Appendix 6

X-Ray Crystallography Reports Relevant to Chapter 4:

Mechanistic Investigations of Ni-Catalyzed Asymmetric

Reductive Cross-Couplings with Alkenyl Bromide Electrophiles

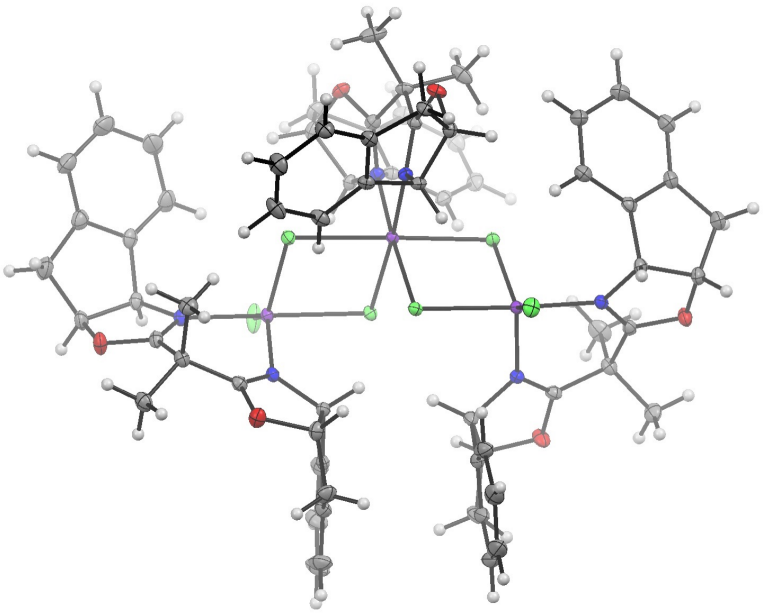
A6.1 STRUCTURAL DETERMINATION AND REFINEMENT DETAILS

Low-temperature diffraction data (ϕ- and ω-scans) were collected on either a Bruker AXS D8 VENTURE KAPPA diffractometer or Bruker AXS KAPPA APEXII diffractometer coupled to a PHOTON 100 CMOS detector with either Mo-$K\alpha$ radiation (λ = 0.71073 Å) or Cu-$K\alpha$ radiation (λ = 1.54178 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 in 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 (1.5 times for methyl groups). Absolute configuration was determined by anomalous dispersion.[6] Graphical representation of the structure with 50% probability thermal ellipsoids was generated using Mercury visualization software.

A6.2 CRYSTALLOGRAPHIC ANALYSIS OF L9·$NiCl_2$

A6.2.1 Special Refinement Details

Figure A6.1 *Rendering of Ni-complex* ***L9***·$NiCl_2$.



L9·$NiCl_2$ crystallizes in the monoclinic space group $P2_1$ with one molecule (consisting of three ligand·nickel subunits) in the asymmetric unit. Data was collected with Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 100 K. Two molecules of dichloromethane (one disordered over two positions) and 0.299 molecules of water are co-crystallized in the unit cell. One chloride atom bound to nickel was disordered over two positions (Cl1, Cl1A), which was refined with the help of a similarity restraint on the Ni-Cl distance. The highest electron density maxima was modeled as a partially occupied water, 0.299(9). The hydrogen atoms for this water could not be located in the difference Fourier synthesis and were not included in the model. Solvent and disorder is omitted for clarity in the graphical representation. Absolute configuration was determined by anomalous dispersion (Flack = 0.004(4)).[6]

A6.2.2 Crystallographic Tables

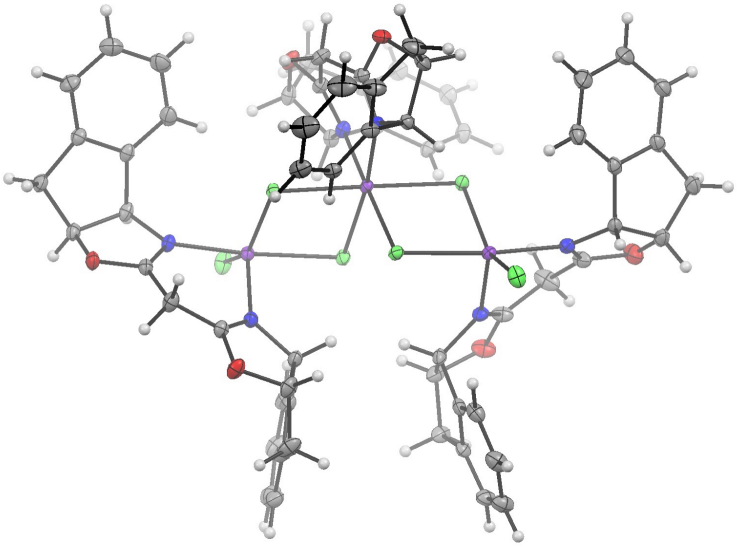
Table A6.1. *Crystal data and structure refinement for* ***L9***·$NiCl_2$.

Identification code	A15003	
Empirical formula	$C_{69}H_{66}Cl_6N_6Ni_3O_6$, $2(CH_2Cl_2)$, $0.30(H_2O)$	
Formula weight	1639.36	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 14.8865(7) Å	α = 90°.
	b = 15.8024(8) Å	β = 112.892(3)°.
	c = 16.5046(8) Å	γ = 90°.
Volume	3576.8(3) $Å^3$	
Z	2	
Density (calculated)	1.522 Mg/m^3	
Absorption coefficient	1.212 mm^{-1}	
F(000)	1686	
Crystal size	0.300 x 0.300 x 0.150 mm^3	
Theta range for data collection	1.485 to 36.533°.	
Index ranges	-24<=h<=24, -26<=k<=26, -27<=l<=27	
Reflections collected	118450	
Independent reflections	34801 [R(int) = 0.0572]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7471 and 0.6710	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	34801 / 2 / 919	
Goodness-of-fit on F^2	0.984	
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.0779	
R indices (all data)	R1 = 0.0604, wR2 = 0.0843	
Absolute structure parameter	0.004(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.023 and -0.795 $e.Å^{-3}$	

A6.3 CRYSTALLOGRAPHIC ANALYSIS OF L20·$NiCl_2$

A6.3.1 Special Refinement Details

Figure A6.2 *Rendering of Ni-complex* ***L20***·$NiCl_2$.



L20·$NiCl_2$ crystallizes in the monoclinic space group $P2_1$ with one molecule (consisting of three ligand·nickel subunits) in the asymmetric unit. Data was collected with Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 100 K. Three molecules of dichloromethane (one was disordered over two positions) are co-crystallized in the unit cell. Solvent is omitted for clarity in the graphical representation. Absolute configuration was determined by anomalous dispersion (Flack = 0.0158(16)).[6]

A6.3.2 Crystallographic Tables

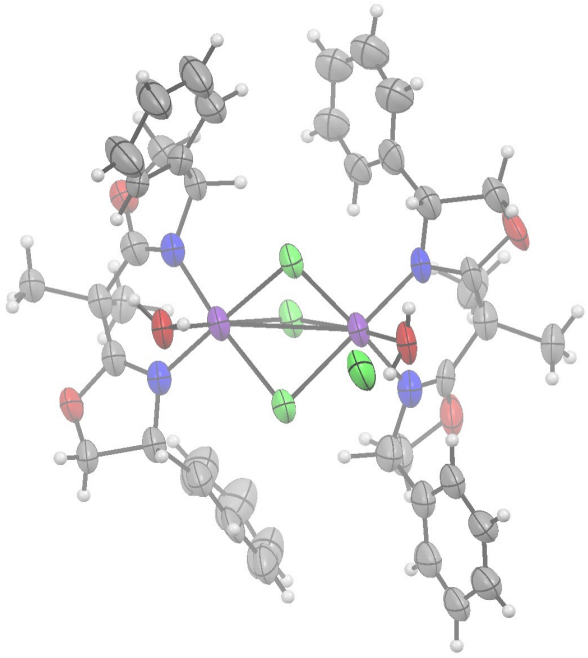
Table A6.2. *Crystal data and structure refinement for* ***L20***·$NiCl_2$.

Identification code	A15002	
Empirical formula	$C_{63}H_{54}Cl_6N_6Ni_3O_6$, $3(CH_2Cl_2)$	
Formula weight	1634.73	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 14.7835(6) Å	α = 90°.
	b = 17.8882(7) Å	β = 90°.
	c = 25.4545(11) Å	γ = 90°.
Volume	6731.4(5) $Å^3$	
Z	4	
Density (calculated)	1.613 Mg/m^3	
Absorption coefficient	1.364 mm^{-1}	
F(000)	3336	
Crystal size	0.45 x 0.34 x 0.22 mm^3	
Theta range for data collection	1.391 to 46.357°.	
Index ranges	-29<=h<=29, -36<=k<=36, -51<=l<=51	
Reflections collected	460634	
Independent reflections	58243 [R(int) = 0.0568]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9071	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	58243 / 0 / 851	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.0937	
R indices (all data)	R1 = 0.0619, wR2 = 0.1025	
Absolute structure parameter	0.0158(16)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.741 and -1.330 e.$Å^{-3}$	

A6.4 CRYSTALLOGRAPHIC ANALYSIS OF L1·$NiCl_2$

A6.4.1 Special Refinement Details

Figure A6.3 *Rendering of Ni-complex* ***L1***·$NiCl_2$.



L1·$NiCl_2$ hydrate crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule (consisting of two ligand·nickel subunits) in the asymmetric unit. Data was collected with Cu-$K\alpha$ radiation (λ = 1.54178 Å) at 100 K. The sample was not stable once removed from the crystallization environment, thus resulting in poor data quality. The structure was refined to R1=13.82% with the aid of enhanced rigid bond restraints. The absolute configuration was determined by anomalous dispersion (Flack = –0.01(5)).[6]

A6.4.2 Crystallographic Tables

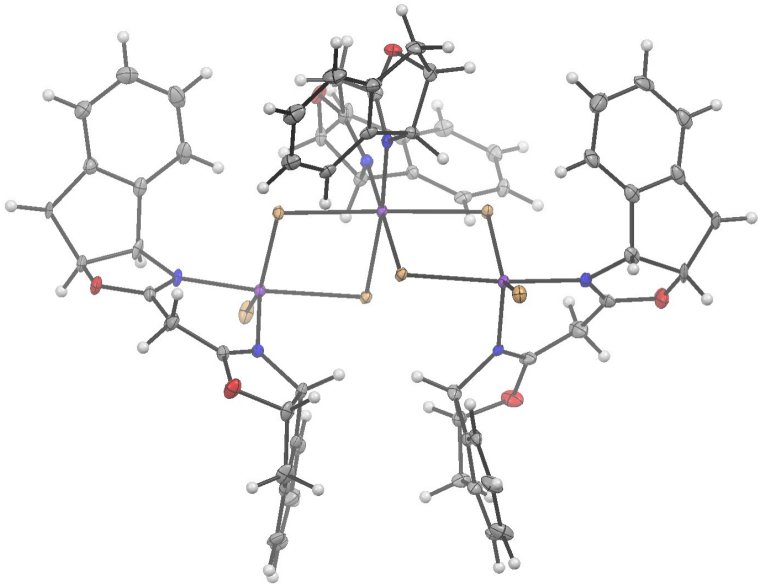
Table A6.3. *Crystal data and structure refinement for* ***L1***·$NiCl_2$.

Identification code	P15389	
Empirical formula	$C_{42}H_{48}C_{l4}N_4Ni_2O_6$	
Formula weight	964.06	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 21.3526(8) Å	α = 90°.
	b = 25.2721(10) Å	β = 90°.
	c = 43.5886(14) Å	γ = 90°.
Volume	23521.5(15) $Å^3$	
Z	16	
Density (calculated)	1.089 Mg/m^3	
Absorption coefficient	2.776 mm^{-1}	
F(000)	8000	
Theta range for data collection	2.304 to 70.265°.	
Index ranges	-18<=h<=25, -30<=k<=27, -27<=l<=52	
Reflections collected	79490	
Independent reflections	38321 [R(int) = 0.3120]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9962 and 0.7879	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	38321 / 2208 / 2113	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.1382, wR2 = 0.3314	
R indices (all data)	R1 = 0.2751, wR2 = 0.4221	
Absolute structure parameter	-0.01(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.734 and -0.918 $e.Å^{-3}$	

A6.5 CRYSTALLOGRAPHIC ANALYSIS OF L20·$NiBr_2$

A6.5.1 Special Refinement Details

Figure A6.4 *Rendering of Ni-complex* ***L20***·$NiBr_2$.



L20·$NiBr_2$ crystallizes in the monoclinic space group $P2_12_12_1$ with one molecule (consisting of three ligand·nickel subunits) in the asymmetric unit. Data was collected with Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 100 K. Three molecules of dichloromethane are co-crystallized in the unit cell. Solvent is omitted for clarity in the graphical representation. Absolute configuration was determined by anomalous dispersion (Flack = -0.011(5)).[6]

A6.5.2 Crystallographic Tables

Table A6.4. *Crystal data and structure refinement for* ***L20***·$NiBr_2$.

Identification code	P15477	
Empirical formula	$C_{21}H_{17}Br_2N_2NiO_2$, CH_2Cl_2	
Formula weight	632.82	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 15.012(2) Å	α = 90°.
	b = 18.064(4) Å	β = 90°.
	c = 25.537(5) Å	γ = 90°.
Volume	6925(2) $Å^3$	
Z	12	
Density (calculated)	1.821 Mg/m^3	
Absorption coefficient	4.557 mm^{-1}	
F(000)	3756	
Crystal size	0.16 x 0.12 x 0.09 mm^3	
Theta range for data collection	2.255 to 41.217°.	
Index ranges	-18<=h<=27, -24<=k<=28, -46<=l<=29	
Reflections collected	67889	
Independent reflections	32678 [R(int) = 0.1370]	
Completeness to theta = 26.000°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	32678 / 0 / 838	
Goodness-of-fit on F^2	0.885	
Final R indices [I>2sigma(I)]	R1 = 0.0520, wR2 = 0.0642	
R indices (all data)	R1 = 0.1243, wR2 = 0.0780	
Absolute structure parameter	-0.011(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.961 and -1.014 $e.Å^{-3}$	

A6.6 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.