Organometallics **1999,** *18,* 5157−5162

Asymmetric Synthesis of Rigid C_2-Symmetric Bis(ferrocenyl) Diol and Diamine Ligands

Andrew O. Larsen, Rebecca A. Taylor, Peter S. White, and Michel R. Gagné*

Department of Chemistry, University of North Carolina,
Chapel Hill, North Carolina 27599-3290

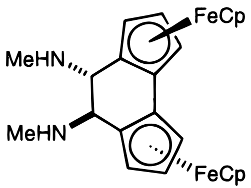
Received July 15, 1999

We report herein the asymmetric synthesis of C_2-symmetric fused diferrocenyl diamine and diol ligands. The synthesis begins with the Cu(II)-mediated coupling of the diastereomerically and enantiomerically pure lithiated derivative of Kagan's ferrocenyl acetal to yield, after deprotection, the C_2-symmetric biferrocenyl dialdehyde **4**. Conversion of dial **4** to a bis(methylimine) followed by a SmI_2 mediated aza−pinacol coupling, yielded the enantio− and diastereomerically pure C_2-symmetric *trans*−diamine **1**. The direct pinacol coupling of dialdehyde **4** by SmI_2 yields the enantio- and diastereomerically pure C_2-symmetric *trans*-diol **2**. The former diamine was coordinated to the Lewis acid $(ArO)_2TiCl_2$ (Ar = 4-vinyl-2,6-dimethylphenyl) and characterized by solution and X-ray methods. The diol ligand was reacted with $(dppe)Pt(CO_3)$ to form a $(dppe)Pt^{II}$ diolate, which was also characterized by solution and solid-state means.

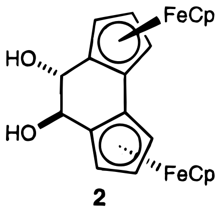
Introduction

The conventional wisdom for the design of efficient chiral ligands for asymmetric catalysis and synthesis points to ligand structures that are rigid and have minimal conformational degrees of freedom.[1] These structure types might most easily be expected to control the relative energetics of competing reaction pathways. Recent studies by Uemura[2] and Riant[3] examining linked planar chiral arene−$Cr(CO)_3$ and linked planar chiral ferrocenes as routes to such rigid structures prompts us to report our own efforts in this area. During the course of these investigations Riant reported a similar route to a key intermediate for our ligand synthesis.[3]

Many C_2-symmetric *trans*-1,2-disubstituted diamine and diol ligands are utilized in asymmetric synthesis and catalysis (e.g. *trans*-1,2-cyclohexanediamine and *trans*-1,2-diphenylethylenediamine).[4,5] Despite some outstanding successes with these ligands, however, the diequatorial orientation of the backbone substituents makes for a subtle and not easily interpreted asymmetric environment. In this context a ligand that incorporates "diaxial" or diametrically opposed substituents, rather than the more common diequatorial situation, should present enhanced steric asymmetry to a coordinated metal. Inspired by the C_2-symmetric bis(azaferrocene) ligands of Fu,[6] and noting that chiral 1,2-diamine and -diol ligands are ubiquitous in asymmetric synthesis and catalysis, we designed a ligand scaffold that can incorporate either of these functionalities while maintaining the highly asymmetric coordination environment of the two *anti*-disposed ferrocene units. We report herein an asymmetric synthesis of the enantio- and diastereomerically pure diamine **1** and the diol **2** along with the coordination chemistry of these ligands to a titanium Lewis acid and a platinum diphosphine complex, respectively.



1



2

Results and Discussion

Ligand Synthesis. Our plan for the synthesis of these ligands began with Kagan's enantio- and diastereomerically pure chiral ferrocenyl acetal, the deprotonation of which (*t*-BuLi) can be selectively directed to a single diastereotopic ortho hydrogen.[7,8] Quenching studies by Kagan indicated that this lithiated species could be selectively quenched with electrophiles to give a variety of planar-chiral 1,2-disubstituted ferrocenes in up to 95% de.

It occurred to us that oxidative quenching of the Kagan anion might form a ferrocene−ferrocene linkage

---

(1) Seyden-Penne, J. *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*; Wiley: New York, 1995.

(2) Taniguchi, N.; Hata, T.; Uemura, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1232−1235.

(3) Neo, A. G.; Gref, A.; Riant, O. *Chem. Commun.* **1998**, 2353−2354.

(4) (a) Lucet, D.; Gall, T. L.; Mioskowski, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 2581−2627. (b) Bennani, Y. L.; Hanessian, S. *Chem. Rev.* **1997**, *97*, 3161−3195. (c) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497−526.

(5) See for example: Duthaler, R. O.; Hafner, A. *Chem. Rev.* **1992**, *92*, 807−832.

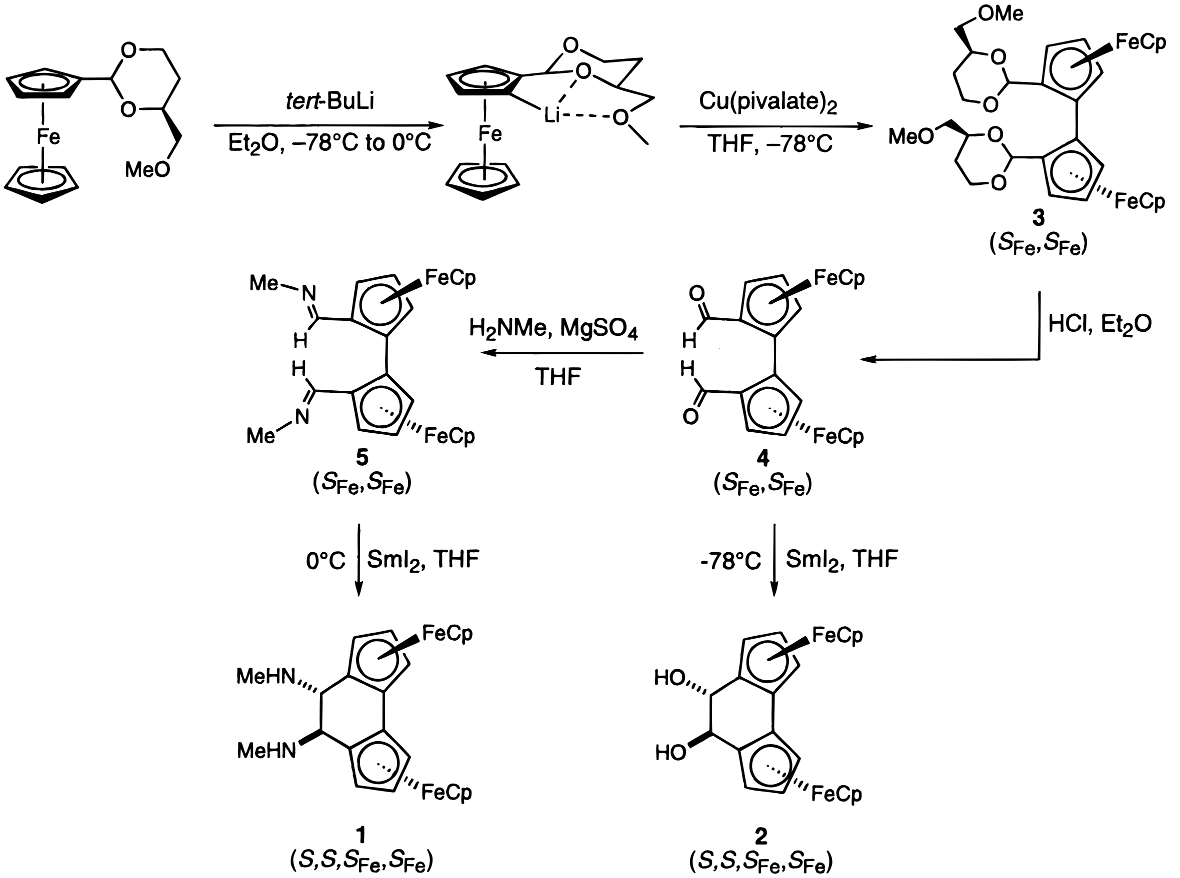
(6) Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 10270−10271.

(7) (a) Riant, O.; Samuel, O.; Flessner, T.; Taudien, S.; Kagan, H. B. *J. Org. Chem.* **1997**, *62*, 6733−6745. (b) Riant, O.; Samuel, O.; Kagan, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 5835−5836.

(8) For an alternative approach to a diastereomerically pure α-lithiated ferrocenecarboxaldehyde equivalent, see: (a) Sammakia, T.; Latham, H. A.; Schaad, D. R. *J. Org. Chem.* **1995**, *60*, 10−11. (b) Sammakia, T.; Latham, H. A. *J. Org. Chem.* **1996**, *61*, 1629−1635.

10.1021/om9905512 CCC: $18.00
Publication on Web 11/05/1999

Scheme 1

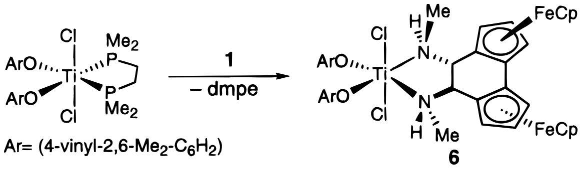


that could selectively access C_2-symmetric planar chiral diferrocenylcarboxaldehydes in high enantiomeric purity (**4**, Scheme 1). Indeed, oxidation of the Kagan anion with Cu(pivalate)$_2$, a soluble copper(II) source, efficiently generated the coupled diacetal **3**, which could be isolated, purified by flash chromatography (62%),[9] and deprotected to yield the desired C_2-symmetric dialdehyde. The ^{1}H and ^{13}C NMR properties of the molecule are consistent with its C_2-symmetric formulation. Recent routes to **3** and **4** relying on an Fe(acac)$_3$-mediated oxidative coupling[3] and an Ullman coupling[10] were reported while the present work was underway.

Conversion of dialdehyde **4** to the bis(methylimine) was accomplished with anhydrous methylamine and MgSO$_4$.[11] Although the bis(imine) could not be purified by chromatography, the isolated product was analytically pure and could be converted to the desired diamine with excess SmI$_2$ in THF at 0 °C.[12] Like the bis(imine), the diamine decomposed upon attempted column chromatography but could be extracted into aqueous solution with tartaric acid and subsequently washed with CH$_2$Cl$_2$. Basification and back-extraction into CH$_2$Cl$_2$ provided the diamine in 59% yield and 90% de. The minor diastereomer could be removed by crystallization from hexanes.

The direct pinacol coupling of **4** using SmI$_2$ at −78 °C, also reported by Riant,[3] yielded the air-sensitive diol **2** (92% yield, 96% de), which was purified by chromatography and recrystallized to analytical purity. ^{1}H and ^{13}C NMR spectroscopy were consistent with a molecule containing C_2 symmetry. On the basis of analogy with intramolecular pinacol couplings of Cr(CO)$_3$-coordinated planar chiral 2,2′-diformylbiphenyls[2] and a crystal structure (vide infra), we assign the major coupling product to be that which orients the vicinal carbinol hydrogen toward the nearest ferrocene unit (Scheme 1). The minor isomers obtained from the SmI$_2$-mediated couplings of both **4** and **5** are assigned to the C_2-symmetric *trans* isomers that orient the formyl and imine H's away from the FeCp unit during the coupling (see Experimental Section).

Coordination Chemistry. To examine the behavior of **1** as a ligand, we chose to first coordinate the diamine to a titanium(IV) Lewis acid known to be a good Diels−Alder catalyst.[13] On the basis of previous studies we expected, and observed, that the *N*,*N*′-dimethyl-substituted aliphatic diamine would cleanly displace coordinated dmpe and bind strongly to the Lewis acid (eq 1).[14]



(1)

By ^{1}H NMR, a single symmetric product is formed in this reaction, suggesting that the prochiral amines

---

[9] Diagnostic for the selectivity of the coupling is the acetal hydrogen, which indicated that in the crude material the desired product was the major diastereoisomer (65%) along with 27% of unreacted starting material.

[10] Patti, A.; Lambusta, D.; Piatelli, M.; Nicolosi, G. *Tetrahedron: Asymmetry* **1998**, *9*, 3073−3080.

[11] Kündig, E. P.; Xu, L. H.; Romanens, P.; Bernardinelli, G. *Synlett* **1996**, 270−272.

[12] See footnote 2 and: (a) Taniguchi, N.; Uemura, M. *Tetrahedron* **1998**, *54*, 12775−12788.

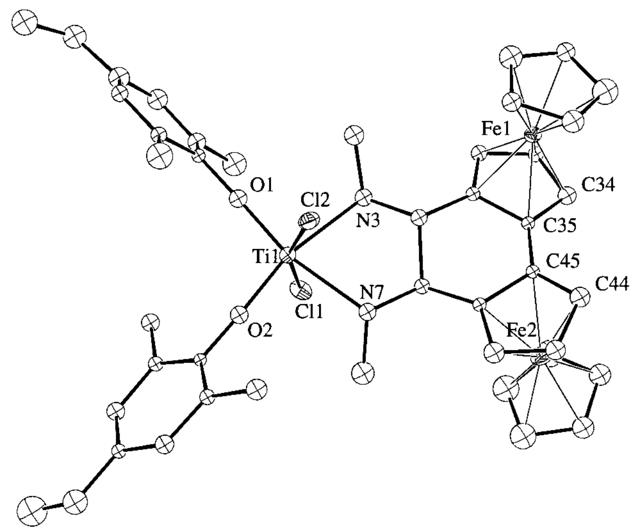


Figure 1. ORTEP diagram of **6**. Selected bond distances (Å) and angles (deg): Ti(1)−N(7) = 2.273(14), Ti(1)−O(1) = 1.799(12), Ti(1)−Cl(1) = 2.355(7); N(3)−Ti(1)−N(7) = 76.8(5), Cl(1)−Ti(1)−Cl(2) = 160.90(25), O(1)−Ti(1)−O(2) = 103.5(5), C(34)−C(35)−C(45)−C(44) = 25.1(22).

coordinate with a single configuration, presumably that which places both *N*-methyl groups in the pseudo-equatorial position.

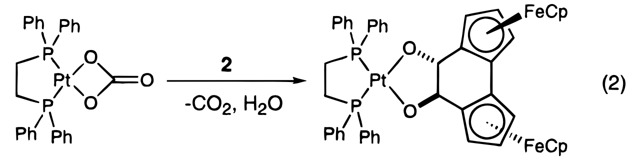
To confirm the ligand stereochemistry in addition to the coordination chemistry, single (weakly diffracting) crystals of **6** were grown from C_6D_6/pentane and subjected to X-ray analysis. An ORTEP representation of the crystal structure is shown in Figure 1, and acquisition/solution parameters are collected in Table 1.[15] As expected, coordination of the diamine leads to a titanium center best described as a distorted octahedron with a compressed Cl−Ti−Cl bond angle (160.90(25)°). Also apparent is the highly asymmetric nature of the bis(ferrocenyl) ligand, as illustrated by the C34−C35−C45−C44 dihedral angle (25(2)°), which describes a ferrocene−ferrocene twist that pushes each ferrocene group slightly away from Ti and in opposite directions. The steric discrimination of the C_2-related quadrants by the *anti*-disposed ferrocenes is best visualized by the partial structure (Chem3D) of **6** shown in Figure 2. Comparison of Bijvoet pairs assigned the absolute configuration of the complex, confirming our expectation for the biaryl bond forming stereochemistry, and that proposed by Riant.[3] The structure of **6** also confirmed the stereochemistry of the aza−pinacol coupling to be that which orients the imine H toward Fe during C−C bond formation[16] and validated our proposed diequatorial coordination mode for the prochiral *N*-methyl amines. Thus, the planar chirality present in the Kagan anion is propagated to the biferrocene linkage, the aza−pinacol coupling, and ultimately to the prochiral diamine upon coordination. Metrical parameters compare favorably to related titanium amine and diamine adducts.[17]

Table 1. Crystallographic Data and Collection Parameters for 6 and 7

	6	7
formula	$TiCl_2C_{44}H_{48}N_2O_2$-Fe_2·$2C_6H_6$	$PtFe_2P_2C_{48}H_{42}$-O_2·C_7H_8
fw	1023.59	1111.71
color, habit	red, cryst	orange, cryst
cryst size, mm	0.15 × 0.15 × 0.20	0.25 × 0.25 × 0.20
cryst syst	orthorhombic	triclinic
space group	$P2_12_12_1$	$P1$
a, Å	11.6026(5)	11.0890(7)
b, Å	20.3883(8)	13.7052(9)
c, Å	21.7999(9)	15.1559(10)
V, Å^3	5156.9(4)	2238.1(3)
Z	4	2
T, °C	−100	−100
D_c, g/cm^3	1.318	1.650
F(000)	2142.07	1111.77
radiation	Mo Kα	Mo Kα
μ, mm^{-1}	0.85	3.86
scan mode	ω	ω
data collected	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
$2\theta_{max}$, deg	50.0	56.0
total no. of rflns	31 832	52 604
no. of unique rflns	9130	21 538
R_{merge}	0.076	0.032
no. of rflns with $I > 2.5\sigma(I)$	3173	19 421
no. of variables	286	1114
R_F^{a}	0.077	0.024
R_w^{b}	0.082	0.026
GOF^c	1.4799	0.8730
max Δ/σ	0.001	0.005
residual density, e/Å^3	−0.520, 1.090	−1.940, 2.190

^{a} $R_F = \Sigma(F_o - F_c)/\Sigma F_o$. ^{b} $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$. ^{c} GOF = $[\Sigma w(F_o - F_c)^2/(n - p)]^{1/2}$.

Reaction of diol **2** with dppePt(CO_3) according to the protocol developed by Andrews[18] afforded the air- and moisture-stable crystalline diolate complex **7** (eq 2).



7 (2)

Unlike our previous experiments using the more acidic binaphthol-type ligands, **2** required more vigorous heating in chlorobenzene (80 °C, 20 min) to generate the desired product. The ^{31}P NMR analysis of **7** indicated a time-averaged symmetric structure (J_{Pt-P} = 3260 Hz), and no coupling between the carbinol hydrogen and platinum ($^3J_{Pt-H} < 5$ Hz), consistent with a diequatorial diolate conformation.[19]

---

(13) (a) Santora, B. P.; Larsen, A. O.; Gagné, M. R. *Organometallics* **1998**, *17*, 3138−3140. (b) Santora, B. P.; White, P. S.; Gagné, M. R. *Organometallics* **1999**, *18*, 2557−2560.

(14) Larsen, A. O.; White, P. S.; Gagné, M. R. *Inorg. Chem.* **1999**, *38*, 4824−4828.

(15) While the structure only allowed anisotropic thermal parameters to be modeled on the heavy atoms, the structure was sufficient to unambiguously assign connectivity, relative, and absolute stereochemistry (Table 1).

(16) The aza−pinacol coupling of a $Cr(CO)_3$-coordinated 2,2′-diiminobiphenyl also yielded a *trans*-diamine product with the same relative stereochemistry.[2]

(17) See the Supporting Information for full tables of metrical parameters.

(18) (a) Andrews, M. A.; Voss, E. J.; Gould, G. L.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1994**, *116*, 5730−5740. (b) Andrews, M. A.; Gould, G. L.; Klooster, W. T.; Koenig, K. S.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5478−5483. (c) Andrews, M. A.; Gould, G. L.; Klooster, W. T.; Koenig, K. S.; Voss, E. J. *Inorg. Chem.* **1996**, *35*, 5478−5483.

(19) Equatorial hydrogens in five-membered platinacycles show $^3J_{Pt-H}$ couplings of 10−60 Hz; see for example: (a) Becker, J. J.; White, P. S.; Gagné, M. R. *Inorg. Chem.* **1999**, *38*, 798−801. (b) Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1971**, *10*, 1717−1725. (c) Erickson, L. E.; McDonald, J. W.; Howie, J. K.; Clow, R. P. *J. Am. Chem. Soc.* **1968**, *90*, 6371−6382.

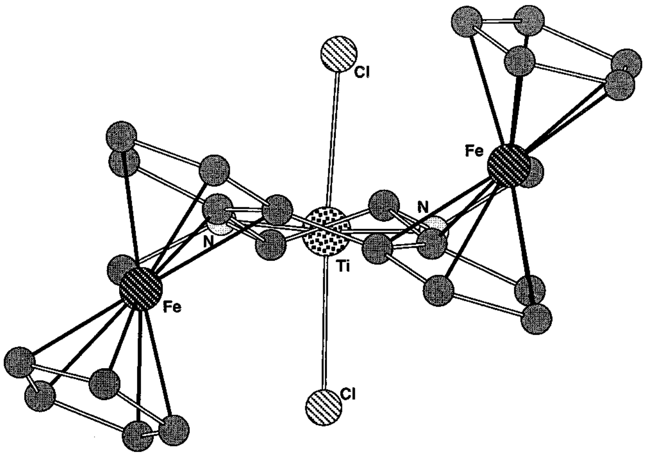


Figure 2. Chem3D picture of **6** highlighting the highly asymmetric nature of the linked bis(ferrocenyl) unit. The aryloxide ligands projecting to the back are omitted for clarity.

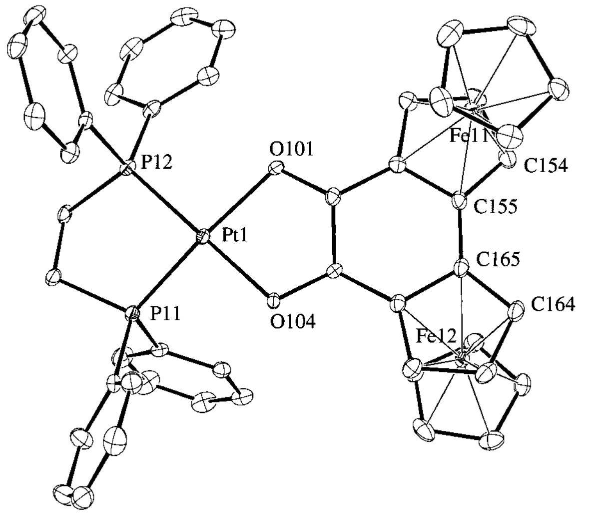


Figure 3. ORTEP diagram of **7**. Selected bond distances (Å) and angles (deg): Pt(1)−P(12) = 2.2332(10), Pt(1)−O(101) = 2.038(3); P(11)−Pt(1)−P(12) = 86.14(4), O(101)−Pt(1)−O(104) = 83.92(10), C(154)−C(155)−C(165)−C(164) = 23.1(5).

Single crystals of **7** suitable for X-ray crystallography were obtained by slow cooling a toluene solution to −20 °C. The ORTEP representation for one of the independent molecules in the asymmetric unit of this structure is shown in Figure 3; the second is nearly identical except for P−Ph rotational differences. The structure highlights many of the topological features observed in the structure of **6**, i.e., the C_2-symmetric disposition of the ferrocenes along with their near-opposite orientations (C154−C155−C165−C164 = 23.1(5)°). The quality of the structure was high, allowing isotropic refinement of hydrogen atoms (Table 1)[17] and assignment of the relative stereochemistry to be that which places the aldehyde CHs toward the Fe during the critical pinacol C−C bond-forming step. The stereochemistry of this pinacol coupling is analogous to that observed for the SmI_2-mediated pinacol coupling of planar chiral (by virtue of $Cr(CO)_3$ coordination) 2,2′-diformylbiphenyl[2] and axially chiral 2,2′-diformylbiphenyls.[20]

Summary

We have demonstrated herein a synthetic protocol for the synthesis of C_2-symmetric bis(ferrocene) ligands which, by virtue of a rigid linkage, are forced to adopt a conformation that orients the two ferrocene units into a highly asymmetric antiperiplanar “diaxial-like” arrangement. The synthetic approach is flexible and allows either *trans*-diamine or -diol functionalities to be selectively incorporated via the SmI_2-promoted pinacol reaction. Coordination studies indicated that both bis(ferrocenes) are good ligands, and structural studies confirm the stereochemical hypotheses that inspired their design.

Experimental Section

(2*S*,4*S*)-4-(Methoxymethyl)-2-ferrocenyl-1,3-dioxane,[7] $Ti(OC_6H_3\text{-}2,6\text{-}(CH_3)_2)_2Cl_2(dmpe)$,[14] $Pt(dppe)CO_3$,[18] SmI_2,[21] and $Cu(pivalate)_2$[22] were prepared according to literature procedures. All other compounds were used as received. THF was distilled from Na/benzophenone ketyl, and all other solvents were dried over activated alumina.[23] $CDCl_3$ and CD_2Cl_2 were stored over 4 Å molecular sieves and K_2CO_3, while C_6D_6 was dried over Na/benzophenone ketyl, vacuum-transferred, and freeze−pump−thaw-degassed prior to use. Superior yields were obtained for each chemical step if the aqueous workup reagents were degassed by sparging with N_2 prior to use. All compounds were synthesized under N_2 using standard Schlenk techniques, and any air-sensitive compounds were handled in an MBraun Lab-Master 100 glovebox.

^1H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or C_6D_6 at ambient temperature on a Bruker AC200, AMX300, or Avance 400 spectrometer. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter. Elemental analyses were performed by E+R Microanalytical Laboratories, Parsippany, NJ.

Synthesis of Bis(acetal) 3. (2*S*,4*S*)-4-(methoxymethyl)-2-ferrocenyl-1,3-dioxane (2 g, 6.3 mmol) was added to a flame-dried Schlenk flask, and a diastereoselective deprotonation was carried out in ether according to the procedure of Kagan.[7] A separate flame-dried 50 mL Schlenk flask was charged with $Cu(Opiv)_2$ (5.0 g, 3 equiv, 19.0 mmol) and Et_2O (50 mL) and precooled to −20 °C. The dark blue solution was then transferred via cannula to the precooled (−20 °C) ferrocenyllithium reagent. The reaction was monitored by TLC until starting material was consumed (~5 h), at which time it was quenched with saturated NH_4Cl, washed with NH_4Cl, $NaHCO_3$ (2×), and brine, and then dried over $MgSO_4$. The solvent was removed in vacuo to yield the crude bis(ferrocene acetal) as a red oil (96% de by integration of acetal resonances in the ^1H NMR).[24] The crude product was purified via flash chromatography (5 → 15 → 35% EtOAc/hexanes) to afford 1.24 g of enantio- and diastereomerically pure **3** as a red-orange solid (62% yield). ^1H NMR (300 MHz, $CDCl_3$): δ 5.71 (s, 2H, $FcCHO_2$), 4.49 (dd, J_{HH} = 2.4, 1.5 Hz, 2H, FcH), 4.37 (dd, J_{HH} = 2.1, 1.5 Hz, 2H, FcH), 4.30 (m, 2H), 4.27 (s, 10H, FeC_5H_5), 4.12 (dd, J_{HH} = 2.4, 2.1 Hz, 2H), 3.93 (m, 4H), 3.43 (dd, J_{HH} = 10.2, 5.7 Hz, 2H), 3.31, (dd, J_{HH} = 10.2, 5.1 Hz, 2H), 3.29 (s, 6H, OCH_3), 1.77

---

[20] Ohmori, K.; Kitamura, M.; Suzuki, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 1226−1229.

[21] (a) Molander, G. A. *Chem. Rev.* **1992**, *92*, 29−68. (b) Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693−2698.

[22] $Cu(pivalate)_2$ was synthesized by refluxing Cu(II) carbonate basic with 4 equiv of pivalic acid in MeOH for 12 h, filtering, recrystallizing from MeOH, and drying under high vacuum. For several recent oxidative couplings of an alkyllithium using this reagent see: (a) Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9075−9076. (b) Corey, E. J.; Chen, Z.; Tanoury, G. J. *J. Am. Chem. Soc.* **1993**, *115*, 11000−11001.

[23] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. *Organometallics* **1996**, *15*, 1518−1520.

(ddd, J_{HH} = 24.5, 12.6, 5.1 Hz, 2H), 1.50 (d, br J_{HH} = 12.6 Hz, 2H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 99.1, 84.1, 83.6, 76.0, 75.3, 71.3, 69.8, 67.0, 66.50, 66.45, 59.2, 28.1 ppm. $[\alpha]_D^{25.4}$ = +182.9 (*c* 1.05, CH_2Cl_2). Anal. Calcd for $C_{32}H_{38}Fe_2O_6$: C, 60.98; H, 6.08. Found: C, 61.18; H, 6.29.

Synthesis of Dialdehyde 4. Bis(acetal) **3** (3.0 g, 4.8 mmol) was dissolved in 50 mL of Et_2O and combined with an equal volume of 1 M HCl. The biphasic mixture was stirred for 30 min, and then the phases were separated. The organic layer was washed with $NaHCO_3$ and brine and then dried over $MgSO_4$. After solvent removal the crude aldehyde was purified by elution through a plug of silica (50% EtOAc/hexanes) to afford 1.85 g of diastereomerically and analytically pure dialdehyde as an orange-red solid (91% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 2H, FcCHO), 4.93 (dd, J_{HH} = 2.8, 1.6 Hz, 2H, FcH), 4.91 (dd, J_{HH} = 2.8, 1.6 Hz, 2H, FcH), 4.71 (dd, J_{HH} = 2.8, 2.4 Hz, 2H, FcH), 4.28 (s, 10H, FeC_5H_5) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 192.2, 85.3, 78.5, 76.6, 71.9, 71.0, 68.8 ppm. $[\alpha]_D^{25.4}$ = −12.6 (*c* 1.02, CH_2Cl_2). Anal. Calcd for $C_{22}H_{18}Fe_2O_2$: C, 62.02; H, 4.21. Found: C, 61.98; H, 4.18.

Synthesis of Diol 2. To a flame-dried Schlenk flask was added dialdehyde **4** (102 mg, 0.23 mmol) and THF (2 mL). To a separate flame-dried Schlenk flask was added a 0.1 M solution of SmI_2 (7.2 mL, 3 equiv, 0.72 mmol). Both flasks were cooled to −78 °C, and the aldehyde was transferred via cannula to the SmI_2 solution. The reaction was monitored by TLC until aldehyde was consumed (~30 min) and then quenched with NH_4Cl, washed with NH_4Cl, $NaHCO_3$, and brine, and then dried over $MgSO_4$. The solvent was removed in vacuo to afford 95 mg of spectroscopically pure (^1H NMR) product as a mixture of *trans*-diol (i.e. *R*,*R* and *S*,*S* configurations at the carbinol carbons) diastereomers (93% yield, 96% de by integration of FeC_5H_5 resonances in the ^1H NMR).[25] Analytically and diastereomerically pure product for analysis was obtained by recrystallization from boiling toluene. ^1H NMR (300 MHz, $CDCl_3$): δ 4.85 (d, J_{HH} = 7.2 Hz, 2H, FcCH), 4.33 (m, 4H, FcH), 4.26 (t, J_{HH} = 2.4 Hz, 2H, FcH), 3.98 (s, 10H, FeC_5H_5), 2.11 (d, J_{HH} = 7.2 Hz, 2H, FcCOH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 81.7, 79.1, 72.2, 69.7, 67.6, 66.5, 62.5 ppm. $[\alpha]_D^{25.4}$ = +446.6 (*c* 1.05, acetone). Anal. Calcd for $C_{22}H_{20}Fe_2O_2$: C, 61.73; H, 4.71. Found: C, 61.80; H, 4.39.

Synthesis of Bis(imine) 5. A flame-dried Schlenk flask was charged with dialdehyde **4** (500 mg, 1.17 mmol) and dissolved in a minimum amount of THF. To the solution was added a small amount of $MgSO_4$ followed by methylamine (2.0 M in THF, ~5 equiv). The reaction was monitored by NMR until quantitative conversion to the bis(imine) was obtained (3 h). The solution was separated from the $MgSO_4$ and transferred to a new flame-dried Schlenk flask via cannula filtration. Solvent and excess methylamine removal gave 530 mg of spectroscopically (^1H NMR) pure bis(imine) (>98% yield) (excessive handling of bis(imine) **5** resulted in decomposition; therefore, it was immediately carried onto the diamine synthesis in situ). ^1H NMR (200 MHz, $CDCl_3$): δ 7.97 (d, J_{HH} = 1.6 Hz, 2H, FcCH), 4.83 (dd, J_{HH} = 2.5, 1.5 Hz, 2H, FcH), 4.67 (dd, J_{HH} = 2.5, 1.5 Hz, 2H, FcH), 4.45 (t, J_{HH} = 2.5 Hz, 2H, FcH), 4.20 (s, 10H, FeC_5H_5), 3.22 (d, J_{HH}= 1.6 Hz, 6H, NCH_3).

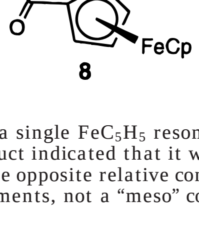
Synthesis of diamine 1. A precooled (0 °C) solution of the bis(imine) **5** from the above procedure (530 mg, 1.17 mmol) in THF (5 mL) was transferred by cannula to a precooled (0 °C) 0.1 M solution of SmI_2 (33 mL, 3 equiv, 3.3 mmol). The reaction was monitored by NMR until the imine was consumed (~30 min) and then quenched with a saturated NH_4Cl solution and washed with NH_4Cl, $NaHCO_3$, and brine. The organic layer was then transferred to an Erlenmeyer flask and combined with an equal volume of a 1 M D-tartaric acid solution. The biphasic mixture was stirred until all of the orange color transferred into the aqueous layer. The phases were then separated, and the aqueous portion was treated with a 6 M solution of NaOH until basic. An equal volume of CH_2Cl_2 was then added, and the diamine was back-extracted into the organic layer, washed with pH 7 buffer and brine, and then dried over $MgSO_4$. The solvent was then removed in vacuo to afford 315 mg of spectroscopically pure (^1H NMR) diamine as a mixture of *trans* (i.e. *R*,*R* and *S*,*S* configurations at the carbinol carbons) diastereomers (59% yield, 90% de by integration of the NCH_3 resonances in the ^1H NMR).[25] Recrystallization from boiling heptane afforded analytically and diastereomerically pure diamine as a yellow-orange solid. ^1H NMR (400 MHz, $CDCl_3$): δ 4.30 (d, J_{HH} = 2.4 Hz, 4H, FcH), 4.18 (t, J_{HH} = 2.4 Hz, 2H, FcH), 3.91 (s, 10H, FeC_5H_5), 3.72 (s, 2H, FcCH), 2.56 (s, 6H, NCH_3), 2.15 (s, br, 2H, NH) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 83.6, 79.3, 69.6, 66.4, 66.2, 62.0, 60.4, 34.5 ppm. $[\alpha]_D^{25.4}$ = −38.0 (*c* 1.06, CH_2Cl_2). Anal. Calcd for $C_{24}H_{26}Fe_2N_2$: C, 63.47; H, 5.77; N, 6.17. Found: C, 63.67; H, 5.89; N, 5.81.

Synthesis of $Ti(OAr)_2Cl_2(1)$ (6). To a flame-dried 25 mL Schlenk flask in a drybox was added Ti(O-4-vinyl-2,6-$(CH_3)_2C_6H_2)_2Cl_2$(dmpe) (86 mg, 0.98 mmol) and toluene (5 mL). To this vigorously stirred solution was added dropwise a solution of **1** (70 mg, 0.98 mmol) in toluene (1 mL). The flask was connected to a Schlenk line and the mixture allowed to react for 30 min. The solvent was then removed in vacuo and the resulting solid triturated with toluene to facilitate the removal of dmpe. The resulting crude product was recrystallized from 3:1 toluene−pentane to give 103 mg of **6** as dark red crystals (83% yield). (Note: **6** crystallizes with 1.5−2.0 equiv of toluene (^1H NMR), which remains after exhaustive drying.) ^1H NMR (200 MHz, C_6D_6); δ 7.03 (s, 4H, OArH), 6.62 (dd, 2H, J_{HH} = 17.6, 10.8 Hz, ArC*H*CH$_2$), 5.59 (dd, 2H, J_{HH} = 17.6, 1.2 Hz, ArCHC*H*H), 5.09 (dd, 2H, J_{HH} = 17.6, 1.2 Hz, ArCHCH*H*), 4.49 (dd, 2H, J_{HH} = 8.5, 3.1 Hz, FcCH), 4.26 (m, br, 2H, NH), 4.10 (t, 2H, J_{HH} = 1.7 Hz, FcH), 3.89 (d, 4H, J_{HH} = 1.7 Hz, FcH), 3.75 (s, 10H, FeC_5H_5), 3.04 (d, 6H, J_{HH} = 5.6 Hz, NCH_3), 2.78 (s, 12H, $OArCH_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 166.7, 137.2, 130.0, 129.5, 127.0, 85.5, 81.0, 71.1, 67.4, 66.0, 64.9, 63.9, 39.7, 18.7 ppm. $[\alpha]_D^{25.4}$ = −14.0 (*c* = 0.95, CH_2Cl_2). Anal. Calcd for $C_{44}H_{48}Cl_2Fe_2N_2O_2Ti\cdot 1.5C_7H_8$: C, 64.10; H, 6.01; N, 2.79. Found: C, 64.47, H, 6.31, N, 2.79.

Synthesis of (dppe)Pt(2) (7). To a 25 mL round-bottom flask equipped with a sidearm and reflux condenser was added (dppe)$PtCO_3$ (153 mg, 0.23 mmol), **2** (100 mg, 0.23 mmol), and chlorobenzene (10 mL). The suspension was then heated to 80 °C while continuously bubbling N_2 through the solution to facilitate the removal of liberated CO_2. Once reaction was complete (^{31}P NMR, 30 min), the homogeneous solution was cooled to room temperature and chlorobenzene was removed in vacuo. The crude product was then recrystallized from boiling toluene to afford 135 mg of spectroscopically pure (^1H NMR) **7** as a bright orange solid (57% yield). ^1H NMR (400

---

(24) Isolation and spectroscopic characterization of the minor diastereomer indicated that it was an asymmetric byproduct containing doubled sets of resonances for the acetal, C_5H_5, and the substituted Cp. Since deprotection of this material yielded a symmetric dialdehyde with no optical rotation, we assign this material to the product of a heterocoupling event between the minor and major lithiated diastereomers (i.e., the meso isomer, **8**).



8

(25) The presence of a single FeC_5H_5 resonance in the ^1H NMR of the isolated minor product indicated that it was likely the product of a *trans* coupling with the opposite relative configuration with respect to the planar chiral elements, not a "meso" coupling.

MHz, CD_2Cl_2): δ 8.32 (dd, 4H, $J_{HH} = 11.6, 7.2$ Hz, ArH), 8.19 (dd, 4H, $J_{HH} = 11.6, 7.2$ Hz, ArH), 7.14 (t, 8H, $J_{HH} = 7.2$ Hz, ArH), 7.04 (t, 4H, $J_{HH} = 1.6$ Hz, ArH), 5.85 (s, 2H, FcCH), 5.18 (dd, 2H, $J_{HH} = 2.2, 1.0$ Hz, FcH), 4.47 (dd, 2H, $J_{HH} = 2.2$, 1.0 Hz, FcH), 4.26 (t, 2H, $J_{HH} = 2.2$ Hz, FcH), 4.06 (s, 10H, FeC_5H_5), 2.10−1.60 (m, br, 4H, PCH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 133.8 (m), 133.0 (m), 131.7, 131.6, 130.7 (d, $J_{CP} = 19.9$ Hz), 130.1 (d, $J_{CP} = 21.4$ Hz), 129.2 (m), 93.1, 87.9, 81.1, 70.3, 66.2, 65.2, 62.8, 26.5 (m) ppm (only seven of the eight expected aromatic carbons were observed). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 28.48 ($J_{PPt} = 3260$ Hz) ppm. $[\alpha]_D^{25.4} = -26.4$ ($c = 1.01$, toluene). Anal. Calcd for $C_{48}H_{42}Fe_2O_2P_2Pt$: C, 56.55; H, 4.15. Found: C, 56.23; H, 4.02.

Crystallography. Suitable crystals were mounted on the tip of a glass fiber using a minimal amount of oil and frozen in place in a stream of N_2 at −100 °C. Diffraction experiments were carried out on a Bruker SMART 1K CCD diffractometer equipped with graphite-monochromated Kα radiation. The experimental conditions are summarized in Table 1. The frame data were converted to intensities using the Bruker routine SAINT and then corrected for absorption effects using SADABS. Direct methods were used to locate the heavy atoms, and the rest of the non-hydrogen positions were located with difference Fourier syntheses. All the non-hydrogen atoms were included in the refinement with anisotropic thermal parameters; hydrogens were included in the final cycles at idealized positions using a riding model. Solution and refinement were performed using the NRCVAX suite of programs.

In the case of **6**, the crystals did not diffract well, and even using long exposure times (120 s frames) only ~$^1/_3$ of the available reflections could be considered observed. As a result only the heavy atoms (Ti, Cl, Fe) could be refined anisotropically. Attempts to include lighter atoms with anisotropic thermal parameters gave unstable refinements and resulted in an unreasonably low data-to-parameter ratio.

Acknowledgment. This work was partially supported by the NSF, under the auspices of a Career Development Award to M.R.G. (Grant No. CHE-9624852), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the DuPont Co. for a Grant in Aid.

Supporting Information Available: Tables of metrical parameters for **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org. These structures have also been deposited in the Cambridge Structural Database.

OM9905512