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Methods for the Synthesis of the Diels−Alder Catalysts $(ArO)_2TiX_2$ (X = Cl, Br, I; Ar = 2-*tert*-Butyl-6-methylphenyl)

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Summary: A procedure for converting titanium diethylamidos to the corresponding dihalides (Cl, Br, I) and a complementary method for converting titanium dichlorides into dibromides and diiodides are reported. These methods were utilized to synthesize a family of homogeneous and polymer-supported Diels−Alder catalysts with the general formula $(ArO)_2TiX_2$ *(X = Cl, Br, I; Ar = 2-tert-butyl-6-methylphenyl).*

In the context of a broader program aimed at developing transition metal catalysts whose selectivity has an outer-sphere component, our lab has recently become interested in the chemical manipulation of titanium aryloxide complexes.[1] As part of these efforts, we wish to report methods for synthesizing and interconverting $(ArO)_2TiX_2$ complexes (good Diels−Alder catalysts) that are amenable to polymer-bound analogues (X = Cl, Br, I; Ar = 2-*tert*-butyl-6-methylphenyl).

$$\underset{\textbf{1a}}{(ArO)_2Ti(NEt_2)_2} + 10\ \text{equiv}\ SiX_4 \xrightarrow[\text{toluene}]{-\,2\ Et_2NSiX_3} (ArO)_2TiX_2 \qquad (1)$$

2a: X = Cl (50 %)
2b: X = Br (42 %)
2c: X = I (13 %)

$$\underset{\textbf{2a}}{(ArO)_2TiCl_2} + 1.1\ \text{equiv}\ BX_3 \xrightarrow[\text{toluene}]{-\,Cl_2BX} (ArO)_2TiX_2 \qquad (2)$$

2b: X = Br (52 %)
2c: X = I (35 %)

Treatment of the bisamido compound **1a** with excess SiX_4 (X = Cl, Br) in toluene at 23 °C results in rapid conversion to the dihalides **2a** and **2b**, respectively (>95% pure by ^1H NMR; eq 1).[2] The silicon-containing byproducts were removed in vacuo, and **2a**/**2b** were purified in modest yield by recrystallization from toluene/hexanes (−35 °C). The synthesis of the diiodide **2c** required more forcing conditions, as the reaction of **1a** with SiI_4 at room temperature stopped at the pale yellow $(ArO)_2Ti(NEt_2)I$. Warming to 60 °C, however, cleanly converted this material to the diiodide **2c**, which was purified by first subliming away the silicon-containing byproducts and then recrystallizing from pentane (−35 °C). The poor yields for these complexes reflect their high solubility.

Another synthetic route into the dihalide compounds **2b** and **2c** is shown in eq 2. Treatment of **2a** with BX_3 (X = Br, I) resulted in immediate conversion to **2b** and **2c** (>95% pure by ^1H NMR).[3] Removal of the boron-containing byproducts in vacuo followed by recrystallization gave the dibromide and diiodide with yields improved over the SiX_4 route. We favor the BX_3 route for scale-up for reasons of yield and ease of preparing **2a** (see Experimental Section, method 1). The former method, however, has several advantages for the synthesis of polymer-immobilized catalysts (vide infra).

The ^1H NMR spectra of the series of dihalide compounds show some interesting features. On going from chloride to bromide to iodide, an upfield shift is seen in the methyl resonances (Cl = 2.15, Br = 2.10, I = 2.0 ppm), while the *tert*-butyl resonances shift downfield (Cl = 1.55, Br = 1.60, I = 1.70 ppm). A similar trend has been observed in the series $Ti(ebmp)X_2$ (ebmp = 2,2′-ethylenebis(6-*tert*-butyl-4-methylphenyl); X = Cl, Br, I).[4]

Red crystals of **2a** suitable for X-ray crystallography were grown from a saturated toluene solution layered with pentane at −35 °C (Figure 1). The pseudo-C_2-symmetric structure is monomeric with a tetrahedral coordination geometry around titanium. The relatively short titanium−oxygen bond lengths (1.753(4) and 1.752(5) Å) as well as the large angles at oxygen (162.2(4)° and 163.4(4)°) suggest substantial $p\pi-d\pi$ donation from oxygen to the formally eight-electron titanium center.[5] The metrical parameters for **2a** are nearly identical to the crystal structure of $Ti(ebmp)Br_2$, suggesting that the chelating ligand in the latter is virtually free of torsional strain.[2b]

We recently reported the use of polymer immobilized $(ArO)_2TiCl_2$ as a catalyst for the Diels−Alder reaction.[1]

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[1] Santora, B. P.; Larsen, A. O.; Gagné, M. R. *Organometallics* **1998**, *17*, 3138−3140.

[2] (a) For the cleavage of $Ti-O^iPr$ with $SiCl_4$, see: Corey, E. J.; Matsumura, Y. *Tetrahedron Lett.* **1991**, *32*, 6289−6292. (b) For the cleavage of $Ti-O^iPr$ with Me_3SiX (X = Br, I), see: Fokken, S.; Spaniol, T. P.; Okuda, J.; Sernetz, F. G.; Mulhaupt, R. *Organometallics* **1997**, *16*, 4240−4242. (c) For the cleavage of $M-NMe_2$ (M = Ti, Zr) with Me_3SiCl, see: Jones, R. A.; Hefner, J. G.; Wright, T. C. *Polyhedron* **1984**, *3*, 1121−1124. (d) For the cleavage of $Ti-NMe_2$ with MeI, see: Johnson, A. R.; Wanandi, P. W.; Cummins, C. C.; Davis, W. M. *Organometallics* **1994**, *13*, 2907−2909. (e) For the cleavage $M-NMe_2$ (M = Ti, Zr) with HCl or $NMe_3\cdot HCl$ see: Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572-1581. (f) For the cleavage of $Zr-NMe_2$ with $Me_2NH\cdot HCl$ see: Scollard, J. D.; McConville, D. H.; Vittal, J. L. *Organometallics* **1995**, *14*, 5478−5480. (g) For the cleavage of $Ti-CH_2Ph$ with I_2, see: Tsuie, B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1997**, *16*, 1392−1400.

[3] For the conversion of Cp_2MCl_2 to Cp_2MX_2 with BX_3 (M = Ti, Zr, Hf; X = Br, I), see: Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. (A)* **1969**, 2106−2110.

[4] Footnote 2b and: Fokken, S. Ph.D. Dissertation, University of Mainz, 1997.

[5] For the effect of $p_\pi-d_\pi$ bonding in Ti−aryloxide complexes, see: (a) Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P. *Inorg. Chem.* **1985**, *24*, 995−1001. (b) Durfee, L. D.; Latesky, S. L.; Rothwell, I. P.; Huffmann, J. C.; Folting, K. *Inorg. Chem.* **1985**, *24*, 4569−4573. (c) For a discussion of the problems associated with utilizing the C−O−M bond angle in early transition metal aryloxide complexes as a probe for the magnitude of $p_\pi-d_\pi$ bonding, see: Steffey, B. D.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1990**, *9*, 963−968.

10.1021/om9808099 CCC: $18.00

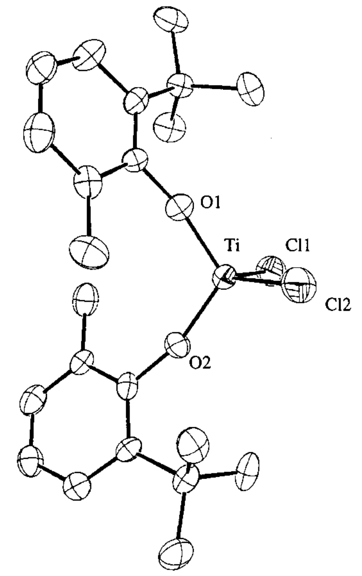
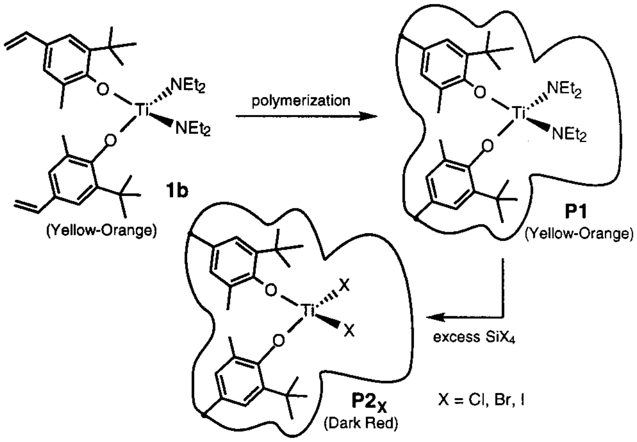
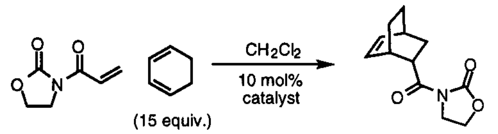


Figure 1. ORTEP drawing of $(ArO)_2TiCl_2$ (**2a**) with ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ti−O1, 1.753 (4); Ti−O2, 1.752(5); Ti−Cl1, 2.217(3); Ti−Cl2, 2.207(3); O1−Ti−O2, 112.63(22); Cl1−Ti−Cl2, 110.33 (11); C−O1−Ti, 162.2(4); C−O2−Ti, 163.4(4).

Scheme 1



To extend this chemistry, we have used the reactions described above to prepare homogeneous and polymer-immobilized dibromide and diiodide catalysts as well. To synthesize the polymer-immobilized catalysts, the strategy in Scheme 1 was employed wherein metallomonomer **1b** was incorporated into a highly cross-linked, yet porous polymer matrix. In analogy with the solution chemistry, treatment of the yellow-orange insoluble polymer **P1** with SiX_4 changes its color to the dark reds characteristic of the dihalide catalysts. Even with large lumps of polymer (~0.5 cm^3), the color changed throughout the polymer. Removal of the silicon byproducts reveals the red, insoluble polymers we formulate as $\mathbf{P2_X}$ (X = Cl, Br, I). Surface area analysis (BET) of these polymers indicates very high surface areas (~500−600 m^2/g polymer), suggestive of a stable porous organic network.



(3)

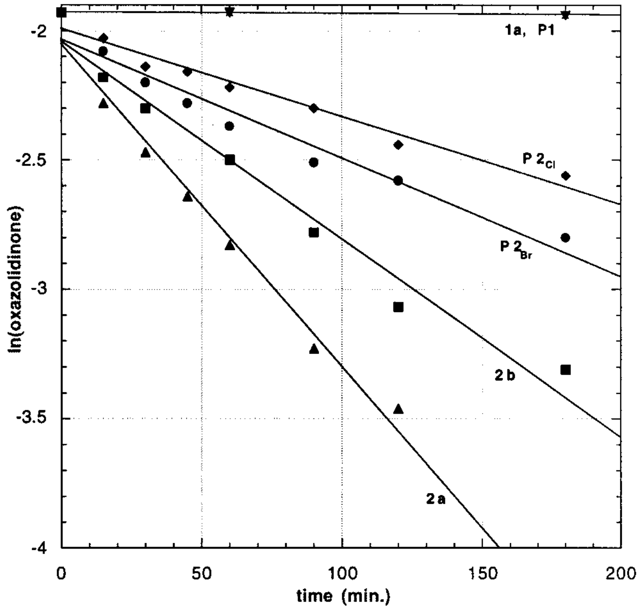


Figure 2. Plots of ln[dienophile] vs time (pseudo-first-order in diene, 33 °C) for the catalysts **1a** (▼), **P1** (×), **2a** (▲), $\mathbf{P2_{Cl}}$ (◆), **2b** (■), and $\mathbf{P2_{Br}}$ (●).

The compounds $(ArO)_2TiX_2$ and the polymers $\mathbf{P2_X}$ were evaluated as catalysts for the Diels−Alder reaction between 3-acryloyloxazolidinone and 1,3-cyclohexadiene (eq 3). Monitoring the rate of disappearance of dienophile by GC yielded the plots highlighted in Figure 2. As expected, the π-basic bisamido ligand set of **1a** and **P1** showed negligible activity.[6] As previously reported, $\mathbf{P2_{Cl}}$ ($k_{obs} = 3.4 \times 10^{-3}$ s^{-1}) is roughly 3 times slower than its solution analogue **2a** ($k_{obs} = 12 \times 10^{-3}$ s^{-1}).[1] Intriguingly, the polymer-bound catalyst $\mathbf{P2_{Br}}$ ($k_{obs} = 4.5 \times 10^{-3}$ s^{-1}) is slightly *faster* than $\mathbf{P2_{Cl}}$, while its solution analogue **2b** ($k_{obs} = 7.5 \times 10^{-3}$ s^{-1}) is *slower* than the dichloride solution catalyst. Poorly behaved kinetics consistent with strong product inhibition or catalyst death were observed with the diiodide catalysts **2c** and $\mathbf{P2_I}$ (not shown). The diiodide-based catalysts were initially competitive, but after 3 or 4 turnovers their activity dropped dramatically and was accompanied (in solution) by an off-white precipitate. Dichloride and dibromide reaction rates (polymer and solution) were reproducible within 5−10%, represent averages of two runs, and were accompanied by only slight clouding of the homogeneous reaction solutions. Control experiments further indicate that SiX_4 (X= Cl, Br, and I) are not Diels−Alder catalysts and that polymer removal midway through catalysis runs halts the conversion to product. The latter controls are consistent with catalysis occurring in the polymer matrix, not from leached complex. All catalysts gave a product endo:exo diastereoselectivity of 98:2, with the solution catalyst **2a** and polymer-bound catalyst $\mathbf{P2_{Cl}}$ giving the Diels−Alder product in 68% and 75% isolated yields, respectively.

In summary, we have developed two complementary methods for synthesizing the Diels−Alder catalysts $(ArO)_2TiX_2$ (X = Cl, Br, I) and their polymer-immobilized analogues. We hope that the synthetic meth-

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[6] Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309−1312.

odologies highlighted herein will be useful in synthesizing dihalide complexes from both dialkylamido and dichloride complexes of titanium.

Experimental Section

All reactions were carried out under an atmosphere of dry argon or nitrogen using standard Schlenck techniques or in a MBraun Lab-Master 100 glovebox. All solvents were dried by passing through a column of activated alumina[7] and stored under argon prior to use. C_6D_6 was vacuum transferred from sodium/benzophenone-ketyl, and CD_2Cl_2 was distilled from CaH_2. Both protiated and deuterated solvents were freeze−pump−thaw degassed before use. 3-Acryloyloxazolidin-2-one was prepared according to literature procedures.[8] All reagents were obtained from Aldrich and stored under a nitrogen atmosphere. $TiCl_4$, $SiCl_4$, and BI_3 were used as received. 2-*tert*-Butyl-6-methylphenol (ArOH) was dried over activated molecular sieves prior to use. $SiBr_4$ was heated under reflux and vacuum transferred. BBr_3 was shaken with mercury, heated under reflux, and distilled.[3] SiI_4 was sublimed under vacuum prior to use. Styrene and technical grade divinylbenzene were distilled from CaH_2 and freeze−pump−thaw degassed before use. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from MeOH and dried under vacuum. Cyclohexadiene was distilled from $NaBH_4$. Gas chromatography was performed on an HP-5 column (30 m × 0.32 mm). NMR spectra were recorded on Bruker WM250 and Bruker AC200 spectrometers for ^1H and ^{13}C, respectively, and referenced to internal solvent signals. Surface area analyses (nitrogen BET) were performed at DuPont CR&D. Elemental analyses of the solution catalysts were performed by E&R Microanalytical Laboratory, Inc., Parsippany, NJ. The polymer catalysts were analyzed by neutron activation at the North Carolina State University nuclear science center, Raleigh, NC.

$(ArO)_2Ti(NEt_2)_2$ (1a). A 25 mL solution of ArOH (2-*tert*-butyl-6-methylphenol, 3.175 g, 19.36 mmol) in toluene was added to a 100 mL solution of $Ti(NEt_2)_4$ (3.257 g, 9.73 mmol) in toluene (23 °C). The orange solution was stirred for 12 h at room temperature, followed by solvent removal in vacuo to yield **1a** as a yellow solid. The product was purified by recrystallization from Et_2O/pentane at −35 °C (4.52 g, 90% yield). ^1H NMR (250 MHz, C_6D_6): δ 7.27 (m, 2H), 7.05 (m, 2H), 6.82 (m, 2H), 3.70 (q, $J = 7.0$ Hz, 8H), 2.34 (s, 6H), 1.58 (s, 18H), 0.81 (t, $J = 7.0$ Hz, 12H). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 13.8, 18.6, 30.5, 35.2, 46.2, 119.9, 124.6, 128.8, 129.2, 137.6, 163.0. Anal. Calcd for $C_{30}H_{50}N_2O_2Ti$: C, 69.48; H, 9.72; N, 5.40. Found: C, 69.76; H, 10.00; N, 5.23.

(p-vinyl-ArO)$_2$Ti(NEt$_2$)$_2$ (1b). A 3 mL solution of *p*-vinyl-ArOH[1] (1.02 g, 5.34 mmol) in toluene was added dropwise to a 10 mL solution of $Ti(NEt_2)_4$ (0.895 g, 2.67 mmol) in toluene (23 °C). The orange solution was stirred for 2 h at 23 °C, followed by solvent removal in vacuo to give the yellow solid **1b**. The yellow product was purified by recrystallization from Et_2O/pentane at −35 °C (1.33 g, 87% yield). ^1H NMR (250 MHz, C_6D_6): δ 0.80 (t, $J = 7.1$ Hz, 12 H), 1.60 (s, 18H), 2.34 (s, 6H), 3.70 (q, $J = 7.1$ Hz, 8H), 5.10 (dd, $J = 10.8$, 1.1 Hz, 2H), 5.68 (dd, $J = 17.6$, 1.1 Hz, 2H), 6.70 (dd, $J = 17.6$, 10.8 Hz, 2H), 7.20 (m, 2H), 7.40 (m, 2H). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 13.3, 18.0, 29.8, 34.6, 45.7, 109.9, 122.5, 126.2, 128.6, 137.0, 162.7. Anal. Calcd for $C_{34}H_{54}N_2O_2Ti$: C, 71.56; H, 9.54; N, 4.91. Found: C, 71.33; H, 9.72; N, 5.05.

$(ArO)_2TiCl_2$ (2a). Method 1.[9] $TiCl_4$ (1.63 mL, 14.6 mmol) was added to 2-*tert*-butyl-6-methylphenol (ArOH, 29.2 mmol) dissolved in 50 mL of Et_2O at 0 °C, and then the homogeneous red solution was stirred for 12 h at room temperature. The solvent was removed in vacuo to give **2a** in >95% purity as a red powder. The product was purified by recrystallization from toluene/pentane at −35 °C (6.08 g, 93% yield).

Method 2. $SiCl_4$ (0.33 mL, 2.8 mmol) was added to $(ArO)_2Ti(NEt_2)_2$ (148 mg, 0.28 mmol) **(1a)** dissolved in 10 mL of toluene at room temperature. The reaction mixture was stirred for 3 h at 23 °C and then concentrated in vacuo to give **2a**. The product was purified by recrystallization from toluene/hexanes at −35 °C (63 mg, 42%). ^1H NMR (250 MHz, C_6D_6): δ 7.05 (m, 2H), 6.70 (m, 4H), 2.15 (s, 6H), 1.50 ppm (s, 18H). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 18.7, 30.5, 35.3, 125.0, 125.1, 129.5, 131.5, 138.0, 168.9 ppm. Anal. Calcd for $C_{22}H_{30}Cl_2O_2Ti$: C, 59.34; H, 6.79. Found: C, 59.19; H, 7.03.

$(ArO)_2TiBr_2$ (2b). Method 1. $SiBr_4$ (1.0 g, 2.8 mmol) was added to $(ArO)_2Ti(NEt_2)_2$ (148 mg, 0.28 mmol) **(1a)** dissolved in 10 mL of toluene at room temperature. The dark red solution was stirred for 2.5 h at 23 °C and then concentrated in vacuo to give the dark red solid **2b**. The product was purified by recrystallization from toluene/hexanes at −35 °C (64.0 mg, 42% yield).

Method 2. BBr_3 (119 mg, 0.47 mmol) was added to $(ArO)_2TiCl_2$ (192 mg, 0.43 mmol) dissolved in 10 mL of toluene at room temperature, followed by stirring for 2 h at ambient temperature. The dark red solution was then concentrated in vacuo to give the dark red solid **2b**, which was purified by recrystallization from toluene/hexanes at −35 °C (120 mg, 52% yield). ^1H NMR (250 MHz, C_6D_6): δ 7.05 (m, 2H), 6.70 (m, 4H), 2.10 (s, 6H), 1.55 ppm (s, 18H). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 19.1, 30.7, 35.5, 125.0, 125.2, 129.6, 131.7, 137.9, 169.5 ppm. Anal. Calcd for $C_{22}H_{30}Br_2O_2Ti$: C, 49.47; H, 5.66. Found: C, 49.62; H, 5.94.

$(ArO)_2TiI_2$ (2c). Method 1. SiI_4 (683 mg, 1.27 mmol) was added to $(ArO)_2Ti(NEt_2)_2$ (132 mg, 0.25 mmol) (**1a**) dissolved in 10 mL of toluene at room temperature. The dark red solution was stirred for 6 h at 60 °C and then concentrated in vacuo to give a dark red tar containing **2c**, SiI_4, and Et_2NSiI_3. The silicon-containing byproducts were removed by sublimation onto a cold probe (60 °C, <1 mTorr), and then the red powder **2c** was recrystallized from pentane at −35 °C (20.0 mg, 12.5% yield).

Method 2. BI_3 (175 mg, 0.45 mmol) was added to $(ArO)_2TiCl_2$ (181 mg, 0.41 mmol) dissolved in 10 mL of toluene at room temperature. The dark red solution was stirred for 3 h at 23 °C and then concentrated in vacuo to give the dark red solid **2c**. The product was purified by recrystallizing from pentane at −35 °C (90 mg, 35% yield). ^1H NMR (250 MHz, C_6D_6): δ 7.05 (m, 2H), 6.75 (m, 4H), 2.00 (s, 6H), 1.65 ppm (s, 18H). $^{13}C\{^1H\}$ NMR (50.28 MHz, CD_2Cl_2): δ 19.7, 31.0, 35.7, 125.0, 125.1, 129.6, 132.0, 137.5, 169.9 ppm. Anal. Calcd for $C_{22}H_{30}I_2O_2Ti$: C, 42.06; H, 4.81. Found: C, 42.37; H, 4.86.

P1. Metallomonomer **1b** (100.0 mg, 0.175 mmol), AIBN (20.0 mg, 0.12 mmol), toluene (1.39 mL), styrene (0.30 mL), and tech grade divinylbenzene (1.09 mL) were combined in a 20 mL scintillation vial under nitrogen and sealed with a Teflon-lined cap. The vial was heated for 12 h at 80 °C followed by 12 h at 120 °C. The yellow-orange insoluble polymer was dried under high vacuum (<1 mTorr) for 12 h at 40 °C to give an isolated yield of 1.32 g of dried polymer. Anal. Calcd for **P1**: Ti, 0.61. Found: Ti, 0.59. Surface area: 570 m^2/g polymer.

$P2_{Cl}$. Under a nitrogen atmosphere, toluene (10 mL) was added to a sample of solvated **P1** (2.55 g polymer, 0.175 mmol Ti), giving a colorless liquid over a yellow polymer. $SiCl_4$ (0.4 mL, 20 equiv) was added at 23 °C, the reaction mixture was slowly stirred for 6 h at room temperature, and then the solvent was removed in vacuo. The red polymer was rinsed with Et_2O in a Soxhlet extractor for 6 h and then dried under vacuum (<1 mTorr) for 12 h at 40 °C to yield 1.32 g of **$P2_{Cl}$**. Anal. Calcd for **$P2_{Cl}$**: Ti, 0.61; Cl, 0.90. Found: Ti, 0.67; Cl, 0.89. Surface area: 530 m^2/g polymer.

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(7) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

(8) Ho, G. J.; Mathre, D. J. *J. Org. Chem.* **1995**, *60*, 2271−2273.

(9) Duff, A. W.; Kamarudin, R. A.; Lappert, M. F.; Norton, R. J. *J. Chem. Soc., Dalton Trans.* **1986**, 489−498.

$P2_{Br}$. Under a nitrogen atmosphere, $SiBr_4$ (0.44 mL, 20 equiv) was added to a sample of **P1** (2.55 g polymer, 0.175 mmol Ti) in toluene at room temperature. The reaction mixture was slowly stirred for 6 h at 23 °C, and then the solvent was removed in vacuo. The red polymer was rinsed with Et_2O in a Soxhlet extractor for 6 h and then dried under vacuum (<1 mTorr) for 12 h at 40 °C to yield 1.33 g of **$P2_{Br}$**. Anal. Calcd for **$P2_{Br}$**: Ti, 0.61; Br, 2.03. Found: Ti, 0.58; Br, 2.74. Surface area: 580 m^2/g polymer.

$P2_I$. Under a nitrogen atmosphere, SiI_4 (2.8 g, 20 eq) was added to a sample of **P1** (2.55 g polymer, 0.175 mmol Ti) in toluene at room temperature. The reaction mixture was slowly stirred for 6 h at 60 °C, and then the solvent was removed in vacuo. The red polymer was rinsed with Et_2O in a Soxhlet extractor for 6 h and then dried under vacuum (<1 mTorr) for 12 h to yield 1.36 g of **$P2_I$**. Anal. Calcd for **$P2_I$**: Ti, 0.61; I, 3.22. Found: Ti, 0.61; I, 4.19. Surface area: 620 m^2/g polymer.

Polymer Analysis. For a concise introduction to neutron activation analysis, visit the North Carolina State University Nuclear Science Center website at www.ne.ncsu.edu/NRP/naa.html. Theoretical amounts of titanium in the dried polymer catalysts were calculated as follows: initial amount of titanium added to the polymerization mixture × (weight of dried polymer sample/(total weight of all polymerizable components + weight of residual toluene)). Control experiments indicate that no styrene, DVB, or metallomonomer **1b** are rinsed out of the polymer, and roughly 0.5% residual toluene remains using the described drying procedure. Analyses of **$P2_{Br}$** and **$P2_I$** are slightly high for halide analysis, possibly due to SiX_4 trapped within the polymer matrix. Extracting the polymers for a longer time period led to decomposition of the titanium complexes. Control experiments also indicated that SiX_4 is not a catalyst for the Diels−Alder reaction (vide supra). Unfortunately, neutron activation is not amenable to silicon and nitrogen analysis.

Solution Catalysis. In the glovebox under a nitrogen atmosphere, $Ti(OAr)_2X_2$ (X = Cl, Br, I, NEt_2; 0.018 mmol), 3-acryloyloxazolidin-2-one (25.5 mg, 0.18 mmol), and 1,3-cyclohexadiene (255 μL, 2.7 mmol) were added to a 20 mL scintillation vial with 1 mL of CH_2Cl_2 at 33 °C. The reactions were monitored by periodically withdrawing aliquots via pipet and quenched by passing through a plug of silica gel with EtOAc, followed by GC analysis. Concentrations of 3-acryloyloxazolidin-2-one and cyclized product were obtained using known relative response factors for these materials (GC response factor was determined to be 1:2.75 for a dienophile:product concentration ratio of 1:1). The $Ti(OAr)_2(NEt_2)_2$-catalyzed reactions remained homogeneous throughout the course of the reaction, but extraneous peaks appeared in the GC after 48 h. Reaction kinetics were determined under pseudo-first-order conditions in dienophile (15-fold excess), and rate constants were obtained by plotting ln[dienophile] vs time (s).

Polymer Catalysis. In the glovebox under N_2 atmosphere, 3-acryloyloxazolidin-2-one (25.5 mg, 0.18 mmol), 1,3-cyclohexadiene (213.0 mg, 2.7 mmol), and 149 mg **$P2_{Br}$** (18 μmol based on 121 μmol Ti/g polymer) were added to a 20 mL scintillation vial with 1 mL of CH_2Cl_2 at 33 °C. The reaction was monitored by periodically taking aliquots via pipet, passing through a plug of silica gel with EtOAc, and analyzing by GC using the same protocol as the solution catalysis studies. The reaction kinetics were determined under pseudo-first-order conditions in dienophile (15-fold excess), and rate constants obtained by plotting ln[dienophile] vs time (s). Internal standards (e.g., decane) were not helpful, as they were observed to adsorb into the polymer matrix. Rate constants therefore reflect the rate of product formation in the solution above the polymer as determined from dienophile:product ratios.

Table 1. Crystallographic Data and Collection Parameters for 2a

formula	$TiCl_2C_{22}H_{30}O_2$
fw	445.28
color, habit	red, crystal
cryst size, mm	0.40 × 0.40 × 0.25
cryst syst	orthorhombic
space group	*Pbca*
a, Å	19.133(9)
b, Å	11.394(7)
c, Å	21.204(6)
V, Å^3	4623(4)
Z	8
T, °C	−100
D_c, g/cm^3	1.280
F(000)	1877.39
radiation, Å	Mo Kα (0.71073)
μ, mm^{-1}	0.61
scan mode	ω
data collected	h, k, l
$2\theta_{max,deg}$	50.0
total no. rflns	13393
no. of unique rflns	4020
R_{merge}	0.112
no. of rflns with $I > 2.5\sigma(I)$	2323
no. of variables	245
R_f[a]	0.066
R_w[b]	0.077
GoF[c]	2.22
max Δ/σ	0.080
residual density, e/Å^3	−0.89, 2.03

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

X-ray Data for 2a. Data were collected at −100 °C on a Rigaku AFC-6/S diffractometer using graphite-monochromated Mo Kα radiation. The structure of this weakly diffracting crystal was solved by direct methods, and non-hydrogen atoms were refined anisotropically (see Table 1).

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Supporting Information Available: Tables of metrical parameters for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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