Conversion of haloform to carbonate by iridium N-heterocyclic carbene complexes and silver(I) oxide


Published in:
Dalton Transactions

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

Publisher rights
© The Royal Society of Chemistry 2019. This work is made available online in accordance with the publisher's policies. Please refer to any applicable terms of use of the publisher.

General rights
Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Open Access
This research has been made openly available by Queen's academics and its Open Research team. We would love to hear how access to this research benefits you. – Share your feedback with us: http://go.qub.ac.uk/oa-feedback

Download date: 15. Sep. 2023
Conversion of haloform to carbonate by iridium N-heterocyclic carbene complexes and silver(I) oxide

Andrew C. Marr,a Patrick J. Morgan,a Graham C. Saunders *b and Hayden P. Thomasb

The reaction between haloform, the complexes [Cp*IrCl2(κC–MeNC3H2NCH2Ar)] (Ar = C6H3F2–2,6, C6H3F–2–Cl–6, C6H3Me2–2,6) and silver(I) oxide proceeded by carbon–halogen bond fission to yield the carbonate complexes [Cp*Ir(κ2O–CO3)(κC–MeNC3H2NCH2Ar)].

Pentamethylcyclopentadienyl imidazol–2–ylidene iridium complexes, Cp*Ir(NHC), display interesting reactivity, such as activation of alkyl carbon–hydrogen bonds1,2 and carbon–fluorine bonds,3 and catalytic activity, including water oxidation,4,5 transfer hydrogenation,6,7 dynamic kinetic resolution,8 hydrogen transfer initiated dehydration,9 the alkylation of amines,10 and dehydrogenative oxidation of alcohols.4,5 Cyclometallation involving carbon–hydrogen bond activation induced by base has been reported for NHC ligands bearing aryl, benzyl and alkyl substituents.2,4,11,12 Recently we reported cyclometallation by carbon–halogen bond activation induced by silver particles for complexes with halogen atoms at both ortho positions of a benzyl substituent.3,13

In a number of in situ NMR studies of carbon–halogen bond activation other minor products were formed when the silver particles were generated mechanically from silver(I) oxide.3 It was considered possible that these were formed by a reaction between the iridium complex and residual silver(I) oxide. In situ NMR experiments, conducted without excluding air and moisture, confirmed that, on treatment with silver(I) oxide, the complex [Cp*IrCl2(κC–MeNC3H2NCH2C6H3F–2–Cl–6)] (1a)13 in deuterio-chloroform underwent a reaction over several hours to afford the carbonate complex [Cp*Ir(κ2O–CO3)(κC–MeNC3H2NCH2C6H3F–2–Cl–6)] (2a) cleanly in high yield. The identity of 2a was confirmed by a single crystal X-ray diffraction study of the dihydrate, and by comparison of its NMR spectral data with an authentic sample prepared by treatment of 1a with silver carbonate, in particular the resonance at δC 168.1, which is consistent with κ2O-bound carbonate of iridium NHC complexes.14

Both metal reagents are necessary for the reaction: no reaction was observed between chloroform and silver(I) oxide, nor between chloroform and 1a. The combination of 1a and silver(I) oxide was also observed to react with dichloromethane to form 2a, although more slowly than with chloroform, and with tetrahydrofuran, albeit much less cleanly. A reaction was observed with dimethylsulphoxide, but this occurred sufficiently slowly to allow an in situ NMR study of the reaction with chloroform to be conducted: adding a drop of chloroform to a deuterio-dimethylsulphoxide solution of 1a with silver(I) oxide produced 2a more rapidly and cleanly than reaction with dimethylsulphoxide alone. Complex 2a was also produced when chloroform was replaced by bromoform or iodoform. Formation of dihalomethane was also evident with these two haloforms. In situ NMR experiments revealed that haloform was consumed as 2a was formed (Fig. 2).
Fig. 2 Portions of $^1$H NMR spectra of the reaction between 1a, silver(I) oxide and bromoform in deuterodimethylsulphoxide, with the methylene hydrogen atoms of 1a and 2a indicated. a) On addition of silver oxide, and after b) after 7 days, c) 20 days and d) 30 days.

The results strongly suggest that the reaction involves the transformation of haloform to carbonate. This is supported by the observation that the reaction also occurred under anaerobic conditions, thus precluding atmospheric carbon dioxide as the source of carbonate. Further, no reaction was observed between the rhodium analogue of 1a and silver(I) oxide from the same batch, but formation of \([\text{Cp}^*\text{Rh}(\kappa^2\text{O}-\text{CO}_3)(\kappa^2\text{C}-\text{MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_3\text{F}-2\text{-Cl}-6)]\) occurred on treatment with silver carbonate. Therefore, contamination of the silver(I) oxide was not the reason for formation of carbonate.

It is proposed that the oxygen atoms of the carbonate are derived from the silver(I) oxide, and the chloride ligands of the iridium complexes dissociate, or are abstracted, and form silver chloride. The halogen atoms of the haloform form silver halide and the haloform carbon atom undergoes a formal oxidation from +II to +IV on formation of carbonate, and so a reduction of two equivalents of silver from +I to 0 is expected (Scheme 1). Consistent with the proposed scheme, analysis of the residue of the reaction involving chloroform was consistent with silver chloride and elemental silver.

Scheme 1 Reaction of haloform with complexes 1a – c and silver(I) oxide.

The reaction mechanism is unknown, but, based on a lack of reaction between chloroform and the individual metal reagents, it is likely that the first step involves a reaction between 1a and silver(I) oxide. Since no obvious intermediate is apparent in the NMR spectra, this would be the rate determining step. It also suggests that the subsequent reaction is rapid. Further studies revealed that the reaction is not restricted to 1a, but occurs for the analogous complexes with fluorine atoms (1b) or methyl groups (1c) at both ortho sites. The requirement for the reaction appears to be the absence of ortho substituents that can undergo base-induced bond activation to give a cyclometallated product.\(^1\)\(^2\)\(^3\)

In summary we have demonstrated that the complex \([\text{Cp}^*\text{IrCl}_2(\kappa^2\text{C}-\text{MeNC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{H}_3\text{F}-2\text{-Cl}-6)]\), and two analogues, convert haloform to carbonate on treatment with silver(I) oxide. The rhodium analogue does not show similar reactivity.

Conflicts of interest
There are no conflicts to declare.

Notes and references