Appendix 4

X-Ray Crystallography Reports Relevant to Chapter 3:

Decarboxylative Asymmetric Ni-Catalyzed Cross-Coupling of Benzylic N-Hydroxyphthalimide Esters and Alkenyl Bromides

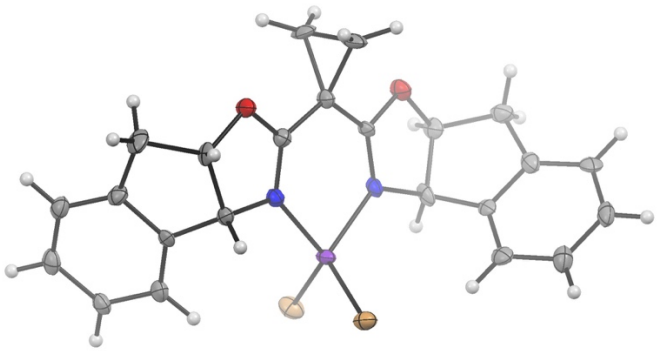
A4.1 STRUCTURAL DETERMINATION AND REFINEMENT DETAILS

Low-temperature diffraction data (ϕ- and ω-scans) were collected on a Bruker AXS KAPPA APEXII diffractometer coupled to a PHOTON 100 CMOS detector with Mo-$K\alpha$ radiation (λ = 0.71073 Å) from an I$_\mu$S HB micro-focused X-ray tube. All diffractometer manipulations, including data collection integration, and scaling were carried out using the Bruker APEXII software.[1] Absorption corrections were applied using SADABS.[2] The structure was solved by intrinsic phasing using SHELXT[3] and refined against F^2 on all data by full-matrix least squares with SHELXL-2014[4] using established refinement techniques.[5] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to. Absolute configuration was determined by anomalous dispersion.[6] Graphical representation of the structure with 50% probability thermal ellipsoids was generated using Mercury visualization software.

A4.2 CRYSTALLOGRAPHIC ANALYSIS OF L2·$NiBr_2$

A4.2.1 Special Refinement Details

Figure A4.1 *Rendering of Ni-complex* ***L2***·$NiBr_2$.



Compound **L2**·$NiBr_2$ crystallizes in the tetragonal space group $P4_1$ with one molecule in the asymmetric unit. Data was collected with Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 100 K. The structure was solved as a merohedral twin with rotation around an axis 45° between a and b. The twin law was defined as the matrix (0.0, 1.0, 0.0, 1.0, 0.0, 0.0, 0.0, 0.0, -1.0). The BASF parameter [0.4980(14)] gave the twin ratio as 0.50:0.50. Absolute configuration was determined by anomalous dispersion (Flack = 0.011(2)).[6]

A4.2.2 Crystallographic Tables

Table A4.1. *Crystal data and structure refinement for* ***L2***·$NiBr_2$.

Identification code	A15178	
CCDC Deposition Number	1501744	
Empirical formula	$C_{23}H_{20}Br_2N_2NiO_2$	
Formula weight	574.94	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_1$	
Unit cell dimensions	a = 9.4823(6) Å	α = 90°.
	b = 9.4823(6) Å	β = 90°.
	c = 24.418(2) Å	γ = 90°.
Volume	2195.5(3) $Å^3$	
Z	4	
Density (calculated)	1.739 Mg/m^3	
Absorption coefficient	4.546 mm^{-1}	
F(000)	1144	
Crystal size	0.31 x 0.27 x 0.14 mm^3	
Theta range for data collection	0.834 to 38.918°.	
Index ranges	-16<=h<=16, -16<=k<=16, -42<=l<=43	
Reflections collected	113308	
Independent reflections	12464 [R(int) = 0.0431]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7476 and 0.5466	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12464 / 1 / 272	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1114	
R indices (all data)	R1 = 0.0580, wR2 = 0.1168	
Absolute structure parameter	0.011(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.381 and -1.019 $e.Å^{-3}$	

A4.3 REFERENCES

(1) *APEX2, Version 2 User Manual, M86-E01078, Bruker Analytical X-ray Systems*, Madison, WI, **2006**.

(2) Sheldrick, G.M. *SADABS (version 2008/1): Program for Absorption Correction for Data from Area Detector Frames*, University of Göttingen, **2008**.

(3) Sheldrick, G. *Acta Crystallogr., Sect. A: Found. Crystallogr*. **2008**, *64*, 112.

(4) Sheldrick, G. M. *Acta Crystallogr., Sect. C: Struct. Chem.* **2015**, *C71*, 3.

(5) Müller, P. *Crystallogr. Rev.* **2009**, *15*, 57.

(6) Parsons, S.; Flack, H. D.; Wagner, T. *Acta Crystallogr., Sect. B: Struct. Sci. Cryst. Eng. Mater.* **2013**, *B69*, 249.