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HYDROGEN BONDING IN TRANSITION METAL FLUORIDES

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SUMMARY

Hydrogen bonding often plays a crucial role in the chemistry of metal complexes and is of particular importance in the interactions of coordination compounds with biological systems. This account will discuss the role of hydrogen bonding in transition metal compounds with particular emphasis on utilizing this aspect of their chemistry to develop new metal based reagents for molecular recognition. After a brief introduction to the role of metal reagents in biochemistry and the influence of hydrogen bonding in the chemistry of organometallic compounds, recent results concerning the hydrogen bonding properties of metal fluorides prepared in my laboratory will be described. Synthetic and mechanistic chemistry relevant to chelate assisted carbon-halogen (Cl, Br, I) activation at tungsten(0) will be discussed along with structural studies of seven coordinate tungsten(II) metallacycles containing either single or double C-N bonds. The synthesis of metal carbonyl fluorides by chelate assisted oxidative addition of C-F bonds to tungsten(0) will be described including recent extensions of this chemistry to difluoro-rather than pentafluoro-substituted aromatics. Alternative synthetic routes to tungsten(II) fluorides by metathesis reactions and the reactivity of the halide in these systems will be noted. Spectroscopic (IR and ^{19}F NMR) and crystallographic characterization of hydrogen bonds involving tungsten(II) and titanium(IV) fluorides, and quantitative assessments of the base strength of fluoride bound to these metals will be included. Remarkably, fluoride bound to tungsten(II) forms 1:1 adducts with 4-chlorophenol with equilibrium association constants that rival that of the organic base pyridine. This work provides the foundation required for the design of more sophisticated receptors for target substrates.

METAL COMPLEXES IN BIOCHEMISTRY

In the past two decades, transition metal complexes have become increasingly important in biochemistry and medicine [1]. Metal containing compounds have been employed as therapeutic drugs and diagnostic agents. They have also become valuable tools for researchers seeking to understand the structures and properties of biomolecules. For example, a structural study showed that $[Co(NH_3)_6]^{3+}$ stabilizes Z-DNA by forming five hydrogen bonds from one octahedral face of the complex to guanine and phosphate groups of the Z-DNA [2]. The chirality of octahedral

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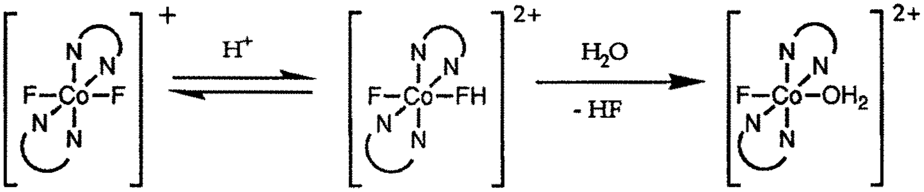
coordination complexes has been exploited to recognize and selectively cleave left-handed DNA [3]. Iron EDTA complexes in concert with organic subunits designed for base specific recognition enable site specific cleavage of right-handed double helical DNA [4]. Noncovalent (hydrophobic or hydrogen bonding) recognition processes are exploited in these examples. Covalent interactions can also form between metal ions and DNA and are thought to be important in the activity of metal based anti-tumor agents.

Perhaps the most dramatic breakthrough in this area is the development of cisplatin as an effective treatment for various forms of cancer [5]. This success has spurred intensive investigations into the coordination chemistry of platinum halides with DNA and interest in the antitumor activity of other metal halides [6]. Structural studies of cisplatin complexed to oligonucelosides indicate an intrastrand crosslink forms between the N7 atoms of two guanosine bases [5]. Interestingly, weak hydrogen bonding between a platinum coordinated ammine N-H to guanosine O(6) has been postulated. This causes more pronounced molecular distortions in the structure of *cis*-$[Pt(NH_3)_2\{d(CpGpG)\}]$ than in *cis*-$[Pt(NH_3)_2\{d(pGpG)\}]$. Intramolecular hydrogen bonding between a coordinated ammine and an oxygen a)tom of the 5'-phosphate group is also evident in the solid state structures and has been observed by solution NMR spectroscopic measurements in a platinum complex of 5'-AMP [7]. These examples indicate that the hydrogen bonding properties of transition metal complexes are important in their interactions with biochemical molecules and in some instances may govern their biological activity. This mode of molecular recognition may also be significant in the chemical behavior of metal based drugs.

HYDROGEN BONDING IN MOLECULAR RECEPTORS

Hydrogen bonding of coordinated primary and secondary amines has been detected by IR spectroscopic and structural studies of cationic coordination compounds [8]. Although the hydrogen bonding properties of coordinated halides have not been as extensively studied, chemical evidence shows that halides, especially fluoride, can act as hydrogen bond acceptors. Networks of hydrogen bonds are frequently detected in crystallographic studies of high valent metal fluorides when suitable proton donors such as the ammonium ion or water are present in the crystal lattice [9]. Structural studies of *cis*-platin analogues show that weak NH···Cl hydrogen bonds link the coordination complexes together in the solid state [10].

Hydrogen bonding is chemically significant even in cationic metal fluorides as evidenced by the classical mechanism for acid catalyzed hydrolysis of these complexes proposed by Basolo and Pearson [11].



Acid catalyzed hydrolysis is not observed for the heavier halogens and the rate of hydrolysis of the fluoride, but not the chloride, is faster in D_2O. Hydrogen bonding to the fluoride may be considered to be on the reaction coordinate to protonation of the halide [12].

Examples of hydrogen bonding in organometallic chemistry are prevalent. Classical organic ligands placed in the coordination sphere of a metal such as carboxylic acids [13], aldehydes [14], ketones [15], alcohols, and phosphates [16] may still participate in hydrogen bonding interactions even though bound to a metal. In addition hydrogen bonding can play a pronounced role in the crystallization of materials for X-ray analysis [17]. Intramolecular hydrogen bonding from a coordinated amine to an iridium halide is proposed to control the is also proposed to control the stereochemistry of C-X oxidative addition to an iridium(I) center [18]. Proton catalysis of methyl migration in $CH_3Mn(CO)_5$ my occur through a hydrogen bonding interaction to the incipient acyl group [19]. A similar rate acceleration is seen in comparing the rate of CO insertion into an α-hydroxyalkyl complex with its α-trimethylsiloxyalkyl analogue again at a manganese carbonyl center [20].

Although the ability of transition metal complexes to engage in hydrogen bonding has been recognized, only scattered quantitative information is available on the strength or specificity of these interactions. Primary or secondary amine ligands in metal carbonyl complexes influence the structures and kinetics of ligand substitution in group 6 metal carbonyl complexes [21]. A surprisingly strong hydrogen bond from phenol to the oxygen of a rhodium(I) phenoxide complex has been characterized by Bergman, Hoff and coworkers with a remarkably large enthalpy of formation of -14 kcal/mol in benzene [22]. A related series of nickel phenoxides exhibit similar chemistry [23]. An intriguing application of the hydrogen bonding ablities of transition metal complexes as receptors for amino acids has also been reported recently [24]. Metalloporphyrin receptors with pendant hyroxynapthyl groups bind amino acid esters with equilibrium constants in the range of $10^5 - 10^6 M^{-1}$. The hydrogen bonding is estimated to stabilize the adduct by 2.1 kcal/mol. Significantly, amino acids can be extracted into chloroform from aqueous solution only in the presence of the pendant hydroxynapthyl groups. Hydrogen bonding also results in selective binding of amino acid esters in the presence of free amines [24].

As outlined below, we have demonstrated that the hydrogen bonding properties of a series of tungsten(II) *cis*-amino halides provide a novel receptor site for organic substrates [25]. Recognition at the molecular level is characteristic of the biochemistry of life processes. Accordingly, chemists have sought to understand the factors that are important in molecular recognition. This field has close intellectual parallels with the design of ligands to selectively bind (or recognize) metal ions. Substantial progress has been made in a number of areas. Synthetic macrocyclic crown ethers which selectively bind metal ions or alkyl ammonium salts have been developed by several groups [26] A similar strategy is seen in the use of molecular cavities such as cyclodextrins [27] or cyclophanes [28] which provide a hydrophobic pocket for organic molecules. The enveloping nature of the recognition process limits potential reaction chemistry (aside from transport) of the guest molecule.

Molecular clefts which are capable of recognizing organic molecules have recently been investigated by several groups [29, 30] Strong binding is achieved by the use of convergent functional groups capable of multiple hydrogen bonding interactions or proton transfer with substrates. The accessibility of the bound molecule may enable reaction chemistry to occur at the guest and lead to catalytic applications. This concept has been developed by Rebek and coworkers [31] utilizing Kemp's triacid derivatives. Systematic alteration of these systems leads to binding of simple organic acids and bases, amino acids, and nucleosides [32, 33].

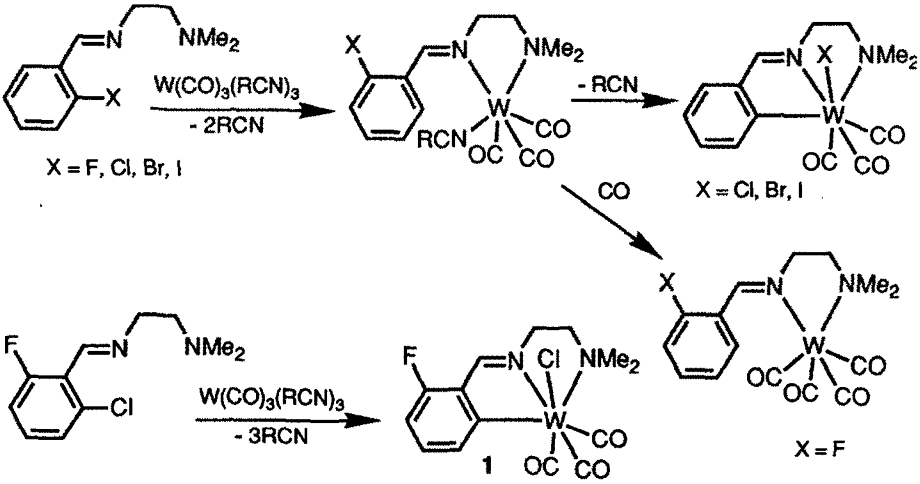
Although the design and understanding of organic receptors has become quite sophisticated, the concept of building hosts from transition metal complexes has largely been ignored. This is surprising given the role of metal complexes in biochemistry alluded to above. Organic receptors have even been designed for metal coordination complexes [34]. We are interested in building and defining the binding characteristics of inorganic receptors for organic molecules of biological interest.

These materials are the first members of a new class of inorganic receptors based on their hydrogen bonding properties. We note that a number of metalloreceptors based on inclusion phenomena [35] as well as more classical ligand binding to a vacant coordination site, particularly in macrocyclic systems, have been reported [36]. The presence of a transition metal center in these hosts may lead to potential reaction chemistry on a guest molecule not possible with wholly organic systems.

CARBON-HALOGEN BOND ACTIVATION

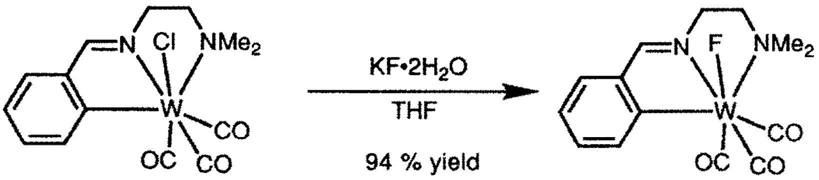
Our interest in the hydrogen bonding properties of organometallic complexes arose from our research on chelate assisted carbon-halogen bond activation in a series of tungsten carbonyl complexes. Although we originally developed [37] this chemistry with a series of symmetrical ligands derived from ethylenediamine, the higher solubility afforded by the unsymmetrical N,N-dimethylethylenediamine based ligands [38] allows us to examine the hydrogen bonding properties of these materials in less polar solvents. This is illustrated in the Scheme 1.

Scheme 1



The Schiff base ligands are easily prepared by condensation of the appropriate aldehyde and amine in ethanol and purified by vacuum distillation. These ligands readily replace two nitriles of the $W(CO)_3(RCN)_3$ starting material to afford isolable red complexes which are characterized by metal carbonyl bands at 1900 and 1775 cm^{-1} as well as a weak C≡N stretch as 2270 cm^{-1} in the case of X = Br and R = CH_3. We usually employ the very soluble propionitrile or butyronitrile reagents developed by Kubas[39]. Facile oxidative addition occurs upon dissolution of the mononitriles in dichloromethane to afford the yellow air stable oxidative addition products in good yields for X = Cl, Br, I. A three band pattern is observed in the infrared spectra of these complexes (ν_{CO} = 2014 (s), 1935 (s), 1894 (m) cm^{-1} for X = Br) consistent with formal oxidation to W(II). These seven coordinate complexes are static on the NMR time-scale (300 MHz ^1H, 75 MHz ^{13}C) and ^{183}W satellites on the order of 8 Hz are observed on the imine protons of the metallacycle. In the case of X = F, tungsten does not readily insert into the C-F bond at room temperature, although the labile nature of the remaining nitrile ligand results in eventual scavenging of CO to afford the tetracarbonyl compound. It should be noted that we can prepare the product of C-F activation by simple halide exchange [40].

Scheme 2



2: ν_{CO} = 2014, 1933 1893 cm^{-1}

3: ν_{CO} = 2007, 1919, 1883 cm^{-1}

In light of these observations, exclusive C-Cl activation is observed in the room temperature reaction of the ligand derived from 2-chloro-6-fluorobenzaldehyde. This is consistent with the stronger aromatic C-F (Bond dissociation energy = 125 kcal/mol) compared to aromatic C-Cl (BDE = 95 kcal/mol) bonds [41]. An ORTEP representation of the structure of this complex is contained in Fig. 1. The geometry about the tungsten metal center can be approximated as a capped octahedron with C4 of the newly formed tungsten-phenyl bond as the capping atom. The bite angles of the ligand [C4-W-N1, 74.3(1)°; N1-W-N2, 71.8(1)°] largely dictates this shape [42]. The metallacycle defined by {W, C4, C9, C10, N1} is planer within ± 0.05 Å. An indication of the steric congestion about the metal center is provided by the acute angles between the carbon atoms: C4-W-C1, 70.1(2)°; C4-W-C2, 68.0(2)°; C4-W-C3, 117.0(2)°; C1-W-C2, 107.4(2); C1-W-C3, 74.8(2); C2-W-C3, 75.3(2)°.

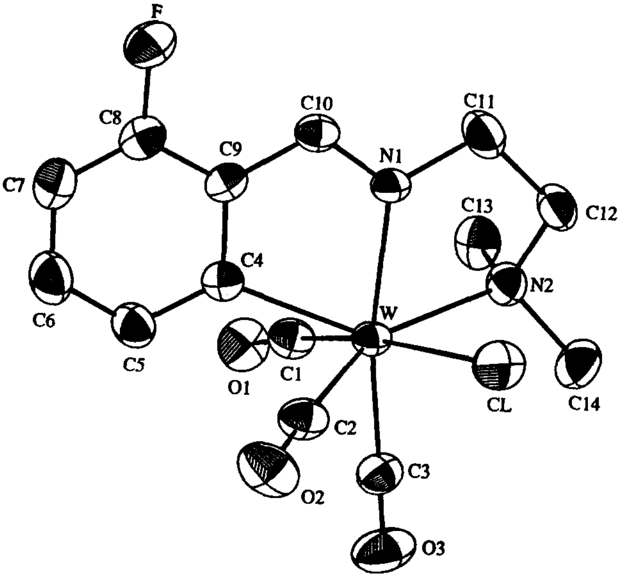
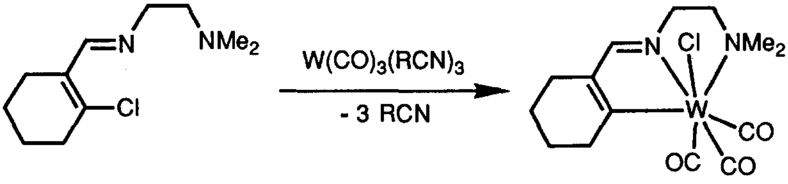


Fig. 1. ORTEP representation of 1 (Space group $P2_1/n$). Selected bond lengths (Å): W-C4, 2.236(4); W-Cl, 2.538(1); W-N1, 2.159(3); W-N2, 2.332(3); W-C1, 1.974(4); W-C2, 1.974(2); W-C3, 1.985(4), N1-C10, 1.304(5). Selected bond angles (deg): Cl-W-C4, 122.3(1); Cl-W-C1, 166.9(1); N1-W-C3, 165.8(2); N2-W-C2, 155.1(2).

In contrast to several of the structures discussed below involving fluoride bound to tungsten, there are no close intermolecular contacts observed in the solid state for 1.

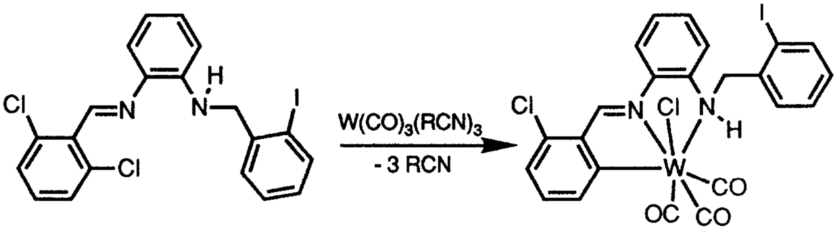
We have also observed facile C-Cl activation in the cyclohexene derived ligand illustrated below [43].

Scheme 3



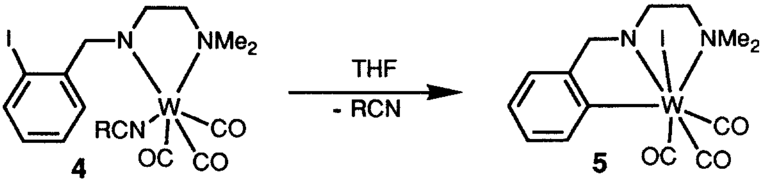
The imine functionality of our ligand system appears to be quite important in directing the regiochemistry of C-X bond activation. For example, in a competition experiment using the unsymmetrical ligand pictured in Scheme 4, exclusive C-Cl bond activation was observed in the presence of the much weaker C-I bond on the aromatic arm of the ligand [44].

Scheme 4



However, a reduced Schiff base ligand can promote C-I bond activation as shown in Scheme 5 if side reactions to afford the substitution inert tetracarbonyl complex $W(CO)_4(L)$ are avoided. Thus C-I activation takes place over the course of several hours at room temperature when **4** is dissolved in anhydrous THF under strictly anaerobic conditions [44]. In contrast, C-I bond activation of the analogous imine ligand is complete within minutes at room temperature. The reduced conformational flexibility of the imine ligand is proposed to account for this rate difference. The flexibility of the saturated ligand in **5** allows the complex to adopt a capped trigonal prismatic geometry with the iodide capping the rectangular face defined by N1, N2, C1, and C2. (Fig. 2). The packing in the solid state is determined by a weak intermolecular N1-H7···O2'-C2' contacts characterized by N1···O2' =3.27(1) Å and N1-H7···O2' = 164(1)° to afford chains of molecules. In contrast to the imine based metallacycles, only a single resonance is observed for the carbonyl ligands in room temperature ^{13}C NMR spectra indicating that the tricarbonyl group of the saturated metallacycle complex is fluxional.

Scheme 5



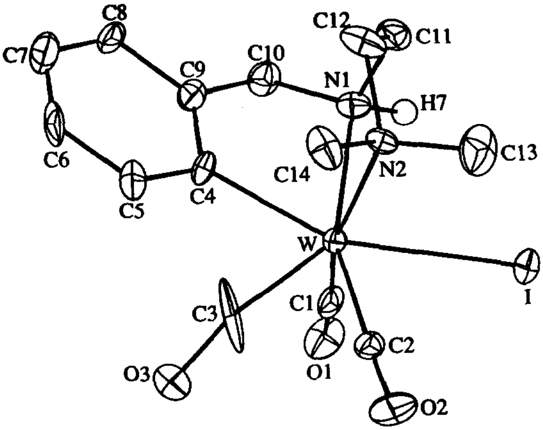
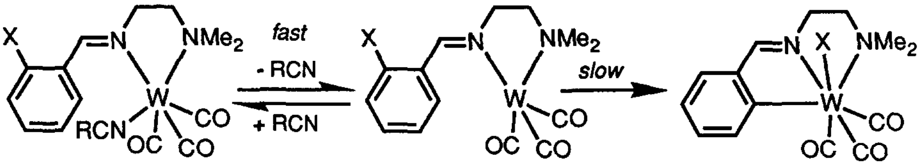


Fig. 2. ORTEP representation of 5 (Space group $P2_1/a$). Selected bond lengths (Å): W-C4, 2.21(1); W-I, 2.906(1); W-N1, 2.256(8); W-N2, 2.364(8); W-C1, 1.94(1); W-C2, 1.97(1); W-C3, 1.86(1), N1-C10, 1.48(1). Selected bond angles (deg): I-W-C4, 157.3(3); I-W-N2, 90.1(2); C4-W-N1, 74.9; C4-W-N2, 82.2(4); N1-W-N2, 77.3(3).

Utilizing the isolated mononitrile complexes, kinetics studies show that the rate of oxidative addition varies inversely with added nitrile and increases in the series F << Cl < Br < I [46]. This is consistent with the two-step mechanism illustrated in Scheme 6.

Scheme 6



Nitrile exchange is rapid and reversible with a half-life for nitrile dissociation of approximately 2 s at room temperature. The coordinatively unsaturated intermediate is not detected by NMR or IR spectroscopic methods. Although interaction of the pendant halide lone pairs with the 16-electron tungsten intermediate is possible in principle, we have been unable to detect such a complex. Despite the favorable entropy for coordination of the pendant halide, it is apparently not sufficient to overcome the much greater coordinating ability of the nitrile ligand.

We note that the chelate stabilized aryl halide complexes reported to date all contain five membered rings in contrast to the present system. In fact, the constrained geometry of our ligand systems may actually disfavor nonproductive aryl halide coordination and thereby promote C-X activation in these systems [45].

Quantitative transformation of a $W(CO)_3(CH_3CN)(L)$ complexe to its corresponding oxidative addition products is illustrated for a symmetrical ligand system in Fig. 3.

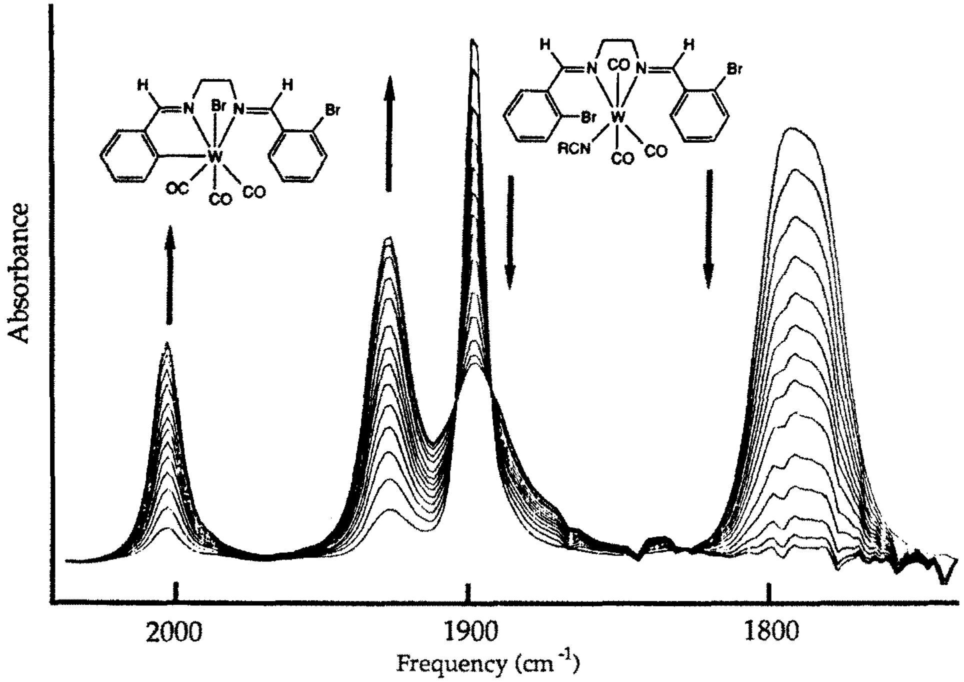


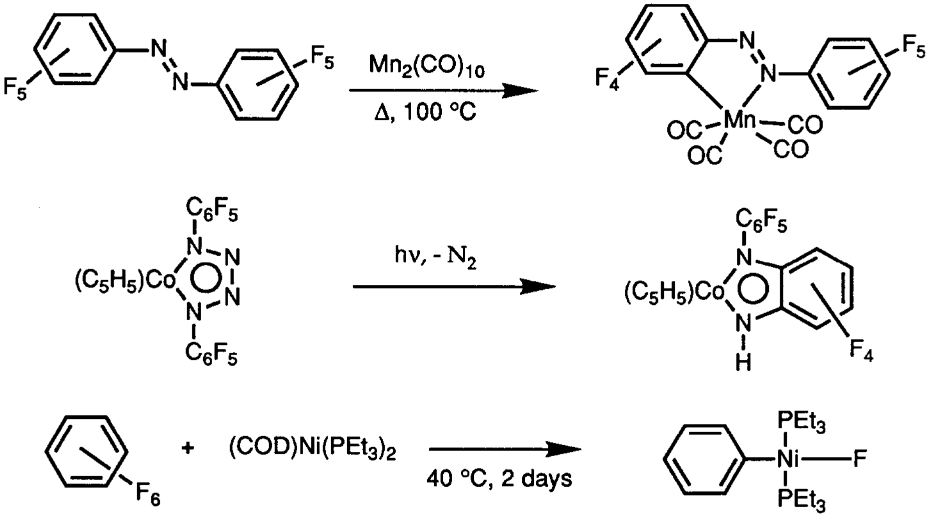
Fig. 3. Sequential infrared spectra showing the formation of a tungsten(II) oxidative addition product from a tungsten(0) precursor.

Thus we were able to study the kinetics of the oxidative addition process. A detailed study of C-Cl activation using a series of ligands with remote substituents on the aromatic ligand was performed to determine the sensitivity of the reaction to electronic effects. A Hammett plot utilizing nine different substituents on the aromatic ring with σ values from -0.3 to +0.8 and rates spanning over three orders of magnitude gave $\rho = 2.8$ with a correlation coefficient of $R = 0.95$. Thus the reaction is quite sensitive to the electronic character of the aromatic ring and is greatly accelerated by electron withdrawing groups. An even better correlation is observed when the highest frequency CO band of the product is plotted as a function of σ which gave had a slope $\rho^* = 8.4$ with $R = 0.99$. There is no correlation between the CO stretching frequencies of the mononitriles and the rate of C-Cl activation. We interpret these results to be indicative of significant W-C bond formation in the transition state. The great rate acceleration as a consequence of the increased ability of the aromatic ring to accept electron density is relevant to our successful quest to activate C-F bonds.

ACTIVATION OF CARBON-FLUORINE BONDS

As mentioned above, room temperature activation of a pendant monofluorophenyl ring does not take place readily at room temperature. However, literature precedent suggests that increasing fluorination of an aromatic ring increases their susceptibility to activation by transition metals (Scheme 7).

Scheme 7

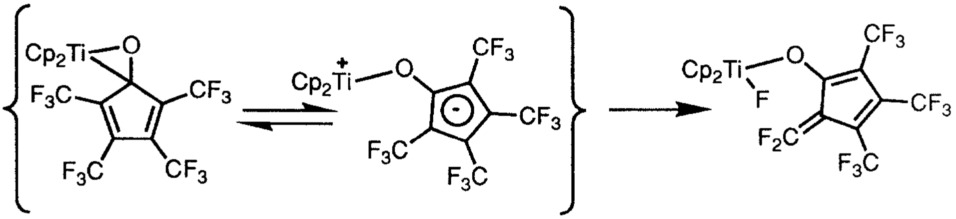


The reaction of perfluoroazobenzene with $Mn_2(CO)_{10}$ in refluxing heptane affords low yields of the metallacycle; the fate of the cleaved fluorine is not known [47]. A related transformation takes place at a cyclopentdienyl ruthenium center [48].

Although inefficient, these early studies provided important guidance in the design of ligands to promote well defined C-F bond activation processes. Photochemical activation is required in the cobalt chemistry and cleaved fluoride is presumed lost as HF [49]. Most intriguing is the intermolecular activation of C_6F_6 by Ni(0). Unfortunately the product was produced only in low yield and reported to be unstable at room temperature and was characterized solely by IR spectroscopy [50]. Thermolysis of $Cp_2Ti(C_6F_5)_2$ at 200 °C is reported to yield $Cp_2Ti(C_6F_5)F$ in modest yield [51]. Most recently intermolecular C-F activation has been reported for C_6F_6 by a Cp^*_2Yb complex to afford $Cp^*_2YbC_6F_5$ and the mixed valance complex $[Cp^*_2Yb]_2F$ [52]. This compound also activates C-F bonds in CH_3F, CH_2F_2, C_2F_4, and $PhCF_3$, but not in C_2F_6 or CF_3CH_3. Interestingly, slow low yield (20 % yield over two weeks time) production of $[Cp_2Yb]_2F$ was observed upon reaction with PhF. Bimolecular fluoride abstraction from perfluorinated olefins by several *bis*-cyclopentadienyl lanthanide complexes has also been reported to take place rapidly at room temperature in inert solvents [53].

Reactions involving metal assisted functionalization of fluorocarbons are often similar in character. Although activation of saturated aliphatic fluorocarbons is rare, electrophiles may induce such transformations as a consequence of possibility of forming strong bonds (e.g. Si-F, B-F) to fluoride. Lewis acids attack the trifluoromethyl group bound to later transition metal carbonyl centers such as $CpMo(CO)_3CF_3$, $Mn(CO)_5CF_3$ and $CpFe(CO)_2CF_3$ to afford cationic difluorocarbene complexes, which may undergo hydrolysis to afford the corresponding cationic carbonyl cations [54]. In addition net halide exchange to yield the metal trihalomethyl (X = Cl, Br, I) compounds is observed upon reaction with BX_3. The intermediacy of the metal carbene is supported by the observation that only α-fluorides are activated in these systems [54]. Stepwise fluoride replacement is observed in trifluoromethyl complexes [55]. Mono- and di-fluoromethyl ligands behave in a similar manner.

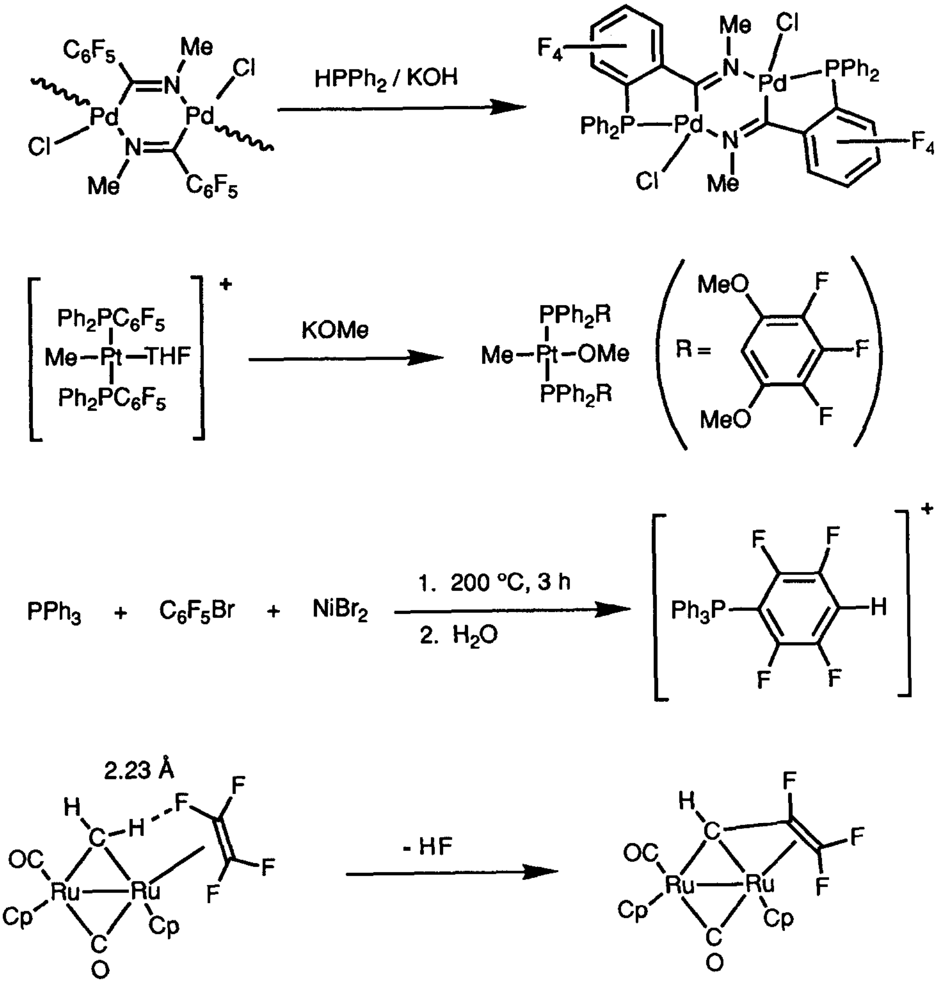
Scheme 8



Roper and co-workers have extensively explored the precious metal chemistry of halocarbenes with protonic and Lewis acids [56]. A conceptually similar reaction involving intramolecular fluoride transfer from a tetrakis(trifluoromethyl)cyclopentadienone to a titanocene fragment (Scheme 8) has been noted [57].

Of the rather diverse group of C-F functionalization reactions reported to take place within the coordination sphere of a metal, one common characteristic is that they frequently involve heavily fluorinated molecules (Scheme 9).

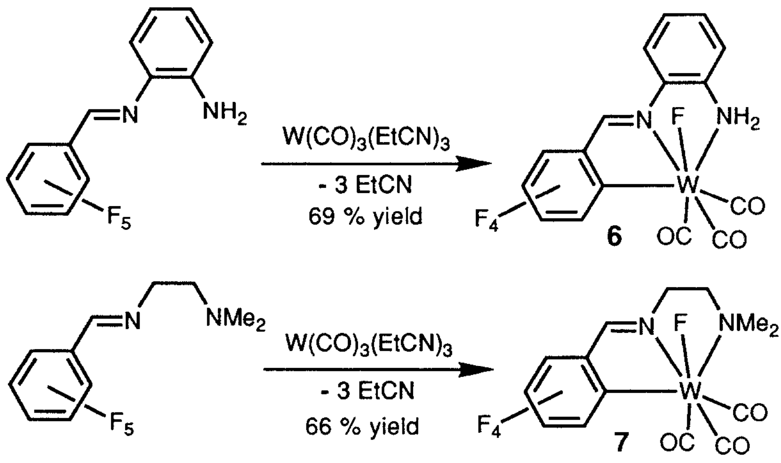
Scheme 9



In the first two reactions, the metal apparently mediates nucleophilic attack at an *ortho*-C-F bond of the pentafluorophenyl ring [58, 59]. Oxidative addition of a C-F bond in the phosphonium salt synthesis is postulated to occur to afford an anionic Ni(II) phenyl fluoride which gives the observed product upon hydrolysis [60]. Perhaps most intriguing transformation of this group is that involving formation of a new C-C bond from a metal carbene and a coordinated tetrafluoroethylene ligand on a diruthenium center [61]. This process may be assisted by a C-H···F hydrogen bond. The 2.33 Å CH···F distance was estimated from the C and F atom positions. Thus hydrogen bonding may influence the reactivity of coordinated fluorocarbons.

Our discovery of a mild high yield system for C-F bond activation is depicted in Scheme 10 utilizing the 1:1 Schiff base ligand derived from pentafluorobenzaldehyde and 1,2-diaminobenzene [62]. Similar reactivity is observed for the ligand derived from N,N-dimethylethylenediamine [40]. These complexes are air and water stable and full characterization by spectroscopic and crystallographic methods has been reported. It is remarkable that the C-F bond of the pentafluorophenyl ring, which has an estimated BDE of 154 kcal/mol, can be cleaved under such mild conditions [64]. A favorable orientation for attack at the C-F bond is readily evident in the structure of $W(CO)_4L$, a model compound for the precursor to C-F bond activation, illustrated in Fig. 4.

Scheme 10



Puddephatt and co-workers have reported similar chemistry at a dimethylplatinum center providing the first examples of aryl carbon-X bond activation at Pt(II) as illustrated in Scheme 11 [65].

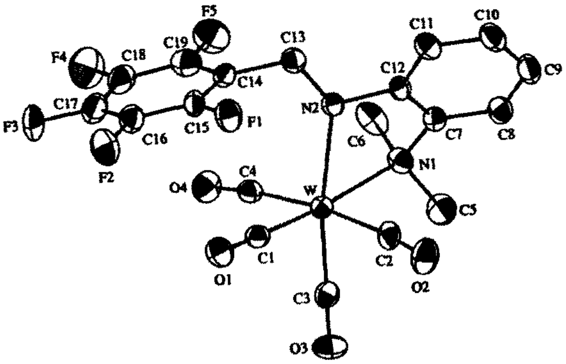
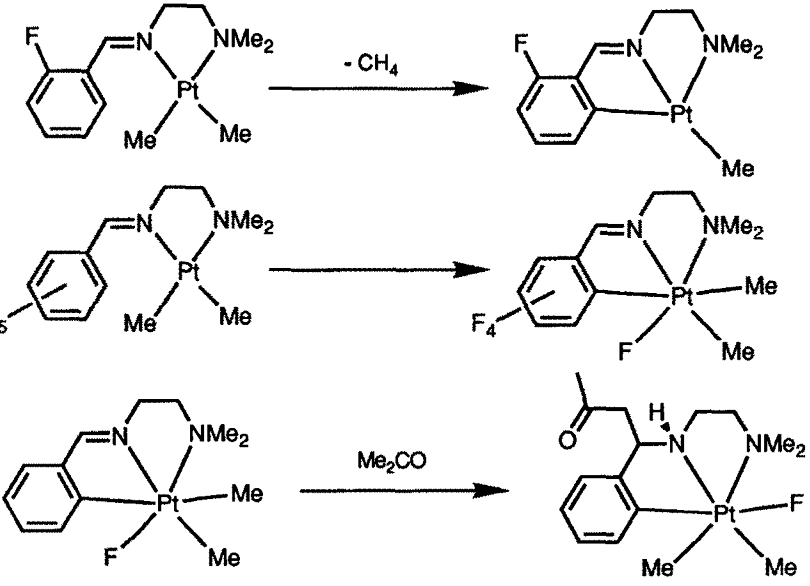


Fig. 4. ORTEP representation of $W(CO)_4L$ (Space group C2/*c*). Selected bond distances (Å): W-N1, 2.351(3); W-N2, 2.241(4); W-C1, 1.954(5); W-C2, 2.027(5); W-C3, 1.953(5); W-C4, 2.012(5); N2-C13, 1.263(6). Selected bond angles (deg): N1-W-N2, 71.3(1); W-N2-C13, 132.6(3); N2-C13-C14, 120.1(4); N1-W-C1, 172.1(2); N2-W-C3, 168.7(2), C2-W-C4, 172.4(2).

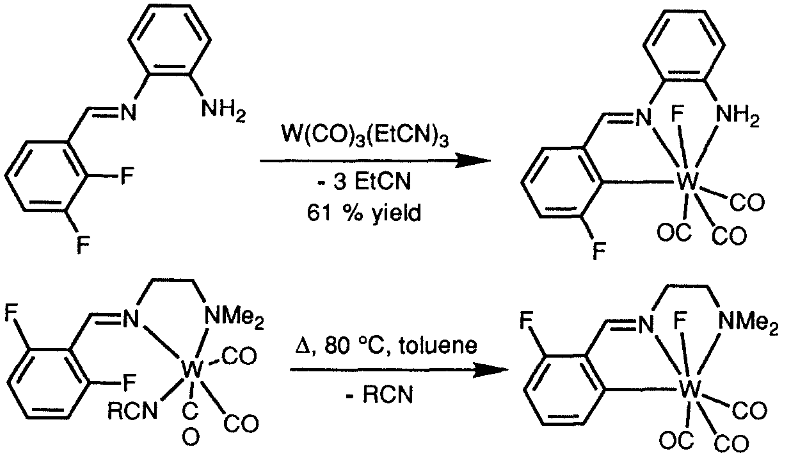
Scheme 11



As noted earlier, activation of a monofluorinated C-F bond has proven to be more difficult than in perfluorinated systems, despite the weaker C-F bond (BDE = 123 kcal/mole [41]) in the former system. In the platinum chemistry discussed above, orthometallation of an aromatic C-H bond (BDE = 105 kcal/mol [41]) and the concomitant formation of methane by reductive elimination occurs in preference to C-F activation. This behavior can be rationalized in light of our kinetic measurements on C-Cl activation which showed a pronounced rate acceleration upon substitution of electron withdrawing groups on the aromatic ring. The increased electrophilicity of the carbon of the C-X bond in the aromatic ring promotes attack by the metal atom.

Our early studies [63] indicated that some C-F activation occurred in ligands derived from 2,6-difluorobenzaldehyde, but separation of the putative oxidative addition product from the reaction mixture could not be achieved. Reinvestigation of the reaction chemistry of less heavily fluorinated ligands has resulted in C-F activation in two instances as shown in Scheme 12 [63,66].

Scheme 12



The aromatic based systems are qualitatively more reactive than related systems based on an aliphatic backbone. The high reactivity of the 2,3-difluoro ligand is similar to that of the 2,3-dichloro ligand studied in the Hammett analysis of C-Cl oxidative addition discussed above. Quantitative spectroscopic yields of the oxidative addition product of the 2,6-difluoro substituted ligand are obtained upon warming in an inert solvent with care taken to avoid decomposition generating CO which results in formation of the tetracarbonyl complex [66]. The activation barrier for the 2,6-

difluoro ligand must be higher than that for the pentafluorophenyl ligand which adds readily at room temperature. This indicates that the electrophilicity of the carbon of the C-F bond is paramount in promoting oxidative addition and the higher BDE of the pentafluorophenyl system is of secondary importance. However, perhaps not unexpectedly, the activation barrier for C-F bond cleavage in the 2,6-difluoro ligand is significantly higher than for C-Cl cleavage in the analogous 2,6-dichloro system. Thus C-F bond activation reactions may be extended to aromatic groups which are less heavily fluorinated than pentafluorophenyl systems.

HYDROGEN BONDING PROPERTIES OF TUNGSTEN(II) FLUORIDES

Our first clue to the potential of these materials to engage in hydrogen bonding came as a result of our spectroscopic investigations of **6** [62]. We noted that the fluorine chemical shift of the tungsten bound fluoride shifts upfield upon addition of proton donors such as H_2O or phenols. This has proved to be quite general and an upfield fluoride shift signals a hydrogen bonding interaction in these systems. We note that the C-F coupling to the CO ligands detected in ^{13}C NMR spectra remains unchanged throughout these measurements indicating that the fluoride remains bound to the metal center. This suggested the possibility of a HOH···FW hydrogen bonding interaction. In addition, the coordinated amine protons are quite acidic and exchange upon mixing with D_2O in acetone-d_6 solution. Further evidence of the potential for this complex to engage in hydrogen bonding is found in its crystal structure (Fig. 5) [62].

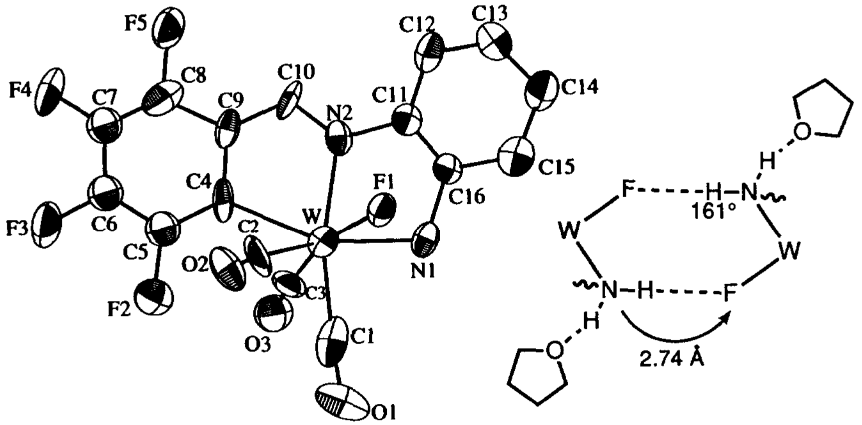


Fig. 5. ORTEP representation of **6** and illustration of the head-to-tail hydrogen bonding and interaction with THF solvate in the solid state.

A similar head-to-tail dimerization is seen in the structure of the N-phenyl substituted derivative **8** shown in Fig. 6 [67]. In this case no solvent of crystallization is found since the hydrogen bonding requirements of the molecule are satisfied by the head-to-tail dimerization.

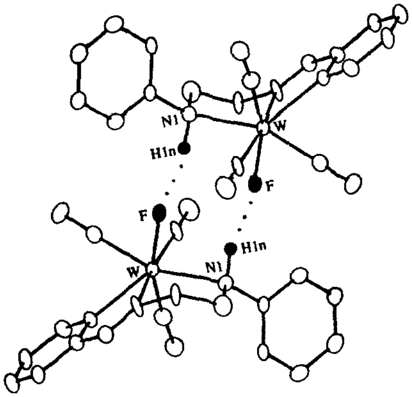
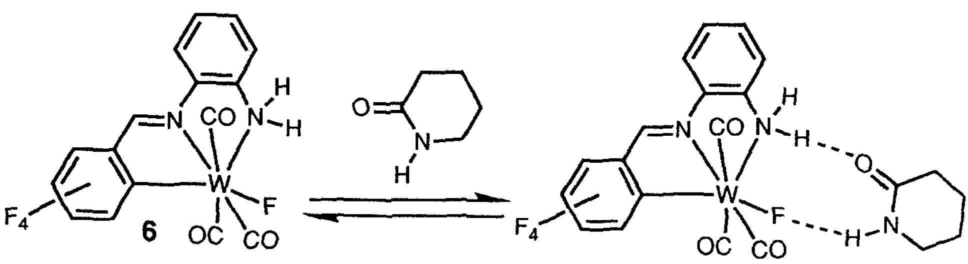


Fig. 6. ORTEP representation of **8** (Space Group P1) depicting head-tail-dimerization observed in the solid state characterized by F···N1 = 2.89 Å, F···H1n = 1.95 Å and <F···H1n-N1 = 167°.

The propensity of these complexes to engage in hydrogen bonding lead us to investigate the possibility that they might function as metal based receptors for organic molecules using hydrogen bonding as the mode of recognition. As a test case, we choose to examine the interactions of **6** with a cyclic amide as a representative substrate for two point hydrogen bonding [25].

Scheme 13



Titration experiments were performed in acetone-d_6 to minimize complications from amide and tungsten complex self-dimerization. Stronger interactions would be expected in less polar solvents more typically employed in the study of hydrogen bonded complexes. Self-dimerization of the amide does take place with K = 1.2 M^{-1} so this provides a lower limit for tungsten-amide association [63]. Downfield shifts of the tungsten amine and organic amide N-H protons and an upfield shift of the W-F resonance are observed upon increasing the amide concentration thereby forcing the equilibrium in Scheme 13 to the right. Based on analysis of the ^{19}F NMR shift data, an equilibrium association of K = 4.5 M^{-1} was determined for this reaction. The tungsten receptor shows a similar affinity for a protected uridine derivative. The N-phenyl derivative **8** interacts with the amide with K = 4.3 M^{-1} in dichloromethane solution. Similar measurements employing derivative of **6** in which the amine protons are replaced by methyl groups or the fluoride is replaced by chloride (**9**) showed only negligible interaction with the amide with apparent binding constants below that of the amide self-dimer. Thus the formation of two hydrogen bonds is crucial in the stability of the host-guest complex.

Additional evidence for the nature of these hydrogen bonded complexes is obtained from an X-ray structural study of the adduct obtained by co-crystallization of **9** and five equivalents of the amide (Fig. 7) [25].

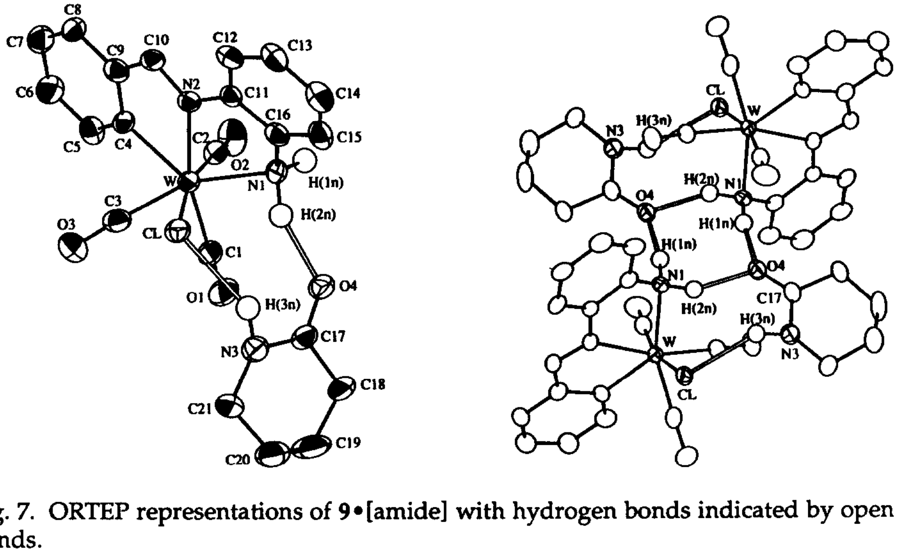


Fig. 7. ORTEP representations of **9**•[amide] with hydrogen bonds indicated by open bonds.

The solid state structure shows the adduct crystallizes as dimers of dimers to afford a total of six hydrogen bonds linking the four molecules. Although the solution studies of the N-phenyl complex 8 indicate that tetramer formation is unimportant in solution, these additional interactions are probably responsible for our success in isolating the host-guest complex in a crystalline state. Attempts to crystallize adducts of the N-phenyl complexes, which only have the possibility of forming a pair of hydrogen bonds between two molecules have been unsuccessful to date [68]. These studies provide a unique example of molecular self-assembly of a host-guest complex. Infrared studies of the solid state adduct show that the highest frequency amide carbonyl band decreases from 1678 to 1632 cm^{-1} upon complex formation.

Since the hydrogen bonding ability of coordinated amines has been long recognized, we were particularly interested in defining the hydrogen bonding properties of the fluoride bound to tungsten in order to assess its utility as a functional group in the design of more sophisticated receptors. Therefore we have examined the interaction of the 3 and 7 with 4-chlorophenol as a reference acid (Scheme 14) [40].

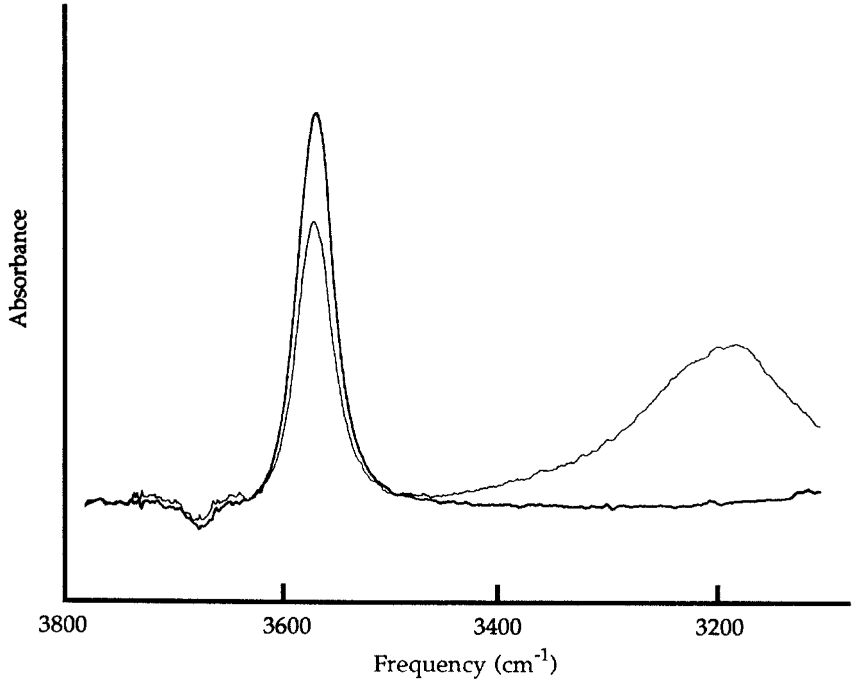
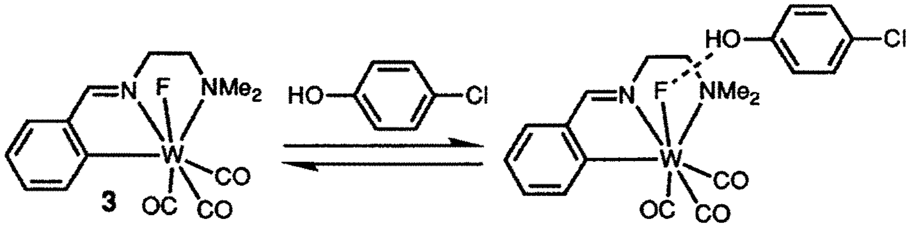


Fig. 8. Infrared spectrum in CH_2Cl_2 of 4-chlorophenol before (ν_{OH} = 3581 cm^{-1}) and after (ν_{OH} = 3177 cm^{-1}) addition of tungsten fluoride 3.

Scheme 14



In addition to a 5-7 cm^{-1} increase in the terminal CO stretching frequencies, classical evidence for a W-F···H-O hydrogen bond is seen in the OH stretching region of the infrared spectra depicted in Fig. 8. Infrared spectra of the chloride **2** and 4-chlorophenol do not reveal any evidence of phenol binding to the chloride [63, 69]. Bulky phenols such as 2,6-di-*tert*-butylphenol do not interact with the sterically crowded tungsten fluoride as indicated by the absence of a shift in the ^{19}F NMR spectra upon addition of excess phenol [63]. NMR titration experiments in several solvents at 25 °C indicate that the fluoride ligand in **3** is quite a respectable base with $K = 32\ M^{-1}$ in CH_2Cl_2 in and $K = 330\ M^{-1}$ in toluene [40]. For comparison purposes, the association constant for the organic base pyridine in CCl_4 is approximately 120 M^{-1} [70]. Thus the fluoride bound to tungsten(II) rivals pyridine in its ability to engage in hydrogen bonding. The electron withdrawing fluorines on the aromatic ring in **7** reduce the basicity of the coordinated fluoride somewhat with $K = 15\ M^{-1}$ in CH_2Cl_2 solution. However, interesting patterns of molecular association in the solid state for **7** relative to its chloride and bromide analogues provide evidence for an unusual sp^2-C-H···F hydrogen bond.

Low temperature (-140 °C) crystallographic characterization of **7** afforded a high quality structure in which the imine hydrogen H1 bound to C10 was located and its position successfully refined as an isotropic contribution [40]. Examination of a unit cell diagram of **7** reveals infinite chains linked by C10'-H1'···F-W interactions characterized by C10'-H = 0.98(9) Å, C10'···F = 3.099(5) Å, C10'-H1'···F = 172(7)° and H1'···F = 2.13(9) Å. This distance is significantly shorter than that defined by the H···F van der Waals[10] separation of 2.6 Å [71]. In contrast the corresponding chloride and bromide complexes show no intermolecular interactions in the solid state. These contrasting packing modes are illustrated in Fig. 9.

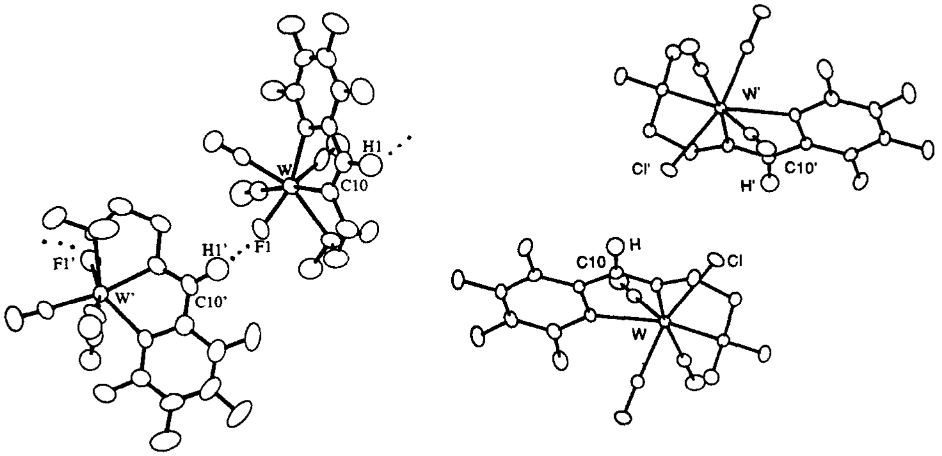


Fig. 9. ORTEP representations of the solid state packing of **7**(left) and **10**(right).

The chloride packs as non-interacting dimers with H···Cl = 3.14 Å, C···Cl = 4.08 Å and <C-H···Cl = 146°. Similarly, the analogous bromide **11** exhibits no unusual intermolecular interactions. We attribute the solid state packing of **7** to the ability of the coordinated fluoride to form an intermolecular hydrogen bond even to the weakly acidic hydrogen on the imine carbon. Of all the carbon-hydrogen groups that have been postulated to participate in hydrogen bonding, those involving sp^2-CH groups have proved to be the most controversial [72]. However, weak interactions such as CH···X hydrogen bonds may be crucial in the three dimensional solid state packing of materials [73].

In order to more fully characterize this unusual interaction, we have examined the IR spectra of the this series of compounds focusing on the imine C-D stretch of selectively deuterated complexes. These results are given in Table 1. In the solid state the C-D band of the fluoride is 17 cm^{-1} *lower* than chloride or bromide complexes consistent with the formation of a weak hydrogen bond. The band for the fluoride is also much more intense than that for the other complexes. This increase in intensity is frequently observed for hydrogen bonded species. Importantly, upon dissolution in 1,2-dichloroethane, the C-D stretch of the fluoride *increases* in frequency by 9 cm^{-1} while that of the bromide *decreases* by 6 cm^{-1}. We interpret the increase in frequency of the fluoride to indicate that the weak C-H···F interaction is broken up by the solvent molecules upon dissolution.

TABLE 1

Imine C-D infrared spectroscopic data in cm^{-1} for **7**, **10**, and **11** in 1,2-dichloroethane solution and mineral oil mulls.

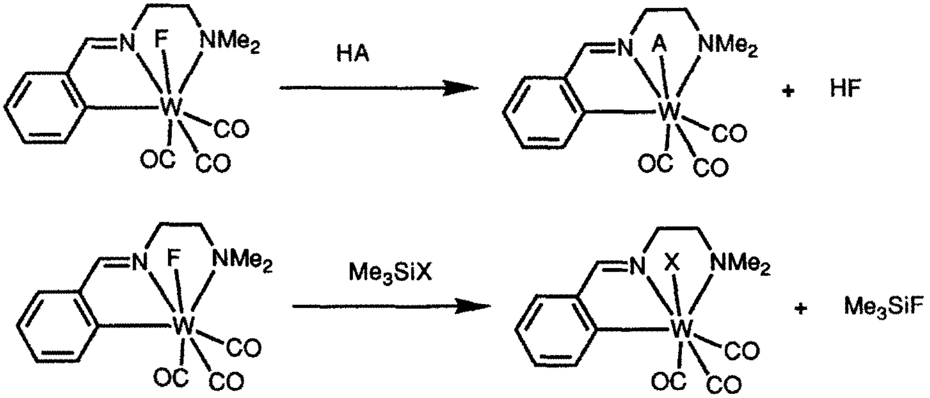
Compound	Halide	Solid State	Solution
X	F	2237	2246
Y	Cl	2255[a]	——
Z	Br	2253	2247

[a] This band is extremely weak making this assignment tentative.

These spectroscopic observations bolster our assessment of the solid state association of the fluoride complex, in contrast to the corresponding chloride and bromide complexes, to be the consequence of a C-H···F hydrogen bond. This emphasizes the basicity of the coordinated fluoride in these tungsten(II) carbonyl complexes.

An intriguing aspect of the study of metal based receptors is the possibility for performing stoichiometric or catalytic chemistry on a bound guest molecule. In the preceding section we have shown that fluoride bound to tungsten(II) can interact with substrates by the formation of hydrogen bonds.

Scheme 15



The chemical reactivity of metal fluorides with electrophiles, as typified by the acid catalyzed hydrolysis of transition metal fluorides [11, 12], provides an opportunity to transform transient information stored in one or more hydrogen bonds to permanent information in the form of a metal-electrophile covalent bond. Accordingly we have explored the reactivity of our tungsten fluorides with acids and silicon reagents [63, 67]. Protonic acids HA where A = Cl, CH_3COO, CF_3COO, and CF_3SO_3 react readily to afford new W-A complexes (Scheme 8). Even the triflate complex is covalent in the solid state as shown by X-ray crystallography [68]. Halide exchange is also effected by silicon reagents to afford Me_3SiF. However, no reaction is observed for Me_3SiOMe or $Me_3SiOSiMe_3$. It remains to be determined if formation of a hydrogen bonded precursor lowers the activation barrier to these types of transformations.

In order to explore the scope of metal fluoride hydrogen bonding interactions, we have investigated several titanocene fluoride complexes [74]. As noted by earlier workers, addition of protic solvents to Cp_2TiF_2 results in a large upfield shift of the ^{19}F NMR signal of the fluorides [75]. Binding isotherms comparing the behavior of 4-chlorophenol and 2,6-di-*tert*-butyl-4-methoxyphenol with Cp_2TiF_2 are shown in Fig. 10.

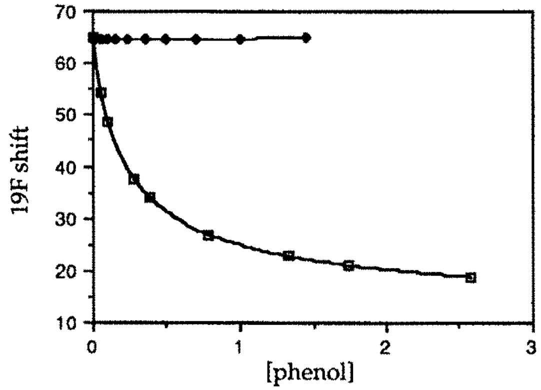


Fig. 10. Binding isotherms at 20 °C for interaction of 4-chlorophenol (•) and 2,6-di-*tert*-butyl-4-methoxyphenol (▫) with Cp_2TiF_2 in $CDCl_3$ solution.

As for the tungsten fluorides, no interaction is detected with a bulky phenol. Solution IR spectra in $CDCl_3$ show a broad band centered at 3326 cm^{-1} assigned to the hydrogen bonded complex 275 cm^{-1} lower than free 4-chlorophenol in $CDCl_3$. An apparent binding constant for Cp_2TiF_2/4-chlorophenol was measured as 5.6 M^{-1}. However no information is available which allows determination of the structure(s) of the adduct(s) since more than one mode of binding is possible. Matrix isolation studies by Ault [76] of the Cp_2TiF_2/HCl system in argon are also indicative of a hydrogen bonding interaction. The ν_{HCl} is red shifted by 440 cm^{-1} upon complex formation. Importantly, a 70 cm^{-1} red shift of one of the Ti-F stretching modes is also detected. No evidence for Ti-HCl interactions nor halide exchange reactions were detected upon warm-up experiments to 157 K at which point the HCl vaporizes to leave a film of Cp_2TiF_2.

In order to study a system with only one metal fluoride, we examined the interaction of $Cp_2Ti(C_6F_5)F$ [51, 73] with 4-chlorophenol. Interestingly, restricted rotation about the pentafluorophenyl ring results in a static structure for this complex at room temperature as illustrated in Fig. 11.

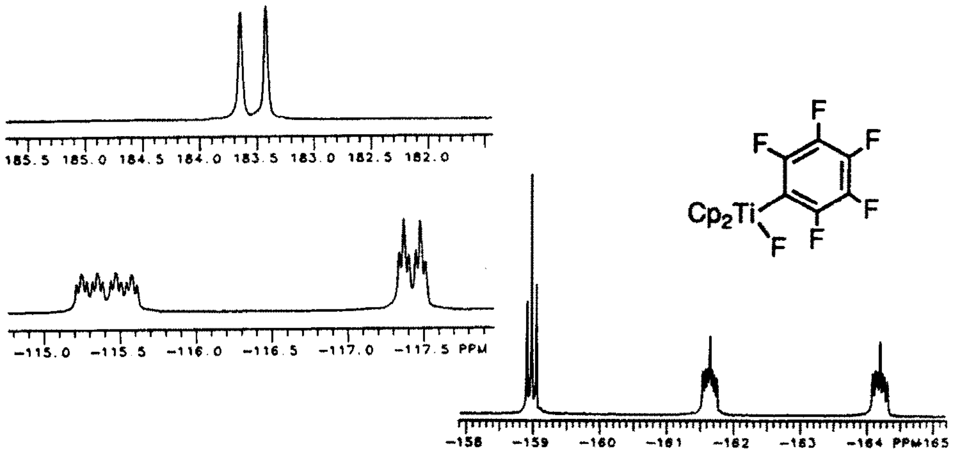


Fig. 11. Slow exchange limit 282 MHz ^{19}F NMR spectra of $Cp_2Ti(C_6F_5)F$ in $CDCl_3$ (CCl_3F reference) solution at 20 °C illustrating the Ti-F resonance (δ 183.5), *ortho*-C-F resonances (δ -115.4, -117.4), *para*-C-F (δ -159.0) and *meta*-C-F resonances(δ -161.7, -164.2).

The fluoride bound to titanium is coupled to the *ortho*-fluorine at -115.4 ppm with $^4J_{FF}$ = 64 Hz. Binding isotherms for this system in toluene solution are shown in Fig. 12. The Ti-F shifts by over 100 ppm over the course of the binding event while the coupled *ortho*-fluorine shifts by only 3 ppm, but the coupling constant remains invariant over the course of the experiment. This is the only instance in which we have noted a shift in an aromatic C-F resonance upon interaction with a phenol [77].

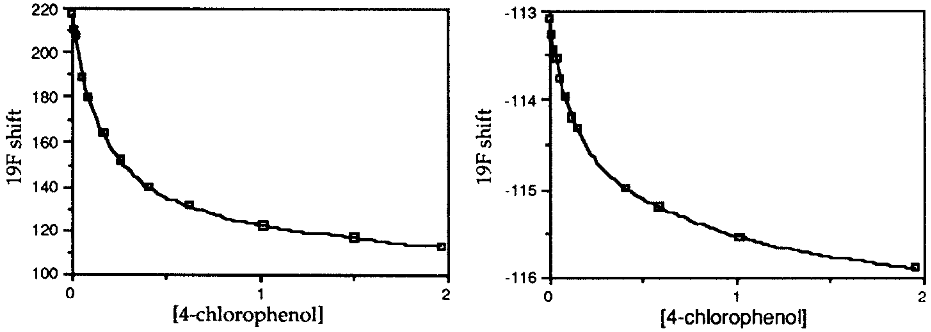


Fig. 12. Binding isotherms showing the change in chemical shift as a function of 4-chlorophenol concentration in toluene of the Ti-F resonance (left) and the coupled *ortho*-CF resonance at 20 °C.

However both curves can be fit to the same equilibrium constant $K = 5.6 \pm 0.1\ M^{-1}$ based on a Scatchard analysis of the data [78]. In $CDCl_3$ $K = 3.9 \pm 0.2\ M^{-1}$ so there is not the dramatic solvent effect observed as in the case of the tungsten fluorides. It is unclear at present why the titanium system is so insensitive to the nature of the solvent.

Using the toluene data as a basis for comparison, the 18-electron tungsten(II) fluoride is significantly more basic than the fluoride ligand in $Cp_2Ti(C_6F_5)F$. Empty orbitals in the 16-electron titanium complex are available for π-donation from the fluoride to titanium thereby reducing its effective charge [79]. We attribute the significant basicity of these low valent metal fluorides to their electronically saturated 18-electron configuration and the lack of suitable vacant orbitals [80] on the metal to accept π-electron density from the fluoride.

CONCLUSION

Our research in the coordination chemistry of a series of nitrogen donor ligands with pendant aryl halide groups has led to the discovery of facile chelate assisted carbon-halogen activation at tungsten(0). Mechanistic studies of C-Cl oxidative addition provided guidance in the design of related ligand to activate even robust C-F bonds under mild conditions. An unusual feature of the our chelating [C, N, N'] ligand set is that it appears to stabilize coordination of the hard fluoride ion in a soft metal carbonyl environment. This is in marked contrast to the chemistry of psuedo-isoelectronic cylopentadienyl metal carbonyl halides, in which the softer halides generally form the more stable complexes. Low valent metal carbonyl fluorides are rather rare and often times not well characterized due to their instability [81]. The propensity of the fluoride to engage in hydrogen bonding is one manifestation of the ionic character of the tungsten(II)-fluoride bond. Our fundamental studies on the hydrogen bonding properties of transition metal fluorides provide the necessary basis for utilizing this novel building block for the design of molecular receptors based on transition metal templates.

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