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SYNTHESIS OF GROUP IV IMIDO COMPLEXES SUPPORTED BY

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SYNTHESIS OF GROUP IV IMIDO COMPLEXES SUPPORTED BY β-DIKETIMINATE LIGANDS

By

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ABSTRACT

SYNTHESIS OF GROUP IV IMIDO COMPLEXES SUPPORTED BY β-DIKETIMINE LIGANDS

By

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In recent years, there has been considerable effort put forth in developing group 4 imido chemistry. Many research groups have focused on developing supporting ligands with the major goal of tailoring chemical reactivity and properties.

β-Diketiminate ligands were used in this research, and a new ligand synthesis that involves deoxygenation of monoketimines by $Ti(NMe_2)_4$ was devised for synthesizing β-diketimines with bulky aryl groups.

A family of titanium imido complexes containing one or two β-diketiminate ligands were synthesized. The synthesis of five-coordinate imido complexes containing two β-diketiminate ligands was achieved for Ti and Zr. The sterically hindered ligand, Dipnacnac, yielded $(Bu^tN)Ti(Dipnacnac)Cl$, a rare example of a four-coordinate group 4 imido complexes.

The chloride in $(Bu^tN)Ti(Dipnacnac)Cl$ could be readily replaced to form a new Ti-E (E = element) bond. From this compound, $(Bu^tN)Ti(Dipnacnac)(OTf)$, $(Bu^tN)Ti(Dipnacnac)(NMe_2)$, $(Bu^tN)Ti(Dipnacnac)Me$ were synthesized.

A reaction between $Ti(NMe_2)_4$ and C_6F_5nacnacH was discovered, wherein *ortho* amination of each C_6F_5 group and fluoride abstraction yielded an unusual Ti difluoride complex. Hydrolysis of this Ti complex gave the ketimine $(2\text{-}NMe_2\text{-}C_6F_5)$nacnac in good yield.

To my family and my parents

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I also want to say thanks to Baixin, my former group member and undergraduate classmate. He guided and helped me a lot on my research. I feel lucky to have this friend. Also, other group members offered me a lot help, which was not limited to chemistry. Especially, I want to express my appreciation to Jian-Yang.

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LIST OF ABBREVIATIONS

Ar	Aryl
Bu	Butyl
BTBA	N,N-bis(trimethylsilyl) benzamidinate
calcd	calculated
C_6F_5nacnacH	2-pentafluorophenylamino-4-pentafluorophenylimino-2-pentene
CCD	Charge Coupled Devise
CN	Coordination Number
Cp	$(C_5H_5)^-$
Cp*	$(C_5Me_5)^-$
d	doublet
decomp	decomposed
Dip	$C_6H_3\text{-2,6-}{}^{i}Pr_2$
DipnacnacH	2-(2,6-$^{i}Pr_2$-phenylamino)-4-(2,6-$^{i}Pr_2$-phenylimino)-2-pentene
equiv	equivalent
e^-	electron
Et	Ethyl
i	iso
IR	Infrared
L	ligand
m	multiplet
Me	Methyl
mp.	melting point
NMR	Nuclear Magnetic Resonance
o	ortho
OTf	triflate

p	para
Ph	Phenyl
Pr	Propyl
py	pyridine
s	singlet
sept	septet
t	triplet
taa	tetraazamacrocycle
tert	tertiary
THF	tetrahydrofuran
TFMnacnacH	2-3,5-di-trifluoromethylamino-4-3,5-trifluoromethylimino-2-pentene
Tol	tolyl
TolnacnacH	2-(*p*-tolylamino)-4-(*p*-tolylimino)-2-pentene
TsOH	*p*-toluenesulfonic acid
VB	Valence Bond

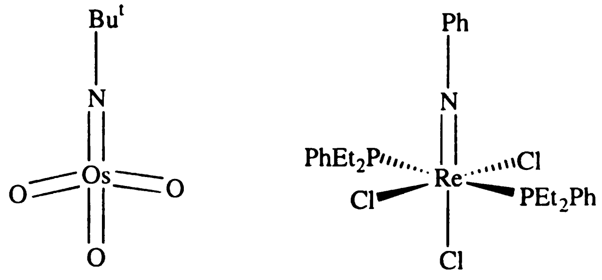
CHAPTER 1

INTRODUCTION

The chemistry of transition metal imido complexes has attracted considerable interest and has experienced exceptional growth in recent years. Such compounds are of interest as intermediates in organic syntheses as well as catalytically active species.[1] A substantial body of research has focused on the group 4 complexes.[2] Terminal zirconium imido complexes were reported in 1988,[3,4] and terminal titanium imido complexes were first structurally characterized in 1990.[5,6] Group 4 compounds containing bridging imide ligands are also well known.[7-13] However, it is generally the terminal M=NR (M = Group 4 Metal, R = Organic fragment) linkage that demonstrates important chemical reactivity such as C-H bond activation[3,4,14,15] and N-C bond forming reactions with unsaturated subtrates.[4,16-20]

A. Transition metal imido complexes

Complexes containing metal-nitrogen multiple bonds are prevalent in transition metal chemistry. Transition metal imido complexes have the general formula $M(=NR)_n(L)_m$ (R = alkyl or aryl group, L = ancillary ligand). They have received significant attention in recent years because of their importance in a wide range of applications that encompass industrial processes, catalysis, and some organic transformations.[1,21] The first transition metal imido complex to be prepared was *tert*-butylimidotrioxo osmium (VIII) (compound **1** in Figure 1), reported by Clifford and Kobyashi in 1956, and in 1962, the arylimido complex $Re(=NPh)Cl_3(PEt_2Ph)_2$ was described by Chatt and Rowe (compound **2** in Figure 1).[22] Since then, numerous imido complexes have been synthesized. In this section, the structural features and synthetic methods to transition metal imido complexes will be described.



1 **2**

Figure 1: Early known transition metal imido complexes

Structural Features of Transition Metal Imido Complexes

Terminal transition metal imido complexes can be considered to bond to a transition metal with one σ and either one or two π interactions. Limiting Valence Bond (VB) descriptions of this interaction[1] are presented in Figure 2, where the hybridization about the nitrogen and the metal-ligand bond order are suggested to impose certain structural parameters on the imido ligand. In addition, three compounds are shown as examples of the limiting VB structures in Figure 2.

In structure **A**, the sp^2 hybridization of nitrogen yields an M=N double bond, with one σ and one π bond. The non-bonding lone pair on nitrogen makes a bent M-N-R linkage. In the closed-shell formalism, the imido dianion $[NR]^{2-}$ acts as a four electron ($4e^-$) donor. There are only a few examples of strongly bent imido complexes. Structure **A** is expected only when the metal center cannot form a bond with the nitrogen lone pair. This case occurs when a linear, triply bonded NR can cause the electron count of the complex to exceed 18 electrons.[23] Wilkinson & Hursthouse reported a tris(imido) complex $Mn(=NBu^t)_3Cl$.[24] The Mn-N-C angles in this compound are very similar, and lie in the range from 138.5(3)° to 141.8(3)°. The bending is consistent with a delocalization of the bonding contributions required from the three imido functions for an 18-electron manganese configuration.

The M-N-R moieties of most known transition metal imido complexes are close to linear. This is consistent with sp hybridization at nitrogen. The M-N-R linkage could be either structure **B** or structure **C** in Figure 2. In structure **B**, there are some restrictions that prevent nitrogen from donating its lone pairs to the metal, thus it retains the one σ and one π double bond configuration. The restrictions could be symmetry imposed, or due to a severe energy mismatch with the available metal orbitals. Bercaw and coworkers[25] reported the synthesis of the imido complex $Cp^*_2Ta(=NPh)H$. They expected a structure with a bent arrangement, because with a single Ta-M π interaction, tantalum would achieve a closed-shell, 18-electron configuration. However, the X-ray structure showed a nearly linear [177.8(9)°] Ta-N-Ph arrangement, with the phenyl group lying nearly in the equatorial plane, indicating that the nitrogen is sp hybridized. The authors suggested that steric interactions, which force the phenyl ring into the equatorial plane, are responsible for sp hybridization at nitrogen. Hence a double [Ta=NPh] bond with a lone electron pair localized in a nitrogen p orbital. Shortly thereafter, Jϕrgensen offered supporting evidence for this description from extended Hückel MO calculations.[24]

Most known transition metal imido complexes resemble structure **C**. Lone pair $p(\pi) \rightarrow M(d)$ donation is very effective leading to a M≡NR bond order of 3. In contrast to structures **A** and **B**, the imido dianion $[NR]^{2-}$ in structure **C** is a formal six electron ($6e^-$)

donor with 1σ and 2π bonds to the metal. Structure **C** is found in many complexes including octahedral mono(imido) complexes with d^0-d^2 electronic configurations, tetrahedral bis(imido) with d^0-d^2 electronic configurations, and d^0 trigonal bipyramidal bis(imides) with equatorial imides. As an example, the d^0 imido complex $Ti(NC_6H_3Me_2\text{-}2,6)(OC_6H_3Me_2\text{-}2,6)_2(Py)_2$[25] is shown in Figure 2. The linear M-N-C linkage shows an sp hybridization of nitrogen, and the lone pair donation from nitrogen to titanium should be described as an M≡NR triple bond.

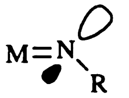
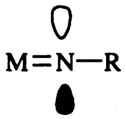
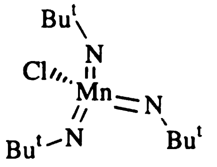
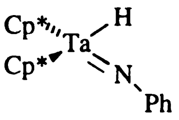
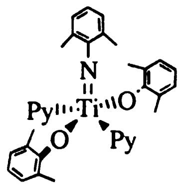
Structure	A	B	C
VB			$M\overset{\leftarrow}{\equiv}N-R$
Hybridization	N (sp^2)	N (sp)	N (sp)
$[NR]^{2-}$	$4e^-$	$4e^-$	$6e^-$
Examples			
M-N-C Angle	138.5(3)-141.8(3)°	177.8(9)°	180°

Figure 2: VB descriptions of metal-imido linkages

Although structure **C** is a fairly accurate depiction of imido bonding for most transition metal imido complexes, "M=NR" is a commonly used generic designation for the metal imido group and is not necessarily an indication of the true bond order.

Synthetic Methods

Chemists have developed various methods for the synthesis of imido complexes. These include (1) α–elimination from amide ligands,[21,26-28] (2) Oxidative nitrene transfer from arylazides[29] and related species,[30,31] (3) "Wittig-like" reactions between phosphin imines and metal ligand double bonds (especially M=O), [23,32-36] and (4) electrophilic attacks on nitrido[37,38] and diazenido ligands.[39]

Among the transition block elements, group 5-8 transition imido chemistry had been reasonably well developed by the end of 1980s. In contrast, well-defined derivatives for group 4 did not appear until about this time.[1,2] The current development of group 4 elements titanium and zirconium imido chemistry will be described in next section.

B. Ti and Zr imido chemistry

Although the first imido titanium complex $Ti(=NSiMe_3)Cl_2(Py)_2$ was reported by Burger and Wannagat[40] as early as 1963 through Me_3SiCl elimination from $Ti[N(SiMe_3)_2]Cl_3$, titanium imidos were still rare at the end of 1980s. Terminal titanium imido complexes were first structurally characterized in 1990.[5] Since then, a number of simple mononuclear, five- and six-coordinate titanium imido derivatives have been reported.[2] The first terminal Zr=NR functional groups were reported in 1988.[3,4] Since then, many research groups have reported a range of new chemical reactivity. In this section, many new developments in Ti and Zr imido chemistry will be described.

Convenient syntheses for Ti and Zr imido complexes

The Mountford group[41,42] reported the compound $[Ti(NR)Cl_2(L)_n]$ ($R=Bu^t$ or aryl; L=py or $NC_5H_4Bu^t$-4; n=2 or 3) (Figure 3), which offers a general route to a series of Ti=NR species. The *tert*-butyl imido complexes $[Ti(NBu^t)Cl_2(L)_n]$ are readily obtained from $TiCl_4$, Bu^tNH_2 and the appropriate ligand(s). Analogous arylimido complexes cannot be obtained directly from $ArNH_2$ and $TiCl_4$, but arylamine/*tert*-butyl imide exchange reactions of $[Ti(NBu^t)Cl_2(Py)_3]$ readily afford the desired complexes, $[Ti(NAr)Cl_2(Py)_3]$.[42,43] The utility of these complexes as synthons for new titanium imido derivatives may partly be attributed to the imido ligand's ability to stabilize higher oxidation states by π donation. Hence, almost none of the anion metathesis reactions are complicated by reduction of the Ti(IV) centers.

The easiest way to access Zr=NR complexes is by reacting 4 equiv of LiNHAr with $ZrCl_4(THF)_2$ in THF / py, which yields $Zr(=NAr)(NHAr)_2(Py)_2$. This complex reacts further with 1 or 2 equiv of Me_3SiCl in THF / py to provide $Zr(=NAr)(NHAr)Cl(Py)_2$ and $Zr(=NAr)Cl_2(Py)_3$ respectively.[44]

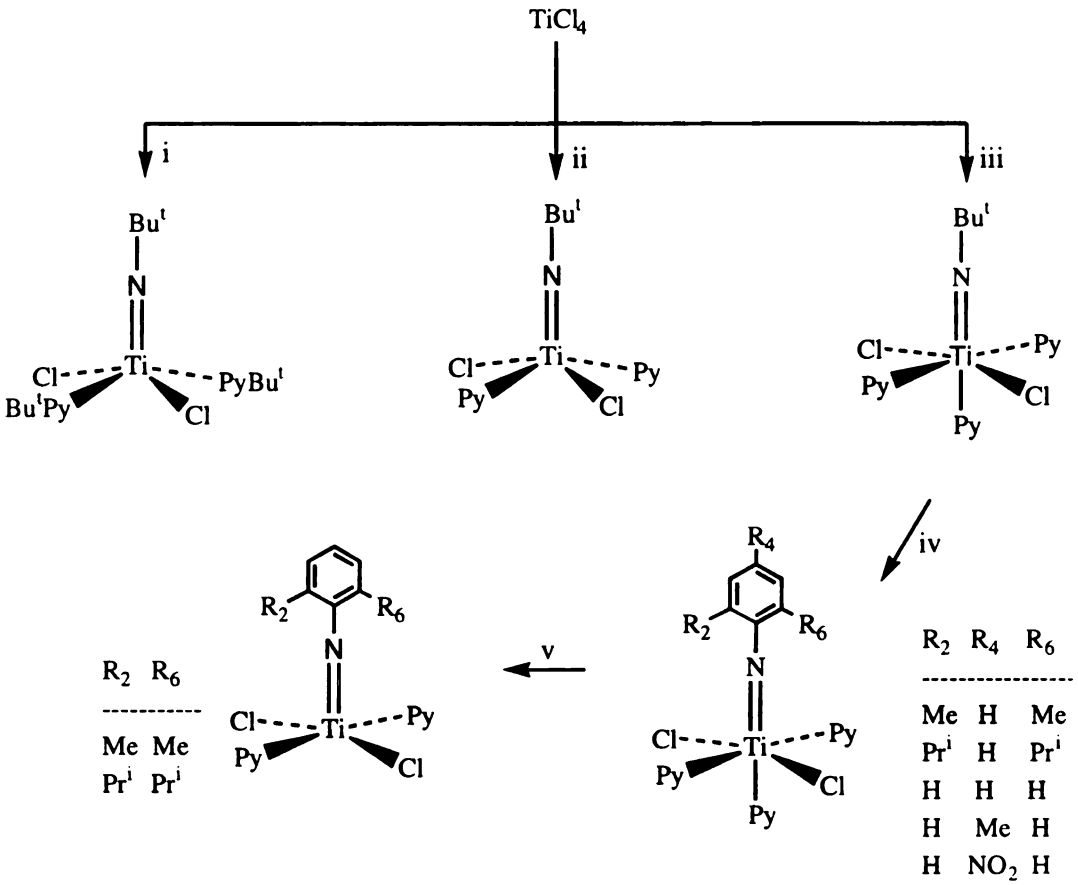


Figure 3: Versatile synthons for titanium imido compound

(i) Bu^tNH_2(6 equiv), py-Bu^t(2.2 equiv.)

(ii) Bu^tNH_2(6 equiv), py(2.3equiv)

(iii) Bu^tNH_2(6.3 equiv), py(4.1equiv)

(iv) aniline or substituted aniline

(v) 65°C, dynamic vacuum.

C-H bond activation

High-valent Ti and Zr imido complexes can activate C-H bonds. In 1991, Wolczanski's group[15] described the preparation and chemistry of highly reactive species $[Ti(NSiBu^t_3)(NHSiBu^t_3)_2]$, which can activate C-H bonds of benzene. The reaction is shown in Figure 4. The group also reported the selectivity in hydrocarbon activation through the kinetic and thermodynamic investigations of reversible 1,2-RH-elimination from $({}^tBu_3SiO)_2({}^tBu_3SiNH)TiR$.[45]

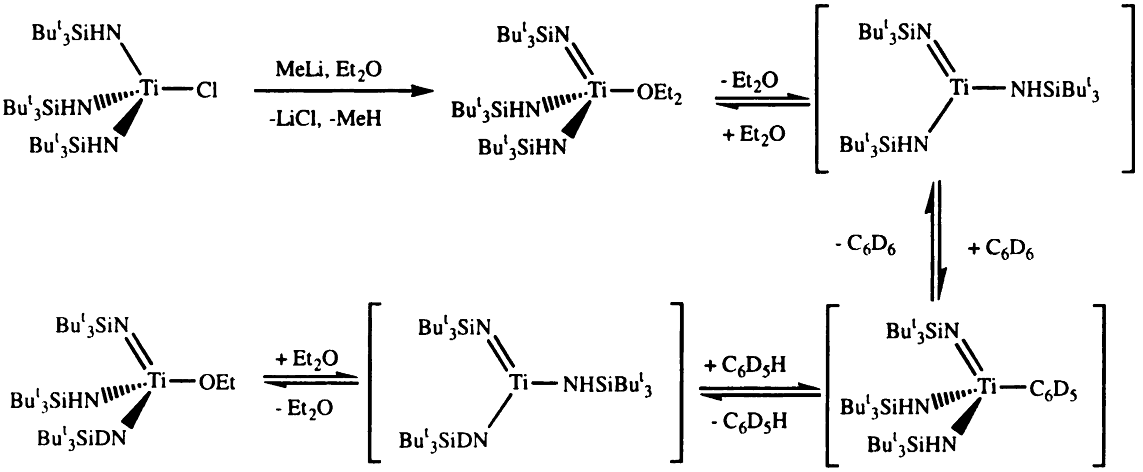


Figure 4: C-H activation with a titanium imido complex

The Zr=N bond can activate the C-H bonds of hydrocarbons through σ-bond metathesis. Bergman's group reported C-H activation by using transient $Cp_2Zr=NR$ in 1988.[31] At the same time, Wolczanski's group reported that a highly reactive zirconium imido complex, $(Bu^t_3SiNH)_2Zr(=NSiBu^t_3)$, effectively mediated the C-H bond activation.[3]

Cycloaddition

Titanium imido complexes also react with alkynes, isocyanates, and isocyanides to produce [2+2] cycloaddition products.[46-48] For example, Mountford's group[49] studied the cycloaddition reactions of the compounds $[Ti(NR)(Me_4taa)]$with a range of organic substrates. Figure 5 shows the cycloaddition reactions with isocynates, di-*p*-tolylcarbodiimide and carbon dioxide.

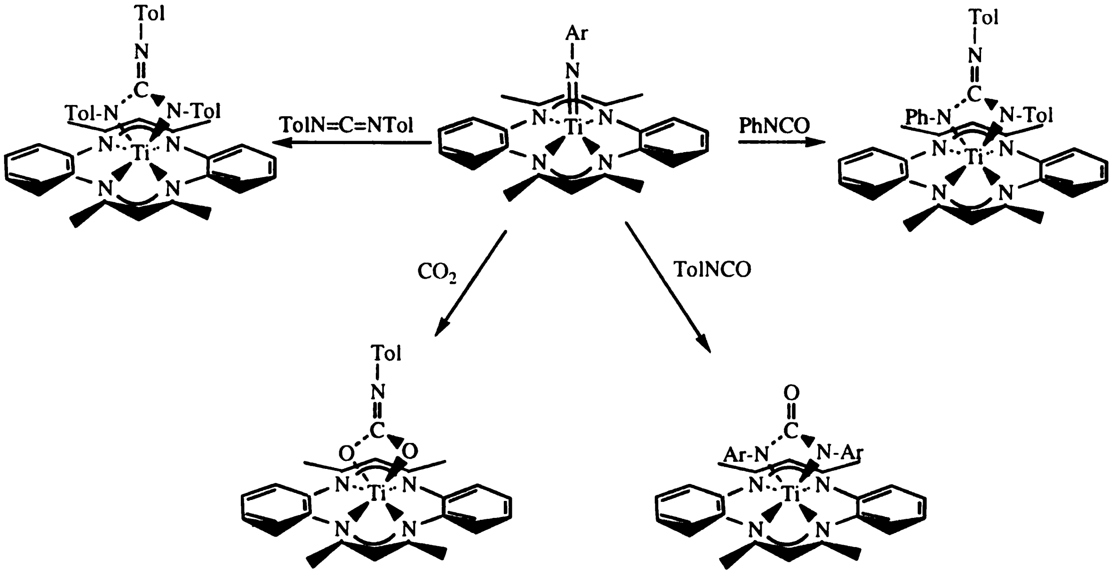


Figure 5: Selected cycloaddition reactions of [Ti(NAr)(Me$_4$taa)]

Zirconium imido complexes undergo cycloaddition reactions with a wide range of unsaturated organic molecules including alkynes, imines, and certain alkenes.[47,50] Several these reactions are believed to be important steps in catalytic transformations (e.g. hydroamination and imine metathesis) mediated by imido compounds.

C. Ligand Considerations

By 1993, research showed that group 4 imido compounds could be isolated but were relatively unreactive, or could be generated in situ and were extremely reactive.[1] In recent years, there has been considerable effort put forth in developing supporting ligands in transition metal imido chemistry, with a major goal being the tailoring of chemical reactivity and properties.[2] Supporting ligands are generally bulky in order to prevent dimerization and to provide the necessary electronic stabilization to the metal center.

Studies utilizing a wide range of ligands have confirmed the influence of the ancillary ligand environment on reactivity, but the accurate prediction of reactivity from a structure remains a challenge. For group 4 metal imido chemistry, N-donor amide and N_4 macrocyclic ligands have been developed, and some representative structures are shown in Figure 6.

A class of ligand that has enjoyed widespread use across a range of transition metal chemistry is "salen"-type Schiff bases **D** (Figure 6).[51,52] The peripheral substituents (i.e. R_1, R_2, R_3) of these N_2O_2-donor ligands are readily modified, and their syntheses from diamines and salicylaldehydes are typically straightforward. A few compounds with group 4 imido chemistry have been reported, and investigations of these compounds are still ongoing.[53]

α-Diimines[54] (**E** in Figure 6) can coordinate as a neutral bidentate ligands, but most commonly they act as mono- or di-anionic moieties owing to their ability to accept electron density into the π_3 lowest unoccupied molecular orbital. This results in shortening of the diimine C-C and lengthening of the C-N bonds in comparison to those of the free ligand.[55,56]

Arnold's group[57] has explored several general classes of amindinate ligands including linked bis(amidinates)[58] and ferrocene-containing derivatives.[59] An example is the N,N-bis(trimethylsilyl) benzamidinate (BTBA) ligand (**F**) shown in Figure 6. This ligand is particularly attractive because it is prepared easily and cheaply on a large scale. Its complexes are nicely soluble and generally highly crystalline, and the ligand contains excellent NMR spectroscopic handles. BTBA complexes are known for a wide range of transition metals in various oxidation states.[60]

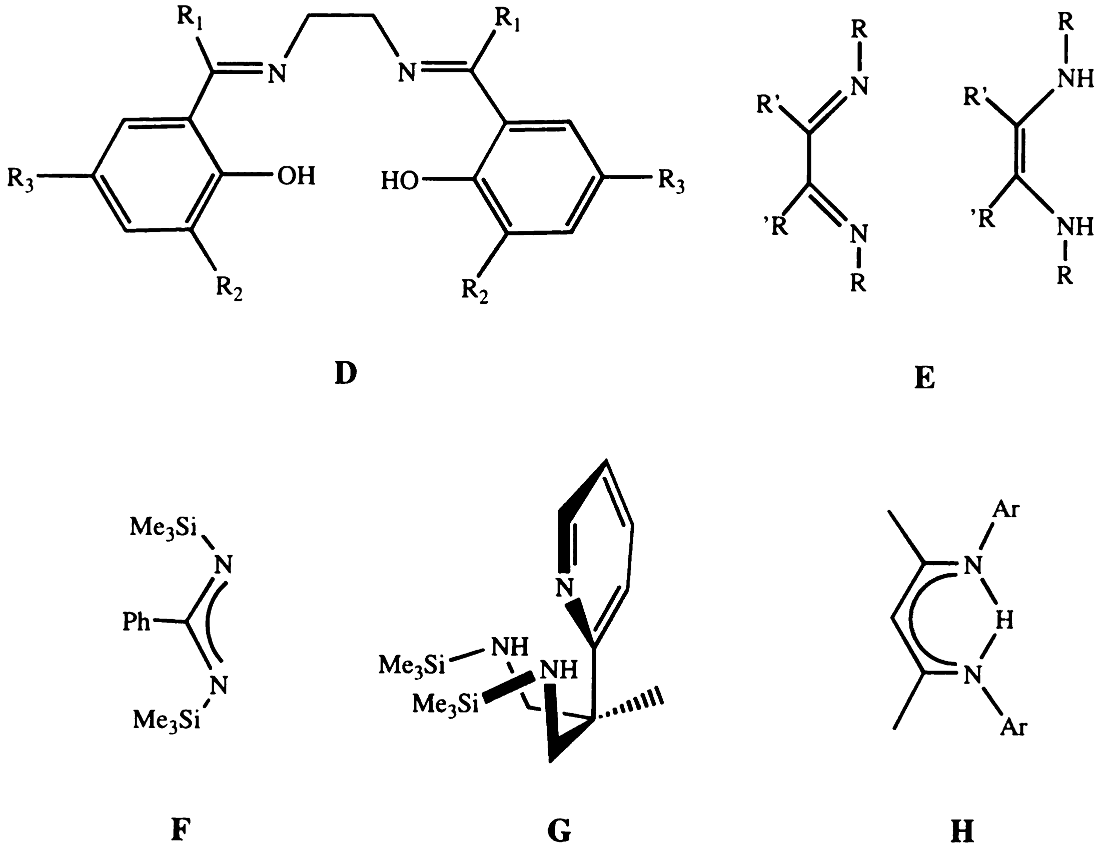


Figure 6: Several supporting ligands used to support group 4 imido complexes

The dianionic diamidoamine ligand $[Me_3SiN(CH_2CH_2NSiMe_3)_2]^{2-}$ (N_2N^{2-}) (**G** in Figure 6) has been used for imido group 4 chemistry.[61] Like its diamidopyridine N_2Npy analog,[62,63] the N_2N ligand can adopt a *fac* coordination geometry. Stable group 4 imido compounds with this ligand were synthesized, and the structures have been reported.

β-Diketiminate ligands

In this research, β-diketiminate ligands (**H** in Figure 6) were used. Applications of β-diketiminate ligands to imido metal complex have been limited despite several attractive features. First, they can be prepared in high yields from cheap and readily available building blocks, 2,4-pentanedione and primary amines. Second, the steric and electronic properties of the β-diketiminate ligands can be altered through appropriate choices of amine and β-diketone used in their syntheses. Lastly, this ligand family can provide kinetic stability while maintaining several accessible oxidation states at the metal since they generally bind as monoanionic ligands.

Diketiminate ligands have been known for a long time, and early investigations involved spectroscopic studies of transition metal complexes.[64-66] In addition to our group's work,[67-74] several groups have recently used the ligands to carry out stoichiometric and catalytic reactions.[75-83]

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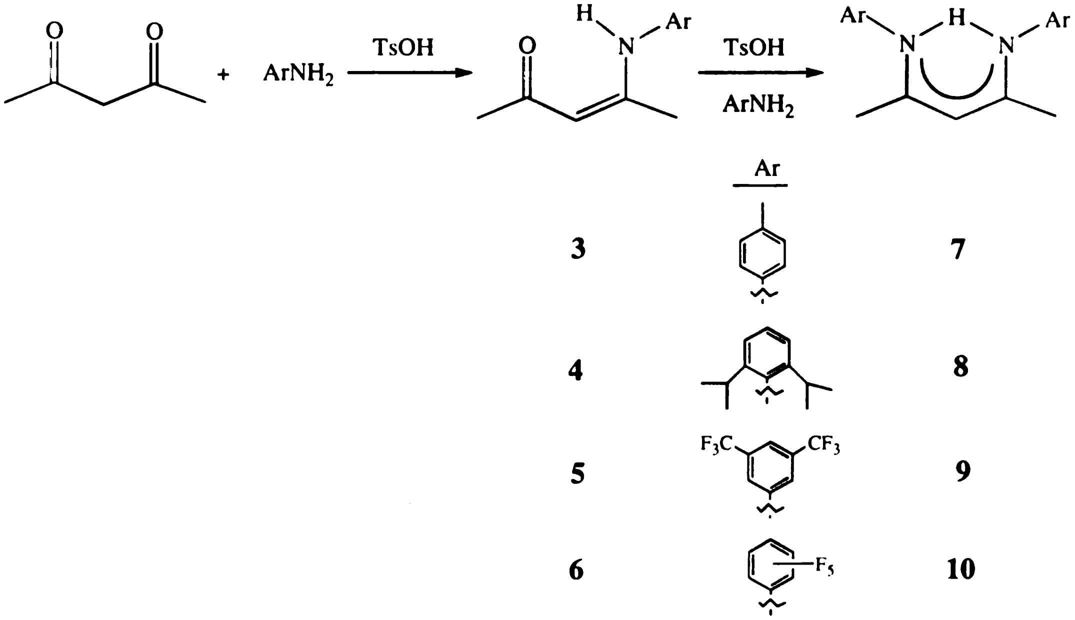
CHAPTER 2

RESULTS AND DISCUSSION

Ligand Synthesis

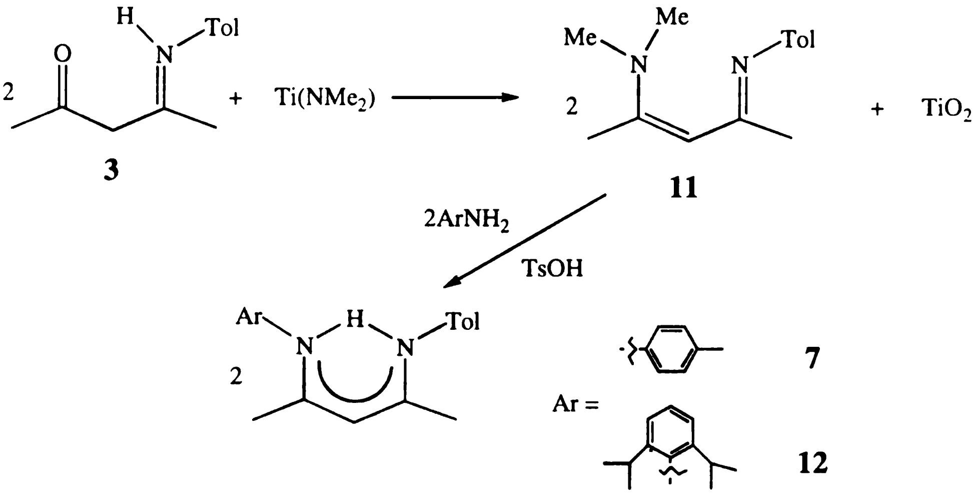
Syntheses of various β-diketiminate ligands were of interest. The general route is from 2,4-pentanedione, through two steps of amine condensation catalyzed by *p*-toluenesulfonic acid (Scheme 1).[1] However, relatively few examples of unsymmetrically substituted ketiminate ligands are known, and most involve reactions of more basic alkyl amines with arylketinines.[1,2] For arylamines, the procedure in scheme 1 is complicated by reversible amine condensations, which can lead to mixtures. Hence, we attempted to devise routes to unsymmetrically substituted ligands.

Scheme 1:



Our group previously found that $Ti(NMe_2)_4$ deoxygenation of monoketiminate complexes, which is thermodynamically driven by formation of TiO_2.[3] For example, two equiv of 4-(*p*-methylphenylamino)-3-pentene-2-one (**3**) react with 1 equiv of $Ti(NMe_2)_4$ to afford colorless 2-Dimethylamino-4-*p*-tolylimino-2-pentene (**11**) in 80% yield after standard workup. With a TsOH mediated reaction, the secondary dimethylamino group could be replaced by primary arylamines, thus TolnacnacH (**7**) was prepared in about 52% yield (Scheme 2).

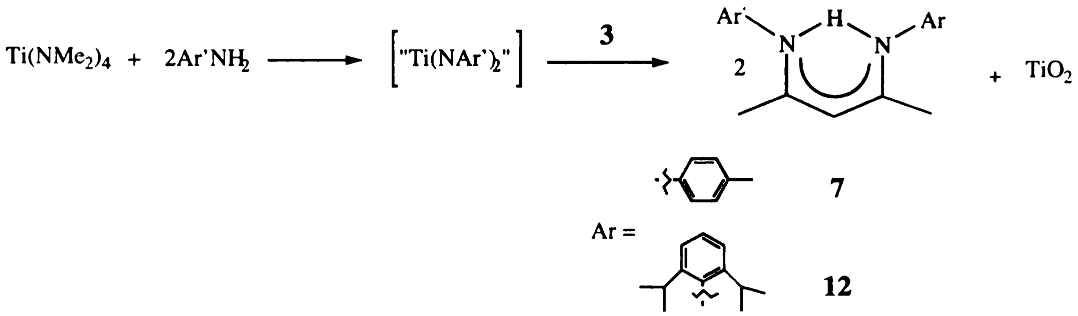
Scheme 2:



After this encouraging result, we designed a new in situ reaction route. To avoid isolation of **11**, we replaced dimethylamino unit at the outset by reacting $Ti(NMe_2)_4$ with two equiv of an aryl amine, and then we reacted the titanium intermediate(s) with 4-amino-3-pentene-2-one to synthesize the desired β-diketiminate ligand (Scheme 3). The result was what we expected, simplifying the syntheses of ligands with bulky aryl groups.

For example, after $Ti(NMe_2)_4$ and *p*-toluidine were stirred in toluene for 8 hours, 4-(2,6-di-*iso*-propylphenylamino)-3-pentene-2-one (**4**) was added and the mixture was refluxed. The desired unsymmetrically substituted ketiminate ligands **12** was obtained after the workup.

Scheme 3:

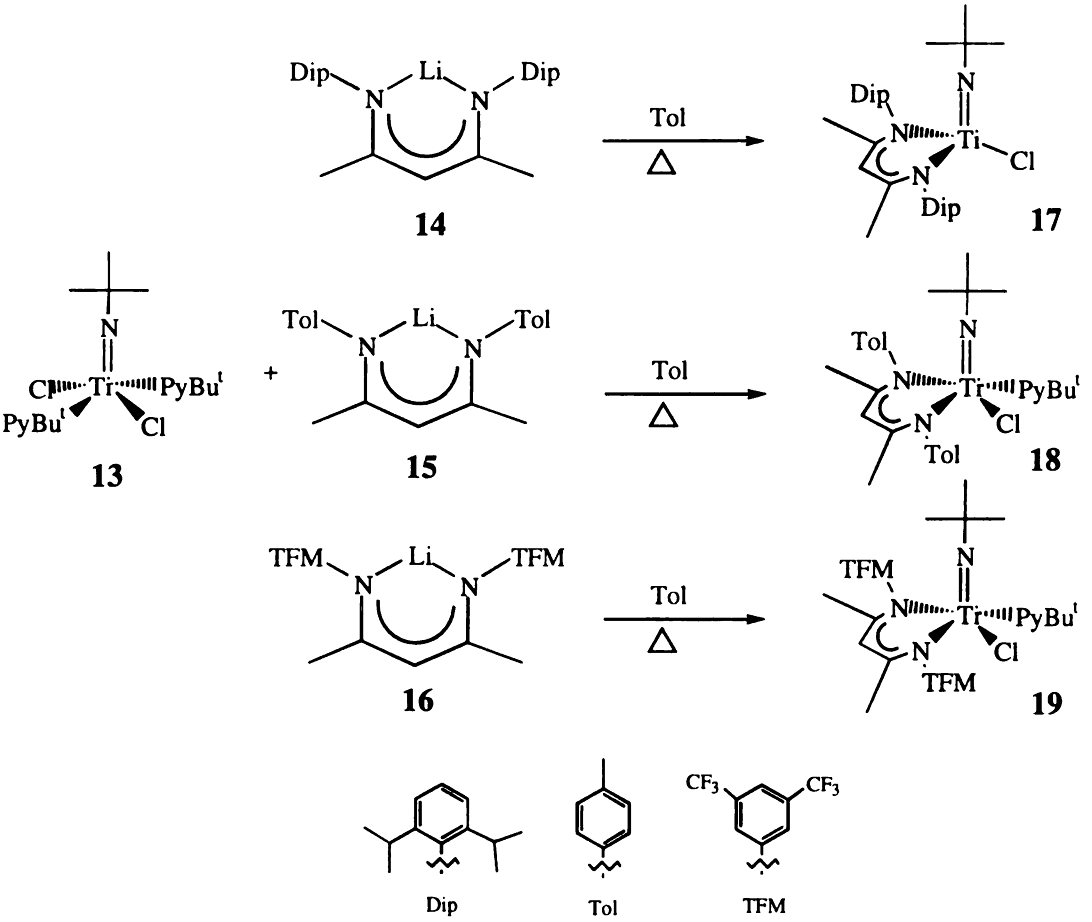


Synthesis of (Arnacnac)Ti(NBu^t)Cl and (Arnacnac)Ti(NBu^t)Cl(Py)

The β-diketiminate ligands are all readily converted to the corresponding lithium salts (**14**, **15** and **16**) in excellent yields through reaction with butyl lithium in toluene/pentane. Filtration and evaporation of volatile materials give products suitable for use without the need for additional purification. Mountford's group[4,5] reported that the compound $Ti(=NBu^t)Cl_2(PyBu^t)_2$ (**13**), which is inexpensive and readily prepared, is an excellent starting material in titanium imido chemistry since the *tert*-butyl pyridine and chloride ligands are usually easily substituted. Therefore, compound **13** was examined as a source of the titanium imido fragment.

The syntheses of β-diketiminate titanium imido chloride complexes were achieved by reacting **13** with lithium salts **14**, **15** and **16** respectively, where a chloride and one or two *tert*-butyl pyridine ligands are replaced by the Arnacnac group. The chemistry is summarized in Scheme 4, and full spectroscopic and analytical data are listed in Chapter 3.

Scheme 4:



Reaction of **13** with **14** in toluene at 70 °C for 16 hours resulted in an orange solution. Standard workup and crystallization from toluene/pentane at –30 °C gave (Bu^{t}N)Ti(Dipnacnac)Cl (**17**) in 66% yield. The NMR spectra for **17** in $CDCl_3$ indicate mirror symmetry in solution. Diffraction-quality crystals of **17** were grown at –30 °C from a saturated pentane solution. Details of data collection, processing, and structure resolution are given in the Appendix. The molecular structure is shown in Figure 7, and selected bond lengths and angles are given in Table 1.

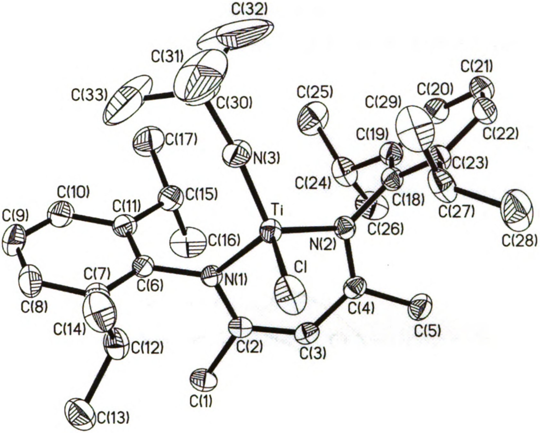


Figure 7: Thermal ellipsoid plot (50% probability) of (Bu^tN)Ti(Dipnacnac)Cl (17).

Table 1. Selected bond lengths (Å) and bond angles (°) for (Bu^tN)Ti(Dipnacnac)Cl (17).

Bond Lengths (Å)		Bond Angles (°)			
N3-Ti-N1	1.695(2)	N3-Ti-N1	106.39(9)	N2-Ti-Cl	115.79(6)
N3-Ti-N2	2.0292(18)	N3-Ti-N2	112.43(10)		
Ti-N2	2.031(2)	N1-Ti-N2	93.83(8)	Ti-N3-C30	171.3(2)
Ti-Cl	2.3268(7)	N3-Ti-Cl	113.17(8)		
N3-C30	1.460(3)	N1-Ti-Cl	113.36(6)		

(Bu^tN)Ti(Dipnacnac)Cl **(17)** has a four-coordinate Ti^{IV} center which possesses a distorted tetrahedral geometry. The $Ti{=}N_{imide}$ bond length [1.695(2) Å] lies in the middle of the range of values (ca. 1.67-1.73 Å) usually found for this linkage.[6,7] The angle subtended at the imido nitrogen atom [Ti-N3-C30] is 171.3(2)°.

The Dipnacnac ligand in **17** has the di-*iso*-propyl substituents on the 2- and 6-aryl positions. We were interested in probing the effects of changing the aryl ring substituents on the properties of titanium imido derivatives. Thus, we also investigated chemistry with less hindered Tolnacnac ligand.

The lithium salt **15** reacted with compound **13** in toluene to afford brown Ti(NBu^t)(Tolnacnac)Cl(PyBu^t) (**18**) in 44% recrystallized yield. Formation of a five-coordinate titanium with one *tert*-butylpyridine in **18** reflects the reduced steric demands of the Tolnacnac ligand relative to Dipnacnac ligand.

A view of the molecular structure of (Bu^{t}N)Ti(Tolnacnac)Cl(PyBu^t) (**18**) is shown in Figure 8, and important bond lengths and angles are listed in Table 2.

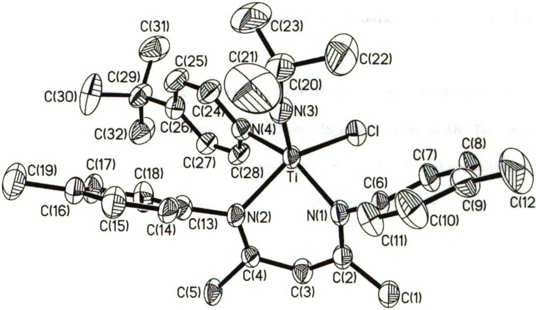


Figure 8: Thermal ellipsoid plot (50% probability) of (Bu^{t}N)Ti(Tolnacnac)Cl(PyBu^t) (18).

Table 2. Selected bond lengths (Å) and bond angles (°) for (Bu^{t}N)Ti(Tolnacnac)Cl(PyBu^t) (18)

Bond Lengths (Å)		Bond Angles (°)			
Ti-N3	1.685(5)	N3-Ti-N1	104.8(3)	N3-Ti-N4	100.5(3)
Ti-N1	2.067(6)	N3-Ti-N2	110.4(3)	N1-Ti-N4	154.0(2)
Ti-N2	2.076(5)	N1-Ti-N2	83.6(2)	N2-Ti-N4	82.4(2)
Ti-N4	2.228(6)	N3-Ti-Cl	111.6(2)	N4-Ti-Cl	84.28(16)
Ti-Cl	2.376(2)	N1-Ti-Cl	91.53(17)		
N3-C20	1.455(9)	N2-Ti-Cl	137.55(17)	Ti-N3-C20	171.6(5)

Compound **18** has the titanium in a square pyramidal geometry with the near-linear *tert*-butylimido ligand in the apical position. The titanium-imido nitrogen bond distance of 1.685(5)Å also falls in the typical range of 1.67-1.73 Å. The two Ti-N bond lengths for the ligand are statistically identical, averaging 2.072 Å.

Lithium salt **16** was also tried to perform the reaction. Under the same condition, the orange compound (Bu^{t}N)Ti(TFMnacnac)(PyBu^t)Cl (**19**) was formed in 53% yield. Compound **19** was obtained with a five-coordinate titanium. The molecular structure of **19** and some important bond lengths and bond angles are shown in Figure 9 and Table 3 respectively.

Similar to that of **18**, the structure of **19** shows a square pyramidal geometry. The titanium-imido nitrogen bond distance is almost identical to that of **18**. The angle of 168.5(7)° at the imido nitrogen atom (Ti-N6-C24) is nearly linear and consistent with a Ti-N triple bond. The titanium-imido nitrogen bond distance is experimentally identical to that in compound **18**.

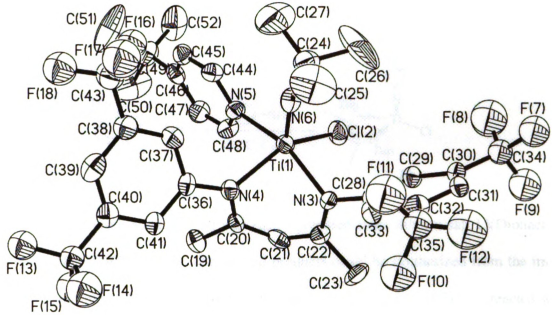


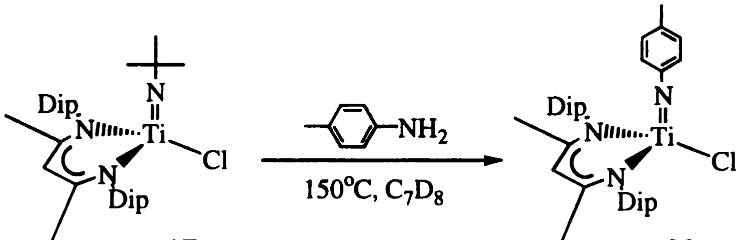
Figure 9: Thermal ellipsoid plot (50% probability) of $(\mathrm{Bu^tN})\mathrm{Ti(TMFnacnac)Cl(PyBu^t)}$ (19).

Table 3. Selected bond lengths (Å) and bond angles (°) for $(\mathrm{Bu^tN})\mathrm{Ti(TMFnacnac)Cl(PyBu^t)}$ (19)

Bond Lengths (Å)		Bond Angles (°)			
Ti1-N6	1.684(8)	N6-Ti1-N3	104.1(3)	N3-Ti1-N5	156.2(3)
Ti1-N3	2.119(7)	N6-Ti1-N4	109.8(3)	N4-Ti1-N5	86.1(3)
Ti1-N4	2.084(7)	N6-Ti-N5	99.5(3)	N4-Ti1-Cl2	139.5(2)
Ti1-N5	2.255(7)	N6-Ti-Cl2	110.6(3)	N5-Ti1-Cl2	85.2(2)
Ti1-Cl2	2.380(3)	N3-Ti1-N4	83.4(3)		
N6-C24	1.483(12)	N3-Ti1-Cl2	89.0(2)	Ti1-N6-C24	168.5(7)

In an attempt to prepare an arylimido analog of $\mathrm{(Dipnacnac)Ti(NBu^t)Cl}$, the NMR reaction between **17** and toluidine was examined in a toluene-d_8 solution. The exchange required forcing conditions. Nevertheless, a clean conversion occurred within 1 hour at 150 °C (Scheme 5).

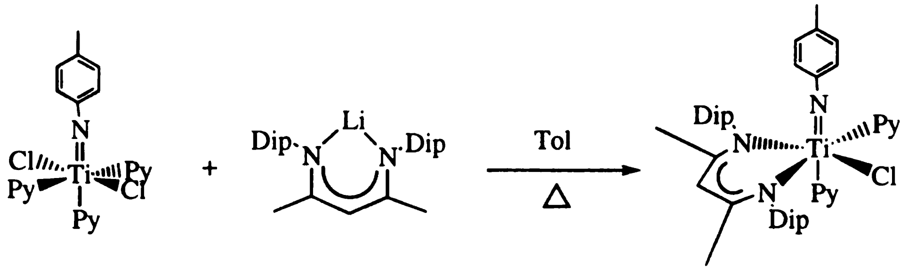
Scheme 5:



17 **20**

The pyridine adduct of **20** was easily prepared from lithium salt Li(Dipnacnac) (**14**) and (NTol)TiCl$_2$Py$_3$ (**21**). The desired products could be synthesized from the imido complex and lithiated β-diketimine ligands. For example, compound **21** was reacted with **14** in toluene for 16 hours at 70°C. After standard workup procedure, the brown compound (TolN)TiDipnacnacClPy$_2$ (**22**) was obtained in 63% yield. With the success of this reaction, a series of arylimido titanium compounds were analogously synthesized with this route.

Scheme 6



21 **14** **22**

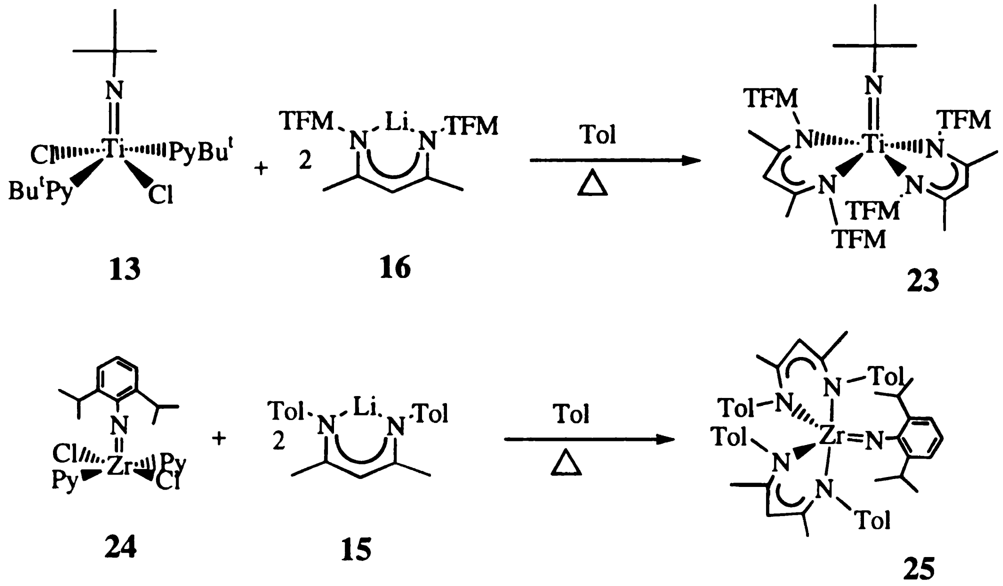
Syntheses of L$_2$M(=NR) through lithium salt metathesis

We tried to coordinate a second β-diketiminate ligand to titanium by further lithium salt metathesis. Addition of **14** to a stirred toluene solution of

(Bu^{t}N)TiCl$_2$(PyBu^t)$_2$ (**13**) gave compound **17** and unreacted **14**. Since steric factors may prevent incorporation of the second dipnacnac ligand, analogous reactions with **15** were examined. However, the desired product Ti(=NBu^t)(Tolnacnac)$_2$ could not be obtained.

Surprisingly, two equiv of **16** reacted with **13** afforded the yellow compound (Bu^{t}N)Ti(TFMnacnac)$_2$ (**23**) in 62% yield (Scheme 7). A singlet methane proton in the ^{1}H NMR spectrum and only one singlet in the ^{19}F NMR suggest a C_{2v}-symmetric structure.

Scheme 7



We also tried the syntheses of zirconium compounds because zirconium has a bigger atomic radius. The complex (DipN)ZrCl$_2$Py$_2$ (**24**)[8] was chosen as the starting material.

Two equiv of **15** were dissolved in toluene, and the solution was added dropwise to a toluene solution of **24**. The yellow-orange compound (DipN)Zr(Tolnacnac)$_2$ (**25**) was obtained in 70% yield (Scheme 7). The solid-state structure of compound **25** is shown in Figure 10 and selected bond lengths and bond angles are listed in Table 4.

Compound **25** has a five-coordinate Zr^{IV} center in a distorted trigonal-bipyramidal arrangement with an approximately linear arylimido ligand (174.95(7)°) occupying an equatorial coordination site. The $Zr\text{-}N_{imido}$ bond length (1.854(2) Å) is within the range of known alkyl- and aryl-substituted imido ligands for Zirconium complexes (1.83-1.88 Å).[6,8-13] The nitrogens of each β-diketimine ligand occupy both axial and equatorial coordination sites, where the averaged axial $Zr\text{-}N_{ligand}$ bond distances (2.60 Å) are longer than the averaged equatorial $Zr\text{-}N_{ligand}$ bond distances (2.35 Å).

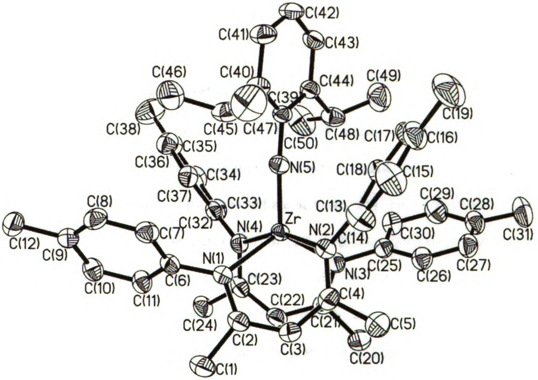


Figure 10: Thermal ellipsoid plot (50% probability) of $(DipN)Zr(Tolnacnac)_2$ (25).

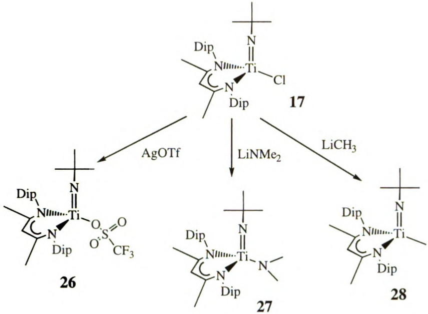
Table 4. Selected bond lengths (Å) and bond angles (°) for (DipN)Zr(Tolnacnac)$_2$ (25)

Bond Lengths (Å)		Bond Angles (°)			
Zr-N1	2.2447(19)	N5-Zr-N1	117.72(8)	N1-Zr-N4	89.93(7)
Zr-N2	2.259(2)	N5-Zr-N2	98.62(8)	N2-Zr-N3	91.04(7)
Zr-N3	2.228(2)	N5-Zr-N3	116.34(8)	N2-Zr-N4	160.30(7)
Zr-N4	2.261(2)	N5-Zr-N4	101.08(8)	N3-Zr-N4	80.33(7)
Zr-N5	1.854(2)	N1-Zr-N2	80.80(7)		
N5-C39	1.395(3)	N1-Zr-N3	125.94(8)	Zr-N5-C39	174.95(17)

Syntheses of LTi(=NR)Cl derivatives

Compounds **17**, **18,** and **19** provide good entries to potentially interesting imidotitanium compounds by exchanging the chloride ligand. As shown in Scheme 8, compound **17** reacts with 1 equiv silver triflate at room temperature to afford the orange compound ($\mathrm{Bu^t}$N)Ti(Dipnacnac)(OTf) (**26**) in 72% yield. Since triflate is usually a better leaving group than chloride, compound **26** may exhibit interesting reactivity. Compound **26** has a similar ^{1}H NMR spectrum to **17**. Therefore, the triflate is almost certainly bound in solution. ORTEP diagram of complex **26** is shown in Figure 11. In Table 5, some selected bond lengths and bond angles are listed.

Scheme 8



The structure of **26** has a distorted pseudo tetrahedral symmetry similar to chloride **17.** The angle subtended at the imido nitrogen atom [Ti-N3-C30] is 177.0 (5)°, which is slightly more linear than in **17** [(171.3(2)°], and the Ti=N$_{imide}$ bond length [1.680(5) Å] is slightly shorter than that of **17** [1.695(2) Å]. These data may reflect a somewhat higher degree of π-interaction between N$_{imido}$ and Ti in **26**.

Table 5. Selected bond lengths (Å) and bond angles (°) for (Bu^{t}N)Ti(Dipnacnac)OTf (26)

Bond Lengths (Å)		Bond Angles (°)			
Ti-N3	1.680(5)	N3-Ti-N1	108.0(2)	N2-Ti-O1	116.3(2)
Ti-N1	1.993(6)	N3-Ti-N2	108.4(2)	Ti-O1-S	163.7(3)
Ti-N2	2.006(5)	N1-Ti-N2	94.8(2)		
Ti-O1	1.982(4)	N3-Ti-O1	113.7(2)	Ti-N3-C30	177.0(5)
N3-C30	1.458(7)	N1-Ti-O1	113.9(2)		

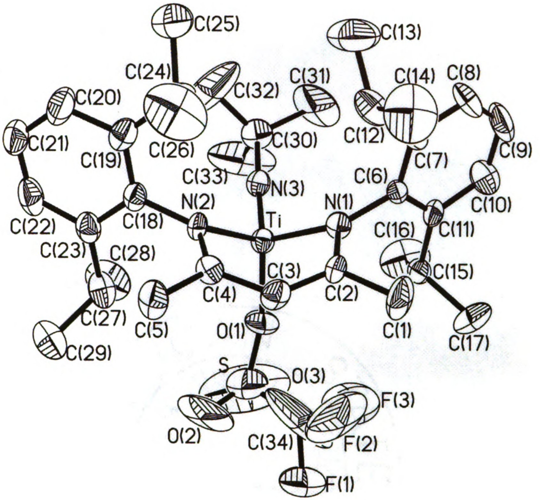


Figure 11: Thermal ellipsoid plot (50% probability) of $(Bu^tN)Ti(Dipnacnac)(OTf)$ (26).

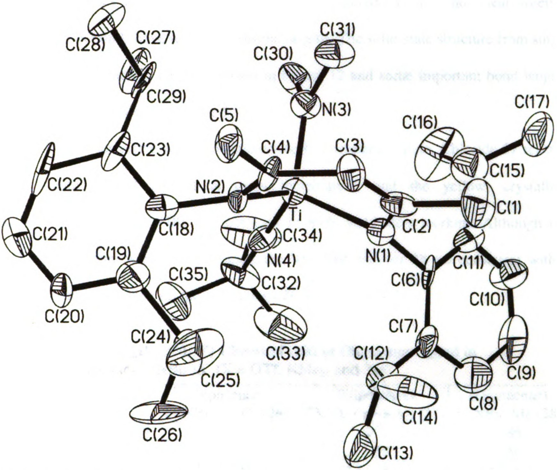


Figure 12: Thermal ellipsoid plot (50% probability) of (Bu^{t}N)Ti(Dipnacnac)(NMe$_2$) (27).

Table 6. Selected bond lengths (Å) and bond angles (°) for (Bu^{t}N)Ti(Dipnacnac)(NMe$_2$) (27)

Bond Lengths (Å)		Bond Angles (°)			
Ti-N4	1.703(4)	N4-Ti-N1	113.8(4)	N2-Ti-N3	114.7(4)
Ti-N1	2.047(9)	N4-Ti-N2	113.2(4)		
Ti-N2	2.080(9)	N1-Ti-N2	92.64(14)	Ti-N4-C32	176.2(9)
Ti-N3	1.922(4)	N4-Ti-N3	108.44(16)		
N4-C32	1.430(6)	N1-Ti-N3	113.6(4)		

The amide derivative (Bu^{t}N)Ti(Dipnacnac)(NMe$_2$) (**27**) was prepared by metathesis between **17** and Li(NMe$_2$) in 62.4% yield. The ^{1}H NMR spectrum showed two

N-CH_3 resonances at 3.93 ppm and 2.61 ppm, respectively. It is not clear whether restricted Ti-N bonds have steric or elctronic origins. The solid-state structure from single crystal X-ray diffraction on **27** is shown in Figure 12 and some important bond lengths and bond angles are listed in Table 6.

A Ti-C derivative was also synthesized by metathesis route. Chloride **17** reacted cleanly with methyl lithium at room temperature, and the yellow, crystalline (Bu^tN)Ti(Dipnacnac)Me (**28**) was obtained in 88% yield after workup. Although the solid-state structure was not determined, the ^1H NMR data for **28** are consistent with a structure similar to those of the compounds **26** and **27** (Table 7).

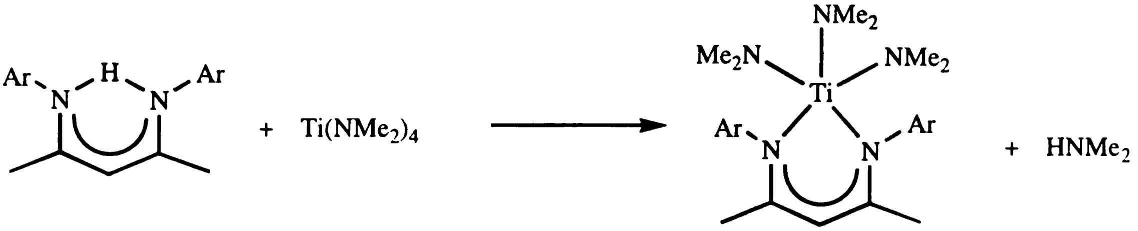
Table 7. ^1H NMR (C_6D_6, 300HZ) Chemical shift of Dipnacnac ligand in (Dipnacnac)Ti(NBu^t)X (X = OTf, NMe_2, and Me)

Compound	(Dipnacnac) Ti(NBu^t)(OTf) (**26**)	(Dipnacnac) Ti(NBu^t)(NMe_2) (**27**)	(Dipnacnac) Ti(NBu^t)Me (**28**)
Backbone (1H)	4.81	4.94	4.86
Methane of petane (6H)	1.51	1.53	1.56
Bond to 1,3-C of isopropyl group (24H)	1.71 (6H)	1.44 (6H)	1.60 (6H)
	1.37 (6H)	1.20 (6H)	1.42 (6H)
	1.30 (6H)	1.13 (6H)	1.19 (6H)
	0.92 (6H)	0.85 (6H)	1.07 (6H)
Bond to 2-C of isopropyl group (4H)	3.11 (2H)	3.61 (2H)	3.36 (2H)
	3.02 (2H)	2.83 (2H)	3.14 (2H)

An unusual reaction between $Ti(NMe_2)_4$ and C_6F_5nacnacH

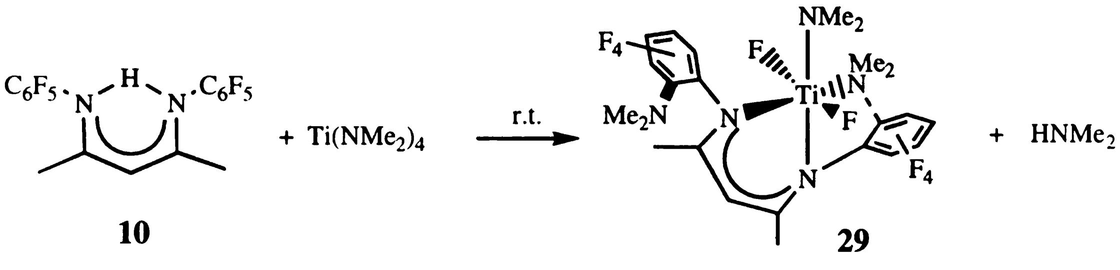
Previously, Our group[14] and Collins' group[15] had examined reactions between various β-diketiminate ligands and $Ti(NMe_2)_4$. Scheme 9 shows the general scheme for these reactions.

Scheme 9



The general scheme 9 holds for many different β-diketiminate ligands. However, when we used the highly fluorinated ligand C_6F_5nacnacH for the reaction, an unusual dark red compound $(NMe_2)Ti[(2\text{-}NMe_2\text{-}C_6F_4)nacnac]F_2$ (**29**) was formed in 93% yield (Scheme 10). ^{1}H NMR spectrum in benzene-d_6 exhibits four sharp singlets and three multiplets between 1.48 ppm and 3.51 ppm. Each resonance integrates as three protons against the β-diketiminate ligand backbone resonance. The typical chemical shift of the backbone hydrogens ranges from 5 ppm to 6 ppm. In this case, the resonance was observed at 5.09 ppm. The ^{19}F NMR spectrum showed ten fluorine resonances.

Scheme 10



To help assign the NMR data, an X-ray diffraction experiment was performed on single crystals of **29** (Figure 13). In Table 8, the selected bond lengths and bond angles are listed.

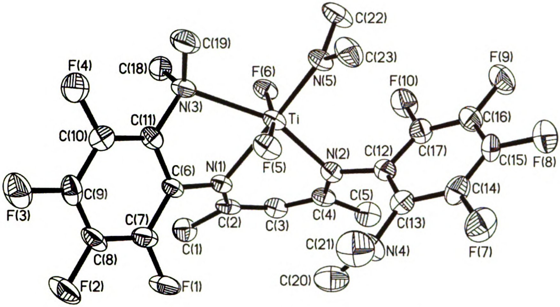


Figure 13: Thermal ellipsoid plot (50% probability) of $(NMe_2)Ti[(2\text{-}NMe_2\text{-}C_6F_4)nacnac]F_2$ (29)..

Table 8. Selected bond lengths (Å) and bond angles (°) for $(NMe_2)Ti[(2\text{-}NMe_2\text{-}C_6F_4)nacnac]F_2$ (29)

Bond Lengths (Å)		Bond Angles (°)			
Ti-N1	2.140(3)	N5-Ti-N1	175.55(13)	N1-Ti-F6	90.54(10)
Ti-N2	2.055(3)	N5-Ti-N2	100.04(13)	N2-Ti-N3	155.62(12)
Ti-N3	2.350(3)	N5-Ti-N3	104.26(12)	N2-Ti-F5	99.26(11)
Ti-N5	1.911(3)	N5-Ti-F5	89.81(12)	N2-Ti-F6	93.51(11)
Ti-F5	1.846(2)	N5-Ti-F6	92.53(11)	N3-Ti-F5	82.88(10)
Ti-F6	1.818(2)	N1-Ti-N2	82.97(12)	N3-Ti-F6	83.58(10)
		N1-Ti-N3	72.89(11)	F5-Ti-F6	166.41(10)
		N1-Ti-F5	86.46(10)		

The ORTEP diagram shows a distorted octahedral geometry with two *trans* fluoride ligands. The β-diketimine ligand C_6F_5nacnac has been aminated twice through *ortho* C-F activation at each pentafluoro phenyl group (Figure 20). Three out of four nitrogens in the $(2\text{-}NMe_2\text{-}C_6F_4)$nacnac ligand coordinate to the central titanium, and inequivalent (2-

NMe_2-C_6F_4) are evident by ^1H and ^{19}F NMR. With five sites of the six-coordinate compound **29** accounted for, the last coordination site is occupied by a dimethylamide.

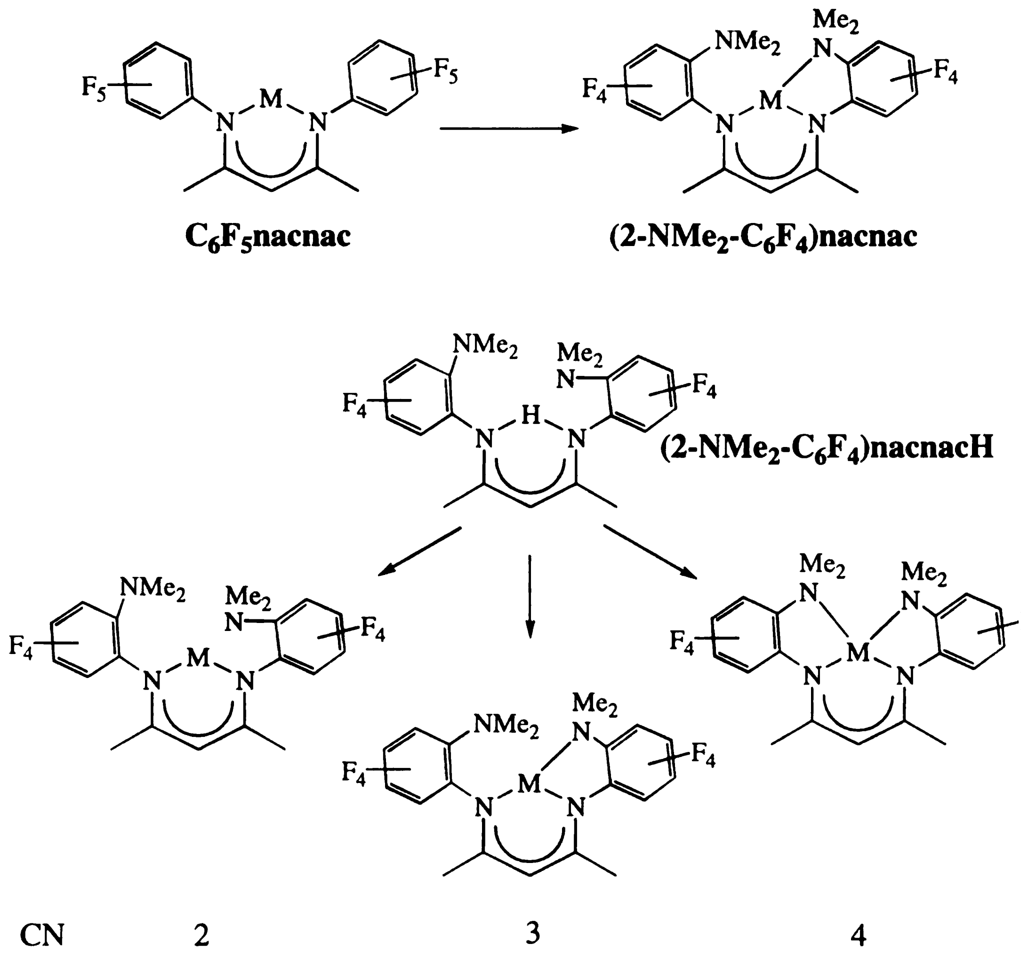


Figure 14: Ligand (2-NMe_2-C_6F_4)nacnac and its potential coordination with metal

Hydrolysis of compound **29** afforded the ligand (2-NMe_2-C_6F_4)nacnacH (**30**) in 90% yield. The ligand **30** has interesting possibilities as a 2-4 coordinate ligand with a valence of −1 (Figure 14).

Summary

In this project, a new method for synthesizing unsymmetrical diketminate ligands from an arylketimine, $Ti(NMe_2)_4$ and an arylamine has been developed. This may be useful for preparing complexes where standard acid catalyzed reactions give mixtures.

A series of four and five-coordinate Ti and Zr imido complexes were prepared with one or two diketiminate ligands. For Ti, a series of compounds with the formula (Dipnacnac)Ti(NBu^t)X (X = OTf, NMe_2, and Me) were prepared from (Dipnacnac)Ti(NBu^t)Cl.

Finally, the fluorinated ligand C_6F_5nacnacH undergoes an *ortho* C-F activation at each C_6F_5 group to give a novel Ti compound, which hydrolyzes to give the new ketamine (2-NMe_2-C_6F_4)nacnacH.

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CHAPTER 3

EXPERIMENTAL METHODS

General Methods and instrumentation

All manipulations, excluding ligand preparations, were carried out under an atmosphere of dinitrogen or argon using standard Schlenk-line or dry-box techniques. Dinitrogen and argon were purified by passing through columns of MnO supported on silica.

Solvents (excluding deuteriated solvents) were freshly distilled over sodium/benzophenone ketyl (toluene, pentane, ether and THF) or over calcium hydride (methylene chloride) and were saturated with dinitrogen before use. Chloroform-d_1, bezene-d_6, toluene-d_8 were dried over activated 3Å sieves, and vacuum transferred. Dichloromethane-d_2 was dried over activated 4Å sieves, and vacuum transferred. Chloroform-d_1 and dichloromethane-d_2 were stored under dinitrogen in air-free flasks in the dry-box. Bezene-d_6 and toluene-d_8 were stored in air-free flask over a sodium mirror in dry-box.

Elemental analyses (C, H, N) were performed on a Perkin Elmer CHN 2400 Series II CHNS/O at the chemistry department of Michigan State University. The following NMR spectrometers were used: Varian Gemini-300, Inova-300 or VXR-300. ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were referenced to the chemical shift of the residual proton and ^{13}C signals of the deuterated solvents. ^{19}F (288 MHz) NMR spectra were referenced to neat $CFCl_3$ (δ 0 ppm) as an external standard. Uncorrected melting points of crystalline samples in sealed capillaries (under a dinitrogen atmosphere) were reported as ranges.

Single Crystal X-Ray Structure Determination

Unless otherwise noted, all crystals were considered to be air sensitive and were collected by filtration and coated with Paratone-N. A suitable single crystal was selected and mounted onto a glass fiber (with Paratone-N). The crystal was then transferred to the goniometer of a Siemens SMART CCD diffractometer using Mo K_λ radiation ($\lambda = 0.71073$ Å). Data frames were collected as 30-second exposures at 173K. The initial cells were calculated from three sets of 20 frames. All data sets were collected over a hemisphere of reciprocal space. SAINT was used to integrate 1025 frames and to generate the raw file. Final unit cell parameters were obtained by least-squares refinement of strong reflections obtained. Absorption correction and time decay were applied to the data by SADABS. The non-hydrogen atoms located by using SHELXS and refined using.

Calculations were based on F^2 data. Unless noted otherwise, all non-hydrogen atoms were refined using anisotropic displacement parameters and all hydrogen atoms were placed in calculated positions and refined as riding models. Three of the parameters are defined below.

$$GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$$

where n is the number of reflections and p the total number of parameters refined.

$$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$$

Starting materials

Common chemicals were purified by established procedures. The compounds $(Bu^tN)TiCl_2(PyBu^t)_2$,[1] $(Bu^tN)TiCl_3Py_3$,[2] $(TolN)TiCl_2Py_3$,[2] $(DipN)ZrCl_2Py_2$,[3] $Ti(NMe_2)_4$,[4] and $Zr(NMe_2)_4$[4] were prepared according to the literature procedures.

2,4-pentanedione, 2,6-diisopropyl aniline were distilled prior to use. *p*-Toluidine was sublimed and AgOTf was recrystallized from ether before use.

Synthesis

4-(*p*-Methylphenylamino)-3-pentene-2-one (3)[5] In a 500 mL round bottom flask, 2,4-pentanedione (40 g, 0.4 mol) and freshly sublimed *p*-toluidine (42.8 g, 0.4 mol) were dissolved in 300 mL toluene. A Dean-Stark apparatus was used to azetropically remove water. The mixture was heated at 130 °C for eight hours to give a brown solution. All the toluene was removed by a rotary evaporator and the subsequent brown oil was diluted with hexane. The hexane solution was put into –30 °C freezer for overnight. The yellow crystallized material was collected by suction filtration (61.3 g, 81.5%). mp 67–68 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 12.38 (br, s, 1H), 7.12 (d, 2H), 6.97 (d, 2H), 5.18 (s, 1H), 2.32 (s, 3H), 2.07 (s, 3H), 1.94 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 195.8. 160.6, 135.9, 135.4, 129.5, 124.7, 97.10, 29.03, 20.81, 19.68.

4-(2,6-Di-*iso*-propylphenylamino)-3-pentene-2-one (4)[5] A 250 mL round bottom flask was charged with 2,4-pentanedione (40 g, 0.40 mol), $TsOH{\bullet}H_2O$ (0.46 g, 2.5 mmol), and 2,6-diisopropyl aniline (47 g, 0.27 mol). The mixture was heated with a minimum amount of toluene in a Dean-Stark apparatus for eight hours. After removing the solvents, the mixture was vacuum distilled (105 °C / 0.01 mmHg) to give a pale yellow ketoamine which solidified upon standing overnight (65 g, 93%). mp 49-51 °C.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.06 (s, br, 1H), 7.26 (m, 1H), 7.15 (d, 2H), 5.18 (s, 1H), 3.00 (sept, 1H), 2.09 (s, 3H), 1.18 (d, 6H), 1.60 (s, 3H), 1.12 (d, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 195.9, 163.2, 146.2, 133.4, 128.2, 123.5, 95.53, 29.03, 28.41, 24.54, 22.61, 19.10.

4-(3,5-Di-trifluoromethylamino)-3-pentene-2-one (5) A 100 mL round-bottom flask was charged with 2,4-pentanedione (0.75 g, 7.5 mmol), 3,5-di-trifluoromethylaniline (1.15 g, 5.0 mmol) and $TsOH•H_2O$ (0.02 g, 0.1 mmol). Dry toluene 50 mL was added to the flask and a Dean-Stark apparatus was used to azetropically remove water. The mixture was heated at 130 °C for eight hours to give a brown solution. All the volatiles were removed by rotary evaporator. The subsequent brown oil was vacuum distilled (75 °C / 0.01 mmHg) to give pale yellow oil which solidified upon standing overnight. (1.45 g, 93%). mp 45-48 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.68 (s, 1H), 7.60 (s, 1H), 7.49 (s, 2H), 5.29 (s, 1H), 2.10 (s, 3H), 2.06 (s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 197.73, 157.74, 147.67, 132.67, 123.37, 121.06, 118.02, 100.09, 29.40, 19.84. ^{19}F NMR ($CDCl_3$, 288MHz) δ –63.71.

4-(Pentafluorophenylamino)-3-pentene-2-one (6) A 250 mL round bottom flask was charged with 2,4-pentanedione (11 g, 0.11 mol), $TsOH•H_2O$ (0.3 g, 1.6 mmol), and pentafluoroaniline (14.2 g, 0.078 mol). Dry toluene (50 mL) was added to the flask and a Dean-Start apparatus was used to azetropically remove water. The mixture was heated at 130°C for ten hours to give a yellow solution. All the volatiles were removed by rotary evaporator leaving a yellow solid, which was washed with pentane (20 mL). Colorless crystals formed after recrystallization overnight from pentane/MeOH at –30 °C. (16.50 g, 80.3%). mp 83-85 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 11.84 (s, 1H), 5.34 (s, 1H), 2.05 (s, 3H), 1.79 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 197.97, 159.80, 145.10, 141.75, 139.42, 138.12, 136.06, 114.41, 99.41, 29.01, 18.59. ^{19}F NMR ($CDCl_3$, 288MHz) δ – 146.63, -156.94, -162.48.

2-*p*-Tolylamino-4-*p*-tolylimino-2-pentene (TolnacnacH) (7)

METHOD 1[5]: A toluene solution of compound **3** (41.0 g, 0.38 mol), TsOH•H_2O (72 g, 0.38 mol), *p*-toluidine (40.7 g, 0.38 mol) was charged in 500 mL round bottom. A Dean-Stark apparatus was used to azetropically remove water. The mixture was heated at 130 °C for 24 hours. After the mixture was cooled to room temperature, it was diluted with ether (40 mL) and washed with aqueous base (100 mL, 18.7% NaOH). After separation from the ether layer, the aqueous layer was back extracted with ether (2 x 20 mL). The combined organics were dried over magnesium sulfate, filtered, and ether was removed using a rotavap. The resultant oil was diluted with 30 mL hexanes, and cooled to –30 °C overnight to induce crystallization. The pale yellow diketimine was obtained after filtration. The product was washed with cold hexane and then dried in vacuo (87 g, 82.4 %).

METHOD 2[6]: A 50ml round bottom flask was charged with compound **11** (216 mg, 1.0 mmol), TsOH·H_2O (190 mg, 1.0 mmol), *p*-toluidine (107mg, 1.0mmol). The mixture was stirred with 20 mL toluene in Dean-Stark apparatus in an oil bath heated at 130 °C for 24 hours. After the mixture was cooled to room temperature, it was diluted with ether (25 mL) and washed with aqueous base (30 mL, 20% NaOH). After separated from the organic layer, the water phase was back extracted with ether (2 x 10 mL). The combined organic phase was dried over $MgSO_4$. The solvent was removed by vacuum.

Yellow analytically pure compound was obtained by recrystallization from Hexane. (146 mg, 52.5%).

<u>METHOD 3</u>: To a stirred solution of $Ti(NMe_2)_4$ (224 mg, 1.0 mmol) in toluene was added a toluene solution of *p*-toluidine (214 mg, 2.0 mmol). The solution quickly turned from yellow to dark red. After 8 hours stirring, compound **3** (378 mg, 2.0 mmol) was added, and the mixture was refluxed 24 hours. A yellow solution with orange precipitate was formed. After filtration, the solvent was removed under vacuum and gave a yellow solid. (453 mg, 81.5%) Samples thus prepared were sufficiently pure (^{1}H NMR spectroscopy) to use in further reactivity studies. mp 67–70 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.62 (s, br, 1H), 7.07 (d, 4H), 6.84 (d, J = 8.1 Hz, 4H), 4.83 (s, 1H), 2.31 (s, 6H), 1.98 (s, 6H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 159.5, 143.1, 132.6, 129.2, 122.6, 96.80, 20.76, 20.60.

2-2,6-Di-*iso*-propylphenylamino-4-2,6-di-*iso*-propylphenylimino-2-pentene (DipnacnacH) (8) A 250 mL round bottom flask was charged with compound **4** (34 g, 0.13 mol), $TsOH{\bullet}H_2O$ (22.6 g, 0.13 mol), and 2,6-diisopropyl aniline (23 g, 0.13 mol). The mixture was stirred with a minimum amount of toluene in a Dean-Stark apparatus in an oil bath heated at 170 °C for 24 hours. After the mixture was cooled to room temperature, it was diluted with ether (100 mL) and washed with aqueous base (100 mL, 12.7% KOH). The water layer was separated from the organic layer, and the water phase was back extracted with ether (20 mL). The combined organics were dried over $MgSO_4$. Colorless, analytically pure compound was obtained by recrystallization from hexane/MeOH (43.4 g, 80%). mp 138–140 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.12 (s, br, 1H), 7.12 (m, 6H), 4.86 (s, 1H), 3.11 (sept, 4H), 1.71 (s, 6H), 1.20 (d, 12H), 1.11 (d, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 161.18, 142.44, 140.69, 125.06, 123.00, 93.18, 28.17, 24.20, 23.22, 20.74.

2-3,5-Di-trifluoromethylamino-4-3,5-trifluoromethylimino-2-pentene (TFMnacnacH) (9) A 100 mL round bottom flask was charged with compound **5** (1.33 g, 4.3 mmol), 3,5-di-trifluoromethylaniline (0.979 g, 4.3 mmol) and TsOH•H_2O (0.813 g, 4.3 mmol). Dry toluene (50 mL) was added to the flask and a Dean-Stark apparatus was used to azetropically remove water. The mixture was heated at 150 °C for 24 hours. After the mixture was cooled to room temperature, it was diluted with ether (20 mL) and washed with aqueous base (50 mL, 1.0% KOH). After separated from ether layer, the aqueous layer was back extracted with ether (2 x 10 mL). The combined organics were dried over $MgSO_4$. A brown solid was formed after removal of the ether under reduced pressure. Colorless analytically pure compound was obtained by crystallization from hexane/MeOH at -30°C. (1.76 g, 78.0%). mp 126-128°C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.51 (s, 1H), 7.56 (s, 2H), 7.34 (s, 4H), 5.04 (s, 1H), 2.02 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ 160.35, 146.79, 132.44, 125.06, 122.33, 116.95, 99.93, 20.96. ^{19}F NMR ($CDCl_3$, 288Hz) δ -63.49. Anal. Calcd for $C_{21}H_{14}N_2F_{12}$: C, 48.29; H, 2.70; N, 5.36. Found: C, 48.32; H, 2.57; N, 5.32.

2-Pentafluorophenylamino-4-pentafluorophenylimino-2-pentene (C_6F_5nacnacH) (10) A 250 mL round bottom flask was charged with compound **6** (3.0 g, 96.5 mmol), pentafluoroaniline (22.1 g, 96.5 mmol) and TsOH•H_2O (0.813 g, 4.3 mmol). Dry toluene 150 mL was added to the flask and a Dean-Stark apparatus was used to azetropically remove water. The mixture was heated at 150 °C for 24 hours. After the mixture was cooled to room temperature, it was diluted with ether (40 mL) and washed with aqueous base (80 mL, 10% NaOH). After separated from ether layer, the aqueous layer was back extracted with ether (2 x 10 mL). The combined organics were dried over $MgSO_4$. A dark brown solid was formed after removal of the ether under reduced pressure. Colorless analytically pure compound was obtained by recrystallization from hexane/MeOH overnight at –30 °C. (17.86 g, 42.9%). mp 85-86 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.06 (s, 1H), 5.18 (s, 1H), 1.93 (s, 6H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 164.28, 142.96, 139.67, 136.27, 120.00, 99.21, 20.90. ^{19}F NMR ($CDCl_3$, 288Hz) δ –149.23, -160.84, -163.31. Anal. Calcd for $C_{17}H_8N_2F_{10}$: C, 47.46; H, 1.87; N, 6.51. Found: C, 47.23; H, 1.87; N, 6.47.

2-Dimethylamino-4-*p*-tolylimino-2-pentene (11) To a stirred solution of $Ti(NMe_2)_4$ (3.150 g, 0.014 mol) in toluene was added a toluene solution of freshly prepared **3** (5.32 g, 0.028 mol). The solution changed from yellow to dark red quickly. After heating and reflux for 24 hours, precipitate formed. After filtration, the solvent was removed under vacuum to give dark red solid. Colorless crystals formed in saturated pentane solution at –80 °C for 24 hours (4.88 g, 80.4%). mp 31-33 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.04 (d, 2H), 6.63 (d, 2H), 4.75 (s, 1H), 2.86 (s, 6H), 2.45 (s, 3H), 2.77 (s, 3H), 1.84(s, 3H). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz) δ 165.39, 154.10, 150.17, 130.43, 128.88, 120.03, 97.32, 39.36, 22.31, 20.46, 16.15.

Li(Dipnacnac) (14) A pentane (200 mL) solution of freshly recrystallized compound **8** (21.1 g, 50 mmol) was treated with a hexane solution of ^{n}BuLi (2.5 M, 20 mL, 50 mmol) at 0 °C with stirring in 30 minutes. The mixture was heated to reflux for one hour, giving a homogeneous pale yellow solution. The volume of solution was concentrated to about 20 mL during which time colorless compound crystallized. After being cooled to –30 °C, the solid was collected by filtration (19.9 g, 93%). mp 158–160 °C (decomp). ^{1}H NMR (C_6D_6, 300 MHz) δ 7.18 (m, 6H), 4.86 (s, 1H), 3.09 (sept, 4H), 1.80 (s, 6H), 1.17 (d, 12H), 1.15 (d, 12H). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz) δ 164.0, 149.2, 140.7, 123.4, 123.3, 93.01, 28.21, 24.08, 24.02, 23.35. Anal. Calcd for $LiC_{29}H_{41}N_2$: C, 82.04; H, 9.73; N, 6.60. Found: C, 82.63; H, 9.64; N, 6.65.

Li(Tolnacnac) (15) A solution of compound **7** (20 g, 72 mmol) in pentane (350 mL) was treated with a hexane solution of ^{n}BuLi (45 mL, 1.6 M, 72 mmol) with stirring at 0 °C. After the addition, the stirring was maintained for another 10 minutes at that temperature. The mixture was allowed to warm to room temperature and was stirred for another two hours. The volume of the yellow mixture was reduced to about 250 mL. Yellow compound was collected by filtration under nitrogen (18 g, 88%). mp 185–187 °C. ^{1}H NMR (C_6D_6, 300 MHz) δ 6.91 (d, 4H), 6.61 (d, 4H), 4.67 (s, 1H), 2.15 (s, 6H), 1.79 (s, 6H). ^{13}C {^{1}H} NMR (C_6D_6, 75 MHz) δ 165.6, 151.4, 131.2, 129.6, 124.3, 95.49, 23.08, 20.87. Anal. Calcd for $LiC_{19}H_{21}N_2$: C, 80.26; H, 7.44; N, 9.85. Found: C, 80.18; H, 7.15; N, 9.50.

Li(TFMnacnac) (16) To a stirred solution of freshly recrystallized compound **9** (3.49 g, 6.69 mol) in toluene was added hexane solution of ^{n}BuLi (1.6 M, 4.2 mL, 6.69 mmol) at 0°C in 30 minutes. The solution was then heated at 55°C for one hour, forming a yellow solution. The solvent was removed under vacuum to afford a yellow solid. The yellow solid was washed with pentane and then dried in vacuo. (3.02 g, 85.6%). Samples thus prepared were sufficiently pure (^{1}H NMR spectroscopy) to use in further reactivity studies. mp 157-160 °C. ^{1}H NMR (C_6D_6, 300 MHz) δ 7.54 (s, 2H), 6.99 (s, 4H), 4.61 (s, 1H), 1.49 (s, 6H). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz) δ 166.90, 155.14, 132.48, 125.73, 124.32, 116.16, 96.99, 22.95. ^{19}F NMR (C_6D_6, 288Hz) δ –63.07. Anal. Calcd for $LiC_{21}H_{13}N_2F_{12}$: C, 47.74; H, 2.48; N, 5.30. Found: C, 47.87; H, 2.53; N, 5.17.

Li(C_6F_5nacnac) (31) To a stirred solution of freshly recrystallized compound **10** (641 mg, 1.49 mmol) in pentane was added a hexane solution of ^{n}BuLi (2.5 M, 0.6 mL, 1.49 mmol) at 0 °C over 30 minutes. The solution was then warmed to room temperature and stirred overnight to give a yellow precipitate. The mixture was allowed to stand at –30 °C for 24 hours. The yellow solid was obtained after filtration. The product was washed with cold pentane and then dried in vacuo. (474 mg, 73%). Samples thus prepared were sufficiently pure (^{1}H NMR spectroscopy) to use. ^{1}H NMR (C_6D_6, 300 MHz) δ 4.60 (s, 1H), 1.51 (s, 6H). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz) δ 170.97, 143.16, 140.11, 136.54, 127.23, 100.68, 23.53. ^{19}F NMR (C_6D_6, 288Hz) δ –154.98, -163.80, -164.34.

(Bu^{t}N)Ti(Dipnacnac)Cl (17) To a stirred solution of (Bu^{t}N)TiCl$_2$(PyBu^t)$_2$ (3.69 g, 8.02 mmol) in toluene, a toluene solution of compound **14** (3.40 g, 8.02 mmol) was added dropwise. After addition, the mixture was heated at 70 °C for 16 hours. After filtration, the solvent was removed under vacuum to give a brown solid, which was washed with pentane two times to give yellow solid after drying in vacuo. (3.02 g, 66%). Samples thus prepared were sufficiently pure (^{1}H NMR spectroscopy) to use. An analytically pure, X-ray quality crystalline sample was obtained from a saturated pentane/toluene solution at –30 °C. mp 230-233 °C (decomp). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.17 (m, 6H), 5.30 (s, 1H), 3.22 (sept, 2H), 3.15 (d, 2H), 1.91 (s, 6H), 1.58 (d, 6H), 1.41 (d, 6H), 1.22 (d, 6H), 1.06 (d, 6H), 0.49 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) δ 167.83, 144.81, 142.18, 140.62, 126.51, 125.05, 123.60, 94.14, 72.46, 30.90, 28.69, 28.40, 26.47, 24.33, 24.05, 23.97, 23.92. Anal. Calcd for $TiC_{33}H_{50}N_3Cl$: C, 69.28; H, 8.81; N, 7.35. Found: C, 69.15; H, 9.04; N, 7.33.

(Bu^tN)Ti(Tolnacnac)($PyBu^t$)Cl (18) To a stirred solution of $Bu^tNTiCl_2(PyBu^t)_2$ (1.298 g, 2.82 mmol) in toluene, a toluene solution of compound **15** (0.801 g, 2.82 mmol) was added dropwise. After addition, the mixture was heated at 70°C for 16 hours. After filtration, the solvent was removed under vacuum to give a dark brown solid, which was recrystallized from saturated pentane/toluene overnight at –30 °C gave a brown crystalline compound. (0.71 g, 44.4%). mp 80-82 °C. ^1H NMR (C_6D_6, 300 MHz) δ 8.64 (br, s, 4H), 6.98 (br, s, 4H), 6.81 (m, 4H), 5.06 (s, 1H), 2.12 (s, 6H), 1.87 (s, 6H), 0.97 (s, 9H), 0.96 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 150.69, 149.51, 133.57, 129.69, 129.00, 125.56, 122.92, 120.78, 98.16, 71.56, 34.45, 31.55, 30.17, 22.66, 22.51, 20.91.

(Bu^tN)Ti(TFMnacnac)($PyBu^t$)Cl (19) To a stirred solution of (Bu^tN)$TiCl_2(PyBu^t)_2$ (200 mg, 0.435 mmol) in toluene, a toluene solution of the compound **16** (230 mg, 0.435 mmol) was added dropwise. The solution turned brown from yellow and some precipitate formed. The mixture was heated at 70 °C for 16 hours. After filtration, the solvent was removed under vacuum to give an orange solid. After washing with pentane two times, yellow solid was dried in vacuo. (185 mg, 52.6%). Samples thus prepared are sufficiently pure (^1H NMR spectroscopy) to use. An analytically pure, X-ray quality crystalline sample was obtained from a saturated pentane/toluene solution at –30 °C. mp 174-177 °C. ^1H NMR (C_6D_6, 300 MHz) δ 8.41 (br, s, 2H), 8.35 (m, 2H), 7.77 (br, s, 1H), 7.50 (br, s, 1H), 7.13 (m, 2H), 6.67 (m, 2H), 4.91 (s, 1H), 1.53 (s, 3H), 1.45 (s, 3H), 0.92 (s, 9H), 0.74 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 178.49, 163.81, 153.36, 150.32, 146.26, 132.03, 128.37, 128.05, 127.73, 126.76, 126.13, 121.67, 118.76, 100.15, 72.77, 34.91, 30.87, 29.84, 22.71, 14.26. ^{19}F NMR ($CDCl_3$, 288Hz) δ -61.83, -62.08. Anal. Calcd for $TiC_{34}H_{35}N_4F_{12}Cl$: C, 50.35; H, 4.35; N, 6.91. Found: C, 50.27; H, 4.39; N, 6.92.

(NTol)Ti(Dipnacnac)ClPy$_2$ (22) To a stirred solution of (TolN)$TiCl_2Py_3$ (127 mg, 0.28 mmol) in toluene, a toluene solution of compound **14** (119 mg, 0.28 mmol) was added dropwise. After addition, the mixture was heated at 70 °C for 16 hours. After filtration, the filtrate was concentrated under vacuum and pentane was added to a saturated the solution. Dark brown crystals formed after standing at –30 °C overnight. (121 mg. 63.0%). mp 184-187 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.46 (d, 2H), 7.11 (m, 3H), 7.03 (m, 2H), 6.77 (m, 3H), 6.70 (m, 3H), 6.44 (m, 2H), 5.35 (s, 1H), 3.76 (sept, 2H), 3.20 (sept, 2H), 2.02 (s, 3H), 1.75 (s, 6H), 1.45 (d, 6H), 1.19 (d, 6H), 1.12 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 166.95, 160.88, 150.63, 147.48, 142.94, 142.28, 136.76, 130.26, 128.55, 126.73, 124.70, 124.38, 123.90, 123.30, 98.66, 29.16, 28.05, 25.28, 24.77, 24.58, 20.98. Anal. Calcd for $TiC_{41}H_{53}N_4Cl$: C, 71.86; H, 7.80; N, 8.18. Found: C, 70.57; H, 7.87; N, 8.13.

(Bu^{t}N)Ti(TFMnacnac)$_2$ (23) To a stirred solution of (Bu^{t}N)$TiCl_2$(PyBu^t)$_2$ (146 mg, 0.317 mmol) in toluene, a toluene solution of the compound ·**16** (335 mg, 0.634 mmol) was added dropwise. The solution turned brown from yellow and some precipitate formed. The mixture was heated at 70 °C for 16 hours. After filtration, the solvent was removed under vacuum to give the yellow solid. After washing with pentane two times, yellow solid was dried in vacuo. (228 mg, 62.0%). Samples thus prepared are sufficiently pure (^1H NMR spectroscopy) to use. An analytically pure, X-ray quality crystalline sample was obtained from a saturated pentane/toluene mixed solution at –30 °C. mp 165-

167 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.56 (s, 4H), 7.17 (s, 8H), 5.012 (s, 2H), 2.00 (s, 12H), 0.52 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 164.02, 151.07, 131.96, 125.41, 121.17, 118.38, 101.74, 77.20, 31.00, 23.39. ^{19}F NMR ($CDCl_3$, 288Hz) δ. -61.45. Anal. Calcd for $TiC_{46}H_{35}N_5F_{24}$: C, 47.56; H, 3.04; N, 6.03. Found: C, 47.45; H, 2.97; N, 5.62.

(DipN)Zr(Tolnacnac)$_2$ (25) To a stirred suspension of (DipN)$ZrCl_2Py_2$ (502 g, 1.04 mmol) in toluene, a toluene solution of compound **15** (593 mg, 2.08 mmol) was added dropwise. Stirring continued overnight. After filtration, the solution was concentrated under reduced pressure. Pentane was added to the saturated solution. Yellow-orange crystals formed upon standing at –30 °C for 24 hours. (598 mg, 70%) mp 232-235 °C. ^{1}H NMR (C_6D_6, 300 MHz) δ 7.00 (d, 2H), 6.94 (d, 8H), 6.82 (d, 8H), 6.77 (m, 1H), 4.87 (s, 2H), 3.94 (sept, 2H), 2.00 (s, 12H), 1.90 (s, 12H), 1.02 (s, 6H), 1.00 (s, 6H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 164.01, 146.91, 141.66, 133.65, 129.72, 125.45, 121.57, 100.25, 27.84, 24.21, 23.70, 20.68. Anal. Calcd for $ZrC_{50}H_{59}N_5$: C, 73.12; H, 7.24; N, 8.53. Found: C, 73.22; H, 7.36; N, 8.31.

(Bu^{t}N)Ti(Dipnacnac)OTf (26) To a stirred solution of compound **17** (0.58 g, 1.0 mmol) in toluene, an ether solution of AgOTf (0.26 mg, 1.0 mmol) was added dropwise. A white precipitate was formed spontaneously. Stirring was continued for an hour, yielding to give an orange solution. The solution was filtered. The solvent was removed under vacuum, and then washed by pentane for two times. The off-white solid was dried in vacuo. (0.497 g, 71.5%). Samples thus prepared were sufficiently pure (^{1}H NMR spectroscopy) to use. An analytically pure, X-ray quality crystalline sample was obtained from a saturated petane/toluene solution at –30 °C. mp 202-205 °C (decomp). ^{1}H NMR (C_6D_6, 300 MHz) δ 7.12 (m, 6H), 4.81(s, 1H), 3.11 (sept, 2H), 3.02 (sept, 2H), 1.71 (d, 6H), 1.51 (s, 6H), 1.37 (d, 6H), 1.30 (d, 6H), 0.92 (d, 6H), 0.58 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 168.08, 145.11, 142.48, 140.29, 131.09, 127.48, 124.46, 123.98, 92.76, 74.04, 30.93, 29.71, 28.65, 25.84, 24.37, 24.15, 23.61, 22.74. ^{19}F NMR (C_6D_6, 288Hz) δ. –78.17.

(Bu^{t}N)Ti(Dipnacnac)(NMe$_2$) (27) To a stirred solution of compound **17** (275 mg, 0.48 mmol) in toluene, $LiNMe_2$ (25 mg, 0.49 mmol) was added slowly. After addition, the mixture was stirred overnight. After filtration, the solvent was removed under vacuum to afford a brown solid. An off-white crystalline compound formed through recrystallization from saturated pentane solution at –30 °C.(272 mg, 62.4%) mp >260 °C. ^1H NMR (C_6D_6, 300 MHz) δ 7.15 (m, 6H), 4.94 (s, 1H), 3.93 (s, 3H), 3.61 (sept, 2H), 2.83 (sept, 2H), 2.61 (s, 3H), 1.53 (s, 6H), 1.47 (d, 6H), 1.44 (d, 6H), 1.20 (d, 6H), 1.13 (d, 6H), 0.85 (s, 9H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 167.23, 144.91, 142.28, 141.38, 126.18, 123.86, 123.28, 96.06, 52.90, 40.11, 32.55, 28.74, 28.45, 25.62, 24.60, 24.34, 24.23, 24.20, 24.11. Anal. Calcd for $TiC_{35}H_{56}N_4$: C, 72.38; H, 9.72; N, 9.65. Found: C, 71.94; H, 9.78; N, 9.39.

(Bu^{t}N)Ti(Dipnacnac)Me (28) To a stirred solution of compound **17** (1.21 g, 2.1 mmol) in toluene, an ether solution of LiMe (1.3 mL, 1.6 M, 2.1 mmol) was added dropwise at –50 °C. After addition, the mixture was allowed to warm to room temperature. After two hours, the mixture was filtered and the filtrate was concentrated. Yellow compound was crystallized after 24 hours at –30 °C. (1.029 g, 88.2%). mp 201-203 °C (decomp) ^1H NMR (C_6D_6, 300 MHz) δ 7.15 (m, 6H), 4.86 (s, 1H), 3.36 (sept, 2H), 3.14 (sept, 2H), 1.60 (d, 6H), 1.56 (s, 6H), 1.42 (d, 6H), 1.19 (d, 6H), 1.07 (d, 6H), 0.90 (s, 9H), 0.76 (s, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 167.78, 145.29, 142.07, 141.02, 126.56, 124.05, 123.87, 93.38, 70.03, 32.40, 28.84, 28.58, 27.44, 26.48, 24.39, 24.30, 23.93, 23.86. Anal. Calcd for $TiC_{34}H_{53}N_3$: C, 74.02; H, 9.68; N, 7.62. Found: C, 73.42; H, 10.03; N, 7.47.

$(NMe_2)Ti[(2\text{-}NMe_2\text{-}C_6F_4)nacnac]F_2$ (29) To a stirred solution of $Ti(NMe_2)_4$ (1.257 g, 5.61 mmol) in pentane, was added compound **10** (2.413 g, 5.61 mmol) toluene solution dropwise at –50 °C. The solution changed from yellow to dark red spontaneously. The mixture was warmed to room temperature and stirred overnight. The volatile materials were removed under vacuum. Then product was crystallized from a saturated pentane/toluene solution at –30 °C to give dark red crystals. (3.19 g, 93.4%) mp 170-173 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.09 (s, 1H), 3.51 (s, 3H), 2.90 (s, 3H), 2.77 (s, 3H), 2.75 (s, 3H), 2.69 (m, 3H), 2.51(m, 3H), 1.66 (m, 3H), 1.48 (s, 3H) . ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 168.10, 166.74, 146.67, 145.42, 143.44, 142.10, 140.78, 138.70, 137.49, 135.41, 134.47, 132.89, 132.08, 130.67, 105.07, 50.55, 49.49, 47.59, 42.63, 34.41, 22.69, 21.84, 14.20. ^{19}F NMR ($CDCl_3$, 288Hz) δ -143.62, -146.88, -148.65, -149.39, -157.79, -159.31, -161.55, -162.10, -163.57, -167.21. Anal. Calcd for $TiC_{23}H_{25}N_5F_{10}$: C, 45.33; H, 4.14; N, 11.50. Found: C, 44.94; H, 4.04; N, 10.55.

$(2\text{-}NMe_2\text{-}C_6F_4)$nacnacH **(30)** Compound **29** (220 mg, 0.36 mmol) was dissolved in an ether/H_2O mixture, and stirred for 10 minutes in air. After separation from the ether layer, the aqueous layer was back extracted with ether two times. The combined ether fractions were dried over $MgSO_4$. The solvent was removed by rotavap to give a yellow solid. Off-white crystals were deposited from a saturated pentane solution after standing at –30 °C overnight. (155 mg, 89.6%). mp 77-80 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 11.97 (s, 1H), 5.037 (s, 1H), 2.739 (s, 12H), 1.854 (s, 6H). ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 75

MHz) δ 162.83, 146.33, 142.95, 139.48, 136.43, 131.58, 126.23, 97.68, 42.98, 20.70. ^{19}F NMR ($CDCl_3$, 288Hz) δ -149.63, -150.45, -162.59, -164.26.

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APPENDIX

X-ray Data structure collection parameters

	TMFnacnacH (**9**)	(Bu^{t}N)Ti(Dipnacnac) Cl (**17**)	(Bu^{t}N)Ti(Tolnacnac) (PyBu^t)Cl (**18**)
Empirical formula	$C_{21}H_{14}F_{12}N_2$	$C_{33}H_{50}ClN_3Ti$	$C_{32}H_{43}ClN_4Ti$
Formula weight	522.34	572.11	567.03
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P-1*	*P2(1)/n*	*P-1*
Cell			
a (Å)	8.3746(17)	10.3135(2)	12.362(3)
b (Å)	8.5077(17)	27.56620(10)	13.428(3)
c (Å)	16.900(3)	12.4202(2)	13.672(3)
α (°)	77.09(3)	90	68.59(3)
β (°)	77.50(3)	106.8840	85.90(3)
χ (°)	65.59(3)	90	73.30(3)
Volume (Å^3)	1058.2(4)	3378.90(9)	2022.3(7)
Z	2	4	3
d (calc.) (Mg/m^3)	1.639	1.125	1.624
Abs. coef. (mm^{-1})	0.172	0.356	0.459
F(000)	524	1232	1056
Crystal size (mm)	0.34 x 0.26 x 0.21	0.21 x 0.16 x 0.10	0.26 x 0.16 x 0.13
2*θ* range (°)	2.50 to 28.30	1.48 to 28.18	1.60 to 28.53
Index ranges	$-10 <= h <= 11$ $-10 <= k <= 11$ $-20 <= l <= 21$	$-13 <= h <= 13$ $-36 <= k <= 36$ $-15 <= l <= 16$	$-16 <= h <=16$ $-17 <= k <=17$ $-18 <= l <= 17$
Reflections collected	9062	29415	24432
Independent reflections	4837 [*R*(int) = 0.0412]	7965 [*R*(int) = 0.0448]	9525 [*R*(int) = 0.1269]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4837 / 0 / 321	7965 / 0 / 343	9525 / 0 / 417
GOF / F^2	0.996	1.130	0.997
Final *R* indices [$I>2\sigma(I)$]	*R*1 = 0.0569, *wR*2 = 0.1237	*R*1 = 0.0568, *wR*2 = 0.1583	*R*1 = 0.1171, *wR*2 = 0.3099
R indices (all data)	*R*1 = 0.1327, *wR*2 = 0.1486	*R*1 = 0.0859, *wR*2 = 0.1741	*R*1 = 0.2658, *wR*2 = 0.3802
Largest diff. peak and hole (e Å^{-3})	0.368 and -0.318	0.883 and –0.492	2.265 and –0.791

	$(Bu^tN)Ti(TFMnacnac)(PyBu^t)Cl$ (**19**)	$(Bu^tN)Ti(Dipnacnac)OTf$ (**26**)	$(DipN)Zr(Tolnacnac)_2$ (**25**)
Empirical formula	$C_{34}H_{35}ClF_{12}N_4Ti$	$C_{34}H_{50}F_3N_3O_3STi$	$C_{50}H_{59}N_5Zr$
Formula weight	811.01	685.73	821.24
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Tetragonal	Monoclinic
Space group	*P2(1)/c*	*P-42(1)c*	*P2(1)/n*
Cell			
a (Å)	9.3094(19)	19.429(3)	11.167(2)
b (Å)	14.324(3)	19.429(3)	19.194(4)
c (Å)	27.812(6)	19.991(4)	21.749(4)
α (°)	90	90	90
β (°)	91.32(3)	90	100.86(3)
χ (°)	90	90	90
Volume ($Å^3$)	3707.8(13)	7547(2)	4578.2(16)
Z	4	8	4
d (calc.) (Mg/m^3)	1.456	1.207	1.191
Abs. coef. (mm^{-1})	0.393	0.331	0.278
F(000)	1656	2912	1736
Crystal size (mm)	0.31 x 0.26 x 0.10	0.16 x 0.18 x 0.21	0.34 x 0.23 x
2θ range (°)	1.46 to 28.63	2.04 to 28.38	1.43 to 28.23
Index ranges			
	$-12 <= h <= 12$	$-25 <= h <= 25$	$-14 <= h <=14$
	$-19 <= k <= 18$	$-25 <= k <= 25$	$-11 <= k <=25$
	$-37 <= l <= 35$	$-25 <= l <= 26$	$-28 <= l <= 27$
Reflections collected	42794	87259	28559
Independent reflections	9047 [*R*(int) = 0.1414]	9259 [*R*(int) = 0.331]	10702 [R(int) = 0.0521]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9047 / 0 / 423	8259 / 0 / 419	10702 / 0 / 518
GOF / F^2	1.459	1.658	0.954
Final *R* indices [$I>2\sigma(I)$]	$R1 = 0.1648$, $wR2 = 0.4541$	$R1 = 0.1017$, $wR2 = 0.0693$	$R1 = 0.0424$, $wR2 = 0.0847$
R indices (all data)	$R1 = 0.2355$, $wR2 = 0.4742$	$R1 = 0.2561$, $wR2 = 0.0768$	$R1 = 0.0922$, $wR2 = 0.0983$
Largest diff. peak and hole ($e\ Å^{-3}$)	1.596 and –0.842	0.567 and –0.556	0.292 and -0.390

	(Bu^{t}N)Ti(Dipnacnac)(NMe$_2$) (**27**)	(NMe$_2$)Ti[(2-NMe$_2$-C$_6$F$_4$)nacnac]F$_2$ (**29**)
Empirical formula	$C_{35}H_{56}N_4Ti$	$C_{23}H_{25}F_{10}N_5Ti$
Formula weight	580.74	609.38
Temperature (K)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P2(1)*	*P2(1)/n*
Cell		
a (Å)	9.4329(19)	13.0595(9)
b (Å)	19.798(4)	9.4528(6)
c (Å)	10.299(2)	21.1353(14)
α (°)	90	90
β (°)	113.20(3)	99.711(2)
χ (°)	90	90
Volume (Å^3)	1768.0(6)	2571.7(3)
Z	2	4
d (calc.) (Mg/m^3)	1.091	1.574
Abs. Coef. (mm^{-1})	0.269	0.428
F(000)	632	1240
Crystal size (mm)	0.51 x 0.16 x 0.13	0.40 x 0.26 x 0.23
2θ range (°)	2.06 to 28.45	1.71 to 28.27
Index ranges	$-12 <= h <= 12$ $-25 <= k <= 25$ $-13 <= l <= 13$	$-17 <= h <= 16$ $-10 <= k <= 12$ $-27 <= l <= 21$
Reflections collected	21251	16039
Independent reflections	8311 [R(int) = 0.0959]	6081 [R(int) = 0.0998]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8311 / 1 / 371	6081 / 0 / 352
GOF / F^2	0.771	0.880
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0703$, $wR2 = 0.1941$	$R1 = 0.0549$, $wR2 = 0.1288$
R indices (all data)	$R1 = 0.1599$, $wR2 = 0.2598$	$R1 = 0.1548$, $wR2 = 0.1536$
Largest diff. peak and hole (e Å^{-3})	0.977 and -0.316	0.536 and -0.400