A series of novel, air-stable ruthenium NHC catalysts with sulfonate and phosphate anions have been prepared easily in one pot at high yields using commercially available precursors. The catalysts were found to be effective for ring-opening metathesis polymerization, ring-closing metathesis, and cross-metathesis. The catalysts showed higher cis-selectivity in olefin cross-metathesis reactions as compared to earlier known ruthenium-based olefin metathesis catalysts, with allylbenzene and cis-1,4-diacetoxybutene as substrates.

**Introduction**

Olefin metathesis has become a standard method in the formation of C–C double bonds. In particular, olefin cross-metathesis (CM) is a convenient route to functionalize higher olefins from simple precursors. CM has gained prominence due to the availability of catalysts of varying activities such as the phosphine-based and the N-heterocyclic carbene (NHC)-based Ru catalysts and the molybdenum/tungsten-based catalysts. However, application of cross-metathesis has been relatively limited when compared to ring-opening metathesis polymerizations (ROMP) and ring-closing metathesis (RCM). This is a result of poor stereoselectivity of the olefin products at high conversions. Z-Selectivity is usually compromised at high conversions, where current ruthenium catalysts have a tendency to give high E/Z ratios (>6) at conversions >75%. Although phosphine-based catalysts give lower E/Z ratios than their NHC counterparts, they tend to decompose at conversions no more than 60%. A highly Z-selective molybdenum catalyst has been recently developed by Hoveyda and Schrock. These very important catalysts have numerous applications. However, as has been seen in the past, ruthenium-based catalysts can be more applicable in many situations. Although there are some ruthenium-based catalysts in recent literature that give better E/Z ratios than the more traditional catalysts, they are generally much less active. Other catalysts tend to have poor control over selectivity at high conversions as a result of secondary metathesis. The precatalysts themselves are also difficult to prepare with multistep synthesis and very low yields, making them less commercially viable. Z-Olefins are commonly found in natural products, and the ability to form Z-olefins from a single catalytic process remains important to synthetic organic chemistry. Hence, there remains an urgent need to develop tolerant catalysts that enable high conversions while delivering low E/Z ratios for production of Z-olefins.

Many metathesis catalysts based on the [L₂X₂Ru=CHR] scaffold have been synthesized in an effort to increase catalyst stability, activity, and selectivity. However, most efforts were concentrated on the modifications of the L₂ units or R group. Chen et al. has very recently reported the use of ruthenium catalysts to give high E/Z ratios (>6) at conversions >75%. Although phosphine-based catalysts give lower E/Z ratios than their NHC counterparts, they tend to decompose at conversions no more than 60%. A highly Z-selective molybdenum catalyst has been recently developed by Hoveyda and Schrock. These very important catalysts have numerous applications. However, as has been seen in the past, ruthenium-based catalysts can be more applicable in many situations. Although there are some ruthenium-based catalysts in recent literature that give better E/Z ratios than the more traditional catalysts, they are generally much less active. Other catalysts tend to have poor control over selectivity at high conversions as a result of secondary metathesis. The precatalysts themselves are also difficult to prepare with multistep synthesis and very low yields, making them less commercially viable. Z-Olefins are commonly found in natural products, and the ability to form Z-olefins from a single catalytic process remains important to synthetic organic chemistry. Hence, there remains an urgent need to develop tolerant catalysts that enable high conversions while delivering low E/Z ratios for production of Z-olefins.
of phosphinephenoxide and sulfoxide anionic ligands to control stereoselectivity in ROMP of norbornene/cyclooctene. Buchmeiser et al. has also reported the use of triflate and trifluoroacetate anions as ligands for Ru complexes for RCM and enyne metathesis reactions. To the best of our knowledge, there have been no other reports on the successful modification of the anions (X2) for improved E/Z selectivities in olefin metathesis reactions, especially in CM reactions. Anion modification is mostly done by replacing a chloride anion by an aryloxide attached to the NHC or PR3 itself. These NHCs or phosphine ligands, however, are often difficult to synthesize, resulting in poor yields of the ligand itself and the final precatalysts prepared. Herein, we report a series of air-stable and easy-to-prepare ruthenium olefin metathesis catalysts bearing bulky sulfonate or phosphate ligands with significantly improved Z-selectivity in CM reactions (eq 1) over other known Ru-based olefin metathesis catalysts.

**Results and Discussion**

It is envisioned that the installation of bulky groups on the anionic ligands on the Ru catalysts would force the resultant metallacyclobutane transition state to adopt a cis-conformation, thereby resulting in the preferential production of cis-olefins (Figure 1). Standard ligand exchange reactions using various silver sulfonate or phosphate salts in a benzene solution of the corresponding Ru precursors result in the formation of the desired metal complexes. The products can be isolated in high yields (> 75%) by simple filtration to remove the AgCl byproduct and unreacted silver salts followed by subsequent removal of solvents (eq 2). Only one chloride ligand is replaced by the bulky sulfonate or phosphate ligand to improve catalytic activity, as substitution of both chlorides by bulky anionic ligands would slow the reaction dramatically (vide infra). Formation of a small amount of dianion exchanged product is inevitable, and their presence in small quantities (<20%) serves to prevent the catalysts from scrambling back to form their precursors. As such, except for (H2IMes)(MesSO3)2RuCHPh(OiPr), 15, which exists as a pure compound, all other complexes (4–14) exist in a mixture of monosulfonate and disulfonate complexes, with the disulfonate complex being a minor component in the mixture. The composition of disulfonate complexes in the product mixture can be controlled by careful control of reaction times and amounts of silver sulfonate used. Microanalytical data for the complexes were not prepared as a result of the mixture of products. These complexes also exist as a mixture of diastereoisomers, especially complexes 4, 7, and 13, which also contain rotamers due to the free rotation of the o-Tol groups on the NHC, resulting in extremely complex 1H NMR spectra for these three complexes. All the complexes are stable in air except for complex 13 (X = binaphthylphosphate), whose solution decomposes after standing in air for ~30 min.

**RROMP Activity.** The ROMP of strained olefinic ring systems is one of the earliest industrial applications of olefin metathesis and remains a popular tool for modern polymer synthesis. Catalysts 4–14 were all highly effective in polymerizing norbornene. The E/Z ratio of poly(norbornene) using 4–14 does not vary much from that of their precursors, the dichloride catalysts, 1–3 (E/Z ~ 0.65). Catalyst 15 was very slow...
to initiate under standard ROMP conditions and achieved only 70% conversion after 6 h.

**RCM Activity.** Given the good activity of catalysts 1–14 in ROMP, we next focused on testing their activity in RCM, which is generally more demanding to the catalyst than ROMP. A standard reaction for testing the RCM activity of a particular catalyst is the ring closing of diethyl diallyl malonate (DEDAM, 18) to the cyclopentene (19) (Figure 2). Catalysts 9 (X = p-tolyl sulfonate) and 11 (X = camphorsulfonate) were extremely effective for RCM, where complete conversion was attained within 30 min of substrate addition at just 1 mol % catalyst loading, 30 °C. 13 (X = binaphthylphosphate) gave very poor conversions in the RCM reaction (50% conversion in 7 h), possibly due to rapid decomposition of the catalyst upon initiation.

**CM Activity.** Our initial studies show that when the mesitylsulfonate ligand is coupled with a bulky NHC such as 1,3-diisopropylphenyl-4,5-dihydroimidazol-2-ylidine on Ru (complex 6), the lowest E/Z ratio of 2.7 at high conversions of >70% (78%) can be attained. This is considerably lower than any of the Ru precursors or even that attainable using the phosphate-based catalysts. Although catalysts with similar E/Z selectivities have been reported prior to this work, higher catalyst loadings and harsher reaction conditions are required. 6 also displays a relatively linear relationship between conversion and E/Z ratio, which is mostly not observed in all other NHC-based Ru catalysts due to secondary metathesis reactions by the catalysts under high olefin product concentrations. When olefin 17 is reacted with 1 mol % of 5, the E/Z ratio of 17 changed by <2% in 1 h and <10% in 3 h (cf. E/Z increased by 20% when 17 is reacted with 2 for 30 min). The lower tendency to carry out the secondary metathesis by the sulfonate catalysts as compared to their dichloride precursors not only enables the formation of more cis-olefin cross-products but also maintains the low E/Z ratios over time.

Besides arylsulfonates, the use of alkylsulfonates such as CamSO₃ (complex 11) may also improve the Z-selectivity in the CM reaction. The binaphthylphosphate-based (BINAPPO₄) catalysts, 13 and 14, also show significant improvements in the Z-selectivities relative to their precursors, despite being slightly less selective when compared to the sulfonate-based catalysts. Secondary metathesis reactions were also minimal when using...
under a nitrogen atmosphere. All solvents and C<sub>6</sub>D<sub>6</sub> used for NMR data collection were purified by passage through solvent purification columns and further degassed with bubbling argon. 2.4,6-Trisopropylbenzenesulfonfonyl chloride was purchased from TCI America, and diphenylphosphate and (S)-1,1’-binaphthylphosphonic acid was purchased from Alfa Aesar. All other reagents were purchased from Aldrich. 2,4,6-Trisopropylbenzenesulfonic acid was prepared according to literature procedures. Catalysts 1–3 were obtained from Materia Inc. Commericially available reagents were used as received with the following exceptions. Allylbenzene, tridecane, and cis-1,4-diacetoxy-2-butene were distilled from anhydrous potassium carbonate and stored under argon in Schlenk flasks. 1H and 13C spectra were recorded on a Varian 500 spectrometer, and the chemical shifts are reported in ppm relative to the appropriate solvent. Reaction conversions for RCM reactions were obtained by comparing the integral values of starting material and product, and no internal standard was used. High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility. Gas chromatography data were obtained using an Agilent 6890 FID gas chromatograph equipped with a DB-Wax polyethylene glycol capillary column (Agilent). Conversions for ROMP and RCM reactions were determined by integration of the olefin proton signals in their 1H NMR spectra. Conversions and E/Z ratios for CM reactions were determined by comparing GC data using tridecane as an internal standard following literature procedures. X-ray crystallographic structures were obtained by Larry M. Henling and Dr. Michael W. Day of the California Institute of Technology Beckman Institute X-ray Crystallography Laboratory.

Representative Procedure for RCM Kinetics. In a glovebox, catalysts 4–14 (0.8 μmol) were dissolved in C<sub>6</sub>D<sub>6</sub> (0.75 mL) and placed in a NMR tube equipped with a rubber septum. The NMR tube was removed from the glovebox, and DEDAM (19.3 μL, 0.08 mmol) was injected, after which the tube was immediately placed in the spectrometer and a spectral array started by arraying the “pad” variable for Varian spectrometers.

Representative Procedure for CM Kinetics. To a flame-dried 1-dram vial, 2.0 μmol of catalyst was added in the glovebox followed by the addition of 1.0 mL of C<sub>6</sub>D<sub>6</sub>. Allylbenzene (1.00 mL, 7.55 mmol) and tridecane (0.920 mL, 3.77 mmol) were combined in a flame-dried, 1-dram vial under an atmosphere of argon. The mixture was stirred before taking a t<sub>0</sub> time point. cis-1,4-Diacetoxy-2-butene (64 μL, 0.40 mmol) and the allylbenzene/tridecane mixture (51 μL, 0.20 mmol 15 0.10 mmol of tridecane) were then added via syringe. The reaction was allowed to stir at 23 °C. Aliquots were taken at the specified time periods. Samples for GC analysis were obtained by adding a ca. 60 μL reaction aliquot to 500 μL of a 3 M solution of ethyl vinyl ether in dichloromethane. The samples was shaken, allowed to stand for 1 min, and then analyzed via GC. All reactions were performed in duplicate to confirm reproducibility. GC retention times were as follows (min): allylbenzene (10.87), tridecane (11.55), cis-diacetoxybutene (18.13), trans-diacetoxybutene (18.70), cis-17 (21.27), trans-17 (21.48), trans-homocoupled allylbenzene (24.09), cis-homocoupled allylbenzene (24.34).

General Synthesis of Silver Sulfonates and Silver Phosphates. The sulfonic acid or hydrogen phosphate (2.5 mmol) was dissolved in the minimal quantity of water required to ensure complete dissolution of all solids. Na<sub>2</sub>CO<sub>3</sub> (1.25 mmol) was added to the solution, and the mixture stirred until effervescence subsided. AgNO<sub>3</sub> (2.5 mmol) was added to precipitate out the silver salt, and the mixture filtered. The residue was washed with a small amount of cold water and dried under high vacuum overnight at 60 °C.

**Synthesis of 4 and 7.** 1 (23 mg, 0.04 mmol) was dissolved in benzene (8 mL) in a 20 mL scintillation vial, and RSO<sub>3</sub> Ag (0.2 mmol) was added to the solution. The mixture was stirred for 5 h, then filtered through a plug of Celite to yield a yellow solution. The...
solvent was removed under vacuum to yield 4 (24 mg, 82%) and 7 (28 mg, 85%) as yellow solids. 4 and 7 exist as multiple diastereomers, resulting in complex 4. 1H NMR spectra. 1H NMR (CD3OD): δ 17.15 (1H), 17.50 (8H), 8.59 (br s, 1H), 7.44–6.5 (m, 14H), 4.23 (sept, maj, J = 6 Hz, 1H), 4.15 (sept, min, J = 6 Hz, 4.08 (sept, min, J = 6 Hz), 3.76–3.68 (m, 2H), 2.63 (s, 3H), 2.58 (br s, 3H), 2.54 (s, 2H), 2.51 (br s, 3H), 2.38 (br s, 2.24 (s, 2.17) (s, 1H), 1.92 (s), 1.88 (s, 3H), 0.97 (d, J = 6 Hz, 1H), 0.93 (d, J = 10 Hz, 1H), 0.89 (δ, J = 6 Hz, 1H), 0.83 (d, J = 6 Hz, 1H). 13C NMR: δ 304.8, 275.0, 210.0, 152.9, 144.0, 143.5, 143.2, 141.9, 140.3, 140.0, 139.9, 139.7, 139.4, 139.1, 139.0, 138.1, 138.9, 137.9, 137.7, 137.4, 137.3, 137.1, 122.2, 121.9, 121.6, 112.6, 112.1, 87.8, 74.3, 69.6, 68.7, 51.5, 22.5, 21.5, 20.9, 20.3, 20.2, 19.3, 18.6. HR-MS (FAB): c 734.1520, found 734.1514.

Synthesis of 5. (25 mg, 0.04 mmol) was dissolved in CH2Cl2 (8 mL) in a 20 mL scintillation vial, silver mesitylsulfonate (MesSO3Ag) (15 mg, 0.048 mmol) was added, and the mixture was stirred overnight. Half an equivalent of MesSO3Ag (6 mg, 0.02 mmol) was added again, and the mixture was stirred overnight, then filtered through a plug of Celite to afford a brown filtrate. The filtrate was evaporated to dryness under high vacuum. The cryst syst monoclinic, space group C2/c, unit cell dimens a (Å) 24.741(19), b (Å) 10.8253(5), c (Å) 23.4557(11) α (deg) 90 β (deg) 120 γ (deg) 90 V (Å3) 9719.4(8).

Synthesis of 6. (28 mg, 0.04 mmol) was dissolved in benzene (8 mL) in a 20 mL scintillation vial, silver naphthysulfonate (NapSO3Ag) (15 mg, 0.048 mmol) was added, and the mixture was stirred overnight. The mixture was then filtered through a plug of Celite to afford a yellow-green filtrate. The filtrate was evaporated to dryness under high vacuum to give a green solid (29 mg, 85%). It exists as a mixture of inseparable mono- and disulfonate complexes in a 5:1 mixture. 1H NMR (CD3OD): δ 18.32 (s, min), 17.18 (s, maj) 1H, 7.42–6.22 (m, 13H), 4.52 (sept, J = 6.5 Hz, 1H), 4.10 (sept, J = 6.5 Hz, 3H), 3.48 (sept, J = 6.5 Hz, 4H), 3.21–3.37 (m, 2H), 3.6–3.57 (m, 2H), 1.56 (d, J = 6 Hz, 6H), 1.43 (d, J = 6 Hz, 6H), 1.24 (d, J = 6 Hz, 6H). 13C NMR (CD3OD): δ 306.7, 275.7, 210.0, 156.5, 154.3, 149.0, 144.1, 146.9, 154.4, 145.1, 138.7, 137.1, 137.6, 137.5, 137.5, 134.3, 135.8, 121.9, 122.9, 122.2, 125.8, 122.8, 120.4, 114.0, 113.4, 75.2, 75.3, 22.7, 22.2, 21.1, 20.9, 20.4. HR-MS (FAB): c 798.1544, found 798.1540.

Synthesis of 7. (25 mg, 0.04 mmol) was dissolved in benzene (8 mL) in a 20 mL scintillation vial, silver naphthysulfonate (NapSO3Ag) (15 mg, 0.048 mmol) was added, and the mixture was stirred overnight. The mixture was then filtered through a plug of Celite to afford a yellow-green filtrate. The filtrate was evaporated to dryness under high vacuum to give a green solid (29 mg, 85%). It exists as a mixture of inseparable mono- and disulfonate complexes in a 5:1 mixture. 1H NMR (CD3OD): δ 18.32 (s, min), 17.18 (s, maj) 1H, 7.42–6.22 (m, 13H), 4.52 (sept, J = 6.5 Hz, 1H), 4.10 (sept, J = 6.5 Hz, 3H), 3.48 (sept, J = 6.5 Hz, 4H), 3.21–3.37 (m, 2H), 3.6–3.57 (m, 2H), 1.56 (d, J = 6 Hz, 6H), 1.43 (d, J = 6 Hz, 6H), 1.24 (d, J = 6 Hz, 6H). 13C NMR (CD3OD): δ 306.7, 275.7, 210.0, 156.5, 154.3, 149.0, 144.1, 146.9, 154.4, 145.1, 138.7, 137.1, 137.6, 137.5, 137.5, 134.3, 135.8, 121.9, 122.9, 122.2, 125.8, 122.8, 120.4, 114.0, 113.4, 75.2, 75.3, 22.7, 22.2, 21.1, 20.9, 20.4. HR-MS (FAB): c 798.1544, found 798.1540.

Synthesis of 10. (25 mg, 0.04 mmol) was dissolved in benzene (8 mL) in a 20 mL scintillation vial, silver naphthysulfonate (NapSO3Ag) (15 mg, 0.048 mmol) was added, and the mixture was stirred overnight under a nitrogen atmosphere. The mixture was then filtered through a plug of Celite to afford a light green filtrate. The filtrate was evaporated to dryness under high vacuum to give a green solid (27 mg, 80%). It exists as a mixture of inseparable mono- and disulfonate complexes in a 5:1 mixture. 1H NMR (CD3OD): δ 18.32 (s, min), 17.18 (s, maj) 1H, 7.42–6.22 (m, 13H), 4.52 (sept, J = 6.5 Hz, 1H), 4.10 (sept, J = 6.5 Hz, 3H), 3.48 (sept, J = 6.5 Hz, 4H), 3.21–3.37 (m, 2H), 3.6–3.57 (m, 2H), 1.56 (d, J = 6 Hz, 6H), 1.43 (d, J = 6 Hz, 6H), 1.24 (d, J = 6 Hz, 6H). 13C NMR (CD3OD): δ 306.7, 275.7, 210.0, 156.5, 154.3, 149.0, 144.1, 146.9, 154.4, 145.1, 138.7, 137.1, 137.6, 137.5, 137.5, 134.3, 135.8, 121.9, 122.9, 122.2, 125.8, 122.8, 120.4, 114.0, 113.4, 75.2, 75.3, 22.7, 22.2, 21.1, 20.9, 20.4. HR-MS (FAB): c 775.2656, found 775.2652 (9 = p-ToSO3–J ).
disulfonate. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 18.32 (min, s), 17.18 (maj, s, 1H), 7.41–7.00 (m, 10H), 4.53 (sept, maj, $J = 6.5$ Hz, 1H), 4.10 (sept, min, $J = 6$ Hz), 3.91–3.76 (m, 4H), 3.62 (br s, 1H), 3.58 (br s, 1H), 3.48 (sept, $J = 7$ Hz, 4H), 1.56 (d, $J = 7$ Hz, 6H), 1.49 (d, $J = 7$ Hz, 4H), 1.43 (d, $J = 6.5$ Hz, 3H), 1.26 (m, 13H), 1.16 (d, $J = 7$ Hz, 4H), 1.07 (d, $J = 7$ Hz, 7H), 0.96 (m, 6H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ 306.0, 275.0, 209.3, 153.6, 148.3, 147.4, 146.2, 144.7, 137.9, 136.4, 135.1, 129.5, 129.1, 128.4, 128.3, 128.2, 127.9, 127.6, 127.4, 127.3, 127.2, 126.9, 125.9, 125.8, 124.5, 124.2, 120.4, 120.3, 114.0, 77.6, 54.2, 28.8, 28.6, 28.3, 26.2, 26.1, 25.8, 24.0, 23.3, 23.1, 21.5, 20.0, 19.6. HR-MS (FAB): found 840.2063. 

Synthesis of 12. 2 (25 mg, 0.04 mmol) was dissolved in benzene (8 mL) in a 20 mL scintillation vial, (PhO)$_2$PO$_2$Ag (23 mg, 0.04 mmol) was dissolved in benzene (8 mL) in a 20 mL scintillation vial, and silver binapthylphosphate (BINAPPO$_2$Ag) (40 mg, 0.18 mmol) was added to the solution. The mixture was stirred for 5 h, then filtered through a plug of Celite to yield a yellow solution. The solvent was removed under high vacuum to give a green solid (28 mg, 82%). $^{12}$ exists as a mixture of mono- and diphasophate complexes in a 5:1 mixture. $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 18.41 (s, min), 17.59 (s, maj, 1H), 7.20–6.63 (m, 6.41 (d, $J = 4$ Hz, min), 6.34 (d, $J = 9$ Hz, maj, 1H), 4.71 (sept, $J = 6$ Hz, min), 4.48 (sept, $J = 6$ Hz, maj, 1H), 3.42 (br s, 6H), 2.75 (br s, 3H), 2.65 (br s, 2.49 (br s), 2.59 (br s, 3H), 2.26 (br s, 5H), 1.24 (br m, 12H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ 303.1, 275.5, 211.7, 210.4, 154.5, 135.9, 135.8, 153.7, 153.6, 146.1, 141.9, 141.5, 140.4, 139.2, 138.9, 134.4, 134.1, 130.3, 130.2, 130.0, 129.7, 123.5, 123.4, 122.8, 122.7, 121.0, 120.8, 113.8, 113.6, 76.4, 75.8, 52.6, 50.7, 21.5, 21.4, 21.1, 20.8, 19.9, 18.9. HR-MS (FAB): found 840.2033, 840.2063. 

Synthesis of 13. 1 (23 mg, 0.04 mmol) was dissolved in benzene (8 mL) in a 20 mL scintillation vial, and silver pinaphosphate (BINAPPO$_2$Ag) (40 mg, 0.08 mmol) was added to the solution. The mixture was stirred for 5 h, then filtered through a plug of Celite to yield a yellow solution. The solvent was removed under vacuum to yield a yellow solid (32 mg, 92%). $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 17.44, 17.10, 8.46–6.86 (m, 4.86 (m), 4.75 (m), 4.51–3.73 (m), 2.65 (br s), 2.54 (br s), 2.37 (s), 2.29 (br s), 2.28 (br s), 1.24 (d, $J = 6$ Hz, 1.15 (d, $J = 6$ Hz), 1.08 (d, $J = 6$ Hz), 0.80 (d, $J = 6$ Hz), 0.78 (d, $J = 6$ Hz). HR-MS (FAB): found 882.1564, 882.1563. $^{13}$ exists as a large mixture of diastereomers, resulting in an extremely complicated $^1$H NMR spectrum. The solution sample of $^{13}$ also decomposed during data collection for $^{13}$C, resulting in the inability to collect an accurate $^{13}$C spectrum for $^{13}$. 

Synthesis of 14. 3 (28 mg, 0.04 mmol) was dissolved in benzene (8 mL) in a 20 mL scintillation vial, BINAPPO$_2$Ag (50 mg, 0.18 mmol) was added, and the mixture was stirred overnight. The mixture was then filtered over a plug of Celite to afford a yellow filtrate. The filtrate was evaporated to dryness under high vacuum to give a dark brown solid (31 mg, 80%). $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 18.22 (s, 1H), 7.45–6.78 (m, 11H), 6.29 (d, $J = 8$ Hz, 1H), 4.30 (s, 2H), 4.13 (sept, $J = 6$ Hz, 1H), 4.78 (s, 4H), 2.56 (br s, 9H), 2.42 (br s, 8H), 2.30 (s, 5H), 2.28 (s, 5H), 1.94 (s, 9H), 0.86 (d, $J = 6$ Hz, 4H). $^{13}$C NMR (CD$_2$Cl$_2$): $\delta$ 323.8, 209.3, 155.3, 145.5, 141.2, 139.6, 139.1, 138.9, 138.4, 137.9, 137.4, 132.1, 130.6, 130.0, 130.9, 130.5, 130.3, 129.7, 129.2, 127.5, 127.3, 123.6, 122.6, 114.0, 75.9, 53.7, 52.7, 50.2, 30.5, 23.5, 21.5, 21.0, 20.5, 20.3, 19.4. HR-MS (FAB): found 954.2886, 954.2896. 

Crystal Structure Determinations. Crystals were mounted on a glass fiber using Paratone oil, then placed on the diffractometer under a nitrogen stream at 100 K. Refinement of $F^2$ is done against all reflections. The weighted $R$-factor ($wR$) and goodness of fit (S) are based on $F^2$. Conventional $R$-factors (R) are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors (gt), etc., and is not relevant to the choice of reflections for refinement. $R$-Factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger. All esd’s (except the esd in the dihedral angle between two least-squares planes) are estimated using the full covariance matrix. The cell esd’s are taken into account individually in the estimation of esd in distances, angles, and torsion angles; correlations between esd’s in cell parameters are used only when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esd’s is used for estimating esd’s involving least-squares planes.

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Supporting Information Available. This material is available free of charge via the Internet at http://pubs.acs.org.