

**Supplementary Information  
for  
“Ruthenium(II) Porphyrin Catalyzed Imine Aziridination and Crystal  
Structures of *Meso*-tetrakis(pentafluorophenyl)porphyrinato Ruthenium(II)  
Complexes Containing PhN=CH(*p*-ClPh), CPh<sub>2</sub> and Pyridine Ligands”**

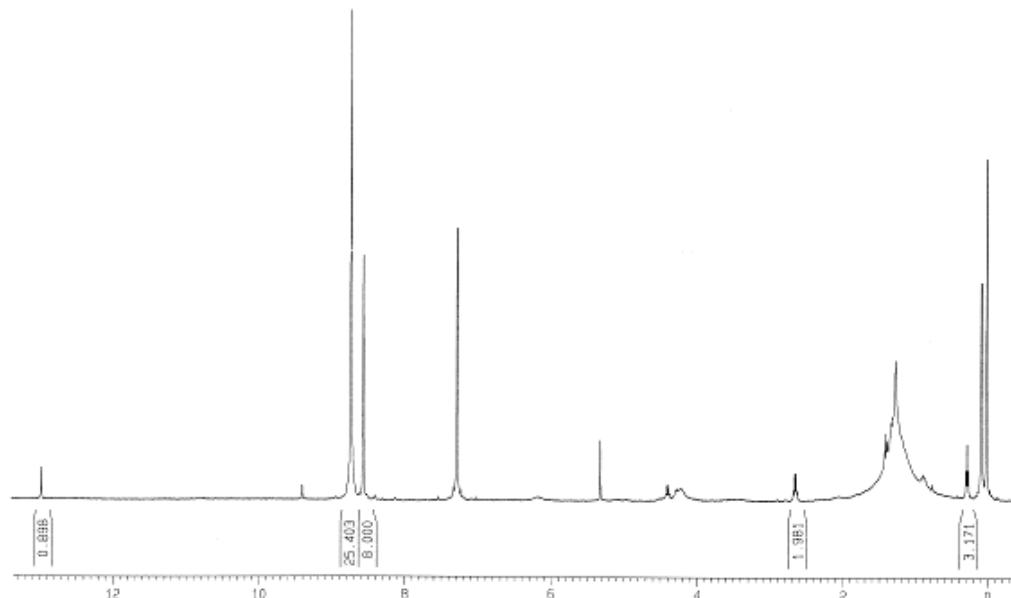
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**General Considerations.** [Ru(F<sub>20</sub>-TPP)(CO)] (**1**) was prepared according to literature methods.<sup>S1</sup> The imines were prepared from the corresponding amines and aldehydes.<sup>S2</sup> The imines were recrystallised from ethanol. EDA was purchased from Aldrich and used as received. Molecular sieves (4Å) were dried over 48h at 350°C and stored in a dry box prior to use. Benzene was dried over sodium and benzophenone and distilled prior to use. Mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. <sup>1</sup>H NMR spectra were obtained on a Bruker DPX-300 FT-NMR spectrometer; the chemical shifts ( $\delta$ , ppm) are relative to tetramethylsilane ( $J$  values are given in Hz).

**Preparation of [Ru(F<sub>20</sub>-TPP)(CHCO<sub>2</sub>Et)]:** To the stirred solution of [Ru(F<sub>20</sub>-TPP)(CO)] (**1**) (22 mg, 0.02 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added EDA (2.1  $\mu$ L, 0.02 mmol) in the same solution (2 mL) by syringe pump for 5 mins at 0°C. The solution was then evacuated under reduced pressure at 0°C. Formation of [Ru(F<sub>20</sub>-TPP)(CHCO<sub>2</sub>Et)] contaminated with [Ru(F<sub>20</sub>-TPP)(CO)] (**1**), was confirmed on the basis of <sup>1</sup>H NMR spectroscopy: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  13.00 (s, 1H), 8.50 (s, 8H), 2.62 (q, 2H), 0.26 (t, 3H).

<sup>1</sup>H NMR spectrum of [Ru(F<sub>20</sub>-TPP)(CHCO<sub>2</sub>Et)].



**Reaction of  $[\text{Ru}(\text{F}_{20}\text{-TPP})(\text{CHCO}_2\text{Et})]$  with  $N$ -(*p*-Chlorobenzylidene)-aniline:** To a solution of  $[\text{Ru}(\text{F}_{20}\text{-TPP})(\text{CHCO}_2\text{Et})]$  in  $\text{CH}_2\text{Cl}_2$  was added excess *p*-ClPhCH=NPh at room temperature. On the basis of  $^1\text{H}$  NMR and GC-MS analysis, formation of the aziridine product was not detected. The major organic product obtained was identified to be  $\text{PhN}=\text{CHCO}_2\text{Et}$ . The inorganic product was rationalized to be  $[\text{Ru}(\text{F}_{20}\text{-TPP})(p\text{-ClPhCH=NPh})]$  based on  $^1\text{H}$  NMR and FAB-MS spectroscopic determination. The ion cluster corresponding to the imine complex  $\{\text{Ru}(\text{F}_{20}\text{-TPP})(\text{CO})[(p\text{-ClPh})\text{CH=NPh}]\}$  (**11**) was found not to be present by FAB-MS analysis.

ORTEP drawing with atomic numbering scheme for 1,5-diphenyl-4,5-dihydro-1*H*-pyrrole-2,3,4-tricarboxylic acid 2-ethyl ester 3,4-dimethyl ester **15b**.

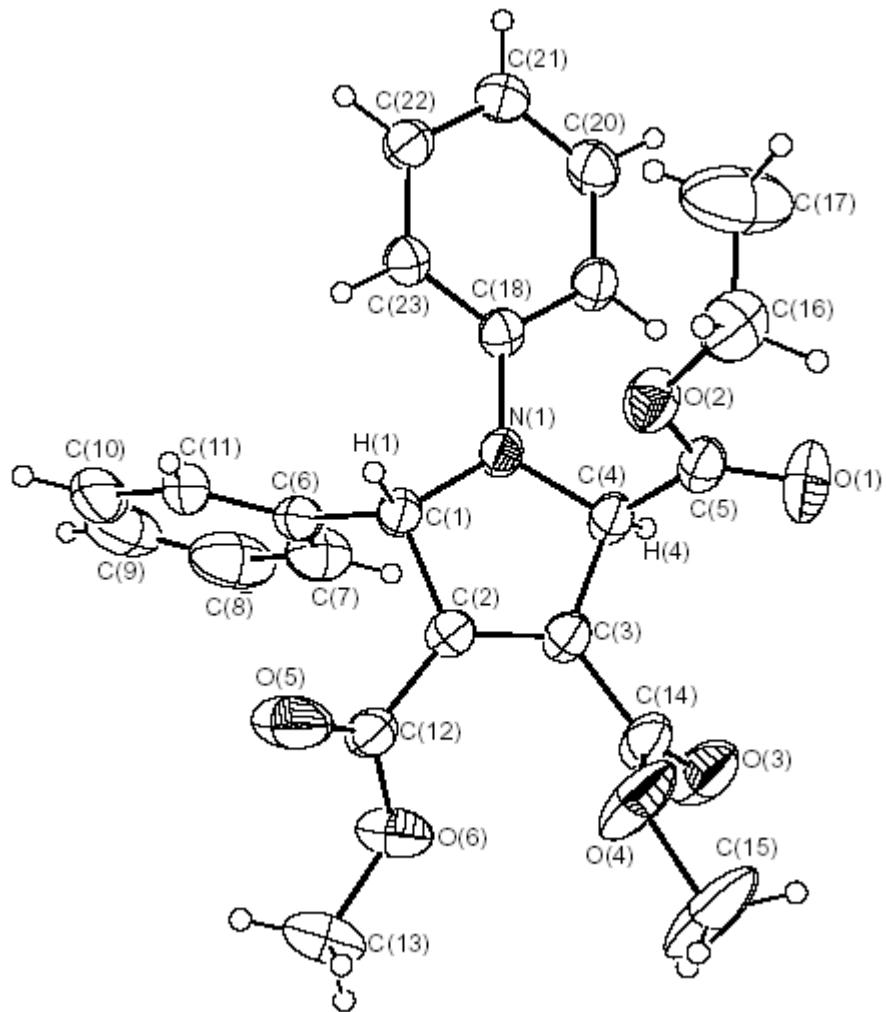


Table 1. Crystal data and structure refinement for **15b**.

Identification code	mar1049a	
Empirical formula	C <sub>23</sub> H <sub>23</sub> N O <sub>6</sub>	
Formula weight	409.42	
Temperature	253(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 <sub>1</sub> /n	
Unit cell dimensions	a = 16.197(3) Å b = 9.203(2) Å c = 16.583(3) Å	$\alpha = 90^\circ$ . $\beta = 118.86(3)^\circ$ . $\gamma = 90^\circ$ .
Volume	2164.9(7) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.256 Mg/m <sup>3</sup>	
Absorption coefficient	0.091 mm <sup>-1</sup>	
F(000)	864	
Crystal size	0.5 x 0.4 x 0.3 mm <sup>3</sup>	
Theta range for data collection	1.44 to 25.32°	
Index ranges	-17≤=h≤=19, -10≤=k≤=10, -19≤=l≤=16	
Reflections collected	10508	
Independent reflections	3398 [R(int) = 0.0337]	
Completeness to theta = 25.32°	86.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3398 / 0 / 274	
Goodness-of-fit on F <sup>2</sup>	1.120	
Final R indices [I>2sigma(I)]	R1 = 0.0655, wR2 = 0.2120	
R indices (all data)	R1 = 0.0831, wR2 = 0.2246	
Largest diff. peak and hole	0.732 and -0.343 e.Å <sup>-3</sup>	

Table 2. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **15b**.

O(1)-C(5)	1.189(3)	C(7)-C(6)-C(1)	120.1(3)
O(2)-C(5)	1.317(3)	C(11)-C(6)-C(1)	120.8(3)
O(2)-C(16)	1.466(4)	C(6)-C(7)-C(8)	120.1(4)
O(3)-C(14)	1.206(4)	C(7)-C(8)-C(9)	119.0(5)
O(4)-C(14)	1.287(4)	C(10)-C(9)-C(8)	120.9(4)
O(4)-C(15)	1.463(4)	C(9)-C(10)-C(11)	119.7(5)
O(5)-C(12)	1.172(3)	C(10)-C(11)-C(6)	121.2(4)
O(6)-C(12)	1.299(3)	O(5)-C(12)-O(6)	122.9(3)
O(6)-C(13)	1.446(4)	O(5)-C(12)-C(2)	123.4(3)
N(1)-C(18)	1.399(3)	O(6)-C(12)-C(2)	113.7(2)
N(1)-C(1)	1.461(3)	O(3)-C(14)-O(4)	124.2(3)
N(1)-C(4)	1.462(3)	O(3)-C(14)-C(3)	122.8(3)
C(1)-C(2)	1.509(3)	O(4)-C(14)-C(3)	112.8(3)
C(1)-C(6)	1.516(3)	C(17)-C(16)-O(2)	109.4(3)
C(2)-C(3)	1.329(3)	C(19)-C(18)-N(1)	120.3(2)
C(2)-C(12)	1.476(4)	C(19)-C(18)-C(23)	118.7(2)
C(3)-C(14)	1.477(4)	N(1)-C(18)-C(23)	121.0(2)
C(3)-C(4)	1.513(3)	C(18)-C(19)-C(20)	120.0(3)
C(4)-C(5)	1.521(4)	C(21)-C(20)-C(19)	121.3(3)
C(6)-C(7)	1.366(4)	C(20)-C(21)-C(22)	118.8(3)
C(6)-C(11)	1.377(4)	C(21)-C(22)-C(23)	121.0(3)
C(7)-C(8)	1.381(6)	C(22)-C(23)-C(18)	120.2(2)
C(8)-C(9)	1.398(8)		
C(9)-C(10)	1.331(7)	Symmetry transformations used to generate equivalent atoms.	
C(10)-C(11)	1.372(5)		
C(16)-C(17)	1.453(6)		
C(18)-C(19)	1.385(4)		
C(18)-C(23)	1.401(4)		
C(19)-C(20)	1.390(4)		
C(20)-C(21)	1.376(4)		
C(21)-C(22)	1.379(4)		
C(22)-C(23)	1.381(4)		
C(5)-O(2)-C(16)	117.9(2)		
C(14)-O(4)-C(15)	117.2(3)		
C(12)-O(6)-C(13)	117.9(3)		
C(18)-N(1)-C(1)	122.07(19)		
C(18)-N(1)-C(4)	121.4(2)		
C(1)-N(1)-C(4)	112.88(18)		
N(1)-C(1)-C(2)	101.58(18)		
N(1)-C(1)-C(6)	112.8(2)		
C(2)-C(1)-C(6)	112.7(2)		
C(3)-C(2)-C(12)	128.0(2)		
C(3)-C(2)-C(1)	111.7(2)		
C(12)-C(2)-C(1)	120.3(2)		
C(2)-C(3)-C(14)	126.8(2)		
C(2)-C(3)-C(4)	111.3(2)		
C(14)-C(3)-C(4)	121.9(2)		
N(1)-C(4)-C(3)	101.52(19)		
N(1)-C(4)-C(5)	115.0(2)		
C(3)-C(4)-C(5)	110.6(2)		
O(1)-C(5)-O(2)	125.2(3)		
O(1)-C(5)-C(4)	122.5(3)		
O(2)-C(5)-C(4)	112.3(2)		
C(7)-C(6)-C(11)	119.1(3)		

## References

- S1. (a) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, 32, 476. (b) Rillema, D. P.; Nagle, J. K.; Barringer, L. F., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, 103, 56. (c) Li, Z.-Y.; Huang, J.-S.; Che, C.-M.; Chang, C.-K. *Inorg. Chem.* **1992**, 31, 2670. (d) Falvo, R. E.; Mink, L.M. *J. Chem. Educ.* **1999**, 76, 237.  
S2. Biglow, L. A.; Eatough, H. *Org. Synth.*, Coll. Vol. 1, **1932**, 73.