantioselective dichlorination of cinnamic alcohols.[10] This spe-

Table 2 Selected Intramolecular Bond Lengths and Angles

Structure^a				
	2d (CCDC 1918404)	**2f** (CCDC 1918405)	**2g** (CCDC 1918406)	**2h** (CCDC 1918407)
Distances (Å)				
C1–I1	2.100(2)	2.095(12)	2.110(2)	2.102(2)
I1–Cl1	2.503(1)	2.471(3)	2.472(1)	2.485(1)
I1–Cl2	2.503(1)	2.500(3)	2.521(1)	2.490(1)
I1–Cl^b	2.5029	2.486	2.497	2.488
Angles θ (°)				
θ_1	87.0(1)	86.7(4)	87.8(1)	89.3(1)
θ_2	87.0(1)	89.6(4)	89.0(1)	88.7(1)
θ_T	174.0(1)	176.1(1)	176.6(1)	177.8(1)
Dihedral angles ϕ^c (°)				
ϕ1a	–81.3	73.7	102.0	–76.0
ϕ1b	98.7	–103.1	–75.0	104.0
ϕ2a	–81.3	–107.5	–79.2	105.0
ϕ2b	98.7	75.7	103.8	–75.0

[a] ORTEP: **2d** and **2g**, thermal ellipsoids are set at 50% probability; **2f**, thermal ellipsoids are set at 30% probability; **2h**, thermal ellipsoids are set at 15% probability.
[b] Average of I1–Cl1 and I1–Cl2 distances.
[c] ϕ1a: Cl1–I1–C1–C2. ϕ1b: Cl1–I1–C1–C6. ϕ2a: Cl2–I1–C1–C2. ϕ2b: Cl2–I1–C1–C6.

cies, together with the three remaining dichloro-λ^3-iodanes, allow the influence of the p-substituent on the structure to be interrogated. Specifically, **2f** contains a p-Br group (CCDC 1918405), **2g** an ester (CCDC 1918406) and **2h** a trifluoromethyl moiety (CCDC 1918407). For the purposes of describing distances and angles in the solid-state study, the solid line (–) corresponds to an intramolecular bond whilst the broken lines (--) refer to intermolecular interactions (Figure 3).

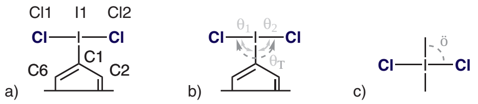


Figure 3 (a) Atom labelling for this study. (b) Nomenclature to describe angles. (c) Representation of torsion angles.

A consistent feature of dichloro-λ^3-iodanes that spans the initial X-ray investigation of the Willgerodt reagent from Archer and van Schalwyk[13a] to the most recent example of *ortho*- and *para*-nitro-substituted reagents,[14d] is the distorted T-shape geometry of the $RICl_2$ unit. In line with previous data (**2d**, **2f**, **2g**, **2h**), the four new structures displayed this characteristic geometry. The C1–I1 bond lengths of compounds **2d**, **2f**, **2g** and **2h** vary between 2.095(12) Å and 2.110(2) Å, and are thus consistent with literature values ranging from 2.00 Å[13a] and 2.125 Å[14a,b] for dichloro(aryl)-λ^3-iodanes and slightly shorter than the fluorinated aliphatic examples[13c,14c] (between 2.140 Å and 2.229 Å).

In addition, symmetrical compound **2d** comprises a I1–Cl1 bond length of 2.503(1) Å, where a θ_T angle of 174.0(1)° was measured. Compounds **2f**, **2g** and **2h** exhibit non-symmetrical angles and distances, which may be a consequence of crystal packing effects.

Hypervalent p-$BrC_6H_4ICl_2$ (**2f**) displays angles θ_1 of 86.7(4)° and θ_2 of 89.6(4)° and an overall θ_T angle of 176.1(1)° for distances of I1–Cl1 (2.471(3) Å) and I1–Cl2 (2.500(3) Å). The ester **2g** has a θ_1 angle of 87.8(1)°, and a θ_2 of 89.0(1)° for a measured θ_T of 176.6(1)°. The three-centre four-electron bond comprises an I1–Cl1 bond length of 2.472(1) Å and an I1–Cl2 bond of 2.521(1) Å. Comparably, the structure of p-CF_3 **2h** consists of two I1–Cl1 and I1–Cl2 bonds of 2.485(1) Å and 2.490(1) Å, respectively, as well as bond angles θ_1 of 89.3(1)°, θ_2 of 88.7(1)° and a measured θ_T of 177.8(1)°.

Interestingly, the four structures in this study display representative dihedral angles that deviate from orthogonality (ϕ1a of –81.3° for **2d**, 73.7° for **2f**, 102.0° for **2g** and –76.0° for **2h**). The unsymmetrical compounds **2f**, **2g** and **2h** exhibit non-equivalent torsion angles of –103.1° (ϕ1b), –107.5° (ϕ2a) and 75.7° (ϕ2b) for **2f**, –75.0° (ϕ1b), –79.2° (ϕ2a) and 103.8° (ϕ2b) for **2g**, and finally 104.0° (ϕ1b), 105.0° (ϕ2a) and –75.0° (ϕ2b) for **2h**. Inspection of the expanded solid-state structures reveals a plenum of intermolecular interactions that are noteworthy.

Compounds with a symmetrical unit in the solid state are organised as a polymeric structure with prominent intermolecular Cl1--Cl1 and Cl1--I1 interactions. In the case of *p*-$PhC_6H_4ICl_2$ (**2d**), two different Cl1--Cl1 interactions with distances of 3.329(1) Å and 3.494(1) Å are observed, while the Cl1--I1 distance measures 3.625(1) Å (Figure 4). It is interesting to note that both Cl1--Cl1 distances are inferior to the sum of the chlorine van der Waals radii (1.75 (Cl) + 1.75 (Cl) = 3.50 Å) and that the same phenomenon is observed for the Cl1–I1 interactions, where the distance is less than 3.71 Å (sum of the chlorine and iodine van der Waals radii: 1.75 (Cl) + 1.96 (I)).[19]

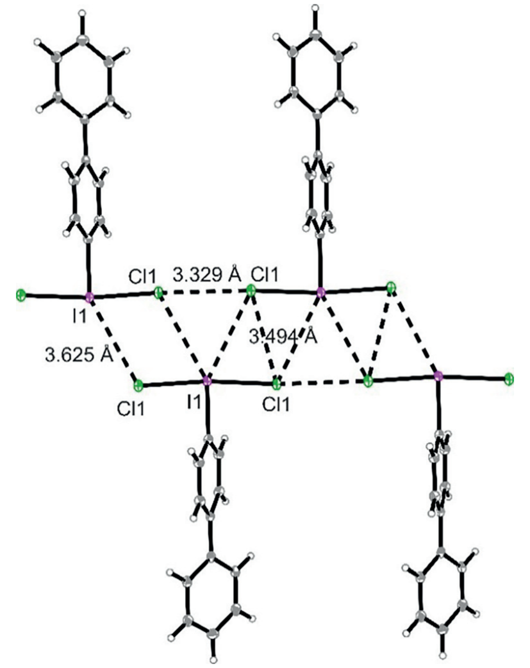


Figure 4 Formation of the halogen-based polymeric chain in **2d**

Structural analyses of the parent Willgerodt reagent **2a** reveal a polymeric zig-zag structure originating from the chlorine atoms at the hypervalent iodine centres.[13] In contrast, the polymeric structure for compound **2d** is built upon two bridging chlorine contacts for each iodine centre. Closer inspection reveals an intermolecular Cl1--I1--Cl1 angle of 54.7° and a torsion angle between the Cl1--I1--Cl1 plane and the T-shaped Cl1–I1(C1)–Cl1 plane of 14.8° for **2d**. Secondary intermolecular C8–H8--Cl1 interactions (3.715(2) Å with an angle C8–H8--Cl1 of 144.9°) allows for the formation of a 2D network based upon halogen chains (Figure 5).

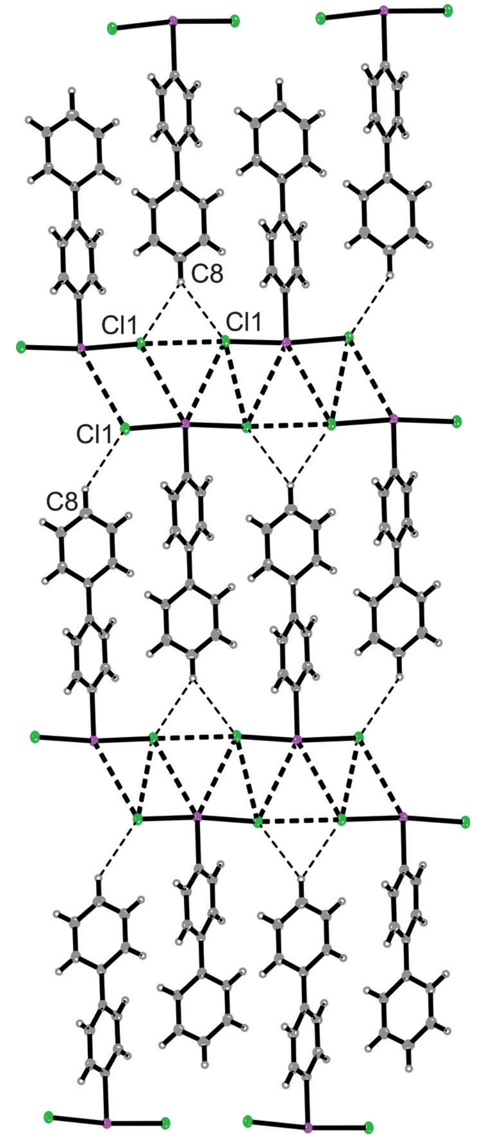


Figure 5 Expansion of the polymeric chain into a 2D network through C8–H8--Cl1 interactions in **2d**

Chlorine--chlorine and chlorine--iodine interactions are also observed in *p*-$BrC_6H_4ICl_2$ (**2f**) with lengths of 3.326(4) Å for Cl1--Cl2 and 3.357(4) Å for Cl2--I1 having been measured (Figure 6, a). Intriguingly, this inter-halogen framework seems to be influenced by a bridging Cl2--Br1 interaction [3.418(4) Å; smaller than the sum of the chlorine and bromine van der Waals radii (1.75 (Cl) + 1.85 (Br) = 3.60 Å)] (Figure 6, b).[19] Expansion of the structure into 3D space via the involvement of a C2–H2--Cl1 interaction (3.797(1) Å for a C2–H2--Cl1 angle of 157.1°) is observed. The chlorine atom Cl2 that is in contact with three different halogens Cl1--Cl2, Cl2--I1 and Cl2--Br1 is also notably the closest to orthogonality (C–I–Cl) with an angle θ_2 of 89.6(3)° (Cl1: θ_1 of 86.7(3)°). The angle between the planes, exemplified by the atoms I1--Cl2--I1 and Br1--Cl2--Cl1, is only 15.3° leading to a *quasi*-planar orientation.

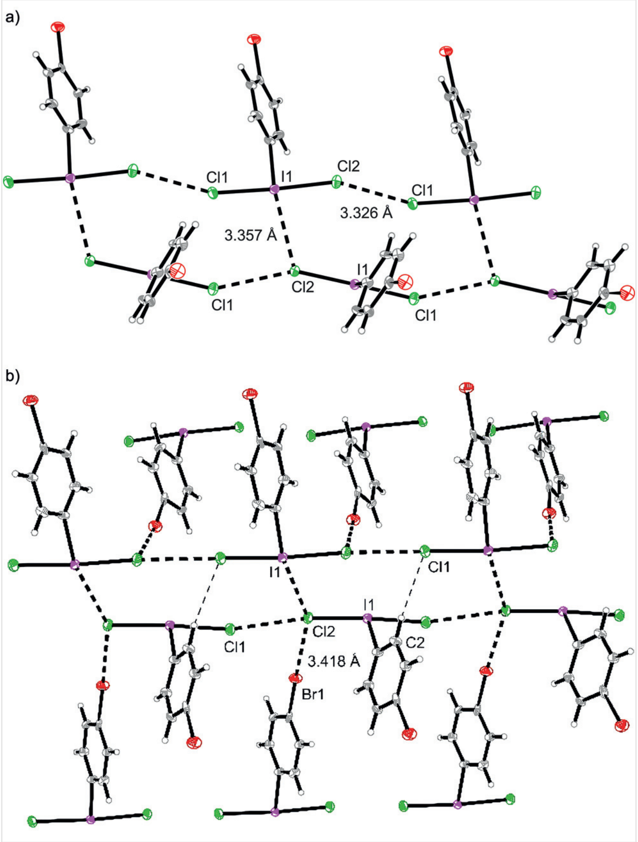


Figure 6 (a) Presentation of the inter-halogen interaction observed in **2f**. (b) Packing diagram representing the bromine–chlorine and hydrogen–chlorine interactions in **2f**.

It is pertinent to mention that dichloro(4-bromobenzene)-λ^3-iodane (**2f**) is the only species in which a chlorine atom engages in three discrete interactions with other halogen atoms, thereby allowing expansion to a complex network (Figure 7).

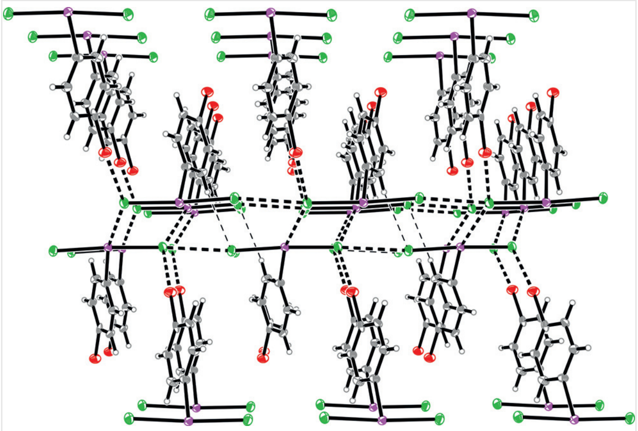


Figure 7 Packing diagram illustrating the expansion of **2f** into a complex 3D network

Analogous to the crystal packing observed for the Willgerodt reagent,[13] *p*-ethyl ester **2g** is a dimer in the solid state in which two intermolecular axial I1--Cl2 interactions of 3.384(4) Å are noted: These are slightly longer than those measured for **2f**. Secondly, Cl1--π interactions with the esters of the adjacent dimers are visible from the X-ray analysis and contrast sharply with the chlorine--chlorine and chlorine--iodine interactions observed in related systems (the distance Cl1--C7(ester) is 3.301(3) Å). This result is interesting when compared with Archer's original report for **2a**[13a] in which the comparable closest contact of the two dimers has a Cl--ArH distance of 3.77 Å. In addition, this scaffold displays a π--π interaction between juxtaposed dimers of 3.384(1) Å (Figure 8). The overall architecture of the crystal **2g** is predicated on a polymer-type structure with alternating halogen contacts.

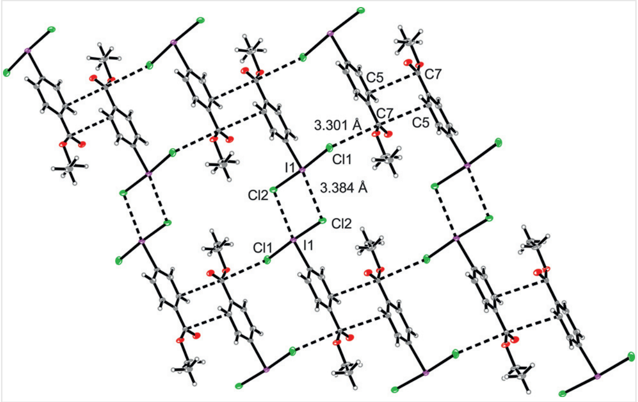


Figure 8 Packing diagram representing the polymer-type structure of **2g** with alternating halogen contacts and π--π interactions

Structural analysis of dichloro(4-trifluoromethylbenzene)-λ^3-iodane (**2h**) again reveals a stair-like, polymeric array based on halogen interactions akin to the Willgerodt reagent. The axial Cl2--I1 interaction of 3.428(1) Å is comparable to the 3.40 Å for the parent molecule **2a**.[13] Despite the initial similarity, closer inspection reveals that **2h** differs from **2a** by a significantly shorter intermolecular Cl2--Cl2 distance (3.293(1) Å compared to 4.15 Å for **2a**)[13] (Figure 9, a).

Whereas crystallographic analysis of compound **2a** reveals a 2D structure based on interlaced polymeric chains, expansion of the **2h** network shows clear interactions between the *p*-CF_3 substituents of each monomer of every polymeric chain. Specifically, a significant C5–H5--F2 interaction measuring 3.508(3) Å (C5–H5--F2 angle of 175.5°) is

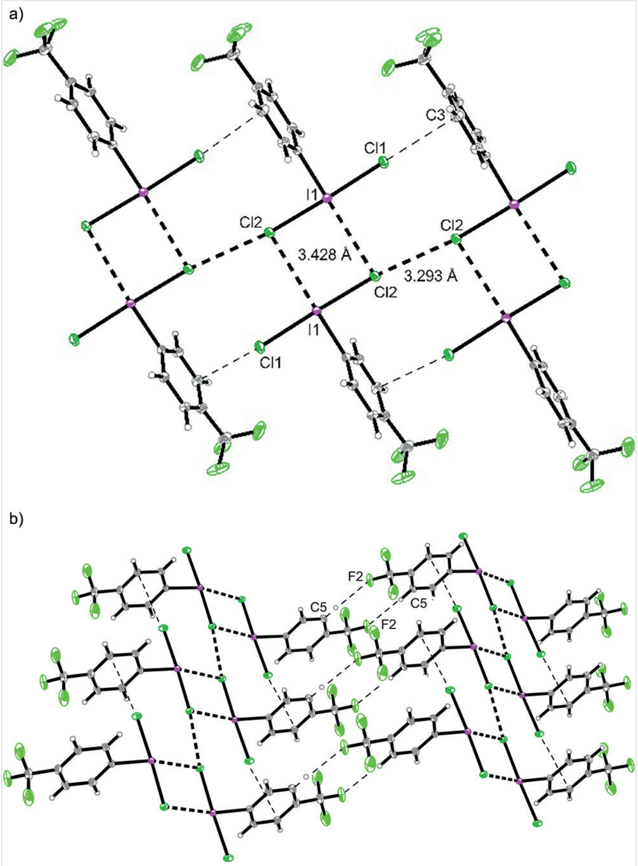


Figure 9 (a) Formation of the halogen-based polymeric chain in **2h**. (b) Expansion of the polymeric chain into a 2D network through C5–H5--F2 interactions

supported by an intermolecular F1--F1 interaction of 2.930 Å: This is comparable to the sum of their van der Waals radii (1.47 (F) + 1.47 (F) = 2.94 Å) (Figure 9, b).[19]

Interestingly, when the intermolecular I1--Cl2 interaction occurs with the axial position of the adjacent hypervalent iodine centre, the angle between the planes Cl1–I1(Cl2)–Cl2 and Cl1–I1(C1)–Cl2 is 20.0° for **2h**, 15.6° for **2f** and only 1.7° for **2g**.

In conclusion, a solution-phase NMR analysis has revealed the influence of *para* substituents on an electronically diverse group of Willgerodt-type chlorination reagents based on the hypervalent dichloro(aryl)-λ^3-iodane scaffold. This is complemented by a crystallographic study for the four novel systems, which demonstrate subtle differences in packing. In addition to providing information on this venerable class of dichlorination reagents, it is envisaged that these data will have implications for crystal engineering and structural chemistry in a broader sense.

All chemicals were purchased as reagent grade and used as received. Solvents were dried using a Grubbs purification system including columns packed with molecular sieves and aluminium oxide. Solvents for extraction or purification were purchased as technical grade and distilled on a rotary evaporator prior to use. Column chromatography was performed using silica gel (40–63 μm; VWR Chemicals) as the stationary phase. Reaction monitoring was achieved by analytical thin-layer chromatography (TLC) on aluminium foil pre-coated with silica gel 60 F254 (Merck). Compounds were visualised with UV light (254 nm) or by chemical staining using a solution of $KMnO_4$ [$KMnO_4$ (10 g), K_2CO_3 (65 g), NaOH (1 N, 15 mL) in water (1 L)] followed by heating. Concentration in vacuo was performed at ~10 mbar at 40 °C unless otherwise stated. Melting points were measured on a Büchi B 545 melting point apparatus in open capillaries (ramp 3 °C/min) and are uncorrected. NMR spectra were measured by the NMR service at the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster on a Bruker Avance II 400 or an Agilent DD2 600 spectrometer. ^1H NMR chemical shifts are given relative to TMS and are referenced to the residual solvent peak as internal standard. Spectra of other nuclides as ^{13}C and ^{19}F are referenced according to the proton resonance of TMS as the primary reference for the unified chemical shift scale. ^1H NMR spectra are reported as follows: chemical shift (δ) in ppm (multiplicity, coupling constant J_{FH} and J_{HH} in Hz, number of protons, assignment of proton). ^{13}C NMR spectra are reported as follows: chemical shift (δ) in ppm (multiplicity, coupling constant J_{FC} in Hz, number of carbons, assignment of carbon). ^{19}F NMR spectra are reported as follows: chemical shift (δ) in ppm (multiplicity, coupling constant J_{FH} in Hz, number of fluorines, assignment of fluorine). Resonance multiplicities are abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet) or m (multiplet). Assignments of unknown compounds are based on COSY, HMBC and HSQC spectra. Mass spectra were measured by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität on a Triplequad TSQ 7000 (MS EI) or a Trace 1310 with ISQ 7000 Single Quad Mass Spectrometer (GC EI-MS).

4-Iodo-1,1′-biphenyl (1d)

The title compound was prepared according to a modified procedure from Yoon et al.[20] 4-Bromo-1,1′-biphenyl (1.2 g, 5.0 mmol, 1.0 equiv) was dissolved in dry tetrahydrofuran (15 mL). The mixture was cooled to –78 °C, *n*-butyllithium (4.7 mL, 1.6 M in hexane, 7.5 mmol, 1.5 equiv) was added dropwise and the reaction mixture was stirred for 1 h. Iodine (252 mg, 7.5 mmol, 1.5 equiv) was dissolved in dry tetrahydrofuran (10 mL) and was then added dropwise to the reaction mixture. The mixture was slowly warmed to room temperature and stirred for 24 h. The reaction was then quenched by addition of water (20 mL) and ethyl acetate (20 mL). The aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over $MgSO_4$ and filtered. The solvent was removed in vacuo and the crude residue was purified by column chromatography using *n*-pentane (100%) to afford 4-iodo-1,1′-biphenyl (**1d**) (1.20 g, 4.2 mmol, 86%) as a yellow solid.

Mp 105–106 °C; $R_f = 0.45$ (*n*-pentane).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (m, 2 H), 7.56 (m, 2 H), 7.45 (m, 2 H), 7.40–7.30 (m, 3 H).

MS (EI): *m*/*z* (%) = 280.0 (84%) $[M]^{+•}$, 153.1 (100) $[M - I]^{+•}$, 77.0 (56) $[M - C_6H_4I]^{+•}$.

The analytical data are in agreement with the literature.[21]

Dichloro(aryl)-λ^3-iodanes; General Procedure

Dichloro(aryl)-λ^3-iodanes were prepared according to a modified procedure from Zhang and Zhao.[15] The corresponding aryl iodide (1.0 mmol, 1.0 equiv) was dissolved in acetonitrile (4 mL). Then water (4 mL) and NaOCl (15% aq, 2 mL) were added slowly to the solution.

Dropwise addition of conc. HCl (2 mL) led to a yellow precipitate. The reaction mixture was stirred for the indicated time (see Table 1), then filtered and washed with *n*-pentane to obtain the desired dichloro(aryl)-λ^3-iodane.

Dichloro(phenyl)-λ^3-iodane (2a)

According to the general procedure using iodobenzene (110 µL, 1.0 mmol, 1.0 equiv), acetonitrile (4 mL), water (4 mL), NaOCl (2 mL) and conc. HCl (2 mL). The reaction mixture was stirred at ambient temperature for 30 min to afford, after work-up, dichloro(phenyl)-λ^3-iodane (**2a**) as a yellow solid (234 mg, 0.85 mmol, 85%).

Mp 80–82 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.19 (m, 2 H, H^2), 7.60 (m, 1 H, H^4), 7.48 (m, 2 H, H^3).*

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 134.0 (2 C, C^2), 132.2 (1 C, C^4), 131.7 (2 C, C^3), 125.5 (1 C, C^1).*

MS (EI): *m*/*z* (%) = 272.0 (1) [M – H$_2$]$^{\bullet+}$, 238.1 (8) [M – HCl]$^{\bullet+}$, 204.1 (100) [M – Cl$_2$]$^{\bullet+}$, 77.0 (92) [M – ICl$_2$]$^{\bullet+}$.

* In agreement with the literature.[22]

Dichloro(4-methoxyphenyl)-λ^3-iodane (2b)

According to the general procedure using 1-iodo-4-methoxybenzene (234 mg, 1.0 mmol, 1.0 equiv), acetonitrile (4 mL), water (4 mL), NaOCl (2 mL) and conc. HCl (2 mL) at 0 °C. The reaction mixture was directly filtered to afford dichloro(4-methoxyphenyl)-λ^3-iodane (**2b**) as a yellow solid (287 mg, 0.94 mmol, 94%).

Mp 68–70 °C.*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.06 (m, 2 H, H^2), 6.94 (m, 2 H, H^3), 3.87 (s, 3 H, H^5).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 162.6 (1 C, C^4), 136.3 (2 C, C^2), 117.3 (2 C, C^3), 114.4 (1 C, C^1), 55.9 (1 C, C^5).

MS (EI): *m*/*z* (%) = 302.0 (1) [M – H$_2$]$^{\bullet+}$, 268.1 (36) [M – HCl]$^{\bullet+}$, 234.0 (100) [M – Cl$_2$]$^{\bullet+}$, 107.0 (8) [M – ICl$_2$]$^{\bullet+}$.

* In agreement with the literature.[15]

Dichloro(*p*-tolyl)-λ^3-iodane (2c)

According to the general procedure using *p*-iodotoluene (219 mg, 1.0 mmol, 1.0 equiv), acetonitrile (4 mL), water (4 mL), NaOCl (2 mL) and conc. HCl (2 mL). The reaction mixture was stirred at ambient temperature for 30 min to afford, after work-up, dichloro(*p*-tolyl)-λ^3-iodane (**2c**) as a yellow solid (248 mg, 0.83 mmol, 83%).

Mp 65 °C (dec.).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.04 (m, 2 H, H^2), 7.27 (m, 2 H, H^3), 2.46 (s, 3 H, H^5).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 143.4 (1 C, C^4), 134.0 (2 C, C^2), 132.5 (2 C, C^3), 122.1 (1 C, C^1), 21.5 (1 C, C^5).

MS (EI): *m*/*z* (%) = 285.9 (18) [M – H$_2$]$^{\bullet+}$, 252.0 (34) [M – HCl]$^{\bullet+}$, 218.1 (100) [M – Cl$_2$]$^{\bullet+}$, 91.0 (75) [M – ICl$_2$]$^{\bullet+}$.

The analytical data are in agreement with the literature.[23]

Dichloro[(1,1′-biphenyl)-4-yl]-λ^3-iodane (2d)

According to the general procedure using 4-iodo-1,1′-biphenyl (280 mg, 1.0 mmol, 1.0 equiv), acetonitrile (4 mL), water (4 mL), NaOCl (2 mL) and conc. HCl (2 mL). The reaction mixture was stirred at ambient temperature for 30 min to afford, after work-up, dichloro[(1,1′-biphenyl)-4-yl]-λ^3-iodane (**2d**) as a yellow solid (308 mg, 0.88 mmol, 88%).

Mp 80–81 °C.*

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.23 (m, 2 H, H^2), 7.66 (m, 2 H, H^3), 7.57 (m, 2 H, H^6), 7.49 (m, 2 H, H^7), 7.43 (m, 1 H, H^8).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 145.7 (1 C, C^4), 138.78 (1 C, C^5), 134.4 (2 C, C^2), 130.3 (2 C, C^3), 129.3 (2 C, C^7), 129.0 (1 C, C^8), 127.6 (2 C, C^6), 123.6 (1 C, C^1).

MS (EI): *m*/*z* (%) = 347.9 (10) [M – H$_2$]$^{\bullet+}$, 314 (82) [M – HCl]$^{\bullet+}$, 280.0 (22) [M – Cl$_2$]$^{\bullet+}$, 153.2 (18) [M – ICl$_2$]$^{\bullet+}$.

* In agreement with the literature.[24]

Dichloro(4-chlorophenyl)-λ^3-iodane (2e)

According to the general procedure using 1-chloro-4-iodobenzene (953 mg, 4.0 mmol, 1.0 equiv), acetonitrile (8 mL), water (16 mL), NaOCl (8 mL) and conc. HCl (8 mL). The reaction mixture was stirred at ambient temperature for 30 min to afford, after work-up, dichloro(4-chlorophenyl)-λ^3-iodane (**2e**) as a yellow solid (1.02 g, 3.3 mmol, 83%).

Mp 100–102 °C (Lit.[15] 113–114 °C).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.11 (m, 2 H, H^2), 7.45 (m, 2 H, H^3).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 139.2 (1 C, C^4), 135.2 (2 C, C^2), 131.9 (2 C, C^3), 121.9 (1 C, C^1).

MS (EI): *m*/*z* (%) = 272.0 (1) [M – HCl]$^{\bullet+}$, 238.1 (100) [M – Cl$_2$]$^{\bullet+}$, 111.1 (71) [M – ICl$_2$]$^{\bullet+}$.

Dichloro(4-bromophenyl)-λ^3-iodane (2f)

According to the general procedure using 1-chloro-4-iodobenzene (1.13 g, 4.0 mmol, 1.0 equiv), acetonitrile (8 mL), water (16 mL), NaOCl (8 mL) and conc. HCl (8 mL). The reaction mixture was stirred at ambient temperature for 30 min to afford, after work-up, dichloro(4-bromophenyl)-λ^3-iodane (**2f**) as a yellow solid (1.34 g, 3.8 mmol, 94%).

Mp 112–114 °C (Lit.[15] 121–122 °C).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.04 (m, 2 H, H^2), 7.61 (m, 2 H, H^3).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 135.3 (2 C, C^2), 134.8 (2 C, C^3), 127.4 (1 C, C^4), 122.9 (1 C, C^1).

MS (EI): *m*/*z* (%) = 281.9 (100) [M – Cl$_2$]$^{\bullet+}$, 155.0 (60) [M – ICl$_2$]$^{\bullet+}$.

Ethyl 4-(Dichloro-λ^3-iodaneyl)benzoate (2g)

The general procedure was modified using ethyl 4-iodobenzoate (276 mg, 1.0 mmol, 1.0 equiv), acetonitrile (2 mL), water (4 mL), NaOCl (2 mL) and conc. HCl (2 mL). The reaction mixture was stirred at ambient temperature for 30 min to afford, after work-up, ethyl 4-(dichloro-λ^3-iodaneyl)benzoate (**2g**) as a yellow solid (335 mg, 0.97 mmol, 97%).

Mp 93–94 °C.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.27 (m, 2 H, H^2), 8.11 (m, 2 H, H^3), 4.42 (q, $^3J_{HH}$ =7.1 Hz, 2 H, H^6), 1.41 (t, $^3J_{HH}$ =7.1 Hz, 3 H, H^7).

^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): δ = 164.7 (1 C, C^5), 134.0 (1 C, C^4), 133.9 (2 C, C^2), 132.5 (2 C, C^3), 128.9 (1 C, C^1), 62.1 (1 C, C^6), 14.4 (1 C, C^7).

MS (EI): *m*/*z* (%) = 311.1 (1) [M – Cl]$^{\bullet+}$, 276.0 (52) [M – Cl$_2$]$^{\bullet+}$, 149.1 (8) [M – ICl$_2$]$^{\bullet+}$.

Dichloro[4-(trifluoromethyl)phenyl]-λ^3-iodane (2h)

According to the general procedure using 1-iodo-4-(trifluoromethyl)benzene (1.09 g, 4.0 mmol, 1.0 equiv), acetonitrile (16 mL), water (16 mL), NaOCl (8 mL) and conc. HCl (8 mL). The reaction mixture was stirred at ambient temperature for 2 h to afford, after work-up, dichloro[4-(trifluoromethyl)phenyl]-λ^3-iodane (**2h**) as a yellow solid (1.27 g, 3.7 mmol, 93%).

Mp 125–127 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (m, 2 H, H^2), 7.74 (m, 2 H, H^3).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 134.4 (2 C, C^2), 134.3 (q, $^2J_{FC}$ = 33.6 Hz, 1 C, C^4), 128.5 (q, $^3J_{FC}$ = 3.7 Hz, 2 C, C^3), 127.5 ($^5J_{FC}$ = 1.3 Hz, 1 C, C^1), 123.0 ($^1J_{FC}$ = 273.1 Hz, 1 C, C^5).

^{19}F NMR (564 MHz, $CDCl_3$): δ = –63.2 (s, 3 F, F^5).

MS (EI): m/z (%) = 307 (1) $[M - Cl]^{\bullet+}$, 272.1 (100) $[M - Cl_2]^{\bullet+}$, 145.0 (92) $[M - ICl_2]^{\bullet+}$.

Dichloro(4-nitrophenyl)-λ^3-iodane (2i)

Acording to the general procedure using 1-iodo-4-nitrobenzene (996 mg, 4.0 mmol, 1.0 equiv), acetonitrile (16 mL), water (16 mL), NaOCl (8 ml) and conc. HCl (8 mL). The reaction mixture was stirred at ambient temperature for 2 h to afford, after work-up, dichloro(4-nitrophenyl)-λ^3-iodane (**2i**) as a yellow solid (1.18 g, 3.7 mmol, 92%).

Mp 174–175 °C.*

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.43 (m, 2 H, H^2), 8.31 (m, 2 H, H^3).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 149.8 (1 C, C^4), 135.0 (2 C, C^2), 129.1 (1 C, C^1), 126.3 (2 C, C^3).

MS (EI): m/z (%) = 284 (1) $[M - Cl]^{\bullet+}$, 249.1 (100) $[M - Cl_2]^{\bullet+}$.

* In agreement with the literature.[15]

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Supporting Information

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