Appendix 2

X-Ray Crystallography Reports Relevant to Chapter 2:

Synthesis and Utility of Chiral Allylic Silanes Prepared

via Ni-Catalyzed Asymmetric Reductive Cross-Coupling

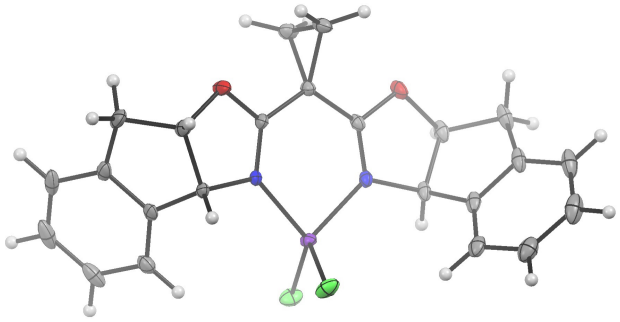
A2.1 STRUCTURAL DETERMINATION AND REFINEMENT DETAILS

Low-temperature diffraction data (ϕ- and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Mo-$K\alpha$ radiation (λ = 0.71073 Å) or a PHOTON II CPAD detector with 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 using 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] and confirmed by Bayesian statistical analysis using the program PLATON.[7] Graphical representation of the structure with 50% probability thermal ellipsoids was generated using Mercury visualization software.

A2.2 CRYSTALLOGRAPHIC ANALYSIS OF L2·$NiCl_2$ (MONOMER)

A2.2.1 Special Refinement Details

Figure A2.1 *Rendering of Ni-complex* ***L2***·$NiCl_2$ *(monomer).*



L2·$NiCl_2$ crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. Data was collected with Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 100 K. Absolute configuration was determined by anomalous dispersion (Flack = 0.017(2)).[6]

A2.2.2 Crystallographic Tables

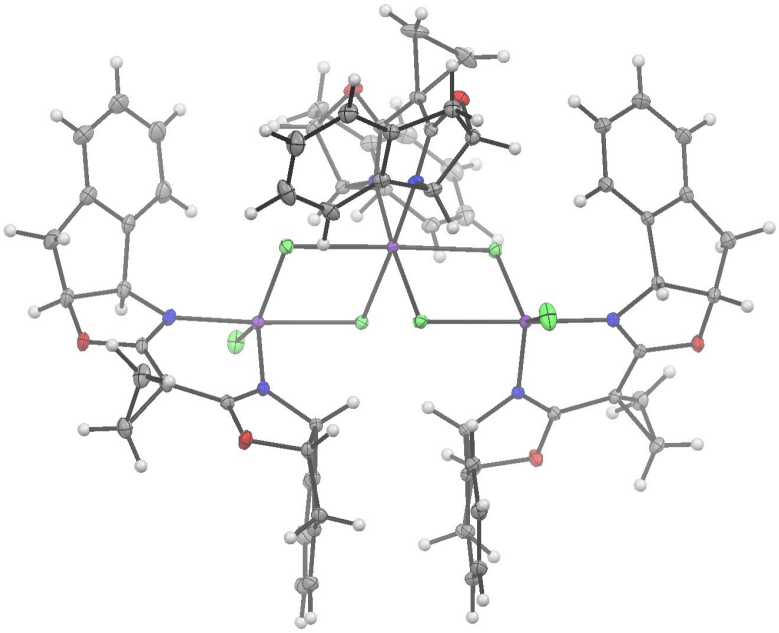
Table A2.1. *Crystal data and structure refinement for* ***L2***·$NiCl_2$ *(monomer).*

Identification code	P15028	
CCDC Number	1547485	
Empirical formula	$C_{23}H_{20}Cl_2N_2NiO_2$	
Formula weight	486.02	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 9.2189(2) Å	α = 90°
	b = 10.5914(3) Å	β = 90°
	c = 22.0654(6) Å	γ = 90°
Volume	2154.49(10) $Å^3$	
Z	4	
Density (calculated)	1.498 Mg/m^3	
Absorption coefficient	1.171 mm^{-1}	
F(000)	1000	
Crystal size	0.22 x 0.18 x 0.17 mm^3	
Theta range for data collection	2.394 to 43.426°	
Index ranges	-17<=h<=16, -20<=k<=20, -42<=l<=42	
Reflections collected	201119	
Independent reflections	16184 [R(int) = 0.0685]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9466	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16184 / 0 / 271	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.0700	
R indices (all data)	R1 = 0.0985, wR2 = 0.0785	
Absolute structure parameter	0.017(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.562 and -0.595 e.$Å^{-3}$	

A2.3 CRYSTALLOGRAPHIC ANALYSIS OF L2·$NiCl_2$ (TRIMER)

A2.3.1 Special Refinement Details

Figure A2.2 *Rendering of Ni-complex* ***L2***·$NiCl_2$ *(trimer).*



L2·$NiCl_2$ 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. The first solvent void was fully occupied by CH_2Cl_2. The second solvent void was occupied by either CH_2Cl_2 or MeCN with relative populations of 27% and 73%, respectively. Solvent is omitted for clarity in the graphical representation. Absolute configuration was determined by anomalous dispersion (Flack = 0.0162(19)).[6]

A2.3.2 Crystallographic Tables

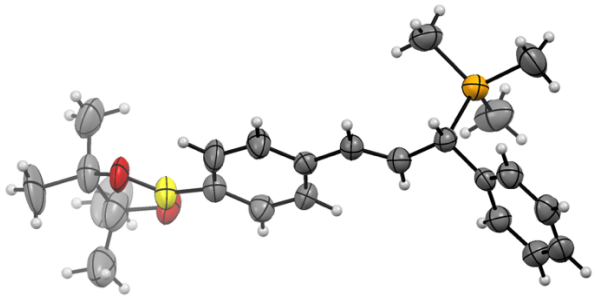
Table A2.2. *Crystal data and structure refinement for* ***L2***·$NiCl_2$ *(trimer).*

Identification code	P16408	
CCDC Number	1547484	
Empirical formula	$C_{69}H_{60}Cl_6N_6Ni_3O_6$, 1.27($CH_2Cl_2$), 0.73($C_2H_3N$)	
Formula weight	1595.88	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 14.8277(18) Å	α = 90°
	b = 15.771(2) Å	β = 116.546(4)°
	c = 16.569(2) Å	γ = 90°
Volume	3466.1(8) $Å^3$	
Z	2	
Density (calculated)	1.529 Mg/m^3	
Absorption coefficient	1.194 mm^{-1}	
F(000)	1639	
Crystal size	0.30 x 0.30 x 0.15 mm^3	
Theta range for data collection	2.476 to 36.402°	
Index ranges	-24<=h<=24, -26<=k<=26, -27<=l<=27	
Reflections collected	214882	
Independent reflections	33574 [R(int) = 0.0487]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7471 and 0.6863	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	33574 / 8 / 894	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0842	
R indices (all data)	R1 = 0.0541, wR2 = 0.0891	
Absolute structure parameter	0.0162(19)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.137 and -1.072 e.$Å^{-3}$	

A2.4 CRYSTALLOGRAPHIC ANALYSIS OF 91c

A2.4.1 Special Refinement Details

Figure A2.3 *Rendering of allylic silane* ***91c****.*



Compound **91c** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. Data was collected with Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 270 K. The structure exhibits significant positional disorder of the pinacol boronate ring, which was satisfactorily modeled over three positions with relative populations of 47%, 34%, and 19%. The 1,2 and 1,3 distances of this moiety were restrained to be equivalent and refined with both U_{ij} and enhanced rigid bond restraints. The absolute configuration was determined by anomalous dispersion (Flack = –0.02(6)); there was no discernible disorder of the chiral center of interest.[6]

A2.4.2 Crystallographic Tables

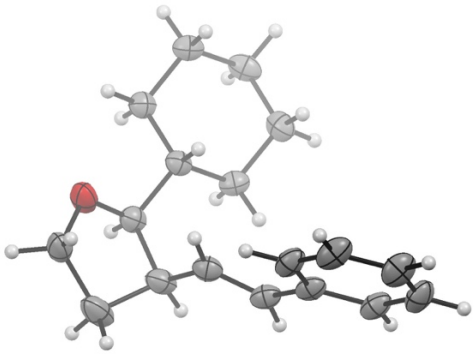
Table A2.3. *Crystal data and structure refinement for* ***91c****.*

Identification code	P16169	
CCDC Number	1547483	
Empirical formula	$C_{24}H_{33}BO_2Si$	
Formula weight	392.40	
Temperature	270 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.4080(3) Å	α = 90°
	b = 12.5679(5) Å	β = 90°
	c = 30.4781(13) Å	γ = 90°
Volume	2454.56(18) $Å^3$	
Z	4	
Density (calculated)	1.062 Mg/m^3	
Absorption coefficient	0.111 mm^{-1}	
F(000)	848	
Crystal size	0.18 x 0.13 x 0.06 mm^3	
Theta range for data collection	2.578 to 27.515°	
Index ranges	-8<=h<=8, -16<=k<=16, -39<=l<=39	
Reflections collected	31898	
Independent reflections	5646 [R(int) = 0.0848]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6970	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5646 / 1045 / 421	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0.1005	
R indices (all data)	R1 = 0.1483, wR2 = 0.1207	
Absolute structure parameter	-0.02(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.141 and -0.193 $e.Å^{-3}$	

A2.5 CRYSTALLOGRAPHIC ANALYSIS OF 123c

A2.5.1 Special Refinement Details

Figure A2.4 *Rendering of tetrahydrofuran* ***123c****.*



Compound **123c** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit. Data was collected with Cu-$K\alpha$ radiation (λ = 1.54178 Å) at 100 K. The secondary α-carbon in the tetrahydrofuran ring was disordered over two positions (68% and 32% occupancy). The disordered tetrahydrofuran ring is omitted for clarity. Absolute configuration was determined by anomalous dispersion (Flack = 0.12(18)).[6] Bayesian statistics further confirm the absolute stereochemistry: P2(true) = 1.000, P3(true) = 0.978, P3(rac-twin) = 0.022, and P3(false) = $0.1\text{x}10^{-7}$.[7]

A2.5.2 Crystallographic Tables

Table A2.4. *Crystal data and structure refinement for* ***123c****.*

Identification code	V18180	
Empirical formula	$C_{18}H_{24}O$	
Formula weight	256.37	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.8196(6) Å	α = 90°.
	b = 14.5241(14) Å	β = 90°.
	c = 17.675(2) Å	γ = 90°.
Volume	1494.0(3) $Å^3$	
Z	4	
Density (calculated)	1.140 Mg/m^3	
Absorption coefficient	0.519 mm^{-1}	
F(000)	560	
Crystal size	0.18 x 0.16 x 0.02 mm^3	
Theta range for data collection	3.939 to 81.258°.	
Index ranges	-5<=h<=6, -14<=k<=16, -22<=l<=13	
Reflections collected	9181	
Independent reflections	2267 [R(int) = 0.0409]	
Completeness to theta = 67.679°	83.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9028	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2267 / 0 / 182	
Goodness-of-fit on F^2	1.083	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1033	
R indices (all data)	R1 = 0.0441, wR2 = 0.1059	
Absolute structure parameter	0.12(18)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.232 and -0.104 $e.Å^{-3}$	

A2.6 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.

(7) Spek, A. L. *Acta Crystallogr., Sect. D: Struct. Biol.* **2009**, *D65*, 148.