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Structurally Well Characterized Binaphtholate Titanium Chloride Lewis Acids: Evidence for Active Dinuclear Catalysts in a Diels–Alder Process

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Well characterized Ti$_2$(diolate)$_2$Cl$_4$ (diolate = 3,3′-dimethyl-1,1′-bi-2-naphtholate (Me$_2$BINO), 10,10′-bi-9-phenanthrolate (BIPHENO), or 5,5′,6,6′,7,7′,8,8′-octahydrobinaphtholate (H$_8$BINO)) complexes have been isolated as red-orange crystalline solids from diethyl ether, toluene, or methylene chloride, respectively. An X-ray crystal structure was performed on the Ti$_2$(Me$_2$BINO)$_2$Cl$_4$ complex, which was found to be a dimer supported by unidentate bridging naphtholate units. Solution molecular weight studies confirmed that the complexes remain dimeric in solution. Homochiral (R^*,R^*)-Ti$_2$(Me$_2$BINO)$_2$Cl$_4$ and (R^*,R^*)-Ti$_2$(H$_8$BINO)$_2$Cl$_4$ are the only spectroscopically observable products from syntheses beginning with either optically pure or racemic ligands. The Me$_2$BINO and BIPHENO Ti$_2$(diolate)$_2$Cl$_4$ complexes establish equilibria with Ti$_2$(diolate)Cl$_6$ in the presence of added TiCl$_4$, although the formation of these monodiolate complexes is less thermodynamically favorable than equilibria leading to related Ti$_2$(diolate)(O-*i*-Pr)$_6$ species. Ti$_2$(Me$_2$BINO)$_2$Cl$_4$ and Ti$_2$(H$_8$BINO)$_2$Cl$_4$ catalyze a Diels–Alder reaction between cyclopentadiene and methyl acrylate. The reactions are rigorously first order in titanium, diene, and dienophile, indicating that the rate determining step for the reaction is the cycloaddition process (Ti$_2$(Me$_2$BINO)$_2$Cl$_4$: $\Delta H^{\ddagger} = 7.1 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -58 \pm 2$ eu). Spectroscopic studies show that the binding constant for the dienophile to the titanium catalysts is very small. The catalyst shows no element of non first order rate dependence, demonstrating that the titanium dimer does not homolytically cleave into mononuclear titanium active sites. The percent enantiomeric excess (ee) of the product prepared with (R,R)-Ti$_2$(Me$_2$BINO)$_2$Cl$_4$ is dependent on the initial dienophile to titanium ratio, suggesting that the catalyst has two similar spacially proximal active sites. This observation favors a dinuclear complex as the catalytically active species. Structural data for Ti$_2$(Me$_2$BINO)$_2$Cl$_4$ at 294 K: $a = 15.307(3)$ Å, $b = 12.007(1)$ Å, $c = 21.948(2)$ Å, $\beta = 99.13(1)°$, $V = 3983(1)$ Å^3, $Z = 4$, $D_{\mathrm{calc}} = 1.438$ g cm^{-3}, space group $P2_1/n$ (No. 14), $R(F) = 0.036$, $R_w(F) = 0.049$ for 4159 unique intensities ($I > 3.00\sigma(I)$).

Introduction

Catalysts derived from high oxidation state early transition metal species have recently become a very important and diverse class of catalyst systems.[1–12] The explosion of asymmetric methodology involving chiral titanates is built upon the initial success achieved in catalytic C–O and C–C bond formation facilitated by early transition metals.[2,12] Beyond the initial successes achieved with the Sharpless–Katsuki asymmetric epoxidation catalyst,[2] other chiral group 4 catalysts have been applied in asymmetric alkylation,[3] aldol condensation,[4] Diels–Alder,[5–7] and glyoxylate ene[8] and related electrocyclic reactions.[9] The recognition that this field represents a rich and, in reality, little explored vein of catalytic chemistry is responsible for the many new reports of synthetic reagents, catalysts and reaction protocols that appear on a monthly basis. It is clear that for many organic transformations the Lewis acidity of high oxidation state early transition metals is key to their wealth of catalytic activity. This high Lewis acidity coupled with designed coordinative unsaturation frequently obviates the need for ligand labilization, resulting in tremendous catalytic activity. Such reactivity can come at the price of selectivity, unless significantly sterically encumbering ligands are introduced into the metal coordination sphere. This strategy has spawned a very successful series of stereo- and enantiospecific catalysts from "piano stool" and bent metallocene templates.[13,14] In combination with conformationally dissymmetric sterically demanding substituents, the Cp-dominated molecular topology clearly defines the stereochemical constraints of the reaction coordinate.[15–17]

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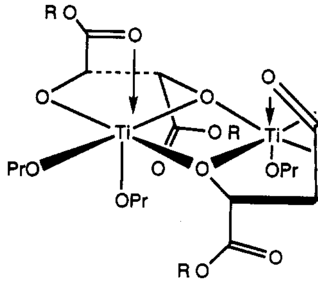
Well-defined catalysts containing chelating diolate ligands are one conceptual step removed from the less fluxional mono- and bis-Cp substituted catalysts. The Sharpless–Katsuki Ti_2(dialkyl tartrate)$_2$(O-*i*-Pr)$_4$ (**1**) catalyst is tolerant of an extremely broad range of allylic alcohols in asymmetric epoxidation processes.[2] The price of this greater conformational flexibility and arguably greater substrate compatibility is a degree of controversy concerning the identity of the active catalyst. Unlike Sharpless, whose structural and mechanistic studies all suggest an active dinuclear epoxidation catalyst, some researchers favor the intermediacy of a more open dinuclear structure (**2**),[18,19] while others favor a heterolytically cleaved four-coordinate cationic active site (**3**).[20]



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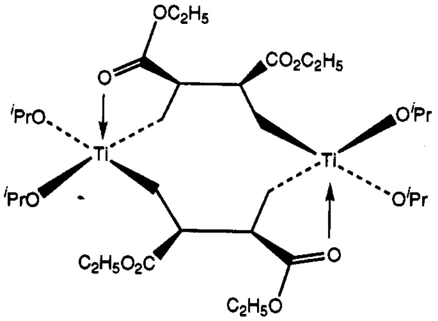

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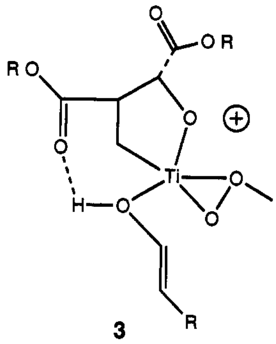

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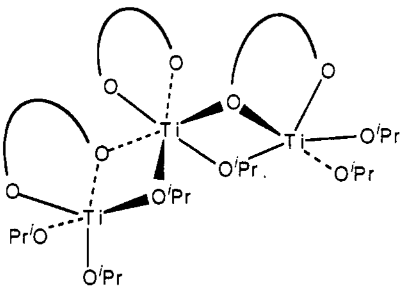
Among the recently developed titanate Lewis acid catalysts, compounds based on the C_2-symmetric binaphtholate ligand are widely employed.[21,22] These complexes are versatile catalysts for a range of electrocyclic and alkyl addition reactions and, along with their precursor, "Ti(O-*i*-Pr)$_2$Cl$_2$", have been used in many synthetic transformations. Despite their utility, relatively little information is available about catalyst structure, reactivity, and the mechanisms of the processes catalyzed by these species.[21,22] The need for additional information about this class of catalyst is exemplified by these three central characteristics of the binaphtholate catalysts: solid state structure, solution state structure, and mechanism of catalysis.

Until our recent studies,[23] the solid state structures of very few binaphtholate substituted titanium complexes were known.[24] Moreover, the structure of the most pivotal Lewis acid catalyst of this class, "Ti(BINO)Cl$_2$", remains to be determined. As a result of this paucity of data, investigators are forced to infer rest-state catalyst structures by logical extension from the structures of known titanium aryloxides, such as the $Ti_2(OPh)_4Cl_4$ dimer.[25,26] This raises the concern that simple phenolate models may not fully incorporate the stereochemical restrictions imposed in the tied-back binaphtholate ligand. The potential complexity of "simple" Ti(diolate)X_2 complexes is illustrated by the structure of Ti_3(BINO)$_3$(O-*i*-Pr)$_6$ (**4**) reported in the Sharpless laboratory.[27] Purifying and structurally characterizing examples of target titanium binaphtholate complexes is the only method for confidently identifying the range of rest-state structures exhibited by potential catalyst species.



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The significant substitutional lability of many titanium procatalysts makes establishing the precise identity of the catalytically active species a challenging, albeit necessary task. As Sharpless and co-workers observed in the titanium tartrate-based epoxidation catalysts, both intramolecular rearrangement and titanium fragment transfer reactions in titanium binaphtholate complexes have small energetic barriers.[28] Seebach's spirotitanate complex also readily participates in ligand redistribution reactions with Ti(O-*i*-Pr)$_4$, generating an apparently mononuclear Ti(4POH)(O-*i*-Pr)$_2$ product (Scheme 1).[29] A collateral concern is that the coordination of even weakly ligating bases, such as esters, aldehydes, and ketones, could tip the balance either between different types of ligand bridged structures or between mono- and dinuclear titanium complexes. This possibility has spawned speculation that polynuclear rest states of binaphtholate substituted titanium Lewis acids may give rise to a homolytically

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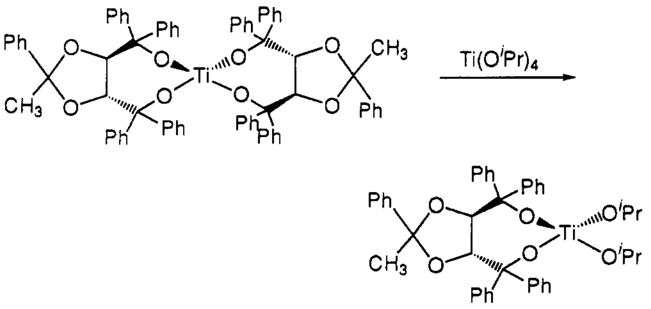
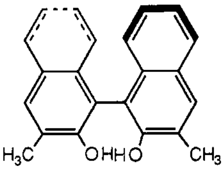
Scheme 1



cleaved monotitanate catalyst.[20] An alternative structure for active catalysts could be more highly Lewis acidic heterolytically cleaved cations. Careful studies of the solution state nuclearity and structure of catalyst species in both the presence and absence of coordinating organic substrates are required before current mechanistic concepts can be rationally extended. Ultimately, this structural information would assist in the interpretation of the kinetics of relevant catalytic reactions and result in the development of reasonable models for the transition states of these processes.

In this paper, we describe the synthesis of "Ti(diolate)Cl_2" complexes (diolate = 3,3′-dimethylbinaphtholate (Me_2BINO) (**5**), biphenanthrolate (BIPHENO) (**6**), and 5,5′,6,6′,7,7′,8,8′-octahydrobinaphtholate (H_8BINO) (**7**)), as an extension of our initial work on the coordination chemistry of titanium complexes of the C_2-symmetric binaphtholate ligand.[23] We have compared the solution state structure and chemistry of (R^*,R^*)-$Ti_2(Me_2BINO)_2Cl_4$ and (R,R)-$Ti_2(H_8BINO)_2Cl_4$ with the solid state structures of the same complexes, as determined by X-ray crystallography. The kinetics of a Diels–Alder reaction catalyzed by the Me_2BINO and H_8BINO derivatives were also examined, and both rate data and activation parameters were obtained from this well-behaved system. This study provides an intimate picture of a Diels–Alder reaction catalyzed by a structurally well characterized chiral titanium complex.



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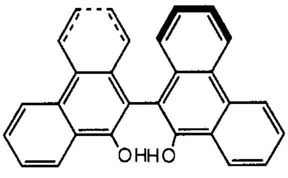

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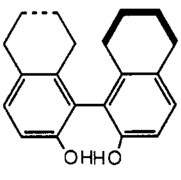

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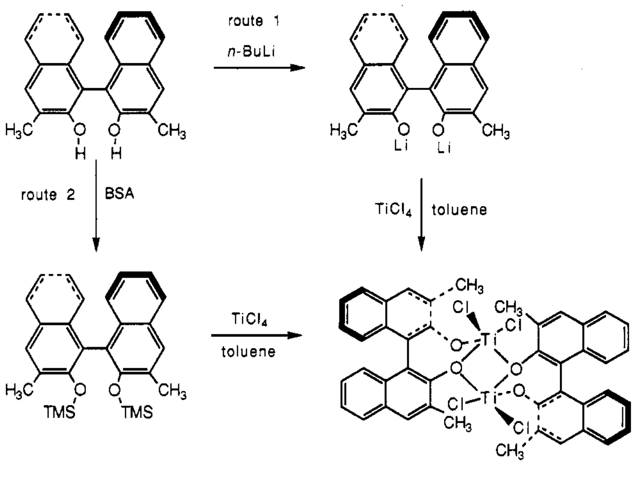
Scheme 2



Results

Synthesis and Characterization of Ti(diolate)Cl_2 Complexes. Dinuclear titanium diolate dichloride complexes were prepared by two standard routes (Scheme 2). (1) Lithium salts of racemic 3,3′-dimethyl-1,1′-bi-2-naphthol ($Me_2BINOLi_2$), prepared in situ, were reacted with $TiCl_4$ in a noncoordinating solvent. (2) Efficient alternative syntheses of "Ti(diolate)Cl_2" and (R^*,R^*)-$Ti(Me_2BINO)_2$ were achieved by the conversion of the diolates into bis(silyl) ethers,[30] followed by reactions with $TiCl_4$ at low temperatures. The *rac*-Ti(Me_2BINO)Cl_2 complex obtained from these syntheses crystallized as red X-ray quality crystals from ether in good yield. Despite the presumed Lewis acidity of the titanium center, there was no evidence of ether coordination in either solution or the solid state. Ti(BIPHENO)Cl_2 is isolated as a pure material after recrystallization in only modest yield, and underwent detectable decomposition over a few hours in dry oxygen free solvents. The source of this instability is currently unknown.

Efforts to prepare crystalline, spectroscopically tractable derivatives of the parent binaphtholate and 3,3′-diphenyl substituted ligands (BINO and Ph_2BINO, respectively) by these routes proved unsuccessful. This is consistent with the problems encountered in our prior attempts to synthesize "(R_2BINO)Ti(O-*i*-Pr)$_2$" complexes, where R = H or Ph.[23] It is noteworthy that Mikami chose to prepare his "(BINO)TiCl_2" catalyst through an alcoholysis protocol modified by the inclusion of 4-Å molecular sieves.[31]

Molecular weight measurements on Ti(Me_2BINO)Cl_2 and Ti(H_8BINO)Cl_2 indicate that they are dinuclear in solution.[32] Studies of an equilibrium process involving Ti(BIPHENO)Cl_2 and $TiCl_4$ (vide infra) confirmed that Ti(BIPHENO)Cl_2 exists as a dimer in solution. Unlike the ^{1}H NMR spectrum of (R^*,R^*)-$Ti_2(Me_2BINO)_2$(O-*i*-Pr)$_4$, which displays two distinct naphthoxide and isopropoxide environments at reduced temperature,[23] the spectra of all three diolate complexes indicate that the molecules retain apparent D_2 symmetry at very low

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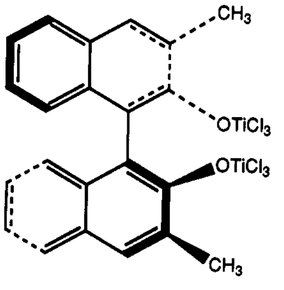
temperatures. Like $Ti_2(Me_2BINO)_2(O\text{-}i\text{-}Pr)_4$, both of the halide complexes show only a single molecular entity in solution within the limits of NMR detection, although they could conceivably adopt both *rac*-(R^*,R^*) and achiral (R,S) diastereomeric structures. This observation indicates that one of the two diastereomeric structures is significantly favored.[23] ^1H NMR spectra of both (R,R)-$Ti_2(Me_2BINO)_2Cl_4$ and (R,R)-$Ti_2(H_8BINO)_2Cl_4$ are identical to those of the respective racemic complexes, confirming that like $Ti_2(Me_2BINO)_2(O\text{-}i\text{-}Pr)_4$,[23] the homochiral dinuclear chloride complexes are substantially more thermodynamically stable than their mixed chirality diastereomers.

Titrations of the $Ti_2(diolate)_2Cl_4$ complexes with additional $TiCl_4$ in either toluene or chloroform cause the growth of a new set of diolate ^1H resonances at the expense of the resonances associated with the $Ti_2(diolate)_2Cl_4$ precursor. Data from titration studies fit an equilibrium expression between a new dinuclear titanium complex, $Ti_2(diolate)Cl_6$, and the $Ti_2(diolate)_2Cl_4$ and $TiCl_4$ starting materials (eq 1). The thermodynamic parameters for these

$$2Ti_2(diolate)_2Cl_6 \rightleftharpoons Ti_2(diolate)_2Cl_4 + 2TiCl_4 \quad (1)$$

equilibria were determined in $CDCl_3$: Me_2BINO $\Delta H° = 4.0$ kcal/mol, $\Delta S° = 4.0$ eu; BIPHENO $\Delta H° = 20.7$ kcal/mol, $\Delta S° = 54.2$ eu. Similar equilibria have been observed for reactions of either (R^*,R^*)-$Ti_2(Me_2BINO)_2(O\text{-}i\text{-}Pr)_4$ or $Ti(3,3'\text{-}(t\text{-}BuMe_2Si)_2BINO)(O\text{-}i\text{-}Pr)_2$ with $Ti(O\text{-}i\text{-}Pr)_4$.[23] The ^1H NMR spectra of both $Ti_2(diolate)Cl_6$ complexes reveal that they maintain apparent C_2 symmetry at very low temperatures. This makes it impossible to determine whether the ground state structure of the complexes has an open C_2-symmetric structure (**8**), or a C_1-symmetric halide bridged structure undergoing rapid intramolecular rearrangement (**9**).



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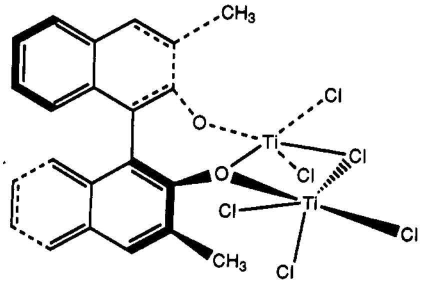

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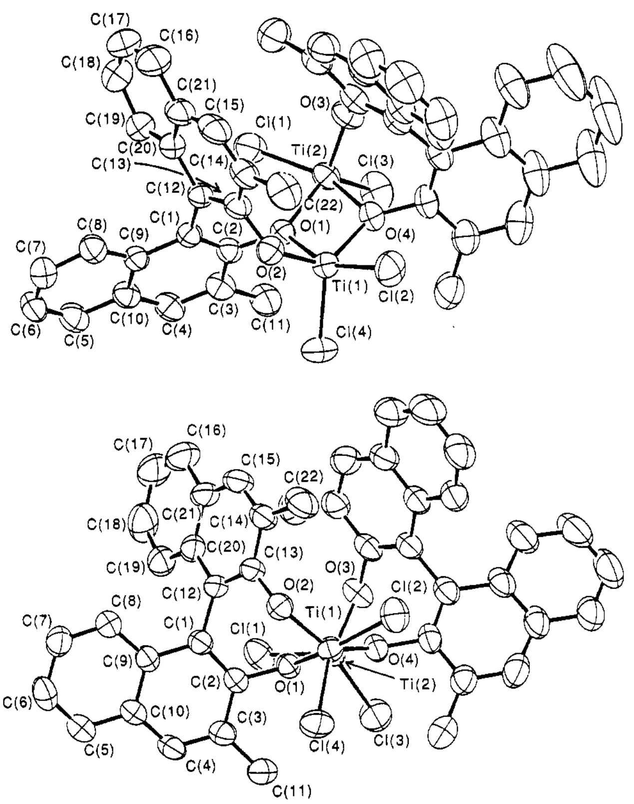

Figure 1. ORTEP representations of (R^*,R^*)-$Ti_2(Me_2BINO)_2Cl_4$: (a, top) obliquely showing the dioxadititanacyclobutane core unit and (b, bottom) viewed down the Ti⋯Ti vector.

Molecular Structure of $Ti_2(Me_2BINO)_2Cl_4$ and $Ti_2(H_8BINO)_2Cl_4$. Two ORTEP representations of the X-ray crystal structure of *rac*-$Ti_2(Me_2BINO)_2Cl_4$ are shown in Figure 1. The structure of this molecule is very similar to the previously determined structure of *rac*-$Ti_2(Me_2BINO)_2(O\text{-}i\text{-}Pr)_4$, and the positional parameters and bond distances and angles collected in Tables 1 and 2 bear a remarkable resemblance to those found in the isopropoxide substituted derivative.[23] The dinuclear titanium structure is supported by identical unidentate-bridging Me_2BINO ligands, whose bridging naphthoxide units generate a classic d^0–d^0 1,3-dioxadititanacyclobutane structure. The geometry about each of the titanium centers (Ti(1)) represents a distorted trigonal bipyramid in which a bridging naphthoxide (O(1)) and its mutually trans chloride ligand (Cl(2)) occupy axial environments, and the remaining chloride (Cl(4)), the terminal naphthoxide ligand (O(2)), and the second bridging naphthoxide unit (O(4)) occupy equatorial positions. Distortions from idealized trigonal bipyramidal geometry, in particular the severely compressed axial Cl(2)–Ti(1)–O(1) angle of 156.23(7)°, are typical of edge-fused bis trigonal bipyramidal titanium complexes.[23,26,33] The structure confirms the homochiral (R^*,R^*) character of the titanium dimer, and this stereochemistry, in turn, enforces a syn relationship between the two terminal naphthoxide units. At least for this complex, the solution and solid state stereochemistry of the molecule are related.

The apparent lesser stability of the alternative (R,S) diastereomer can be understood in terms of the favorability of transannular interactions between the two dimethylbinaphtholate ligands. In the observed (R^*,R^*) diastereomer, the syn terminal naphtholate units are virtually parallel, both avoiding sterically destabilizing interligand contact and producing a narrowly spaced aromatic cleft

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Table 1. Positional and Isotropic Thermal Parameters for $Ti_2(Me_2BINO)_2Cl_4$

atom	*x*	*y*	*z*	*B*(eq), Å^2	atom	*x*	*y*	*z*	*B*(eq), Å^2
Ti(1)	0.56978(4)	0.03542(5)	0.77887(3)	3.54(3)	C(34)	0.3643(2)	–0.0626(3)	0.8535(2)	4.3(2)
Ti(2)	0.38944(4)	–0.06906(5)	0.69661(3)	3.65(3)	C(35)	0.3861(2)	0.0275(3)	0.8207(2)	4.1(2)
Cl(1)	0.39119(7)	–0.16117(9)	0.60826(4)	5.05(4)	C(36)	0.3557(2)	0.1370(4)	0.8279(2)	4.8(2)
Cl(2)	0.58475(7)	0.0600(1)	0.88040(4)	5.58(5)	C(37)	0.3023(3)	0.1525(5)	0.8711(2)	6.1(2)
Cl(3)	0.27609(7)	0.0428(1)	0.66877(5)	6.17(5)	C(38)	0.2154(5)	0.0794(8)	0.9480(3)	10.1(4)
Cl(4)	0.61166(7)	0.19663(8)	0.74631(5)	5.42(5)	C(39)	0.1874(5)	–0.0064(9)	0.9786(4)	13.3(6)
O(1)	0.5117(1)	–0.0232(2)	0.6936(1)	3.4(1)	C(40)	0.2101(4)	–0.1149(8)	0.9661(3)	10.6(4)
O(2)	0.6558(2)	–0.0616(2)	0.7775(1)	4.0(1)	C(41)	0.2668(3)	–0.1344(6)	0.9252(2)	7.1(3)
O(3)	0.3554(2)	–0.1790(2)	0.7412(1)	4.5(1)	C(42)	0.3016(3)	–0.0472(4)	0.8948(2)	5.3(2)
O(4)	0.4414(1)	0.0111(2)	0.7763(1)	3.9(1)	C(43)	0.2729(3)	0.0625(5)	0.9050(2)	6.3(2)
C(1)	0.6276(2)	–0.1115(3)	0.6506(2)	3.4(1)	C(44)	0.3837(4)	0.2328(4)	0.7910(3)	6.4(3)
C(2)	0.5647(2)	–0.0296(3)	0.6472(1)	3.4(1)	H(4)	0.597(2)	0.106(3)	0.526(2)	3.6(7)
C(3)	0.5511(2)	0.0525(3)	0.6002(2)	3.8(2)	H(5)	0.726(2)	0.023(3)	0.486(2)	4.5(9)
C(4)	0.6061(3)	0.0494(3)	0.5573(2)	4.2(2)	H(6)	0.837(2)	–0.097(3)	0.490(2)	4.3(8)
C(5)	0.7327(3)	–0.0280(4)	0.5149(2)	4.5(2)	H(7)	0.865(3)	–0.229(4)	0.569(2)	7(1)
C(6)	0.8004(3)	–0.1010(4)	0.5183(2)	4.9(2)	H(8)	0.766(2)	–0.236(3)	0.639(2)	5(1)
C(7)	0.8144(3)	–0.1785(3)	0.5660(2)	4.8(2)	H(11A)	0.422(3)	0.098(4)	0.592(2)	7(1)
C(8)	0.7590(3)	–0.1839(3)	0.6086(2)	4.3(2)	H(11B)	0.487(3)	0.197(4)	0.569(2)	9(1)
C(9)	0.6871(2)	–0.1098(3)	0.6065(1)	3.4(1)	H(11C)	0.478(2)	0.179(3)	0.636(2)	6.0(8)
C(10)	0.6754(2)	–0.0285(3)	0.5592(2)	3.7(1)	H(15)	0.685(3)	–0.420(4)	0.826(2)	6(1)
C(11)	0.4782(3)	0.1362(4)	0.5970(2)	5.1(2)	H(16)	0.645(3)	–0.550(4)	0.754(2)	7(1)
C(12)	0.6358(2)	–0.1991(3)	0.6993(2)	3.5(1)	H(17)	0.589(3)	–0.60695)	0.651(2)	8(2)
C(13)	0.6554(2)	–0.1724(3)	0.7608(2)	3.8(2)	H(18)	0.549(3)	–0.472(3)	0.577(2)	5(1)
C(14)	0.6765(2)	–0.2522(3)	0.8093(2)	4.5(2)	H(19)	0.573(3)	–0.300(3)	0.596(2)	5(1)
C(15)	0.6714(3)	–0.3598(4)	0.7930(2)	5.2(2)	H(22A)	0.720(2)	–0.280(3)	0.904(2)	9(1)
C(16)	0.6285(4)	–0.5090(4)	0.7170(3)	6.6(3)	H(22B)	0.752(4)	–0.155(2)	0.883(2)	9(1)
C(17)	0.5943(4)	–0.5402(4)	0.6602(3)	7.4(3)	H(22C)	0.655(4)	–0.183(4)	0.894(2)	9(1)
C(18)	0.5741(4)	–0.4628(4)	0.6135(3)	6.8(3)	H(26)	0.487(2)	–0.470(3)	0.835(2)	5(1)
C(19)	0.5899(3)	–0.3514(4)	0.6246(2)	5.2(2)	H(27)	0.562(3)	–0.454(4)	0.945(2)	6(1)
C(20)	0.6241(2)	–0.3148(3)	0.6839(2)	4.2(2)	H(28)	0.584(3)	–0.363(4)	1.034(2)	7(1)
C(21)	0.6426(3)	–0.3952(3)	0.7323(2)	4.9(2)	H(29)	0.541(3)	–0.183(3)	1.037(2)	5(1)
C(22)	0.7034(4)	–0.2129(5)	0.8750(2)	6.1(2)	H(30)	0.454(2)	–0.096(3)	0.961(2)	3.9(8)
C(23)	0.4053(2)	–0.1744(3)	0.8487(2)	4.0(2)	H(33A)	0.3732	–0.3540	0.6976	22(3)
C(24)	0.3957(2)	–0.2310(3)	0.7940(2)	4.1(2)	H(33B)	0.4575	–0.4263	0.7152	28(3)
C(25)	0.4238(2)	–0.3433(3)	0.7877(2)	4.6(2)	H(33C)	0.3679	–0.4658	0.7323	24(3)
C(26)	0.4671(3)	–0.3915(4)	0.8404(2)	5.1(2)	H(37)	0.284(3)	0.228(3)	0.881(2)	6(1)
C(27)	0.5354(3)	–0.3856(5)	0.9491(2)	6.2(3)	H(38)	0.213(4)	0.154(5)	0.958(3)	9(2)
C(28)	0.5552(3)	–0.3308(5)	1.0027(3)	6.8(3)	H(39)	0.161(5)	0.014(6)	1.010(3)	12(2)
C(29)	0.5260(3)	–0.2231(5)	1.0079(2)	6.2(3)	H(40)	0.192(3)	–0.178(4)	0.986(2)	8(1)
C(30)	0.4776(3)	–0.1710(4)	0.9591(2)	5.1(2)	H(41)	0.285(2)	–0.204(3)	0.919(2)	4(1)
C(31)	0.4450(2)	–0.2255(3)	0.9021(2)	4.4(2)	H(44A)	0.359(3)	0.285(3)	0.803(2)	7(1)
C(32)	0.4853(2)	–0.3363(3)	0.8967(2)	4.7(2)	H(44B)	0.446(4)	0.256(4)	0.797(3)	9(2)
C(33)	0.4044(4)	–0.4036(4)	0.7275(2)	6.0(2)	H(44C)	0.390(4)	0.221(5)	0.745(3)	11(2)

Table 2. Selected Intramolecular Distances and Angles for $Ti_2(Me_2BINO)_2Cl_4$

	Bond Distances (Å)		
Ti(1)–Ti(2)	3.2973(2)	Ti(2)–Cl(1)	2.236(1)
Ti(1)–Cl(2)	2.223(1)	Ti(2)–Cl(3)	2.203(1)
Ti(1)–Cl(4)	2.194(1)	Ti(2)–O(1)	1.962(2)
Ti(1)–O(1)	2.064(2)	Ti(2)–O(3)	1.771(2)
Ti(1)–O(2)	1.762(2)	Ti(2)–O(4)	2.045(2)
Ti(1)–O(4)	1.979(2)		
	Bond Angles (deg)		
Cl(2)–Ti(1)–Cl(4)	102.72(5)	O(1)–Ti(1)–O(4)	69.00(9)
Cl(2)–Ti(1)–O(1)	156.23(7)	O(2)–Ti(1)–O(4)	130.1(1)
Cl(2)–Ti(1)–O(2)	98.42(8)	Ti(1)–O(1)–Ti(2)	109.9(1)
Cl(2)–Ti(1)–O(4)	89.52(7)	Ti(1)–O(1)–C(2)	117.6(2)
Cl(4)–Ti(1)–O(1)	96.42(7)	Ti(2)–O(1)–C(2)	132.4(2)
Cl(4)–Ti(1)–O(2)	108.67(8)	Ti(1)–O(1)–C(13)	132.1(2)
Cl(4)–Ti(1)–O(4)	117.46(8)	Ti(2)–O(3)–C(24)	132.3(2)
O(1)–Ti(1)–O(2)	88.5(1)		

that disfavors solvation of the juxtaposed naphtholate faces. In the alternative (*R*,*S*) diastereomer, the terminal naphthoxide ligands would presumably adopt an anti relationship, generating C_i molecular symmetry (Figure 2). This would result in a destabilizing steric interaction between the methyl group of a bridging naphthoxide unit and the methyl group of the syn-terminal naphthoxide on the other Me_2BINO unit. A combination of this steric contact and a reduced ability to exclude solvent probably accounts for the lower stability of the (*R*,*S*) isomer of $Ti_2(Me_2BINO)_2Cl_4$.

While Figure 1a provides the best view of the near-planar dioxadititanacycle unit, Figure 1b, plotted from the perspective of the Ti···Ti vector, clearly illustrates the C_2 symmetry of $Ti_2(Me_2BINO)_2Cl_4$. Like its isopropoxide substituted structural analog, this molecule possesses an incipient vacancy trans to the equatorial chloride ligand on each titanium center. Were an approaching organic substrate to attack titanium to generate a ligated dinuclear species, this space seems to provide a logical binding site.

The structure of $Ti_2(H_8BINO)_2Cl_4$, which has been briefly described elsewhere,[34] differs significantly from that of $Ti_2(Me_2BINO)_2Cl_4$. The significant torsional restriction of the H_8BINO ligand will not support the ligand in a unidentate-bridging bonding mode. Instead, the complex forms a 14-membered metallamacrocycle, in which the aryloxide ligand shows evidence of substantial π-donation to titanium.

Application of $Ti_2(Me_2BINO)_2Cl_4$ and $Ti_2(H_8BINO)_2Cl_4$ as Lewis Acid Catalysts. $Ti_2(Me_2BINO)_2Cl_4$ and $Ti_2(H_8BINO)_2Cl_4$ act as catalysts for the Diels–Alder reaction between methyl acrylate and cyclopentadiene in chloroform solution. Figure 3 shows plots of rate studies

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(34) Eilerts, N. W.; Heppert, J. A.; Kennedy, M. L.; Takusagawa, F. Submitted for publication.

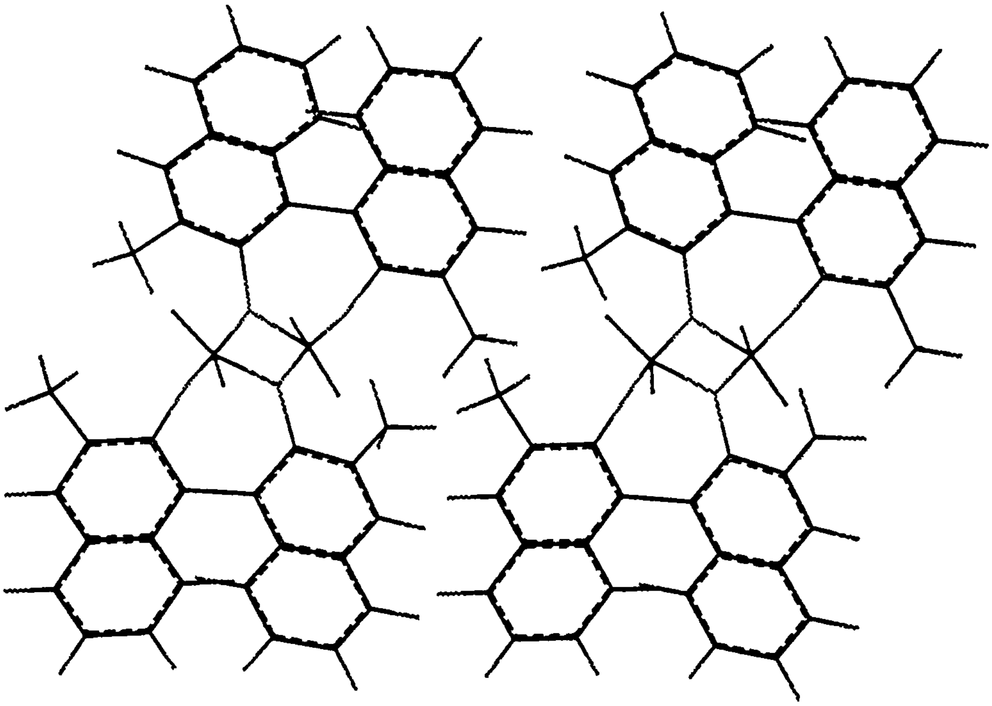


Figure 2. Stereoview of a molecular model of a hypothetical (*R*,*S*)-$Ti_2(Me_2BINO)_2Cl_4$ diastereomer.

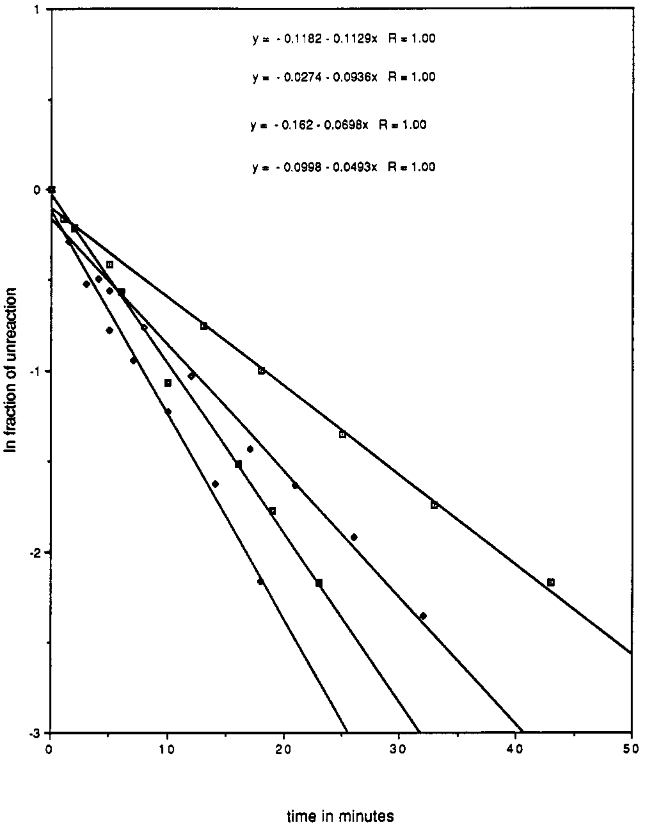


Figure 3. Rate studies of methyl acrylate disappearance in the presence of varying concentrations of $Ti_2(Me_2BINO)_2Cl_4$.

for the Diels–Alder reaction in the presence of varying amounts of $Ti_2(Me_2BINO)_2Cl_4$. Similar kinetic data were acquired for $Ti_2(H_8BINO)_2Cl_4$. All of these studies were run under pseudo first order conditions (excess cyclopentadiene). The plots indicate that, over the conditions studied, the reactions remain strictly first order in dienophile. Moreover, doubling the concentration of diene doubles the rate of the catalyzed process, indicating that the reaction is also first order in diene. The rate of the reaction in chloroform was that in benzene, indicating that a more polar solvent slightly accelerates the reaction. The rate of the same Diels–Alder reaction in the presence of either $Ti_2(Me_2BINO)_2(O\text{-}i\text{-}Pr)_4$ or $Ti_2(Me_2BINO)(O\text{-}i\text{-}Pr)_6$ was no greater than that observed for the uncatalyzed reaction. Either the increased crowding of the coordination sphere or the greater π-donor character introduced by the isopropoxide ligands substantially reduces the Lewis acidity of these complexes.

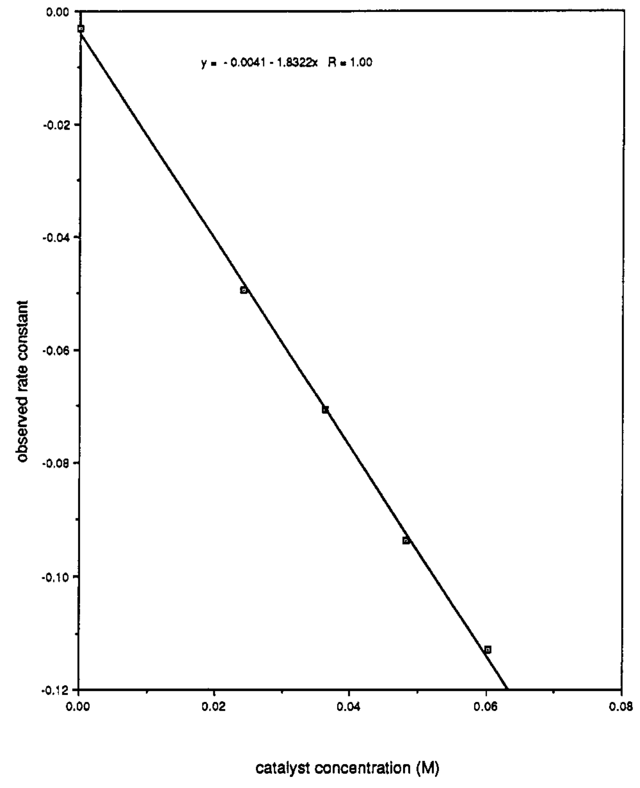
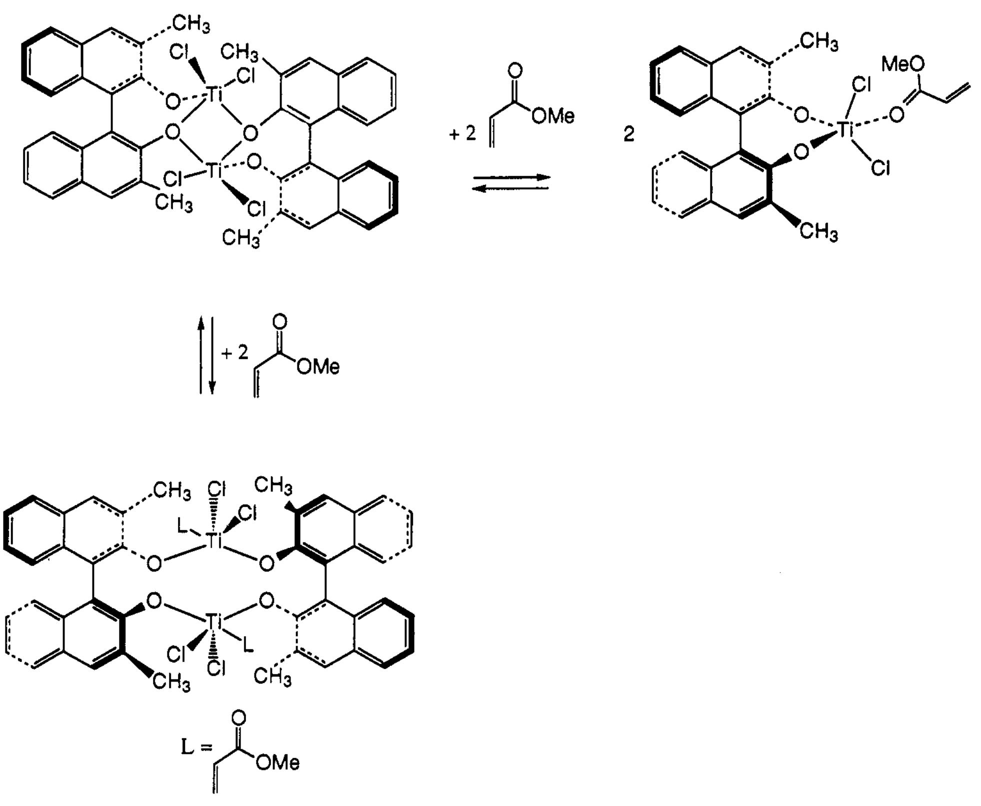


Figure 4. Rates of disappearance of methyl acrylate as a function of $Ti_2(Me_2BINO)_2Cl_2$ concentration.

Scheme 3



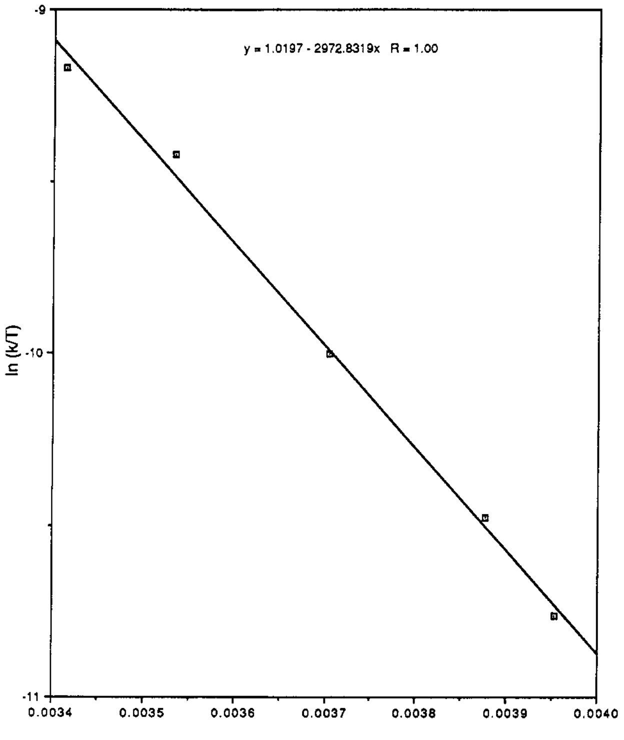


Figure 5. Eyring plot of the rate of methyl acrylate disappearance in the $Ti_2(Me_2BINO)_2Cl_4$ catalyzed Diels–Alder reaction.

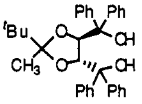
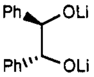
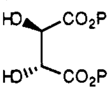
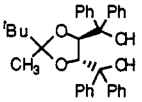
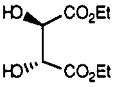
Plotting the determined rates of product formation against the $Ti_2(Me_2BINO)_2Cl_4$ concentration gives the simple first order relationship shown in Figure 4. The linearity of this plot indicates that for titanium to dienophile ratios exceeding 1:10, a single catalyst species is involved in the reaction. Were a monomer/dimer equilibrium responsible for generating several catalytically active species, the plots would have exhibited nonlinear character. This first order behavior has two possible interpretations: either the dimer undergoes complete scission to generate an active mononuclear catalyst in the presence of coordinating methyl acrylate substrate, or the catalyst maintains its dinuclear structure during the reaction (Scheme 3). Rate data spanning a 50-deg temperature range at a 1:10 titanium to dienophile concentration for $Ti_2(Me_2BINO)_2Cl_4$ are collected in the Eyring plot shown in Figure 5. The good linear correlation of these data also suggests that a single catalyst species is active under these reaction conditions. Activation parameters for the Diels–Alder reaction obtained from the rate data ($\Delta H^{\ddagger} = 7.1 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -58 \pm 2$ eu) are consistent with the cycloaddition step being rate determining. These differ somewhat from the activation parameters for the uncatalyzed Diels–Alder process ($\Delta H^{\ddagger} = 12.6 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -35 \pm 2$ eu). The higher entropic barrier for the catalyzed process is consistent with the additional requirements for organization, while the reduced enthalpic barrier is consistent with the Lewis acid induced polarization of the dienophile.

Binding of the dienophile to the titanium center was also examined for the two dinuclear catalysts. NMR spectroscopic studies performed at the concentrations employed in the catalytic experiments show no evidence of methyl acrylate binding to titanium. Moreover, spectra of the catalyst acquired in the presence of up to a 30-fold excess of methyl acrylate and at temperatures as low as −55 °C showed no perceptible changes, as would be expected if significant populations of acrylate-bound metal species were being formed. Marked spectroscopic changes in $Ti_2(Me_2BINO)_2Cl_4$ are observed on addition of a more reactive chelating oxazolidinone crotanoate dienophile.[35] Although this product has not yet been fully characterized,

Table 3. Percent ee of Methyl-5-carboxynorbornene as a Function of the Ratio of Optically Pure Catalyst to Methyl Acrylate Substrate

Titanium: dienophile ratio	% ee, absolute configuration	Titanium: dienophile ratio	% ee, absolute configuration
1:20	7, (+)-(*R*)	1:1	21, (–)-(*S*)
1:5	4, (+)-(*R*)	2:1	26, (–)-(*S*)

Table 4. Percent ee of Methyl-5-carboxynorbornene in the Context of Other Asymmetric Diels–Alder Catalysts

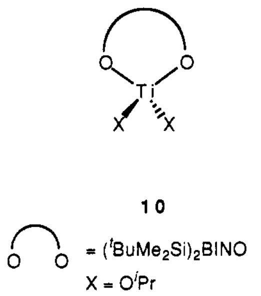
catalyst or catalyst components	isolated yield	% ee, absolute configuration	ref
(R)-BINOH$_2$ + "TiCl$_2$(O^{i}Pr)$_2$"	77	50, (+)-(*R*)	3
 + "TiCl$_2$(O^{i}Pr)$_2$"	74	42, (–)-(*S*)	3
 + "TiCl$_2$(O^{i}Pr)$_2$"	85	36, not reported	43b
[(*R*)-Me$_2$BINO)TiCl$_2$]$_2$	100	26, (–)-(*S*)	this work
 + TiCl$_4$	95	17, (–)-(*S*)	3
 + TiCl$_4$	30	14, (–)-(*S*)	3
 + TiCl$_4$	87	10, (–)-(*S*)	3

the interaction of oxazolidinone dienophiles with titanium Lewis acids is a subject of continuing study.

Finally, the influence of titanium dimer concentration on the percent enantiomeric excess (ee) of the reaction catalyzed by optically pure (*R,R*)-Ti$_2$(Me$_2$BINO)$_2$Cl$_4$ was examined. Table 3 shows the results of studies in which the ratio of optically pure catalyst to methyl acrylate was varied from 5 mol % metal to 200 mol % metal.[36] As is sometimes observed with metal-derived Lewis acids, the sign of the product enantiomeric excess showed a reversal on proceeding from a catalytic stoichiometry to one in which the metal acts as a promoter for the reaction.[37] The best enantioselectivities for these well characterized catalysts were obtained at higher titanium to dienophile ratios. Table 4 places the 26% ee obtained with a 2:1 titanium to methyl acrylate stoichiometry in the context of results found with other asymmetric Lewis acid catalysts. The results in Table 3 represent the approximate functional range of enantioselectivity accessible with the (*R,R*)-Ti$_2$(Me$_2$BINO)$_2$Cl$_4$ catalyst.

Discussion

Structure of the Titanium Catalyst. Prior to our studies, the only structurally well characterized group 4 binaphtholate complexes were the *ansa*-metallocene derivatives prepared to resolve the C_2-symmetric bis(indenyl) complexes.[13,38] A combination of structural and spectroscopic studies have now characterized four distinct structural types for binaphtholate–chloride and binaphtholate–isopropoxide complexes of titanium: a mononuclear complex containing a simple binaphtholate chelate (**10**), a bridging binaphtholate bound to two otherwise noninteracting titanium centers (**11**), a trinuclear complex containing a unidentate bridging binaphtholate ligand and one other bridging ligand (**12**), and the dinuclear complexes containing two unidentate bridging ligands (**13**), as exemplified by Ti$_2$(Me$_2$BINO)$_2$Cl$_4$. A number of common principles can be extracted from these studies. (1) More sterically demanding ligands, such as (t-BuMe$_2$Si)$_2$BINO, favor either lower nuclearity complexes or complexes supported by fewer bridging ligands. In this context, it is noteworthy that an X-ray structure from the Sharpless group shows that "(*R*)-Ti(BINO)(O-*i*-Pr)$_2$" exists in a trimeric form,[27] demonstrating a logical progression in the aggregation of the $\{(R_2BINO)Ti(O\text{-}i\text{-}Pr)_2\}_n$ subunit (R = t-BuMe$_2$Si, n = 1; R = Me, n = 2; R = H, n = 3). (2) There can be a direct structural correspondence between chloride and isopropoxide substituted complexes bearing like R$_2$-BINO ligands, as illustrated by the structural similarity of the Ti$_2$(Me$_2$BINO)$_2$X$_4$ (X = Cl and O-*i*-Pr) derivatives. If this principle extends to unsubstituted BINO ligands, then the rest-state structure of the classic Mikami "Ti(BINO)Cl$_2$" catalyst[25] would be related to the trimeric (*R,R,R*)-Ti$_3$(BINO)$_3$(O-*i*-Pr)$_6$ (**4**) complex.[27] (3) Complexes containing either a 2:1 or 1:1 ratio of binaphtholate ligands to titanium centers freely incorporate additional TiX$_4$ fragments (X = Cl or *i*-PrO), ultimately generating complexes containing two titanium centers per binaphtholate ligand. This result is consistent with the observation of Ti$_2$(tartramide)(O-*i*-Pr)$_6$ complexes by Sharpless[39] and with Seebach's discovery that homoleptic Ti(4POH)$_2$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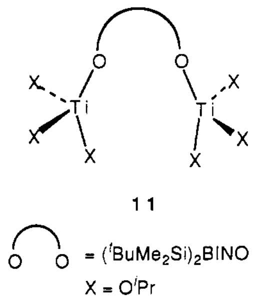
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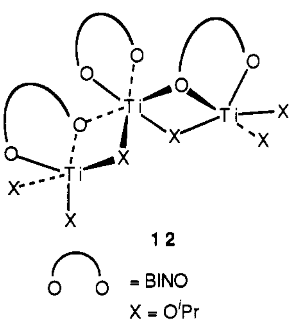
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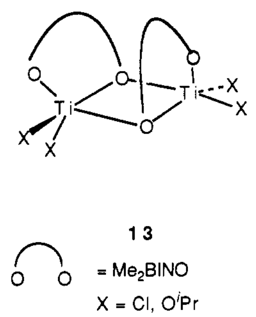
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(35) We thank professor Tom Engler for a gift of this reagent.

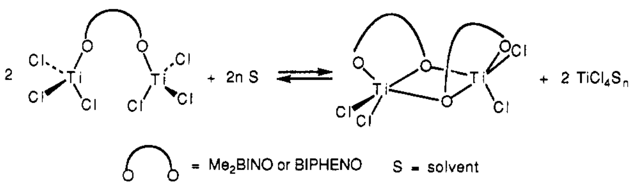
(36) The addition of activated 4-Å molecular sieves to the five mole percent experiment had no effect on the enantiomeric excess of the resulting norbornene ester.

(37) (a) Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967. (b) Oh, T.; Devine, P. *J. Org. Chem.* **1992**, *57*, 396.

(38) Brintzinger, H. H.; Schnutenhaus, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 777.

(39) Lu, L. D.-L.; Johnson, R. A.; Finn, M. G.; Sharpless, K. B. *J. Org. Chem.* **1984**, *49*, 728.

Scheme 4

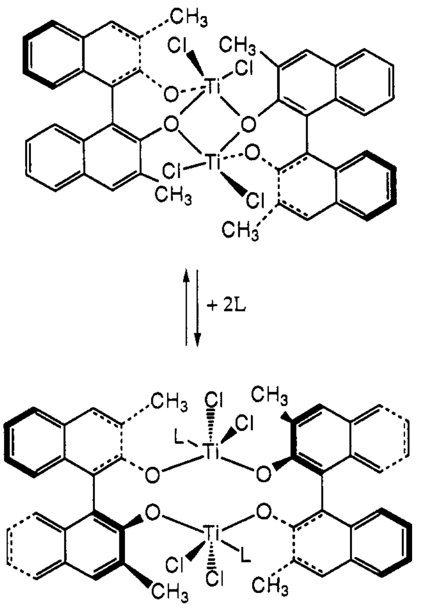


complexes react with Ti(O-*i*-Pr)$_4$ to generate Ti(4POH)(O-*i*-Pr)$_2$.[29] On the basis of these equilibria, it seems clear that the role of the added TiX_4 is to establish (diolate)Ti_2X_6 as the predominant rest-state species in solution.

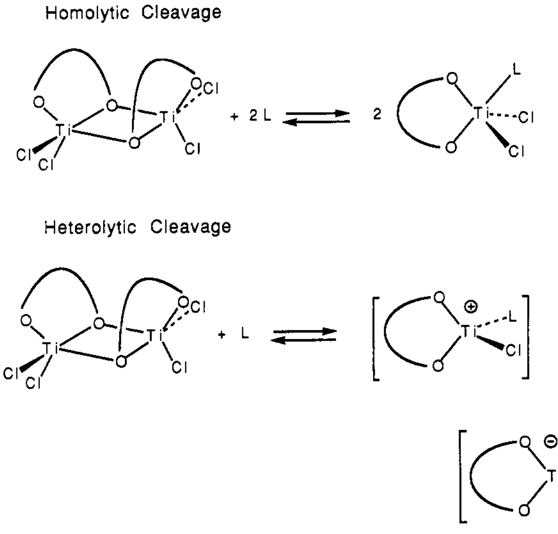
Relationship between the Observed Equilibria and Lewis Acid Catalysis. The nature of the observed equilibria for the halide and isopropoxide substituted complexes also provides some insight into the characteristics of the complexes as catalysts. Ti(O-*i*-Pr)$_4$ is not, by itself, a very active Lewis acid catalyst. In contrast, $TiCl_4$ is so highly reactive that complexes of intermediate Lewis acidity, such as "Ti(O-*i*-Pr)$_2$Cl$_2$" are employed in its place. This spectrum of catalytic activities imposes different requirements on asymmetric catalysts containing chloride and isopropoxide ligands. Catalysts prepared from $TiCl_4$ must not engage in equilibria that produce significant concentrations of free $TiCl_4$, for fear that all productive catalysis will be channeled through this achiral molecule. By comparison, Ti(O-*i*-Pr)$_4$ undergoes a demonstrable increase in Lewis acidity on substitution by less sterically demanding ligands. This ligand-induced rate acceleration is probably operative in other asymmetric catalytic systems that produce high product ee's even in the presence of excess achiral Ti(O-*i*-Pr)$_4$. While all of the equilibria favor the formation of the monodiolate substituted dititanium complexes, the equilibrium is enthalpically less favorable for $Ti_2(Me_2BINO)Cl_6$ than for $Ti_2(Me_2BINO)$(O-*i*-Pr)$_6$.[23] This could be due to differences in the energies of μ-Cl and μ-O-*i*-Pr bridging interactions. The entropies of the related equilibria are also startlingly different. The surprisingly low entropies of reaction observed for $Ti_2(Me_2BINO)Cl_6$ may stem from the greater tendency of $TiCl_4$ to form weak σ- or π-interactions with suitable donor sites on solvent molecules.[40] Consequently, more accurate representations for equilibria involving $TiCl_4$ may reduce the overall change in molecularity through the participation of solvent molecules (Scheme 4).

Due to the fluxional behavior and facile intermolecular ligand exchange exhibited by these molecules, it is best to consider the apparent structures of the pure group 4 complexes in solution merely as rest-state structures. Examples of this principle are found for (*R**,*R**)-$Ti_2(Me_2BINO)_2$(O-*i*-Pr)$_4$ and other complexes bridged by tartrate and ethylene glycolate ligands that show facile intramolecular ligand exchange.[23] These fluxional processes are believed to proceed through symmetrically bridged diolate intermediates. Given that these intermediates are frequently energetically close to the ground state structures ($\Delta G^{\ddagger} < 13$ kcal/mol), it is possible that the coordination of additional ligands to the metal center might favor a more open form of the complex (Scheme 5). This distinction is further illustrated by structural variations in $Ti_2(R_2BINO)$(O-*i*-Pr)$_6$ species, where R = Me generates a classic dioxadititanacycle structure through bridging O-*i*-Pr groups, while R = *t*-BuMe$_2$Si supports an "open" complex with two isolated Ti(O-*i*-Pr)$_3$ units.[23] Spectroscopic studies of the Ti_2(diolate)Cl_6 complexes unfortunately do not provide such detailed structural information. The weaker bond strengths of bridging chloride ligands might result in lower activation barriers for intramolecular rearrangement than those found in alkoxide bridged complexes.

Scheme 5



Scheme 6



Ligand induced molecular fragmentation is another potential pathway for the formation of an active catalyst species.[20] TiX_4 fragments both induce molecular fragmentation, as is demonstrated in the equilibrium studies outlined above, and participate in independent intermolecular exchange processes, as was observed for $Ti_2(Me_2BINO)$(O-*i*-Pr)$_6$. It is possible that ligating organic substrates could favor the formation of mononuclear complexes (Scheme 6). The heterolytic cleavage pathway would generate potentially highly active cationic Lewis acids, albeit at the thermodynamic expense of generating ion pairs.

All of these structural conclusions support many of Mikami's suppositions about his "Ti(BINO)Cl$_2$" catalyst.[25] The highly enantiomerically enriched products of the glyoxylate ene reaction observed even in the presence of

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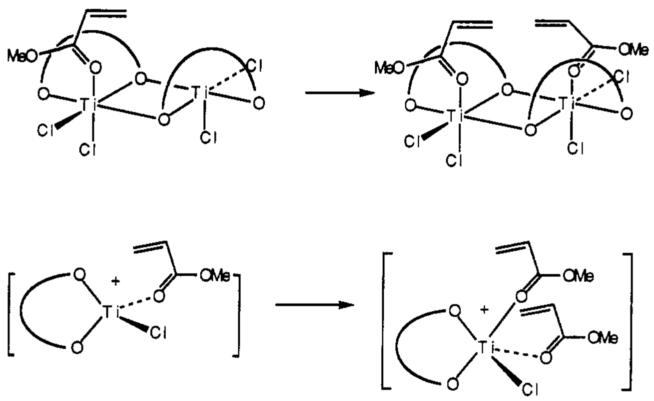
[40] Solari, E.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1989**, 1747.

a partially optically pure catalyst ("enantiomeric amplification") probably stem from the presence of diastereomeric titanium aggregates, in which the homochiral diastereomer is significantly more reactive than the racemic diastereomer.[25] This amplification mechanism could not operate for $Ti_2(Me_2BINO)_2Cl_4$, because both the racemic and optically pure forms of the Me_2BINO catalyst favor the same diastereomeric structure in solution. Our study does, however, raise some interesting questions about the rest-state structure of the BINO-substituted catalyst. On the basis of the available structural data, there is no compelling reason to believe that a *rac*-$Ti_2(BINO)_2Cl_4$ complex would either be formed in preference to or have a greater barrier to scission than its (R^*,R^*)-$Ti_2(BINO)_2Cl_4$ diastereomer. Moreover, if the BINO system follows the structural analogy established by $Ti_2(Me_2BINO)_2X_4$ (X = Cl or O-*i*-Pr), then "(*R*)-Ti(BINO)Cl_2" may adopt the trinuclear structure previously noted (4).[27]

Mechanistic Considerations in the Catalyst Behavior of $Ti_2(Me_2BINO)_2Cl_4$. Before embarking on a discussion of the kinetics of the metal catalyzed Diels–Alder reaction, it is worth examining the information that can be gained from the initial spectroscopic studies of the dititanium catalysts. The catalyst is dinuclear in solution in the absence of added Lewis bases and is unaltered spectroscopically over a range of temperatures by the addition of the methyl acrylate dienophile. Subsequent kinetic studies of the Diels–Alder process confirm that the methyl-5-carboxynorbornene product fails to significantly alter the spectroscopy of the titanium dimer. From these studies, we can infer that during the catalytic reaction the titanium Lewis acid exists primarily in its dinuclear rest state. This does not directly address the question of whether the catalyst is acting as a mononuclear or dinuclear species.

The existence of a mononuclear catalyst, formed through the homolytic fragmentation of the dititanium precursor, is ruled out by the strict first order dependence of the reaction on titanium concentration. Were a homolytic cleavage process to occur spontaneously as a prelude to methyl acrylate binding, or through ligand induced catalyst cleavage, the reaction would exhibit deviations from first order behavior in titanium. The same behavior would be expected for the heterolytic cleavage of the titanium dimer if the ions formed were independently solvated.[41] Given the relatively nonpolar nature of both the reaction medium and the catalyst, it seems very likely that any ionic species formed by heterolytic dissociation would exist as a tight ion pair, exhibiting kinetics similar to those of an intact dinuclear complex. The elimination of "Ti(Me_2BINO)Cl_2" as a potential catalytically active species also has implications in Mikami's proposed mechanism for the "Ti(BINO)Cl_2" catalyst.[25] If the Me_2BINO substituted catalyst fails to undergo homolytic scission to generate an active moiety, then it seems unlikely that complexes containing the less sterically demanding BINO ligand would proceed through a related dissociative process. The catalyzed reaction is clearly favored at low temperatures, and over the temperature range relevant to the asymmetric catalysis and kinetic studies, the barrier to the uncatalyzed reaction remains between 3 and 4 kcal/mol higher than that of the catalyzed process. Calculated rate constants covering the temperature range of the asymmetric reactions indicate that the catalyzed reaction maintains a 10^3–10^2 rate advantage over the uncatalyzed Diels–Alder process, demonstrating that product ee is not significantly affected by the uncatalyzed reaction.

Scheme 7



This leads to the conclusion that variations in the product ee as a function of catalyst to dienophile ratio probably result from the ability of the active catalyst species to bind either 1 or 2 equiv of organic substrate. The rapid reversible binding of either a second equivalent of dienophile or an equivalent of norbornene ester product at a site proximal to the reactive dienophile could account for this effect. Such multiple binding could occur at either an intact dinuclear catalyst or at a heterolytically cleaved fragment (Scheme 7). The mechanism involving the heterolytically cleaved mononuclear catalyst seems unlikely in that the binding of a second equivalent of substrate or product might be expected to affect more directly the kinetics of cycloaddition at the reactive dienophile. In contrast, an intact dinuclear catalyst would separate the second substrate from the adjacent active site. For this reason, we most strongly favor the intact dimer as the likely catalyst for the cycloaddition reaction.

This study emphasizes that Lewis acid catalysts that generate organic products with consistent enantioselectivity regardless of catalyst to substrate stoichiometry need to possess a single type of binding site that is sterically isolated from adjacent active sites. This factor adds further weight to arguments against the formulation of such catalysts, particularly those with nonsterically demanding ligands, as mononuclear. If we again reflect on the potential trinuclear structure for the "Ti(BINO)Cl_2" glyoxylate ene catalyst, it is noteworthy that the five-coordinate titanium centers, which are logical sites for dienophile binding, are positioned at opposing ends of the trinuclear structure and are probably sufficiently remote to act as independent binding sites. On the basis of this criterion, 4 might be considered a good candidate for the structure of the active species in the BINO catalyst mixture.

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[41] Note that equilibria for the formation of both heterolytically cleaved mononuclear ions and the homolytically cleaved neutral monomers both have a second order concentration dependence:

$$\text{heterolytic cleavage } A \rightleftharpoons B^+ + C^- \quad K_{eq} = [B^+][C^-]/[A]$$

$$\text{homolytic cleavage } A \rightleftharpoons 2B \quad K_{eq} = [B]^2/[A]$$

In contrast, the formation of a tight ion-paired catalyst species has a first order concentration dependence:

$$A \rightleftharpoons [B^+C^-] \quad K_{eq} = [B^+C^-]/[A]$$

Conclusions

(1) The structurally well characterized $Ti_2(Me_2BINO)_2Cl_4$ complex acts as a Lewis acid catalyst in the Diels–Alder cycloaddition of cyclopentadiene to methyl acrylate.

(2) An X-ray structural analysis of the complex shows the formation of a dioxadititanacycle through unidentate bridging binaphtholate ligands of like stereochemistry for molecules prepared with both racemic and optically pure Me_2BINO. Solution molecular weight studies indicate that the molecule maintains a dinuclear rest state in solution.

(3) The rate law for the catalytic process is rigorously first order in titanium catalyst, dienophile, and diene, indicating that the cycloaddition step is rate determining.

(4) Spectroscopic studies in the presence of excess methyl acrylate show no evidence for the formation of new metal complexes in solution. This result, taken together with the first order dependence on titanium concentration, indicates that the active form of the catalyst is not a small concentration of a mononuclear species, but is instead some form of dinuclear molecule.

(5) The maximum ee obtained with the catalyst is 26% at a 2:1 titanium ion to methyl acrylate ratio. Moreover, the enantiomeric purity of the Diels–Alder product is dependent on the methyl acrylate to titanium stoichiometry, suggesting that the active catalyst possesses proximate dienophile binding sites.

(6) Because the rate acceleration engendered by increased solvent polarity is minor, we favor the dinuclear structure observed in a solid phase as the best structural model for the active catalyst.

This catalyst exhibits many principles of structure and reactivity common to other diolate substituted titanium catalyst systems. The most important of these observations appears to be that asymmetric catalysts with multiple stereochemically interacting ligand binding sites will not demonstrate uniform enantioselectivities over a broad range of catalyst:substrate ratios. We are currently investigating other models of group 4 Lewis acid catalyst systems.

Experimental Section

All manipulations were performed under an inert atmosphere of N_2 using standard Schlenk, vaccum line, and glovebox techniques. NMR spectra were recorded on a Varian XL-300 or a Bruker AM-500 spectrometer, with ^1H chemical shift values referenced against the residual proton resonances of chloroform-*d* or toluene-d_8 and ^{13}C resonances referenced against the methyl carbon resonance of toluene-d_8 or the methine carbon resonance of chloroform-*d*. Solvents were distilled over the appropriate drying agents and degassed prior to use, while NMR solvents were degassed and dried over 5-Å molecular sieves. Optical rotations were recorded with a Perkin-Elmer 241 polarimeter and referenced to literature values.[42] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, 56-19 37th Ave., Woodside, NY 11377. 1,1′-Bi-2-naphthol,[43] biphenanthrol,[44] 3,3′-dimethyl-1,1′-bi-2-naphthol,[45] and the corresponding silyl ethers[30] were prepared by literature methods. (*R*)-(+)-1,1′-bi-2-naphthol and $TiCl_4$ were purchased from Aldrich and used as received.

$Ti_2(Me_2BINO)_2Cl_4$. Method A. To a solution of $TiCl_4$ (0.58 g, 3.1 mmol) in dichloromethane (30 mL) at −78 °C was added solid Li_2Me_2BINO (1.0 g, 3.1 mmol) over a 10-min period. The resulting red solution was allowed to warm to room temperature and then was filtered. The filtrate was dried in vacuo, redissolved in Et_2O, and cooled to yield red crystals in a 68% yield.

Method B. A solution of $Me_2BINO(TMS)_2$ (1.42 g, 3.1 mmol) in toluene at −78 °C was added dropwise to a solution of $TiCl_4$ (0.58 g, 3.1 mmol) in toluene at −78 °C. The solution was allowed to warm to room temperature and then was stripped to dryness. The red solid was redissolved in toluene, layered with hexane, and cooled to yield red crystals in a 70% yield. ^1H NMR data (toluene-d_8, 20 °C): δ 7.59 (2H, d, J = 4.1 Hz), 7.36 (2H, s), 7.15 (2H, t, J = 7.0 Hz), 7.09 (2H, d, J = 4.2 Hz), 6.88 (2H, t, J = 7.2 Hz), 2.13 (6H, s, *Me*$_2$BINO). ^{13}C NMR data (toluene-d_8, 20 °C): δ 164.8, 132.1, 131.9, 130.7, 127.8, 127.5, 127.4, 126.6, 126.2, 17.8. Anal. Calcd: C, 61.28; H, 3.74. Found: C, 61.48; H, 4.18.

$Ti_2(Me_2BINO)Cl_6$. A solution of $Me_2BINO(TMS)_2$ (1.42 g, 3.1 mmol) in toluene was added to $TiCl_4$ (1.16 g, 6.2 mmol) in toluene at −78 °C. The solution was allowed to warm to room temperature and then was dried in vacuo. When the reaction is performed with optically pure $Me_2BINO(TMS)_2$, crystals can be isolated from a solution in toluene layered with hexane in 52% yield. ^1H NMR data ($CDCl_3$, 20 °C): δ 7.86 (2H, d, J = 8.3 Hz), 7.83 (2H, s), 7.48 (2H, td, J = 6.8 Hz, 1.4 Hz), 7.34 (2H, td, J = 6.8 Hz, 1.4 Hz), 7.24 (2H, d, J = 8.3 Hz), 2.74 (6H, s, *Me*$_2$BINO). ^{13}C NMR data ($CDCl_3$, 20 °C): δ 158.6, 132.0, 131.8, 130.2, 128.5, 127.9, 127.2, 127.1, 126.0, 121.7, 18.1. Anal. Calcd: C, 42.56; H, 2.60. Found: C, 42.09; H, 2.76.

$Ti_2(BIPHENO)_2Cl_4$. Solutions of $BIPHENO(TMS)_2$ (1.0 g, 1.88 mmol) and $TiCl_4$ (0.72 g, 1.88 mmol) in toluene were mixed at −78 °C and then warmed to room temperature. The solution was then heated to reflux for 18 h. It was stripped to dryness and redissolved in toluene to yield red crystals in a 10% yield. ^1H NMR data ($CDCl_3$, 20 °C): δ 8.74 (4H, overlapping doublets, J = 3.6 Hz), 7.61 (4H, m, J = 8.5 Hz), 7.31 (4H, m, J = 3.8 Hz), 7.13 (2H, d, J = 8.0 Hz), 7.0 (2H, t, J = 8.0 Hz), 7.0 (2H, t, J = 8.0 Hz). ^{13}C NMR data ($CDCl_3$, 20 °C): δ 166.4, 131.6, 131.0, 129.4, 128.9, 128.4, 128.3, 128.1, 127.9, 127.4, 125.2, 123.5, 123.3, 122.9.

$Ti_2(BIPHENO)Cl_6$. To a solution of $[(BIPHENO)TiCl_2]_2$ in $CDCl_3$ was added 2 equiv of $TiCl_4$. This complex is stable only in solution and cannot be isolated in the solid state. ^1H NMR data ($CDCl_3$, 20 °C): δ 8.84 (2H, d, J = 7.8 Hz), 8.79 (2H, d, J = 7.8 Hz), 8.61 (2H, d, J = 7.6 Hz), 7.86 (4H, m, J = 7.8 Hz, 1.8 Hz), 7.70 (2H, m, J = 2.8 Hz), 7.47 (4H, m, J = 2.4 Hz). ^{13}C NMR data ($CDCl_3$, 20 °C): δ 159.6, 128.1, 131.5, 130.9, 129.3, 128.8, 128.3, 128.2, 127.9, 127.2, 125.1, 123.4, 123.2, 122.7.

Diels–Alder Reactions. The catalyst was dissolved in CH_2Cl_2, and the solution was cooled to −78 °C. Methyl acrylate was added by syringe, and the mixture was stirred at −78 °C for 10 min. Freshly distilled cyclopentadiene was then added, and the mixture was stirred at −78 °C for 10 h and then at −20 °C for 12 h. HCl (2 M) was added (5 mL), and the organic layer was extracted with 3 × 3-mL aliquots of 10% NaOH. The organic solvent was removed by distillation to yield the product. Conditions for the catalytic reaction (20 methyl acrylate:1 Ti): mass of catalyst, 0.14 g; volume of methyl acrylate, 0.60 mL; volume of cyclopentadiene, 0.87 mL; volume of CH_2Cl_2, 2.8 mL. $[\alpha]_D^{20} = +10.3$ (c = 1, 95% ethanol). Conditions for the stoichiometric reaction (1 methyl acrylate:1 Ti): mass of catalyst, 0.380 g; volume of methyl acrylate, 0.08 mL; volume of cyclopentadiene, 0.14 mL; volume of CH_2Cl_2, 1.0 mL. $[\alpha]_D^{20} = -28.9$ (c = 0.6, 95% ethanol).

Kinetic Studies. The kinetics of the Diels–Alder reactions were monitored by measuring the disappearance of the methyl acrylate methyl resonance and the appearance of the methyl resonance of the product by ^1H NMR at 20 °C.

Structure Determination on (R^*,R)-$Ti_2(Me_2BINO)_2Cl_4$. A red-brown prismlike crystal of $Ti_2(Me_2BINO)_2Cl_4$ of approximate dimensions 0.2 × 0.2 × 0.3 mm was sealed into a thin walled glass capillary under nitrogen gas. All measurements were

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[42] Berson, J. A.; Ben-Efraim, D. A. *J. Am. Chem. Soc.* **1959**, *81*, 4083.

[43] Brussee, J.; Groenendijk, J. L. G.; te Koppele, J. M.; Jansen, A. C. A. *Tetrahedron* **1985**, *41*, 3313.

[44] Yamamoto, K.; Fukushima, H.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1490.

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Table 5. Summary of Crystal Data for $Ti_2(Me_2BINO)_2Cl_4$

empirical formula	$Ti_2Cl_4O_4C_{44}H_{32}$
color of cryst, habit	brown, prism
cryst dimens, mm	0.2 × 0.2 × 0.3
space group, syst	$P2_1/n$, monoclinic
cell dimens (25 °C)	
a, Å	15.307(3)
b, Å	12.007(1)
c, Å	21.948(2)
β (°)	99.13
V, $Å^3$	3983(1)
Z, molecules/cell	4
d(calculated), g/cm^3	1.438
X-ray radiation (λ, Å)	Cu Kα (1.541 78)
MW	862.35
linear abs coeff cm^{-1}	63.07
av ω scan width, deg	0.40
scan speed, deg/min	8.0
scan width, deg + dispersion background range	1.15 + 0.30 tan θ
aperture size (vert × horiz) mm	6.0 × 6.0
$2\theta_{max}$, deg	112.6
total no. of reflns collcd	5781
no. of unique intensities	5541
$R(F)$	0.036
$R_w(F)$	0.049
goodness of fit for last cycle	1.19
Δ/s for last cycle	0.21
temp, °C	21

made on a Rigaku AFC5R diffractometer with graphite monocromated Cu Kα radiation from a 12-kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least squares refinement using 23 centered reflections in the range $69.73 < 2\theta < 69.99°$. On the basis of systematic absences of $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$) and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (No. 14). Cell constants and structural data are collected in Table 5. Of the 5781 reflections measured, 5541 were unique ($R_{int} = 0.031$). Equivalent reflections were merged. Monitoring three representative reflections indicated that no decay correction was required. An empirical absorption correction, based on azimuthal scans of several reflections, was applied. Transmission factors ranged from 0.55 to 1.00. The data were also corrected for Lorentz and polarization effects. The structure was solved by direct methods.[46] The non-hydrogen and hydrogen atoms were refined anisotropically and isotropically, respectively. The final cycle of full-matrix least squares refinement[47] was based on 4159 observed reflections ($I > 3.00\sigma(I)$) and 607 variable parameters and converged with unweighted and weighted agreement factors of

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.036$$

$$R_w = [(\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)]^{1/2} = 0.049$$

The largest shift of positional parameters was 0.21 times its esd. The standard deviation of an observed unit weight[48] was 1.19. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$ and various other classes of indices showed no unusual trends. The maximum and minimum peaks in the final difference Fourier map corresponded to +0.31 and −0.22 e A^{-3}, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[49] Anomalous dispersion effects were included in F_c;[50] the values of $\Delta f\, m$ and $\Delta f''$ were those of Cromer.[51] All calculations were performed using the TEXSAN[52] crystallographic software package of the Molecular Structure Corp.

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Supplementary Material Available: Tables of experimental data, anisotropic thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

OM9402123

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(46) Structure Solution Methods: Gilmore, C. J. MITHRIL—an integrated direct methods computer program. *J. Appl. Crystallogr.* **1984**, *17*, 42–46 (University of Glasgow, Scotland). Beurskens, P. T. DIRDIF: Direct Methods for Difference Structures—an automatic procedure for phase extension and refinement of difference structure factors. Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, Netherlands.

(47) Least-squares: The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$ (S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, and p = p factor).

(48) Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

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(52) TEXSAN-TEXRAY Structure Analysis Package. Molecular Structure Corp., 1985.