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Cationic PCP iridaepoxide and carbene complexes for facile water elimination and activation processes †

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Iridaepoxide dihydride complexes of a PCP ligand bearing benzo[*b*]thiophene linkers are synthesized through ligand coopertive N₂O and H₂ activations. These neutral complexes also eliminate water at elevated temperatures to form the corresponding $PC_{carbene}P$ complexes which results in the formal hydrogenation of N₂O to water. The synthesis of cationic iridaepoxide dihydride complexes are reported herein where the room temperature elimination of water is observed when a donating solvent is used. This supports a previously proposed mechanism for this water elimination where hydrides *cis* to the epoxide are required. Ir(i) and Ir(iii) cationic $PC_{carbene}P$ complexes are also synthesized through protonation and through O–H oxidation additions of water and phenol.

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Introduction

Tridentate pincer ligands have become ubiquitous in transition metal catalysis,¹ having near endless potential for steric and electronic modifications with capability for supporting elements across the periodic table. Strategic ligand design has led to extensive use of cooperative ligands, resulting in efficient small molecule activations and selective bond transformations.²⁻⁴ Incorporating metal carbene bonds into traditional PCP frameworks has proven to be advantageous for difficult small molecule activations.⁵⁻⁹ Recently, we have reported the synthesis of diaryl $\ensuremath{\text{PC}_{\text{carbene}}}\xspace{\text{P}}$ ligands bearing electron-rich dialkylphosphine donors.¹⁰ These ligands, bearing an array of aryl linkers (I and II, for example), have now been installed on iridium,^{11–14} rhodium,¹⁵ nickel^{16,17} and palladium,18-20 and have demonstrated several challenging bond activations including the heteroatom-H bonds of water, alcohols, ammonia and silanes as well as the reversible addition of H₂.

Taking advantage of this metal-ligand cooperativity, N₂O has been activated across this carbon-iridium bond to afford new "iridaepoxide" (1-Cl, Scheme 1) complexes with the release of N_2 gas.^{12,13} For ligands I bearing no linker (Z = H, H) these iridaepoxides underwent decomposition processes involving C-C bond cleavages in the pincer ligand framework¹³ but by employing a linker (Z = O) or the rigid benzo[b]thiophene groups in the pincer ligand backbone (II) extensive reactivity studies on the reactions of these iridaepoxide complexes with hydrogen has been possible.²¹ These studies have revealed a rapid label scrambling process when a mixture of hydrogen and deuterium are introduced and, at elevated temperatures, water elimination from the dihydride complex 2-Cl, regenerating the carbene moiety 3-Cl. It has been proposed that these processes both occur through pathways that involve ligand cooperativity at the carbene moiety (Scheme 1).²¹

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[†]Electronic supplementary information (ESI) available: Description of general methods, Fig. S1–S24 and crystallographic data for **2-NTf₂**, **4-Cl** and **6-acetone**. CCDC 1530796 and 1530797. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt00563f



Scheme 1 Hydrogenation of N_2O to H_2O and N_2 through epoxy dihydride intermediates.

Paper

In a recent report,¹² data was presented that indicated the major barrier towards water elimination from the epoxy dihydride complex 2-Cl was the need to generate the kinetic dihydride isomer 2'-Cl, which has the appropriate geometry (*i.e.*, the hydrides *cis* to the iridaepoxide oxygen) for O-H bond formation and water elimination. This isomerization from the thermodynamic isomer to the kinetic isomer occurs through hydrogen elimination from the former, requiring elevated temperatures. It is thus logical to suggest that if the competition between these two isomers were to be removed, the barrier for water elimination would be lowered considerably. The synthesis of a cationic epoxy dihydride complex was therefore targeted wherein a halide abstracting agent could be used to remove the chloride ligand in 2-Cl resulting in a cationic species, preferably with a weakly coordinating anion. Exploring cationic iridium carbene complexes is also of interest due to their differing reactivity as compared to their neutral counterparts.²²⁻²⁴ Herein we describe the reactions of 2-Cl with various chloride abstracting agents and the behaviour of the resulting cationic complexes.

Results and discussion

Dihydride complex 2-Cl was reacted with a number of different halide abstracting agents $(NaB(Ar^{F})_{4} (Ar^{F} = 3,5-bis(trifluoro$ methyl)phenyl), AgBPh₄, $[CPh_3][B(C_6F_5)_3]$, $B(C_6F_5)_3$), with mixed results. However, addition of one equivalent of Me₃SiNTf₂ to 2-Cl at -20 °C led immediately and cleanly to the formation of a single product. The NMR spectroscopic signatures of this product pointed to the formation of a carbene species rather than an epoxy dihydride complex. This was not entirely surprising considering the previously reported²¹ reactivity of iridaepoxide 1-Cl with Me₃SiOTf to form an Ir(III) chloro bis(triflate) carbene complex. While in that case, two equivalents of Me₃SiOTf were required, resulting in O(SiMe₃)₂ as the byproduct, here dihydride 2-Cl reacts quantitatively with one equivalent of Me₃SiNTf₂. The product of this reaction exhibits a singlet in the ¹H NMR spectrum that ranges from 3 to 6.5 ppm and a broad hydride signal that appears between -19and -27 ppm (Fig. S1[†]). A broad resonance in the ${}^{31}P{}^{1}H{}$ NMR spectrum ranges from 40 to 52 ppm. These key chemical shifts observed for the product of this reaction are thus extremely sensitive to small changes in concentration, temperature and how much Me₃SiNTf₂ or byproduct is present in solution.

Initially, we hypothesized that the product was the five coordinate hydrido hydroxo complex (4-OH, Scheme 2) and that the signal between 3 and 6.5 ppm corresponded to the OH proton. When the product was isolated, however, this signal disappeared and any further reactivity led to complexes bearing chloride ligands. It is therefore proposed that rather than 4-OH, a hydrido chloride carbene product 4-Cl is formed upon reaction of 2-Cl with Me₃SiNTf₂. The byproduct of this reaction is the volatile Me₃SiOH, accounting for the signal at 3–6.5 ppm that disappeared when the solvent was removed *in vacuo* upon isolation. It is not clear from these data whether



Scheme 2 Synthesis of compounds 4-Cl and 5 through multiple pathways.

this reaction proceeds through a hydrido hydroxo intermediate (4-OH) followed by reaction with the Me₃SiCl byproduct (Scheme 2), or through an alternative pathway involving direct interaction between the epoxide oxygen and the Me₃Si group. To ensure that the chloride source was in fact Me₃SiCl (or originating from 2-Cl) and not the CH₂Cl₂ solvent, the reaction was repeated using acetone- d_6 as the solvent, leading to the same result.

The cationic hydrido chloride carbene complex 4-Cl can also be synthesized through protonation of carbene chloride 3-Cl with HNTf₂. Furthermore, when reacted with triethylamine, 4-Cl is easily deprotonated to regenerate carbene chloride 3-Cl. In a CH₂Cl₂ solution at room temperature, this protonation occurs immediately with a colour change from deep brown to deep red-pink. Here, broad hydride and phosphorus resonances appear at -27.75 and 52.5 ppm in the ¹H and ³¹P{¹H} NMR spectra, respectively. Additionally, a diagnostic carbene signal appears at 224.2 ppm in the ¹³C¹H NMR spectrum and a sharp singlet is present at -78.53 ppm in the ¹⁹F NMR spectrum. The chemical shifts in this reaction vary somewhat based on concentration and stoichiometry of HNTf₂, but not as severely as described above for the products of reaction of **2-Cl** and Me₃SiNTf₂. The broadness of the ${}^{31}P{}^{1}H{}$ and hydride NMR signals are consistent with the fluxional behaviour expected (and previously observed¹⁰) in such five-coordinate iridium complexes. Additionally, the presence of a single sharp resonance observed in the ¹⁹F NMR spectrum of 4-Cl suggests that in solution, the NTF₂ anion is at most weakly interacting with the metal center in solution. When the NMR spectra of 4-Cl were acquired at temperatures as low as -75 °C, the hydride and ³¹P{¹H} resonances became sharper and shifted moderately with temperature (Fig. S2[†]). X-ray crystallographic data was obtained for complex 4-Cl, indicating that in the solid state the NTf2 anion coordinates to the iridium center through an oxygen atom (Fig. S3[†]). Only connectivity information could be gathered from this structure, however, due to incomplete data collection, but the formulation of the complex as 4-Cl was confirmed.

When this fluxional species was reacted with a chloride source, such as tetrabutylammonium chloride, an anion exchange took place, resulting in a sharpening of all NMR spectra and formation of an Ir(III) carbene hydrido dichloride complex 5 (Scheme 2). A clear triplet $({}^{2}J_{HP} = 11.8 \text{ Hz})$ integrating to ¹H is present in the hydride region of the ¹H NMR spectrum at -13.31 ppm in addition to a diagnostic carbene signal at 220.6 ppm in the ¹³C{¹H} NMR spectrum. The geometry of complex 5 as assigned in Scheme 2 with the hydride ligand trans to a chloride rather than the carbene moiety is consistent with expectations based on the trans directing properties of the ligands involved and is further supported by an asymmetric pattern of resonances in the ¹H NMR spectrum corresponding to the iso-propyl groups of the ligand. Complex 5 can also be formed through reaction of carbene chloride 3-Cl with one equivalent of HCl from a 4 M dioxane solution. This conversion occurs cleanly and quantitatively resulting in the same spectroscopic features as 5.

Given the complications arising from the oxophilicity of the Me₃Si electrophile and/or the non-innocence of the Me₃SiCl by-product, AgNTf₂ was explored as an alternative halide abstracting agent for 2-Cl. The AgCl byproduct of this reaction should precipitate out of solution and not interfere with further chemistry. Accordingly, reaction of 2-Cl with one equivalent of AgNTf₂ resulted in the room temperature, quantitative conversion to a single new product, identified as an epoxy dihydride triflimide complex 2-NTf₂ (Scheme 3). ¹H and ³¹P{¹H} NMR spectroscopy indicate that a new dihydride species was formed cleanly as evidenced by two new resonances in the hydride region at -7.05 and -20.16 ppm and a modest shift from 24.5 for 2-Cl¹² to 32.0 ppm in the ³¹P{¹H} NMR spectrum. It should be noted that the phosphorus and hydride signals were significantly broadened, likely indicating dynamic behaviour. In addition, the ¹⁹F NMR spectrum exhibits two broad signals at -77.97 and -79.67 ppm. The presence of two signals in the 19F NMR spectrum is characteristic of an oxygen-bound NTf₂ ligand, rendering the two CF₃ groups inequivalent. The lability of this bond is likely responsible for the observed broadness of the NMR spectra. Furthermore, the



Scheme 3 Halide abstraction from 2-Cl to form cationic epoxy dihydride complexes followed by room temperature water elimination.

 CF_3 carbon resonances are not observable in the ${}^{13}C{}^{1}H$ NMR spectrum, likely due to broadening of the inequivalent quartets. The ${}^{13}C{}^{1}H$ NMR chemical shift for the iridaepoxide carbon appears at 114.2 ppm which is somewhat downfield from that of the chloride derivative at 99.5 ppm. 12 This is consistent with the downfield shifts observed for the carbone resonances on going from neutral to cationic species.

The structure of **2-NTf**₂ was confirmed by X-ray crystallography as shown in Fig. 1. In the solid state, the NTf₂ ligand is indeed coordinated to iridium through an oxygen atom,^{25,26} and the Ir1–O2 bond distance of 2.259(2) Å is longer than any of the other Ir–O bonds observed crystallographically thus far with this ligand framework, ranging from 2.157(3) to 2.200(4) Å.^{12,21}

While the dihydride complex $2-NTf_2$ appears to be contact ion pair in solution, the greater lability of this ion in comparison to chloride should lower the barrier to water elimination by providing an alternate pathway to the required O-H bond forming reaction necessary. Accordingly, the tendency of 2-NTf₂ to eliminate water was explored. At room temperature, 2-NTf₂ is stable indefinitely in solutions of CD_2Cl_2 or $C_6D_5Br_1$, but when dissolved in the more polar, donating solvent acetone- d_6 , slow conversion to a new carbene product is observed at room temperature over the course of ca. 16 hours. This new carbene species was identified as the Ir(I) acetone adduct 6-acetone shown in Scheme 3. This complex is only moderately stable in solution and decomposes over the course of several hours to a mixture of unidentified products. This is likely due to the accessibility of a 14 electron Ir(I) fragment, which are known to be highly reactive and unstable,²⁷⁻³¹ through dissociation of acetone from 6-acetone. Full NMR spectra of 6-acetone could be obtained before decomposition



Fig. 1 Molecular structure of **2-NTf**₂. Iso-propyl carbon atoms and all hydrogen atoms except for H0 and H1 have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ir(1)-P(1), 2.3094(9); Ir(1)-P(2), 2.3306(9); Ir(1)-C(9), 2.157(3); Ir(1)-O(1), 2.157(2); Ir(1)-O(2), 2.259(2); C(9)-O(1), 1.305(4). Selected bond angles (°): C(9)-Ir(1)-O(1), 35.2(1); C(9)-O(1)-Ir(1), 72.4(2); Ir(1)-C(9)-O(1), 74.2(2); C(9)-Ir(1)-O(2), 120.4(1); P(1)-Ir(1)-P(2), 165.20(3).

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however, and exhibit typical features of a C_{2v} symmetric molecule as well as a singlet at 43.7 ppm in the ³¹P{¹H} NMR spectrum. The ¹³C{¹H} signals corresponding to the coordinated acetone ligand could not be identified, likely due to rapid exchange with free acetone. Additionally, the structure of **6-acetone** was determined *via* X-ray crystallography; the molecular structure of this species is shown in Fig. 2, along with selected metrical data. Finally, a spectroscopically identical species was generated when a solution of carbene chloride **3-Cl** in acetone-*d*₆ was reacted with AgNTf₂ at room temperature (Scheme 3); leaving this reaction mixture in solution at room temperature led to the same mixture of decomposition products as mentioned above.

The room temperature conversion of **2-NTf**₂ to **6-acetone** is presumably accompanied by loss of one equivalent of H₂O, although definitive proof of this was not obtained. It is possible that the eliminated water is involved in the undefined decomposition vectors **6-acetone** undergoes. Assuming that water is eliminated in this conversion, it occurs under much milder conditions than previously observed for **2-Cl**,^{12,21} suggesting that the rate limiting step for water loss becomes dissociation of the weakly coordinating anion, rather than loss of H₂ from **2-Cl**.

The conversion of **2-NTf**₂ to **6-acetone** with loss of water may proceed through the cationic hydrido hydroxo species **4-OH**, depicted in Scheme 2. We thus sought other ways to generate this potentially key species. Considering the facile protonation of carbene chloride **3-Cl** to form the cationic hydrido chloride complex **4-Cl** (Scheme 2), we hypothesized that protonation of the previously described²¹ carbene hydroxo

complex 3-OH might be an alternate route to generate 4-OH. The room temperature addition of HNTf2 to a solution of carbene hydroxo 3-OH in acetone- d_6 immediately led to a colour change from deep brown to deep red/pink and complete conversion to a new product was evidenced by a shift from 34.6 to 43.6 ppm in the ${}^{31}P{}^{1}H$ NMR spectrum. The ${}^{1}H$ and ³¹P{¹H} NMR spectroscopic signatures of this new product match exactly with those of adduct 6-acetone, as described above, with an additional singlet at 3.74 ppm in the ¹H NMR spectrum attributed to the loss of a water molecule. Here, it is likely that protonation of 3-OH led to the formation of a cationic aquo complex (6-H₂O, Scheme 4) followed by a rapid exchange of the L donor in the acetone solvent. It is not clear whether or not direct protonation of the hydroxo group occurs, or whether kinetic protonation at the iridium center precedes formation of 6-H₂O but the clean formation of 6-acetone is the ultimate result.

When this same protonation reaction was performed in CD_2Cl_2 rather than acetone- d_6 , a very different result was observed. Upon addition of HNTf2 to carbene hydroxo 3-OH dissolved in degassed CD₂Cl₂ that has not undergone any drying procedure ("wet" CD₂Cl₂), rapid conversion to a new species with a broad resonance at 38.4 ppm in the ${}^{31}P{}^{1}H{}$ NMR spectrum took place. Interestingly, the ¹H NMR spectrum (Fig. S4^{\dagger}) features a broad hydride signal at -20.74 ppm as well as two broad signals at 4.60 and 5.06 ppm. When this product is cooled to -55 °C, the broad signals in the ¹H and ³¹P{¹H} NMR spectra become somewhat sharper. Most notably, phosphorus coupling to the hydride signal becomes apparent as a triplet (${}^{2}J_{PH}$ = 13.2 Hz) is resolved. When performed in carefully dried CD2Cl2, this reaction was not as clean, resulting in the formation of three very broad resonances in the ³¹P{¹H} NMR spectrum. These results are consistent with protonation of 3-OH at the iridium center to form 4-OH, which is trapped with another molecule of water present in the "wet" CD₂Cl₂ to form a six coordinate species formu-



Fig. 2 Molecular structure of **6-acetone**. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Ir(1)-P(1), 2.305(1); Ir(1)-P(2), 2.304(1); Ir(1)-C(9), 1.901(3); Ir(1)-O(1), 2.125(2); O(1)-C(31), 1.236(4). Selected bond angles (°): C(9)-Ir(1)-O(1), 178.4(1); Ir(1)-O(1)-C(31), 135.2(2); P(1)-Ir(1)-P(2), 170.97(3).



Scheme 4 Protonation of 3-OH with $HNTf_2$ in acetone- d_6 or wet CD_2Cl_2 .

lated as III, Scheme 4. A related aquo cation was previously synthesized through the addition of two equivalents of HOTf to the iridaepoxide 1-Cl.^{12,21} This product was structurally characterized as an octahedral chloro triflate aquo complex with a second triflate group as the counter anion. Unfortunately, all attempts to isolate these compounds led to decomposition and so they were only characterizable via in situ spectroscopy.

Although neither 4-OH nor its aquo adduct III could be isolated, their assignment is corroborated by the fact that spectroscopically similar species can be obtained by generating a highly reactive 14-electron PCcarbeneP iridium fragment in the presence of water. A similar strategy was employed by Jensen et al. to achieve water activation in a PCP iridium pincer complex.²⁷ When AgNTf₂ is slowly added to a solution of carbene chloride 3-Cl in dry CD₂Cl₂ at -20 °C, no colour change from deep brown is observed but the NMR spectra (Fig. S5–S7[†]) did show quantitative conversion to a new C_{2v} symmetric compound within 5 minutes. The ³¹P{¹H} NMR spectrum features a somewhat broadened resonance at 45.5 ppm and a single resonance is observed in the ¹⁹F NMR spectrum at -79.52 ppm. This new complex is assigned as the carbene triflimide complex 3-NTf₂ (Scheme 5) where the NTf_2 ligand is weakly coordinated to the iridium center. If left in solution, this complex decomposes over the course of a few hours. Due to this decomposition, only a low quality ${}^{13}C{}^{1}H{}$ NMR spectrum could be obtained, where the carbene carbon as well as most splitting patterns could not be identified.

When wet, rather than dry, CD₂Cl₂ was used in this reaction (Scheme 5), the addition of $AgNTf_2$ resulted in a rapid colour change from deep brown to deep red/pink. The ${}^{31}P{}^{1}H$ NMR spectrum showed some unreacted 3-NTf₂ as well as a number of other unidentified products, including a broad resonance at 39.9 ppm as well as a broad hydride signal in the ¹H NMR spectrum at -24.97 ppm. The NMR chemical shifts of these signals vary each time the reaction is repeated, likely due to varying amounts of water present. Considering that no hydride



Scheme 5 Synthesis of 3-NTf₂ and addition of water to form 4-OH.

signals were observed while monitoring the decomposition of dry 3-NTf₂ over time, it appears as though a water molecule is being activated resulting in a hydride product,³²⁻³⁴ albeit not very cleanly. The addition of excess (ca. 10 equivalents) degassed water to a sample of 3-NTf₂ in CD₂Cl₂ led to a cleaner mixture of three products as shown in the ${}^{31}P{}^{1}H$ NMR spectrum. A signal at 37.0 ppm in the ³¹P{¹H} NMR spectrum corresponds to a triplet $({}^{2}J_{HP} = 12.6 \text{ Hz})$ at -20.33 ppm inthe hydride region of the ¹H NMR spectrum. Immediately after mixing, this product accounted for ca. 40% of the observed products, based on integration of the ${}^{31}P{}^{1}H$ NMR spectrum (Fig. S8[†]). After 24 hours at room temperature however, the signal at 37.0 ppm as well as the hydride resonance disappeared. The spectroscopic details of these reactions are very close to those observed during the protonation reaction of carbene hydroxo 3-OH with HNTf2 and these observations suggest that addition of H2O to 3-NTf2 to give 4-OH/III is reversible.

The drifting in the chemical shifts of the key resonances in 4-OH as described above likely arises from variability in the amount of water present in the different experiments. In addition to affecting the position of the equilibrium with III, hydrogen bonding effects in the relatively non-polar solvent medium are expected to be significant with changing $[H_2O]$. Thus, although the spectroscopy is consistent with the notion that protonation of 3-OH and water addition to 3-NTf₂ give the same species (Schemes 4 and 5), the variability in the chemical shifts with minor changes in water concentration render these observations admittedly somewhat inconclusive. Accordingly, we sought to demonstrate the activation of another O-H bond and chose that of phenol, since primary alcohols would lead to alkoxy hydrides susceptible to well-known \beta-hydride elimination and decarbonylation processes.^{30,35,36} Reacting phenol at -20 °C with 3-NTf₂, formed *in situ* with AgNTf₂, again led to an immediate colour change from deep brown to deep red/ pink. In this case, only one product was observed by NMR spectroscopy and it has been assigned as the hydrido phenoxide cation 4-OPh (Scheme 6). The ³¹P{¹H} NMR spectrum exhibits a broad signal at 51.4 ppm, characteristic of a fluxional five coordinate complex. Also, the ¹⁹F NMR spectrum features a sharp singlet at -80.4 ppm indicating that the NTf₂ anion is likely not coordinated to the iridium centre in solution. The ¹H NMR spectrum, as shown in Fig. S9,† features the expected phenoxide resonances as well as a broad hydride signal at -27.64 ppm. Additionally, a characteristic carbene signal appears at 224.1 ppm in the ${}^{13}C{}^{1}H$ NMR spectrum. Elemental analysis and HRMS could not be obtained for this compound, but further evidence for this assignment could be found in the reactivity of carbene phenoxide 3-OPh. This phenoxide derivative was synthesized separately through salt metathesis of 3-Cl with NaOPh and fully characterized. When **3-OPh** was reacted with $HNTf_2$ in CD_2Cl_2 at room temperature, two products containing hydrides were observed in the ¹H and ³¹P{¹H} NMR spectra. One of these products, amounting to 63% of the mixture matches the spectroscopic signatures of the hydrido phenoxide 4-OPh. Furthermore, when this reaction



was performed in acetone- d_6 , a process analogous to that described in Scheme 4 took place. Here, the acetone adduct **6-acetone** was identified by ¹H and ³¹P{¹H} NMR spectroscopy as well as free phenol at 7.18, 6.81 and 3.79 ppm in the ¹H NMR spectrum in acetone- d_6 . The formation of **6-acetone** accounted for 42% of the product formed in this reaction in addition to two other unidentified products, neither of which appear to contain hydride ligands.

Thus, the O–H bond of phenol undergoes a clean oxidative addition to **3-NTf**₂. A similar oxidative addition of phenol was reported by Nozaki and coworkers³⁷ using a PBP rhodium complex stabilized only by an intermolecular C–H σ -coordination. This system is comparable to **3-NTf**₂ where the active 14-electron species is readily available through the displacement of a weakly-coordinating ligand. It is notable that the O–H oxidative additions described herein, and by Nozaki, occur rapidly at low temperatures. This is in contrast to a 1993 report by Merola *et al.*.³⁵ where oxidative addition of phenol to [IrCOD(PMe₃)₃][Cl] (COD = cyclooctadiene) took place. In this case, heating to 60 °C for three hours was required for full conversion, as removal of the COD ligand was necessary for further reactivity.

Conclusions

The elimination of water from the iridaepoxide 2-Cl was hampered by the need for access to the kinetic isomer (2'-Cl) to facilitate O–H bond formation (Scheme 1^{12,21}). Since 2-Cl was prepared from N₂O oxidation of the carbene chloride 1-Cl, this sequence was in principle a novel ligand cooperative mechanism for homogeneous N₂O reduction to water.^{38–41} In order to find lower barrier pathways to water elimination from 2-Cl, we have studied here the chemistry of analogs of 2-Cl with more weakly coordinating anions that would provide access to lower coordinate cationic iridaepoxide dihydrides. The NTf₂ anion provides the right balance between lability and coordinative stability and when dissolved in a donating solvent, the elimination of water from 2-NTf₂ occurred at room temperature over several hours as opposed to temperatures above 100 °C for 2-Cl. These investigations also led to the formation of a series of Ir(I) and Ir(III) cationic carbene complexes, including the synthesis of a highly reactive iridium triflimide complex (3-NTf₂). The NTf₂ ligand is easily displaced in the presence of other small molecules resulting in Ir(I) cations with neutral L-donor capping ligands or Ir(III) cations formed through the O-H bond activation of water or phenol. Further investigations into the reactivity potential of 3-NTf₂ are an obvious extension of this work and are currently underway.

Experimental

For general experimental details, see the ESI.†

Synthesis of 2-NTf₂

AgNTf₂ (5 mg, 0.013 mmol) was added as a solid to a solution of 2-Cl (10 mg, 0.013 mmol) in CH₂Cl₂ in a J-Young NMR tube. Slowly there was a colour change from pale yellow to darker orange as well as formation of a precipitate. The reaction was left to mix for five hours at room temperature or until full conversion was observed by ³¹P{¹H} NMR spectroscopy. The solution was then filtered through Celite and the volatile components were removed in vacuo. The product was isolated as an orange/brown solid in 98% yield (13 mg, 0.013 mmol). ¹H NMR (500 MHz, CD₂Cl₂) δ 7.93 (m, 4H, ArH), 7.49 (m, 4H, ArH), 2.86 (m, 4H, CH(CH₃)₂), 1.44 (dvt, ${}^{3}J_{HH} = J_{HP} = 7.2$ Hz, 6H, CH(CH₃)₂), 1.38 (dvt, ${}^{3}J_{HH}$ = 6.8 Hz, J_{HP} = 9.3 Hz, 6H, CH $(CH_3)_2$, 1.24 (dvt, ${}^{3}J_{HH} = 7.4$ Hz, $J_{HP} = 8.5$ Hz, 6H, $CH(CH_3)_2$), 0.80 (dvt, ${}^{3}J_{HH} = 7.1$ Hz, $J_{HP} = 8.7$ Hz, 6H, CH(CH₃)₂), -7.05 (br s, 1H, IrH), -20.16 (br s, 1H, IrH). ¹³C{¹H} NMR (126 MHz, CD_2Cl_2) δ 157.7 (vt, J_{CP} = 10.0 Hz, aryl C), 143.1 (vt, J_{CP} = 4.3 Hz, aryl C), 138.1 (vt, J_{CP} = 2.0 Hz, aryl C), 132.0 (vt, J_{CP} = 18.6 Hz, aryl C), 126.4 (s, aryl CH), 126.3 (s, aryl CH), 124.6 (s, aryl CH), 124.0 (s, aryl CH), 114.2 (br s, C(O)Ir) 26.3 (vt, J_{CP} = 12.9 Hz, $CH(CH_3)_2$), 22.1 (vt, $J_{CP} = 17.9$ Hz, $CH(CH_3)_2$), 20.1 (s, CH(CH₃)₂), 19.4 (s, CH(CH₃)₂), 18.8 (s, CH(CH₃)₂), 18.4 (s, $CH(CH_3)_2$). Note: there was no evidence of a $N(CF_3SO_2)_2$ ¹³C signal. ³¹P{¹H} NMR (203 MHz, CD_2Cl_2) δ 32.0 (s). ¹⁹F NMR (471 MHz, CD_2Cl_2) δ -77.97 (br s), -79.67 (br s). HRMS (APCI) calculated C₂₉H₃₈IrOP₂S₂ (M): 721.1469, found 721.1491.

Synthesis of 3-OPh

NaOPh (3 mg, 0.027 mmol) was added as a solid to a solution of **3-Cl** (20 mg, 0.027 mmol) in CH₂Cl₂ (0.7 mL) and transferred to a J-Young NMR tube. The mixture was left to mix at room temperature for 36 hours after which full conversion to **3-OPh** was observed by ³¹P{¹H} NMR. The product was then filtered through Celite and the volatiles were removed *in vacuo*. The desired product was isolated at a dark brown solid in 97% yield (21 mg, 0.026 mmol). ¹H NMR (500 MHz, CD₂Cl₂) δ 8.64 (d, ³*J*_{HH} = 8.1 Hz, 2H, LigArH), 8.25 (t, ³*J*_{HH} = 7.6 Hz, 2H, LigArH), 7.50 (d, ³*J*_{HH} = 8.1 Hz, 2H, LigArH), 7.25 (t, ³*J*_{HH} = 7.6 Hz, 2H, LigArH), 6.98 (t, ³*J*_{HH} = 7.7 Hz, 2H, OPh ArH), 6.40 (t, ³*J*_{HH} = 7.2 Hz, 1H, OPh ArH), 5.92 (d, ³*J*_{HH} = 7.8 Hz, 2H, OPh

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ArH), 3.35 (septvt, ${}^{3}J_{HH} = 6.9 \text{ Hz}$, $J_{HP} = 1.6 \text{ Hz}$, 4H, CH(CH₃)₂), 1.40 (m, 24H, CH(CH₃)₂). ${}^{13}C{}^{1}H$ **NMR** (126 MHz, CD₂Cl₂) δ 187.0 (vt, $J_{CP} = 21.6 \text{ Hz}$, Lig aryl C), 174.4 (t, J = 2.3 Hz, Ir=C), 173.5 (s, OPh aryl C), 145.7 (vt, $J_{CP} = 3.8 \text{ Hz}$, Lig aryl C), 142.6 (vt, $J_{CP} = 1.3 \text{ Hz}$, Lig aryl C), 139.9 (vt, $J_{CP} = 17.6 \text{ Hz}$, Lig aryl C), 128.8 (s, OPh aryl CH), 127.6 (s, Lig aryl CH), 126.5 (s, Lig aryl CH), 126.0 (s, Lig aryl CH), 124.5 (s, Lig aryl CH), 122.7 (s, OPh aryl CH), 115.4 (s, OPh aryl CH), 23.7 (vt, $J_{CP} = 13.4 \text{ Hz}$, CH(CH₃)₂), 20.6 (s, CH(CH₃)₂), 20.2 (vt, $J_{CP} = 3.0 \text{ Hz}$, CH(CH₃)₂). ³¹P{¹H} NMR (203 MHz, CD₂Cl₂) δ 38.3 (s). HRMS (APCI) calculated C₃₅H₄₁IrOP₂S₂ (M + H)+: 797.1776, found 797.1808.

Synthesis of 3-NTf₂

2-Cl (20 mg, 0.027 mmol) was dissolved in ca. 0.5 mL CH₂Cl₂ and cooled to -20 °C in the freezer. A solution of AgNTf₂ (11 mg, 0.027 mmol) in ca. 0.5 mL CH₂Cl₂ was also cooled to -20 °C and then added dropwise to the solution of 2-Cl. 3-NTf₂ was formed in situ but was not isolated. ¹H NMR (600 MHz, CD_2Cl_2) δ 8.69 (d, ${}^{3}J_{HH}$ = 8.3 Hz, 2H, ArH), 8.34 (t, ${}^{3}J_{\rm HH}$ = 7.7 Hz, 2H, ArH), 7.56 (d, ${}^{3}J_{\rm HH}$ = 8.1 Hz, 2H, ArH), 7.36 $(t, {}^{3}J_{HH} = 7.7 \text{ Hz}, 2H, \text{ArH}), 3.65 (q, J = 7.2 \text{ Hz}, 4H, CH(CH_{3})_{2}),$ 1.51 (dq, J = 15.2, 7.8 Hz, 24H, CH(CH₃)₂). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂) δ 180.7 (aryl C), 147.4 (aryl C), 143.9 (aryl C), 141.5 (aryl C), 128.4 (aryl CH), 128.1 (aryl CH), 126.2 (aryl CH), 126.1 (aryl CH), 119.7 (q, ${}^{1}J_{CF} = 321.2$ Hz, N(CF₃SO₂)₂), 23.8 (vt, J_{CP} = 13.6 Hz, CH(CH₃)), 20.8 (s, CH(CH₃)₂), 20.7 (s, $CH(CH_3)_2$). Note: the C=Ir signal could not be found and select splitting patterns could not be resolved due to decomposition over time. ³¹P{¹H} NMR (243 MHz, CD_2Cl_2) δ 45.4 (br s). ¹⁹F NMR (471 MHz, CD_2Cl_2) δ –79.52 (s). HRMS (ESI) calculated for $C_{29}H_{36}IrP_2S_2$ (M + H)+: 703.1357 found 703.1364.

Synthesis of 4-Cl

A solution of HNTf₂ (8 mg, 0.027 mmol) in CH₂Cl₂ (0.5 mL) was added to a solution of 2-Cl (20 mg, 0.027 mmol) in CH₂Cl₂ (0.5 mL) upon which a colour change from dark brown to deep red-pink was observed. The solvent was removed in vacuo and the product was isolated as a deep red-pink solid in 94% yield (26 mg, 0.026 mmol). ¹H NMR (600 MHz, CD_2Cl_2) δ 8.29 (d, ${}^{3}J_{\rm HH}$ = 8.3 Hz, 2H, ArH), 8.04 (d, ${}^{3}J_{\rm HH}$ = 8.3 Hz, 2H, ArH), 7.97 (t, ${}^{3}J_{HH}$ = 7.6 Hz, 2H, ArH), 7.66 (t, ${}^{3}J_{HH}$ = 7.7 Hz, 2H, ArH), 3.65 (sept, ${}^{3}J_{HH} = 6.7$ Hz, 2H, CH(CH₃)₂), 3.52 (m, 2H, CH(CH₃)₂), 1.47 (m, 12H, CH(CH₃)₂), 1.31 (dvt, ${}^{3}J_{HH} = J_{HP} =$ 8.2 Hz, 6H, CH(CH₃)₂), 1.11 (dvt, ${}^{3}J_{HH} = J_{HP} = 8.9$ Hz, 6H, CH(CH₃)₂), -27.75 (s, 1H, IrH). ¹³C{¹H} NMR (151 MHz, CD_2Cl_2) δ 224.2 (s, C=Ir), 171.4 (vt, J_{CP} = 17.2 Hz, aryl C), 154.8 (vt, J_{CP} = 16.1 Hz, aryl C), 150.4 (vt, J_{CP} = 4.1 Hz, aryl C), 139.72 (s, aryl C), 131.8 (s, aryl CH), 129.2 (s, aryl CH), 126.6 (s, aryl CH), 126.5 (s, aryl CH), 120.0 (q, ${}^{1}J_{CF} = 321.6 \text{ Hz}, \text{ N}(\text{CF}_{3}\text{SO}_{2})_{2})$, 25.8 (vt, J_{CP} = 13.3 Hz, CH(CH₃)₂), 24.6 (vt, J_{CP} = 15.0 Hz, CH(CH₃)₂), 19.8 (s, CH(CH₃)₂), 19.7 (s, CH(CH₃)₂), 19.2 (vt, $J_{\rm CP}$ = 2.9 Hz, CH(CH₃)₂), 19.1 (s, CH(CH₃)₂). ³¹P{¹H} NMR (243 MHz, CD₂Cl₂) δ 52.5 (br s). ¹⁹F NMR (376 MHz, CD₂Cl₂) δ -78.5 (s). HRMS (APCI) calculated for C₂₉H₃₇ClIrP₂S₂ (M+): 739.1124, found 739.1138. Elemental Anal. Calcd (%) for

Synthesis of 4-OH

A solution of HNTf₂ (4 mg, 0.014 mmol) in CD₂Cl₂ (0.5 mL) was added to a solution of 3-OH (10 mg, 0.014 mmol) in wet CD_2Cl_2 (0.5 mL) upon which a colour change from dark brown to deep red-pink was observed. ¹H NMR (600 MHz, CD_2Cl_2) δ 8.23 (d, ${}^{3}J_{HH}$ = 8.3 Hz, 2H, ArH), 8.04 (d, ${}^{3}J_{HH}$ = 8.3 Hz, 2H, ArH), 7.90 (t, ${}^{3}J_{HH}$ = 7.7 Hz, 2H, ArH), 7.66 (t, ${}^{3}J_{HH}$ = 7.7 Hz, 2H, ArH), 5.06 (s, 2H), 4.59 (s, 1H), 3.64 (m, 2H, CH(CH₃)₂), 3.11 (m, 2H, CH(CH₃)₂), 1.41 (m, 12H, CH(CH₃)₂), 1.28 (dvt, ${}^{3}J_{\text{HH}} = 9.7, J_{\text{HP}} = 7.0 \text{ Hz}, 6\text{H}, \text{CH}(\text{CH}_{3})_{2}), 1.11 \text{ (dvt, } {}^{3}J_{\text{HH}} = J_{\text{HP}} = 100 \text{ Hz}$ 8.0 Hz, 6H, CH(CH₃)₂), -20.74 (br s, 1H, IrH). ¹³C{¹H} NMR (126 MHz, CD_2Cl_2) δ 169.9 (aryl C), 156.3 (vt, J_{CP} = 15.5 Hz, aryl C), 151.3 (aryl C), 139.4 (aryl C), 132.0 (aryl C), 129.0 (aryl CH), 126.8 (aryl CH), 126.2 (aryl CH), 119.4 (q, ${}^{1}J_{CF} = 321.7$ Hz, $N(CF_3SO_2)_2)$, 26.6 (CH(CH₃)₂), 25.8 (CH(CH₃)₂), 19.5 $(CH(CH_3)_2)$, 19.1 $(CH(CH_3)_2)$. The C=Ir signal could not be located due to poor signal to noise. ³¹P{¹H} NMR (243 MHz, CD_2Cl_2) δ 37.8 (s). ¹⁹F NMR (471 MHz, CD_2Cl_2) δ -78.17 (s). Elemental analysis could not be obtained due to the instability of this complex under vacuum. Conditions for ESI and APCI HRMS were too harsh to see the 4-OH cation, peaks corresponding to the $C_{29}H_{36}IrP_2S_2$ cation (no H_2O) were found instead.

Synthesis of 4-OPh

A mixture of 2-Cl (20 mg, 0.027 mmol) and PhOH (3 mg, 0.027 mmol) was dissolved in ca. 0.5 mL CH₂Cl₂ and cooled to -20 °C in the freezer. A solution of Me₃SiNTf₂ (6.2 µL, 0.027 mmol) in ca. 0.5 mL CH₂Cl₂ was also cooled to -20 °C and then added dropwise to the mixture resulting in a colour change from dark brown to deep pink-red. The volatile components were removed in vacuo resulting in a dark pink-red solid in 93% yield (27 mg, 0.025 mmol). ¹H NMR (500 MHz, CD_2Cl_2) δ 8.29 (d, ${}^{3}J_{HH}$ = 8.3 Hz, 2H, Lig ArH), 8.03 (d, ${}^{3}J_{HH}$ = 8.3 Hz, 2H, Lig ArH), 7.97 (t, ${}^{3}J_{HH}$ = 7.8 Hz, 2H, Lig ArH), 7.66 (t, ${}^{3}J_{HH}$ = 7.6 Hz, 2H, Lig ArH), 7.23 (t, ${}^{3}J_{HH}$ = 7.3 Hz, 2H, OPh Ar**H**), 6.95 (t, ${}^{3}J_{HH}$ = 7.3 Hz, 1H, OPh Ar**H**), 6.83 (t, ${}^{3}J_{HH}$ = 7.3 Hz, 2H, OPh ArH), 3.64 (sept, ${}^{3}J_{HH} = 7.1$ Hz, 2H, CH(CH₃)₂), 3.52 (m, 2H, CH(CH₃)₂), 1.47 (m, 12H, CH(CH₃)₂), 1.31 (dvt, ${}^{3}J_{\text{HH}}$ = 7.1 Hz, J_{HP} = 9.2 Hz, 6H, CH(CH₃)₂), 1.10 (dvt, ${}^{3}J_{\text{HH}}$ = 7.0 Hz, $J_{\rm HP}$ = 9.3 Hz, 6H, CH(CH₃)₂), -27.64 (br s, 1H, IrH). ¹³C{¹H} NMR (126 MHz, CD_2Cl_2) δ 224.1 (s, C=Ir), 171.5 (vt, $J_{\rm CP}$ = 17.2 Hz, Lig aryl C), 156.1 (s, OPh aryl C), 154.8 (vt, $J_{\rm CP}$ = 16.0 Hz, Lig aryl C), 150.4 (vt, *J*_{CP} = 4.0 Hz, Lig aryl C), 139.7 (s, Lig aryl C), 131.7 (s, Lig aryl CH), 130.0 (s, OPh aryl CH), 129.1 (s, Lig aryl CH), 126.6 (s, Lig aryl CH), 126.5 (s, Lig aryl CH), 121.8 (s, OPh aryl CH), 120.5 (s, OPh aryl CH), 120.3 (q, ${}^{1}J_{CF}$ = 321.0 Hz, (CF₃SO₂)N), 25.8 (vt, J_{CP} = 13.3 Hz, CH(CH₃)₂), 24.6 (vt, $J_{CP} = 15.0$ Hz, CH(CH₃)₂), 19.8 (s, CH(CH₃)₂), 19.7 (s, $CH(CH_3)_2$, 19.2 (vt, J_{CP} = 2.6 Hz, $CH(CH_3)_2$), 19.1 (s, $CH(CH_3)_2$). ³¹P{¹H} NMR (203 MHz, CD_2Cl_2) δ 51.4 (br s). ¹⁹F NMR (471 MHz, CD_2Cl_2) δ –80.4 (s). Elemental analysis could not be obtained due to residual Me₃SiCl (or AgCl when done with AgNTf₂). Conditions for ESI and APCI HRMS were too harsh to

see the **4-OPh** cation, peaks corresponding to the $C_{29}H_{36}IrP_2S_2$ cation (no PhOH) were found instead.

Synthesis of 5

Method 1: One equivalent of tetrabutylammonium chloride was added as a solid to a solution of 4-Cl in CD_2Cl_2 . An immediate colour change from deep pink/red to deep green/ brown was observed and quantitative conversion to a new product was shown by ¹H and ³¹P{¹H} NMR spectroscopy. The volatiles were removed *in vacuo*, leaving a dark green/brown solid. Due to the similar solubilities of the product and the ^{*n*}BuN₄NTf₂ byproduct, the two could not be separated.

Method 2: A 4 M dioxane solution of HCl (5 µL, 0.020 mmol) was added via syringe to a solution of 3-Cl (15 mg, 0.020 mmol) in CH₂Cl₂ (ca. 0.7 mL) at room temperature. A slight colour change from deep brown to deep green/ brown was observed immediately upon addition. The volatiles were removed in vacuo and 5 was isolated as a green/brown solid in 95% yield (15 mg, 0.019 mmol). ¹H NMR (600 MHz, CD_2Cl_2) δ 8.24 (d, ${}^{3}J_{HH}$ = 8.2 Hz, 2H, ArH), 7.91 (d, ${}^{3}J_{HH}$ = 8.2 Hz, 2H, ArH), 7.83 (t, ${}^{3}J_{HH}$ = 7.7 Hz, 2H, ArH), 7.52 (t, ${}^{3}J_{HH}$ = 7.7 Hz, 2H, ArH), 3.64 (m, 2H, CH(CH₃)₂), 2.96 (m, 2H, $CH(CH_3)_2$), 1.76 (dvt, ${}^{3}J_{HH}$ = 7.6, J_{HP} = 8.7 Hz, 6H, $CH(CH_3)_2$), 1.53 (dvt, ${}^{3}J_{HH} = J_{HP} = 7.6$ Hz, 6H, CH(CH₃)₂), 1.46 (dvt, ${}^{3}J_{HH} =$ 7.4, $J_{\rm HP}$ = 8.6 Hz, 6H, CH(CH₃)₂), 0.99 (dvt, ${}^{3}J_{\rm HH}$ = 7.4, $J_{\rm HP}$ = 8.4 Hz, 6H, CH(CH₃)₂), -13.31 (t, ${}^{2}J_{HP}$ = 11.8 Hz, 1H, IrH). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂) δ 220.6 (s, C=Ir), 174.9 (vt, $J_{\rm CP}$ = 18.5 Hz, aryl C), 152.5 (vt, $J_{\rm CP}$ = 15.3 Hz, aryl C), 147.2 (vt, J_{CP} = 3.8 Hz, aryl C), 140.1 (s, aryl C), 128.3 (s, aryl CH), 128.0 (s, aryl CH), 126.4 (s, aryl CH), 125.04 (s, aryl CH), 27.7 (vt, $J_{\rm CP}$ = 15.6 Hz, CH(CH₃)₂), 27.6 (vt, $J_{\rm CP}$ = 13.6 Hz, CH(CH₃)₂), 21.4 (s, CH(CH₃)₂), 20.5 (vt, J_{CP} = 1.8 Hz, CH(CH₃)₂), 20.0 (s, CH(CH₃)₂), 19.6 (s, CH(CH₃)₂). ³¹P{¹H} NMR (243 MHz, CD_2Cl_2) δ 23.7 (s). HRMS (APCI) calculated for $C_{29}H_{37}ClIrP_2S_2$ (M*+): 739.1124, found 739.1091 (missing Cl ligand).

Synthesis of 6-acetone

Method 1: 2-NTf₂ was dissolved in acetone- d_6 and allowed to sit at room temperature for 16 hours during which time a colour change from orange-brown to deep brown took place. Full conversion to **6-acetone** was observed by NMR spectroscopy.

Method 2: AgNTf₂ (5 mg, 0.014 mmol) was added as a solid to a solution of **3-Cl** (10 mg, 0.014 mmol) in acetone- d_6 at room temperature. After ten minutes, a pink-brown precipitate was formed and full conversion to **6-acetone** was observed by NMR spectroscopy.

Method 3: HNTf₂ (4 mg, 0.014 mmol) was added as a solid to a solution of **3-OH** (10 mg, 0.014 mmol) in acetone- d_6 at room temperature. After five minutes, full conversion to **6-acetone** was observed by NMR spectroscopy. ¹H NMR (600 MHz, acetone- d_6) δ 8.90 (d, ³ J_{HH} = 8.1 Hz, 2H, ArH), 8.42 (t, ³ J_{HH} = 7.6 Hz, 2H, ArH), 7.78 (d, ³ J_{HH} = 8.2 Hz, 2H, ArH), 7.48 (t, ³ J_{HH} = 7.6 Hz, 2H, ArH), 3.67 (septvt, ³ J_{HH} = 6.9 Hz, J_{HP} = 1.5 Hz, 4H, CH(CH₃)₂), 1.47 (m, 24H, CH(CH₃)₂). ¹³C{¹H} NMR (151 MHz, acetone- d_6) δ 181.0 (t, ² J_{CP} = 1.7 Hz, C=Ir),

180.6 (vt, J_{CP} = 22.1 Hz, aryl C), 146.7 (vt, J_{CP} = 4.2 Hz, aryl C), 142.5 (vt, J_{CP} = 18.2 Hz, aryl C), 141.0 1 (vt, J_{CP} = 1.6 Hz, aryl C), 128.3 (s, aryl CH), 128.1 (s, aryl CH), 126.3 (s, aryl CH), 125.1 (s, aryl CH), 120.2 (q, ${}^{1}J_{CF}$ = 321.4 Hz, N(CF₃SO₂)₂), 23.7 (vt, J_{CP} = 14.3 Hz, CH(CH₃)₂), 19.8 (s, CH(CH₃)₂), 19.7 (vt, J_{CP} = 2.8 Hz, CH(CH₃)₂). Signals corresponding to the acetone adduct could not be identified, likely due to broadness. ³¹P{¹H} NMR (243 MHz, acetone- d_6) δ 43.8 (s). ¹⁹F NMR (471 MHz, acetone- d_6) δ –80.82 (s).

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