Halogen Bonding Effects on the Outcome of Reactions at Metal Centres‡†

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Key findings regarding the effects of ligand preorganisation *via* halogen bonding on the outcome of reactions at rhodium are reported. An unprecedented halogen bonding-mediated oxidative addition of C_{Ar}–I bonds to rhodium with efficient formation of cyclometallated species deserves special mention.

Non-covalent interactions are at the core of supramolecular chemistry.[1,2] Whilst interactions such as hydrogen bonding,[2b] ionic,[2c-g] metal-ligand,[2h-j] anion-π[3] or cation-π[4] interactions have been widely exploited, non-conventional interactions such as halogen,[5] chalcogen,[6] pnictogen[7] or tetrel bonding[8] have been less extensively studied.[9] Of the latter interactions, halogen bonding has recently gained importance due to its inherent supramolecular directionality and strength that is independent of solvent polarity.[5] In contrast to the numerous reports of halogen bonding applied to crystal engineering or functional materials,[10] its application to solution chemistry has progressed at a much slower pace and mainly involves molecular recognition events,[11] organocatalysis[11] and, to a lesser extent, transition metal based catalysis.[12,13] Our group has pioneered the use of halogen bonding as the driving force to construct the backbone of rhodium chelates.[12] As indicated in Scheme 1, our approach relies on the halogen-bond-mediated assembly of a metal centre and two suitably engineered building blocks (each of which incorporates an appropriate halogen-bond donor and acceptor group, respectively, together with a P-based ligating group for the metal centre). We successfully used the resulting rhodium complex **XBphos-Rh** as an efficient catalyst for the hydroboration of terminal alkynes.[12] This breakthrough in the use of halogen bonding for easily constructing metal catalysts prompted us to further explore the use of this interaction for influencing the coordination sphere at the metal centre. By expanding the structural diversity of our approach, we aimed to gain new insights into the reactivity of these complexes and induce transformations at the metal that would not take place in the absence of halogen bonding. Herein, we report our work on the formation of five- and six- coordinate rhodium complexes, in which halogen bonding drives ligand preorganisation and determines the structure of the final products.

The underlying strategy for the preparation of **XBphos-Rh**, relied on the *in situ* preparation of a putative $[Rh(CO)_2]X$ intermediate from $[Rh(Cl)(CO)_2]_2$ and a halide scavenger (*i.e.* NaBArF). Although this strategy proved to be useful for the preparation of four-coordinate rhodium complexes such as **XBphos-Rh**, herein we broaden our approach to include a wider array of rhodium precursors.

We began by studying $[Rh(nbd)_2]BF_4$ as the rhodium precursor in the complexation reaction, since phosphorus-containing complexes derived from this cationic metal precursor have found wide application in pivotal organic transformations[14] such as (enantioselective) hydrogenations.[15] When an equimolar mixture of ligands **1** and **2** were added to stoichiometric amounts of $[Rh(nbd)_2]BF_4$, heterocomplex $[Rh(nbd)(\textbf{1})(\textbf{2})]BF_4$ **3** was isolated in 90% yield (Scheme 2, *top*). X-ray analysis confirmed the structure of the rhodium complex derived from **1** and **2** (Scheme 2, *bottom*) as a 5-coordinate square-pyramidal complex. In addition to a coordinated norbornadiene unit, X-ray analysis also revealed

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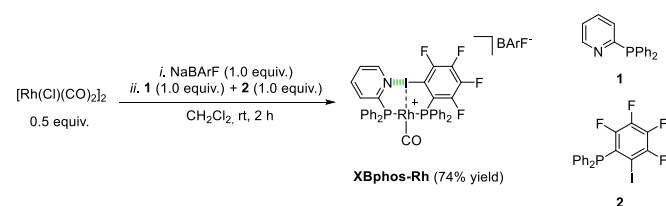*[c]LPCNO, INSA-Toulouse, 135 Avenue de Rangueil, F-31077 Toulouse, France.*
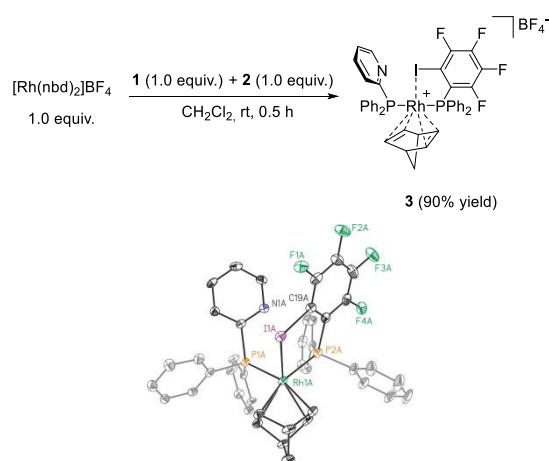*[d]ICREA, Pg. Lluís Companys 23, 08010 Barcelona, Spain.*
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Scheme 1. Supramolecular halogen-bonded **XBphos-Rh** catalyst.

Scheme 2. *Top:* Preparation of [Rh(nbd)(**1**)(**2**)]BF$_4$ complex **3**. *Bottom:* X-Ray structure of **3** with hydrogen atoms and the BF$_4^-$ unit having been omitted for the sake of clarity. Colour scheme: C: black, P: orange, Rh: green, F: green, N: blue, I: purple. Atomic displacement ellipsoids are drawn at a 50% probability.

Scheme 3. *Top*: reaction of ligands **1** and **2** with [Rh(acac)(CO)$_2$]. *Bottom*: reaction of ligand **1** with complex **5**.

phosphines **1** and **2** coordinated in a relative *cis*-arrangement as well as a I–Rh interaction in the apical position (2.7726(5) Å). This arrangement of the P-ligands containing the halogen-bond donor and acceptor motifs in the slightly distorted square-pyramidal environment (P–Rh–P angle = 95.31(5)°) does not allow the required linear N···I–C alignment for effective halogen bonding (N···I–C angle = 59.1(2)°). However, preorganisation of ligands **1** and **2** *via* halogen bonding interactions (*i.e. in situ* formation of supramolecular bisphosphine **1·2**) before coordination to the rhodium centre accounts for the high selectivity obtained in the formation of heterocomplex [Rh(nbd)(**1**)(**2**)]BF$_4$ **3** (90% yield), with the corresponding homocomplexes not being detected.[16] These observations are in agreement with the results of DOSY experiments of ligands **1**, **2** and a 1:1 mixture of **1** and **2**, in which the value of the diffusion coefficient of the ligand mixture is lower than the same values for free ligand **1** or **2**. A lower diffusion coefficient is associated to a larger molecular size, thus pointing to a favourable halogen-bond-mediated assembly of the two ligands in solution (see ESI†).

We then turned our attention to the use of [Rh(acac)(CO)$_2$] as the rhodium precursor. The combination of this derivative and P-ligands has been widely employed to generate active hydroformylation catalysts.[17] In this case, when an equimolar mixture of ligands **1** and **2** was added to stoichiometric amounts of [Rh(acac)(CO)$_2$], ^{31}P{^{1}H} NMR analysis showed that complex [Rh(acac)(CO)(**1**)] **4** was formed, with iodo-substituted phosphine **2** remaining uncoordinated (Scheme 3, *top*). Therefore, we envisaged that a stepwise coordination protocol using first ligand **2** followed by phosphine **1** could lead to the target complex [Rh(acac)(**1**)(**2**)]. The reaction between [Rh(acac)(CO)$_2$] and ligand **2** efficiently led to complex [Rh(acac)(CO)(**2**)] **5**, which was successfully isolated. Unfortunately, the reaction of **5** with equimolar amounts of the ligand **1** led to complex **4** (Scheme 3, *bottom*) by ligand displacement. The halogen bonding interaction between ligands **1** and **2** does not appear to be strong enough to displace the acetylacetonate ligand. Furthermore, the lower
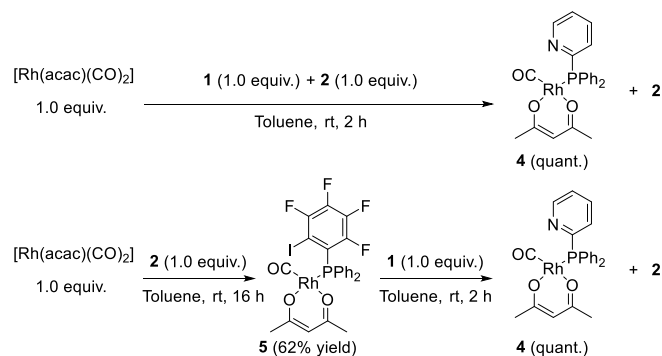
donicity of the P-electron pair in **2** (see ESI† for the determination of the Tolman electronic parameter[18] and the percent buried volume[19]) compared to **1** ensured that **2** remained uncoordinated.

We then moved to the [Rh(acac)(C$_2$H$_4$)$_2$] precursor,[20] with the reasoning that the ethylene ligands would be more labile and thus more readily displaced by the supramolecular phosphine assembly compared to carbonyl ligands. Interestingly, the reaction of [Rh(acac)(C$_2$H$_4$)$_2$] with phosphines **1** and **2** led to complex **6** that incorporated both phosphines and an acetylacetonate unit. A closer inspection of the NMR spectral data pointed to the formation of a Rh(III) complex in which a C–I oxidative addition process had taken place (Scheme 4, *left*). Single crystals of complex **6** suitable for X-ray analysis were obtained and the structure of the Rh(III) complex was confirmed (Fig. 1a). Indeed, it is reported in the literature that *ortho*-haloarylphosphines such as **2** undergo oxidative addition (OA) processes with rhodium (and other transition metals) at high temperatures or under UV/Vis irradiation.[21] According to these literature reports, the mild conditions employed in the complexation reaction of [Rh(acac)(C$_2$H$_4$)$_2$] with **1** and **2** should not favour the C$_{Ar}$–I oxidative addition process.[22] However, as we observed OA even at 25 °C, we wondered whether ligand preorganisation around the rhodium centre due to halogen bonding between **1** and **2** could be facilitating the OA process.

It has been demonstrated for ligands **1** and **2** that the geometry of the resulting complexes depends on the nature of the precursor. Moreover, the iodine atom is coordinated to the metal centre in both **XBphos-Rh** and **3**. In the case of six-coordinate complex **6**, we reasoned that a transient N···I–C alignment *via* halogen bonding with simultaneous coordination of the I-atom to the rhodium centre could be taking place, ultimately favouring the oxidative addition of the C–I bond to the electron-rich rhodium centre. To support this statement, we decided to study the interplay between [Rh(acac)(C$_2$H$_4$)$_2$], ligand **2** and 3-pyridyldiphenyl-phosphine **7**, where alignment of the N···I–C atoms with simultaneous coordination of the P-ligating groups is not possible. Therefore, oxidative addition using ligand **7** should be disfavoured with respect to the same process employing halogen-bond complementary ligand **1**. Unlike in the case of the reaction of **1** with **2**, where chemoselective formation of the oxidative addition Rh(III) complex **6** was observed, the reaction of **7** and
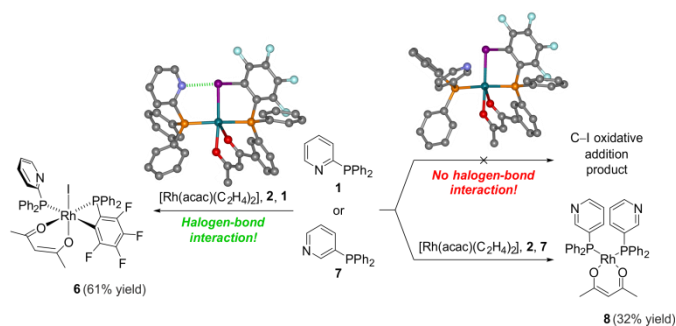
Scheme 4. Reactivity of 2-iodo-3,4,5,6-tetrafluorophenyldiphenylphosphine **2** and [Rh(acac)(C₂H₄)₂] with 2-pyridyldiphenylphosphine **1** and 3-pyridyldiphenylphosphine **7**.

2 led to homocomplex **8** (Scheme 4, *right*) with no traces of the OA product being detected by NMR analysis. To further demonstrate the influence of halogen bonding in this transformation, we monitored both complexation reactions by ^{31}P NMR spectroscopy. It is interesting to note that, whilst no heterocomplex for **7** and **2** was observed by ^{31}P NMR analysis, this technique clearly demonstrated the formation of rhodium species containing the halogen-bonded **1·2** assembly (see ESI† for details).

Theoretical calculations were also carried out in order to understand the selective formation of complex **6** (see ESI† for details). The examination of the reaction path reveals the formation an intermediate displaying a short and directional halogen bonding contact N···I–C (see Fig. 2a). In fact, the molecular electronic potential (MEP) surface of ligand **2** reveals the existence of a strong σ-hole (*ca.* 30 kcal·mol⁻¹, see Fig. SI 50) on the extension of the C–I bond. This halogen bonding interaction enlarges the C–I distance from 2.11 Å in the ligand to 2.14 Å in the intermediate thus facilitating the subsequent oxidative addition. Interestingly, the calculation of the equivalent intermediate using phosphine **7** (no halogen-bond is possible, see Fig. SI 51) is 6.9 kcal·mol⁻¹ less stable, thus explaining the absence of oxidative addition reaction (see Scheme 4). The TS structure is characterised by a lengthening of the C$_{Ar}$–I bond (from 2.14 to 2.20 Å) as well as a shortening of the C–Rh distance (1.06 Å). The N···I–C halogen- bond is less directional and longer in the TS, but the interaction still exists as evidenced by the non-covalent interaction plot (NCIplot, see Fig. SI 52). Overall, these results illustrate that the combined use of an electron-rich metal precursor such as [Rh(acac)(C₂H₄)₂] together with complementary ligands **1** and **2**
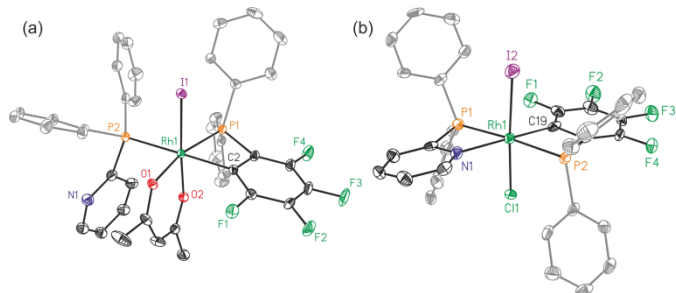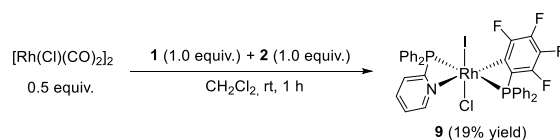

Fig. 1. Crystal structures of **6** (a) and **9** (b). Hydrogen atoms have been omitted for the sake of clarity. For the colour scheme, see caption to Scheme 4.

Scheme 5. Preparation of complex **9**.

efficiently leads to a new class of cyclometallated rhodium(III) complexes.[23]

Analogous behaviour was observed for the reaction between **1** and **2** and [Rh(Cl)(CO)₂]₂ in the absence of a halide scavenger.[12] In this case, the CO ligands were preferentially displaced by phosphines **1** and **2**. The complementarity of the halogen-bonded complex **1·2** for simultaneous complexation of the two phosphine groups to the rhodium centre and the absence of strong pi-backbonding carbonyl ligands facilitated the formation of complex **9** arising from coordination of the P-atoms and a C$_{Ar}$–I oxidative addition process. The structure of the final complex was determined by standard spectroscopic techniques and confirmed by X-ray analysis (Scheme 5 and Fig. 1b). Interestingly, the pyridine group is coordinated to the rhodium centre with the two halogen ligands placed axially and the two phosphino groups coordinated in a *trans*-arrangement.[24]

In conclusion, these results illustrate how the careful selection of the rhodium precursor and the geometry of the halogen-bond donor and acceptor ligands determines the outcome of the Rh–P complexation chemistry, either to P–I–P pincer-like Rh(I) complexes with a permanent halogen bonding interaction (**XBphos-Rh**),[12] or to the P–P Rh(III) complexes described in this work that arise from an unprecedented halogen-bond-driven C$_{Ar}$–I oxidative addition process. It has been both experimentally and computationally demonstrated that the N···I-halogen-bond interaction and the electron density at the metal centre are key factors that control the reactivity towards oxidative addition processes as observed in
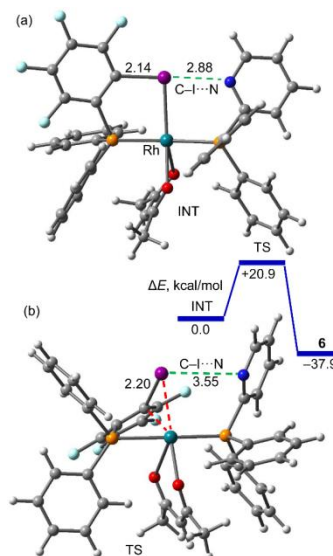

Fig. 2. M06-2X/LANL2DZ optimised structures of the intermediate and transition state to yield **6**. Distances in Å. Halogen bonds are represented by green dashes.

6 and 9. Selectivity in the primary sphere coordination chemistry at rhodium has also been controlled by employing building blocks 1 and 2. Ligand preorganisation by *in situ* formation of supramolecular halogen-bonded complex 1·2 appears to translate to a selective formation of complex 3. Further work is currently underway to study the application[23] and catalytic activity of these new complexes, to ultimately set the basis for the use of halogen bonding in transition metal chemistry and catalysis.

Conflicts of interest

There are no conflicts to declare.

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