Studies on Selective Nucleophilic Substitution Reactions of [(Cyclopentadienyl)(1,3-dichlorobenzene)M]$^+$ PF_6^- Complexes (M = Fe, Ru)

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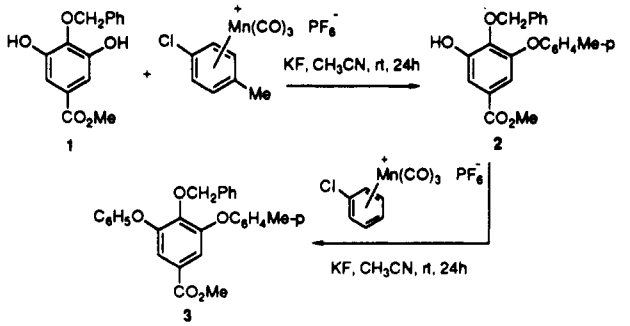
Reactions of [cyclopentadienyl)(1,3-dichlorobenzene)M]$^+PF_6^-$ complexes (M = Fe, Ru) with phenoxide nucleophiles were found to proceed with excellent selectivity under mild conditions to give products of monosubstitution. Using aminophenoxides, a preference for O-arylation was observed, while amino alcohols such as prolinol react selectively on nitrogen. Methodology for sequential selective displacement of both chlorides by different nucleophiles is reported.

The selective formation of diaryl ethers under mild conditions in the presence of sensitive functional groups is of current interest because of the presence of such ether linkages in a number of important cyclic peptide/aryl ethers, exemplified by the vancomycin group of antibiotics,[1] antitumor agents such as bouvardin[2] and OF4949,[3] and the angiotensin converting enzyme inhibitor K-13.[4] Methods presently employed for preparing diaryl ethers include the Ullmann coupling reaction,[5] in which an aryloxide is coupled with an aryl halide in the presence of a copper salt at high temperatures, often in basic solvents such as pyridine, and thallium(II)-promoted oxidative coupling procedures.[6] We have been investigating the uses of chloroarene–metal π complexes as reactive intermediates for the selective formation of diaryl ethers and triaryl diethers.[7] One approach is illustrated in Scheme I, in which construction of an unsymmetrical triaryl diether was accomplished by sequential monoarylations of the protected methyl gallate 1 with chloroarene–$Mn(CO)_3$ cations, followed by demetalation, both of which are performed under very mild conditions.[8]

The use of arene–manganese complexes is, however, limited to monochloro substitution; a number of attempts

Scheme I



Scheme II

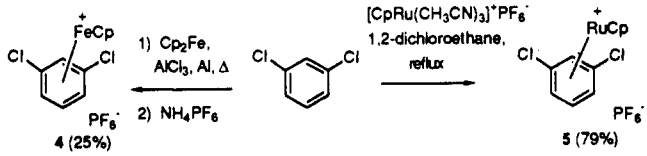


Table I. Nucleophilic Disubstitution of 1,3-Dichlorobenzene–MCp PF_6 Complexes 4 and 5

complex	base	conditions	product (yield, %)
4	K_2CO_3	THF, 50 °C, 16 h	6 (43)
4	K_2CO_3	CH_3CN, reflux, 30 min	6 (70)
4	NaH	THF, 0 °C (20 min), rt (2 h)	6 (87)
4	NaH	THF, 0 °C (30 min), rt (30 min)	6 (98)
5	NaH	THF, −30 °C (30 min), rt (2 h)	7 (74)

to prepare 1,2-, 1,3-, and 1,4-dichlorobenzene–$Mn(CO)_3$ complexes in our laboratory under a variety of conditions have so far been unsuccessful.[9] On the other hand, [arene–FeCp]$^+PF_6^-$ and [arene–RuCp]$^+PF_6^-$ complexes of dichlorobenzenes are known, and the iron complexes have been shown to undergo nucleophilic displacement of chloride, although the selectivity of these reactions and demetalation of the product complexes have not been thoroughly investigated.[10] We report herein studies on the selective construction of diaryl ethers and triaryl diethers under conditions that allow the use of protected amino acid derivatives, which has been undertaken as part of a systematic investigation of methodology for synthesis of the aforementioned antibiotics. We also include studies

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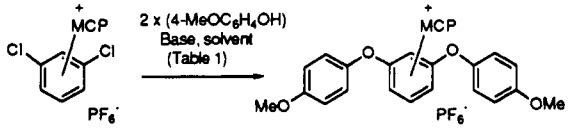
on the selectivity of N vs O arylation of amino alcohols and amino phenols.

Results and Discussion

The 1,3-dichlorobenzene–MCp complexes 4 (M = Fe)[10] and 5 (M = Ru)[11] were prepared using the literature procedures, or slight modifications thereof, as indicated in Scheme II. While the yield of 5 is higher than that of 4, the expense of ruthenium compounds compared to iron, coupled with the low cost of the dichlorobenzene, makes the use of 5 less attractive. However, we have shown[12] that efficient decomplexation allows recycling of $[CpRu(CH_3CN)_3]PF_6$ and that arene–RuCp complexes of chlorophenylalanine derivatives can be prepared. Consequently, Cp–ruthenium provides a useful activation system in cases where harsh reaction conditions, which are necessary for the preparation of 4, cannot be tolerated.

The reactions of 4 and 5 with various nucleophiles were next investigated. Optimum conditions were established by treating 4 with 2 equiv of 4-methoxyphenol in the presence of base in different solvents to give the triaryl diether complex 6. The results of this study are summarized in Table I, from which it can be seen that quite mild conditions allow high yield conversion of 4[13] and that sodium hydride is the base of choice for these reactions. Similarly mild conditions allow the conversion of 5 to 7.



4 M = Fe
5 M = Ru

6 M = Fe
7 M = Ru

Ether substituents attached to the arene of arene–metal complexes are known to deactivate the aromatic ring toward nucleophilic attack at the ortho and para positions,[14] owing to resonance electron donation, but whether the ring is overall sufficiently deactivated to allow selective displacement of one of the chlorides from complexes 4 and 5 is not fully established.[15] Reaction of these complexes with 1 equiv of aryloxide nucleophile was examined, and the results are summarized in Figure 1. In general, for the more reactive phenoxides, the reaction was run at −78 °C for ca. 2 h, followed by stirring at room temperature for ca. 2 h. Under these conditions, excellent yields of stable monosubstitution products 8–10 were obtained; since the arene–metal system is chiral in some of these complexes, a mixture of diastereomers is obtained with chiral or prochiral nucleophiles (see Experimental Section). The less reactive phenoxides derived from 4-nitrophenol and 2-nitrophenol gave no reaction under these mild reaction conditions; at higher temperatures, extensive decomposition occurred and no characterizable products were obtained, indicating that *very* unreactive phenoxides will not add to the arene complex. On the other hand, treatment of 4 with an excess of 3-nitrophenol/sodium hydride gave the triaryl diether complex 11. It was not possible to control this reaction to give the product of monosubstitution; the use of 1 equiv of nucleophile gave an approximately 2:1 mixture in favor of monosubstituted product 12 in 56% combined yield. The somewhat more reactive 2-amino-5-nitrophenol did give monosubstituted product 13. This complex was very unstable, precluding purification, and the structure (O vs N arylation) was established using the diaryl ether obtained after demetalation (see later).

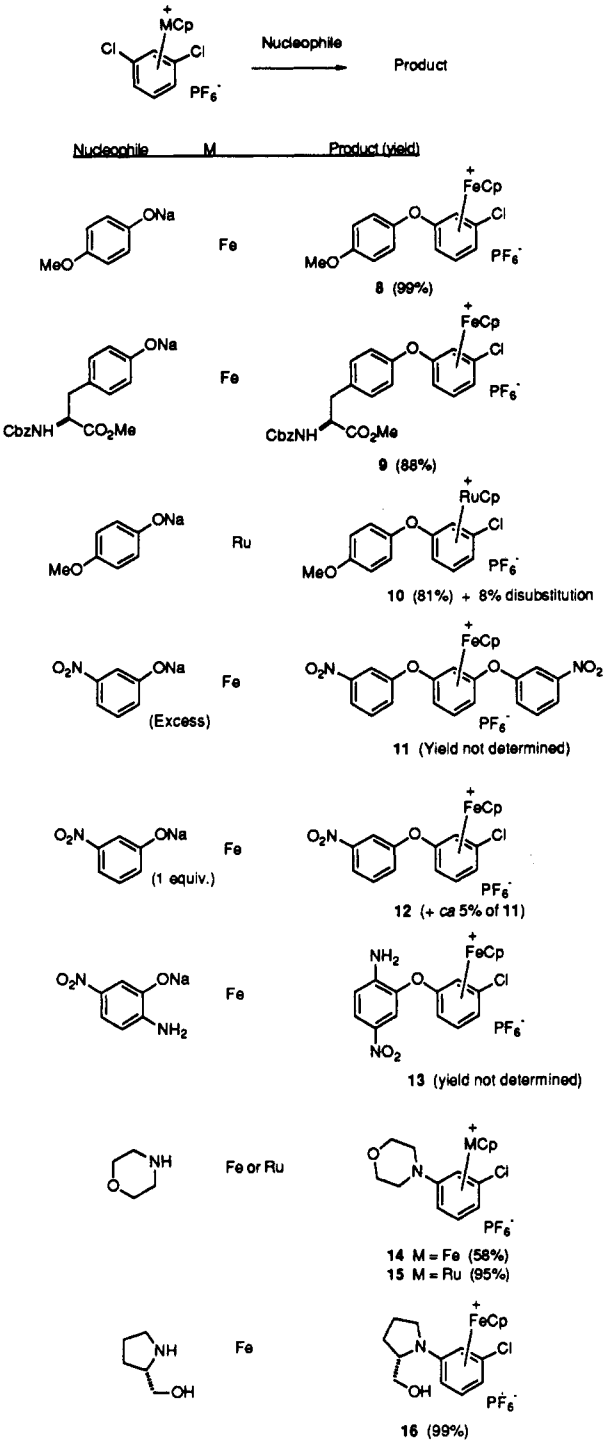


Figure 1. Selective reactions of complexes 4 and 5 with nucleophiles.

Sutherland and co-workers[10] have reported the reaction of monochloroarene–FeCp complexes with morpholine to give nucleophilic substitution. Complexes 4 and 5 underwent monosubstitution to give 14 and 15, respectively. Double selectivity was observed during the reaction of 4 with L-prolinol. Thus, treatment of 4 with 1.0 equiv of the amine in the presence of 2.5 equiv of K_2CO_3 (THF, rt,

(11) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.
(12) Park, J. G. Ph.D. Dissertation, Case Western Reserve University, 1991. Pearson, A. J.; Park, J. G. *J. Org. Chem.* In press.
(13) These reactions conditions are much milder than those reported by Sutherland and co-workers (ref 10), who generally carry out such nucleophilic displacement at much higher temperatures.
(14) Khan, M. M.; Watts, W. E. *J. Organomet. Chem.* **1976**, *108*, C11.
(15) Sutherland and co-workers (ref 10) have not examined selectivity during the reaction of 4 with phenoxide nucleophiles, although the reactions of this complex with diethyl alkylmalonates have been studied.

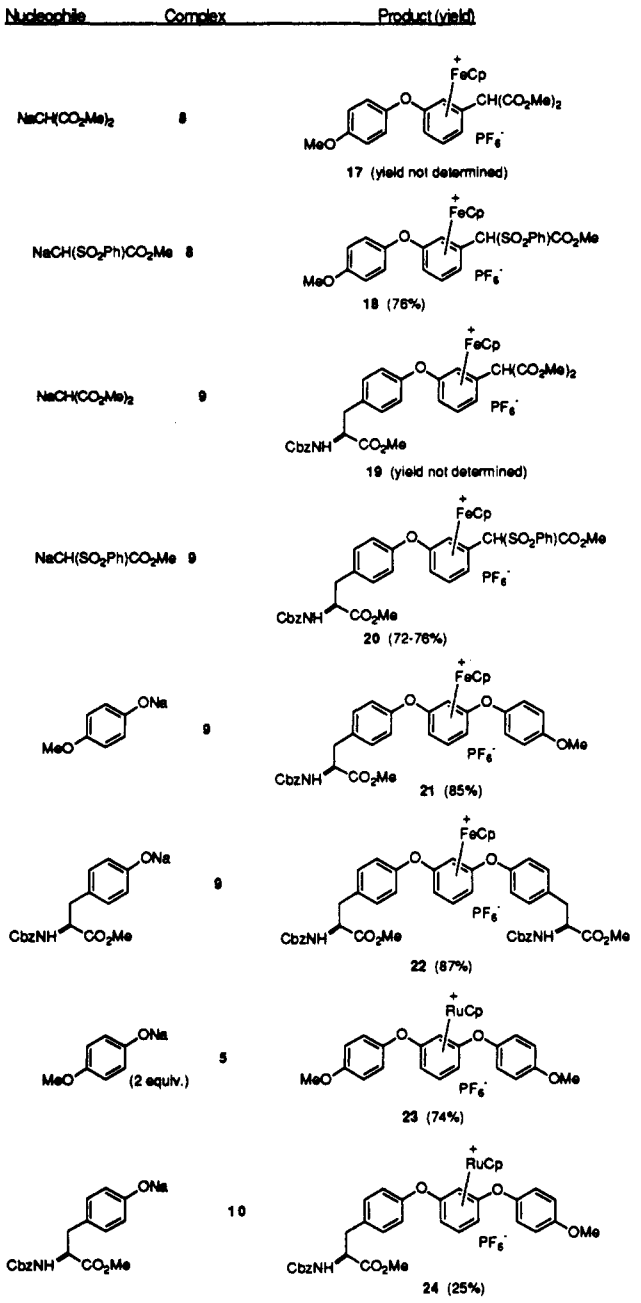
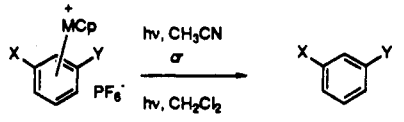


Figure 2. Preparation of 1,3-disubstituted arene–MCp complexes.

overnight) gave exclusively the N-arylated product **16** in 99% yield. The structure was rigorously established using the aromatic compound resulting from demetalation. These results are consistent with the greater nucleophilicity of secondary amine vs alcohol, while the selectivity observed during the formation of **13** is consistent with the more facile deprotonation of phenolic OH to give the nucleophilic aryloxide.

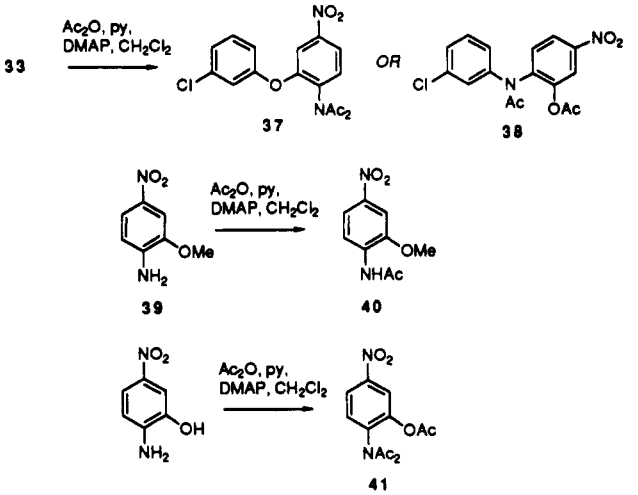
Further reactions of complexes **8–10** with nucleophiles were studied. The results are summarized in Figure 2 and are self-explanatory. Reactions with stabilized enolates (malonates, (phenylsulfonyl)acetates) proceeded satisfactorily with the iron complexes **8** and **9**, and no problems were encountered with the protected amino acid substituent of the latter. In several cases, it was more convenient to purify the products of demetalation. The ruthenium complex **10** did not react with dimethyl malonate anion under a variety of conditions (from room temperature to 50 °C in a variety of solvents: THF, DMF, DMSO, HMPA). We observed either no reaction at all or considerable decomposition to give intractible product mixtures. All complexes **8–10** reacted satisfactorily with phenoxide nucleophiles to give triaryl diether derivates **21–24**, although better yields were obtained from the iron complexes. This, together with their lower cost, make them more attractive as synthetic intermediates.

Demetalation of the arene–MCp complexes was readily accomplished by irradiation (sunlamp, 275 W) in the presence of suitable donor ligand (usually acetonitrile as solvent).[16] In the case of the ruthenium complexes, this leads to a convenient method of recovery and recycling the metal, since it is collected in 80–90% yield as the ether-insoluble complex $[CpRu(CH_3CN)_3]^+PF_6^-$. The results of decomplexation are summarized in eq 1.



25 X = 4-MeOC$_6$H$_4$O, Y = CH(CO$_2$Me)$_2$ (20%)
26 X = 4-MeOC$_6$H$_4$O, Y = CH(SO$_2$Ph)CO$_2$Me (33%)
27 X = 4-MeOC$_6$H$_4$O, Y = (L)-tyrosyl-O (81%)
28 X = (L)-tyrosyl-O, Y = CH(CO$_2$Me)$_2$ (45%)
29 X = (L)-tyrosyl-O, Y = CH(SO$_2$Ph)CO$_2$Me (33%)
30 X = Y = (L)-tyrosyl-O (45%)
31 X = Y = 3-(O$_2$N)C$_6$H$_4$O (59%)
32 X = 3-(O$_2$N)C$_6$H$_4$O, Y = Cl (38%)
33 X = Cl, Y = 2-(NH$_2$)-5-(NO$_2$)-C$_6$H$_3$O (51%)
34 X = Cl, Y = N(CH$_2$CH$_2$)$_2$O (79%)
35 X = Cl, Y = N-prolinyl (100%)
36 X = Cl, Y = N-(O-acetyl)prolinyl (100%)

The decomplexed materials **33** and **36** were used for further verification of the structures of **13** and **16**, respectively. We were fairly confident that **13** was the product of O-arylation, because complex **4** did not react with either aniline or *p*-nitroaniline under the conditions used for these reactions. Thus, in view of the fact that *m*-nitrophenol gave complexes **11** and **12** on reaction with **4**, there is clearly a strong preference for reaction with phenoxide nucleophiles rather than aromatic amines. Acetylation of **33**, however, gave a *diacetate*, showing IR bands at 1779 and 1687 cm^{-1}, acetyl CH$_3$ ^{1}H resonances at δ 2.24 and 2.15 ppm and ^{13}C resonances at δ 23.13 and 20.67. Thus, there was some doubt as to whether the diacetate was **37** or **38**; this was further questioned by the



fact that acetylation of commercially available 2-meth-

(16) Alternative methods of decomplexation involve pyrolysis in a suitable donor solvent, but these reaction conditions are too harsh for use in the presence of sensitive functionality. See: Helling, J. F.; Braitsch, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 7207 and 7209. For earlier work on photochemical demetalation, see: Nesmeyanov, A. N.; Vol'kenau, N. A.; Shilovtseva, L. S. *Izv. Akad. Nauk, SSSR Ser. Khim.* **1969**, 726. Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1983**, *248*, C9. Gill, T. P.; Mann, K. R. *J. Organomet. Chem.* **1981**, *216*, 65.

oxy-4-nitroaniline (39) gave a monoacetate (40) (IR, 1705 cm^{-1}; ^1H NMR, 2.24 ppm; ^{13}C NMR 25.05 ppm). Further support for the structure of 33 was gained from the acetylation of 2-hydroxy-4-nitroaniline itself which gave *triacetate* 41 (IR, 1782 and 1722 cm^{-1}; the latter band is twice as intense as the earlier compounds, suggesting overlapping NAc and OAc bands; ^1H NMR, 2.29, 9 H, s; ^{13}C NMR, 26.26, 20.54, 2:1 intensity ratio). Thus, it appears that an electron-withdrawing substituent ortho to the amino group (OAc in 41 and 3-ClC_6H_4O in 33) induces a second N-acetylation to give the imide, while the absence of such a substituent leads to N-monoacetylation. A plausible explanation for this rather unexpected result is that a weakly electron-withdrawing group results in somewhat greater acidity of the NH proton of the amide intermediate, thereby leading to deprotonation under the acetylation conditions and subsequent formation of the imide. These experiments support the assignment of structure 37 to the diacetyl derivative of 33.

The structure of 35, resulting from selective N-arylation of L-prolinol, was more easily established. Acetylation (Ac_2O, py, DMAP, CH_2Cl_2) gave the acetate 36 in quantitative yield. Spectroscopic studies confirmed this to be the *O*-acetyl compound: IR, 1736 cm^{-1}; ^1H NMR, 2.06 ppm, OAc; 4.23 (dd, J = 10.4, 3.7 Hz) and 3.79 (dd, J = 10.4, 8.4 Hz), CH_2OAc. This diastereotopic methylene is observed as a 2 H multiplet at 3.66–3.63 ppm for the alcohol 35; its downfield shift on acetylation is in full agreement with the assigned structure.

In conclusion, we have shown that highly selective sequential nucleophilic displacement of chloride occurs on reaction of 1,3-dichlorobenzene–MCp cations (M = Fe and, to a lesser extent, Ru) with certain nucleophiles. A dual selectivity is also observed, whereby aliphatic amino alcohols such as prolinol react exclusively on nitrogen, while aminophenoxides react on oxygen. The 1,3-dichlorobenzene complexes are sufficiently reactive to allow arylation of *m*-nitrophenols, but not the less reactive ortho or para derivatives. This contrasts with chlorobenzene–FeCp which, in our hands, is completely unreactive toward all nitrophenols. The coupling and subsequent decomplexation reactions proceed under conditions that are sufficiently mild to accommodate the use of relatively sensitive functionality.

Experimental Section

NMR (proton or ^{13}C) spectra were recorded on a Varian XL 200 (200 MHz) or Varian Gemini-300 (300 MHz) spectrophotometer using $CDCl_3$, acetone-d_6, CD_3CN, or DMSO-d_6 as solvent with internal TMS standard. Infrared spectra were recorded on a Perkin-Elmer 1420 or Perkin-Elmer 1600 series FTIR spectrophotometer. Optical rotations were recorded on a Perkin-Elmer 141 polarimeter. Mass spectral analyses were performed by the Chemistry Department of Case Western Reserve University using a Kratos MS25A instrument; elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN. The purity of compounds not submitted for combustion analysis was assessed from their proton or carbon NMR spectra. Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected.

All reactions were conducted under an inert atmosphere of dry, oxygen-free argon or nitrogen unless otherwise noted. Organic solvents were purified prior to use as follows: ether and THF were freshly distilled from Na/benzophenone; CH_3CN and CH_2Cl_2 were distilled from CaH_2; DMF was vacuum distilled after stirring over 4-Å molecular sieves then stored over 4-Å molecular sieves under nitrogen. Complex 4 was prepared according to the literature procedure.[4]

(η^6-1,3-Dichlorobenzene)(η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (5). To a stirred solution of 1.2 mL (10 equiv) of 1,3-dichlorobenzene in 1,2-dichloroethane (degassed, 10 mL) was added 434.3 mg (1.0 mmol) of $(CH_3CN)_3RuCpPF_6$, and the mixture was then refluxed under Ar for 17 h. Solvent was removed in vacuo. The residue was diluted with ether. The precipitate was collected, washed with ether, and then dried. The crude product was eluted through columns of neutral alumina (acetone) and then silica gel (acetone) to give a colorless solution. Further purification by recrystallization from 95% ethanol gave 360.5 mg (78.7%) of a pale brown-grey solid: mp 265–70 °C dec; IR (Nujol) 3100, 1130, 1065, 850 cm^{-1}; ^1H NMR (200 MHz, acetone-d_6) δ 7.35 (1 H, t, J = 1.1 Hz, 2-H), 6.80 (2 H, dd, J = 6.4 and 1.1 Hz, 4- and 6-H), 6.61 (1 H, dd, J = 6.4 and 6.4 Hz, 5-H), 5.73 (5 H, s, *Cp*). Anal. Calcd for $C_{11}H_9Cl_2F_6PRu$: C, 28.84; H, 1.98. Found: C, 28.95; H, 1.91.

[η^6-1,3-Bis(4-methoxyphenoxy)benzene](η^5-cyclopentadienyl)iron Hexafluorophosphate (6). To a stirred suspension of 4.13 g (10 mmol) of (*m*-dichlorobenzene)$CpFe^+$ complex 4 in 10 mL of THF was added a solution of 4-methoxyphenol sodium salt [from 1.06 g (22 mmol, 2.2 equiv) of 50% NaH in oil and 3.10 g (25 mmol) of 4-methoxyphenol] in 10 mL of THF at 0 °C over 30 min. The mixture was stirred for an additional 30 min at 0 °C and then quenched with 2 mL of water. After THF was evaporated on a rotary evaporator, the residue was redissolved in CH_2Cl_2 and washed with 1 N NaOH (2 × 50 mL) to remove unreacted phenol and then with water until neutral. The organic phase was dried over $MgSO_4$ and then concentrated to give 5.76 g (97.9%) of yellow powder. This was pure enough for characterization: IR ($CHCl_3$) 3100, 2940, 1590, 835 cm^{-1}; ^1H NMR (200 MHz) in CD_3CN δ 7.17 and 7.05 (4 H each, d, J = 9.2 Hz, uncomplexed aromatic Hs), 6.10 and 5.87 (2 H each, m, complexed aromatic Hs), 5.03 (5 H, s, *Cp*), 3.83 (6 H, s, OCH_3); in $CDCl_3$ δ 7.00 (8 H, br s, uncomplexed aromatic Hs), 6.27 (1 H, t, J = 6 Hz, complexed aromatic 5-H), 5.96 (1 H, s, complexed aromatic 2-H), 5.86 (2 H, d, J = 6 Hz, complexed aromatic 4- and 6-H), 4.99 (5 H, s, *Cp*), 3.82 (6 H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 145.8, 133.7, 121.5, 115.9, 84.0, 77.1, 72.2, 65.9, 55.7.

[η^6-3-Chloro-1-(4-methoxyphenoxy)benzene](η^5-cyclopentadienyl)iron Hexafluorophosphate (8). 4-Methoxyphenol sodium salt (12.11 mmol, from 4-methoxyphenol and NaH) in 15 mL of THF was added dropwise into a stirred suspension of (1,3-dichlorobenzene)$CpFePF_6$ in 15 mL of THF at −78 °C. After the addition, the reaction was allowed to reach to room temperature and then quenched with 5 mL of water. THF was removed in vacuo, and the residue was taken up into CH_2Cl_2. The organic layer was washed with water and then dried over $MgSO_4$. CH_2Cl_2 was evaporated in vacuo to give 5.97 g (98.5% yield) of a very thick, dark brown oil: IR ($CHCl_3$) 3100, 3050, 2990, 1500, 1260, 850 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.06 (4 H, s, uncomplexed aromatic Hs), 6.50–6.43 (2 H, m, 4- and 5-H), 6.24 (1 H, s, 2-H), 6.16 (1 H, d, J = 6.3 Hz, 6-H), 5.15 (5 H, s, *Cp*), 3.86 (3 H, s, OCH_3); MS m/z (rel int) 129.1 (76), 234.0 (100), $[M]^+$ not found.

[η^6-3-Chloro-1-[4-L-[2-[*N*-(benzyloxycarbonyl)amino]-3-methoxy-3-oxopropyl]phenoxy]benzene](η^5-cyclopentadienyl)iron Hexafluorophosphate (9). *N*-(Benzyloxycarbonyl)-L-tyrosine methyl ester (500 mg, 1.52 mmol) in 5 mL of dry THF was added dropwise to a stirred slurry of NaH (50% in oil, 70.7 mg, 1.47 mmol, 0.97 equiv) in dry THF (5 mL) at 0 °C. The resulting clear solution was transferred with a cannula to a stirred solution of (1,3-dichlorobenzene)$CpFePF_6$ (4, 626.8 mg, 1.52 mmol) in 10 mL of dry THF at −78 °C. After the addition of the aryloxide solution, the dry ice–acetone bath was removed to allow the reaction to come to room temperature. The color of the solution turned to cloudy yellow upon warming. Stirring was continued for an additional 30 min at room temperature. The reaction was quenched by adding 0.5 mL of water. Solvent was removed in vacuo, and the residue was taken up into CH_2Cl_2, washed with water until neutral, and then dried over $MgSO_4$. The solution was filtered and evaporated to 5 mL on a rotary evaporator. The concentrated solution was added to 200 mL of ether. The product was obtained as a yellow solid (916.3 mg, 85.5% yield). Because the product is sensitive to light, it should be stored in the dark: mp 83–5 °C; IR ($CHCl_3$) 3420, 3100, 2950, 1740, 1720, 1500, 850 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.34 (5 H, s, CO_2CH_2Ph), 7.26 (2 H, d, J = 8.3 Hz, uncomplexed aromatic Hs, meta to O), 7.04 (2 H, d, J = 8.3 Hz, uncomplexed aromatic Hs,

ortho to O), 6.45 (2 H, br s, 2-H and 4-H), 6.28 (1 H, d, J = 5.9 Hz, 6-H), 6.17 (1 H, t, J = 6.4 Hz, 5-H), 5.43 (1 H, d, J = 7.6 Hz, N-H), 5.14 (5 H, s, *Cp*), 5.10 (2 H, s, OCH_2Ph), 4.62 (1 H, apparently br q with J = 7 Hz) 3.76 (3 H, s, CO_2Me), 3.20 (1 H, dd, J = 9.6 and 4.8 Hz, ArC*H*HCHNH), 3.08 (1 H, dd, J = 15 and 9.6 Hz, ArCH*H*NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 155.6, 151.6, 136.2, 135.4, 133.2, 131.9, 131.8, 128.5, 128.2, 128.0, 120.4, 106.2, 86.4, 85.4, 79.4, 75.7, 66.9, 54.8, 52.6, 37.4; MS m/z (rel int) $[M]^+$ not found, 129.1 (100), 239.2 (48), 368.3 (65).

[η^6-1-Chloro-3-(4-methoxyphenoxy)benzene](η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (10). To a stirred solution of 200 mg (0.44 mmol) in **5** in 5 mL of THF was added dropwise a solution of 4-methoxyphenol sodium salt [from 65 mg of 4-methoxyphenol and 21 mg of NaH (50% in oil)] in 5 mL of THF at −78 °C. The mixture was stirred for 2 h at −78 °C and 2 h at room temperature. The reaction mixture was filtered through a Celite pad (THF) and then the solvent was removed in vacuo. The residue was dissolved in 2 mL of acetone and the solution was added to 30 mL of ether to give 212.5 mg of pale yellow oil. An NMR spectrum showed a 15:1 mixture of mono:disubstituted products. Total yield = 89%. **10**: ^1H NMR (200 MHz, acetone-d_6) δ 7.31 and 7.11 (2 H each, d, J = 9.1 Hz, uncomplexed aromatic Hs), 6.80 (1 H, t, J = 1.2 Hz, complexed aromatic 2-H), 6.66 (1 H, dd, J = 1.1 and 5.5 Hz, complexed aromatic 6-H), 6.48 (1 H, t, J = 6 Hz, complexed aromatic 5-H), 6.30 (1 H, dd, J = 1.5 and 6 Hz, complexed aromatic 4-H), 5.70 (5 H, s, *Cp*), 3.86 (3 H, s, OCH_3).

(Cyclopentadienyl)(1-chloro-3-morpholinobenzene)iron Hexafluorophosphate (14). A mixture of complex **4** (1.239 g, 3.0 mmol) and K_2CO_3 (1.035 g, 7.5 mmol) was stirred in dry THF (50 mL) at room temperature, and a solution of morpholine (0.5226 g, 0.54 mL, 6.0 mmol) in THF (75 mL) was added dropwise over a period of 1 h. Stirring was continued overnight, the resulting solution was filtered and concentrated by rotary evaporation, and the residue was dissolved in the minimum volume of methylene chloride. This solution was added dropwise to ether (450 mL) and the mixture was set aside in the refrigerator overnight. The yellow precipitate was removed by filtration and the powder was washed with ether and dried in vacuo to give complex **14** (0.8043 g, 58%): mp 171–174 °C dec; ^1H NMR (acetone-d_6) 6.57 (1 H, dd, J = 6.3, 1.6 Hz), 6.47 (1 H, t, J = 1.6 Hz), 6.38 (1 H, t, J = 6.6 Hz), 6.07 (1 H, dd, J = 6.8, 1.6 Hz), 5.24 (5 H, s), 3.84 (4 H, t, J = 5.0 Hz), 3.6–3.54 (4 H, m); ^{13}C NMR (acetone-d_6) 127.17, 107.34, 85.98, 83.41, 78.13, 70.16, 67.67, 66.42, 47.37.

(Cyclopentadienyl)(1-chloro-3-morpholinobenzene)ruthenium Hexafluorophosphate (15). With use of an identical procedure to the preceding reaction, 91.6 mg (0.2 mmol) of complex **5** gave the morpholine adduct **15** (101.7 mg, 95%): ^1H NMR (acetone-d_6) 6.6–6.4 (2 H, m), 6.27 (1 H, t, J = 6.0 Hz), 6.11 (1 H, dd, J = 6.5, 1.6 Hz), 5.59 (5 H, s), 3.80 (4 H, t, J = 5.0 Hz), 3.24 (4 H, m); ^{13}C NMR (acetone-d_6) 126.73, 104.97, 84.09, 83.95, 81.29, 72.29, 69.66, 66.13, 47.86.

(Cyclopentadienyl)[1-chloro-3-[2-(hydroxymethyl)-pyrrolidinyl]benzene]iron Hexafluorophosphate (16). With use of an identical procedure to that in the preceding reaction, 413 mg (1.0 mmol) of **4** was treated with L-prolinol (101.2 mg, 1.0 mmol) in the presence of K_2CO_3 (345 mg, 2.5 mmol) to give complex **16** (473 mg, 99%): ^1H NMR (acetone-d_6) 6.42 (1 H, d, J = 6.2 Hz), 6.32–6.21 (2 H, m), 5.87 and 5.83 (1 H, 2 × dd, J = 6.3, 1.3 Hz diastereomers), 5.11 (5 H, s), 4.27–4.20 (2 H, m), 3.77–3.51 (4 H, m), 2.2–2.05 (4 H, m); ^{13}C NMR (acetonitrile-d_3, diastereomers) 85.65, 85.59, 81.38, 78.10, 73.98, 69.30, 66.83, 63.32, 63.23, 61.73, 61.62, 50.23, 28.77, 23.75.

1-(4-Methoxyphenoxy)-3-(1,3-dimethoxy-1,3-dioxo-2-propyl)benzene (17). Dimethyl sodiomalonate (1.21 mmol, from dimethyl malonate and NaH) in 5 mL of THF was added dropwise to a stirred solution of [3-chloro-1-(4-methoxyphenoxy)-benzene]$CpFe^+$ complex **8** in 5 mL of THF at −78 °C. After the addition of the aryloxide the reaction was allowed to come to room temperature (solution turned to cloudy dark red). Stirring was continued for an additional 30 min at room temperature, and then the mixture was cooled to −78 °C. The reaction mixture was irradiated with UV light (sunlamp, 275 W) for 90 min. Solvent was removed in vacuo and then the residue was dissolved into 10 mL of CH_2Cl_2 and filtered through silica gel to remove polar byproducts. Flash chromatography on silica gel (25% EtOAc–hexanes) gave 75.9 mg (20% yield, unoptimized) of pale yellow oil: R_f 0.21 (25% EtOAc–hexanes); IR (neat) 3000, 2950, 1750, 1730, 1600, 1500 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.23 (1 H, t, J = 8.0 Hz, 5-H), 7.06–6.88 (7 H, m, aromatic Hs), 4.60 (1 H, s, $CH(CO_2Me)_2$), 3.81 (3 H, s, OCH_3) 3.75 (6 H, s, CO_2CH_3); MS m/z (rel int) 330.111 (76.6, $[M]^+$, $C_{18}H_{18}O_6$ requires 330.1103), 112 (31), 129.1 (100), 331.1 (11.7, $[M + 1]^+$). Anal. Calcd for $C_{18}H_{18}O_6$: C, 65.39; H, 5.45. Found: C, 65.52; H, 5.34.

[η^6-1-(4-Methoxyphenoxy)-3-[1-(phenylsulfonyl)-2-methoxy-2-oxoethyl]benzene](η^5-cyclopentadienyl)iron Hexafluorophosphate (18). To a stirred solution of 0.50 g of (3-chloroarene)$CpFePF_6$ **8** (1 mmol) in THF (at −30 °C) was added dropwise a solution of methyl (phenylsulfonyl)sodioacetate (1 mmol, from methyl (phenylsulfonyl)acetate and NaH) in THF. After the addition the reaction was allowed to come to room temperature. Stirring was continued for an additional 30 min and then the reaction was quenched with 0.5 mL of water. Solvent was removed in vacuo and the residue was taken up into 5 mL of CH_2Cl_2 and then dried over $MgSO_4$ (deep red solution). The product was isolated as a deep red oil (493 mg, 76.4% yield) by dropping a concentrated CH_2Cl_2 solution of the reaction mixture into 150 mL of ether: IR (neat) 3100, 2950, 1740, 1300, 850 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.06 (9 H, SO_2Ph and uncomplexed aromatic Hs), 6.58 (1 H, t, J = 6.4 Hz, 5-H), 6.45 (1 H, d, J = 6.4 Hz, 4-H), 6.24 (1 H, s, 2-H), 6.17 (1 H, dd, J = 6.4 and 1.1 Hz, 6-H), 5.16 (5 H, s, *Cp*), 5.04 (1 H, s, $CHSO_2$), 3.87 (3 H, s, $ArOCH_3$), 3.86 (3 H, s, CO_2CH_3).

[η^6-1-(4-Methoxyphenoxy)-3-[4-L-[2-[*N*-(benzyloxycarbonyl)amino]-3-methoxy-3-oxopropyl]phenoxy]-benzene](η^5-cyclopentadienyl)iron Hexafluorophosphate (21). To a stirred solution of 500 mg (0.71 mmol) of the starting (3-chloroarene)$CpFePF_6$ **8** in 10 mL of THF at −78 °C was added dropwise a solution of 4-methoxyphenol sodium salt in 5 mL of THF. The reaction was allowed to come to room temperature and then stirred for an additional 1 h. The reaction was quenched with 1 mL of water and then THF was evaporated in vacuo. The residue was dissolved in 5 mL of CH_2Cl_2 and then dried ($MgSO_4$). The solution was concentrated to 2 mL and added dropwise to 100 mL of ether. The yellow-brown precipitate was collected and dried to give 478 mg (85%) of powder: mp 85–7 °C; IR ($CHCl_3$) 3677, 3425, 3033, 2950, 1716, 1500, 848 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.35 (5 H, s, CH_2Ph), 7.24–7.0 (8 H, m, uncomplexed aromatic Hs), 6.34 (1 H, td, J = 8 and 1.4 Hz, 5-H), 6.0 (3 H, m, 2-, 4-, and 6-H), 5.40 (1 H, br d, J = 8 Hz, N-H), 5.11 (2 H, s, CH_2Ph), 5.03 (5 H, s, *Cp*), 4.68 (1 H, m, C*H*NHZ), 3.85 (3 H, s, $ArOCH_3$), 3.76 (3 H, s, CO_2CH_3), 3.23 (1 H, dd, J = 14 and 5.5 Hz, ArC*H*HCHNHCbz), 3.08 (1 H, dd, J = 14 and 6 Hz, ArCH*H*CHNHCbz). Anal. Calcd for $C_{36}H_{34}O_7NF_6PFe$: C, 54.44; H, 4.28; N, 1.76. Found: C, 54.44; H, 4.37; N, 1.79.

[η^6-1,3-Bis[4-L-[2-[*N*-(benzyloxycarbonyl)amino]-3-oxo-3-methoxypropyl]phenoxy]benzene](η^5-cyclopentadienyl)iron Hexafluorophosphate (22). *N*-Cbz-tyrosine methyl ester Na salt (from *N*-Cbz-tyrosine methyl ester and NaH) in 5 mL of dry THF (0.71 mmol) was added dropwise to a stirred solution of the (chloroarene)Fe^+Cp complex **9** (500 mg, 0.71 mmol) in 5 mL of THF at −78 °C. The reaction mixture was allowed to come to room temperature by removing the dry ice–acetone bath (40 min). The reaction was quenched with 2 mL of water, the product was extracted with CH_2Cl_2, and the combined extracts were washed with water, dried over $MgSO_4$, and concentrated to 5 mL and then slowly added to 200 mL of ether to give 614.9 mg (86.9%) of yellow powder: mp 92–95 °C; IR ($CHCl_3$) 3400, 3060, 2920, 1720, 1700, 1485, 830 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.34 (10 H, s, CH_2Ph), 7.23–6.99 (8 H, m, uncomplexed aromatic Hs), 6.35 (1 H, t, J = 6 Hz, 5-H), 6.03 (1 H, s, 2-H), 5.96 (2 H, apparently t, 4- and 6-H), 5.40 (2 H, d, J = 12.8 Hz, N-H), 5.10 (4 H, s, CH_2Ph), 5.04 (5 H, s, *Cp*), 4.64 (2 H, br q, J = 7 Hz, C*H*NHZ), 3.76 (6 H, s, CO_2Me), 3.20 (1 H, dd, J = 14 and 6 Hz, ArC*H*HCH), 3.08 (1 H, dd, J = 14 and 6 Hz, ArC*H*HCH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 155.2, 151.5, 135.7, 134.6, 132.3, 131.4, 128.1, 127.8, 127.6, 119.8, 84.3, 77.3, 73.1, 66.7, 66.6, 54.4, 52.1, 37.0. Anal. Calcd for $C_{47}H_{45}F_6FeN_2O_{10}P$: C, 56.47; H, 4.51; N, 2.80. Found: C, 56.13; H, 4.50; N, 2.62.

[η^6-1,3-Bis(4-methoxyphenoxy)benzene](η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (23). To a stirred solution of 4-methoxyphenol Na salt (from 81.3 mg, 0.66

mmol, of 4-methoxyphenol and 36.7 mg of 50% NaH in oil) in 10 mL of THF was added 100 mg (0.22 mmol) of (1,3-dichlorobenzene)FeCpPF$_6$ as a solid in one portion at −30 °C. The mixture was stirred for 30 min at −30 °C and 2 h at room temperature. The reaction was quenched with 1 drop of water, filtered through a Celite pad, and then THF was removed in vacuo. The residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. Solvent was evaporated, the residue was eluted through a neutral alumina column with acetone, and then the product was isolated by dropping the concentrated solution into 100 mL of ether to give 102.9 mg (74.4%) of white foam after drying in vacuo: IR ($CHCl_3$) 3020, 1500, 1210, 750 cm^{-1}; ^{1}H NMR (200 MHz, acetone-d_6) δ 7.24 and 7.06 (4 H each, d, J = 9.1 Hz, uncomplexed aromatic Hs), 6.32 (1 H, t, J = 1.4 Hz, 5-H), 6.25 (1 H, dd, J = 6.5 and 5.5 Hz, 2-H), 6.04 (2 H, dd, J = 5.9 and 1.4 Hz, 4- and 6-H), 5.59 (5 H, s, *Cp*), 3.83 (6 H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.03, 145.37, 133.42, 121.56, 115.68, 81.70, 80.56, 72.60, 67.01, 55.65. Anal. Calcd for $C_{25}H_{23}F_6O_4PRu$: C, 47.40; H, 3.66. Found: C, 47.51; H, 3.96.

[η^6-1(*S*)-[4-[2-[*N*-(Benzyloxycarbonyl)amino]-3-methoxy-3-oxopropyl]phenoxy]-3-(4-methoxyphenoxy)benzene](η^5-cyclopentadienyl)ruthenium Hexafluorophosphate (24). To a stirred solution of L-*N*-Cbz-tyrosine methyl ester sodium salt [from 22.2 mg (67.4×10^{-6} mmol, 2 equiv) of L-*N*-Cbz-tyrosine and 3.2 mg of NaH (50% in oil) in 5 mL of THF] was added 18.4 mg (33.7×10^{-6} mmol) of 1-chloro-3-(aryloxy)-benzene RuCp complex **10** as a solid in one portion at room temperature; then the mixture was stirred for 30 min. Solvent was removed in vacuo and then the residue was dissolved in acetone and filtered through Celite and neutral alumina (acetone). Attempted crystallization from acetone–ether resulted in a gum (7.1 mg, 25% yield) which turned into white foam during drying under vacuum: IR ($CHCl_3$) 3420, 3200, 2950, 1720, 1500, 750 cm^{-1}; ^{1}H NMR (200 MHz, acetone-d_6) δ 7.49–7.06 (13 H, m, uncomplexed aromatic Hs), 6.76 (1 H, br d, J = 8.4 Hz, N-H), 6.39–6.04 (4 H, m, complexed aromatic Hs), 5.59 (5 H, s, *Cp*), 5.04 (2 H, s, CH_2Ph), 4.50 (1 H, m, C*H*NH), 3.84 (3 H, s, ArOCH_3), 3.70 (3 H, s, CO_2CH_3), 3.24 (1 H, dd, J = 14 and 5.3 Hz, ArC*H*H), 3.05 (1 H, dd, J = 14 and 9.2 Hz, ArC*H*H).

1-(4-Methoxyphenoxy)-3-[1-(phenylsulfonyl)-2-methoxy-2-oxoethyl]benzene (26). The starting (arene)Cp Fe$^+$ complex **18** (493 mg, 0.73 mmol) in CH_2Cl_2 was cooled to −78 °C and then irradiated with UV light for 1 h (dark brown). Solvent was removed in vacuo and the product was isolated by preparative TLC (5% EtOAc–benzene) to give 99.4 mg (33%) of pale yellow oil: R_f 0.22 (25% EtOAc–hexanes), 0.37 (5% EtOAc–benzene); IR (neat) 3060, 2950, 1740, 1585, 1500, 1330 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67–6.86 (8 H, m, aromatic Hs), 5.05 (C*H*SO$_2$Ph), 3.81 (3 H, s, ArO*Me*), 3.76 (3 H, s, CO_2Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 158.4, 156.0, 149.2, 136.2, 130.1, 129.8, 129.7, 129.2, 128.6, 124.1, 120.8, 119.2, 118.6, 114.8, 74.9, 55.6, 53.2; MS m/z 412.0998 ([M]$^+$, $C_{22}H_{20}O_6S$ requires 412.0980).

L-(+)-*N*-(Benzyloxycarbonyl)-4-[3-(4-methoxyphenoxy)-phenoxy]phenylalanine Methyl Ester (27). The starting bis(aryloxy) CpFePF$_6$ **21** (200 mg, 0.25 mmol) in 10 mL of CH_2Cl_2 was irradiated with UV light at 0 °C for 2 h. The reaction mixture was filtered through silica gel and then the solvent was evaporated in vacuo. Purification by preparative TLC (10% EtOAc–hexanes) gave 108 mg (81.4%) of thick pale yellow oil: R_f 0.42; $[\alpha]_D$ +4.73° (*c* 0.47, THF); IR ($CHCl_3$) 3420, 3020, 2950, 1720 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34 (5 H, s, CH_2*Ph*), 7.0–6.6 (12 H, m, aromatic Hs), 5.24 (1 H, br d, J = 8 Hz, N-H), 5.10 (2 H, s, CH_2Ph), 4.66 (1 H, m, C*H*NHCbz), 3.80 (3 H, s, ArOCH_3), 3.71 (3 H, s, CO_2CH_3), 3.15 (1 H, dd, J = 14 and 5.5 Hz, ArC*H*HCHNHCbz), 3.05 (1 H, dd, J = 14 and 6 Hz, ArCH*H*CHNHCbz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 158.1, 155.5, 136.1, 135.0, 131.3, 131.0, 130.7, 130.5, 128.5, 128.2, 128.1, 127.8, 123.3, 119.4, 118.9, 116.7, 67.0, 54.8, 52.4, 38.1, 37.5; MS m/z (rel int) 527.1943 ([M]$^+$, $C_{31}H_{29}O_7N$ requires 527.1944), 108.1 (71.1), 322.1 (100), 395.1 (23.8). Anal. Calcd for $C_{31}H_{29}O_7N$: C, 70.51; H, 5.50; N, 2.65. Found: C, 69.25; H, 5.49; N, 2.75.

L-(−)-(Benzoyloxycarbonyl)-4-[3-(1,3-dimethoxy-1,3-dioxo-2-propyl)phenoxy]phenylalanine Methyl Ester (28). To a stirred solution of dimethyl sodiomalonate (from 34 mg, 0.71 mmol, of NaH and 93.6 mg, 81 μL of dimethyl malonate) in 5 mL of THF was added 500 mg (0.71 mmol) of arene–Fe$^+$Cp complex **9** in one portion. The mixture was stirred for 30 min at room temperature. The resulting solution was irradiated with a UV light (sunlamp, 275 W) for 40 min at room temperature. The color changed from deep red to very dark brown. Flash chromatography on silica gel (50% EtOAc–hexanes) gave 22.2 mg of L-(−)-*N*-(benzyloxycarbonyl)-4-(3-chlorophenoxy)phenylalanine methyl ester and 171 mg of product **28** [45.1% yield based on the unreacted demetalated product]: R_f 0.43 (50% EtOAc–hexane); $[\alpha]_D$ −8.5° (*c* 1.03, EtOH); IR ($CHCl_3$) 3360, 3020, 2950, 1750, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.34 (5 H, s, CH_2*Ph*), 7.29–6.90 (8 H, m, aromatic Hs), 5.24 (1 H, d, J = 8.3 Hz, N-H), 5.11 (2 H, s, CH_2Ph), 4.67 (1 H, m, C*H*NHCbz), 4.61 (1 H, s, C*H*($CO_2Me)_2$), 3.75 (6 H, s, CH($CO_2Me)_2$), 3.73 (3 H, s, CO_2Me), 3.10 (1 H, dd, J = 10.6 and 5.3 Hz, ArC*H*HCH), 3.03 (1 H, dd, J = 10.6 and 5.3 Hz, ArCH*H*CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 168.2, 157.2, 155.9, 155.6, 136.1, 134.2, 130.6, 129.8, 128.5, 128.2, 128.0, 124.0, 119.8, 119.0, 118.4, 66.9, 57.3, 54.8, 52.9, 52.3, 37.4; MS m/z (rel int) 207.1 (61.8), 313.1 (96.5), 402.1 (57.6, [M − CO_2Bn]$^+$), 462.2 (35.4, [M − ($C_3H_6O_2$)]$^+$), 492.2 (51, [M − (CO_2)]$^+$), 536.2 (100, [M + 1]$^+$).

L-(+)-*N*-(Benzyloxycarbonyl)-4-[3-[1-(phenylsulfonyl)-2-oxo-2-methoxyethyl]phenoxy]phenylalanine Methyl Ester (29). To a stirred solution of 300 mg (0.43 mmol) of the starting 3-chloroareneCpFe$^+$ complex **9** in 5 mL of THF was added a solution of methyl (phenylsulfonyl)sodioacetate (from methyl (phenylsulfonyl)acetate and NaH, 0.43 mmol) in 5 mL of THF at room temperature. The solution turned to cloudy red-brown. Stirring was continued for 1 h. The reaction was quenched with 1 mL of water. Solvent was evaporated in vacuo and then the residue was dissolved into 5 mL of CH_2Cl_2 and dried over $MgSO_4$. The solution was filtered using a disposable pipette with cotton plug and the filtrate was directly introduced into 50 mL of ether to give 269 mg of yellow powder. Then 100 mg of the crude product was dissolved into 15 mL of CH_2Cl_2 and irradiated with UV light (sunlamp, 275 W), at −78 °C for 1 h. The demetalated compound was isolated by preparative TLC (10% EtOAc–benzene) to give 23.4 mg (33% based on crude intermediate complex) of a pale yellow oil: R_f 0.43 (50% EtOAc–hexanes), 0.207 (10% EtOAc–benzene); $[\alpha]_D$ +3.10° (*c* 0.58, THF); IR ($CHCl_3$) 3420, 3020, 2950, 1720, 1500, 1320 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.7–6.8 (18 H, aromatic Hs), 5.26 (1 H, br d, J = 8 Hz, N-H), 5.14 (2 H, s, CH_2Ph), 5.10 (1 H, s, C*H*SO$_2$), 4.68 (1 H, m, C*H*NH), 3.80 (3 H, s, $SO_2CHCO_2CH_3$), 3.78 (3 H, s, CO_2CH_3), 3.12 (2 H, m, ArCH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 159.9, 158.3, 156.0, 155.9, 155.5, 149.4, 136.1, 130.5, 130.1, 128.4, 128.1, 128.0, 121.0, 119.0, 114.8, 112.4, 112.0, 108.2, 66.9, 55.5, 54.8, 52.3, 37.4. Anal. Calcd for $C_{33}H_{31}O_9NS$: C, 64.11; H, 5.02: N, 2.27. Found: C, 64.33; H, 5.48; N, 2.15.

L,L-(+)-1,3-Bis[4-[2-[*N*-(benzyloxycarbonyl)amino]-3-methoxy-3-oxopropyl]phenoxy]benzene (30). Dityrosylbenzene–Fe$^+$Cp complex **22** was dissolved in a mixed solvent of 5 mL of CH_2Cl_2 and 5 mL of CH_3CN and then irradiated with UV light (sunlamp 275 W) at room temperature for 30 min. The color changed from brown to black. The solvent was removed in vacuo and then the black residue was redissolved in CH_2Cl_2 (in the presence of polar solvent, colored byproduct can not be removed). The solution was filtered through silica gel to give a pale yellow solution. The product was further purified by flash chromatography on silica gel (50% EtOAc–hexanes) and preparative TLC (50% EtOAc–hexanes) to give 172.6 mg (45.3% yield) of a pale yellow oil: R_f 0.49 (50% EtOAc–hexanes); $[\alpha]_D$ +41.8° (*c* 0.51, CH_2Cl_2); IR (neat) 3420, 3020, 2950, 1740, 1715, 1500 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.33 (10 H, s, CH_2*Ph*), 7.24 (1 H, t, J = 8.4 Hz, 5-H), 7.05 (4 H, d, J = 8.6 Hz, phenoxy ring H, meta to O), 6.92 (4 H, d, J = 8.6 Hz, phenoxy ring H, ortho to O), 6.75–6.63 (3 H, m, 2-, 4-, and 6-H), 5.25 (2 H, d, J = 8 Hz, N-H), 5.10 (4 H, m, CH_2Ph), 4.64 (2 H, br q, J = 6 Hz, C*H*NH), 3.71 (6 H, s, CO_2Me), 3.12 (2 H, dd, J = 14 and 6 Hz, ArC*H*HCH), 3.04 (2 H, dd, J = 14 and 6 Hz, ArC*H*HCH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 158.5, 155.7, 155.6, 136.2, 131.0, 130.6, 130.4, 128.5, 128.2, 128.1, 119.1, 113.2, 109.4, 66.9, 54.9, 52.3, 37.4; MS m/z (rel int) [M]$^+$ not found, 129.1 (100), 236.2 (60), 368.3 (68). Anal. Calcd for $C_{42}H_{40}N_2O_{10}$: C, 68.78; H, 5.46; N, 3.82. Found: C, 68.40; H, 5.37; N, 3.61.

(Cyclopentadienyl)[1,3-bis(3-nitrophenoxy)benzene]iron Hexafluorophosphate (11) and 1,3-Bis(3-nitrophenoxy)-

benzene (31). The reaction of **4** (82.6 mg, 0.2 mmol) with 3-nitrophenol (83.5 mg, 0.6 mmol; using 14.4 mg of NaH) was carried out in THF (20 mL) at room temperature for 2 h, followed by the usual workup, to give complex **11**. The instability of this complex prevented full characterization and so the crude material was decomplexed according to the general procedure (irradiate, CH_3CN) to give **31**, which was purified by flash chromatography (yield: 125 mg, 59% overall). Spectroscopic data for **11**: ^1H NMR (acetone-d_6) 8.23–8.18 (2 H, obscured m), 8.19–8.16 (2 H, observed m), 7.9–7.8 (4 H, m), 6.88 (1 H, t, J = 1.7 Hz), 6.59 (1 H, dd, J = 7.6, 5.4 Hz), 6.47 (2 H, ddt, J = 7.6, 5.4, 1.7 Hz), 5.46 (5 H, s); ^{13}C NMR (acetone-d_6) 155.56, 150.48, 132.78, 132.53, 127.37, 121.68, 116.26, 85.68, 79.47 (Cp), 76.82, 71.43. Analytical data for **31**: R_f 0.21 (20% EtOAc/hexane); ^1H NMR ($CDCl_3$) 7.96 (2 H, ddd, J = 8.1, 2.2, 1.0 Hz), 7.83 (2 H, t, J = 2.2 Hz), 7.50 (2 H, t, J = 8.1 Hz), 7.4 (3 H, m), 6.86 (2 H, dd, J = 8.3, 2.3 Hz), 6.74 (1 H, t, J = 2.3 Hz); ^{13}C NMR ($CDCl_3$) 157.6, 157.23, 149.27, 131.44, 130.53, 124.65, 118.31, 115.29, 113.39, 110.81; HRMS (M^+) calcd for $C_{18}H_{12}N_2O_6$ 352.0695, found 352.0697.

(Cyclopentadienyl)[1-chloro-3-(3-nitrophenoxy)benzene]iron Hexafluorophosphate (12) and 1-Chloro-3-(3-nitrophenoxy)benzene (32). An identical procedure as for the preparation of **11**, but employing 1 equiv of 3-nitophenoxide, gave a mixture of **12** and **11** (approximately 2.5:1). Decomplexation of the mixture, followed by preparative TLC (silica gel, 10% EtOAc/hexane), gave **31** (38 mg, 18% overall) and **32** (57 mg, 38% overall). Analytical data for **32**: R_f 0.30 (10% EtOAc/hexane); ^1H NMR ($CDCl_3$) 7.97 (1 H, ddd, J = 8.1, 2.0, 1.0 Hz), 7.80 (1 H, t, J = 2.2 Hz), 7.50 (1 H, t, J = 8.2 Hz), 7.32 (1 H, J = 8.0 Hz), 7.32 (1 H, ddd, J = 8.2, 2.3, 1.0 Hz), 7.17 (1 H, ddd, J = 8.0, 2.0, 1.0 Hz), 7.04 (1 H, t, J = 2.1 Hz), 6.93 (1 H, ddd, J = 8.2, 2.3, 1.1 Hz); ^{13}C NMR ($CDCl_3$) 157.55, 156.40, 149.24, 135.44, 130.92, 130.49, 124.82, 124.54, 119.85, 118.29, 117.57, 113.37; HRMS (M^+) calcd for $C_{12}H_8NO_3Cl$ 249.0193, found 249.0194.

2-(3-Chlorophenoxy)-4-nitroaniline (33). The crude complex **13**, obtained from 413 mg (1 mmol) of complex **4**, was dissolved in CH_3CN (50 mL) in a Pyrex flask and irradiated (125 W sunlamp) for 1 h. The solution was filtered through a Celite pad, solvent was removed in vacuo, and the residue was purified by flash chromatography (silica gel, 20% EtOAc/hexane) to give **33** (135 mg, 51% overall yield) as a yellow powder: R_f 0.1 (20% EtOAc/hexane); IR ($CHCl_3$) n_{max} 3588, 3407, 1586, 1532, 1499, 1326, 872, 854, 832, 818 cm^{-1}; ^1H NMR (acetone-d_6) 7.8–7.7 (2 H, m), 7.4–7.3 (5 H), NH_2 not observed; ^{13}C (acetone-d_6) 145.64, 143.25, 140.45, 139.86, 135.24, 131.52, 123.50, 121.20, 119.70, 118.08, 112.37, 110.08; HRMS (M^+) calcd for $C_{12}H_9N_2O_3Cl$ 264.0302, found 264.0308.

***N*-(3-Chlorophenyl)morpholine (34).** Irradiation of complex **14** dissolved in CH_3CN with a sunlamp according to the general procedure afforded **34** (79% yield): ^1H NMR ($CDCl_3$) 7.18 (1 H, t, J = 8 Hz), 6.92–6.80 (3 H, m), 3.86, (4 H, t, J = 4.8 Hz), 3.16 (4 H, t, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) 152.29, 135.0, 130.07, 119.67, 115.47, 113.57, 66.70, 48.85; HRMS (M^+) calcd for $C_{10}H_{12}NOCl$ 197.0607, found 197.0610.

Acetylation of Compound 33. To a solution of compound **33** (24.7 mg, 0.093 mmol) in methylene chloride (3 mL) was added acetic anhydride (10 mL), pyridine (8 mL), and (*N*,*N*-dimethylamino)pyridine (DMAP) (10 mol %). After being stirred overnight at room temperature, the reaction mixture was poured into methylene chloride (20 mL), washed with H_2O (3×40 mL), and saturated aqueous $NaHCO_3$ (30 mL), and dried ($MgSO_4$). Removal of solvent in vacuo, followed by purification by flash chromatography (silica gel, 30% EtOAc/hexane), gave the diacetyl derivative **37** (32.3 mg, quantitative): R_f 0.09 (30% EtOAc/hexane); IR ($CHCl_3$) 1779, 1687, 1590, 1532, 1491, 1475, 1430, 1371, 1349, 1314, 1220, 1177, 1082, 1012; ^1H NMR ($CDCl_3$) 8.14–8.1 (2 H, m), 7.42–7.05 (5 H, m), 2.24 (3 H, s), 2.15 (3 H, s); ^{13}C NMR ($CDCl_3$) 169.7, 167.7, 147, 146.7, 145, 142.5, 140.5, 138. 135.5, 130.5, 128, 126, 121.7, 120.3, 23.1, 20.7; HRMS (M^+) calcd for $C_{16}H_{13}O_5N_2Cl$ 348.0513, found 348.0509.

2-Methoxy-4-nitroacetanilide (40). Treatment of 2-methoxy-4-nitroaniline (336 mg) with acetic anhydride, pyridine, and DMAP in CH_2Cl_2 in the above manner afforded compound **40** (420 mg, quantitative): mp 154.5–156 °C; IR ($CHCl_3$) 3421, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) 8.56 (1 H, d, J = 9.1 Hz), 7.95 (1 H, br s, NH), 7.90 (1 H, dd, J = 9.0, 2.3 Hz), 7.73 (1 H, d, J = 2.3 Hz), 3.98 (3 H, s), 2.24 (3 H, s); ^{13}C NMR 168.58, 147.06, 142.96, 133.72, 118.25, 117.72, 105.11, 56.30, 25.05; HRMS (M^+) calcd for $C_9H_{10}O_4N_2$ 210.0641, found 210.0647.

Acetylation of 2-Hydroxy-4-nitroaniline. Treatment of 2-hydroxy-4-nitroaniline (154 mg, 1 mmol) with acetic anhydride, pyridine, and DMAP as above, followed by extractive workup and chromatographic purification, afforded the triacetyl derivative **41** (280 mg, quantitative) as a yellow crystalline solid: mp 137–138 °C (95% EtOAc/hexane); IR ($CHCl_3$) n_{max} 1782, 1722 cm^{-1}; ^1H NMR ($CDCl_3$) 8.23–8.18 (2 H, m), 7.42 (1 H, dd, J = 7.7, 1.4 Hz), 2.29 (9 H, s); ^{13}C NMR ($CDCl_3$) 171.65, 167.71, 148.22, 147.37, 137.48, 131.04, 121.75, 119.71, 26.26 (2C), 20.54; HRMS (M^+) calcd for $C_{12}H_{12}N_2O_6$ 280.0695, found 280.0660.

***N*-(3-Chlorophenyl)-L-prolinol (35).** Irradiation of a solution of complex **16** (384 mg) in CH_3CN (20 mL) with a sunlamp (125 W) for 4 h, followed by the usual workup and chromatographic purification, gave **35** (170 mg, quantitative) as an oil: R_f 0.22 (30% EtOAc/hexane); ^1H NMR ($CDCl_3$) 7.12 (1 H, t, J = 8.3 Hz), 6.7–6.58 (3 H, m), 3.84–3.77 (1 H, m), 3.66–3.63 (2 H, m), 3.54–3.44 (1 H, m), 3.16–3.07 (1 H, m), 2.06–1.96 (4 H, m); ^{13}C NMR ($CDCl_3$) 148.87, 135.01, 130.07, 116.11, 112.11, 110.49, 63.36, 60.14, 49.33, 28.60, 23.56; HRMS (M^+) calcd for $C_{11}H_{14}ClNO$ 211.0764, found 211.0757.

***N*-(3-Chlorophenyl)-L-prolinyl Acetate (36).** Treatment of **35** (114 mg, 0.54 mmol) with acetic anhydride (5 mL, 53 mmol), pyridine (0.05 mL, 0.54 mmol), and DMAP (6.6 mg, 0.1 equiv) at room temperature overnight, followed by the usual extractive workup and chromatography, afforded the acetate **36** (137 mg, quantitative) as an oil: IR ($CHCl_3$) n_{max} 1736 cm^{-1}; ^1H NMR ($CDCl_3$) 7.11 (1 H, t, J = 8.1 Hz), 6.66–6.54 (3 H, m), 4.23 (1 H, dd, J = 10.4, 3.7 Hz), 3.96–3.88 (1 H, m), 3.79 (1 H, dd, J = 10.4, 8.4), 3.46–3.36 (1 H, m), 3.11 (1 H, q, J = 8.5 Hz), 2.06 (3 H, s), 2.04–1.91 (4 H, m); ^{13}C NMR ($CDCl_3$) 170.91, 148.24, 134.96, 130.07, 116.0, 111.90, 110.22, 63.84, 56.90, 48.40, 28.51, 23.00, 20.85; HRMS (M^+) calcd for $C_{13}H_{16}ClNO_2$ 253.0870, found 253.0891.

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Supplementary Material Available: ^1H and/or ^{13}C NMR spectra of compounds **6**, **8**, **9**, **10**, **14**, **15**, **16**, **18**, **22**, **23**, **24**, **26**, **27**, **28**, **31**, **32**, **33**, **34**, **35**, **36**, **37**, **40**, and **41** (38 pages). Ordering information is given on any current masthead page.