

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Fluoride, Bifluoride and Trifluoromethyl Complexes of Iridium(I) and Rhodium(I)

Cite this: DOI: 10.1039/x0xx00000x

Byron J. Truscott, Fady Nahra, Alexandra M. Z. Slawin, David B. Cordes and Steven P. Nolan*

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Herein we report robust methods for the preparation and full characterisation of a range of Ir(I) and Rh(I) fluoride and bifluoride complexes using *N*-heterocyclic carbenes (NHCs) as ancillary ligands. The processes that link the fluoride and the bifluoride species are investigated and reports of the first Ir-bifluoride and Ir(I)-NHC and Rh(I)-NHC trifluoromethyl complexes are revealed.

Fluorinated organometallic complexes are highly interesting species. Fluorides are known to confer unique properties to the metal and their coordination can lead to fascinating reactivity. Nevertheless metal fluorides remain the least understood member of the metal-halide family.¹

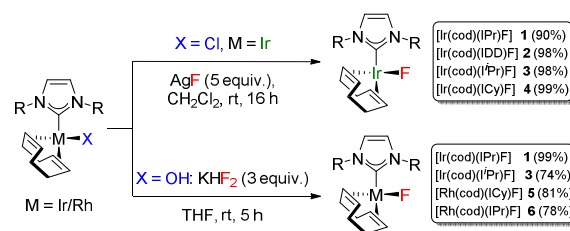
Additionally, the catalytic preparation of fluorinated organic compounds is an area of great importance, particularly for the radio therapeutic, pharmaceutical and agrochemical sectors.² The isolation of fluorinated organometallic complexes permits us to study the behaviour of potential catalysts and catalytic intermediates under homogeneous conditions.³ This knowledge is of paramount importance in designing new catalytic cycles and improving existing fluorination methods.^{2b,4}

The interaction between a hard base such as fluoride and a low-oxidation state metal (behaving as a soft Lewis acid) should lead to weak metal-fluoride bonds.^{1a,5} Stabilisation of M-F bonds and isolation of LTM-fluorides has mostly been reported using phosphine, *N*-donor or σ -aryl ancillary ligands.^{1,6} Some of the most extensively investigated fluoride complexes are analogues of Vaska's complex ($[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$) and related rhodium complexes.^{1a,6c,7} In contrast, fluoride complexes bearing olefinic ligands remain scarce,⁸ and even more scarce are those containing *N*-heterocyclic carbenes (NHCs).^{6a,9} NHC ligands have featured extensively in the literature as electron-rich donor ligands, and have proven particularly useful in stabilising hard/soft metal-ligand mismatches such as metal hydroxides.¹⁰

Bifluoride complexes $[\text{M}(\text{FHF})]$ are very interesting, and since the first report by Coulson¹¹ on Pt, several examples of metal bifluorides have been reported, including Mn,¹² W,¹³ Pd,¹⁴ Ru,¹⁵ Mo,¹⁶ Ni,¹⁷ and Rh,^{7a,8b,18} mostly bearing phosphine or amine based supporting ligands. The only examples of LTM-HF₂ complexes bearing NHC ligands are those reported by the groups of Leyssens on Cu,¹⁹ and by Whittlesey on Rh (bearing

ring expanded six-membered NHC ligands).^{18c,20} Furthermore, reports of LTM(NHC) complexes bearing trifluoromethyl (CF₃) groups are exclusive to Cu.²¹ In order to build on the reactivity of Ir(I) and Rh(I) compounds, we aimed to establish robust methods for the preparation of fluorinated Ir(I)- and Rh(I)-complexes bearing F, HF₂ and CF₃ moieties.

Based on previous success in stabilising M-OH bonds on Rh(I) and Ir(I), our strategy was to use the $[\text{M}(\text{cod})(\text{NHC})(\text{X})]$ scaffold (M = Rh, Ir; cod = 1,5-cyclooctadiene; X = Cl, OH) to gain access to M(I)-F bonds.¹⁰ Gratifyingly, a transmetalation/halide substitution reaction between $[\text{Ir}(\text{cod})(\text{NHC})\text{Cl}]$ and AgF^{6b} delivered $[\text{Ir}(\text{cod})(\text{NHC})\text{F}]$ complexes **1** - **4** as yellow solids in excellent yields (Scheme 1). Multinuclear NMR spectroscopy and elemental analysis were used to unambiguously confirm the identity of the products with the ¹⁹F NMR signals corresponding to the Ir(I)-F moiety resonating between -221 and -227 ppm (see ESI).



Scheme 1. Preparation of Ir(I) and Rh(I)-fluoride complexes

It was clear that the three species were intrinsically linked and we were able to convert the fluoride complex to either the Ir(I)-OH (via reaction with CsOH or KOH), or to the Ir(I)-Cl (via reaction with NaCl). However, when we attempted to extend the methodology to rhodium, the reactions were at best very slow (65% conversion after 60 h for $[\text{Rh}(\text{cod})(\text{IPr})\text{Cl}]$). Treating either of the metal chlorides or hydroxides with fluoride salts such as KF or CsF was also unsuccessful and a new approach had to be devised. To our delight, the Rh(I)-OH reacted with cheap and readily available KHF₂ to deliver the desired Rh(I)-F in high yield in just 5 h. This method proved general for both metals (Scheme 1) and analysis by ¹⁹F NMR

indicated that Rh(I)-F signals resonated at a higher field than the analogous Ir(I)-F complexes (δ -258, br (**5**); δ -253, d, $^1J_{RhF}$ = 77 Hz (**6**)).

X-ray analysis of complexes **1**, **3**, **5** and **6** (Figure 1 and Figure S56-57) indicated $16e^-$, square planar geometries. Compared to the parent complexes, the M(I)-F bonds (1.991 – 2.032 Å for Ir and 2.016 – 2.092 Å for Rh) are shorter than M(I)-Cl bonds (2.334 – 2.382 Å)²² and closer in magnitude to the corresponding M(I)-hydroxides (2.014 – 2.038 Å).^{10, 23}

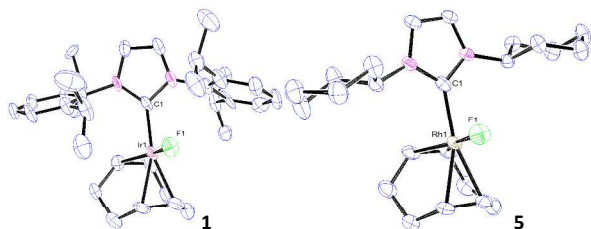
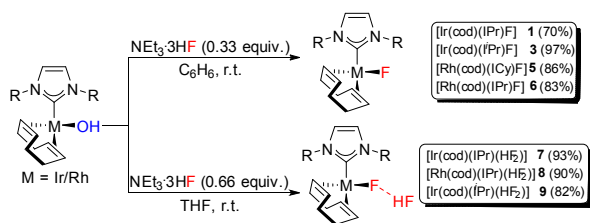


Figure 1. Thermal ellipsoid representations (50%) of **1** and **5**. H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$), numbers in parentheses are for second independent molecule: **1**: Ir(1)-C(1) 2.014(16), [2.029(17)]; Ir(1)-F(1) 2.023(9), [2.002(11)]; C(1)-Ir(1)-F(1): 87.5(5), [88.2(6)]. **5**: Rh(1)-C(1) 2.022(3); Rh(1)-F(1) 2.018(2); C(1)-Rh(1)-F(1) 88.20(11).

As a third method, we examined the reaction between the Rh(I) and Ir(I)-hydroxides and $Et_3N \cdot 3HF$. Ir(I)-OH and Rh(I)-OH complexes were reacted with $Et_3N \cdot 3HF$ (0.33 equiv.) in benzene to successfully deliver the Rh(I) and Ir(I)-fluorides in good to excellent yields (Scheme 2).

As described by Riant and Leysens,^{19b} changing the solvent to THF and increasing the relative concentration of $Et_3N \cdot 3HF$ (0.66 equiv.) afforded the expected bifluoride species, $[Ir(cod)(IPr)(HF_2)]$ (**7**) and $[Rh(cod)(IPr)(HF_2)]$ (**8**) from the corresponding M-hydroxides (Scheme 2). NMR spectroscopic analyses of these new complexes showed subtle differences to the analogous fluoride complexes (**1** and **5**). At room temperature the 1H NMR spectrum for each compound contained a low-field broad doublet (δ 11.4, $^1J_{FH}$ = 395 Hz (**7**); δ 12.3, $^1J_{FH}$ = 350 (**8**)). Upon cooling (200K, CD_2Cl_2) the signals partially resolved into doublets of doublets in each case with a spin-spin coupling of 395 and 40 Hz for **7** and 350 and 25 Hz for **8** (see ESI). These 1H NMR signals were assigned to the acidic proton of the bifluoride moiety; with a strong bond to one fluoride and a weaker bond to a second fluoride. The assignment was confirmed by the identification of two fluoride groups by ^{19}F NMR analysis of **7** and **8**.



Scheme 2. Reaction of Rh(I) and Ir(I) hydroxides with $Et_3N \cdot 3HF$

In each case, a ^{19}F NMR signal was observed in the same region as that found for **1** and **6**, corresponding to the metal-bound (proximal) fluoride. In addition, a doublet resonated further downfield with a spin-spin coupling constant of 395 Hz on **7** and 350 Hz on **8**. These signals were assigned to the distal fluoride, showing a strong bond to the acidic proton. At 200 K, all ^{19}F NMR signals resolved into distinct doublets of doublets,

e.g. for **7**: δ -178 (dd, $^1J_{HF}$ = 395, $^2J_{FF}$ = 120, Ir-F \cdots HF), -239 (dd, $^2J_{FF}$ = 120, $^1J_{HF}$ = 40, Ir-F \cdots HF, see ESI). Based on these results, we proposed the composition of **7** and **8** as $[Ir(cod)(IPr)(FHF)]$ and $[Rh(cod)(IPr)(FHF)]$, respectively (Scheme 2) with the HF_2 moieties comprising a strong bond between the metal and the proximal fluoride, and a relatively weak hydrogen bond to the HF moiety (i.e. $[M]-F\cdots HF$ as opposed to $[M]\cdots F-HF$), in agreement with literature reports.^{15b, 18a, 18b, 19b, 20}

X-ray crystallographic analysis of **7** and **8** (Figure 2) showed square planar complexes, similar to the mono-fluorides. The X-ray structure for **7** shows a significantly elongated M-F bond. This weakening of the M-F bond is a consequence of the hydrogen bond to HF.^{15b} The F-F separation on **7** is in the range of 2.35 – 2.39 Å and 2.32 – 2.33 Å for complex **8**. These values are considerably less than the sum of the van der Waals radii of two F atoms (2.94 Å)²⁴ and are indicative of strong hydrogen bonds to the two fluorides, in agreement with reports for other metal bifluorides including those of Mo and Rh.^{13, 14c, 15b, 15c, 16-18, 18c, 19b, 20}

The unsymmetrical nature of the bifluoride ligand is further supported by FTIR analyses of **7** and **8**, which showed two broad bands each (**7**: ν = 2623 and 1807 cm^{-1} ; **8**: ν = 2530 and 1890 cm^{-1}) corresponding to the H-F modes of the bifluoride (absent from FTIR of **1** or **6**, see ESI).^{14b, 16, 20} Compared to the IR bands expected for free HF (ν = 3896 and 3895 cm^{-1} in an Ar matrix),²⁵ it is clear that there is weakened hydrogen bonding within the HF moiety as a result of the H-bond to the proximal fluoride, causing a shift to lower wavenumber.

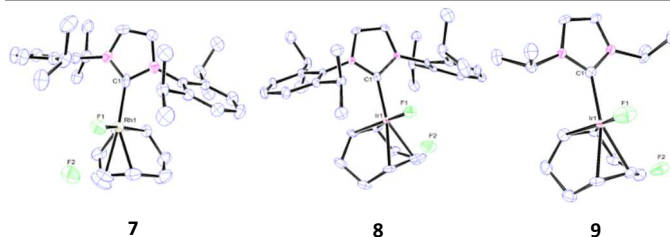


Figure 2. Thermal ellipsoid representations of **7**, **8** and **9** showing 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles ($^\circ$): **7**: Ir(1)-C(1) 2.033(4), [2.049(4)]; Ir(1)-F(1) 2.057(3), [2.062(2)]; C(1)-Ir(1)-F(1) 88.92(13), [92.59(12)]. **8**: Rh(1)-C(1) 2.047(5), [2.035(6)]; Rh(1)-F(1) 2.089(3), [2.069(3)]; C(1)-Rh(1)-F(1) 93.09(16), [89.14(18)]. **9**: Ir(1)-C(1) 2.045(6), [2.053(6)]; Ir(1)-F(1) 2.064(5), [2.082(4)]; C(1)-Ir(1)-F(1) 91.0(2), [87.5(2)].

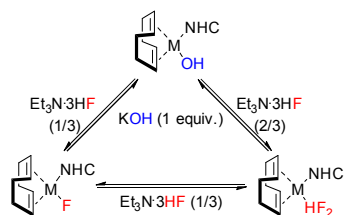
Compared to symmetrical inorganic bifluoride salts, for example Cs^+ , K^+ or Na^+ HF_2^- (1372 – 1284 cm^{-1}),²⁶ the IR bands of **7** and **8** are considerably higher in wavenumber, indicating that the HF_2 moiety in these complexes is highly unsymmetrical, with a stronger hydrogen bond to one fluorine atom than the other.

In addition to **7** and **8**, an alkyl-substituted NHC complex of Ir(I)-(HF₂) was prepared in the form of $[Ir(cod)(IPr)(HF_2)]$ (**9**) (Scheme 2). The less sterically encumbered **9** exhibited different structural characteristics to **7** and **8**, both in the solid-state and in solution. For example, at room temperature the 1H NMR signal corresponding to the acidic proton resonates as a broad unresolved peak, as do both signals on the ^{19}F NMR spectrum (see ESI). Upon cooling to 200 K, the signals resolved into doublets of doublets in the same way as **7** and **8**.

From the X-ray structure for **9** (Figure 2), it is apparent that while the Ir-F bond is comparable in length to **7**, the F-F separation (2.457(6), [2.587(6)] Å) is considerably larger, even

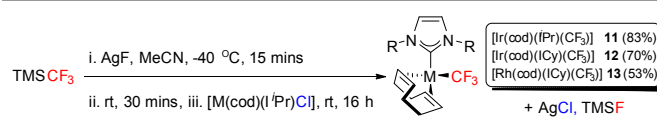
compared to the values for most metal bifluorides reported to date.^{8b, 13-16, 18a-c, 19b, 20} On closer inspection of the X-ray structures of **7** and **8**, it is clear that F(1) and the *isopropyl* proton on each side of the IPr ligand are in very close proximity to each other (*ca.* 2.33 – 2.49 Å in **7**; 2.32 – 2.43 Å in **8**). This is considerably less than the sum of the van der Waals radii for H and F (2.67 Å)²⁴ Such a close contact is not possible in **9** and the added flexibility may account for the fluxional behaviour in solution that is associated with **9** (this close contact is not observed on the monofluoride complexes).

Next we studied the link between the fluoride and bifluoride complexes. The ease with which the bifluoride can be generated from the monofluoride and the lability of the HF molecule is especially important for catalytic fluorination and fluorination/ring-opening processes,²⁷ where catalysts, particularly metal fluorides are coupled with an HF source. In order to examine the persistence of the bifluoride moiety in the presence of a base, both the Rh(I) and Ir(I)-bifluorides (**7** and **8**) were reacted with a stoichiometric amount of KOH. In both cases, full conversion to the corresponding M-F (**1** and **6**) was seen within 2 h. Interestingly, the addition of a second equivalent of KOH yielded the corresponding M(I)-OH; whilst addition of Et₃N·3HF (0.33 equiv.) to **1** or **6** regenerated M-HF₂ (**7** and **8**). Hence, the three species are inherently linked (Scheme 3) and in the presence of an excess of Et₃N·3HF, a metal fluoride or hydroxide will more than likely deliver the metal bifluoride.



Scheme 3. Processes linking M(I)-OH, M(I)-F and M(I)-HF₂

Having established reliable routes to mono and bifluoride complexes of Ir(I) and Rh(I), our final goal was to access the first examples of Ir(I)- and Rh(I)-NHC trifluoromethyl complexes. Our initial attempts were conducted using Ruppert-Prakash's reagent, trifluoromethyl(trimethyl)silane (TMSCF₃). Unfortunately all attempts to transfer the CF₃ moiety from Si to Ir or Rh failed. The only complex that reacted with TMSCF₃ was [Ir(cod)(IⁱPr)(OH)], delivering [Ir(cod)(IⁱPr)(OSiMe₃)] (**10**) (96%).^{10b} Reactions between TMSCF₃ and the other Ir(I)- or Rh(I)-hydroxides, -chlorides, or -bifluorides were all unsuccessful and clearly a new approach was necessary. Roper has previously prepared Ir(I)-CF₃ complexes from [Ir(CO)₂(PPh₃)₂H] using Hg(CF₃)₂²⁸ and similar strategies have been employed on other metals using Cd(CF₃)₂. In an attempt to avoid such toxic reagents, we considered the use of Ag to transfer the CF₃. Hence AgCF₃ was prepared *in situ* from AgF and TMSCF₃ at -40 °C²⁹ and reacted with [Ir(cod)(IⁱPr)Cl] to give Ir(I)-CF₃ (**11**) as a bright red solid (Scheme 4). All attempts at isolating the Ir-IPr and Rh-IPr analogues using this procedure failed. In order to rationalise these results we studied the structure of the isolated compound, **11**. Hence, single crystals of **11** were grown and analysed by X-ray diffraction (Figure 3).



Scheme 4. Preparation of [M(cod)(NHC)(CF₃)] complexes (**11** - **13**)

In the solid-state it was apparent that two of the fluorine atoms were in very close proximity to a methine proton on each side of the NHC ligand (*ca.* 2.45 Å). This distance is considerably less than the sum of the Van der Waals radii of H and F (2.67 Å)²⁴ and may indicate an interaction between the two groups. Furthermore, in the ¹³C{¹H} NMR spectrum of **11**, a spin-spin coupling interaction causes one of the methyl signals to split into a quartet (δ 22.8 ppm, *J*_{FC} = 1 Hz). Since the methyl group is separated from the fluorine atoms by six bonds, the interaction must be a "through-space" coupling.³⁰ This evidence indicates that there are considerable steric factors to take into account and that the presence of bulky NHC ligand substituents such as *disopropyl*(phenyl) might hinder the coordination of a CF₃ group to the metal centre.

To test this hypothesis, we investigated the reaction between [M(cod)(ICy)Cl] and AgCF₃, which delivered [M(cod)(ICy)(CF₃)] **12** and **13** (Scheme 4). The same structural features were evident on the ¹³C{¹H} NMR spectrum, showing a spin-spin coupling interaction between a methylene on the cyclohexyl ring and the fluoride groups of the CF₃ on **12**. Furthermore, an X-ray crystal structure of **13** (Figure 3) indicated a similar close proximity between the fluorides and a proton on each of the cyclohexyl rings (2.51 – 2.52 Å). Hence, this synthetic method is somewhat limited by the steric bulk of the NHC ligands and therefore, independent of the metal used. These structural investigations have given us further insights into the stability of this scaffold and the viability of the method.

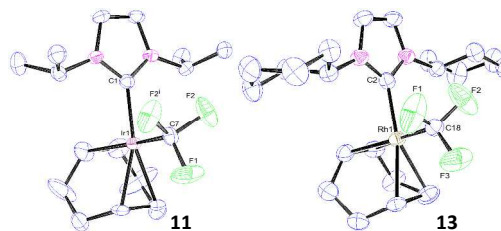


Figure 3. Thermal ellipsoid representations of **11** and **13** showing 50% thermal ellipsoid probability. H atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): **11**: Ir(1)-C(1) 2.065(8); Ir(1)-C(7) 2.086(8); C(7)-F(1) 1.357(10); C(1)-Ir(1)-C(7) 88.3(3). **13**: Rh(1)-C(2) 2.042(5); Rh(1)-C(18) 2.067(5); C(18)-F(1) 1.366(6); C(8)-Rh(1)-C(29) 87.3(2).

In conclusion, we have demonstrated three methods for accessing Ir(I)-NHC fluoride compounds, two of which were effective on rhodium. The first examples of Ir(I)-bifluorides are reported in high yields, *via* a general method. Access to Ir(I) and Rh(I)-F and -HF₂ complexes enabled examination of the link between the two species. This knowledge could prove paramount in developing new fluorination strategies since the bifluoride can be quantitatively generated from the monofluoride in solution and *vice versa*. A new method was also established to access the first examples of Ir(I)-NHC trifluoromethyl complexes. This method was also applied to access the first 5-membered NHC-based Rh(I)-CF₃ complex. Consequently, we have assembled a toolbox for the preparation of fluorinated complexes to take advantage of the reactivity of already successful Ir(I)- and Rh(I)-NHC scaffolds. This will

enable us to pursue fluorination strategies and may well provide active catalytic species or catalytic intermediates in the future.

Notes and references

^a *EaStCHEM, School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST. E-mail: snolan@st-andrews.ac.uk*

The ERC (Advanced Researcher Award FUNCAT to SPN), the EPSRC and Sasol (Stipend to BJT) are gratefully acknowledged for support. Umicore AG are thanked for their gift of materials. We thank Prof. Andrew Smith for access to FTIR spectrometry. Thank you to Dr A. Collado and S.R. Patrick for helpful discussions. SPN is a Royal Society Wolfson Award holder.

[†] *Electronic Supplementary Information (ESI) available: detailed synthetic procedures and full characterisation details for new complexes. See DOI: 10.1039/b000000x/*

‡ CCDC- 1000750 (1), 1000751 (3), 1000752 (5), 1001354 (6), 1000753 (7), 1000754 (8), 1000755 (9), 1000756 (11), 1000757 (13), contain structural data for complexes characterized by X-ray diffraction.

- For reviews on fluorination see: (a) N. M. Doherty and N. W. Hoffmann, *Chem. Rev.*, 1991, **91**, 553-573; (b) E. F. Murphy, R. Murugavel and H. W. Roesky, *Chem. Rev.*, 1997, **97**, 3425-3468.
- (a) K. Müller, C. Faeh and F. Diederich, *Science*, 2007, **317**, 1881-1886; (b) T. Furuya, A. S. Kamlet and T. Ritter, *Nature*, 2011, **473**, 470-477; (c) O. A. Tomashenko and V. V. Grushin, *Chem. Rev.*, 2011, **111**, 4475-4521.
- M. G. Campbell and T. Ritter, *Org. Process Res. Dev.*, 2014, **18**, 474-480.
- Articles demonstrating fluorination strategies: (a) E. J. Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson and S. L. Buchwald, *Science*, 2010, **328**, 1679-1681; (b) H. G. Lee, P. J. Milner and S. L. Buchwald, *J. Am. Chem. Soc.*, 2014, **136**, 3792-3795; (c) M.-G. Braun and A. G. Doyle, *J. Am. Chem. Soc.*, 2013, **135**, 12990-12993; (d) M. H. Katcher and A. G. Doyle, *J. Am. Chem. Soc.*, 2010, **132**, 17402-17404; (e) P. S. Fier and J. F. Hartwig, *J. Am. Chem. Soc.*, 2012, **134**, 10795-10798; (f) K. L. Hull, W. Q. Anani and M. S. Sanford, *J. Am. Chem. Soc.*, 2006, **128**, 7134-7135; (g) J. R. Brandt, E. Lee, G. B. Boursalian and T. Ritter, *Chem. Sci.*, 2014, **5**, 169-179; (h) T. Liang, C. N. Neumann and T. Ritter, *Angew. Chem. Int. Ed.*, 2013, **52**, 8214-8264.
- (a) K. Fagnou and M. Lautens, *Angew. Chem. Int. Ed.*, 2002, **41**, 26-47; (b) M. Gorol, Nadia C. Mösch-Zanetti, Herbert W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Eur. J. Inorg. Chem.*, 2004, **2004**, 2678-2682; (c) R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533-3539; (d) C. Becker, I. Kietlsch, D. Broggin and A. Mezzetti, *Inorg. Chem.*, 2003, **42**, 8417-8429.
- (a) J. Fawcett, D. A. J. Harding, E. G. Hope, K. Singh and G. A. Solan, *Dalton Trans.*, 2010, **39**, 10781-10789; (b) C. J. Bourgeois, S. A. Garratt, R. P. Hughes, R. B. Larichev, J. M. Smith, A. J. Ward, S. Willemssen, D. Zhang, A. G. DiPasquale, L. N. Zakharov and A. L. Rheingold, *Organometallics*, 2006, **25**, 3474-3480; (c) V. V. Grushin, *Acc. Chem. Res.*, 2009, **43**, 160-171.
- (a) S. A. Macgregor, D. C. Roe, W. J. Marshall, K. M. Bloch, V. I. Bakhmutov and V. V. Grushin, *J. Am. Chem. Soc.*, 2005, **127**, 15304-15321; (b) V. V. Grushin and W. J. Marshall, *J. Am. Chem. Soc.*, 2004, **126**, 3068-3069.
- (a) P. Kläring, A.-K. Jungton, T. Braun and C. Müller, *Eur. J. Inorg. Chem.*, 2012, **2012**, 1430-1436; (b) J. Vicente, J. Gil-Rubio and D. Bautista, *Inorg. Chem.*, 2001, **40**, 2636-2637.
- Examples of TM-NHC fluoride complexes (a) J. R. Herron and Z. T. Ball, *J. Am. Chem. Soc.*, 2008, **130**, 16486-16487; (b) D. S. Laitar, PhD Thesis, Massachusetts Institute of Technology, 2006; (c) D. S. Laitar, P. Müller, T. G. Gray and J. P. Sadighi, *Organometallics*, 2005, **24**, 4503-4505; (d) T. Schaub, M. Backes and U. Radius, *J. Am. Chem. Soc.*, 2006, **128**, 15964-15965; (e) T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius and A. Mix, *J. Am. Chem. Soc.*, 2008, **130**, 9304-9317; (f) S. L. Chatwin, M. G. Davidson, C. Doherty, S. M. Donald, R. F. R. Jazzar, S. A. Macgregor, G. J. McIntyre, M. F. Mahon and M. K. Whittlesey, *Organometallics*, 2005, **25**, 99-110; (g) S. P. Reade, D. Nama, M. F. Mahon, P. S. Pregosin and M. K. Whittlesey, *Organometallics*, 2007, **26**, 3484-3491; (h) J. Fawcett, D. A. J. Harding, E. G. Hope, K. Singh and G. A. Solan, *Dalton Trans.*, 2009, 6861-6870.
- (a) B. J. Truscott, G. C. Fortman, A. M. Z. Slawin and S. P. Nolan, *Org. Biomol. Chem.*, 2011, **9**, 7038-7041; (b) B. J. Truscott, D. J. Nelson, C. Lujan, A. M. Z. Slawin and S. P. Nolan, *Chem. Eur. J.*, 2013, **19**, 7904-7916.
- D. R. Coulson, *J. Am. Chem. Soc.*, 1976, **98**, 3111-3119.
- U. Bentrup, K. Harms, W. Massa and J. Pebler, *Solid State Sci.*, 2000, **2**, 373-377.
- V. J. Murphy, D. Rabinovich, T. Hascall, W. T. Klooster, T. F. Koetzle and G. Parkin, *J. Am. Chem. Soc.*, 1998, **120**, 4372-4387.
- (a) N. D. Ball and M. S. Sanford, *J. Am. Chem. Soc.*, 2009, **131**, 3796-3797; (b) N. A. Jasim and R. N. Perutz, *J. Am. Chem. Soc.*, 2000, **122**, 8685-8693; (c) D. C. Roe, W. J. Marshall, F. Davidson, P. D. Soper and V. V. Grushin, *Organometallics*, 2000, **19**, 4575-4582.
- (a) M. K. Whittlesey, R. N. Perutz, B. Greener and M. H. Moore, *Chem. Commun.*, 1997, 187-188; (b) N. A. Jasim, R. N. Perutz, S. P. Foxon and P. H. Walton, *Dalton Trans.*, 2001, 1676-1685; (c) M. S. Kirkham, M. F. Mahon and M. K. Whittlesey, *Chem. Commun.*, 2001, 813-814.
- V. J. Murphy, T. Hascall, J. Y. Chen and G. Parkin, *J. Am. Chem. Soc.*, 1996, **118**, 7428-7429.
- T. Braun, S. P. Foxon, R. N. Perutz and P. H. Walton, *Angew. Chem. Int. Ed.*, 1999, **38**, 3326-3329.
- (a) J. Vicente, J. Gil-Rubio, D. Bautista, A. Sironi and N. Masciocchi, *Inorg. Chem.*, 2004, **43**, 5665-5675; (b) W. J. Marshall and V. V. Grushin, *Organometallics*, 2004, **23**, 3343-3347; (c) C. Segarra, E. Mas-Marzá, J. P. Lowe, M. F. Mahon, R. C. Poulten and M. K. Whittlesey, *Organometallics*, 2012, **31**, 8584-8590; (d) D. Noveski, T. Braun and S. Krückemeier, *J. Fluorine Chem.*, 2004, **125**, 959-966.
- (a) T. Vergote, F. Nahra, D. Peeters, O. Riant and T. Leyssens, *J. Organomet. Chem.*, 2013, **730**, 95-103; (b) T. Vergote, F. Nahra, A. Welle, M. Luhmer, J. Wouters, N. Mager, O. Riant and T. Leyssens, *Chem. Eur. J.*, 2012, **18**, 793-798; (c) T. Vergote, F. Nahra, A. Merschaert, O. Riant, D. Peeters and T. Leyssens, *Organometallics*, 2014, **33**, 1953-1963.
- N. Bramanathan, M. Carmona, J. P. Lowe, M. F. Mahon, R. C. Poulten and M. K. Whittlesey, *Organometallics*, 2014, **33**, 1986-1995.
- (a) G. G. Dubinina, H. Furutachi and D. A. Vici, *J. Am. Chem. Soc.*, 2008, **130**, 8600-8601; (b) A. Zanardi, M. A. Novikov, E. Martin, J. Benet-Buchholz and V. V. Grushin, *J. Am. Chem. Soc.*, 2011, **133**, 20901-20913.
- (a) W. A. Herrmann, C. Köcher, L. J. Gooßen and G. R. J. Artus, *Chem. Eur. J.*, 1996, **2**, 1627-1636; (b) M. Ahmed, C. Buch, L. Routaboul, R. Jackstell, H. Klein, A. Spannenberg and M. Beller, *Chem. Eur. J.*, 2007, **13**, 1594-1601; (c) R. A. Kelly III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo and S. P. Nolan, *Organometallics*, 2008, **27**, 202-210.
- B. J. Truscott, A. M. Z. Slawin and S. P. Nolan, *Dalton Trans.*, 2013, **42**, 270-276.
- A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.
- L. Andrews and G. L. Johnson, *J. Phys. Chem.*, 1984, **88**, 425-432.
- B. S. Ault, *Acc. Chem. Res.*, 1982, **15**, 103-109.
- (a) J. J. Topczewski, T. J. Tewson and H. M. Nguyen, *J. Am. Chem. Soc.*, 2011, **133**, 19318-19321; (b) J. Zhu, G. C. Tsui and M. Lautens, *Angew. Chem. Int. Ed.*, 2012, 12353-12356; (c) C. Hollingworth and V. Gouverneur, *Chem. Commun.*, 2012, **48**, 2929-2942; (d) J. A. Akana, K. X. Bhattacharyya, P. Müller and J. P. Sadighi, *J. Am. Chem. Soc.*, 2007, **129**, 7736-7737; (e) J. A. Kalow and A. G. Doyle, *Tetrahedron*, 2013, **69**, 5702-5709.
- P. J. Brothers, A. K. Burrell, G. R. Clark, C. E. F. Rickard and W. R. Roper, *J. Organomet. Chem.*, 1990, **394**, 615-642.
- Y. Zeng, L. Zhang, Y. Zhao, C. Ni, J. Zhao and J. Hu, *J. Am. Chem. Soc.*, 2013, **135**, 2955-2958.
- J.-C. Hierso, *Chem. Rev.*, 2014, **114**, 4838-4867.

TOC:

New methods for the preparation of a range of NHC-based Ir(I) and Rh(I) fluoride, bifluoride and trifluoromethyl complexes are reported.

