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Pincer-ligated Iridium Complexes with Low-Field Ancillary Ligands: Complexes of (^{iPr}PCP)IrCl$_2$ and Comparison with (^{iPr}PCP)IrHCl

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Abstract

Pincer-ligated iridium complexes have been widely developed, and (pincer)Ir(III) complexes, particularly five-coordinate, are central to their chemistry. Such complexes typically bear two formally anionic ligands in addition to the pincer ligand itself. Yet despite the prevalence of halides as anionic ligands in transition metal chemistry there are relatively few examples in which both of these ancillary anionic ligands are halides or even other monodentate low-field anions. We report a study of the fragment (^{iPr}PCP)IrCl$_2$ (^{iPr}PCP = κ^3-2,6-$C_6H_3(CH_2P^iPr_2)$), and adducts thereof. These species are found to be thermodynamically disfavored relative to the corresponding hydridohalides. For example, DFT calculations and experiment indicate that one Ir-Cl bond of (^{iPr}PCP)IrCl$_2$ complexes will undergo reaction with H_2 to give the (^{iPr}PCP)IrHCl or an adduct thereof. In the presence of aqueous HCl, (^{iPr}PCP)IrCl$_2$ adds a chloride ion to give an unusual example of an anionic transition metal complex ((^{iPr}PCP)IrCl$_3^-$) with a Zundel cation ($H_5O_2^+$). (^{iPr}PCP)IrCl$_2$ is not stable as a monomer at room temperature but exists in solution as a mixture of clusters which can add various small molecules. DFT calculations indicate that dimerization of (^{iPr}PCP)IrCl$_2$ is more favorable than dimerization of (^{iPr}PCP)IrHCl, in accord with its observed tendency to form clusters.

Keywords: iridium; pincer ligands; halide ligands; Zundel cation; clusters

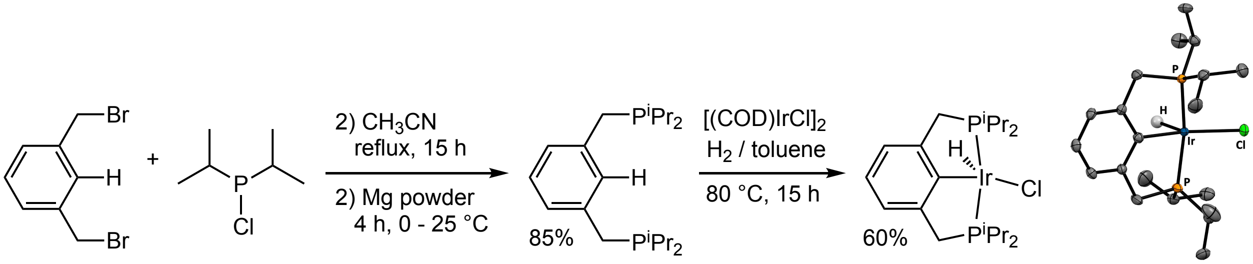
INTRODUCTION

Pincer-ligated iridium complexes have been extensively developed over the past several decades, as catalysts for the functionalization of C-H bonds[1-3] and many other reactions[4-32], as well as for other applications[9,33-35] such as optoelectronics[36-37]. In almost all of this chemistry (pincer)Ir(III) species play a critical role, for example in catalytic cycles that are all-Ir(III), Ir(III)/Ir(V), or Ir(I)/(III), or as synthetic precursors. One of the earliest examples of pincer complexes in general and an archetypal example of a (pincer)Ir(III) complex is (^{tBu}PCP)IrHCl (^{R}PCP = κ^3-2,6-$C_6H_3(CH_2PR_2)$), first reported by Shaw in 1976.[38] Typically, (pincer)Ir(III) complexes bear two formally anionic ligands in addition to the pincer ligand itself, e.g. (^{R}PCP)IrHCl, (phebox)Ir$(OAc)_2(H_2O)$ (phebox = 2,6-bis-oxazolinephenyl)[39], or (^{tBu}P^{py}NP)IrPhH$^+$ (^{tBu}P^{py}NP = κ^3-2,6-bis(dialkylphosphinomethyl)pyridine)[40]. Given the prevalence of halides as anionic ligands in transition metal chemistry, it is therefore surprising that there are few examples in which both of the ancillary anionic ligands are halides or even other monodentate low-field anions such as alkoxide or various "pseudo-halides". In particular, five-coordinate Ir(III) complexes play a critical role in (pincer)Ir chemistry yet to our knowledge there is only one report of (pincer)IrX_2 complexes where both ancillary ligands are halides,[41] specifically bis-NHC-pincer complexes, (C^C^C^{Mes})IrX_2. The corresponding six-coordinate ligand adducts are much less rare though still not particularly common[42-49] and there are a few examples in which six-coordination results from halide bridging of the (pincer)IrX_2 units.[50-52] In view of our interest in both high-oxidation catalytic cycles[3,53-55] and synthetic precursors for species such as bis-hydrocarbyl (pincer)Ir complexes[56], our attention has been drawn to such dihalide complexes. Here we report spectroscopic evidence of the five-coordinate complex (^{iPr}PCP)$IrCl_2$, and a study of the chemistry of this species and six-coordinate adducts thereof.

RESULTS AND DISCUSSION

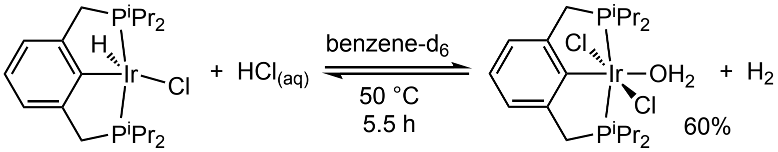
The (^{iPr}PCP)Ir(I) fragment has been found in many instances to be catalytically more active than the iconic (^{tBu}PCP)Ir(I) analogue,[57-58] presumably due to lesser crowding at the iridium center. In the case of Ir(III) complexes, with the metal center bearing ancillary anionic ligands in addition to the pincer, we would expect that the less sterically demanding ^{iPr}PCP ligand would confer an even greater advantage with respect to intermolecular reactivity.[59] Accordingly, we began our study with the synthesis of (^{iPr}PCP)IrHCl[57] (**1-HCl**; **1** = (^{iPr}PCP)Ir). Although this complex is well known, previously reported synthetic routes in our experience lead to mixtures of **1-HCl** and **1-HBr**, where the bromide is derived from 1,3-bis(bromomethyl)benzene starting material[58]. **1-HCl** is typically used as a precursor of the fragment (^{iPr}PCP)Ir(I), via treatment with a hydride or base; for such a purpose the presence of **1-HBr** is not problematic, but for the present work we required the pure hydridochloride. Pure proligand (^{iPr}PCP-H) was prepared by the method of Ozerov[60] and then allowed to react with $[(COD)IrCl]_2$[40] (Scheme 1; COD = 1,5-cyclooctadiene). Pure **1-HCl** was obtained, and X-ray quality crystals were grown by vapor diffusion of pentane into benzene. The molecular structure determined by scXRD is typical of (^{R}PCP)IrHCl complexes and related complexes of the type (pincer)IrHCl.[38,61-64] In particular both molecules in the unit cell show the characteristic "Y" geometry[65-67] formed by the chloride, hydride, and Ir-bound carbon, with wide angles Cl-Ir-C (164.81(9)°, 165.54(9)°) and Cl-Ir-H (120(2)°, 112(2)°), for molecules 1 and 2, respectively.

Scheme 1. Synthesis of (^{iPr}PCP-H) Pro-ligand and Metalation to give 1-HCl (ORTEP Diagram shown, 50% Probability Level, Molecule 1)



We initially attempted to generate **1-Cl₂** by the addition of anhydrous HCl to **1-HCl**. However, even after heating at 80 °C for 1 h, and then addition of 3,3-dimethylbutene (TBE) as a potential hydrogen acceptor and further heating overnight, no reaction was observed by ^{1}H and ^{31}P NMR spectroscopy. The reaction of **1-HCl** with 1 equiv aqueous $HCl_{(aq)}$ (36% w/w), however, led to partial conversion to what was believed to be (^{iPr}PCP)$IrCl_2 \cdot H_2O$ (**1-Cl₂(H₂O)**). The reaction with 3 equiv of HCl(aq) at 50 °C went to 51 % completion in 230 min and reached 60% completion in 330 min (Scheme 2). Removing the atmosphere of the J-young NMR tube in vacuo, followed by further heating at 50 °C for 90 min resulted in 95% conversion to a mixture of **1-Cl$_2$(H$_2$O) and [1-Cl$_3$$^-$]**. These observations indicated that the failure of the reaction to proceed to completion in a sealed system was due to the buildup of H_2, and presumably an equilibrium in which the back reaction, surprisingly, includes hydrogenolysis of an Ir-Cl bond.

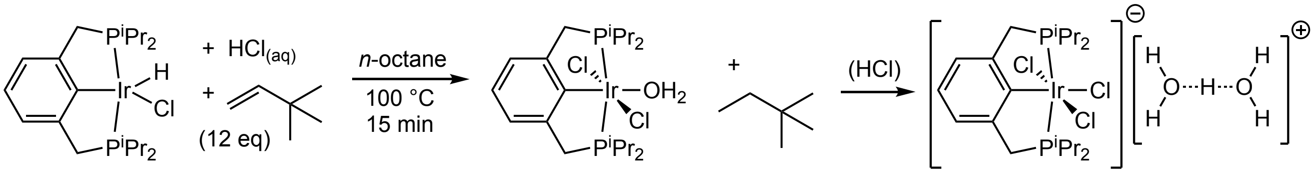
Scheme 2. Reaction of 1-HCl with HCl$_{(aq)}$ (no added hydrogen acceptor)



To more effectively remove H_2 and drive the reaction fully to completion, the reaction with HCl$_{(aq)}$ was conducted with 3,3-dimethylbutene (TBE) added to act as a hydrogen acceptor. After 330 min at 50 °C, 97% loss of **1-HCl** was observed by ^{1}H NMR spectroscopy and after an additional 90 min, no **1-HCl** could be detected (> 99% conversion).

Attempts to grow crystals from *n*-octane led to individual crystals of two different materials, determined by scXRD to be **1-Cl$_2$(H$_2$O)** and [**1-Cl$_3$**][H_5O_2] (Scheme 3, Figure 1). The latter contains anionic **1-Cl$_3$**$^-$ and, interestingly, the Zundel cation[68-69], $[H_5O_2]^+$. There are only a few crystallographically characterized examples of anionic metal complexes with a Zundel cation.[70-71]

Scheme 3. Reaction of 1-HCl with HCl$_{(aq)}$ (3 equiv) and TBE



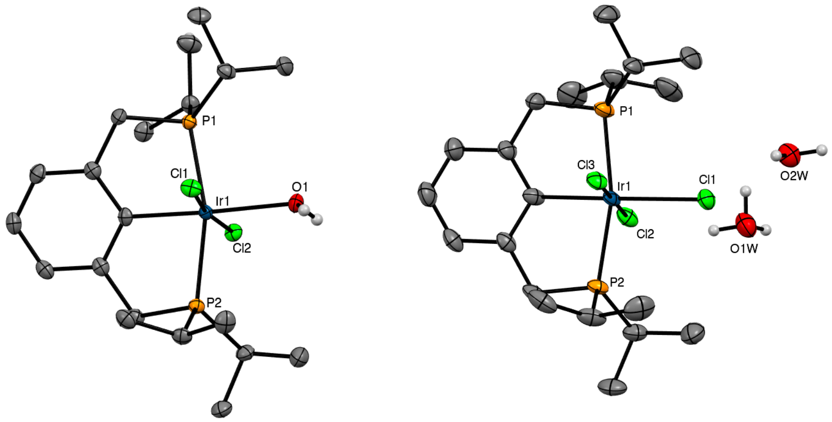
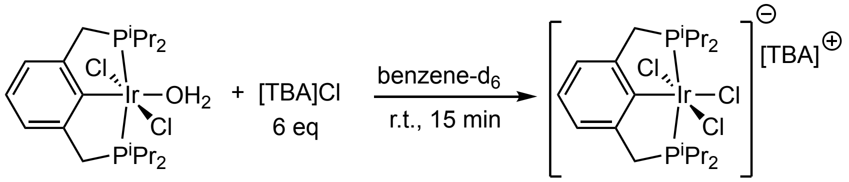


Figure 1. Molecular structure of **1-Cl$_2$(H$_2$O)** and **1-Cl$_3$(H$_5$O$_2$)** determined by scXRD. Hydrogen atoms other than those on water molecules omitted for clarity.

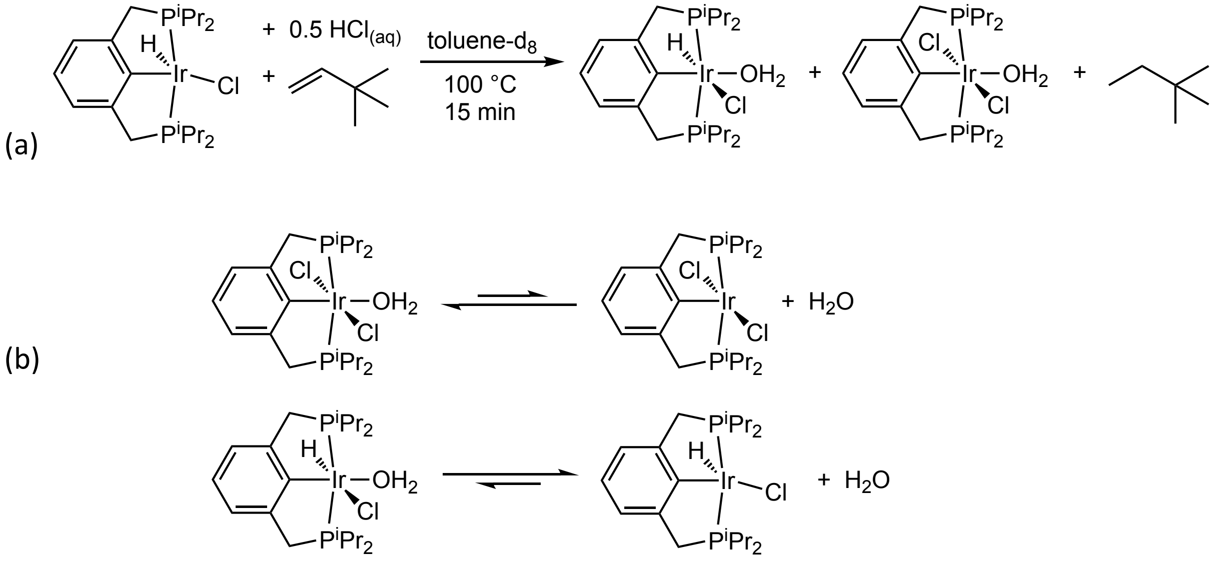
The anionic complex **[1-Cl$_3^-$]** was also independently generated by the reaction of **1-Cl$_2$(H$_2$O)** with *tert*-butylammonium chloride (Scheme 4).

Scheme 4. Synthesis of [1-Cl$_3$][TBA]



When only 0.5 eq HCl$_{(aq)}$ was added to **1-HCl** (along with 1.75 eq TBE; Scheme 5) it was noted that both the **1-Cl$_2$(H$_2$O)** product and the “unreacted” **1-HCl** formed adducts of H$_2$O. At 25 °C the H$_2$O adduct **1-HCl(H$_2$O)** appeared to be in equilibrium with free **1-HCl**, while no evidence of free **1-Cl$_2$** was observed. When the solution was heated above 75 °C, the broad signal in the ^{31}P NMR spectrum, attributable to **1-HCl** and **1-HCl(H$_2$O)** undergoing rapid exchange, gave rise to a sharp signal attributable to free **1-HCl** (with no significant coordination of water) at δ 57. In the case of **1-Cl$_2$** a sharp signal at δ 25.2 was observed at room temperature, attributable to **1-Cl$_2$(H$_2$O)**. Upon increasing temperature the signal shifted downfield and broadened giving rise to a broad signal at δ 34.5 at 135 °C, which we attribute to **1-Cl$_2$** and **1-Cl$_2$(H$_2$O)** undergoing rapid exchange (SI, Figure S3.20). Thus H_2O is found to bind much more strongly to **1-Cl₂** than to **1-HCl** in the given solution.

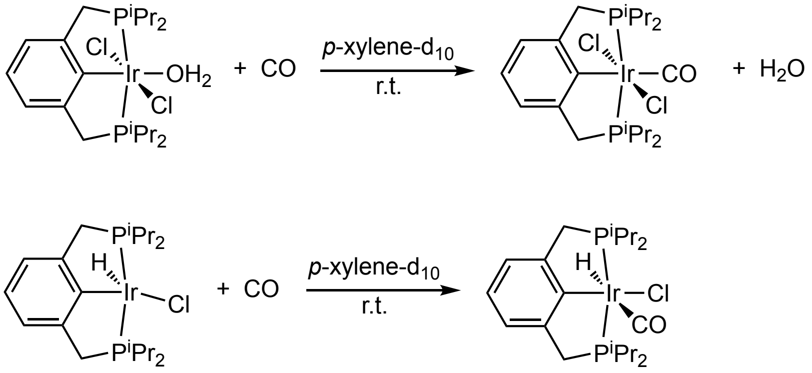
Scheme 5. (a) Generation of (^{iPr}PCP)IrHCl·H_2O and (^{iPr}PCP)IrCl$_2$·H_2O. (b) Binding affinity of H_2O to (^{iPr}PCP)IrHCl and (^{iPr}PCP)IrCl$_2$.



Attempts to quantify the binding constants of H_2O to **1-Cl₂** and to **1-HCl** in individual solutions were stymied by the difficulty of reproducibly obtaining solutions with a known concentration of water in hydrocarbon solvent. The experiment described above, with both complexes present in a single solution, therefore appears to be a more meaningful (albeit qualitative) indicator of the greater binding affinity of water for **1-Cl₂**.

Addition of CO to a *p*-xylene-d_{10} solution of **1-Cl₂(H₂O)** resulted in rapid substitution of the water to give **trans-1-Cl₂(CO)**. For comparison, CO was added to a solution of **1-HCl** resulting in immediate formation of **cis-1-HCl(CO)** (Scheme 6). Assignments were based on ^{1}H and ^{31}P NMR spectroscopy. X-ray quality crystals were obtained in both cases by vapor diffusion of pentane to saturated solutions of the complexes in benzene solvent, and the NMR solution-phase assignments were in agreement with solid-phase molecular structures obtained by scXRD for both carbonyl complexes (Figure 2).

Scheme 6. Synthesis of 1-Cl$_2$(CO) and 1-HCl(CO)



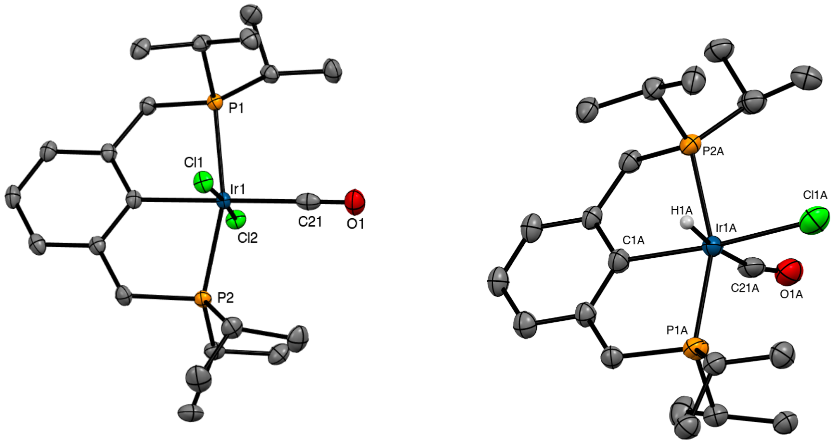


Figure 2. Molecular structure of **1-Cl$_2$(CO**) and **1-HCl(CO)** determined by scXRD. Hydrogen atoms, except the hydride of **1-HCl(CO)** omitted for clarity.

We found the trans geometry of **1-Cl$_2$(CO)** to be somewhat surprising since one might expect that mutually cis coordination of the two weak-trans-influence chloride ligands would be more favorable. Accordingly, DFT calculations were conducted, initially for the very uncrowded analogue (^{Me}PCP)IrCl$_2$(CO); the *cis*-chloride configuration was calculated to be more favorable for this complex, although by only 1.8 kcal/mol (Table 1). The calculated difference between *cis*-and *trans*-chloride isomers was greater in the case of the very crowded analogue (^{tBu}PCP)IrCl$_2$(CO) with the former being 4.8 kcal/mol lower in free energy. This result is in good agreement with calculations indicating that for (^{tBu}PCP)IrX$_2$L complexes the coordination sites cis to the Ir-bound carbon are significantly more crowded than the trans site.[64] Surprisingly however – but consistent with the experimentally determined geometry – the trans-chloride configuration was calculated to be more favorable than cis for **1-Cl$_2$(CO)**, by 2.4 kcal/mol, even though this complex is expected to be intermediate between (^{Me}PCP)IrCl$_2$(CO) and (^{tBu}PCP)IrCl$_2$(CO) with respect to steric crowding. Inspection of the calculated structures of **1-Cl$_2$(CO)** reveals five individual contact distances between PCP ligand hydrogen atoms and each chloride ligand between 2.61 Å and 2.97 Å (Figure 3). These close contact distances reflect *favorable* interactions[72-74], possibly with H-bonding character[75]. Thus the modest "crowding" found in **1-Cl$_2$(CO)** can account for the greater stability of the trans chloride configuration, as opposed to the *lack of crowding* in (^{Me}PCP)IrCl$_2$(CO) or the severe crowding in (^{tBu}PCP)IrCl$_2$(CO).

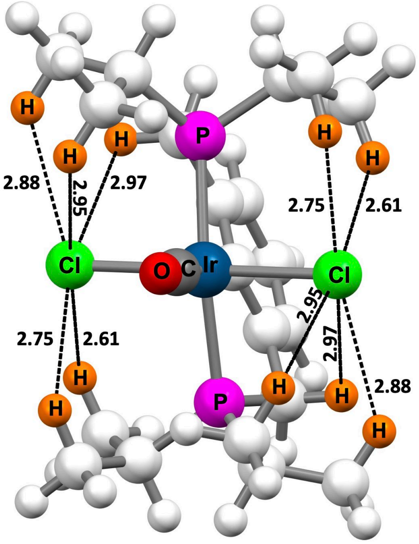
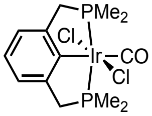
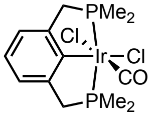
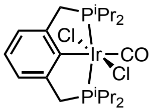
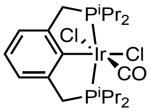
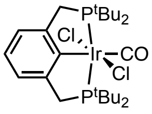
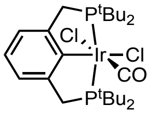


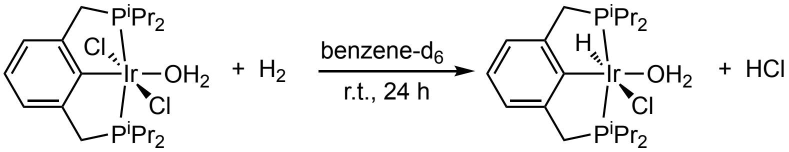
Figure 3. Calculated structure of **1-Cl$_2$(CO)**, colored to highlight close CH-Cl distances (given in Å).

Table 1. Calculated relative stability of *trans*- versus *cis*-(^{R}PCP)$IrCl_2(CO)$ for R = Me, ^{i}Pr, ^{t}Bu

trans-isomer	*cis*-isomer	ΔG(*cis-trans)*
		-1.8 kcal/mol
		2.4 kcal/mol
		-4.8 kcal/mol

Transition metal hydrides typically react with acids to yield H_2. As indicated in Scheme 2, however, **1-Cl$_2$(H$_2$O)** appears to react with H_2 to yield **1-HCl(H$_2$O)**, i.e. the reverse of acidolysis resulting in formation of H_2. Confirming this proposal, addition of 1 atm H_2 to a solution of **1-Cl$_2$(H$_2$O)**, resulted in complete conversion to **1-HCl(H$_2$O)** within 24 h (Scheme 7). Our DFT calculations predict that hydrogenolysis of Ir-Cl bonds of both **1-Cl$_2$** and **1-Cl$_2$(H$_2$O)** is very slightly endergonic (ΔG° = 2.9 kcal/mol and 2.4 kcal/mol, respectively; Figure 4) in the gas phase, while with the use of a solvent (toluene) continuum model, the reactions are calculated to be essentially ergoneutral (ΔG° = 0.3 kcal/mol and -1.3 kcal/mol respectively).[76] In contrast, hydrogenolysis of the Ir-Cl bond of either **1-HCl** or **1-HCl(H$_2$O)** is very highly endergonic (ΔG° = ca. 30 kcal/mol; Figure 5).

Scheme 7. Reaction of (^{iPr}PCP)$IrCl_2(H_2O)$ with 1 atm of H_2 to Generate (^{iPr}PCP)$IrHCl(H_2O)$



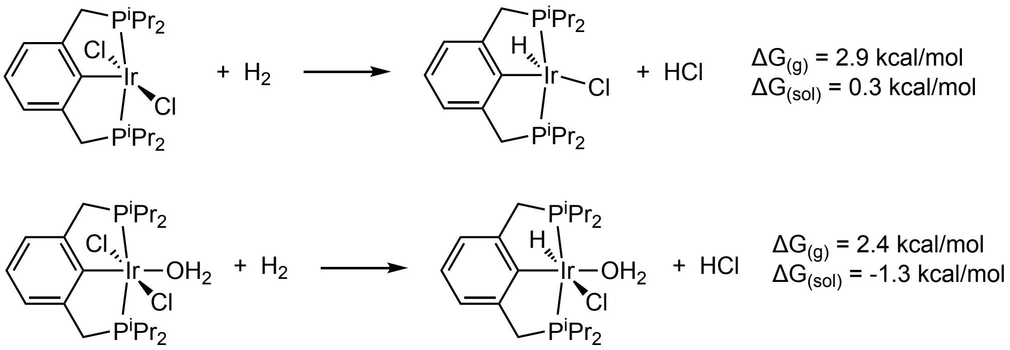


Figure 4. Thermodynamics of hydrogenolysis of **1-Cl$_2$** and **1-Cl$_2$(H$_2$O)**

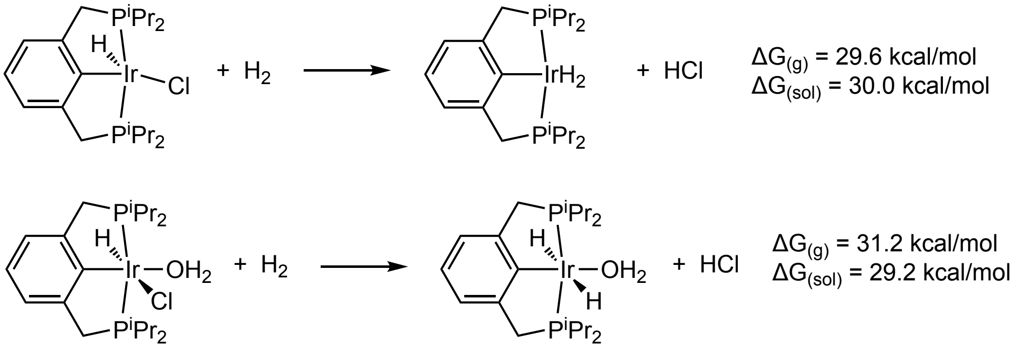


Figure 5. Thermodynamics of hydrogenolysis of **1-HCl** and **1-HCl(H$_2$O)**

From the relative thermodynamics of the hydrogenolysis reactions of Figures 4 and 5 it follows that the comproportionation reactions shown in Figure 6 are extremely favorable. This result is consistent with chemistry of other hydride/halide pincer metal complexes, including those that we have recently reported of ruthenium complexes (PPP)RuXY (XY = H_2, HCl, Cl_2).[77] In all these cases we attribute the favorability of the pincer hydridohalides (5- or 6-coordinate) to the coordination of two strong-trans-influence ligands (hydride and the metal-bound carbon or phosphorus in the case of PCP and PPP respectively) positioned mutually cis, and trans to weak trans-influence ligands (H_2O or chloride) or to a vacant coordination site.

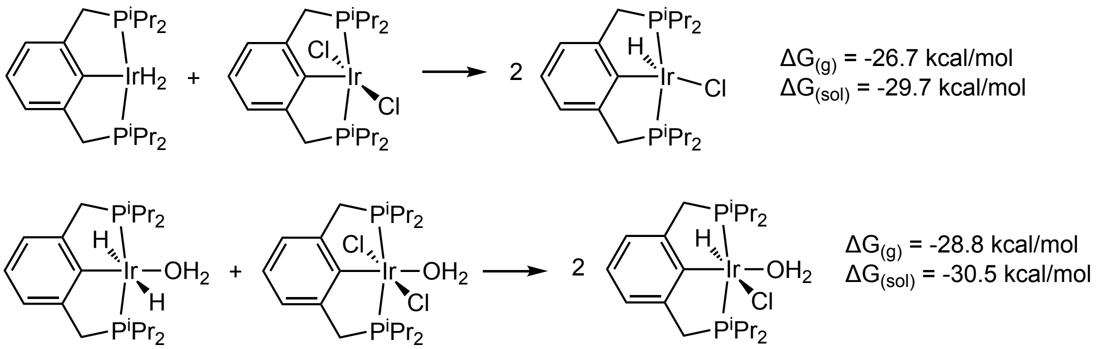


Figure 6. Thermodynamics of Comproportionation of **1-HCl/1-H$_2$** and **1-HCl(H$_2$O)/1-H$_2$(H$_2$O)**

The synthesis of **1-Cl$_2$** was attempted via removal of H_2O from **1-Cl$_2$(H$_2$O)** in vacuo. The resulting solid could be redissolved in *p*-xylene-d$_{10}$. The ^{31}P NMR spectrum comprised ten discrete signals (all but one of which was relatively sharp). Of these, eight were in the range δ 23 – δ 36, and two at ca. δ 47 (SI, Figure S3.18). Upon heating the solution to 135 °C, these signals converged to a single broad signal at ca. δ 40. When the solution was allowed to return to room temperature the same spectrum with ten discrete signals reappeared. Addition of H_2O to this solution yielded **1-Cl$_2$(H$_2$O)** and addition of CO then yielded **1-Cl$_2$(CO)**. We propose that upon loss of H_2O from **1-Cl$_2$(H$_2$O)** a complex mixture of oligomers, **[1-Cl$_2$]$_n$** is formed. Upon heating, this material dissociates reversibly to give an equilibrium with monomeric **1-Cl$_2$** (Scheme 8).

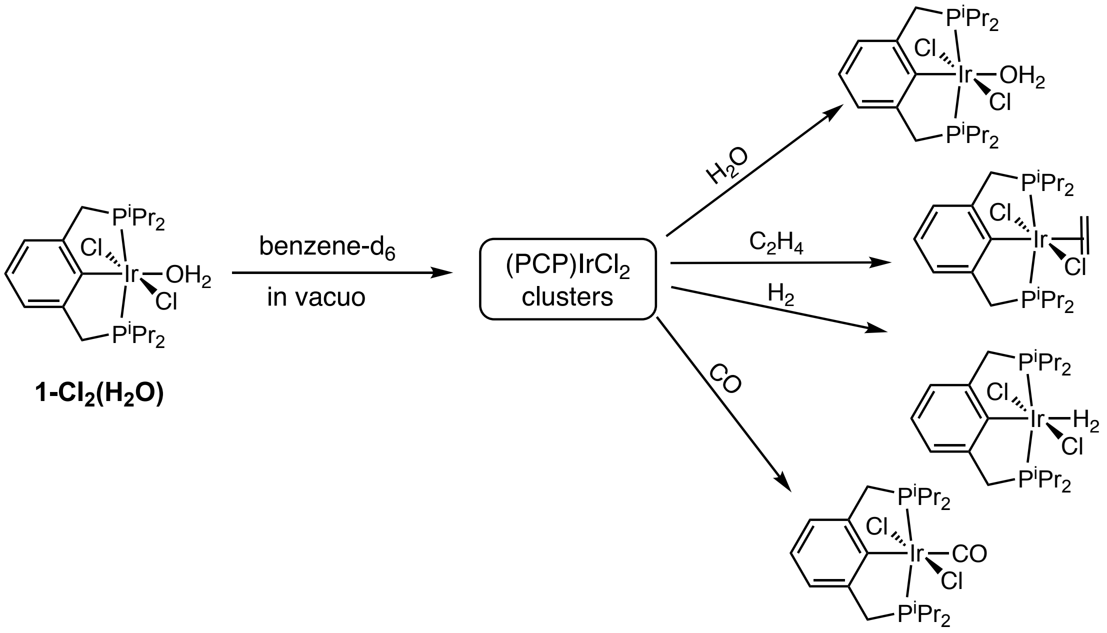
Scheme 8. Reversible Formation of (^{iPr}PCP)IrCl$_2$ Clusters

$$[\mathbf{1\text{-}Cl_2}]_\mathbf{n} \xrightleftharpoons[\text{decreased T}]{\text{increased T}} \mathbf{n\ 1\text{-}Cl_2}$$

This conclusion is in agreement with the observation, discussed above, that heating a solution of **1-Cl$_2$(H$_2$O)** results in a downfield shift of the ^{31}P NMR signal from δ 25.25 to ca. δ 35. The difference between the chemical shifts, δ 35 versus δ 40, reflects that, due to the presence of H_2O, even at 135 °C there remains a significant concentration of **1-Cl$_2$(H$_2$O)** in solution (Scheme 5b).

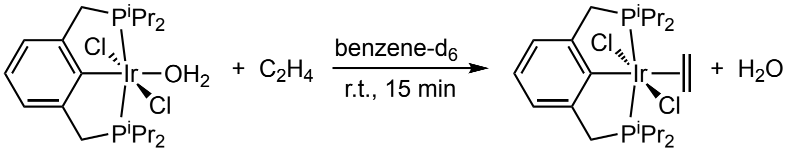
The putative **[1-Cl$_2$]$_n$** acts as a synthetic precursor of **1-Cl$_2$**. In addition to the reactions with H_2O and CO noted above, the addition of ethylene (1 atm) affords **1-Cl$_2$(C$_2$H$_4$)** (Scheme 9). The same species can be obtained directly via the displacement of H_2O from **1-Cl$_2$(H$_2$O)** by ethylene (Scheme 10). The addition of H_2 atmosphere to **[1-Cl$_2$]$_n$** initially results in the formation of a single species, which we assign as **1-Cl$_2$(H$_2$)** (SI, Figure S3.21), which then apparently undergoes loss of HCl to afford **1-HCl**.

Scheme 9. Formation of (^{iPr}PCP)IrCl$_2$ Clusters and Reactions to form Adducts



1-Cl$_2$(H$_2$O)

Scheme 10. Independent Synthesis of 1-Cl$_2$(C$_2$H$_4$)



DFT calculations of simple dimerization may shed light on the conclusion that **1-Cl$_2$** tends to form clusters, in contrast with the observed behavior of **1-HCl**. A dimer of **1-Cl$_2$** was computed, showing a single bridging chloride and a σ-C-H bonding interaction between a phosphino-*i*-propyl group of the Ir center accepting the bridging chloride with the Ir center donating the bridging chloride. In the case of **1-HCl**, a strikingly analogous dimeric structure is found.

Formation of such dimers (**1-XCl**)$_2$ (X = H or Cl) requires that for both monomeric units of each dimer, X and Cl are positioned mutually trans. In the case of **1-Cl$_2$** this is essentially no different than in the monomer (calculated C$_{PCP}$-Ir-Cl angles of 95.2°) whereas dimerization requires a complete rearrangement of the coordination sphere of **1-HCl**. In particular, dimerization of **1-HCl** requires repositioning of the chloride to the empty coordination site approximately trans to the strong-trans-influence hydride ligand (which is reflected in the longer Ir-Cl distances of (**1-HCl**)$_2$; Figure 7. Accordingly, dimerization of **1-Cl$_2$** is calculated to be 5.6 kcal/mol more exergonic ($\Delta G°$ = -0.9 kcal/mol) than that of **1-HCl** ($\Delta G°$ = 4.8 kcal/mol), although this is only a tentative and possibly partial explanation of the apparently greater tendency of **1-Cl$_2$** to form clusters. We also suspect that favorable CH-Cl interactions play a role. This could include interactions between **1-Cl$_2$** units as well intramolecular interactions, such as seen in Figure 3, that are favored by the configuration with mutually trans chloride ligands. Lastly, we note that (**1-Cl$_2$**)$_2$ has three terminal chlorides available for further bridging whereas (**1-HCl**)$_2$ obviously only has one.

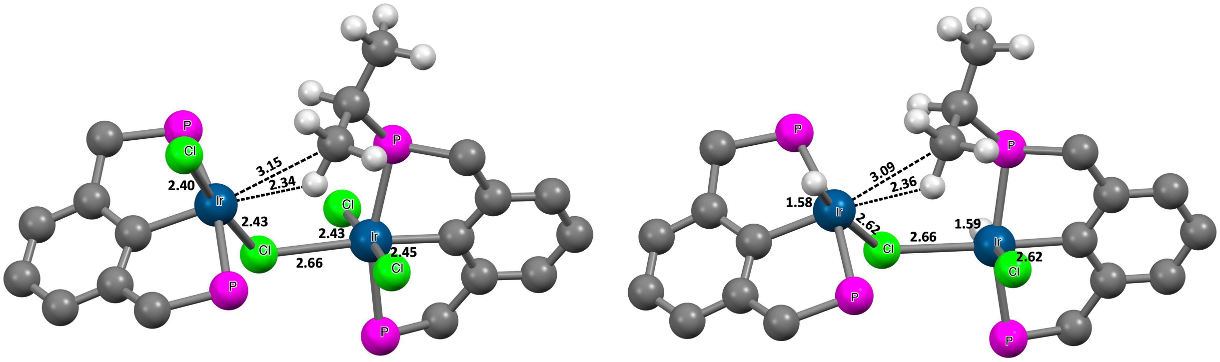


Figure 7. Calculated lowest-energy structures of dimers of **1-Cl$_2$** and **1-HCl**. Phosphinoisopropyl groups (other than the *i*-Pr group engaged in σ-C-H bonding with the complementary iridium center) and backbone H atoms omitted for clarity. Selected distances (to Ir) in Å.

SUMMARY

Attempts to generate the complex **1-Cl$_2$** have revealed insight into the nature of this species, likely applicable in part to other high-oxidation-state pincer complexes with halide ligands. **1-Cl$_2$** and adducts thereof are found to be thermodynamically very disfavored relative to **1-HCl** and adducts thereof; this is manifest for example in the need to add a hydrogen acceptor to drive the reaction of **1-HCl** with excess HCl to form **1-Cl$_2$** or, conversely, the formation of **1-HCl** from the reaction of **1-Cl₂** with H_2. **1-Cl₂** is not stable as a monomer but exists in solution as a mixture of clusters which can add various small molecules. In the presence of aqueous HCl, **1-Cl₂** adds chloride ion to give an unusual example of an anionic transition metal complex with a Zundel cation ($H_5O_2^+$). DFT calculations indicate the favorability of formation of a dimer of **1-Cl₂** with terminal chloride ligands that are potentially available for further bridging with additional monomeric units.

■ ASSOCIATED CONTENT

Supporting Information

Complete experimental details and synthetic procedures, NMR data, computational details and data, computed energies and thermodynamic quantities (**PDF**)

Optimized structures for calculated species (.mol format) (**ZIP**)

Accession Codes

CCDC 2309473, 2309474, 2309483, 2309501, 2311745 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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