Ruthenium(II) Porphyrin Catalyzed Imine Aziridination and Crystal Structures of (*meso*-Tetrakis(pentafluorophenyl)porphyrinato)ruthenium(II) Complexes Containing PhN=CH(*p*-ClPh), CPh_2, and Pyridine Ligands

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A (*meso*-tetrakis(pentafluorophenyl)porphyrinato)ruthenium(II) complex of PhN=CH(*p*-ClPh) is prepared by reacting [Ru(F_{20}-TPP)(CO)] (**1**) with a benzene solution of *N*-(*p*-chlorobenzylene)aniline. The crystal structure of {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (**10**) shows the coordinated imine ligand in a cis configuration. Comparison with X-ray crystallographic data for [Ru(F_{20}-TPP)($py)_2$] (**11**) revealed the axial Ru−N bond length of the imine complex (2.203 Å) to be slightly longer than that of the bis(pyridine) complex (2.108 Å). Spectral and structural data revealed the Ru−N(imine) bond to have single-bond character, and the Ru=C bond in [Ru(F_{20}-TPP)(CPh_2)] (**7**) has a bond distance of 1.842 Å, indicative of multiple-bond character. In the presence of diazo compounds, {Ru(F_{20}-TPP)(CO)[PhN=CH-(*p*-ClPh)]} (**10**) and other related complexes mediated diastereoselective imine aziridination with product yields up to 86%. The mechanism is suggested to involve activation of the imine and diazo compounds by the ruthenium(II) porphyrin catalyst followed by nucleophilic addition of the imine to the diazo ester and subsequent cyclization to give the aziridine.

Introduction

The ability of aziridines to undergo regio- and stereoselective ring-opening reactions renders them invaluable building blocks in organic synthesis.[1] Aziridines are found in a number of biologically active products such as mitomycins and azinomycins.[1,2] However, in contrast to extensive investigations on organic oxidations and C−C bond formation reactions, studies on stereoselective C−N bond formations remain sparse. Recent studies by us[3] and others[4−12] demonstrated the simplicity and versatility of transition-metal catalysts for nitrene transfer reactions. Works by Du Bois[11] and in our laboratory[3i,j] recently described examples of such processes for the intramolecular amidation of saturated C−H bonds and aziridination of alkenes catalyzed by rhodium(II,II) dimers in high product yields and enantioselectivity.

In comparison to alkene aziridination, the addition of metallocarbenoids to imines has been less successful. Jacobsen and co-workers showed that a copper-catalyzed protocol gave aziridines either with high enantioselectivity or as a racemate.[13] Wulff et al. demonstrated that a similar outcome could be accomplished from Lewis acid mediated cyclopropanation of imines with

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ethyl diazoacetate (EDA) using a biaryl boronate catalyst.[14] Other Lewis acids such as boron, iron, molybdenum, and tin complexes have been less successful in asymmetric aziridination.[15,16] More recently, Aggarwal and co-workers reported an alternative approach that utilized the reaction of sulfur ylides with imines. The rhodium(II,II) dimer catalyzed aziridination procedure afforded a variety of aziridines in excellent enantioselectivity, albeit with modest diastereoselectivity.[17]

Ruthenium(II) porphyrin catalyzed carbenoid transformations using diazo compounds have been receiving growing interest (Figure 1).[18,19] We recently described a highly regio- and enantioselective ruthenium porphyrin catalyzed alkene cyclopropanation reaction that both gives good yields and is accomplished with high product turnovers.[18a,d] In light of this work, we wondered whether ruthenium(II) porphyrin catalysts could be applied to the catalytic cyclopropanation of imines.

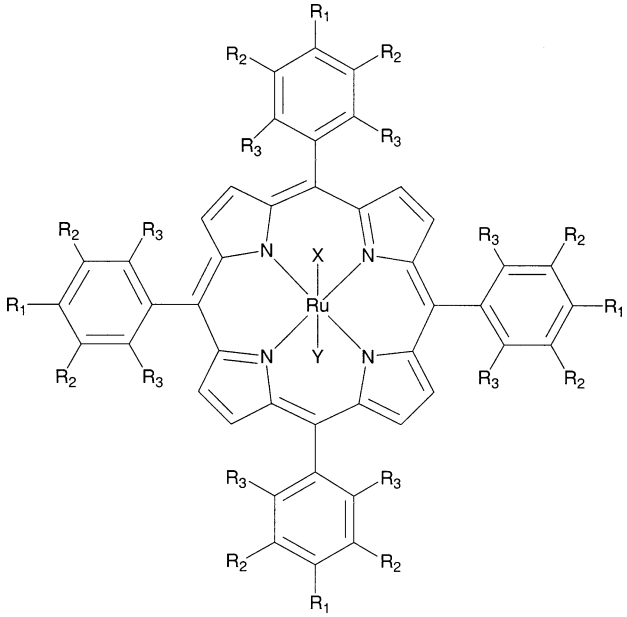

Figure 1. Ruthenium porphyrin catalysts **1**−**9**. Abbreviations (*): $H_2(F_{20}$-TPP) = *meso*-tetrakis(pentafluorophenyl)porphyrin; H_2(TTP) = *meso*-tetrakis(tolyl)porphyrin; H_2(*p*-F-TPP) = *meso*-tetrakis(*p*-fluorophenyl)porphyrin; H_2(*p*-Cl-TPP) = *meso*-tetrakis(*p*-chlorophenyl)porphyrin. For **1**−**3** and **5**−**7**, the complexes could be five-coordinate or Y = solvent molecule.

Ruthenium(II) porphyrins have previously been shown to catalyze the enantio- and diastereoselective aziridination of C=C bonds using (*N*-(*p*-tolylsulfonyl)imino)-phenyliodinane as the nitrogen source.[3b,c,g,18f] Herein, we report the first Ru-catalyzed aziridination reactions of aryl imines with diazo compounds and, in the course of this work, the isolation and characterization by X-ray crystallography of a stable (porphyrinato)ruthenium(II) imine complex (Scheme 1).

Results and Discussion

A. Synthesis, Isolation, and Spectra of {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (10). In contrast to the vast number of metal complexes with chelating imines[20] and simple monodentate imines[15e,21] reported in the literature, studies examining the binding behavior of

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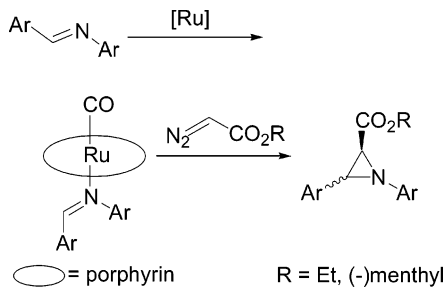
Scheme 1



ruthenium porphyrins to imines are sparse. In fact, only a few mononuclear cationic metal complexes that contain two or three simple imine ligands have been reported.[21c,d,g,h] Simonneaux and co-workers observed the formation of ruthenium porphyrins bearing imino and amino ester groups as axial ligands.[19a,d] In these metalloporphyrin species the strongly electron-withdrawing groups on the imino carbon were suggested to enhance imine coordination to Ru due to a π-back-bonding interaction. More recently, we reported the crystal structures of air-stable bis(imine)(porphyrinato)-ruthenium(II) complexes obtained through an unprecedented oxidative N-dealkylation of triethylamine by dioxoruthenium(VI) porphyrins.[18c] The C═N bond geometries of the coordinated imines in these complexes were shown to exclusively adopt a cis configuration.

In this work, the addition of [Ru(F_{20}-TPP)(CO)] (**1**) to a C_6H_6 solution containing *N*-(*p*-chlorobenzylene)-aniline gave {Ru(F_{20}-TPP)(CO)[PhN═CH(*p*-ClPh)]} (**10**) in 80% yield. Complex **10** is stable in solution and in the solid state for several weeks. As expected, it is diamagnetic with well-resolved ^{1}H NMR signals at normal fields, consistent with known literature data for ruthenium(II) porphyrins. The spectral data are summarized in Table 1. For comparison, the data for [Ru(F_{20}-TPP)(CO)] (**1**), free PhN═CH(*p*-ClPh), [Ru(F_{20}-TPP)(CPh_2)] (**7**), [Ru(F_{20}-TPP)(py)$_2$] (**11**; py = pyridine), and pyridine are also included in the table. Complexes **7** and **11** were obtained from the reaction of diphenyldiazomethane with [Ru(F_5-TPP)(CO)] and [Ru(F_5-TPP)-($CPhCO_2Et$)][22] with pyridine, respectively.

Figure 2 depicts the ^{1}H NMR spectrum of **10** in deuteriochloroform. This spectrum features the pyrrole protons of the porphyrinato ligand shifted slightly upfield to 8.65 ppm relative to that of **1** (8.71 ppm). The aryl proton signals of the imine are significantly shifted upfield, assignable to the porphyrin ring current effect. A similar effect can be seen for the aryl proton signals of [Ru(F_{20}-TPP)(CPh_2)] (**7**) and [Ru(F_{20}-TPP)(py)$_2$] (**11**) (Table 1). In contrast, the proton resonance of (*p*-ClPh)-C*H*═N in *N*-(*p*-chlorobenzylene)aniline shifts downfield to 8.73 ppm relative to that of free (*p*-chlorobenzylidene)-aniline (8.38 ppm). This is similar to the data observed for [(η^5-C_5H_5)Fe(CO)$_2$(PhN═CHPh)][16d] and monosubstituted carbene-ligated metalloporphyrins.[20] However, for other reported imine-coordinated ruthenium(II) porphyrins, the opposite was found for the proton resonance of the imino carbon.[18c] The ^{13}C NMR of **10** exhibits a carbon resonance for Ph*C*H═N at 176.7 ppm. In the free imine, the corresponding signal is at 160.4 ppm. For the imine-ligated $SnCl_4$ and BF_3 complexes,[16c] the imino carbon resonance was found further upfield, whereas for [(η^5-C_5H_5)Fe(CO)$_2$(PhN═CHPh)], it is downfield at 186.4 ppm.[16d]

The UV/vis absorption spectrum of **10** exhibits a slightly red shifted Soret band at λ 406 nm. The spectrum, shown in Figure 3, is characteristic of ruthenium(II) porphyrins with σ-donating axial ligands, such as amines and nitriles. This Soret band is slightly lower in energy than those observed for [Ru(F_{20}-TPP)(CO)] (**1**; λ 402 nm) and [Ru(F_{20}-TPP)(py)$_2$] (**11**; λ 399 nm). As is evident from the inset in Figure 3, the spectrum of **10** is similar to that of **1** but significantly different from those of **7** and **11**.

At this juncture, it is worth mentioning the effect of axial imine ligation on the M→N═C π-back-bonding interaction. In general, the strength of M→L increases with increasing π-acidity of L. Previous works by us[18c,23] and Gouterman et al.[24] showed that, for iron, ruthenium, and osmium *meso*-tetraaryl- and octaethylporphyrins, both the β band wavelength in the UV/vis spectrum and the H_{meso} chemical shift in the ^{1}H NMR spectrum systematically decrease as the π-acidity of the axial ligand decreases. Thus, while a comparison of the β band wavelengths and H_{meso} chemical shifts of [Ru(F_{20}-TPP)(CO)] (**1**) with those of **11** reveals that there might be weak Ru→py back-bonding in **11**, the same comparison made for **1** and **10** reveals that the Ru→N═C back-bonding in **10** is negligible (see Table 1 and Figure 3).

The IR spectrum of **10** gives an absorption at 1967 cm^{-1} for ν(CO) that is at a frequency slightly higher than that observed for **1** (1963 cm^{-1}). A similar change in ν(CO) stretching frequency has previously been reported for [Ru(TTP)(CO)] (**2**) and [Ru(TTP)(CO)(py)] (ν(CO) 1934 and 1939 cm^{-1}, respectively).[25] The "oxidation state marker" band of **10** at ν 1011 cm^{-1} is identical with that observed for **1**, **7**, and **11**. Interestingly, for all these complexes bearing a *meso*-tetrakis(pentafluo-

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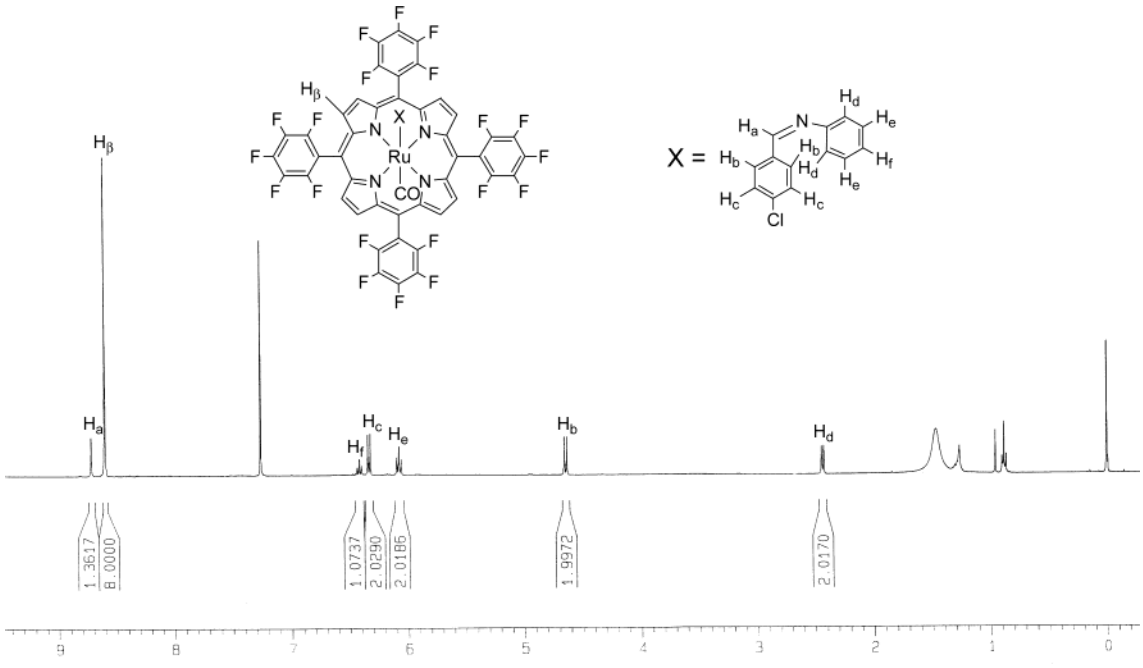


Figure 2. ^{1}H NMR spectrum of {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (**10**) in $CDCl_3$.

Table 1. ^{1}H NMR Spectrum of Complex 10 As Compared with Those of [Ru(F_{20}-TPP)(CO)] (1), Free PhN=CH(*p*-ClPh), [Ru(F_{20}-TPP)(CPh_2)] (7), [Ru(F_{20}-TPP)($py)_2$] (11), and Pyridine

		PhN=CH(*p*-ClPh)					
	H_β (s, 8H)	H_a (s, 1H)	H_b (d, 2H)	H_c (d, 2H)	H_d (d, 2H)	H_e (t, 2H)	H_f (t, 1H)
1	8.71						
10	8.65	8.73	4.66	6.35	2.45	6.09	6.43
PhN=CH-(*p*-ClPh)		8.38	7.18−7.25 (m, 3H), 7.35−7.43 (m, 4H), 7.80−7.82 (m, 2H)				

	H_β (s, 8H)	Ph H_p (t, 2H)	Ph H_m (t, 4H)	Ph H_o (d, 4H)
7	8.32	6.39	6.14	3.14

	H_β (s, 8H)	py H_p (t, 2H)	py H_m (t, 4H)	py H_o (d, 4H)
11	8.08	6.07	5.20	2.55
pyridine		7.67	7.28	8.61

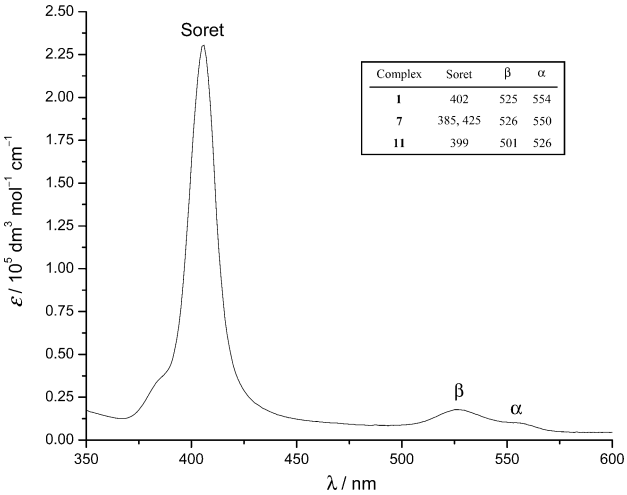


Figure 3. UV/vis spectrum of {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (**10**) in CH_2Cl_2. A comparison of the spectral data with those of Ru(II) complexes **1**, **7**, and **11** is shown in the inset.

rophenyl)porphyrin ligand, the "oxidation state marker" bands are identical with related values observed for ruthenium(IV) *meso*-tetraarylporphyrin complexes.[18c] Furthermore, they are at a higher frequency than the "oxidation state marker" bands typically observed for ruthenium(II) *meso*-tetraarylporphyrins (ca. 1000 cm^{-1}), reflecting the effect of the electron-withdrawing fluorine substituent on the ruthenium(II) porphyrin core.[18c] The positive ion FAB spectrum of **10** exhibits three signals that can be attributed to the parent ion $[M]^+$ and the $[M - CO]^+$ and $[M - C_{13}H_{10}ClN - CO]^+$ fragments.

B. X-ray Crystal Structure of {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (10).[26] Complex **10** was recrystallized from CH_2Cl_2/*n*-hexane at room temperature. A perspective view of **10** is depicted in Figure 4. The crystal data and structural refinement details are given in Table 2.[26] For comparison, the crystal structures of [Ru(F_{20}-TPP)(CPh_2)] (**7**) and [Ru(F_{20}-TPP)($py)_2$] (**11**) are included. Perspective views of **7** and **11** are shown in Figures 5 and 6, respectively.[26]

As shown in Figure 4, the PhN=CH(*p*-ClPh) ligand adopts a cis configuration, presumably to minimize unfavorable steric interaction with the porphyrinato ligand.[27] The Ru−N(imine) bond is nearly perpendicular to the plane of the porphyrin ring, with the N(imine)−Ru−C(CO) angle being 178.5°. As expected for sp^2-hybridized N atoms, the sum of the C(2)−N(5)−C(9), Ru−N(5)−C(2), and Ru−N(5)−C(9) angles is 358°, which is close to the 360° value required for a planar configuration. For the coordinated imine, both the aniline and benzylidene rings reside in planes that traverse the plane of the C=N moiety. The dihedral

(26) The files CCDC 211007, 211008, and 211189 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving-.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk).

(27) In solution, free imines preferentially occupy the more stable trans configuration; see: Bjørgo, J.; Boyd, D. R.; Watson, C. G. *J. Chem. Soc., Perkin Trans 2* **1974**, 1081.

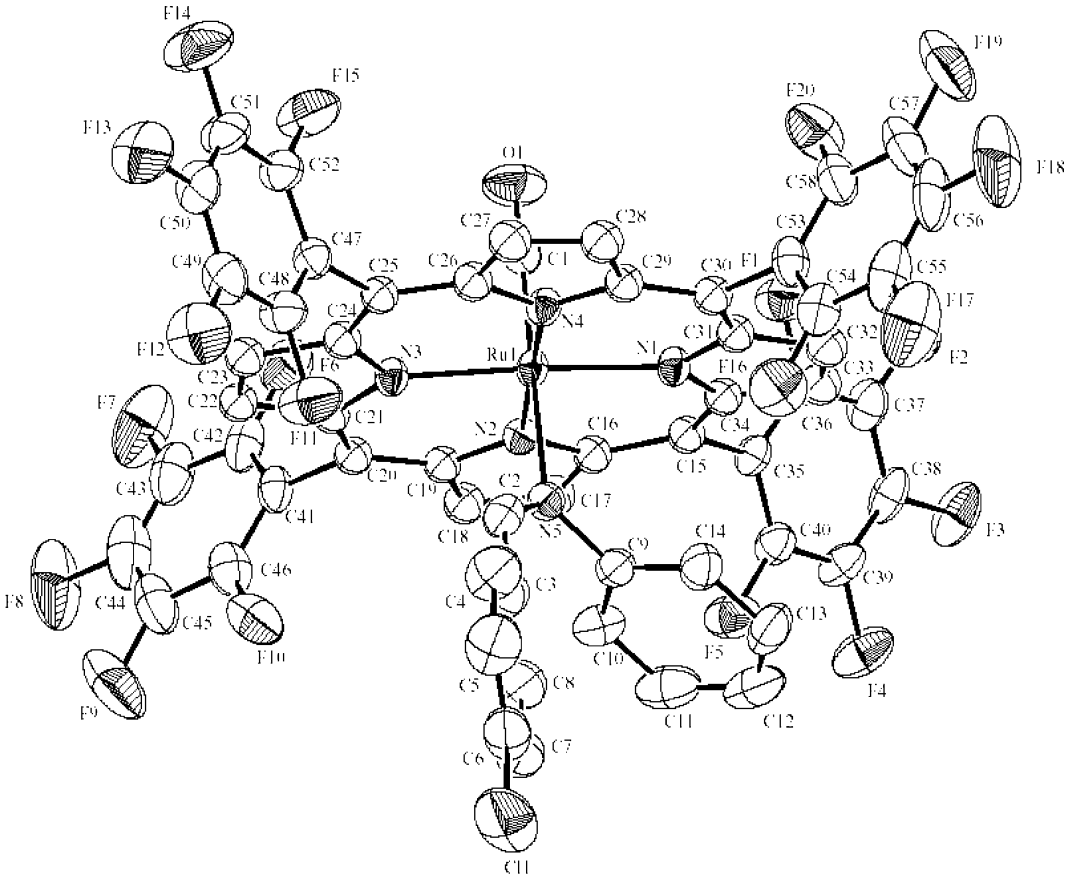


Figure 4. Perspective view of {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (**10**). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−N(5) = 2.203(7), Ru−C(1) = 1.860(10), Ru−N(1) = 2.059(6), Ru−N(2) = 2.050(6), Ru−N(3) = 2.059(6), Ru−N(4) = 2.045(6), C(1)−O(1) = 1.130(1), N(5)−C(2) = 1.300(1), N(5)−C(9) = 1.4500(1); C(2)−N(5)−C(9) = 117.9(7), Ru−N(5)−C(2) = 120.9(6), Ru−N(5)−C(9) = 120.2(5), N(5)−Ru-C(1) = 178.5(3), N(5)−Ru−N(1) = 88.2(2), N(5)−Ru−N(2) = 90.2(3), N(5)−Ru−N(3) = 88.7(2), N(5)−Ru−N(4) = 86.8(3), N(1)−Ru−N(3) = 177.0(3), N(2)−Ru−N(4) = 177.0(3).[26]

Table 2. Crystal Data and Structure Refinement Details for [Ru(F_{20}-TPP)(CPh_2)] (7), {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (10), and [Ru(F_{20}-TPP)($py)_2$] (11)

	7·0.5C_4H_9OH	**10**·C_6H_{14}·C_2H_5OH	**11**·2CH_2Cl_2·2H_2O
empirical formula	$C_{57}H_{18}F_{20}N_4Ru$·0.5C_4H_9OH	$C_{58}H_{18}ClF_{20}N_5ORu$·$C_6H_{14}$·$C_2H_5OH$	$C_{54}H_{32}F_{20}N_6O_2Ru$·2$CH_2Cl_2$·2$H_2O$
formula wt	1276.88	1449.55	1437.70
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	Cc
a, Å	18.768(4)	10.399(3)	26.593(3)
b, Å	14.491(3)	14.908(4)	8.8500(10)
c, Å	18.936(4)	23.480(5)	27.101(3)
α, deg	90	100.24(2)	90
β, deg	90.64(3)	101.51(2)	113.669(2)
γ, deg	90	107.83(2)	90
V, Å^3	5149.6(18)	3282(1)	5841.7(12)
Z	4	2	4
F(000)	2532	1452	2880
density (calcd), g/cm^3	1.647	1.467	1.644
abs coeff, cm^{-1}	0.424	3.83	0.564
cryst size, mm^{-3}	0.25 × 0.2 × 0.1	0.25 × 0.15 × 0.1	0.14 × 0.12 × 0.06
no. of rflns collected	33 747	12 068	9202
no. of indep rflns	8699	6119	9202
no. of data/restraints/params	8699/0/763	6119/0/711	9202/36/803
$R^a/R_w{}^b$	0.047/0.13 ($I > 2\sigma(I)$)	0.06/0.09 ($I > 3\sigma(I)$)	0.048/0.12 ($I > 2\sigma(I)$)
$R^a/R_w{}^b$ (all data)	0.08/0.14	0.06/0.09	0.088/0.15
goodness of fit	0.97	2.4	0.81
largest diff peak/hole, e Å^{-3}	0.508/−0.573	0.97/−0.60	0.504/−0.594

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(||F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

angle between the plane of the aniline ring and the plane of the C=N moiety is 36°, and that between this latter plane and the plane of the benzylidene ring is 106°. This would suggest *π*-conjugation between the aromatic rings and the imine C=N bond that would be present in the free imine is negligible upon ligation to ruthenium. Despite this, coordination of the imine ligand results in minimal distortion of the Ru atom from

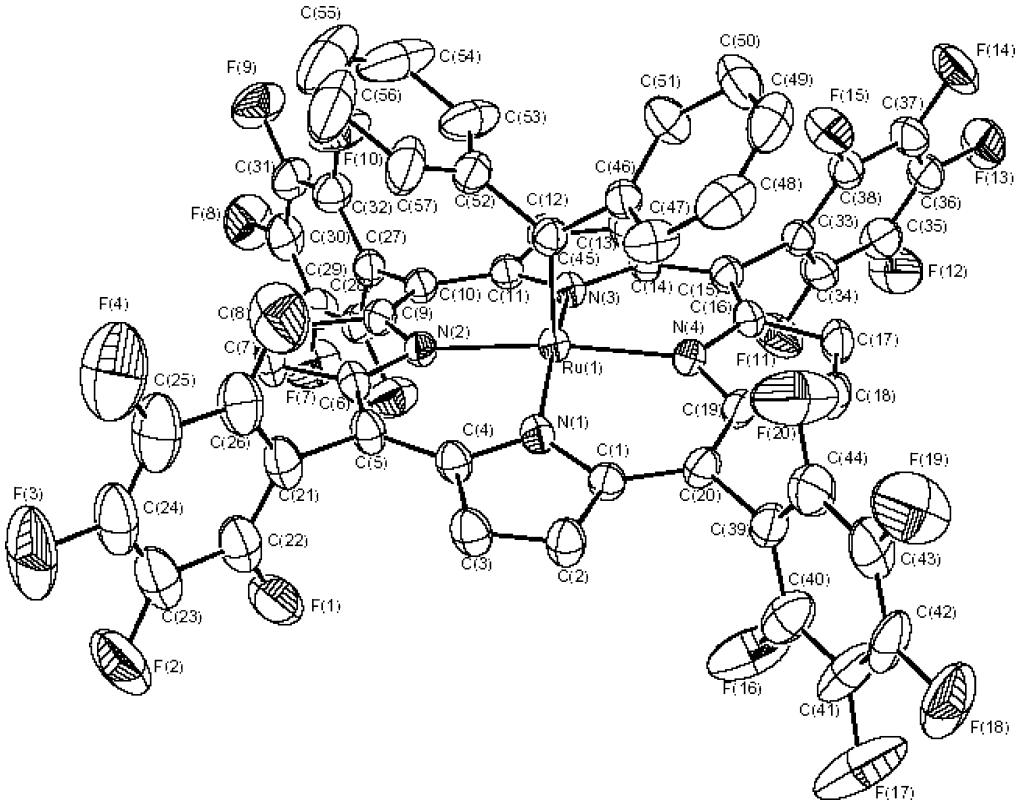


Figure 5. Perspective view of [Ru(F_{20}-TPP)(CPh_2)] (**7**). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−C(45) = 1.842(4), Ru−N(1) = 2.046(3), Ru−N(2) = 2.054(3), Ru−N(3) = 2.047(3), Ru−N(4) = 2.045(3), C(45)−C(46) = 1.491(5), C(45)−C(52) = 1.509(6); C(45)−Ru−N(1) = 99.94(14), C(45)−Ru−N(2) = 94.26(13), C(45)−Ru−N(3) = 95.05(14), C(45)−Ru−N(4) = 94.30(14), N(1)−Ru−N(3) = 165.0(1), N(2)−Ru−N(4) = 171.44(11), C(46)−C(45)−C(52) = 113.4(3), C(46)−C(45)−Ru = 125.1(3), C(52)−C(45)−Ru = 121.5(3).[26]

the calculated least-squares plane of the porphyrinato ring (0.0544 Å), offsetting the metal slightly toward the CO ligand. A similar mode of coordination is found in both **7** and **11**. For [Ru(F_{20}-TPP)($py)_2$] (**11**) the two axial pyridine ligands are close to right angles to the plane of the porphyrin ring with N(py)−Ru−N(pyrrole) angles ranging from 87.23 to 93.35°. The two pyridine rings are located in the same plane with respect to each other, with a dihedral angle between these two planes equal to 1.28°. For both **10** and **11**, the dihedral angles between the C(2)−N(5)−C(9) and N(5)−Ru−N(1)−N(3) planes in **10** and C(45)−N(5)−C(49) and N(5)−Ru−N(1)−N(3) planes in **11** are 43.1 and 47.8°, respectively. Thus, there is no apparent unfavorable steric interaction between the porphyrin ring and the axial ligands; the imine and bis pyridine ligands are located in planes that bisect the Ru−N bonds of the porphyrin ring in **10** and **11**, as shown in parts a and b of Figure 7, respectively. As shown in Figure 5, the carbon donor atom of the diphenylcarbene ligand in **7** adopts an sp^2-hybridized configuration, as evidenced by the sum of the C(46)−C(45)−C(52), C(46)−C(45)−Ru, and C(52)−C(45)−Ru angles equal to 360°. In contrast to **10** and **11**, coordination of the carbene ligand results in greater distortion of the ruthenium atom from the calculated least-squares plane of the porphyrin ring in a direction toward the carbene ligand (0.2099 Å). This results in the ruthenium atom adopting a slightly distorted-square-pyramidal coordination sphere with the carbene C atom at the vertex site. Furthermore, with the dihedral angle between the C(46)−C(45)−C(52) and C(45)−Ru−N(2)−N(4) planes equal to 20.8°, the axial ligand is situated much more closely to the C(45)−Ru−N(2)−N(4) plane in comparison to that found in **10** and **11**. Presumably in this conformation any unfavorable steric interaction with the porphyrin ring is kept to a minimum (Figure 7c).

The N(imine)−Ru distance in **10** is 2.203 Å. This is comparable to the Ru−N distances in [Ru(TPP)(CO)(py)] (2.193 Å) and [Ru(TPP)(CO)(1-MeIm)] (2.187 Å) (1-MeIm = 1-methylimidazole)[29] but longer than those observed for [Ru(F_{20}-TPP)($py)_2$] (**11**; 2.108 and 2.1085 Å),[26] [Ru(TTP)(EtN=CHMe)$_2$] (2.115 Å), and [Ru(*p*-Cl-TPP)(N=CPh_2)$_2$] (1.896 Å).[18c] The imine C=N distance (1.30 Å) is the same as that in [Ru(TTP)(EtN=CHMe)$_2$] (1.30 Å) but slightly longer than those in free imines (ca. 1.28 Å), [$SnCl_4$(*o*-MeOPhN=CHPh)] (1.285 Å),[16b] and [$SnCl_4$(*p*-ClPhN=CHPh)] (1.288 Å).[16c] In addition, the Ru−C(carbonyl) distance of 1.86 Å is longer than those in [Ru(TPP)(CO)(EtOH)] (1.72 Å),[29] [Ru(TFPPCl_8)(CO)(H_2O)] (H_2(TFPPCl_8) = octa-*β*-chlorotetrakis(pentafluorophenyl)porphyrin; 1.828 Å),[30] [Ru(TPP)(CO)(py)] (1.838 Å), and [Ru(TPP)(CO)(1-MeIm)] (1.828 Å).[29]

C. [Ru(F_{20}-TPP)(CO)] (1) Catalyzed Aziridination Reactions of Imines with EDA. When EDA (1 equiv) was slowly added to a C_6H_6 solution containing *N*-(benzylidene)aniline (2 equiv), [Ru(F_{20}-TPP)(CO)] (**1**; 0.5 mol %), and 4 Å molecular sieves at room temper-

(28) Scheidt, W. R.; Lee, Y. J. *Struct. Bonding (Berlin)* **1987**, *64*, 1.
(29) (a) Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 8583. (b) Slebodnick, C.; Seok, W. K.; Kim, K.; Ibers, J. A. *Inorg. Chim. Acta* **1996**, *243*, 57.
(30) Birnbaum, E. R.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 1751.

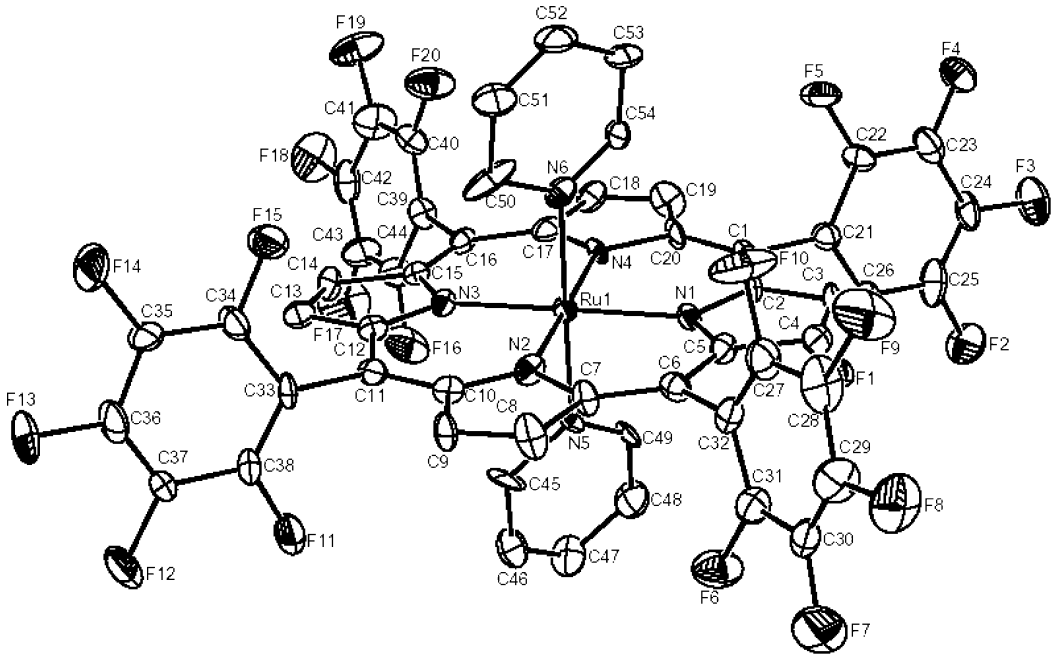


Figure 6. Perspective view of [Ru(F_{20}-TPP)($py)_2$] (**11**). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−N(5) = 2.1085(19), Ru−N(6) = 2.108(2), Ru−N(1) = 2.0368(17), Ru−N(2) = 2.028(3), Ru−N(3) = 2.0441(18), Ru−N(4) = 2.056(2), N(5)−C(45) = 1.436(4), N(5)−C(49) = 1.317(3), N(6)−C(50) = 1.438(5), N(6)−C(54) = 1.281(4); N(5)−Ru−N(6) = 178.87(1), N(5)−Ru−N(1) = 91.78(7), N(5)−Ru−N(2) = 92.12(8), N(5)−Ru−N(3) = 87.63(7), N(5)−Ru−N(4) = 88.11(8), N(6)−Ru−N(1) = 87.23(8), N(6)−Ru−N(2) = 88.45(9), N(6)−Ru−N(3) = 93.35(8), N(6)−Ru−N(4) = 91.33(9), N(1)−Ru−N(3) = 179.41(9), N(2)−Ru−N(4) = 179.32(8), C(45)−N(5)−Ru = 117.14-(17), C(45)−N(5)−C(49) = 119.9(2), C(49)−N(5)−Ru = 122.8(2), C(50)−N(6)−Ru = 116.1(2), C(50)−N(6)−C(54) = 120.0-(2), C(54)−N(6)−Ru = 123.7(2).[26]

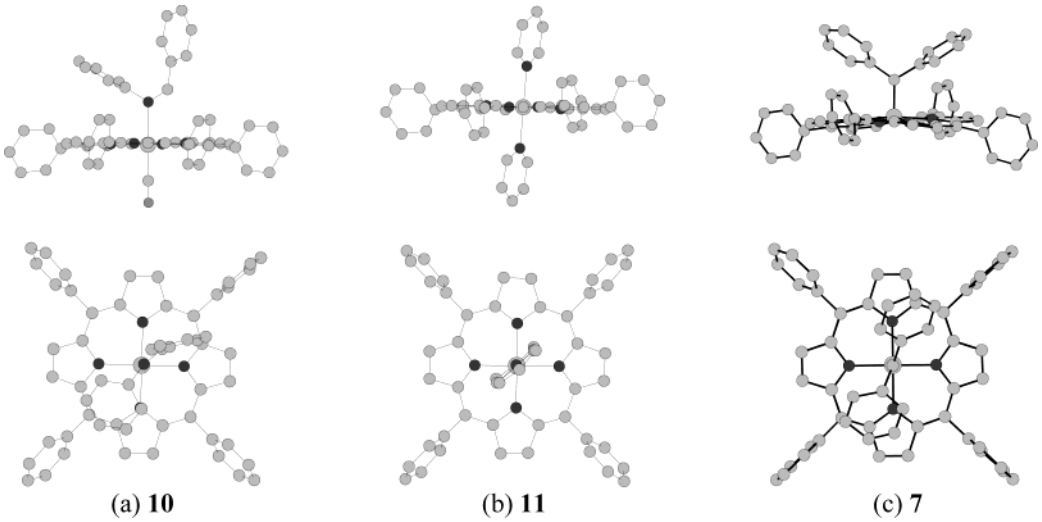
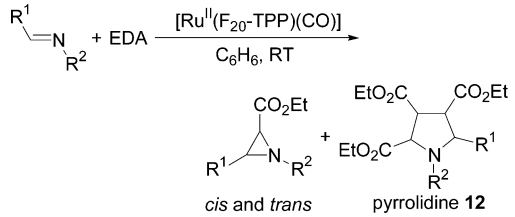


Figure 7. Ball-and-stick drawings showing the orientations of the axial ligands in (a) {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (**10**), (b) [Ru(F_{20}-TPP)($py)_2$] (**11**), and (c) [Ru(F_{20}-TPP)(CPh_2)] (**7**). The ϕ angle is defined as described in ref 28.

ature, ethyl 1,3-diphenylaziridine-2-carboxylate was isolated in 69% yield and with a cis:trans ratio of 2.7:1. Under these conditions, the pyrrolidine **12**, presumably from 1,3-dipolar cycloaddition of the imine intermediate and EDA dimer generated in situ, was also furnished in 10% isolated yield (Table 3, entry 1). The analogous reactions conducted in CH_2Cl_2 and the same solvent system in the absence of molecular sieves gave markedly lower yields, while higher yields of the cycloadduct **12** were found (entries 2 and 3). Similarly, when the reaction was conducted at 50 °C, the aziridine product was afforded in lower yield and cis selectivity along with an increased isolated yield of **12** (entry 4).

In turning our attention to exploring the generality of the present procedure, we examined the Ru-catalyzed aziridination of a series of aryl imines under similar conditions. These reactions afforded the corresponding ethyl 1-phenyl-3-(substituted phenyl)aziridine-2-carboxylate products in moderate to good yields and stereoselectivity (entries 5−16). It was interesting to note that in all these reactions competitive formation of the corresponding pyrrolidine **12** in yields up to 31% was also isolated or detected by ^{1}H NMR analysis of the crude reaction mixtures. Other reaction side products detected by GC-MS analysis include the corresponding ArCHO, $ArNCHCO_2Et$, and $ArNHCH_2CO_2Et$. In one

Table 3. [Ru(F_{20}-TPP)(CO)] (1) Catalyzed Cyclopropanation of Imines with EDA[a]



entry	imine R¹	imine R²	conversion (%)[c]	aziridine[b] cis:trans	aziridine[b] yield (%)	pyrrolidine **12** yield (%)[d]
1	Ph	Ph	39	2.7:1	69	10
2[e]	Ph	Ph	32	2.5:1	20	25
3[f]	Ph	Ph	35	2.5:1	30	31
4[g]	Ph	Ph	44	1.4:1	37	24
5	*p*-CH_3Ph	Ph	41	2.3:1	72	6
6	*p*-$C(CH_3)_3$Ph	Ph	31	2.5:1	13	15[h]
7	*p*-OCH_3Ph	Ph	45	2.2:1	74	3
8	*p*-FPh	Ph	41	3.8:1	83	5
9	*p*-ClPh	Ph	40	7:1	78	8
10	*p*-BrPh	Ph	37	6.5:1	79	27
11[i]	*p*-BrPh	Ph	74	6.5:1	58	21
12	*o*-ClPh	Ph	38	*j*	12[k]	3
13	Ph	*p*-ClPh	38	3:1	76	6
14	Ph	*p*-CH_3Ph	40	2:1	69	10
15	Ph	*p*-OCH_3Ph	33	1.8:1	57	19[h]
16	Ph	*o*-OCH_3Ph	36	1.6:1	80	13

[a] Reaction conditions: catalyst:EDA:imine = 1:200:400, benzene, 4 Å molecular sieves, room temperature, addition of EDA for 18 h and then stirring for 3 h. [b] Cis:trans ratios, product yields, and conversions were determined by ^{1}H NMR of the crude product using bibenzyl as a standard and based on imine conversion. [c] Maximum conversion 50%. [d] ^{1}H NMR yield. [e] CH_2Cl_2 solvent and no 4 Å molecular sieves. [f] CH_2Cl_2 solvent. [g] Reaction conducted at 50 °C. [h] Isolated yield. [i] Catalyst:EDA:imine = 1:200:200. [j] Could not be determined by ^{1}H NMR analysis. [k] Diethyl maleate isolated as the main product in 63% yield along with recovery of PhN=CH(*o*-ClPh) in 63% yield.

instance, the employment of equimolar quantities of imine and EDA was also found to result in markedly higher substrate conversion, although no significant increase in product yield was observed (entry 11). More notably, imines bearing an electron-withdrawing substitutent at the para position of the benyzlidene ring were found to undergo aziridination with higher cis selectivity (cis:trans ratios up to 7:1) (entries 8−11). However, for imines bearing either an electron-withdrawing or -donating group at the para position of the aniline ring or electron-donating substituents at the para position of the benzylidene ring, the effect of substitution on reaction diastereoselectivity was found to be minimal (entries 5−7 and 13−16). The aziridinations of the sterically demanding imines *N*-(*p*-*tert*-butyl)- and *N*-(*o*-chlorobenzylidene)aniline are the only examples that gave low product yields and conversions (entries 6 and 12).

The effect of the porphyrinato ring and axial ligand on the yield and selectivity of the present protocol was examined (Table 4). Reactions catalyzed by ruthenium(II) porphyrins where the axial CO ligand was replaced with diphenylcarbene preferentially gave diethyl maleate in yields up to 85% (entries 1−3). The desired aziridine product was only afforded in 32% yield under reflux conditions along with the pyrrolidine **12** in 22% yield (entry 4). The difference in reactivity among catalysts **5**−**7** could be the absence of imine ligation at room temperature, as suggested by ^{1}H NMR analysis

Table 4. Aziridination Reactions of Imines with EDA by [Ru(Por)(X)] (1−9) Catalysts[a]

entry	catalyst	imine R¹	imine R²	aziridine[b] cis:trans	aziridine[b] yield (%)[c]	pyrrolidine **12** yield (%)
1	[Ru(4-F-TPP)(CPh_2)] (**5**)	Ph	Ph	1.7:1	1[d]	3
2	[Ru(4-Cl-TPP)(CPh_2)] (**6**)	Ph	Ph	1.5:1	2[e]	5
3	[Ru(F_{20}-TPP)(CPh_2)] (**7**)	Ph	Ph		<1[f]	8
4[g]	[Ru(F_{20}-TPP)(CPh_2)] (**7**)	Ph	Ph	1:1	32 (44)	22[h]
5	[Ru(4-F-TPP)(CO)] (**3**)	Ph	Ph	2.5:1	60 (36)	8
6	[Ru(TTP)(CO)] (**2**)	Ph	Ph	2:1	43 (31)	10
7	[Ru(F_{20}-TPP)(NO)(OH)] (**4**)	Ph	Ph	7.2:1	77 (45)	2
8[i]	[Ru(4-F-TPP)(O_2)] (**8**)	Ph	Ph	2.7:1	86 (46)	1
9[i]	[{Ru(4-F-TPP)(OH)}$_2$(O)] (**9**)	Ph	Ph	2.5:1	75 (48)	1

[a] Reaction conditions: catalyst:EDA:imine= 1:200:400, C_6H_6, 4 Å molecular sieves, room temperature, addition of EDA over 18 h and then stirring for 3 h. [b] Cis:trans ratios and yields were determined by ^{1}H NMR of the crude product using bibenzyl as a standard and based on imine conversion (maximum 50%). [c] Yields in parentheses denote conversion. [d] Diethyl maleate isolated as the main product in 85% yield. [e] Diethyl maleate isolated as the main product in 82% yield. [f] Diethyl maleate isolated as the main product in 76% yield. [g] Reaction carried out at reflux. [h] $Ph_2CHNHPh$ detected by GC analysis. [i] Addition of EDA over 12 h.

of solutions of "**7** + PhN=CH(*p*-ClPh)" (molar ratios 1:1 and 1:10) in deuteriochloroform (Figure 8). The ^{1}H NMR spectrum shows the aryl proton resonances of *N*-(*p*-chlorobenzylidene)aniline as multiplets at 7.15−7.20, 7.32−7.45, and 7.80−7.85 ppm and the imino−carbon proton resonance as a singlet at 8.40 ppm. These chemical shifts are consistent with those observed for the free imine as reported in Table 1. Imine coordination would be expected to result in the aryl proton signals to significantly shift upfield as a result of the porphyrin ring current effect in a manner similar to that observed in the ^{1}H NMR spectrum of {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]}(**10**), shown in Figure 2. It is conceivable the degree of distortion of the Ru atom from the porphyrin ring toward the axial carbene ligand is sufficient to prevent or at least contribute to preventing effective coordination of the sterically bulky imine. The low yields and conversions observed for the reactions of *N*-*p*-*tert*-butyl- and *N*-(*o*-chlorobenzylidene)aniline (Table 3, entries 6 and 12) are consistent with this suggestion. With [Ru(4-F-TPP)(CO)] (**3**) as catalyst, ethyl 1-phenyl-3-phenylaziridine-2-carboxylate was afforded in a slightly lower yield (entry 5). The same reaction catalyzed by [Ru(TTP)(CO)] (**2**) gave the aziridine in 43% yield (entry 6). In contrast, higher product yield and cis selectivity were observed for the analogous reaction catalyzed by [Ru(F_{20}-TPP)(NO)(OH)] (**4**)[31] (entry 7). Presumably, this systematic increase in product yields as the electrophilicity of the Ru atom increases suggests product formation would be affected by axial ligand to ruthenium coordination. For reactions catalyzed by ruthenium porphyrins **8** and **9**,[32] markedly higher product yields (up to 86%) were obtained (entries 8 and 9). Interestingly, while attempts to isolate the bis(imine) complex of **8** were unsuccessful, the reaction of this catalyst (1 equiv) in the presence of excess *N*-(*p*-chlorobenzylidene)aniline (4 equiv) in C_6H_6 at room temperature gave [{Ru(*p*-F-TPP)(OH)}$_2$(O)] (**9**) in 88%

(31) Ho, C.; Leung, W.-H., Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1991**, 2993.
(32) Collman, J. A.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151.

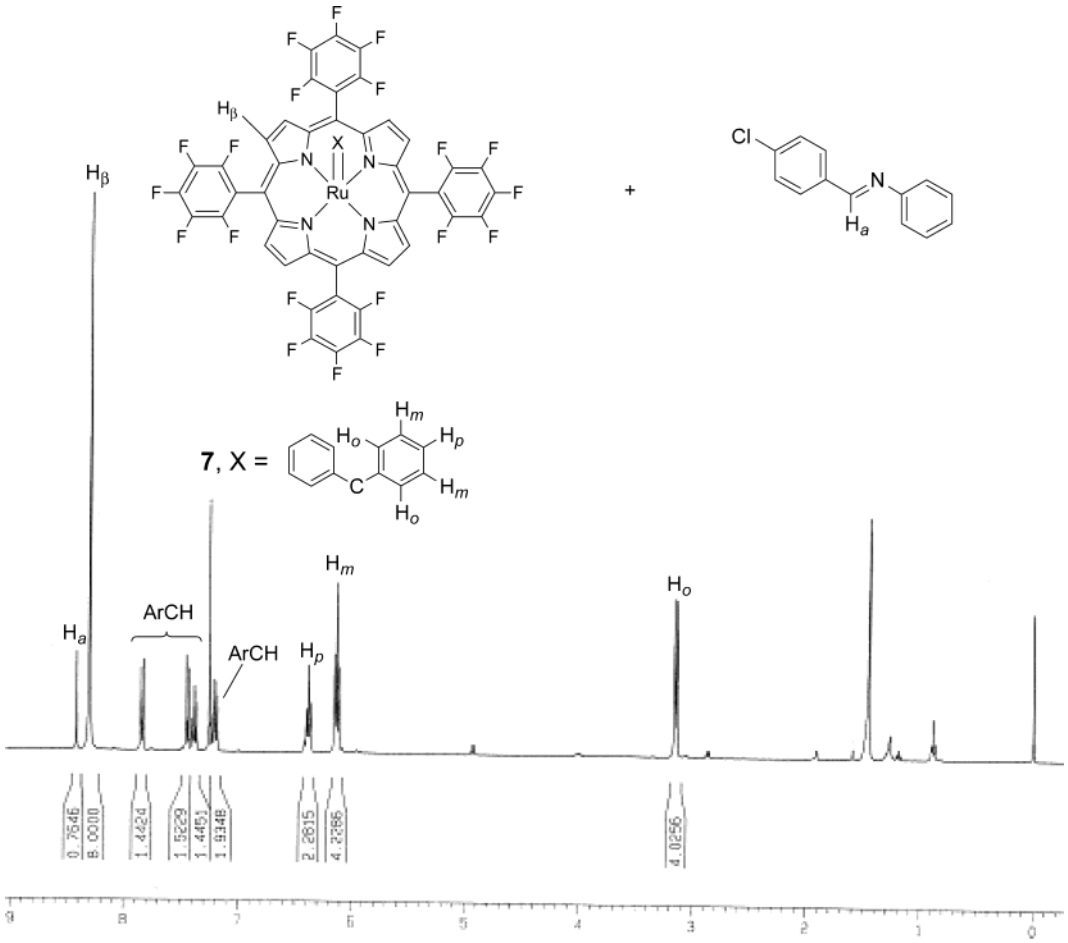


Figure 8. ^{1}H NMR spectrum of a $CDCl_3$ solution of [Ru(F_{20}-TPP)(CPh_2)] (**7**) and PhN=CH(*p*-ClPh) (molar ratio 1:1).

yield. In this instance, rather than undergoing axial ligation, the imine seems to act as an electron source for the reduction of Ru(VI) to Ru(IV), leading to the formation of the dimeric ruthenium(IV) complex **9**.

These results suggest a mechanism involving ruthenium porphyrin activated imine aziridination.[13−16] Thought to involve ylide formation as a result of initial nucleophilic addition of the imine to EDA, the newly formed intermediate is also thought to subsequently cyclize to give the aziridine. Indeed, this is supported by the following experiments. In the absence of Ru catalyst, the reaction of PhCH=NPh with EDA resulted in the recovery of both starting materials in near-quantitative yields. The addition of either (*p*-ClPh)CH=NPh or (*p*-MePh)CH=NPh to a solution of [Ru(F_{20}-TPP)($CHCO_2Et$)] generated in situ from the stoichiometric addition of EDA to **1** was also examined. These reactions gave $PhN{=}CHCO_2Et$[33] in up to 93% yield along with recovery of the corresponding benzaldehydes in 90−92% yield. The formation of {Ru(F_{20}-TPP)[PhN=CH(*p*-ClPh)]} was also detected by ^{1}H NMR analysis and mass spectrometry (FAB).[34] Aziridine product formation would have suggested a mechanism similar to that proposed for the analogous copper-catalyzed reactions, whereby the azomethine ylide is derived from addition of the imino nitrogen to a carbene intermediate.[13] Furthermore, when 1.2 equiv of EDA was slowly added to a C_6H_6 solution containing dimethyl fumerate (1.2 equiv), *N*-(*p*-chlorobenzylidene)aniline (1.2 equiv), and **1** (0.5 mol %) at room temperature, pyrrolidine **14a** was afforded as the sole product in 90% yield (Table 5, entry 1). The structure of **14a** was confirmed by comparing its ^{1}H NMR data with the literature data.[35−37] Under similar conditions, trapping of the imino ylide derived from PhN=CHPh with dimethyl acetylenedicarboxylate (DMAD) gave **14b** in 92% yield and as a single diastereomer (entry 2). The structure of **14b** was established by X-ray crystallography.[38] ^{1}H NMR analysis of the crude reaction mixture detected **14b** as a single diastereomer under our experimental conditions, the stereochemistry of which was determined to be trans on the basis of comparison with known literature data.[35−37] Slightly lower product yields were obtained for the analogous cycloaddition reactions of DMAD with either (*p*-^{t}BuPh)CH=NPh or {3,4,5-$(MeO)_3$Ph}CH=NPh as the imine source (entries 3 and 4). In these last two cases, exclusive trans product selectivity was deter-

(33) Borrione, E.; Prato, M.; Scorrano, G.; Stivanello, M. *J. Heterocycl. Chem.* **1988**, *25*, 1831.

(34) See the Supporting Information for full experimental details.

(35) (a) Deyrup, J. A. *J. Org. Chem.*, **1969**, *34*, 2724. (b) Dostal, J.; Potacek, M.; Humpa, O.; Marek, J. *Bull. Soc. Chim. Belg.* **1994**, *103*, 343.

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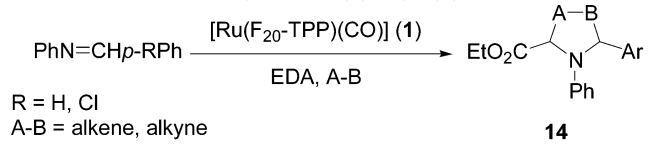
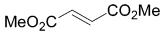
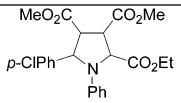
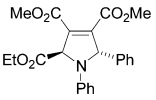
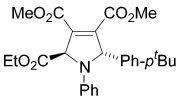
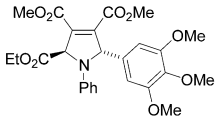
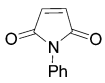
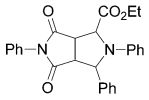
(38) See the Supporting Information for full X-ray crystallographic details. Also: CCDC 217583 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk).

Table 5. 1,3-Dipolar Cycloaddition of Aryl Imines with Dipolarophiles A−B Catalyzed by [Ru(F_{20}-TPP)(CO)] (1)[a]



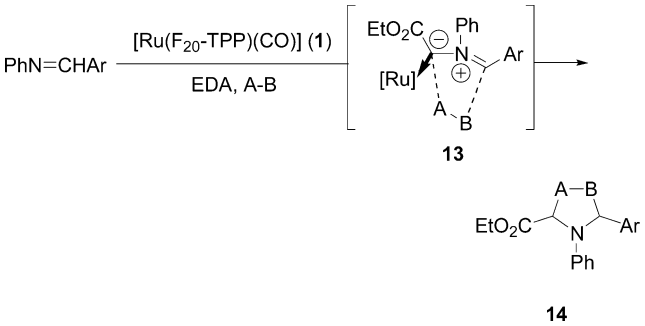
14

Entry	Imine	Dipolarophile A-B	Product **14**	Yield (%)[b]
1	(*p*-ClPh)CH=NPh		 **14a**	90
2	PhCH=NPh	DMAD	 **14b**	92
3	(*p*-^{t}BuPh)CH=NPh	DMAD	 **14c**	83
4	(3,4,5-(OMe)$_3$Ph)CH=NPh	DMAD	 **14d**	80
5	PhCH=NPh		 **14e**	86

[a] Reaction conditions: catalyst:EDA:imine:dipolarophile A−B = 1:200:240:240, C_6H_6, 4 Å molecular sieves, room temperature, addition of EDA for 12 h and then stirring for 1 h. [b] Isolated yield.

mined on the basis of ^{1}H NMR analysis of the respective crude reaction mixtures. With *N*-phenylmaleimide as the dipolarophile, the corresponding cycloadduct **14d** was obtained in 86% yield and as a single isomer on the basis of ^{1}H NMR analysis of the crude reaction mixture (entry 5). At this juncture, it is worth noting that the present 1,3-dipolar cycloaddition procedure provides a powerful method for the regio- and stereoselective synthesis of highly functionalized nitrogen heterocycles such as pyrrolidine alkaloids.[39] Furthermore, among the various literature procedures to generate reactive azomethine ylides in situ,[40] the present methodology provides an attractive approach because of the mild reaction conditions employed and excellent regio- and stereocontrol achieved by catalyst design.[36] Indeed, works in our laboratory[36] and by Scheidt and co-workers[37] recently demonstrated ruthenium(II) porphyrins and copper(I) salts as efficient catalysts for

Scheme 2



effecting this one-pot, three-component transformation with high yields and diastereoselectivity.

The delivery of **14** in all these reactions thus supports a mechanism for the present imine aziridination reac-

(39) Selected examples: (a) Katritzky, A. R.; Cui, X.-L.; Yang, B.; Steel, P. J. *J. Org. Chem.* **1999**, *64*, 1979. (b) Chan, P. W. H.; Cottrell, I. F.; Moloney, M. G. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2997. (c) Chan, P. W. H.; Cottrell, I. F.; Moloney, M. G. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3007. (d) Amat, M.; Llor, N.; Hidalgo, J.; Escolano, C.; Bosch, J. *J. Org. Chem.* **2003**, *68*, 1919. (e) Harris, J. M.; Padwa, A. *J. Org. Chem.* **2003**, *68*, 4371.

(40) (a) Huisgen, R.; Grashey, R.; Steingruber, E. *Tetrahedron Lett.* **1963**, *4*, 1441. (b) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565. (c) Heine, H. W.; Peavy, R. *Tetrahedron Lett.* **1965**, *6*, 3123. (d) Padwa, A.; Hamilton, L. *Tetrahedron Lett.* **1965**, *6*, 4363. (e) Huisgen, R.; Scheer, W.; Mäder, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 602. (f) Grigg, R.; Kemp, J.; Sheldrick, G.; Trotter, J. *J. Chem. Soc., Chem. Commun.* **1978**, 109. (g) Grigg, R.; Kemp, J. *Tetrahedron Lett.* **1980**, *21*, 2461. (h) Vedejs, E.; West, F. G. *Chem. Rev.* **1986**, *86*, 941.

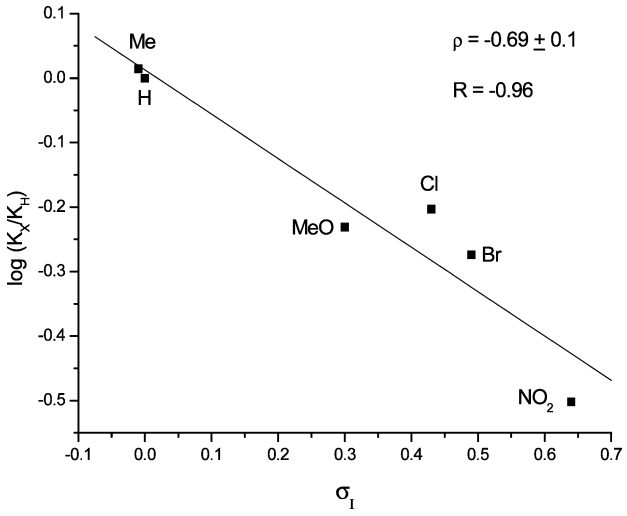


Figure 9. Hammett correlation studies for the ruthenium-mediated aziridination of para-substituted arylimines.

tion that involves the formation of the ylide intermediate **13** (Scheme 2). However, in contrast to the reaction pathway proposed by Jacobsen et al. involving imino attack onto a carbene intermediate,[13] we postulate the generation of **13** to occur via substitution of EDA by the imino nitrogen under the present conditions. Recall that no aziridine products were detected from the reaction of either (*p*-ClPh)CH═NPh or (*p*-MePh)CH═NPh with a stoichiometric solution of [Ru(F_{20}-TPP)($CHCO_2Et$)] and when the Ru catalyst was removed from the reaction conditions. While currently unclear, the role of the ruthenium catalyst here seems to be in some capacity other than that for facilitating carbenoid formation. Furthermore, the triethyl pyrrolidine species **12** was isolated as a side product in all the Ru-catalyzed imine aziridination reactions with EDA (Table 3). The ylide is achiral. In the case of Cu catalysts, the ylide may remain closely associated to the catalyst and allow a limited degree of asymmetric induction to be achieved.[13] However, this appears not the case in the present ruthenium-catalyzed imine aziridination protocol. As with the analogous Lewis acid catalyzed reactions,[15,16] the ylide is thought to be weakly associated to the Ru catalyst. This is supported by the marked influence of different porphyrinato ring systems on reaction diastereoselectivity, as shown in Tables 3 and 4. Presumably, this systematic increase in stereoselectivity as the electrophilicity of the Ru atom increases suggests the effect of the spatial distance between the metal center and the imino carbon on the extent of stereochemical control exerted by the catalyst.

A series of competition experiments were performed to investigate the product ratios of the aziridines formed by reaction of PhCH═NPh vs *p*-X-PhCH═NPh (X = OMe, Me, Br, Cl, NO_2) with EDA in the presence of **1** (imine:EDA:**1** = 100:100:1) as the catalyst. The ratios of the corresponding aziridines were determined on the basis of ^{1}H NMR spectroscopy. The formation of these aziridines was found to correlate with the Hammett σ_I values as shown in Figure 9.

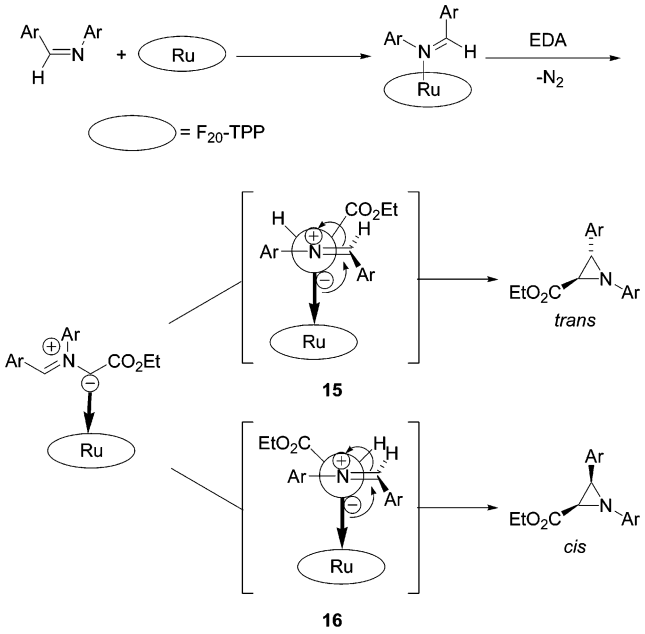
The Hammett plot in Figure 9 shows that, in general, aziridines derived from imines substituted with an electron-donating group formed much more quickly than those with an electron-withdrawing substituent. Fitting

Table 6. Variation of log K_R with σ_I and σ^+ for the [Ru(F_{20}-TPP)(CO)] (1) Catalyzed Aziridination of Para-Substituted Imines (*p*-XPhCH═NPh) with EDA

p-X	K_X/K_H	log(K_X/K_H)	σ_I	σ^+	log K_R(calcd)[a]
MeO	0.588	−0.231	0.30	−0.78	−0.192
Me	1.034	0.014	−0.01	−0.31	0.011
H	0	0	0	0	0
Cl	0.627	−0.203	0.43	0.11	−0.291
Br	0.532	−0.274	0.49	0.15	−0.332
NO_2	0.315	−0.502	0.64	0.79	−0.501

[a] log K_R(calcd) = $-0.67\sigma_I - 0.01\sigma^+$.

Scheme 3



(by the least-squares method) the log K_X/K_H data in Table 6 to the σ_I scale results in a linear correlation (R = 0.96) with the ρ value calculated to be −0.69 (±0.1). The Hammett $\sigma\rho$ correlation with a negative value for ρ supports a mechanism where imines having electron-donating substituents coordinated more efficiently to the ruthenium atom than electron-withdrawing substituted imines. Furthermore, the negative ρ value is indicative of the electronic nature of the active ruthenium species. The results of the correlation studies and the trapping experiments suggest that a metal-bound ylide intermediate is generated upon addition of EDA to the ruthenium(II) imine complex. The electronic nature of the imine should have an influence on the cis:trans ratio of the aziridines formed; however, the present results indicate that there is no simple correlation between this ratio and the electronic structure of the imine. Nevertheless, preferential cis product selectivity is thought to arise from the metal-bound ylide intermediate favoring to reside in the conformer **16** upon formation. Intramolecular attack of the carbanion onto the imino carbon atom resulting in ring closure is thought to give the aziridine with the observed stereochemistry as shown in Scheme 3.

Conclusion

In this article, we describe a (tetrakis(pentafluorophenyl)porphyrinato)ruthenium(II) complex of PhN═CH(*p*-

ClPh) prepared from the direct addition of [Ru(F_{20}-TPP)(CO)] (**1**) to a C_6H_6 solution containing *N*-(*p*-chlorobenzylene)aniline. The crystal structure of {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (**10**) reveals the coordinated imine ligand to be in a cis configuration. When treated with EDA, complex **10** and other closely related imine ligated ruthenium(II) porphyrins undergo aziridination in moderate to good yields and cis selectivity. Our studies suggest activation of the imine by the ruthenium catalyst followed by nucleophilic substitution of the imine to the diazo compound and subsequent cyclization to give the aziridine. Product formation was shown to occur more quickly for reactions derived from imines with electron-donating substituents compared to electron-withdrawing substituted imines.

Experimental Section

General Considerations. All (porphyrinato)ruthenium(II) carbonyl complexes were prepared according to literature methods.[41] The imines were prepared from the corresponding amines and aldehydes.[42] The imines were recrystallized from ethanol. EDA was purchased from Aldrich and used as received. Molecular sieves (4 Å) were dried over 48 h at 350 °C and stored in a drybox prior to use. Benzene was dried over sodium and benzophenone and distilled prior to use. UV−visible spectra were recorded on a HP 8453 diode array spectrophotometer. Infrared spectra were obtained on a BIO-RAD FTS 165 spectrometer. Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker DPX-300 FT-NMR spectrometer; the chemical shifts (δ, ppm) are relative to tetramethylsilane (*J* values are given in Hz). Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences.

Synthesis of [Ru(F_{20}-TPP)(CPh_2)] (7).[26] To a CH_2Cl_2 solution (5 mL) of [Ru(F_5-TPP)(CO)] (50 mg, 0.045 mmol) was slowly added a CH_2Cl_2 solution (10 mL) containing diphenyldiazomethane (17.5 mg, 0.09 mmol) by syringe pump for 8 h at room temperature. The resulting solution was further stirred for 2 h and then evacuated under reduced pressure. The residue was purified by chromatography on a silica gel column using a CH_2Cl_2/*n*-hexane mixture (1:2 v/v) as eluent to give the desired product in 95% yield. Crystals suitable for X-ray structure determination were isolated from a solution of CH_2Cl_2 and *n*-hexane. ^{1}H NMR ($CDCl_3$): δ 8.32 (s, 8H), 6.39 (t, 2H, J = 7.4 Hz), 6.14 (t, 4H, J = 7.7 Hz), 3.14 (d, 4H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$): δ 328.70 (Ru=C). ^{19}F NMR ($CDCl_3$): δ −136.2 (d), −137.1 (d), −152.3 (t), −161.8 (m). UV/vis (CH_2Cl_2): λ_{max}/nm (log ϵ) 385 (4.90), 425 (4.89), 526 (4.11), 550 (sh, 4.10), 613 (3.13). IR (KBr, cm^{-1}): 1012 (oxidation state marker band). MS (FAB): *m*/*z* 1239 [M]$^+$. Anal. Calcd for $C_{57}H_{18}F_{20}N_4Ru$: C, 55.21; H, 1.45; N, 4.52. Found: C, 55.77; H, 1.92; N, 4.40.

Synthesis of {Ru(F_{20}-TPP)(CO)[PhN=CH(*p*-ClPh)]} (10).[26] To a flask containing C_6H_6 (50 mL) was added [Ru(F_{20}-TPP)(CO)] (**1**; 0.05 mmol) and *N*-(4-chlorobenzylidene)aniline (0.06 mmol). The mixture was stirred for 30 min and then evacuated to give the product in 80% yield. Crystals suitable for X-ray determination were isolated from a solution of CH_2Cl_2 and *n*-hexane at room temperature. ^{1}H NMR ($CDCl_3$): δ 8.73 (s, 1H), 8.65 (s, 8H), 6.43 (t, 1H, J = 7.3 Hz), 6.35 (d, 2H, J = 8.7 Hz), 6.09 (t, 2H, J = 7.8 Hz), 4,66 (d, 2H, J = 8.6 Hz), 2.45 (d, 2H, J = 7.9 Hz). ^{13}C NMR ($CDCl_3$) δ 176.70, 161.43, 148.08, 144.45, 143.82, 143.58, 140.48, 140.25, 139.31, 135.77, 132.11, 130.75, 127.86, 127.62, 127.06, 124.97, 116.34, 116.01, 115.03, 105.03. UV/vis (9.72 μM, CH_2Cl_2): λ_{max}/nm (log ϵ) 406 (5.36), 527 (4.20), 555 (sh, 3.48). IR (KBr, cm^{-1}): 1967 (CO), 1011 (oxidation state marker band). MS (FAB): *m*/*z* 1319 [M]$^+$, 1290 [M − CO]$^+$, 1074 [M − $C_{13}H_{10}ClN$ − CO]$^+$. Anal. Calcd for $C_{58}H_{18}ClF_{20}N_5ORu$: C, 52.88; H, 1.38; N, 5.32. Found: C, 52.39; H, 1.24; N, 5.65.

Synthesis of [Ru(F_{20}-TPP)($py)_2$] (11).[26] To a CH_2Cl_2 solution (5 mL) of the complex [Ru(F_5-TPP)($CPhCO_2Et$)] (20 mg, 0.016 mmol) was added 1 drop of pyridine, and the mixture was evaporated immediately. The residue was purified by chromatography on a silica gel column using a 1:2 solution of CH_2Cl_2 and *n*-hexane as eluent to give the desired product in 72% yield. ^{1}H NMR ($CDCl_3$): δ 8.08 (s, 8H), 6.07 (t, 2H, J = 7.4 Hz), 5.20 (t, 4H, J = 7.0 Hz), 2.55 (d, 4H, J = 5.3 Hz). ^{13}C NMR ($CDCl_3$): δ 148.66, 147.18, 143.97, 143.28, 142.41, 139.14, 138.50, 135.15, 131.80, 131.38, 120.36, 115.32, 105.02. UV/vis (CH_2Cl_2): λ_{max}/nm (log ϵ) 399 (5.24), 501 (4.13), 526 (4.16). IR (KBr, cm^{-1}): 1011 (oxidation state marker band). MS (FAB): *m*/*z* 1233 [M]$^+$, 1154 [M − C_5H_5N]$^+$, 1075 [M − C_5H_5N − C_5H_5N]$^+$. Anal. Calcd for $C_{54}H_{18}F_{20}N_6Ru$: C, 52.65; H, 1.47; N, 6.82. Found: C, 52.93; H, 1.80; N, 6.57.

General Procedure for Catalytic Cyclopropanation of Imines with EDA. A flask containing imine (2 mmol), catalyst (0.005 mmol), and 4 Å molecular sieves was evacuated and filled with Ar. C_6H_6 (10 mL) was added, and the mixture was stirred for 10 min at room temperature. EDA (1 mmol, in 6 mL of benzene) was then added to the flask by syringe pump over 18 h, and then the mixture was stirred for another 3 h. After addition of bibenzyl (0.2 mmol), the reaction mixture was filtered and eluted with $CHCl_3$. The solution was evacuated and analyzed by ^{1}H NMR. The crude product was purified by flash chromatography on silica gel using 2% EtOAc in *n*-pentane as eluent to give the pure aziridine.[16e,f]

Ethyl *cis*-1-Phenyl-3-(*p*-bromophenyl)aziridine-2-carboxylate. ^{1}H NMR ($CDCl_3$): δ 7.46−7.49 (m, 2H), 7.38−7.41 (m, 2H), 7.25−7.30 (m, 2H), 7.02−7.05 (m, 5H), 4.01−4.07 (m, 2H), 3.53 (d, 1H, J = 6.7 Hz), 3.20 (d, 1H, J = 6.7 Hz), 1.05 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 167.42, 152.04, 133.70, 131.24, 129.45, 129.27, 123.65, 121.94, 119.89, 61.22, 46.52, 45.54, 14.02. HRMS (EI): *m*/*z* calcd for $C_{17}H_{16}BrNO_2$ 345.0364, found 345.0345.

Ethyl *trans*-1-Phenyl-3-(*p*-bromophenyl)aziridine-2-carboxylate. ^{1}H NMR ($CDCl_3$): δ 7.43−7.48 (m, 2H), 7.18−7.25 (m, 5H), 6.96−7.01 (m, 1H), 6.84−6.87 (m, 2H), 4.07−4.15 (m, 2H), 3.76 (d, 1H, J = 2.4 Hz), 3.18 (d, 1H, J = 2.4 Hz), 1.15 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 167.27, 148.17, 135.39, 131.65, 128.95, 128.44, 123.00, 122.02, 119.86, 61.48, 45.93, 45.62, 14.05. HRMS (EI): *m*/*z* calcd for $C_{17}H_{16}BrNO_2$ 345.0364, found 345.0335.

Ethyl *cis*-1-Phenyl-3-(*p*-*tert*-butylphenyl)aziridine-2-carboxylate. ^{1}H NMR ($CDCl_3$): δ 7.44 (d, 2H, J = 8.3 Hz), 7.36 (d, 2H, J = 8.5 Hz), 7.27−7.25 (q, 2H), 7.07−7.04 (m, 3H), 4.10−3.95 (m, 2H), 3.57 (d, 1H, J = 6.8 Hz), 3.18 (d, 1H, J = 6.8 Hz), 1.32 (s, 9H), 0.95 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 167.77, 151.56, 143.96, 129.42, 129.27, 126.31, 125.10, 118.31, 113.13, 61.42, 46.00, 45.67, 31.43, 31.18, 14.30. HRMS (EI): *m*/*z* calcd for $C_{21}H_{25}NO_2$ 323.1885, found 323.1877.

Ethyl *trans*-1-Phenyl-3-(*p*-*tert*-butylphenyl)aziridine-2-carboxylate. ^{1}H NMR ($CDCl_3$): δ 7.36 (d, J = 8.4 Hz, 2H), 7.26−7.19 (m, 4H), 6.99−6.95 (m, 1H), 6.89−6.87 (q, 2H), 4.14−4.08 (q, 2H), 3.78 (d, 1H, J = 2.5 Hz), 3.22 (d, 1H, J = 2.5 Hz), 1.31 (s, 9H), 1.15 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 167.78, 151.27, 148.71, 133.37, 128.96, 126.57, 125.59, 122.79, 120.06, 61.39, 46.38, 45.99, 34.70, 31.41, 14.16. HRMS (EI): *m*/*z* calcd for $C_{21}H_{25}NO_2$ 323.1885, found 323.1879.

5-(4-*tert*-Butylphenyl)-1-phenylpyrrolidine-2,3,4-tricarboxylic Acid Triethyl Ester. ^{1}H NMR ($CDCl_3$): δ 7.22−

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7.17 (m, 2H), 7.11−7.01 (m, 4H), 6.67 (t, 1H, J = 7.3 Hz), 6.59 (d, 2H, J = 7.8 Hz), 5.41 (d, 1H, J = 7.9 Hz), 5.35 (d, 1H, J = 6.6 Hz), 4.19−4.14 (m, 2H), 4.08−4.03 (q, 2H, J = 14.3, 7.1 Hz), 3.75−3.67 (m, 2H), 3.62 (t, 1H, J = 7.6 Hz), 3.51−3.43 (m, 1H), 1.24 (s, 9H), 1.22 (t, 3H, J = 7.6 Hz), 1.08 (t, 3H, J = 7.1 Hz), 0.74 (t, 3H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$): δ 173.93, 170.75, 169.99, 150.54, 145.10, 134.22, 128.40, 126.83, 125.21, 117.44, 114.26, 65.74, 65.63, 61.40, 61.23, 60.58, 53.04, 49.71, 34.54, 31.44, 31.41, 31.28, 14.15, 14.08, 13.63. HRMS (EI): *m*/*z* calcd for $C_{29}H_{37}NO_6$ 495.2021, found 495.2630.

1-(4-Methoxyphenyl)-5-phenylpyrrolidine-2,3,4-tricarboxylic Acid Triethyl Ester. ^{1}H NMR ($CDCl_3$): δ 7.38−7.19 (m, 5H), 6.66 (d, 2H, J = 9.1 Hz), 6.51 (d, 2H, J = 9.1 Hz), 5.27 (d, 1H, J = 4.9 Hz), 5.22 (d, 1H, J = 2.5 Hz), 4.23−4.04 (m, 6H), 3.80−3.77 (q, 1H, J = 3.7, 2.3 Hz), 3.66 (s, 3H), 3.54−3.51 (q, 1H, J = 4.7, 4.0 Hz), 1.30 (t, 3H, J = 7.1 Hz), 1.17−1.11 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 172.41, 171.72, 171.24, 152.56, 142.24, 139.40, 128.76, 127.42, 126.35, 116.91, 114.43, 65.97, 65.24, 61.74, 61.54, 61.24, 55.71, 55.57, 48.75, 14.27, 14.16, 14.08. HRMS (EI): *m*/*z* calcd for $C_{26}H_{31}NO_7$ 469.2100, found 469.2095.

General Procedure for the Preparation of Pyrrolidines Catalyzed by [Ru(F_{20}-TPP)(CO)] (1). A flask containing the imine (1.2 mmol), dipolarophile A−B (1.2 mmol), catalyst **1** (0.005 mmol), and 4 Å molecular sieves was evacuated and filled with Ar. C_6H_6 (10 mL) was added, and the mixture was stirred for 10 min at room temperature. A solution of EDA (1 mmol) dissolved in C_6H_6 (6 mL) was then added to the flask by syringe pump over 12 h, and the mixture was stirred for a further 1 h. The reaction mixture was filtered and eluted with $CHCl_3$. The solution was evacuated and analyzed by ^{1}H NMR. The crude product was purified by flash chromatography on silica gel using 10% EtOAc in *n*-pentane as eluent to give the pure pyrrolidine.

5-(4-Chlorophenyl)-1-phenylpyrrolidine-2,3,4-tricarboxylic Acid 2-Ethyl Ester 3,4-Dimethyl Ester (14a). Purification by flash column chromatography gave the title compound in 90% yield as a 1.3:1 mixture of diastereomers. Major stereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.27−7.23 (m 4H), 7.11−7.07 (q, 2H), 6.71 (t, 1H, J = 7.3 Hz), 6.49 (d, 2H, J = 7.9 Hz), 5.35 (d, 1H, J = 4.1 Hz), 5.28 (d, 1H, J = 2.0 Hz), 4.15−4.02 (m, 2H), 3.83 (t, 1H, J = 2.5 Hz), 3.78 (s, 3H), 3.65 (s, 3H), 3.54 (t, 1H, J = 3.5 Hz), 1.13 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 171.99, 171.79, 171.45, 144.98, 140.74, 133.13, 129.03, 128.06, 126.90, 118.80, 115.37, 65.10, 64.59, 64.40, 61.50, 55.23, 52.94, 48.40, 14.11; HRMS (EI) *m*/*z* calcd for $C_{23}H_{24}ClNO_6$ 445.1292, found 445.1288. Minor stereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.25 (d, 2H, J = 6.9 Hz), 7.16 (d, 2H, J = 8.5 Hz), 7.10 (t, 2H, J = 7.4 Hz), 6.71 (t, 1H, J = 7.3 Hz), 6.43 (d, 2H, J = 8.0 Hz), 5.29 (d, 1H, J = 9.5 Hz), 5.00 (d, 1H, J = 8.1 Hz), 4.25 (dd, 1H, J = 12.6, 9.6 Hz), 4.18−4.07 (m, 2H), 4.01 (dd, 1H, J = 12.6, 8.0 Hz), 3.75 (s, 3H), 3.40 (s, 3H), 1.20 (t, 3H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 170.89, 169.68, 169.59, 144.06, 137.46, 133.87, 129.19, 128.80, 128.34, 118.34, 113.45, 63.20, 62.57, 61.64, 52.52, 51.88, 49.84, 46.20, 14.14; HRMS (EI) *m*/*z* calcd. for $C_{23}H_{24}ClNO_6$ 445.1290, found 445.1290.

1,5-Diphenyl-4,5-dihydro-1*H*-pyrrole-2,3,4-tricarboxylic Acid 2-Ethyl Ester 3,4-Dimethyl Ester (14b). Purification by flash column chromatography gave the title compound in 92% yield. ^{1}H NMR ($CDCl_3$): δ 7.35−7.22 (m, 5H), 7.11−7.06 (q, 2H, J = 8.6, 7.2 Hz), 6.68 (t, 1H, J = 7.2 Hz), 6.54 (d, 2H, J = 7.9 Hz), 6.01 (d, 1H, J = 6.9 Hz), 5.76 (d, 1H, J = 6.9 Hz), 4.22−4.07 (m, 2H), 3.83 (s, 3H), 3.63 (s, 3H), 1.11 (t, 3H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 169.61, 162.92, 162.27, 143.94, 143.45, 137.95, 130.88, 129.03, 128.87, 128.41, 127.30, 118.29, 113.89, 71.02, 69.73, 61.79, 52.61, 52.34, 14.05; HRMS (EI) *m*/*z* calcd for $C_{23}H_{23}NO_6$ 409.1525, found 409.1518.

5-(4-*tert*-Butylphenyl)-1-phenyl-2,5-dihydro-1*H*-pyrrole-2,3,4-tricarboxylic Acid 2-Ethyl Ester 3,4-Dimethyl Ester (14c). Purification by flash column chromatography gave the title compound in 83% yield. ^{1}H NMR ($CDCl_3$): δ 7.30−7.22 (m, 4H), 7.12−7.08 (m, 2H), 6.69 (t, 1H, J = 7.3 Hz), 6.55 (d, 2H, J = 7.9 Hz), 5.99 (d, 1H, J = 6.9 Hz), 5.75 (d, 1H, J = 6.9 Hz), 4.20−4.08 (m, 2H), 3.82 (s, 3H), 3.63 (s, 3H), 1.26 (s, 9H), 1.10 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 169.69, 162.98, 162.33, 151.23, 144.07, 143.58, 134.74, 130.59, 129.00, 126.84, 125.76, 118.11, 113.87, 70.65, 69.73, 61.75, 52.57, 52.30, 34.53, 31.27, 14.04. HRMS (EI): *m*/*z* calcd for $C_{27}H_{31}NO_6$ 465.2151, found 465.2150.

1-Phenyl-5-(3,4,5-trimethoxyphenyl)-2,5-dihydro-1*H*-pyrrole-2,3,4-tricarboxylic Acid 2-Ethyl Ester 3,4-Dimethyl Ester (14d). Purification by flash column chromatography gave the title compound in 80% yield. ^{1}H NMR ($CDCl_3$): δ 7.14−7.10 (m, 2H), 6.73 (t, 1H, J = 7.4 Hz), 6.58 (d, 2H, J = 8.0), 6.53 (s, 2H), 5.94 (d, 1H, J = 6.8 Hz), 5.76 (d, 1H, J = 6.8 Hz), 4.19−4.06 (m, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 3.79 (s, 6H), 3.67 (s, 3H), 1.08 (t, 3H, J = 7.1 Hz). ^{13}C NMR ($CDCl_3$): δ 169.70, 163.21, 162.24, 153.70, 144.55, 143.78, 137.98, 133.48, 130.29, 129.13, 118.65, 114.16, 104.18, 71.40, 69.82, 61.84, 60.90, 56.27, 52.70, 52.49, 14.12. HRMS (EI): *m*/*z* calcd for $C_{26}H_{29}NO_9$ 499.1842, found 499.1831.

4,6-Dioxo-2,3,5-triphenyloctahydropyrrolo[3,4-*c*]pyrrole-1-carboxylic Acid Ethyl Ester (14e). Purification by flash column chromatography gave the title compound in 86% yield. ^{1}H NMR ($CDCl_3$): δ 7.50−7.23 (m, 10H), 7.14−7.08 (q, 2H, J = 8.9, 7.6 Hz), 6.77 (t, 1H, J = 7.3 Hz), 6.68 (d, 2H, J = 7.6 Hz), 5.53 (t, 1H, J = 3.3 Hz), 5.28 (d, 1H, J = 9.9 Hz), 4.13−4.03 (m, 3H), 3.61−3.56 (q, 1H, J = 13.6, 4.0 Hz), 1.04 (t, 3H, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$): δ 175.68, 174.06, 170.98, 144.57, 141.56, 131.73, 129.23, 129.15, 128.97, 128.87, 127.72, 126.53, 126.10, 119,97, 117.01, 65.42, 64.97, 61.75, 60.41, 54.54, 46.21, 13.90. HRMS (EI): *m*/*z* calcd for $C_{27}H_{24}N_2O_4$ 440.1736, found 440.1734.

Procedure for Aziridination Competition Experiments. A flask containing the imines PhCH=NPh (0.3 mmol) and *p*-X-PhCH=NPh (X = OMe, Me, Br, Cl, NO_2; 0.3 mmol), [Ru(F_{20}-TPP)(CO)] (0.003 mmol), and 4 Å molecular sieves was evacuated and filled with Ar(g). The mixture was diluted with C_6H_6 (10 mL) and stirred for 10 min at room temperature. EDA (0.3 mmol, in 10 mL of C_6H_6) was then added to the flask by syringe pump over 18 h. The reaction mixture was filtered, and the 4 Å molecular sieves were eluted with $CHCl_3$. The solution was evacuated, and the resultant mixture was used to determine aziridine product ratios by ^{1}H NMR analysis.

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Supporting Information Available: Text giving detailed experimental procedures and characterization data for [Ru(F_{20}-TPP)($CHCO_2Et$)] and tables giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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