

Syntheses and structural studies of η^5 -pentamethylcyclopentadienyl rhodium(III) and iridium(III) complexes of a Schiff-base expanded porphyrin

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X-RAY EXPERIMENTAL

Complex 2. CCDC deposition number: 709220. Crystals grew as yellow-orange plates by slow evaporation from dichloromethane. The data crystal was cut from a larger crystal and had approximate dimensions; $0.35 \times 0.17 \times 0.07$ mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 480 frames of data were collected using ω -scans with a scan range of 0.8° and a counting time of 85 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.¹ The structure was solved by direct methods using SIR97² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.³ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times U_{\text{eq}}$ of the attached atom ($1.5 \times U_{\text{eq}}$ for methyl hydrogen atoms).

A number of the trifluoromethyl groups were disordered. In addition, several fluorine atoms exhibited highly anisotropic displacement parameters. The disordered CF_3 - groups were all modeled alike. The C-F bond lengths and the F-C-C bond angles were restrained to be equivalent for all CF_3 groups. For a given CF_3 - group, the site occupancy factor for one component of the disorder was assigned the variable x , while the site occupancy factor for the alternate component was set to $(1-x)$. A common isotropic displacement parameter was refined for all six F atoms. Once the variable x was refined, the site occupancies were fixed and the displacement parameters were refined. Anisotropic displacement parameters for all fluorine atoms were refined with restraints to keep them approximately isotropic.

One of the dichloromethane molecules was also disordered. The disorder was the result of a rotation about one of the Cl-C bonds. The geometry of the dichloromethane was restrained to be equivalent to the ordered dichloromethane molecule throughout the refinement. The hydrogen atoms associated with this molecule were not included in the refinement model.

The function, $\sum w(|F_{\text{O}}|^2 - |F_{\text{C}}|^2)^2$, was minimized, where $w = 1/[(\sigma(F_{\text{O}}))^2 + (0.0411*P)^2 + (11.4564*P)]$ and $P = (|F_{\text{O}}|^2 + 2|F_{\text{C}}|^2)/3$. $R_{\text{w}}(F^2)$ refined to 0.142, with $R(F)$ equal to 0.0689 and a goodness of fit, S , = 1.06. Definitions used for calculating $R(F)$, $R_{\text{w}}(F^2)$ and the goodness of fit, S , are given below.⁴ The data checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁵ All figures were generated using SHELXTL/PC.⁶

Complex 3. CCDC deposition number: 709221. Crystals grew as yellow-orange plates by slow evaporation from dichloromethane. The data crystal was cut from a larger crystal and had approximate dimensions; $0.20 \times 0.13 \times 0.10$

mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 397 frames of data were collected using ω -scans with a scan range of 1.1° and a counting time of 102 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.¹ The structure was solved by direct methods using SIR97² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.³ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom ($1.5 \times U_{eq}$ for methyl hydrogen atoms).

A number of the trifluoromethyl groups were disordered. In addition, several fluorine atoms exhibited highly anisotropic displacement parameters. The disordered CF₃- groups were all modeled alike. The C-F bond lengths and the F-C-C bond angles were restrained to be equivalent for all CF₃ groups. For a given CF₃- group, the site occupancy factor for one component of the disorder was assigned the variable x , while the site occupancy factor for the alternate component was set to $(1-x)$. A common isotropic displacement parameter was refined for all six F atoms. Once the variable x was refined, the site occupancies were fixed and the displacement parameters were refined. Anisotropic displacement parameters for all fluorine atoms were refined with restraints to keep them approximately isotropic.

One of the dichloromethane molecules was also disordered. The disorder was the result of a rotation about one of the Cl-C bonds. The geometry of the dichloromethane was restrained to be equivalent to the ordered dichloromethane molecule throughout the refinement. The hydrogen atoms associated with this molecule were not included in the refinement model.

The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0562 * P)^2 + (18.8245 * P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.135, with $R(F)$ equal to 0.0602 and a goodness of fit, S , = 1.11. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁴ The data checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁵ All figures were generated using SHELXTL/PC.⁶

Table S1. Crystal data and structure refinement parameters for complexes **2** and **3**

	2	3
empirical formula	C ₁₂₄ H ₉₄ B ₂ Cl ₆ F ₄₈ N ₈ Rh ₂	C ₁₂₄ H ₉₄ B ₂ Cl ₆ F ₄₈ N ₈ Ir ₂
formula weight	3048.21	3226.79
crystal system	Monoclinic	Monoclinic
space group	P21	P21
<i>a</i> , Å	13.5078(3)	13.5372(2)
<i>b</i> , Å	26.2580(8)	26.2793(6)
<i>c</i> , Å	18.6348(6)	18.6279(4)
α , °	90	90
β , °	104.457(2)	104.549(2)
γ , °	90	90
<i>V</i> , Å ³	6400.2(3)	6414.3(2)
<i>Z</i>	2	2
<i>D</i> (Calc'd), mg/m ³	1.582	1.671
abs. coeff., mm ⁻¹	0.505	2.320
<i>F</i> (000)	3056	3184
crystal size, mm	0.35 × 0.17 × 0.07	0.20 × 0.13 × 0.10
θ for data collection, °	2.14 – 27.48	2.14 – 27.47
limiting indices	-17 ≤ <i>h</i> ≤ 17 -34 ≤ <i>k</i> ≤ 33 -24 ≤ <i>l</i> ≤ 24	-17 ≤ <i>h</i> ≤ 17 -34 ≤ <i>k</i> ≤ 33 -21 ≤ <i>l</i> ≤ 24
reflections collected	26327	67201
independent reflections	26237	27926
completeness to θ_{max}	98.6%	99.2%
absorption correction	Semi-empirical	Analytical
data/restraints/parameters	26327 / 4522 / 1890	27926 / 3326 / 1809
goodness-of-fit on <i>F</i> ²	1.054	1.035
<i>R</i> , <i>R</i> _w	0.0689, 0.1425	0.0603, 0.1350

REFERENCES

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2. SIR97. (1999). A program for crystal structure solution. Altomare A, Burla MC, Camalli M., Cascarano GL, Giacovazzo C, Guagliardi A, Moliterni AGG, Polidori G and Spagna R *J. Appl. Cryst.* 32; 115-119.
3. Sheldrick GM (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.
4. $R_w(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^4)\}^{1/2}$ where w is the weight given each reflection. $R(F) = \Sigma(|F_o| - |F_c|) / \Sigma |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$. $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
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