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Binding of Chlorohydrocarbons to Metal Centers: Quantitative Evaluation of Relative Binding Constants and Structural Characterization of the First Isolable Transition Metal−Chloromethane Adduct

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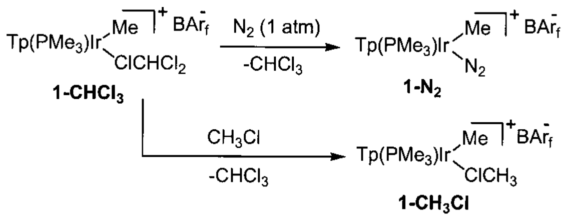
During the past 50 years halogenated hydrocarbons have been synthesized by industry in massive quantities, due primarily to their use as solvents, refrigerants, and precursors for polymeric and molecular organic materials.[1] Their prevalence in soil, water, living organisms, and the atmosphere is increasingly evident and the harmful effects of many of these materials is well established.[2−4] As efforts are developed to control the emissions of halocarbons, it is important to create methods for their sequestration, activation, and functionalization.

One approach to this problem involves the development of metal complexes that are capable of selective and reversible binding of halocarbons to metal centers. Halocarbons typically either react irreversibly with or bind only weakly to most metal centers. However, a few molecules, such as iodomethane and dichloromethane, do form reasonably stable adducts with certain metals.[5−9] Little information has been available about whether other halocarbons can be found that also bind reversibly to metals, and more importantly, whether their relative binding abilities can be quantified.[9]

Herein we report the synthesis of a unique series of chlorohydrocarbon−metal complexes. These utilize the cationic iridium(III) fragment $[Tp(PMe_3)IrMe]^+$ (**1**, Tp = hydridotris(pyrazolyl)borate) as a binding center. We find that this cation forms complexes not only with several chlorocarbons, including chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), and chloromethane (CH_3Cl), but also with gaseous nitrogen (N_2). These materials can be characterized and quantified in solution by NMR spectroscopy, and some are isolable. The fact that CH_3Cl is in the latter category has allowed us to fully characterize, including by X-ray diffraction, the first isolable chloromethane−metal complex. Finally, we have been able to measure the relative binding constants for two chlorocarbons toward the iridium center in **1** and compare our experimental numbers with theoretical estimates for these affinities.

We recently reported the synthesis of the surprisingly stable dichloromethane complex $[Tp(PMe_3)IrMe(CH_2Cl_2)][BAr_f]$ (**1-CH$_2$Cl$_2$**; BAr_f = $B[3,5\text{-}C_6H_3(CF_3)_2]_4$).[10] The iridium-bound dichloromethane molecule was observed by ^{13}C NMR spectroscopy at room temperature, indicating that exchange with the solvent is slow on the NMR time scale. The slow rate of CH_2Cl_2 dissociation from the iridium center is further evidenced by the fact that the synthesis of the thermodynamically more stable dinitrogen complex **1-N$_2$** from **1-CH$_2$Cl$_2$** necessitated the use of high dinitrogen pressures (50 atm, $t_{1/2}$ = 3 h). The stability of **1-CH$_2$Cl$_2$** prompted us to explore the ability of the cationic fragment $Tp(PMe_3)IrMe^+$ (**1**) to act as a template for binding other chlorohydrocarbons.

Scheme 1



We first explored chloroform as a potential ligand for **1** with the hope that its decreased electron donor capability and increased steric bulk would make it a more labile ligand for the iridium cation. Dissolution of **1-CH$_2$Cl$_2$** in chloroform resulted in the liberation of dichloromethane (δ 5.30 ppm) and the formation of a new, very sensitive iridium-containing product that we formulate as $[Tp(PMe_3)IrMe(CHCl_3)][BAr_f]$ (**1-CHCl$_3$**).[11] Chloroform complex **1-CHCl$_3$** decomposes over the course of 4 h at room temperature to an insoluble brown oil. Attempts to detect the bound $CHCl_3$ carbon resonance of **1-CHCl$_3$** utilizing low-temperature ^{13}C NMR spectroscopy (−60 °C) were unsuccessful, probably because exchange with the bulk chloroform solvent is still fast on the NMR time scale at this temperature. The reactivity of **1-CHCl$_3$** is consistent with the presence of a weakly bound $CHCl_3$ ligand. Allowing a solution of **1-CHCl$_3$** to stir under N_2 (1 atm) resulted in formation of **1-N$_2$** ($t_{1/2}$ ~ 1.5 h, 90% yield) (Scheme 1). Consequently, **1-N$_2$** can be synthesized on preparative scale by simply dissolving **1-CH$_2$Cl$_2$** in chloroform under 1 atm of dinitrogen (instead of the 50 atm of N_2 required in CH_2Cl_2 solution).

Since chloroform proved to be an effective solvent for the synthesis of **1-N$_2$**, it was used as the solvent for carrying out preparative reactions between **1-CHCl$_3$** and chloromethane. In the absence of N_2, chloromethane (5 equiv) was added to a chloroform solution of **1-CHCl$_3$** (Scheme 1) to produce $[Tp(PMe_3)IrMe(CH_3Cl)][BAr_f]$ (**1-CH$_3$Cl**). This is a much more stable complex than **1-CHCl$_3$**, and in $CDCl_3$ solution, the bound chloromethane resonance was observed at 2.65 ppm (free CH_3Cl = 3.02 ppm) in the room temperature ^1H NMR spectrum. Additionally, a singlet at 33.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum assigned to the bound chloromethane carbon was observed (free CH_3Cl = 24.9 ppm). To confirm the identity of **1-CH$_3$Cl**, a $^1H-^1H$ NOESY spectrum was acquired. As expected, through-space coupling was observed between the resonance assigned to the bound $ClCH_3$ and those of the $P(CH_3)_3$ and Ir-CH_3 groups. Finally, an isotopic perturbation of equilibrium (IPE) experiment with $ClCH_2D$ was performed to ascertain the solution state binding mode of CH_3Cl in **1-CH$_3$Cl**.[12] In particular, we wished to confirm

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[11] No change in the ^1H NMR spectrum of **1-CDCl$_3$** was observed when CH_2Cl_2 was removed.

[12] We prefer the term isotopic perturbation of equilibrium over "isotopic perturbation of resonance (IPR)". As originally described by Saunders and co-workers, IPR refers to a perturbation of resonance *structures*, not the resonance *frequency* in the NMR spectrum. See: Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8071−8072.

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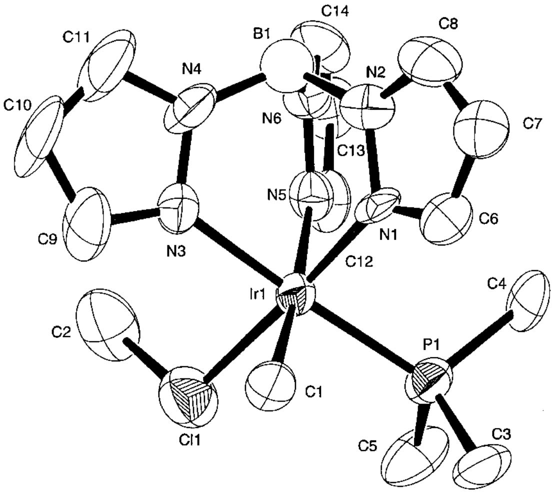

Figure 1. ORTEP diagram of the cationic portion of **1-CH$_3$Cl**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å): Ir−Cl1 2.364(3); Ir−C1 2.117(9); Cl1−C2 1.77(1). Selected bond angles (deg): Ir−Cl1−C2 109.3(5); Cl1−Ir−C1 86.8(3).

that chloromethane was bound to iridium through a chlorine lone pair and not a C−H bond.[13] Treatment of a CDCl$_3$ solution of **1-CDCl$_3$** with CH$_2$DCl (5 equiv) resulted in quantitative formation of **1-CH$_2$DCl** by ^{1}H NMR spectroscopy. The bound chloromethane resonance in **1-CH$_2$DCl** was observed at 2.63 ppm (t, $^2J_{D-H} = 2$ Hz, 2H) only 0.02 ppm upfield from the CH$_3$Cl resonance observed in **1-CH$_3$Cl** (2.65 ppm). This small difference is consistent with the M−Cl−CH$_3$ binding mode in which the C−H bond is not perturbed significantly by coordination of CH$_3$Cl to iridium.

Chloromethane complex **1-CH$_3$Cl** can be isolated on a preparative scale in 63% yield by dissolving **1-CH$_2$Cl$_2$** in chloromethane. Single crystals of **1-CH$_3$Cl** suitable for X-ray crystallographic analysis were obtained by allowing pentane to diffuse into a CHCl$_3$ solution saturated with CH$_3$Cl at −40 °C. The ORTEP diagram of **1-CH$_3$Cl** is shown in Figure 1 and provides definitive evidence for the molecular architecture illustrated in Scheme 1.

To our knowledge this is the first isolable chloromethane adduct. Gladysz and co-workers spectroscopically characterized a rhenium chloroethane adduct in dichloromethane solution as a 40:60 mixture of the chloroethane and dichloromethane complexes.[14] The unusual stability of chloromethane adduct **1-CH$_3$Cl** reflects the strongly Lewis acidic character of the "Tp(PMe$_3$)IrMe$^+$" fragment.

While chloroform was an effective solvent for the synthesis of **1-CH$_3$Cl**, dichloromethane proved to be a less convenient solvent for this synthesis. Addition of a large excess (~100 equiv) of CH$_3$Cl to a degassed CH$_2$Cl$_2$ solution of **1-CH$_2$Cl$_2$** resulted in the formation of **1-CH$_3$Cl**. In CD$_2$Cl$_2$, the bound chloromethane resonance was observed at 2.80 ppm (free CH$_3$Cl = 3.03 ppm). In the absence of excess CH$_3$Cl, **1-CH$_3$Cl** was converted back to **1-CH$_2$Cl$_2$** with concomitant liberation of chloromethane ($t_{1/2} \sim 2$ h). This reversibility prompted us to measure the equilibrium between **1-CH$_2$Cl$_2$** and **1-CH$_3$Cl**. Addition of CH$_3$Cl to a dichloromethane solution of **1-CH$_2$Cl$_2$** (0.012 mM) resulted in the formation of a mixture of **1-CH$_2$Cl$_2$** and **1-CH$_3$Cl** ($K_{eq} = 90 \pm 10$). Thus, the chloromethane adduct **1-CH$_3$Cl** is 2.6 kcal/mol (ΔG_{295}) more stable than **1-CH$_2$Cl$_2$**.[9]

As demonstrated above, the relative ligand binding affinity for **1** is CH$_3$Cl > CH$_2$Cl$_2$ > CHCl$_3$. The instability of the chloroform complex **1-CHCl$_3$** prohibited attempts to quantify the energetic differences between chloroform and the other chlorohydrocarbons. As a result, density functional theory calculations were carried out on **1-CH$_3$Cl**, **1-CH$_2$Cl$_2$**, **1-CHCl$_3$**, CH$_3$Cl, CH$_2$Cl$_2$, and CHCl$_3$. The minimum-energy geometries were calculated at the BP86/LACVP* level of theory in Jaguar[15] and single-point energy calculations were carried out on the optimized structures at the BP86/LACVP**+ level of theory. The difference in free energy (ΔG_{298}) between **1-CH$_2$Cl$_2$/CH$_3$Cl** and **1-CH$_3$Cl/CH$_2$Cl$_2$** was calculated to be 3.2 kcal/mol. This value is in good agreement with the experimentally obtained value of 2.6 kcal/mol and supports the postulate that CH$_3$Cl is a stronger ligand than CH$_2$Cl$_2$ for **1**. The difference in free energies between **1-CH$_3$Cl**/CHCl$_3$ and **1-CHCl$_3$**/CH$_3$Cl was calculated to be 6.0 kcal/mol (ΔG_{298}). Therefore, each additional chlorine atom destabilizes the iridium chlorohydrocarbon interaction by ~3 kcal/mol. This is likely the result of both steric and electronic factors; the additional chlorine atoms attenuate the Lewis basicity and increase the steric demand of CH$_2$Cl$_2$ and CHCl$_3$. An analogous trend has been observed by Yang and Yang in their study of the photochemically generated, charge-neutral "CpMn(CO)$_2$" fragment.[16] At 195 K, they determined that dihalomethanes (CH$_2$Cl$_2$ and CH$_2$Br$_2$) are less strongly bound than monohaloalkanes (*n*-BuBr, *n*-BuCl).[17]

In summary, we have quantified the relative binding affinities of three simple chlorohydrocarbon ligands toward positively charged iridium. Complementary to use of a noncoordinating anion, the use of a poorly coordinating solvent is essential to increasing the reactivity of cationic transition metals.[18] Utilizing this concept, we were able to access **1-N$_2$** and **1-CH$_3$Cl** from **1-CHCl$_3$**. Future work will focus on the design and use of more inert, weakly coordinating solvents. It is our hope that with the appropriate polar solvent, isolation of cationic complexes bearing weakly coordinating ligands, such as alkanes, will be possible.

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Supporting Information Available: Structural data for **1-CH$_3$Cl** and experimental data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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