Stereoselective Chloro-Deboronation Reactions Induced by Substituted Pyridine–Iodine Chloride Complexes

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A novel class of charge-transfer complexes based on iodine chloride and substituted pyridines, which possess a number of interesting and unique structural features, can be employed to bring about a stereocontrolled chloro-deboronation of certain vinyl boronates to generate the (1Z)-alkenyl chlorides in good yields.

Introduction

An ongoing program in our research group has focused on the stereocontrolled synthesis of polyene natural products[1] which featured the total synthesis of the antibiotic and selective herbicide phthoxazolin A.[2] The strategy currently under development utilizes palladium-catalysed Heck coupling of the two-carbon building block, 4,4,6-trimethyl-2-vinyl-1,3,2-dioxaborinane (a vinyl boronate ester and vinyl dianion equivalent), to a number of electrophiles.[3] Conditions have been developed to bring about stereocontrolled iodo-deboronations of the coupled Heck products to generate either (*E*)- or (*Z*)-iodoalkenes, which in turn allow further coupling and therefore building of polyene chains. This transformation is performed by treatment of the boronate ester with ICl and NaOMe, with the order of reagent addition determining the stereochemical outcome of the reaction.[4,5]

To develop the potential and diversity of this strategy further substrates and reagents were examined. Having noted the presence of pyridine– and bipyridine–iodine chloride complexes in the literature,[6–8] and in the case of pyridine–iodine chloride, its successful application to the iodination of a number of aromatics,[7] it was envisaged that Py·ICl could be applied to iodo-deboronation reactions believing it would act as a cleaner and more electropositive source of ICl to bring about the conversion of sensitive substrates. Recently reported preliminary studies[5] involving pyridine–iodine chloride showed that for certain boronates, the complex could be used to give direct conversion to the (*Z*)-alkene without the need for further addition of base (NaOMe). However, there was a change in regioselectivity which resulted in the favoured formation of the (*Z*)-1-chloroalkene. Thus this reagent allows the stereoselective chloro-deboronation of certain vinyl boronate esters.

In this paper we report on the synthesis and novel structural features of a number of substituted pyridine–iodine chloride complexes, and investigate how the substituents on the pyridine ring affect the selectivity of the chloro-deboronation vs. iodo-deboronation reaction.

Results and Discussion

Synthesis and Structural Characterisation of the Complexes

The different pyridine–iodine chloride complexes were prepared by stirring equimolar quantities of each pyridine analogue in DCM with iodine chloride before the addition of hexane, which resulted in precipitation of the complexes as yellow solids. A slow recrystallisation method afforded yellow crystalline materials with characterisations, which were identical to the powdered form but produced single crystals suitable for crystallographic studies to be performed. Samples were prepared from 3-bromopyridine (**1**), pyridine (**2**), 2,2′-bipyridine (**3**), 2,6-lutidine (**4**), 2,4,6-collidine (**5**) and dimethylaminopyridine (**6**) according to Equation (1), with yields shown in Table 1. The structures of pyridine–iodine chloride complexes **8** and **11**–**13** have been determined, and that of **10**[6c] redetermined at low temperature by single-crystal X-ray diffraction; major structural parameters are summarised in Table 2.

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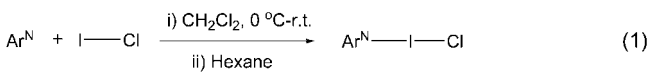


1 3-Bromopyridine **7**
2 Pyridine
3 2,2-Bipyridine
4 2,6-Lutidine
5 2,4,6-Collidine
6 DMAP

8 3-Bromopyridine-ICl
9 Pyridine-ICl
10 2,2-Bipyridine-ICl
11 2,6-Lutidine-ICl
12 2,4,6-Collidine-ICl
13 DMAP-ICl

Table 1. Yields for each pyridine–iodine chloridecomplex produced as shown in Equation (1).

Entry	Complex	Yield [%]
1	**8**	73
2	**9**[a]	90
3	**10**[a]	94
4	**11**	82
5	**12**	75
6	**13**	87

[a] See ref.[6]

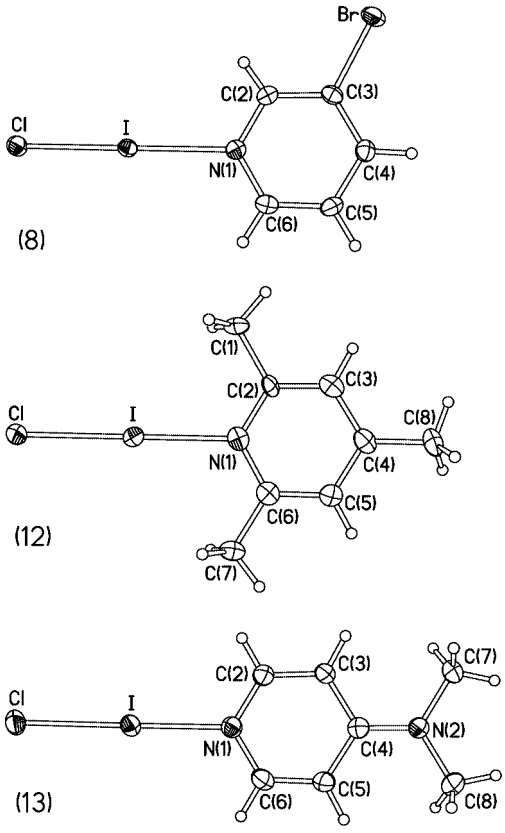


Figure 1. Molecular structures of ICl complexes of 3-bromopyridine (**8**), 2,4,6-collidine (**12**) and 4-(dimethylamino)pyridine (**13**). Thermal ellipsoids are drawn at the 50% probability level.

The structures of **8**, **10**, **12** and **13** (Figure 1 and Figure 2) are typical for charge-transfer complexes between *n* donors and dihalogen or interhalogen molecules.[11] The N–I–Cl moiety is linear and nearly coplanar with the (coordinated) pyridine ring. The structure of **10** does not differ substantially from that at room temperature.[6c] Whilst the uncoordinated bipyridine molecule adopts a planar *trans* conformation in the crystal,[12] the bipyridine moiety in **10** is twisted by 92.0(2)° with respect to the former. In the chemically (but not crystallographically) isostructural 2,2-bipyridine–bis(iodine bromide) complex the twist angle is 127.1°, i.e. the conformation is closer to *cis*, due to intramolecular halogen–halogen attractions.[6c] Our study confirms the earlier observation that *one* N–I–Cl moiety in **10** is slightly nonlinear.

The N–I bond is longer than the sum of covalent radii (2.03 Å) but much shorter than the sum of van der Waals radii[13] (3.67 Å). At present, there is no structurally characterised compound with a N(sp^2)–I bond to a strictly monocoordinate iodine atom. This is apparently the case in solid *N*-iodosuccinimide[14] [N–I 2.059(6) Å] and diiodoformamide[15] [N–I 2.041(8) and 2.100(7) Å], but in fact, both structures contain short intermolecular I···O contacts [2.580(6) and 2.565(7)–3.130(8) Å, respectively], which can be regarded as secondary donor–acceptor interactions. Comparison with these two structures highlights the shortening of N–I bonds in the complexes **8**–**13** (see Table 2). Similarly, the I–Cl bonds in the complexes are much longer than that in the ICl molecule in the gas phase (2.321 Å), which is practically equal to the sum of covalent radii.[16] Indeed, the former are even longer than in the crystal structures of ICl[17] [2.353(2) and 2.450(2) Å in the α-phase,[17a] 2.35(1) and 2.44(1) Å in the β-phase[17b]] which are characterised by strong intermolecular I···I and I···Cl interactions and hence by reduced order of the intramolecular I–Cl

Table 2. Bond lengths [Å] and angles [°] for the pyridine–iodine chloride complexes.

Compound	I–Cl	I–N	N–C ave.	N–I–Cl	C–N–C	φ[a]
8	2.4734(7)	2.344(2)	1.341(3)	178.43(5)	120.0(2)	5.2
10	2.4974(7)	2.321(2)	1.344(3)	179.41(5)	119.8(2)	4.5
	2.4878(9)	2.337(2)		175.33(5)	119.6(2)	6.6
10[b]	2.479(4)	2.336(7)	1.36(1)	179.6(3)	119.8(8)	5.5
	2.477(11)	2.344(7)		176.2(2)	118.8(9)	5.8
11	2.5421(5)	2.300(1)	1.358(2)	–	120.9(1)	7.1
12	2.531(2)	2.294(5)	1.367(8)	179.05(14)	119.8(5)	1.5
13	2.5615(7)	2.246(2)	1.351(3)	179.24(5)	117.9(2)	0.4
Py·ICl[c]	2.510(4)	2.29(1)	1.33(2)	178.7(3)	120(1)	0.1
L·ICl[d]	2.44(1)	2.34(3)	1.33(5)	177(5)	–	1.7
L′·ICl[e]	2.446(3)	2.432(8)	1.36(2)	179.9(4)	121.2(8)	2.1

[a] φ is the angle between the N–I bond and the heterocycle plane. [b] Ref.[6c] [c] Ref.[8] [d] Ref.[9], L = (pentamethylene)tetrazole. [e] Ref.[10], L′ = 2-chloroquinoline.

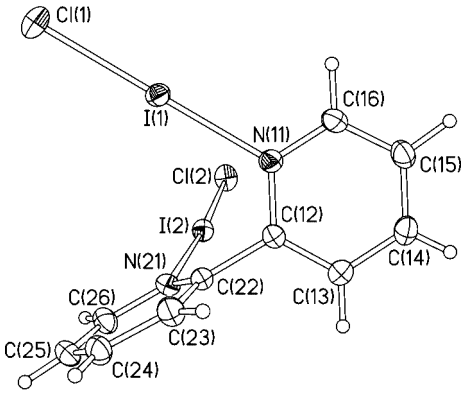


Figure 2. Molecular structure of the ICl complex of 2,2′-bipyridine **10**.

bonds. The N–I–Cl interaction can be described as a three-centre four-electron bond, involving one bonding and one nonbonding electron pair.[18] The C–N–C angles in all complexes are significantly wider than in uncoordinated pyridine[19] [116.6(2)°] or bipyridine[12] (117.4°).

The amino atom N(2) in **13** has a planar-trigonal geometry, its plane is coplanar with the pyridine ring, as in pure 4-(dimethylamino)pyridine.[20] The molecule of **12** is disordered by a 120° rotation in its own plane, the minor position of the ICl group (I′Cl′) nearly overlapping with the major positions of the ICl group of the adjacent molecule, related by the *a* translation (Figure 3). The occupancy of the minor position is estimated as only 3%, and its geometry is imprecise, hence all discussion refers to the major position only.

The structure of **11** (Figure 4 and Figure 5) is basically different: the structure comprises discrete bis(2,6-lutidino) iodinium cations and ICl_2^- anions. In either ion, the central iodine atom lies at a crystallographic inversion centre hence the N–I–N and Cl–I–Cl bond angles equal exactly 180°. The cation is not quite planar: The N–I bond is tilted out of the pyridine plane by 7.1°, thus the two pyridine rings are parallel but not coplanar, with an interplanar separation of 0.60 Å. The N–I bond lengths are comparable with those in the cations of bis(pyridine)iodonium [2.259(3) Å][21] and bis(2,4,6-collidine)iodonium [2.29(1) and 2.30(1) Å],[22] as well as in the complexes with N–I–Cl coordination. Likewise, the I–Cl bond length in the anion of **11** lies in the

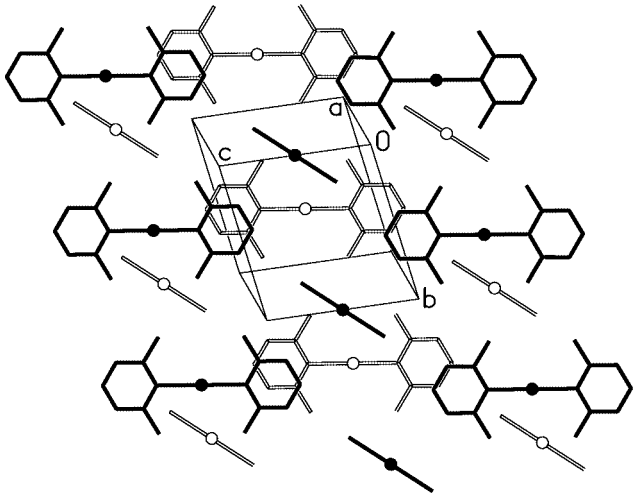


Figure 5. Crystal structure of **11**, showing two successive layers of ions, parallel to the (20–1) plane.

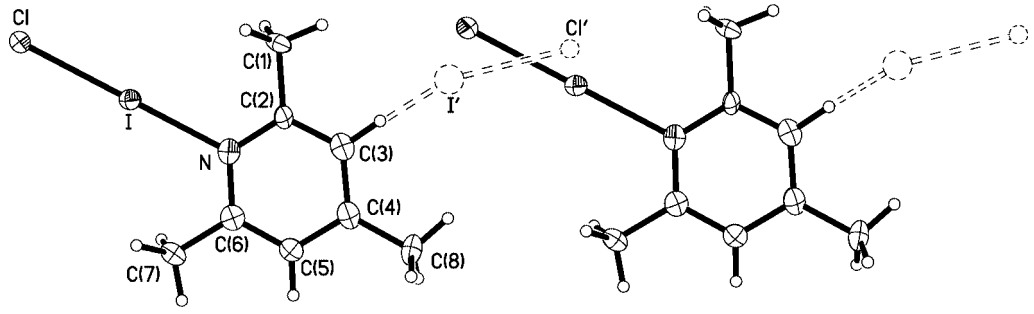


Figure 3. Disorder in the structure of the ICl complex of 2,4,6-collidine (**12**).

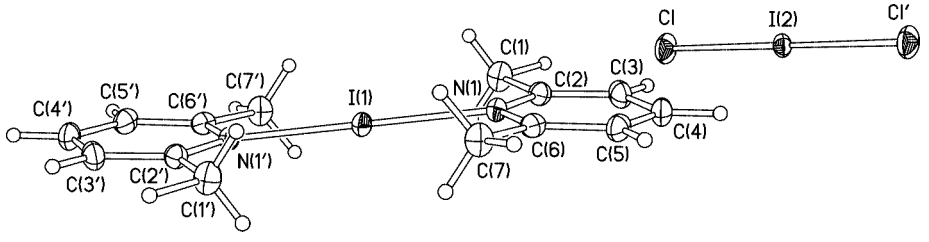
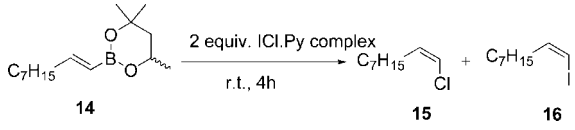


Figure 4. Molecular structure of the complex **11**. Primed atoms are generated by inversion centres.

usual range for such anions (2.53 to 2.57 Å, although distances of up to 2.69 Å also occur)[23] and in fact is very similar to that in N–I–Cl moieties of other complexes. None of the structures contains any intermolecular halogen–halogen contact shorter than the sum of van der Waals radii.[13]

Application of Py-ICl Complexes for Stereoselective Chloro-Deboronations

Each complex was used to carry out the deboronation of 4,4,6-trimethyl-2-non-1-enyl-1,3,2-dioxaborinane (**14**), which was prepared from 1-nonyne by a catechol–hydroboration, transesterification sequence. As outlined earlier, direct conversion to the (*Z*)-alkenyl products was expected on the basis of initial experiments with pyridine–iodine chloride complex,[5] i.e. following an initial addition of ICl across the double bond followed by elimination, assisted by pyridine. The important question was what would be the effect of the different pyridine–iodine chloride complexes upon the overall conversion and the chemoselectivity. The procedure followed to examine this process involved stirring the boronate and the complex in dichloromethane at room temperature, using two equivalents of the pyridine–iodine chloride complex [except in the case of 2,2′-Bipy·$(ICl)_2$ (**10**), where one equivalent was used]. This was required in order to achieve (in most cases) complete consumption of the starting boronate **14**. The results for the deboronation reaction described by Equation (2) are shown in Table 3.



14 **15** **16** (2)

Table 3. Yields and product distributions for the reaction of different pyridine–iodine chloride complexes with alkenylboronate ester **14**.

Entry	Reagent(s)		Product ratio[a] (% isolated yield[b]) **15**	**16**
1	ICl/NaOMe	0	63 (45)	37
2	8	0	84	16
3	9	0	95 (48)	5
4	10	0	94	6
5	11	0	100 (69)	0
6	12	0	100 (60)	0
7	13	38	39	23
8	Py·ICl/BF_3/NaOMe	0	66	34

[a] Determined by ^{1}H NMR of the crude product. [b] Isolated yield after purification by silica gel chromatography.

For comparison, an iodo-deboronation reaction was performed under standard conditions[4] involving treatment with ICl alone, followed by NaOMe (Entry 1, Table 3). As can be observed from Table 3, this resulted in a mixture of (*Z*)-1-iodo-1-nonene and (*Z*)-1-chloro-1-nonene in a ratio of 37:63, respectively, i.e. favouring the alkenyl chloride (N.B.: increased temperatures favoured the iodide[5]) and giving a moderate isolated yield of 45%. This reaction was then performed and compared with each of the pyridine–iodine chloride complexes.

With the exception of DMAP·ICl (**13**, Entry 7, Table 3), all of the pyridine–iodine chloride complexes resulted in complete consumption of the alkenyl boronate **14** substrate, and there was a concommittent increase in the chemoselectivity for formation of the (*Z*)-chloride compared to the ICl/NaOMe system (Entry 1, Table 3). The product ratio obtained for each complex is, to a large degree, dependent on the structure of the pyridine–iodine chloride complex used, which clearly shows that the pyridine plays a significant role in the reaction mechanism, and hence in determining the regioselectivity of the ICl addition across the double bond which ultimately controls the chemoselectivity of the reaction. It is interesting to note that the chemoselectivity for formation of chloride **15** increases through Entries 2–6 (Table 3), with the increasing electron-donating ability of the substituents on the pyridine ring, i.e. the more electron-rich pyridine favours addition of chloride ion to the boron-substituted end of the alkene. If one examines the different crystal structures for each of the different pyridine–iodine chloride complexes (Figure 1, Figure 2, Figure 3 and Figure 4) one can observe stronger N–I coordination, shown by a shorter N–I bond length. The shorter N–I bond lengths also result in concommittent increases in the I–Cl bond length (see Table 2). Indeed, the use of both the 2,6-lutidine–ICl (**11**) and 2,4,6-collidine–ICl (**12**) complexes (Entries 5 and 6, respectively, Table 3) gave complete selectivity and high yields for the (*Z*)-chloride **15**. Both of these complexes exhibit the shortest N–I bond length and the weakest chloride coordination, with the 2,6-lutidine complex actually dissociating into a Py^N–I–^NPy cation/Cl–I–Cl anion system. Given this seeming trend in reactivity vs. N–I and I–Cl distances, the use of DMAP·ICl (**13**) complex (Entry 7, Table 3) gave surprising results considering it exhibits the shortest N–I bond length (see Table 2); use of this reagent resulted in both low conversion of the starting material and very poor selectivity for formation of the (*Z*)-chloride, i.e. in a ratio 39:23.

In order to further probe the mechanism of the iodo/chloro-deboronation reaction and to identify why two equivalents of each complex were required for complete conversion of the boronate, the reaction was performed with a single equivalent of 2,2′-Bipy·$(ICl)_2$ (**10**) complex (Entry 4, Table 3). It was anticipated that comparison of the results from this reaction would indicate whether the two equivalents of pyridine–iodine chloride complex required for complete consumption of the starting material worked in tandem, since the 2,2′-Bipy·$(ICl)_2$ (**10**) complex clearly provides the correct molar equivalents required for complete boronate consumption. However, the bipyridyl structure also effectively locks the two ICl equivalents into close proximity yet prevents potential intermolecular interactions between pyridine rings. The reaction of 2,2′-Bipy·$(ICl)_2$ (**10**) complex (Entry 5, Table 3) gave virtually the same results as with pyridine–iodine chloride (**9**) com-

plex (Entry 3, Table 3), showing that the predefined orientation of the bipyridine system has no effect on the conversion or selectivity of the reaction.

After studying the results obtained for the effect of the complexes on the chloro-deboronation vs. iodo-deboronation reaction, a final experiment was undertaken to probe further the role of the pyridine (Entry 8, Table 3). The study was performed by reacting boronate **14** with one equivalent of Py·ICl in the presence of borontrifluoride–diethyl ether, prior to the addition of sodium methoxide to effect the final elimination step. It was envisaged that the Lewis acid would decomplex the ICl through coordination to the pyridine, and therefore prevent the pyridine from taking further part in the iodo-deboronation or chloro-deboronation reaction. Under these conditions, it was found that complete conversion of the substrate occurred to give a mixture of the (*Z*)-chloro- and iodoalkenes **15** and **16** in a 66:34 ratio, respectively, i.e. almost identical to that obtained when ICl alone was used (Entry 1, Table 3). This demonstrates that the Py·ICl/BF_3 system acts effectively as a "clean" source of ICl, i.e. the shelf-stable pyridine–iodine chloride complex can be used to regenerate ICl in situ by decomplexation of the pyridine. However, this result also adds further support to the idea that the pyridine plays a crucial role in the addition of ICl to the alkene, which in turn controls selectivity of the chloro- vs. iodo-deboronation.

Speculation on the mechanism of the deboronation reaction using ICl has been carried out in some detail,[5] however, the results presented here show an even more complex situation than first envisaged, but one which broadly follows our previous proposal.[3] The present results suggest that the mechanism operating is as outlined in Scheme 1.

Hence, the more hindered and generally electron-rich pyridines that have shorter N–I bonds and longer I–Cl bonds are the more reactive systems, resulting in them behaving as reasonable I^+ sources. Hence, with the pyridine–iodine chloride complexes in general, alkenylboronates react initially to form the pyridine-stabilised iodonium ion **18**, which is more stabilised than with ICl alone.[5] The exception is for the DMAP·ICl complex **13**, which due to the much greater stabilisation of the positively-charged iodine complex (Figure 6), only reacts very sluggishly, i.e. it behaves as a poor source of I^+. Once formed, the resulting iodonium complexes **18** either react directly with chloride ion to give **23** (more favoured with the less-hindered pyridines), or the complex **18** undergoes boronate complexation by chloride ion to give **19**. It is expected that chloride ion complexation is more favoured, especially with the more hindered pyridine systems, however, the competing coordination of the pyridine to boron to give pyridine–boronate complex analogues of intermediates **21** and **24** can not be ruled out. In the case of boronate–chloride complex **19**, the complex rapidly undergoes *anti* elimination to give the (*Z*)-chloride **22**, whereas, its regioisomer **23** eliminates to give the (*Z*)-iodide **25**.

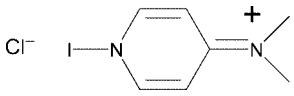


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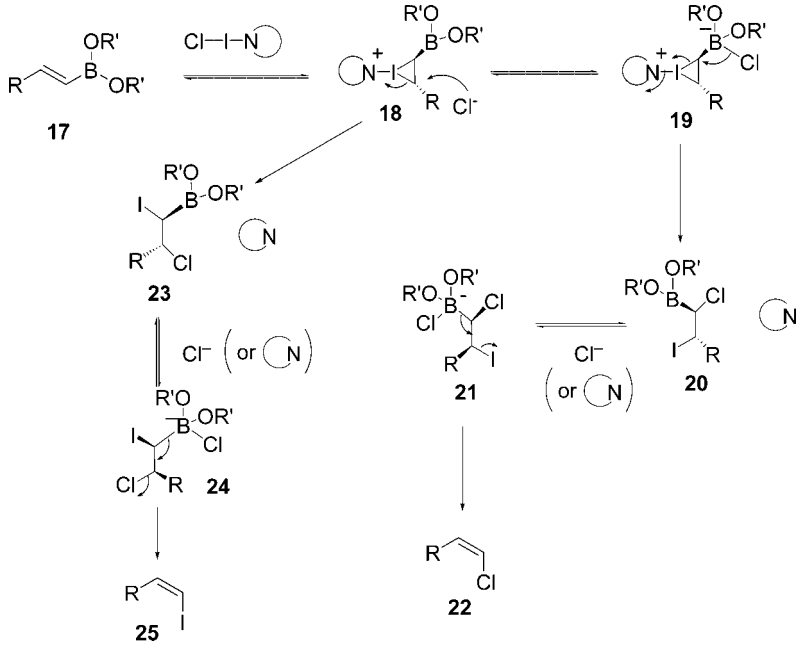
Figure 6. DMAP-stabilised ICl complex.

Hence, the overall chemoselectivity for the iodo- vs. chloro-deboronation is controlled by complexes **18** vs. **19**. More hindered pyridines will favour chloride ion coordinating boron to derive **19**, and hence, preferentially forming the alkenyl chloride **22**. In contrast, the less hindered pyridines or no pyridine tend to favour more participation of



Scheme 1. Proposed mechanism for the chloro- vs. iodo-deboronation reaction using Py·ICl complexes.

chloride ion in assisting with iodonium stabilisation and therefore direct attack on **18** to give **23** and hence resulting in an increased likelihood of producing the vinyl iodide **25**.

Conclusions

A simple and straightforward procedure allows the preparation of a number of pyridine-based ICl charge transfer complexes. Crystallographic studies have identified the interesting and unique structures of some of these complexes, particularly those derived from 2,6-lutidine and 2,4,6-collidine. These more hindered complexes can be used to produce a chemoselective preparation of (*Z*)-alkenyl chlorides by a chloro-deboronation reaction from alkenylboronate esters. Alkenyl chlorides and their derivatives have a number of synthetic applications and can be utilized to further diversify our strategy towards the synthesis of polyene natural products. Although chlorides are less reactive than iodides and bromides under standard palladium coupling conditions, the coupling of vinyl chlorides has been demonstrated in palladium catalysed Negishi couplings with a range of aryl and alkylzinc reagents.[24,25] In addition nickel-phosphane-catalysed systems allow the Kumada–Corriu coupling of alkenyl chlorides with Grignard reagents.[26]

Experimental Section

General: All ^{1}H and ^{13}C NMR were recorded with either a Varian Mercury-400, Bruker Avance-400 or Varian Inova-500 spectrometers. ^{11}B NMR were recorded with the Bruker Avance-400 at a frequency of 128 MHz. Chemical shifts are expressed as parts per million (ppm) downfield from the internal standard TMS. EI mass spectrometry was performed with a Micromass Autospec. All IR spectra were recorded with a Perkin–Elmer 298 spectrometer employing NaCl plates or KBr discs. Elemental analysis was performed using an Exeter Analytical E-440 Elemental Analyser. Melting points were determined using an electrothermal melting point apparatus. Column chromatography was performed on Davisil Silica gel, 60 mesh. TLC was performed on Polygram SIL G/UV_{254} plastic-backed silica gel plates with visualisation achieved using a UV lamp, or by staining with $KMnO_4$. All glassware was oven-dried (130 °C) before use and cooled under a positive pressure of argon. Dry solvents were dried by distillation from CaH_2 (CH_2Cl_2) or sodium-benzophenone ketyl (THF). All reactions were performed at room temperature unless otherwise stated. All other materials were purchased directly from either Aldrich or Lancaster and used without further purification, unless stated otherwise.

General Procedure for the Preparation of Substituted Pyridine–Iodine Chloride Complexes: The appropriate pyridine (30 mmol) was dissolved with stirring under argon in freshly distilled CH_2Cl_2 (10 mL) before cooling to 0 °C. Over 30 minutes the dropwise addition of ICl (1.0 M soln., 30 mL, 30 mmol) was performed before warming to room temp. and stirring for a further 30 minutes. Hexane was added, and the product precipitated out of solution allowing filtration and isolation of the yellow solid. Crystallisation was performed from CH_2Cl_2/hexane.

3-Bromopyridine–Iodine Chloride Complex 8: Yield: 73%. M.p. 95–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (ddd, J = 8.4, 5.2, 0.4 Hz, 1 H, Ar-H), 8.11 (ddd, J = 8.0, 2.4 Hz, 1.6 Hz, 1 H, Ar-H), 8.58 (dd, J = 5.2 Hz, 1.2 Hz, 1 H, Ar-H) and 8.73 (dd, J = 2.0 Hz, 0.4 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.1 (Ar-C), 127.6 (Ar-CH), 142.7 (Ar-CH), 146.8 (Ar-CH) and 149.8 (Ar-CH) ppm. IR (KBr disc): $\tilde{\nu}$ = 2961, 1610, 1538, 1450, 1411, 1260, 1094, 1021 and 800 cm^{-1}. $C_5H_4NBrClI$ (320.35): calcd. C 18.75, H 1.26, N 4.37; found C 18.85, H 1.24, N 4.31.

Pyridine–Iodine Chloride Complex 9: Yield 90%. All spectroscopic and analytical data was identical to that reported in the literature.[27]

2,2-Bipyridine–Diiodine Chloride Complex 10:[6b,6c] Yield: 94%. M.p. 130–131 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (t, J = 6.0 Hz, 2 H, H-5), 7.80 (d, J = 8.0 Hz, 2 H, H-3), 8.17 (t, J = 7.5 Hz, 2 H, H-4) and 8.95 (d, J = 5.0 Hz, 2 H, H-6) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 126.2 (2 Ar-CH), 127.1 (2 Ar-CH), 140.6 (2 Ar-CH), 150.2 (2 Ar-CH) and 154.0 (2 Ar-C) ppm. IR (KBr disc): $\tilde{\nu}$ = 3092, 3071, 1654, 1637, 1589, 1490, 1463, 1297, 1074, 1007 and 794 cm^{-1}. $C_{10}H_8Cl_2I_2N_2$ (480.90): calcd. C 24.98, H 1.68, N 5.83; found C 25.28, H 1.71, N 5.84.

2,6-Lutidine Complex 11: Yield: 82%. M.p. 103–105 °C (ref.[28] 112–113 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.81 (s, 6 H, 2 × CH_3), 7.17 (d, J = 8.0 Hz, 2 H, Ar-H) and 7.66 (t, J = 8.0 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 29.1 (CH_3), 123.6 (2 Ar-CH), 140.0 (Ar-CH) and 158.3 (Ar-C) ppm. IR (KBr disc): $\tilde{\nu}$ = 2974, 1601, 1577, 1482, 1465, 1377, 1161 and 792 cm^{-1}. $C_{14}H_{18}Cl_2I_2N_2$ (269.51): calcd. C 31.20, H 3.37, N 5.20; found C 31.21, H 3.38, N 5.09.

2,4,6-Collidine–Iodine Chloride Complex 12: Yield: 75%. M.p. 110–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 2.77 (s, 6 H, 2 × CH_3) and 7.00 (s, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1 (2 CH_3), 27.5 (CH_3), 124.4 (Ar-CH) and 156.9 (Ar-C) ppm. IR (KBr disc): $\tilde{\nu}$ = 2962, 1613, 1560, 1457, 1431, 1378, 1313, 999 and 849 cm^{-1}. $C_8H_{11}ClIN$ (283.54): calcd. C 33.89, H 3.91, N 4.94; found C 33.69, H 3.90, N 4.94.

DMAP–Iodine Chloride Complex 13: Yield: 87%. M.p. 140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.10 (s, 6 H, 2 × CH_3), 6.44 (d, J = 7.2 Hz, 2 H, Ar-H) and 8.08 (d, J = 7.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.8 (CH_3), 108.6 (2 Ar-CH), 147.9 (2 Ar-CH) and 155.3 (Ar-C) ppm. IR (KBr disc): $\tilde{\nu}$ = 2918, 1607, 1527, 1508, 1458, 1389, 1335, 1215, 1005 and 811 cm^{-1}. $C_7H_{10}N_2ClI$ (284.52): calcd. C 29.55, H 3.55, N 9.84; found C 29.58, H 3.53, N 9.75.

4,4,6-Trimethyl-2-non-1-enyl-1,3,2-dioxaborinane (14): Catecholborane (0.86 mL, 8.05 mmol) was added dropwise to 1-nonyne (1.32 mL, 8.05 mmol) with stirring under argon at 0 °C. The reaction was then heated to 70 °C for 2 h before cooling to room temp. and diluting with CH_2Cl_2 (8 mL) allowing the addition of 2-methyl-2,4-pentanediol (1.03 mL, 8.05 mmol) and satd. aq. $NaHCO_3$ (6 mL). After vigorous stirring at room temperature for 2 h the two phases were separated and the organic layer washed with satd. aq. $NaHCO_3$ (6 mL) and water (6 mL) before drying ($MgSO_4$) and solvent removal to yield the product as a yellow oil. Flash silica gel column chromatography (petroleum ether/EtOAc, 10:1) furnished **14** as a clear oil (1.569 g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.0 Hz, 3 H, alkyl CH_3), 1.26–1.29 (m, 17 H, 3 × CH_3, 4 × CH_2), 1.38–1.41 (m, 2 H, CH_2), 1.50 (t, J = 11.5 Hz, 1 H, boronate CH_2), 1.77 (dd, J = 13.5 Hz, 2.5 Hz, 1 H, boronate CH_2), 2.10 (q, J = 7.0 Hz, 2 H, CH_2–CH=), 4.17–4.23 (m, 1 H boronate O–CHRCH_3), 5.33 (d, J = 17.5 Hz, 1 H, =CHB) and 6.53 (dt, J = 18.0 Hz, 6.5 Hz, 1 H, CH_2CH=) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 25.7 ppm. ^{13}C NMR (126 MHz,

$CDCl_3$): δ = 14.4 (alkyl CH_3), 22.9 (CH_2), 23.5 (boronate CH_3), 28.4 (CH_2), 28.7 (boronate CH_3), 29.5 (CH_2), 29.4 (CH_2), 31.5 (boronate CH_3), 32.1 (CH_2), 35.8 (CH_2), 46.2 (boronate CH_2), 64.8 ($OCHRCH_3$), 70.8 [$OC(CH_3)_2$] and 151.5 (CH_2CH=) ppm. MS (EI): m/z = 252.2259 (M^+, $C_{15}H_{29}BO_2^+$ calcd. 252.2261), 237, 168, 153, 83, 55 and 43 (100). IR (neat): $\tilde{\nu}$ = 2972, 2925, 2855, 1639, 1457, 1413, 1387, 1368 and 1302 cm^{-1}.

Synthesis of (*Z*)-1-Chloro-1-nonene (15) Using ICl/NaOMe: Boronate **14** (2.0 g, 7.94 mmol) was added to a solution of ICl (1.55 g, 9.52 mmol) in THF (50 mL) with stirring under argon and in the absence of light. The reaction was stirred for 4 h before the addition of NaOMe (19.04 mL, 0.5 M solution in MeOH, 9.52 mmol). After 30 minutes the reaction was diluted with Et_2O (150 mL) before washing with 5% $Na_2S_2O_5$ (2×100 mL), water (2×100 mL) and brine (2×100 mL). Drying ($MgSO_4$) and solvent removal yielded the crude product as a yellow oil. Flash silica gel column chromatography (hexane as eluent) furnished a clear oil (0.896 g, 45%). Characterisation data for both (*Z*)-1-chloro-1-nonene (**15**) and (*Z*)-1-iodo-1-nonene (**16**) were consistent with the literature.[29]

General Procedure for the Synthesis of (*Z*)-1-Chloro-1-nonene 15 Using a Py·ICl Complex: The Py·ICl variant (3.97 mmol, 1.98 for 2,2-Bipy·$(ICl)_2$) was dissolved in CH_2Cl_2 (15 mL) with stirring under argon in the absence of light before the addition of the boronate **5** (0.50 g, 1.98 mmol). After 4 h the reaction was diluted with Et_2O (35 mL) and washed with 5% $Na_2S_2O_5$ (50 mL), water (50 mL) and brine (50 mL). Drying ($MgSO_4$) and solvent removal yielded the crude product. Purification was performed by flash silica gel column chromatography (hexane as eluent). Characterisation data for both 1-(*Z*)-chlorononon-1-ene (**15**) and 1-(*Z*)-iodonon-1-ene (**16**) were consistent with the literature.[29]

Synthesis of (*Z*)-1-Chloro-1-nonene (15) Using Py·ICl/BF_3/NaOMe: Py·ICl (0.77 g, 3.17 mmol) was dissolved with stirring under argon in dry CH_2Cl_2 (20 mL) before the addition of BF_3·Et_2O (0.38 mL, 3.01 mmol,) followed by boronate **14** (0.8 g, 3.17 mmol) and the reaction stirred in the absence of light for 4 h. NaOMe (25.4 mL, 0.5 M solution in methanol, 12.7 mmol) was added and the reaction stirred for a further 30 minutes. Dilution of the reaction with Et_2O (100 mL) allowed washing with 5% $Na_2S_2O_5$ (100 mL), water (100 mL) and brine (100 mL). Drying ($MgSO_4$) and solvent removal yielded the crude product as a yellow oil, its constituents were determined by ^1H NMR.

X-ray Crystallography: X-ray diffraction data for **8** and **10**–**12** were collected with Bruker 3-circle diffractometer with a ProteumM APEX CCD area detector, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) from a 60-W microfocus Bede Microsource® with glass polycapillary optics. For **13**, a SMART 6000 CCD area detector and a sealed Mo-anode tube were used. The low temperature of the crystals was maintained with Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. Full sphere of the reciprocal space for $2\theta \leq 60°$ (**8**, **10**, **12**) or $2\theta \leq 61°$ (**11**, **13**) was covered by three series of 0.3° ω scans. Reflection intensities were corrected for absorption by numerical integration based on crystal face-indexing. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data, using SHELXTL[30] software. All non-H atoms were refined in anisotropic approximation. All H atoms were refined in isotropic approximation (**8**, **10**, **11**) or treated in riding model (**12**, **13**). The absolute structure of **12** was determined from anomalous scattering of I and Cl; Flack parameter[31] 0.03(4). Crystal data and experimental details are listed in Table 4. CCDC-253719 to -253723 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 4. Crystal data and refinement parameters for the different pyridine–iodine chloride complexes.

Compound	**8**	**10**[a]	**11**	**12**	**13**
Formula	$C_5H_4BrClIN$	$C_{10}H_8Cl_2I_2N_2$	$C_{14}H_{18}IN_2^+ \cdot Cl_2I^-$	$C_8H_{11}ClIN$	$C_7H_{10}ClIN_2$
Formula mass	320.35	480.88	539.00	283.53	284.52
T [K]	120	120	120	120	120
Crystal system	monoclinic	monoclinic	triclinic	hexagonal	monoclinic
Space group	*C*2/*c* (# 15)	*P*2$_1$/*n* (# 14)	*P1*(# 2)	*P*6$_1$ (# 169)	*P*2$_1$/*c* (# 14)
a [Å]	21.337(3)	10.073(1)	7.307(1)	9.1915(12)	4.4864(9)
b [Å]	4.174(1)	12.141(7)	8.253(1r)	9.1915(12)	7.4207(7)
c [Å]	18.384(3)	11.859(1)	8.537(1)	21.005(3)	15.867(2)
α [°]	90	90	98.46(1)	90	90
β [°]	94.38(1)	101.67(1)	103.50(1)	90	105.19(2)
γ [°]	90	90	111.92(1)	120	90
V [Å^3]	1632.5(5)	1420.3(8)	448.5(1)	1536.8(4)	964.3(2)
Z	8	4	1	6	4
$\rho_{calcd.}$ [g·cm^{-3}]	2.607	2.249	1.996	1.838	1.960
μ [mm^{-1}]	9.06	4.78	3.80	3.33	3.54
Total reflections	9303	19301	5502	18238	16640
Unique reflections	2372	4128	2699	3120	2813
Reflections $I > 2\sigma(I)$	2054	3867	2498	3015	2541
Parameters	98	177	130	111	104
Transmission range	0.170–0.818	0.152–0.760	0.486–0.677	0.535–0.911	0.236–0.896
$R_{int.}$[b]	0.082, 0.054	0.135, 0.094	0.040, 0.014	0.088, 0.086	0.102, 0.025
R [F, $I > 2\sigma(I)$]	0.020	0.024	0.016	0.045	0.022
wR (F^2, all data)	0.039	0.062	0.039	0.101	0.056
$\Delta\rho_{min.,max.}$ [e·Å^{-3}]	0.86, –0.69	1.19, –0.73	0.38, –0.66	1.41, –1.33	1.54, –0.66

[a] cf. findings for room temperature[6c] a = 10.163(5), b = 12.427(7), c = 11.833(7) Å, β = 101.76(3)°, V = 1427.8(14) Å^3. [b] Before and after the absorption correction.

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