Acid−Base Adducts of Catalytically Active Titanium(IV) Lewis Acids

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A series of monomeric Lewis acid−base adducts of the Diels−Alder catalyst Ti(O-2,6-$Me_2C_6H_3)_2Cl_2$ have been synthesized from bidentate diphosphines and diamines, Ti(O-2,6-$Me_2C_6H_3)_2Cl_2L_2$ (L_2 = dmpe, depe, dpeda, and dmeda). X-ray crystal structures of Ti(O-2,6-$Me_2C_6H_3)_2Cl_2$(dmpe) and Ti(O-2,6-$Me_2C_6H_3)_2Cl_2$(dpeda) establish a distorted octahedral coordination environment with *trans*-chloride ligands. Bidentate ligands that were also studied but did not form isolable complexes with the Ti(IV) Lewis acid include dppe, tmeda, and binam. Through pairwise exchange reactions a qualitative ranking of relative bidentate ligand binding strengths to the Lewis acid were obtained (dmeda ≥ dpeda > dmpe ≥ depe > tmeda > binam > dppe). The ranking is readily rationalized using hard−soft electronic arguments except for tmeda, which requires that unfavorable steric interactions be invoked.

Introduction

The ability of titanium(IV) Lewis acids to act as efficient catalysts for various organic transformations has led to considerable interest in exploring their reactivity, especially in the context of asymmetric catalysis.[1] We have been particularly interested in titanium(IV) bisaryloxide complexes as Lewis acid catalysts for processes such as the Diels−Alder reaction.[2] Simple titanium phenoxy (e.g., $[(PhO)_2TiCl_2]_2$)[3] and binaphtholate[4] complexes, however, are aggregated in solution and in the solid state, a phenomenon that can contribute to reduced catalytic activity, solubility, and moreover lead to complex reaction dynamics (e.g. nonlinear effects in asymmetric catalysis).[5,6] Lappert, Rothwell, and others[7,8] have utilized sterically demanding aryloxide ligands to favor monomeric complexes, and resultant well-behaved reactivity. With the most bulky ligands, however, the high steric congestion inhibits the binding of simple Lewis bases such as pyridine[7b] and restricts their utility as Lewis acid catalysts. Thus, one would like monomeric Lewis acids with high levels of steric and electronic unsaturation; however, the above observations point to a delicate balance between maintaining the monomeric state and promoting rich coordination chemistry.

It is known that Lewis bases (e.g., tmeda, dmpe) convert titanium aryloxides that are otherwise aggregated in their free-base forms into monomeric Lewis acid−base complexes.[9] Building on these observations we wish to incorporate polymerizable versions of monomeric Lewis acid−base complexes into highly cross-linked organic polymer networks to yield site-isolated complexes.[2,10] Subsequent removal of the coordinated Lewis base should generate monomeric Lewis acids that would otherwise be inaccessible (i.e., they are aggregated) in solution. Moreover, using chiral bidentate bases and the concept of molecular imprinting,[11] we additionally aim to associate with these site-isolated titanium catalysts, chiral cavities capable of controlling the enantioselectivity of transformations mediated by the Lewis acid. To this end we chose to first investigate the acid−base chemistry of Ti(O-2,6-$Me_2C_6H_3)_2Cl_2$, (**1**) since (1) it is a well-behaved Diels−Alder catalyst;[12] (2) its aggregation state was, until recently[8] unknown[7b] and so **1** might be amenable to the above-mentioned strategy; and (3) the 2,6-dimethyl substituents provide a convenient spectroscopic handle for adduct characterization. We have examined the Lewis acid character of **1** with chiral, and potentially chiral bidentate Lewis bases to systematically document the relative binding affinities of different structure types to titanium(IV) Lewis acids. Such studies are scarce,[13] despite the fact that these data shed light

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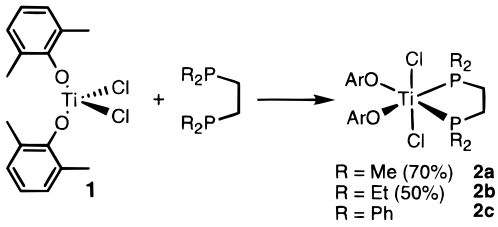
on the fundamentals of Lewis acid activation of 2-point binding organic substrates.[14]

Results and Discussion

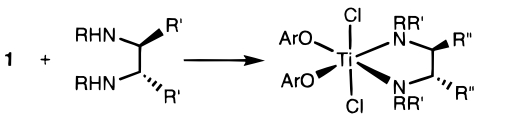
Synthesis of Coordination Complexes. The Lewis acid Ti(O-2,6-$Me_2C_6H_3)_2Cl_2$ (**1**), prepared by the method of Lappert,[7b] was treated with stoichiometric quantities of several nitrogen and phosphorus containing bidentate Lewis bases. These reactions have precedence as $(Ti(OPh)_2Cl_2)_2$ has been previously shown to react with bisdimethylphosphinoethane (dmpe) and tmeda to form stable, presumably monomeric adducts.[9,15] Similarly, when **1** was treated with dmpe in CD_2Cl_2, rapid formation of **2a** was observed as characterized by diagnostic downfield shifts in the dmpe ^{31}P (−47.8 → −9.6 ppm) and aryloxide ^1H NMR methyl resonances (2.25 → 2.48 ppm) (eq 1). In situ



(1)

monitoring indicated that although the desired 1:1 adduct was the major product, a small amount (∼10%) of a 1:2 (Ti/dmpe) complex (^{31}P NMR: 5.0, 9.9 ppm) was also formed.[16] When preparatory reactions are carried out in toluene, however, the impurity conveniently precipitates from solution to yield the clean 1:1 adduct after filtration. Recrystallization from toluene:pentane yields a highly crystalline orange compound that is monomeric in the solid state by single-crystal X-ray diffraction (vide infra). Heating pure samples of **2a** in toluene-d_8 leads to a gradual broadening of the ^{31}P NMR which upon recooling generates traces (<10%) of free dmpe and the 1:2 adduct. The fate of the necessary titanium byproduct is unknown. These observations are suggestive of dmpe "on/off" dynamics.

Similar adducts could be obtained with 1,2-bisdiethylphosphinoethane (depe) (**2b**, eq 1), (1*S*,2*S*)-diphenylethylenediamine (dpeda), and *N*,*N*′-dimethylethylenediamine (dmeda) (**3a** and **3b**, eq 2).[17] In the case of the diamines, however, the crude



(2)

(14) Footnote 1b, Chapter 9.

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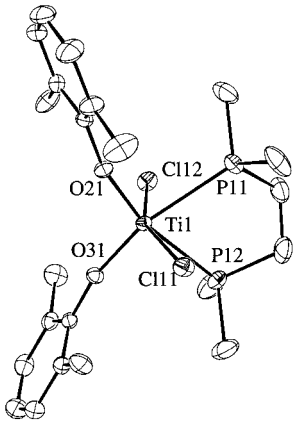


Figure 1. ORTEP diagram of **2a**.

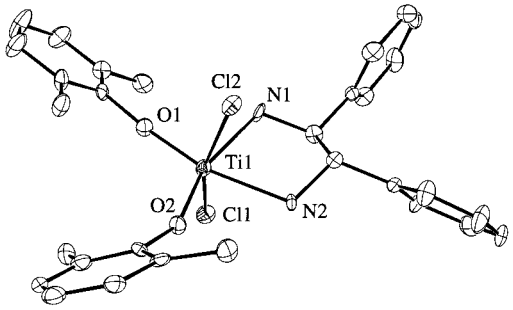
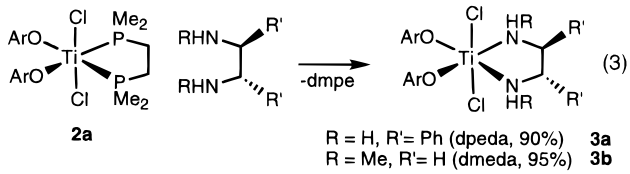


Figure 2. ORTEP diagram of **3a**.

material required fractional crystallization to provide material of high purity; the low yields reflect this. Each of these reactions yielded crystalline products that were well behaved. Unlike **2a**, the diamine adduct **3a** maintained sharp resonances in the ^1H NMR up to 100 °C with no sign of decomposition.

In contrast to the above ligands, attempts to synthesize adducts of **1** with bisdiphenylphosphinoethane (dppe), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), and 1,1′-binaphthyl-2,2′-diamine (binam) led to products that were dynamic in the NMR at room temperature, and could not be satisfactorily purified by selective recrystallization. Attempts to isolate these complexes invariably led to additional decomposition. These adducts, however, could be generated in situ, and provided that they were not concentrated, they led to solutions containing minimal impurities.

The diamine complexes **3a** and **3b** could also be cleanly prepared by selective displacement of dmpe from **2a** (eq 3).



(3)

Although direct reaction of these ligands with **1** led to traces of byproducts that were difficult to separate from the desired adduct, the dmpe displacement protocol was clean and quantitative (^1H and ^{31}P NMR). This route was therefore chosen as the more convenient method of synthesizing **3a** and **3b**.

X-ray analysis. To structurally characterize these acid−base adducts, single-crystal X-ray analyses were performed on **2a** and **3a**. Their respective ORTEP representations are shown in Figures 1 and 2; data acquisition parameters are listed in Table 1. Both complexes adopt a distorted octahedral geometry with

Table 1. Crystallographic Data and Collection Parameters for **2a** and **3a**

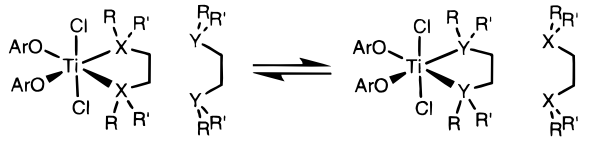
	2a	**3a**
formula	$TiP_2Cl_2C_{22}H_{34}O_2$	$TiCl_2C_{30}H_{30}N_2O_2$
fw	511.26	615.45
space group	$P4_32_12$	$P2_1$
a, Å	16.3617(10)	14.3132(17)
b, Å	−	13.7468(16)
c, Å	38.8262(23)	16.1350(19)
β, deg	−	99.158(1)
V, Å^3	10394.0(9)	3134.3(6)
Z	16	4
T, °C	−100	−100
D_c, g/cm^3	1.307	1.304
λ, Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	0.67	0.48
R indices (all data)	$R_f{}^a = 0.039$	0.058
	$R_w{}^b = 0.038$	0.068
R indices (sig. rflcns)	$R_F = 0.033$	0.045
	$R_w = 0.038$	0.055
GoF	2.22	2.12

[a] $R_F = \sum(F_o - F_c)/\sum F_o$. [b] $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$, GoF = $[\sum w(F_o - F_c)^2/(n - p)]^{1/2}$, where n = number of reflections and p = number of parameters.

trans chloride ligands. From a *trans*-effect perspective, the latter enables the strong aryloxide ligands to be trans to the neutral phosphine and amine ligands, a trend that is consistently observed in a variety of titanium(IV) coordination complexes.[18−20] The metrical parameters in **2a** and **3a** are unexceptional as the Ti−O, Ti−Cl, and C−O−Ti bond lengths and angles are similar to previously reported bisaryloxide titanium(IV) dichloride complexes.[7a,c,e,18] The recent structural characterization of **1** by Rothwell,[8] however, allows a more careful analysis of the effects of a bidentate ligand on the metrical parameters of this Lewis acid. Not surprisingly, addition of two donors to the coordination sphere increases the Ti−O and Ti−Cl bond lengths, on the average by 0.075 and 0.15 Å, respectively (Table 2). Consistent with a more octahedral-like geometry in the adducts is the decrease in the Cl−Ti−O bond angles from ∼109 in **1** to ∼98° in **2a** and 92−99° in **3a**. On the other hand the O−Ti−O bond angles only decrease 3−4° upon transitioning from tetrahedral to octahedral (Table 2).

The Ti−N[17,21] and Ti−P[22] bond lengths in **2a** and **3a** are also normal, with the average Ti−P (2.62 Å), not surprisingly, being longer than the average Ti−N (2.26 Å) bond lengths, reflecting the larger van der Waals radius of phosphorus. It is interesting to note that in **2a**, the aryloxides adopt a conformation that minimizes the steric interactions between the aryl and phosphorus methyl groups. This orientation is best described by the angle relating the orientation of the aryl and O−Ti−O planes (75.9 and 91.4°, respectively). Two independent conformations are observed in the asymmetric unit of **3a**, the one shown in Figure 2 with the aryl rings rotated 52.6 and 31.8° clockwise, and a second isomer (not shown) with the aryloxides rotated 52.3 and 38.6° counterclockwise. The nearly perpendicular arrangement of aryloxides in the former case, however, introduces unfavorable interactions between the aryl methyl and the axial chloride ligands, perhaps helping to distort the chlorides away from the strongest ligands (Cl−Ti−Cl = 154.69(4)°). Similar Cl−Ti−Cl angle distortions are observed in the X-ray crystal structures of **3a** (161.57(8)°), **1**·THF_2 (165.0(2)),[18] Ti(salen)Cl_2 (168.7(1)°),[23] Ti(TADDOL)Cl_2dppe (157.2(1)°),[13b] and Ti(TADDOL)Cl_2(3-*E*-3-cinnamoyl-1,3-oxazolidin-2-one) (164.3°).[19a] On the other hand, electronic structure calculations predict an axial bond compression to the weaker neutral ligands, and so the origin of the effect may in fact be purely electronic.[24,25]

Competitive Binding Experiments. NMR experiments were carried out between the Lewis acid **1** and pairs of bidentate bases to assess their relative binding affinities (e.g. eq 4, Table 3).



(4)

Initial studies focused on the competition established by adding various ligands to **2a**, and determining relative binding constants by integrating the amounts of free and bound ligand (^{1}H and/or ^{31}P NMR). Binding kinetics were rapid as equilibrium was reached in <5 min, and remained constant over at least 48 h. In the case of dpeda, dmeda, dmpe, and depe, on/off rates were also slower than the NMR time scale as sharp resonances were observed for the free and bound ligand.

From these experiments, two classes of bidentate ligands emerged, those that quantitatively displaced dmpe (dmeda, dpeda) and those that did not. In the latter cases, 10 equiv. of the addend ligands were used to establish an upper limit of the equilibrium constant at 10^{-4} (see Experimental Section). Similarly, the competition set up by **2a**, 9 equiv of dmpe, and 1 equiv of the stronger binding bases yielded minimum equilibrium constants of 10^4. The relative binding strengths of the sets of ligands that were stronger and weaker than dmpe were established by a series of pairwise competition experiments with **1**. Although competition experiments with the weaker ligands gave somewhat broadened NMR spectra and traces of impurities, a reasonable qualitative analysis could be obtained from spectrum appearance. For example, in the competition between tmeda and binam, the ^{1}H NMR spectrum of the aromatic region contained peaks solely due to free binam, whereas for binam vs dppe, the binam aromatic resonances corresponded solely to **3d**. *In toto*, these experiments establish a semiquantitative range of binding strengths for Lewis acid **1**.

dmeda ≥ **dpeda** > **dmpe** ≥ **depe** > **tmeda** > **binam** > **dppe**

Basicity and hard−soft arguments account for most of the orderings in this series with the exception of tmeda. The fact

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**,[a] **2a**, and **3a**

	1[a]	**2a**[b]	**3a**[b]
Ti−O	1.734(7), 1.736(8)	1.8143(19), 1.8255(20) 1.8165(20), 1.81315(19)	1.804(4), 1.787(4) 1.788(4), 1.802(4)
Ti−Cl	2.192(4), 2.211(4)	2.3524(8), 2.3644(8) 2.3512(8), 2.3605(9)	2.3524(18), 2.3960(18) 2.3536(17), 2.3960(17)
O−Ti−O	109.1(4)	105.16(9) 104.10(9)	106.07(21) 104.64(21)
Cl−Ti−Cl	111.0(2)	154.69(4) 154.34(4)	161.57(8) 162.02(9)
Ti−O−C	167.3, 168.9	165.28(18), 166.76(18) 157.80(17), 168.12(19)	173.5(4), 152.6(4) 174.6(4), 152.9(4)
Cl−Ti−O	∼109	∼98	92−99

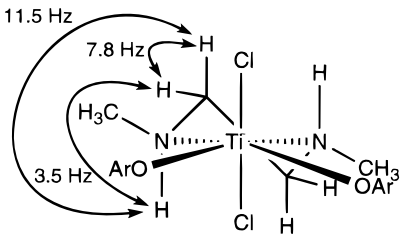
[a] Reference 8. [b] Two independent molecules per asymmetric unit.

Table 3. Ligand−Ligand Competition for Lewis Acid **1**

complex	ligand	K_{eq}
2a	dmeda[a]	$>10^4$
	dpeda[a]	$>10^4$
	depe[b]	0.1
	tmeda[c]	2×10^{-3}
	binam[c]	$\sim 10^{-4}$
	dppe[c]	$<10^{-4}$
3a	dmeda	1.5
2b	tmeda	0.01
3c[d]	binam	favors tmeda[e]
3d[d]	dppe	favors binam[e]

[a] 10:1 dmpe/ligand. [b] 5:1 depe/dmpe. [c] 10:1 ligand/dmpe. [d] Generated in situ. [e] Qualitative due to broadened NMR line widths (vide infra).

Scheme 1



that this most basic ligand does not form an isolable complex with **1**, and does not effectively compete with the isostructural (but soft) dmpe, suggests that factors other than electronics are operative.

The most reasonable interpretation for this observation is that the shortened Ti−N and N−Me bond lengths in the tmeda adduct leads to steric congestion that destabilizes it relative to the isostructural dmpe complex. Consistent with this argument is the X-ray structure of $TiCl_4$(*N*,*N*′*N*′′-Me_3-ethylenediamine)[17] wherein the Ti−NHMe bond length (2.227(4) Å) is shorter than the Ti−NMe_2 bond length (2.316(4) Å). These bond length variations go counter to simple basicity arguments. Unlike tmeda, however, dmeda forms the strongest adduct of any of the bidentate ligands studied. In this case, orienting the N−Me substituents into pseudoequatorial positions must enable the aryloxide methyl groups to rotate away from the axial chlorides toward the relatively unhindered pseudoaxial hydrogens. The dmeda adduct can thus take advantage of a slightly enhanced basicity, without paying the steric price of having pseudoaxial N−Me substituents. Securing the argument of pseudoequatorial positioning of the N−Me group are the relative coupling constants obtained between the diastereotopic backbone CHs and the single NH resonance in **3b** (Scheme 1); the large coupling between the NH and backbone CH (11.5 Hz) suggesting an axial NH.

Summary

The synthesis and characterization of several acid−base adducts of the Diels−Alder catalyst **1** have been realized. X-ray crystallography on the dmpe and dpeda adduct point to a series of structures wherein the neutral bidentate ligands occupy positions trans to the aryloxide ligands, and are thus consistent with proposed transition structures for the (TADDOL)$TiCl_2$-catalyzed Diels−Alder and 1,3-dipolar cycloaddition of 2-point binding dieneophiles.[26] Relative binding affinities to the Lewis acid can generally be explained using electronic hard−soft acid concepts, with the exception of bulky ligands such as tmeda.

Experimental Section

Reagents and General Techniques. $Ti(O\text{-}2,6\text{-}Me_2C_6H_3)_2Cl_2$[7b] and (*S*,*S*)-1,2-diphenylethylenediamine[27] were prepared according to literature procedures. Dmeda and tmeda (Aldrich) were freshly distilled from CaH_2 prior to use. All other compounds were used as received. Solvents were dried over activated alumina,[28] stored under argon and degassed by freeze−thaw techniques prior to use. Deuterated solvents were dried over and vacuum transferred from Na/benzophenone-ketyl (C_6D_6) or CaH_2 (CD_2Cl_2) and were degassed by freeze−pump−thaw techniques prior to use. All compounds were synthesized under N_2 using standard Schlenk-techniques and were handled in an MBraun Lab-Master 100 glovebox.

^1H, ^{13}C, and ^{31}P NMR were recorded in C_6D_6 or CD_2Cl_2 at ambient temperature on either a Bruker AMX300 or Bruker Avance 400 spectrometer. Optical rotation measurements were taken on a Jasco DIP-1000 digital polarimeter. Elemental analyses were performed by E+R Microanalytical Laboratories (Parsippany, NJ).

Synthesis of $Ti(OAr)_2Cl_2$(dmpe) (2a). A 50-mL flame-dried Schlenk flask was charged with $Ti(OAr)_2Cl_2$ (1.00 g, 2.77 mmol) and toluene (20 mL) in the glovebox. A separate 25-mL Schlenk flask was similarly charged with dmpe (0.416 g, 2.77 mmol) and toluene (10 mL). Both flasks were connected to a Schlenk line and the dmpe solution was added dropwise via cannula to the precooled (0 °C) Ti-$(OAr)_2Cl_2$ suspension. The pale red suspension clears to a dark red solution from which a small amount of orange solid precipitated. The reaction solution was stirred an additional 1 h at room temperature after which time the supernatant was separated from the precipitate via cannula filtration. The solution was pumped to dryness, and the resulting solid recrystallized from a 1:1 mixture of toluene/pentane to give 0.991 g of a bright orange solid (70% yield). ^1H NMR (300 MHz, C_6D_6) δ 6.88 (d, J_{HH} = 7.5 Hz, 4H, ArH), 6.72 (t, J_{HH} = 7.5 Hz, 2H, ArH), 2.66 (s, 12H, Ar−CH_3), 1.19 (d, J_{PH} = 15.2 Hz, 4H, PCH_2), 1.03 (m, 3 line pattern, 12H, PCH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2-

(26) See ref 21a, and also: (a) Seebach, D.; Dahinden, R.; Marti, R. E.; Beck, A. K.; Plattner, D. A.; Kühnle, F. N. M. *J. Org. Chem.* **1995**, *60*, 1788−1799. (b) Haase, C.; Sarko, C. R.; DiMare, M. *J. Org. Chem.* **1995**, *60*, 1777−1787.
(27) Pikul, S.; Corey, E. J. *Org. Synth.* **1992**, *71*, 22−28.
(28) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. *Organometallics* **1996**, *15*, 1518−1520.

Cl_2) δ 165.9, 129.1, 128.2, 121.9, 25.9 (t, J_{CP} = 15.4 Hz), 18.4, 11.7 (t, J_{CP} = 6.7 Hz); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6) δ 11.34 (s); Anal. Calcd. for $C_{22}H_{34}Cl_2O_2P_2Ti$: C, 51.68; H, 6.70. Found: C 51.59; H 6.72.

Synthesis of Ti(OAr)$_2$Cl$_2$(depe) (2b). To a 50-mL flame-dried Schlenk flask in a drybox was added $Ti(OAr)_2Cl_2$ (1.05 g, 2.77 mmol) and toluene (20 mL). To a separate 25 mL Schlenk flask in a drybox was added bisdiethylphosphinoethane (0.601 g, 2.77 mmol) and toluene (10 mL). Both flasks were connected to a Schlenk line and the depe solution was added dropwise to the precooled (0 °C) $Ti(OAr)_2Cl_2$ suspension via cannula. The pale red suspension becomes a dark red homogeneous solution. Upon removal of toluene in vacuo a red-orange solid began to precipitate from solution. After approximately 15 mL of toluene was removed, the supernatant was separated from the precipitate via cannula filtration. The filtrate was pumped to dryness, and the resulting solid recrystallized from a 1:1 mixture of toluene/pentane to give 0.745 g of a dark red solid (50% yield). ^1H NMR (300 MHz, C_6D_6) δ 6.87 (d, 4H, J_{HH} = 7.5 Hz, ArH), 6.70 (d, 1H, J_{HH} = 7.5 Hz, ArH), 6.63 (d, 1H, J_{HH} = 7.5 Hz, ArH), 2.72 (s, 12H, $ArCH_3$), 1.83 (m, 4H, PCH_2CH_3), 1.70 (m, 4H, PCH_2CH3), 1.27 (d, 4H, J_{PH} = 12.3 Hz, PCH_2CH_2), 0.79 (t, 6H, J_{HH} = 5.8 Hz, PCH_2CH_3), 0.71 (t, 6H, J_{HH} = 6.7 Hz, PCH_2CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 165.9, 129.1, 128.2, 121.9, 25.9 (t, J_{CP} = 13.5 Hz), 18.4, 11.7 (t, J_{CP} = 5.8 Hz); $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6) δ 11.34 (s); Anal. Calcd. for $C_{26}H_{42}Cl_2O_2P_2Ti$: C, 55.04; H, 7.46. Found: C, 55.23; H, 7.65.

Synthesis of Ti(OAr)$_2$Cl$_2$((*S*,*S*)-dpeda) (3a). To a flame-dried 25 mL Schlenk flask in a drybox was added $Ti(OAr)_2Cl_2$(dmpe) (500 mg, 0.98 mmol) and toluene (10 mL). To this vigorously stirred solution was added dropwise a solution of (*S*,*S*)-diphenylethylenediamine (211 mg, 0.98 mmol) and toluene (2 mL) and an immediate color change from orange-red to dark red was observed. The flask was connected to a Schlenk line and allowed to react for an additional 30 min. The solvent was then reduced to ~2 mL in vacuo and was then layered with 5 mL of pentane via syringe and allowed to stand for 1 h, after which the solution was cooled to 0° C. Dark red crystals immediately precipitated and the supernatant was removed via cannula filtration. Crude product was recrystallized from 1:1 toluene:pentane to give 0.509 g of dark red crystals (90% yield). ^1H NMR (300 MHz, CD_2Cl_2) δ 6.86 (d, 4H, J_{HH} = 7.5 Hz, OArH) 6.81−6.69 (m, 12H, OArH, $H_2NCHArH$), 4.61 (m, 2H, three-line pattern, H_2NCH), 3.82 (t, 2H, J_{HH} = 10.5 Hz, HHN), 3.30 (dd, 2H, J_{HH} = 10.5 Hz, J_{HH} = 1.5 Hz, HHN), 2.60 (s, 12H, $OArCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 166.1, 139.3, 129.5, 129.2, 129.0, 128.6, 127.5, 122.9, 63.7, 17.9; $[\alpha]_D^{25.4} = -31.3$ (*c* 0.55, CH_2Cl_2); Anal. Calcd. for $C_{30}H_{34}Cl_2N_2O_2Ti \cdot 1/2(C_7H_8)$: C, 64.95; H, 6.18; N, 4.52. Found: C, 64.79; H, 5.91; N, 4.35.

Synthesis of Ti(OAr)$_2$Cl$_2$(dmeda) (3b). To a flame-dried 25 mL Schlenk flask in a drybox was added a solution of $Ti(OAr)_2Cl_2$(dmpe) (500 mg, 0.98 mmol) and toluene (10 mL). To this vigorously stirred solution was added dropwise a solution of *N*,*N*′-dimethylethylenediamine (211 mg, 0.98 mmol) and toluene (2 mL) and an immediate color change from orange-red to dark red was observed. The flask was then placed on a Schlenk line and allowed to react for an additional 30 min. The solvent was then reduced to ~2 mL in vacuo and then layered with 5 mL of pentane via syringe, allowed to stand for 1 h, and then cooled to 0 °C. The dark red crystals were isolated via cannula filtration and recrystallized from 1:1 toluene/pentane to give 0.418 g of dark red crystals (95% yield). ^1H NMR (400 MHz, CD_2Cl_2) δ 6.90 (d, 4H, J_{HH} = 7.5 Hz, ArH), 6.71 (t, 2H, J_{HH} = 7.5 Hz, ArH), 4.07 (m, br, 2H, NH), 3.20 (dd, 2H, J_{HH} = 11.5 Hz, 7.8 Hz, $NCHH$), 3.08 (dd, 2H, J_{HH} = 7.8 Hz, 3.5 Hz, $NCHH$), 2.77 (d, 6H, J_{HH} = 6.0 Hz NCH_3), 2.39 (s, 12H, $ArCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 166.0, 129.5, 128.6, 122.6, 52.0, 39.3, 17.9; Anal. Calcd. for $C_{20}H_{28}N_2O_2Ti$: C, 53.47; H 6.73, N 6.24. Found: C 53.39, H 6.95, N 6.03

Characterization of 2c, 3c, and 3d. General procedure for characterizing nonisolable complexes. To a 2 mL vial was added 15 mg (41.5 μmol) of **1** in of CD_2Cl_2 (0.5 mL) resulting in a light red solution. To this solution was added tmeda (4.3 mg, 41.5 μmol) in CD_2Cl_2 (0.5 mL). **3c**: ^1H NMR (400 MHz, CD_2Cl_2) δ 6.86 (d, 4H, J_{HH} = 7.5 Hz, ArH), 6.72 (d, 1H, J_{HH} = 7.5 Hz, ArH), 6.68 (d, 1H, J_{HH} = 7.5 Hz, ArH), 2.92 (s, br, 12H, NCH_3), 2.85 (s, br, 4H, NCH_2-CH_2), 2.45 (s, 12H, $ArCH_3$); **3d**: ^1H NMR (400 MHz, CD_2Cl_2) δ 7.99 (d, 2H, J_{HH} = 8.7 Hz, Ar−H), 7.94 (d, 2H, J_{HH} = 8.1 Hz, ArH), 7.45−7.39 (m, 4H, ArH), 7.25 (t, 2H, J_{HH} = 8.1 Hz, ArH), 7.06 (d, 2H, J_{HH} = 8.7 Hz, ArH), 6.95 (d, 4H, J_{HH} = 7.5 Hz, OAr), 6.82 (d, 2H, J_{HH} = 7.5 Hz, OAr), 6.80 (d, 2H, J_{HH} = 7.5 Hz, OAr,), 5.39 (s, br, 4H, NH_2), 2.47 (s, 12H, $OArCH_3$); **2c**: ^1H NMR (400 MHz, CD_2Cl_2) δ 7.48−7.38 (s, br, 20 H, PPh), 6.73 (d, *J* = 7.5 Hz, 4H, OAr), 6.69 (t, *J* = 7.5 Hz, 2H, OAr), 2.28 (s, 4H, PCH_2), 2.23 (s, 12H, $ArCH_3$); $^{31}P\{^1H\}$ NMR (121.471 MHz) δ −9.69 (s, br).

Competition Experiments. All competition experiments were carried out in NMR tubes with CD_2Cl_2 as the solvent. In the case of competition experiments with **2a**, a solution (0.5 mL CD_2Cl_2) of the bidentate ligand was added dropwise to a solution of **2a** (0.5 mL CD_2Cl_2). For ligands binding weaker than dmpe, 10 equivalents of the ligand were used, and the ratio of released dmpe and bound dmpe obtained from ^{31}P NMR (relaxation delay = 10 s), were used to calculate the equilibrium constant (K_{eq}) according to the formula:

$$K_{eq} = [\text{dmpe}]^2/[\text{Ti-dmpe}](x[\text{dmpe}_{\text{total}}] - [\text{dmpe}])$$

where x represents the ratio of ligand to $\text{dmpe}_{\text{total}}$ and $[\text{dmpe}_{\text{total}}] = [\text{dmpe}] + [\text{Ti-dmpe}]$ (x = 10 for tmeda, binam, and dppe, and 5 for depe). A lower limit of K_{eq} (10^{-4}) for the weak binders was established by assuming a 2% detection limit for free dmpe.

For stronger binding ligands (dmeda and dpeda), 1 equiv of **2a**, 9 equiv of dmpe, and 1 equiv of the ligand were used to establish a net competition between 10 equiv of dmpe and 1 equiv of the addend (i.e., x = 0.1). The equilibrium constant was then calculated according to the equation:

$$K_{eq} = [\text{dmpe}](x[\text{dmpe}_{\text{total}}] - [\text{Ti-dmpe}])/[\text{Ti-dmpe}]^2$$

For these ligands we set an upper limit to K_{eq} at 10^4 by assuming a 2% detection limit for **2a** in the ^{31}P NMR. Similarly, the competition experiment between **3a** and dmeda was established by adding a 1:1 ratio of the ligands to **1**, and measuring relative adduct concentrations by ^1H NMR (relaxation delay = 10 s). For the weakest ligands a qualitative analysis was carried out by inspection of the ^1H NMR. For example, for tmeda vs binam, ^1H NMR signals were diagnostic of the bound tmeda complex and free binam, indicating that tmeda was a stronger binder than binam.

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Supporting Information Available: Tables of metrical parameters and fully labeled ORTEP diagrams of **2a** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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