Electronic Supplementary Information for:

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

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Experimental details

Materials
Complexes 1a, 1b, and 1c were prepared as previously described. Silver(I) oxide (Aldrich), chloroform (Aldrich), bromoform (BDH) and iodoform (BDH) were used as supplied.

NMR tube reactions between silver(I) oxide and 1a, 1b and 1c
Silver(I) oxide (ca. 0.025 g, 0.1 mmol) was added to a solution of 1a, 1b or 1c (ca. 20 mg, 0.03 mmol) in deuterochloroform (ca. 1 cm³) in an NMR tube. The solution was monitored regularly over 7 to 10 days and by ¹H and ¹⁹F NMR spectroscopy. Once the reaction had reached completion, the solution was diluted with CHCl₃ and filtered through Celite. The product was obtained as a brown-beige or yellow solid on slow evaporation of the solvent, or on precipitation by addition of petroleum ether (b.p. 60-80°C).

η⁵-Pentamethylcyclopentadienyliridium(1-(2-chloro-6-fluorophenylmethyl)-3-methylimidazolin-2-ylidene) carbonate (2a)
Calculated for C₂₄H₂₅ClFIrN₂O₃: C, 43.2; H, 4.1; N, 4.6. Found: C, 43.8; H, 5.3; N, 4.9%. Repeated recrystallization failed to give satisfactory analyses. Mass spectrometric analysis of 2a did not produce a recognisable anion or cation.

¹H NMR (CDCl₃): δ 7.36 (1H, d. t. JHF 5.8, JHH 8.1, C₆H₃ClF), 7.31 (1H, m, C₆H₃ClF), 7.07 (1H, m, C₆H₃ClF), 6.85 (1H, d, JHH 2.0, HCC₇H), 6.37 (1H, d, JHH 2.0, HCC₇H), 5.69 (1H, dd, JHH 14.5, JHF 1.7, NCH), 5.34 (1H, dd, JHH 14.5, JHF 1.6, NCH), 3.79 (3H, s, NCH₃), 1.78 (15H, s, C₅(CH₃)₅).

¹³C{¹H} NMR (CDCl₃): δ 168.1 (CO₃), 163.8 (IrCcarbene), 162.3 (d, JCF 252, CF), 137.1 (d, JCF 5, CₛH₃ClF), 131.3 (d, JCF 10, CₛH₃ClF), 126.1 (d, JCF 3, CₛH₃ClF), 121.9 (NCH), 120.9 (d, JCF 17, CₛH₃ClF), 119.4 (NCH), 114.8 (d, JCF 22, Ph), 86.2 (Cₛ(CH₃)₃), 45.2 (d, JCF 3, NCH₂), 37.8 (NCH₃), 9.8 (Cₛ(CH₃)₃).

¹⁹F NMR (CDCl₃): δ -110.29 (1F, m).

Shifts for the carbonate complex obtained in the NMR tube reaction between 1a, Ag₂O and a drop of chloroform in deutero-dimethylsulphoxide:
¹H NMR ((CD₃)₂SO): δ 7.56 (1H, d. t. JHH 6.1, JHH 8.2, C₆H₃ClF), 7.48 (1H, m, C₆H₃ClF), 7.35* (1H, m, CₛH₃ClF), 7.35* (1H, d, JHH 2.0, HCC₇H), 6.62 (1H, d, JHH 2.0, HCC₇H), 5.48 (1H, d. d, JHH 14.9, JHF 1.2, NCH), 5.18 (1H, d, d, JHH 14.9, JHF 1.2, NCH), 3.70 (3H, s, NCH₃), 1.70 (15H, s, Cₛ(CH₃)₃).

*These resonances are coincident.

¹⁹F NMR ((CD₃)₂SO): δ -111.77 (1F, m).
Figure S1. $^1$H NMR spectrum of 2a in CDCl$_3$

Figure S2. $^{19}$F NMR spectrum of 2a in CDCl$_3$
Figure S3. $^{13}$C($^1$H) NMR spectrum of 2a in CDCl$_3$.

$\eta^5$-Pentamethylcyclopentadienyliridium(1-(2,6-difluorophenylmethyl)-3-methylimidazolin-2-ylidene) carbonate (2b)

Calculated for C$_{22}$H$_{25}$F$_2$IrN$_2$O$_3$: C, 44.4; H, 4.2; N, 4.7. Found: C, 44.0; H, 5.2; N, 5.0%. Repeated recrystallization failed to give satisfactory analyses. Mass spectrometric analysis of 2b did not produce an recognisable anion or cation.

$^1$H NMR (CDCl$_3$): $\delta$ 7.38 (1H, m, H$_{para}$), 6.97 (2H, m, H$_{meta}$), 6.89 (1H, d, $^3$J$_{HH}$ 2.1, HCCH), 6.47 (1H, d, $^3$J$_{HH}$ 2.0, HCCH), 5.46 (1H, d, $^2$J$_{HH}$ 15.2, NCHH), 5.26 (1H, d, $^2$J$_{HH}$ 15.2, NCHH), 4.78 (3H, s, NCH$_3$), 1.77 (15H, s, C$_5$(CH$_3$)$_5$).

$^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 168.1 (CO$_3$), 164.3 (IrC$_{carbene}$), 162.1 (dd, $^1$J$_{CF}$ 251, $^3$J$_{CF}$ 8, CF), 131.3 (t, $^1$J$_{CF}$ 10, C$_6$H$_3$F$_2$), 122.2 (NCH), 119.5 (NCH), 112.0 (dm, $^1$J$_{CF}$ 25, C$_6$H$_3$F$_2$), 111.2 (t, $^1$J$_{CF}$ 25, C$_6$H$_3$F$_2$), 86.3 (C$_5$(CH$_3$)$_5$), 42.1 (NCH$_2$), 37.8 (NCH$_3$), 9.7 (C$_5$(CH$_3$)$_5$).

$^{19}$F NMR (CDCl$_3$): $\delta$ -112.46 (2F, br t, J 6.7, F).
Figure S4. $^1$H NMR spectrum of 2b in CDCl$_3$

Figure S5. $^{19}$F NMR spectrum of 2b in CDCl$_3$
Figure S6. $^{13}$C($^1$H) NMR spectrum of 2b in CDCl$_3$

$\eta^5$-Pentamethylcyclopentadienyliridium(1-(2,6-dimethylphenylmethyl)-3-methylimidazolin-2-ylidene) carbonate (2c)

Calculated for C$_{24}$H$_{31}$IrN$_2$O$_3$: C, 49.05; H, 5.3; N, 4.8. Found: C, 48.8; H, 6.2; N, 3.9%. Repeated recrystallization failed to give satisfactory analyses. Mass spectrometric analysis of 2c did not produce a recognisable anion or cation.

$^1$H NMR (CDCl$_3$): $\delta$ 7.19 (1H, m, H$_{para}$), 7.08 (2H, m, H$_{meta}$), 6.79 (1H, d, J$_{HH}$ 2.0, HCCCH), 6.22 (1H, d, J$_{HH}$ 2.0, HCCCH), 5.78 (1H, d, $^2$J$_{HH}$ 14.0, NCHH), 4.89 (1H, d, $^2$J$_{HH}$ 14.0, NCHH), 3.78 (3H, s, NCH$_3$), 2.27 (6H, s, C$_6$CH$_3$), 1.78 (15H, s, C$_5$(CH$_3$)$_5$).

$^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 167.9 (CO$_3$), 163.1 (IrC$_{\text{carbene}}$), 130.6 (C$_6$H$_3$Me$_2$), 129.8 (C$_6$H$_3$Me$_2$), 129.1 (C$_6$H$_3$Me$_2$), 128.8 (C$_6$H$_3$Me$_2$), 121.5 (NCH), 119.3 (NCH), 86.0 (C$_5$(CH$_3$)$_5$), 47.9 (NCH$_2$), 37.6 (NCH$_3$), 19.8 (C$_6$(CH$_3$)$_2$), 9.9 (C$_5$(CH$_3$)$_5$).
**Figure S7.** $^1$H NMR spectrum of 2c in CDCl$_3$

**Figure S8.** $^{13}$C($^1$H) NMR spectrum of 2c in CDCl$_3$
**Synthesis of 2a, 2b and 2c using silver(I) carbonate**

Complexes 2a, 2b and 2c were generated in NMR tubes by the reaction of 1a, 1b and 1c with silver(I) carbonate in deutero-chloroform. The NMR data are identical to those obtained by the reaction of 1a, 1b and 1c with silver(I) carbonate in deutero-chloroform.

**Synthesis of η5-pentamethylcyclopentadienylrhodium(1-(2,6-difluorophenylmethyl)-3-methylimidazolin-2-ylidene) carbonate**

The rhodium analogue of complex 2a was generated in an NMR tube by the reaction of 1a with silver(I) carbonate in deutero-chloroform. 

$^1$H NMR (CDCl$_3$): $\delta$ 7.36 (1H, d. t. $J_{HF}$ 5.8, $J_{HH}$ 8.1, C$_6$H$_3$ClF), 7.28 (1H, m, C$_6$H$_3$ClF), 7.05 (1H, m, C$_6$H$_3$ClF), 6.91 (1H, d, $J_{HH}$ 2.0, HCC), 6.38 (1H, d, $J_{HH}$ 2.0, HCC), 5.67 (1H, dd, $J_{HH}$ 14.5, $J_{HF}$ 1.7, NCHH), 5.34 (1H, dd, $J_{HH}$ 14.5, $J_{HF}$ 1.4, NCHH), 3.80 (3H, s, NCH$_3$), 1.75 (15H, s, C$_5$(CH$_3$)$_5$).

$^{13}$C{$_1$H} NMR (CDCl$_3$): $\delta$ 174.8 (d, $J_{RhC}$ 60, RhC$_{carbene}$), 166.4 (CO$_3$), 162.3 (d, $J_{CF}$ 253, CF), 137.0 (d, $J_{CF}$ 5, C$_6$H$_3$ClF), 131.3 (d, $J_{CF}$ 10, C$_6$H$_3$ClF), 126.1 (s, C$_6$H$_3$ClF), 122.7 (NCH), 120.8 (d., $J_{CF}$ 17, C$_6$H$_3$ClF), 120.0 (NCH), 114.8 (d, $J_{CF}$ 22, Ph), 93.7 (C$_5$(CH$_3$)$_5$), 45.5 (d, $J_{CF}$ 3, NCH$_3$), 37.9 (NCH$_3$), 9.6 (C$_5$(CH$_3$)$_5$).

$^{19}$F NMR (CDCl$_3$): $\delta$ -110.17 (1F, m).

**Reaction between 1a and haloform in deutero-dimethylsulphoxide**

Silver(I) oxide (ca. 0.025 g, 0.1 mmol) was added to a solution of 1a (ca. 20 mg, 0.03 mmol) in deutero-dimethylsulphoxide (ca. 1 cm$^3$) in an NMR tube. A drop of chloroform or bromoform or a few crystals of iodoform (ca. 25 mg, 0.06 mmol) was added. Integration of appropriate NMR resonances was used to determine the ratio of 1a to haloform, and the amount of haloform adjusted to achieve a ratio close to 1:1. The reaction was monitored regularly over several days by $^1$H and $^{19}$F NMR spectroscopy.

Shifts for the carbonate complex obtained in the NMR tube reaction between 1a, Ag$_2$O and a drop of chloroform in deutero-dimethylsulphoxide:

$^1$H NMR (CD$_3$$_2$SO): $\delta$ 7.56 (1H, d. t. $J_{HH}$ 6.1, $J_{HH}$ 8.2, C$_6$H$_3$ClF), 7.48 (1H, m, C$_6$H$_3$ClF), 7.35* (1H, m, C$_6$H$_3$ClF), 7.35* (1H, d, $J_{HH}$ 2.0, HCC), 6.62 (1H, d, $J_{HH}$ 2.0, HCC), 5.48 (1H, d, $J_{HH}$ 14.9, $J_{HF}$ 1.2, NCHH), 5.18 (1H, d, $J_{HH}$ 14.9, $J_{HF}$ 1.2, NCHH), 3.70 (3H, s, NCH$_3$), 1.70 (15H, s, C$_5$(CH$_3$)$_5$).

*These resonances are coincident.

$^{19}$F NMR (CD$_3$$_2$SO): $\delta$ -111.77 (1F, m).
Figure S9. $^1$H NMR spectra of the reaction between 1a, silver oxide and CHCl$_3$ in (CD$_3$)$_2$SO.

a) 0 hours

b) 3 days
c) 17 days

1a:2a:CHCl₃ 1:2.3:2.4

1a CHH'
2a CHH'
2a NCH₃
1a NCH₃

d) 50 days

2a:CHCl₃ 1.0:0.6

CHCl₃
2a CHH'
2a CHH''
2a NCH₃
Figure S10. Variation of the concentrations of 1a, 2b and CHCl₃ (relative to the initial concentration of 1a) with time the reaction between 1a, silver oxide and CHCl₃ in (CD₃)₂SO.
Figure S11. $^1$H NMR spectra of the reaction between 1a, silver oxide and CHBr$_3$ in (CD$_3$)$_2$SO.

a) 0 hours

b) 7 days
c) 20 days

\[ \text{1a:2a:CHBr}_3: \text{CH}_2\text{Br}_2 \ 1.0:2.8:1.5:1.4 \]

\[ \text{CH}_2\text{Br}_2 \]

\[ \text{CHBr}_3 \]

\[ 2a \]

\[ 1a \text{ CHH}^' \]

\[ 2a \text{ CHH}^' \]

\[ 2a \text{ CHH}^' \]

d) 30 days

\[ \text{2a:CHBr}_3: \text{CH}_2\text{Br}_2 \ 1.0:0.1:0.4 \]

\[ \text{CH}_2\text{Br}_2 \]

\[ \text{CHBr}_3 \]

\[ 2a \]

\[ 2a \text{ CHH}^' \]

\[ 2a \text{ CHH}^' \]
Figure S12. Variation of the concentrations of 1a, 2b and CHBr₃ (relative to the initial concentration of 1a) with time the reaction between 1a, silver oxide and CHBr₃ in (CD₃)₂SO.
Figure S13. $^1$H NMR spectra of the reaction between 1a, silver oxide and CHI$_3$ in (CD$_3$)$_2$SO.

a) 0 hours

b) 3 days
c) 7 days

1a:2a:CHI₂:CHJ₂ 1.0:2.7:0.5:0.8

2a NCH₃

1a CHH⁺
2a CHH⁺
2a CHH⁺

1a NCH₃

CHI₂

2a CHJ₂

16


d) 18 days

2a:CHI₂:CHJ₂ 1.0:0.0:0.3

2a NCH₃

2a CHH⁺
2a CHH⁺

CHJ₂

Figure S14. Variation of the concentrations of 1a, 2b and CHI$_3$ (relative to the initial concentration of 1a) with time the reaction between 1a, silver oxide and CHI$_3$ in (CD$_3$)$_2$SO.
Identification of silver and silver chloride in the residue of the reaction between 1a and chloroform

The black solid residue (Fig. S15a) remaining after the reaction between 1a, chloroform and silver oxide in deutero-dimethylsulphoxide was treated with dilute (2M) aqueous ammonia, in which both silver chloride and silver oxide are soluble. Most of the material dissolved to produce a colourless solution leaving a small amount of black solid (Fig. S15b). Nitric acid added was added to the decanted solution resulting in a white precipitate (Fig. S15c). The observations are consistent with the presence of silver chloride. The black solid was found to dissolve in nitric acid (Fig. S15d), which is consistent with elemental silver. [CARE: While no adverse incidents occurred during these experiments, dissolution of silver(I) oxide in aqueous ammonia can lead to the formation of explosive and shock sensitive silver nitride (fulminating silver). Dilute (2 M) aqueous ammonia was used, and the samples were treated with acid immediately after each experiment had been completed to prevent the formation of the nitride.]
Figure S15. Analysis of the residue from the reaction between 1a, silver oxide and CHCl₃ in (CD₃)₂SO.

a Black residue

b Addition of NH₃(aq)

Insoluble material

c Addition of HNO₃ to ammoniacal solution

d Addition of HNO₃ to insoluble solid
X-ray crystallographic study

Crystals of 2a were obtained by vapour diffusion of pentane into a chloroform solution. Crystal data are listed in Table S1. Diffraction data were collected on an Agilent SuperNova, single source at offset, Atlas diffractometer with graphite-monochromated Cu—Kα radiation. The structure was solved using Olex2 and refined with the olex2.refine refinement package using Gauss-Newton minimization. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were added in idealized positions and a riding model with fixed thermal parameters (Uij = 1.2Ueq for the atom to which they are bonded (1.5 for CH₃)) was used for subsequent refinements. The function minimized was ∑[w(|Fo|^2 - |Fc|^2)] with reflection weights \( w^{-1} = [\sigma^2 |Fo|^2 + (g1P)^2 + (g2P)] \) where \( P = \text{max} |Fo|^2 + 2|Fc|^2/3 \).

CCDC 1864957 contains 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](http://www.ccdc.cam.ac.uk/data_request/cif).

Figure S16. Molecular structure of 2a
Table S1. Crystallographic data for \([\eta^5-C_5Me_5]Ir(\kappa^2O-CO_3)(\kappaC-MeNC_2H_2NCH_2C_6H_3F-2-Cl-6)].2H_2O (2a.2H_2O).

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References


