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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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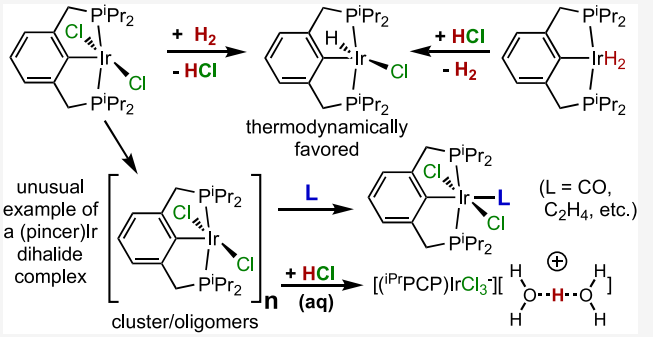
ABSTRACT: Pincer-ligated iridium complexes have been widely developed, and (pincer)Ir(III) complexes, particularly five-coordinate, are central to their chemistry. Such complexes typically bear two formally anionic ligands in addition to the pincer ligand itself. Yet despite the prevalence of halides 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$_6$H$_3$(CH$_2$P^{i}Pr$_2$)) and adducts thereof. These species are found to be thermodynamically disfavored relative to the corresponding hydridohalides. For example, DFT calculations and experiments indicate that one Ir−Cl bond of (^{iPr}PCP)IrCl$_2$ complexes will undergo reaction with H$_2$ to give (^{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 and trimerization of (^{iPr}PCP)IrCl$_2$ are more favorable than the analogous reactions of (^{iPr}PCP)IrHCl, in accord with cluster formation being observed only for the dichloride complex.



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$_6$H$_3$(CH$_2$PR$_2$)), 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$_2$O) (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, (CCC^{Mes})IrX$_2$ (CCC^{Mes} = [κ^3-1,3-(CH$_2$NHC^{Mes})$_2$C$_6$H$_3$]; NHC^{Mes} = *N*-mesitylimidazol-2-ylidene). The corresponding six-coordinate ligand adducts are much less rare, although 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.[57]

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,[58,59] presumably due to lesser crowding at the iridium center. In the case of Ir(III) complexes, with the metal center

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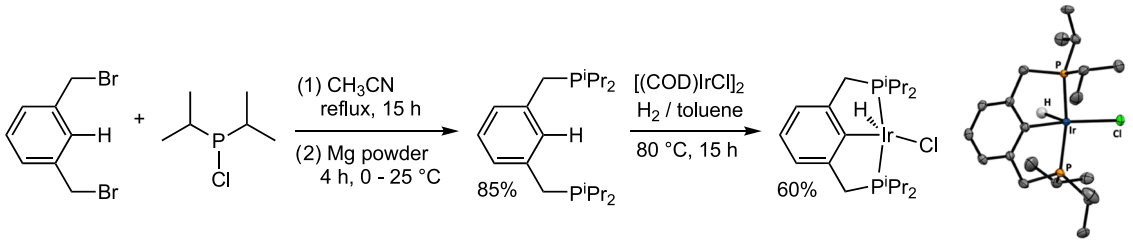
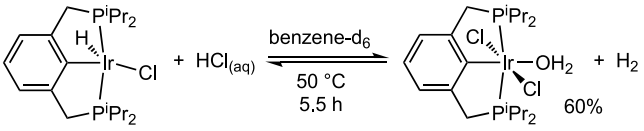
Scheme 1. Synthesis of (^{iPr}PCP-H) Pro-Ligand and Metalation to Give 1-HCl (ORTEP Diagram Shown, 50% Probability Level, Molecule 1)



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.[60] Accordingly, we chose to investigate (^{iPr}PCP)Ir(III) complexes, and we began our study with the synthesis of (^{iPr}PCP)IrHCl[58] (**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.[59] **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 pro-ligand (^{iPr}PCP-H) was prepared by the method of Ozerov[61] 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.[38,62−65] In particular, both molecules in the unit cell show the characteristic "Y" geometry[66−68] 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)°) and an acute H−Ir−C angle (75(2), 83(2)°) for molecules 1 and 2, respectively.

We initially attempted to generate **1-Cl$_2$** by the addition of anhydrous HCl to **1-HCl**. However, even after heating at 80 °C for 1 h and then adding 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$_2$·H$_2$O (**1-Cl$_2$(H$_2$O)**). 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

Scheme 2. Reaction of 1-HCl with $HCl_{(aq)}$ (No Added Hydrogen Acceptor)



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.

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$_5$O$_2$] (Scheme 3 and Figure 1). The latter contains anionic **1-Cl$_3$**$^-$ and, interestingly, the Zundel cation,[69,70] $[H_5O_2]^+$. There are only a few crystallographically characterized examples of anionic metal complexes with a Zundel cation.[71,72]

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).

When only 0.5 equiv $HCl_{(aq)}$ was added to **1-HCl** (along with 1.75 equiv 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 the temperature, the signal shifted downfield and broadened, giving rise to a broad signal at δ 29.8 at 100 °C, which we attribute to **1-Cl$_2$** and **1-Cl$_2$(H$_2$O)** undergoing rapid exchange (SI, Figure S20). Thus, H$_2$O is found to bind much more strongly to **1-Cl$_2$** than to **1-HCl** in the given solution.

Attempts to quantify the binding constants of H$_2$O to **1-Cl$_2$** 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-Cl$_2$** versus **1-HCl**.

Addition of CO to a *p*-xylene-d_{10} solution of **1-Cl$_2$(H$_2$O)** resulted in rapid substitution of the water to give ***trans*-1-Cl$_2$(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

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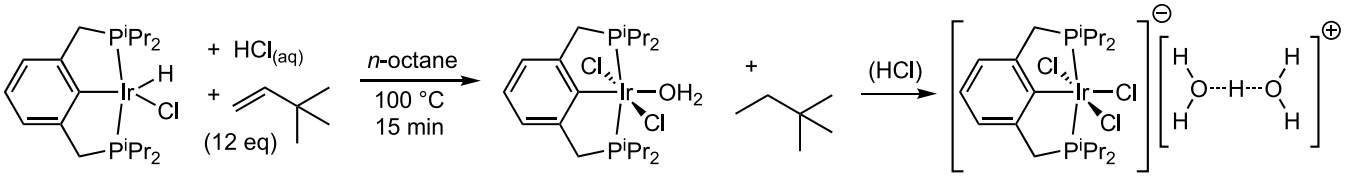
Scheme 3. Reaction of 1-HCl with $HCl_{(aq)}$ (3 Equiv) and TBE



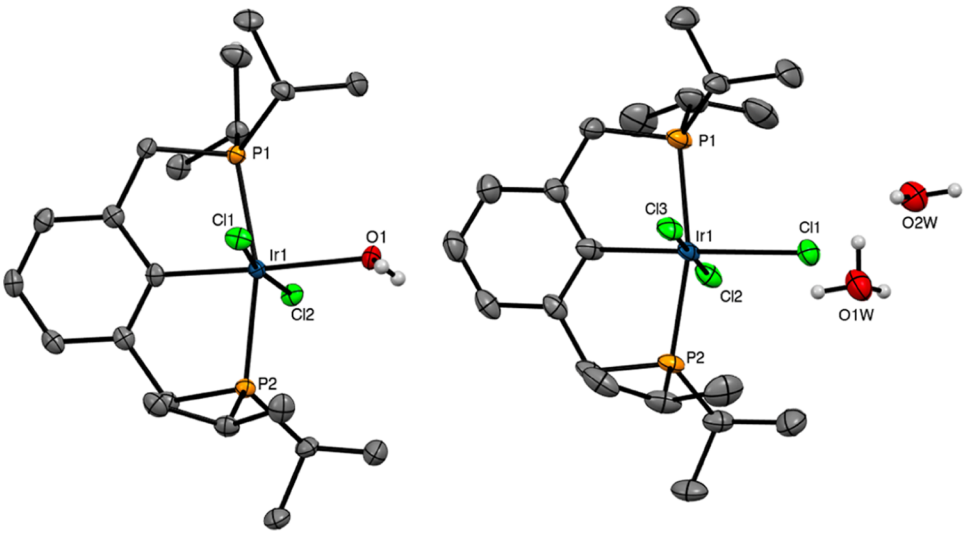
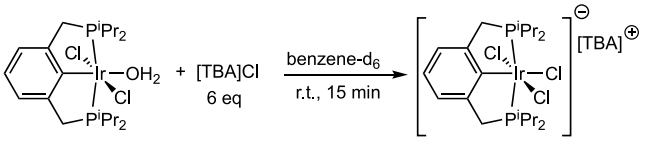


Figure 1. Molecular structure of **1-Cl_2(H_2O)** and **1-Cl_3(H_5O_2)** determined by scXRD. Hydrogen atoms other than those on water molecules omitted for clarity.

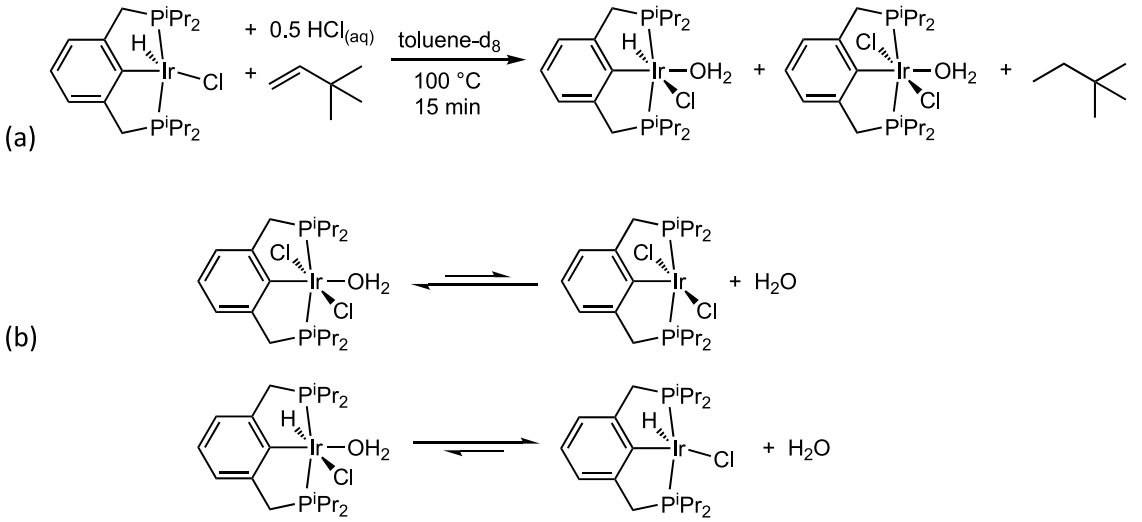
Scheme 4. Synthesis of [1-Cl_3][TBA]



assignments were in agreement with solid-phase molecular structures obtained by scXRD for both carbonyl complexes (Figure 2).

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 indeed 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 *cis* isomer being 4.8 kcal/mol lower in free energy. This result is in good

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)$IrCl_2$



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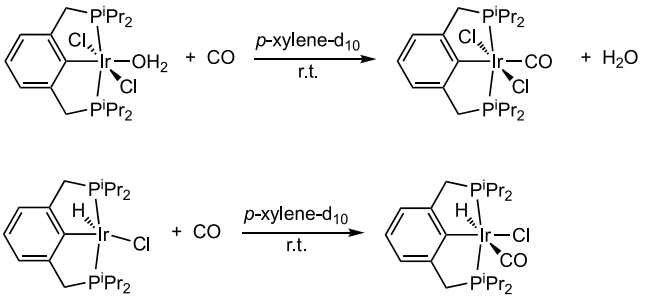
Scheme 6. Synthesis of 1-Cl_2(CO) and 1-HCl(CO)



agreement with calculations indicating that for (^{tBu}PCP)IrX_2L and related complexes the coordination sites *cis* to the Ir-bound carbon are significantly more crowded than the trans site.[65,73] 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 and 2.97 Å (Figure 3). These close contact distances reflect favorable interactions,[74−76] possibly with H-bonding character.[77] 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 more severe crowding in (^{tBu}PCP)IrCl_2(CO).

Transition metal hydrides typically react with acids to yield H_2. As indicated in Scheme 2, however, **1-Cl_2(H_2O)** appears to react with H_2 to yield **1-HCl(H_2O)**, i.e., the reverse of acidolysis resulting in the formation of H_2. Confirming this proposal, addition of 1 atm H_2 to a solution of **1-Cl_2(H_2O)** resulted in complete conversion to **1-HCl(H_2O)** within 24 h (Scheme 7). Our DFT calculations predict that hydrogenolysis of one Ir−Cl bond of both **1-Cl_2** and **1-Cl_2(H_2O)** is very slightly endergonic ($\Delta G°$ = 2.9 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 ($\Delta G°$ = 0.3 and −1.3 kcal/mol respectively).[78] In contrast, hydrogenolysis of the Ir−Cl bond of either **1-HCl** or **1-HCl(H_2O)** is very highly endergonic ($\Delta G°$ = ca. 30 kcal/mol; Figure 5).

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).[79] In all of 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. In contrast, having three (or more) strong-trans-influence ligands coordinated in the same plane inevitably leads to unfavorable trans interactions between at least two of these ligands. In the present case, this leads to the hydrogenolysis reactions of **1-HCl** and **1-HCl(H_2O)** (Figure 5) being much less favorable than the hydrogenolyses of **1-Cl_2** and **1-Cl_2(H_2O)** (Figure 4).

The synthesis of **1-Cl_2** was attempted via the removal of H_2O from **1-Cl_2(H_2O)** 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 S19). 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. DOSY ^{1}H NMR spectroscopy indicates the presence of significant concentrations of high-MW species, specifically with MW corresponding approximately to $[(^{iPr}PCP)IrCl_2]_n$ (n = 2, 3, 4) in addition to monomer. Addition of H_2O to this solution yielded **1-Cl_2(H_2O)**, and addition of CO then yielded **1-Cl_2(CO)**. We

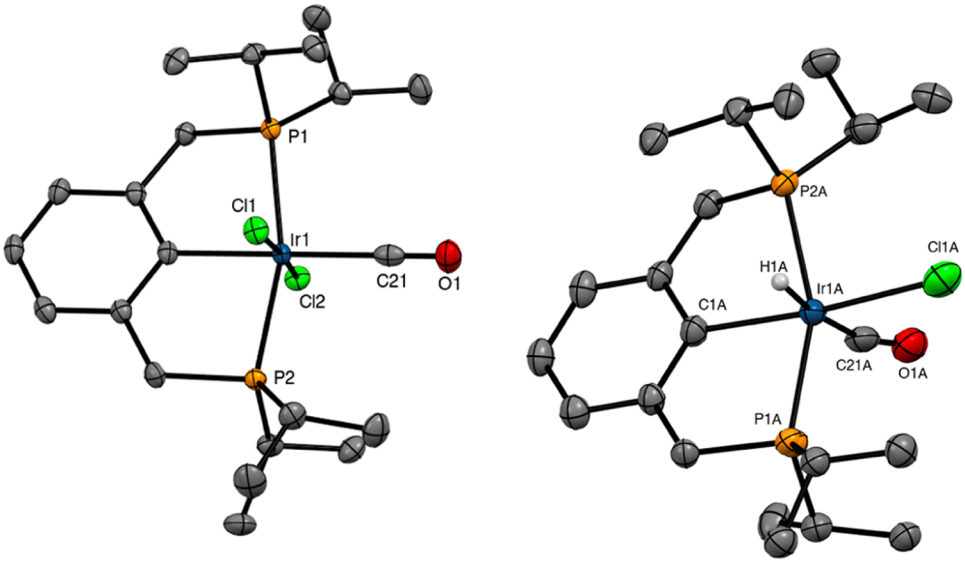


Figure 2. Molecular structure of **1-Cl_2(CO)** and **1-HCl(CO)** determined by scXRD. Hydrogen atoms, except the hydride of **1-HCl(CO)**, omitted for clarity.

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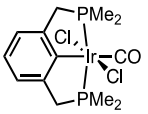
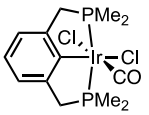
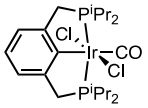
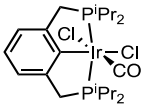
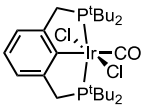
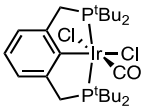
Table 1. Calculated Relative Stability of *trans*- Versus *cis*-(^{R}PCP)IrCl$_2$(CO) for R = Me, ^{i}Pr, ^{t}Bu

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

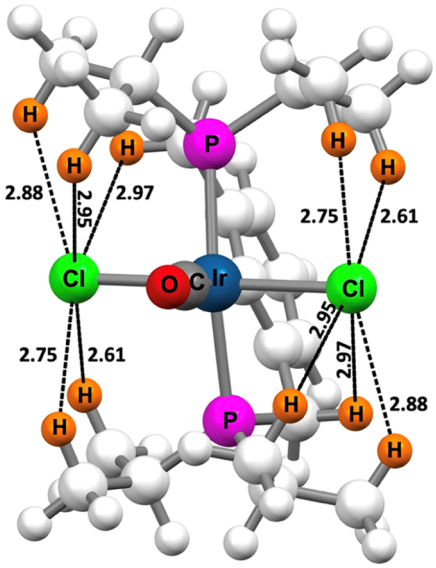
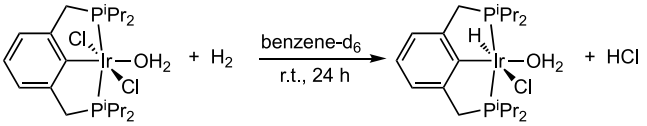


Figure 3. Calculated structure of **1-Cl$_2$(CO)**, colored to highlight close CH-Cl distances (given in Å).

Scheme 7. Reaction of (^{iPr}PCP)IrCl$_2$(H$_2$O) with 1 atm of H$_2$ to Generate (^{iPr}PCP)IrHCl(H$_2$O)



propose that upon loss of H$_2$O from **1-Cl$_2$(H$_2$O)**, a complex mixture of aggregates, [**1-Cl$_2$**]$_n$, is formed. Upon heating, this material dissociates reversibly to give an equilibrium with monomeric **1-Cl$_2$** (Scheme 8).

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 δ 29.8; further heating to 135 °C leads to a signal at δ 34.5. The difference between the chemical shifts, δ 34.5 versus δ 40, reflects that due to the presence of H$_2$O, 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$_2$O 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$_2$O from **1-Cl$_2$(H$_2$O)** by ethylene (Scheme 10).

The addition of H$_2$ atmosphere to [**1-Cl$_2$**]$_n$ initially results, as indicated by ^{31}P and ^{1}H NMR spectroscopy, in the reversible formation of a single new species, "**1-Cl$_2$H$_2$**." Removal of H$_2$ atmosphere returned the original NMR spectra of [**1-Cl$_2$**]$_n$ aggregates. Notably, even under H$_2$ atmosphere, the characteristic signal of H$_2$ in solution (δ 4.50) was not observed in the ^{1}H NMR spectrum, consistent with the exchange between bound and free (solution-phase) H$_2$ occurring rapidly on the NMR time scale. When CO was added to the NMR tube (without removal of H$_2$ atmosphere), H$_2$ was apparently displaced from the complex (Scheme 11),

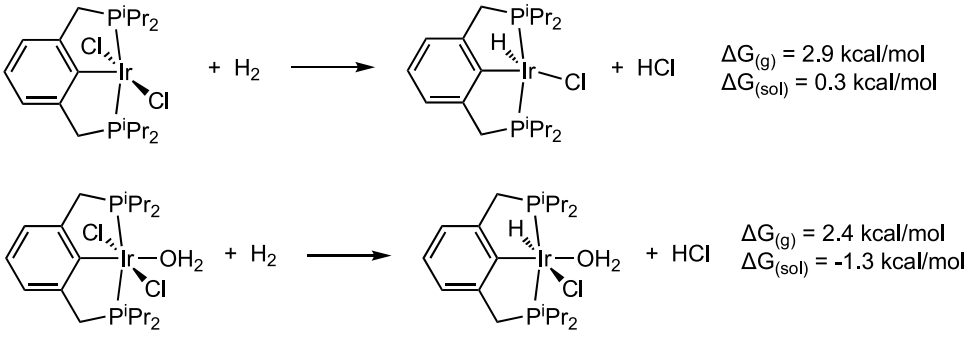


Figure 4. Thermodynamics of hydrogenolysis of **1-Cl$_2$** and **1-Cl$_2$(H$_2$O)**.

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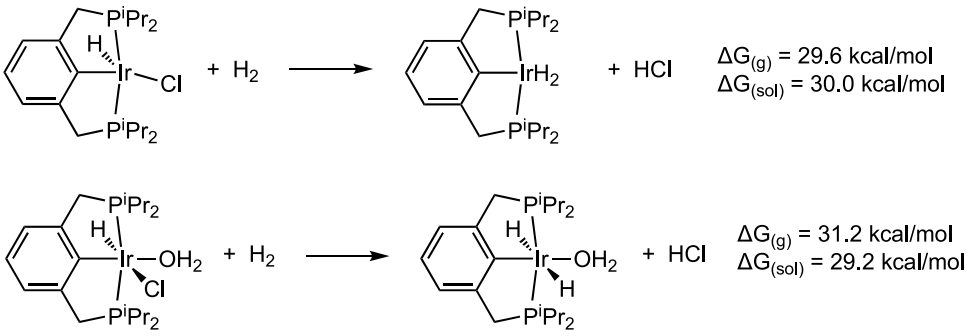


Figure 5. Thermodynamics of hydrogenolysis of **1-HCl** and **1-HCl(H_2O)**.

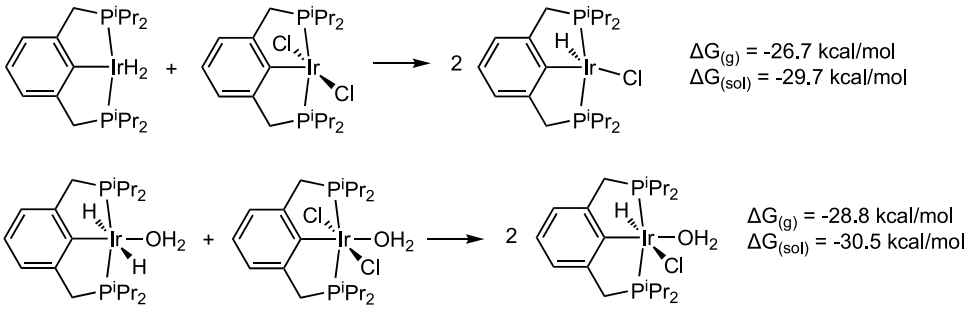
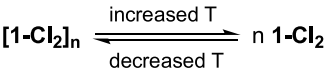


Figure 6. Thermodynamics of comproportionation of **1-HCl**/**1-H_2** and **1-HCl(H_2O)**/**1-H_2(H_2O)**.

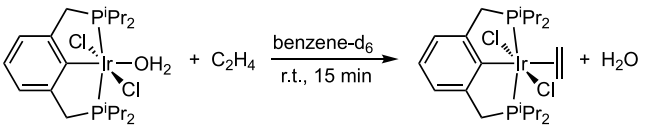
Scheme 8. Reversible Formation of (^{iPr}PCP)$IrCl_2$ Clusters



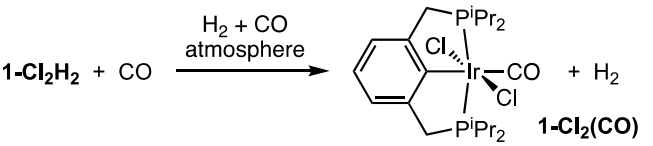
and, as would be expected, the solution-phase H_2 was now clearly observable in the ^{1}H NMR spectrum.

When the solution of **1-Cl_2H_2** under pure H_2 atmosphere was cooled to −85 °C, a sharp signal attributable to dissolved H_2 was observed in the ^{1}H NMR spectrum, indicating that exchange was slow on the NMR time scale at this temperature. Surprisingly, however, no signal attributable to hydrides or coordinated dihydrogen was observed. This suggested that **1-Cl_2H_2** was undergoing some intramolecular exchange process and that the hydrogens were chemically inequivalent (and **1-Cl_2H_2** was not, in analogy with **1-CO** or **1-C_2H_4**, *trans*-(^{iPr}PCP)$IrCl_2(H_2)$ or *trans*-(^{iPr}PCP)$IrCl_2(H)_2$). DFT calculations shed some light on this issue. Several isomers of the proposed empirical formula were calculated to have energy minima that could account for the reversible addition at room temperature and the stability at −85 °C (Figure 7). Most

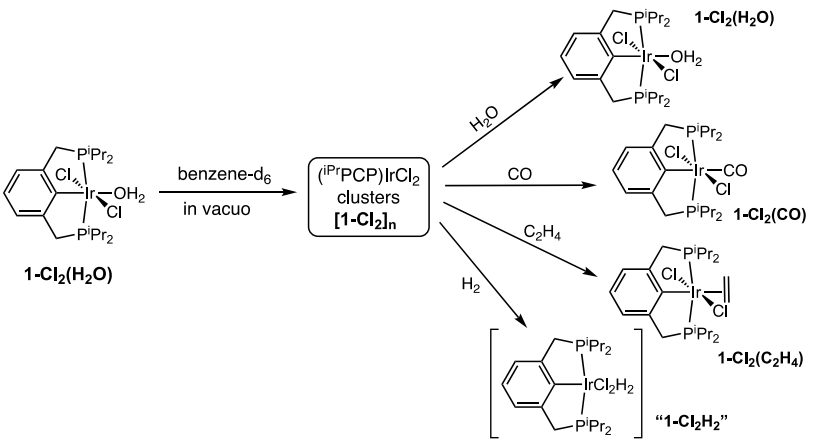
Scheme 10. Independent Synthesis of 1-Cl_2(C_2H_4)



Scheme 11. Reaction of 1-Cl_2H_2 with CO



Scheme 9. Formation of (^{iPr}PCP)$IrCl_2$ Clusters and Reactions to Form Adducts



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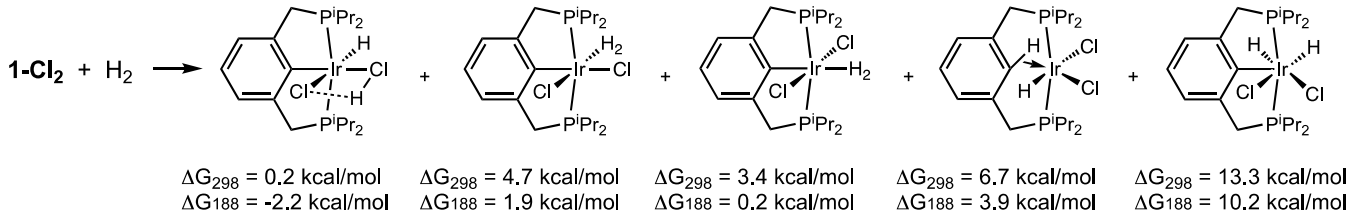

Figure 7. Calculated free energies of addition of H_2 to **1-Cl$_2$** to give isomers with composition **1-Cl$_2$H$_2$**.

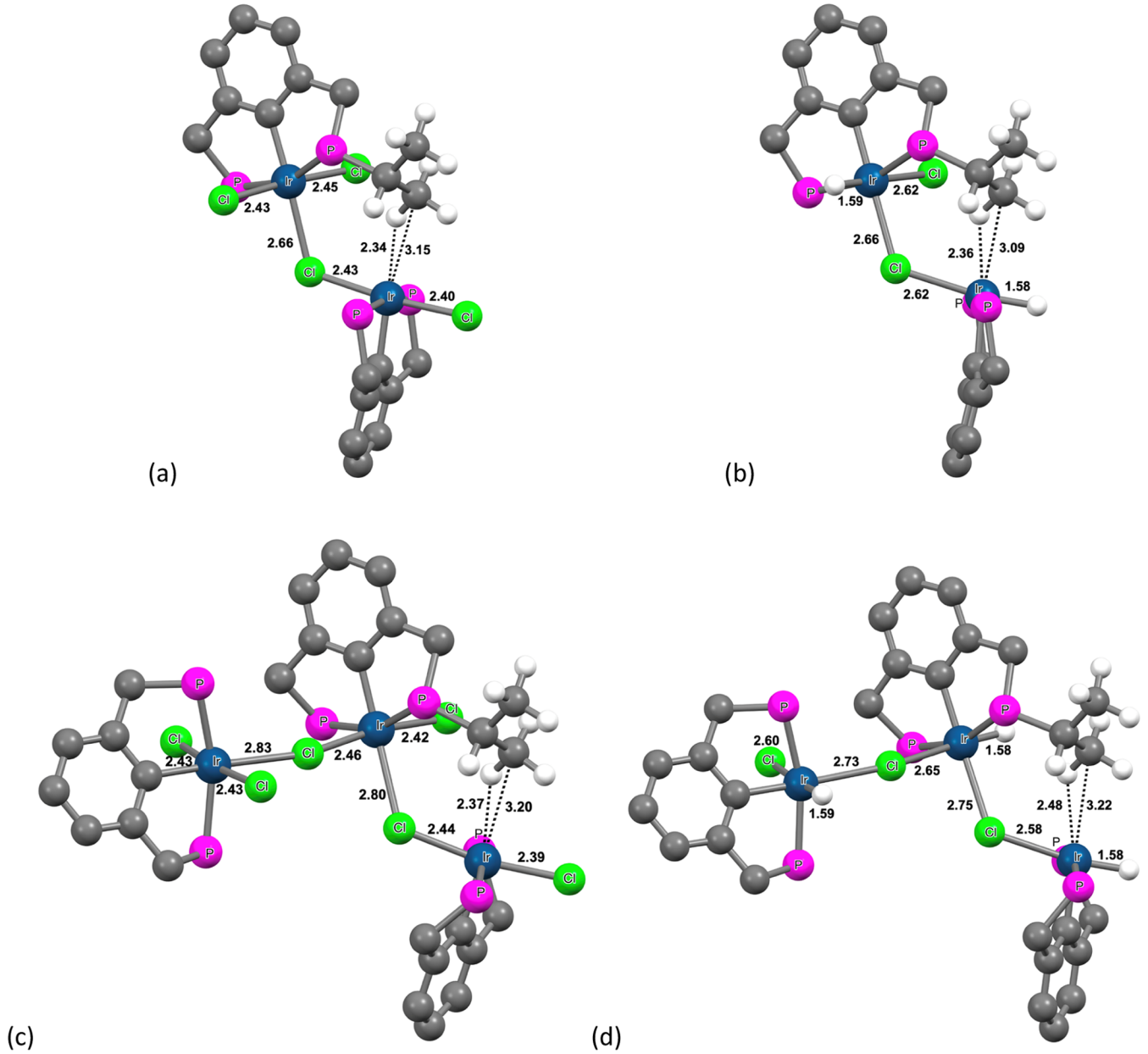

Figure 8. Calculated lowest-energy structures of dimers (a, b) and trimers (c, d) of **1-Cl$_2$** and **1-HCl**, respectively. Phosphino-isopropyl groups (other than the *i*-Pr group engaged in σ−C-H bonding with another iridium center) and backbone H atoms omitted for clarity. Selected distances (to Ir) in Å.

interestingly, the isomer calculated to be of lowest energy was *trans*-(^{iPr}PCP)IrHCl(ClH), i.e., an Ir(III) complex with a datively bound molecule of HCl engaged in H-bonding with the terminal chloride ligand (Figure 7). However, more conventional species of the same composition were calculated to be very slightly higher in energy. Although the dynamics of interconversion between such species is beyond the scope of this work, any such interconversions may result in H/H exchange. This could result in line-broadening that precludes observation of the hydride ligand in the ^{1}H NMR spectrum.

DFT calculations of simple dimerization and trimerization may also shed light on the conclusion that **1-Cl$_2$** tends to form

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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 (Figure 8a). A strikingly analogous structure is found for the dimer of **1-HCl** (Figure 8b). Formation of such dimers (**1-XCl**)$_2$ (X = H or Cl) requires X and Cl to be positioned mutually trans in both monomer units. In the case of **1-Cl$_2$**, this geometry is essentially no different than in the free monomer (calculated C_{PCP}−Ir-Cl angles of 95.2°), whereas dimerization of **1-HCl** requires a significant rearrangement of its coordination sphere. In particular, dimerization of **1-HCl** requires repositioning of the chloride to occupy 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 8). Accordingly, dimerization of **1-Cl$_2$** is calculated to be 5.7 kcal/mol more exergonic ($\Delta G°$ = −0.9 kcal/mol) than that of **1-HCl** ($\Delta G°$ = 4.8 kcal/mol). Additionally, we suspect that favorable C−H···Cl−Ir interactions play a role. This could include interactions between the **1-Cl$_2$** units as well as resulting intraunit interactions, such as seen in Figure 3, that are favored by the configuration with mutually trans-chloride ligands.

As with dimerization, trimerization is calculated to be more favorable for **1-Cl$_2$** than for **1-HCl** ($\Delta G°$ = −15.7 versus −1.8 kcal/mol). The same factors appear to be in play for trimerization as for dimerization, including the need for rearrangement to allow coordination of the additional **1-HCl** unit, and the formation of numerous additional close contacts of C−H bonds with the terminal chlorides of the additional **1-Cl$_2$** unit in (**1-Cl$_2$**)$_3$. The trimers are readily viewed as the product of the dimers adding an additional monomer unit via a terminal chloride of the **1-XCl** unit in (**1-XCl**)$_2$ (specifically the unit that has accepted a chloride from its partner for bridging; Figure 8). The structure of the initial dimeric unit is largely maintained in the trimers. Higher oligomers may form following the same pattern and presumably with similar thermodynamics for "chain growth." Thus, in the context of oligomer/cluster formation, it is noteworthy that the addition of the monomeric unit to dimer is significantly more favorable for **1-Cl$_2$** ($\Delta G°$ = −14.8 kcal/mol) than for **1-HCl** ($\Delta G°$ = −6.6 kcal/mol).

SUMMARY

Attempts to generate the complex **1-Cl$_2$** have revealed insight into the nature of this species, possibly applicable to other high-oxidation-state pincer complexes with halide ligands. **1-Cl$_2$** and adducts thereof are found to be thermodynamically 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, by the formation of **1-HCl** from the reaction of **1-Cl$_2$** with H_2. **1-Cl$_2$** is not stable as a monomer but exists in solution as a mixture of clusters which react with H_2O, CO, or C_2H_4 to give the corresponding monomeric six-coordinate species **1-Cl$_2$L**. In the presence of aqueous HCl, **1-Cl$_2$** adds a 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 the formation of dimers and trimers of **1-Cl$_2$** relative to those of **1-HCl**, which likely relates to the much greater tendency of the former to form clusters.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.4c00162.

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

Optimized structures for calculated species (ZIP)

Accession Codes

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

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Notes

The authors declare no competing financial interest.

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(78) For purposes of simplifying the comparative analysis we consider hydrogenolysis of ***trans*-1-$Cl_2(H_2O)$** to give ***trans*-1-HCl(H_2O)**. However, ***cis*-1-HCl(H_2O)** is calculated to be more stable than ***trans*-1-HCl(H_2O)**, by 1.7 kcal/mol (gas phase) and 2.3 kcal/mol (solvent continuum).

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