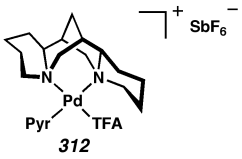
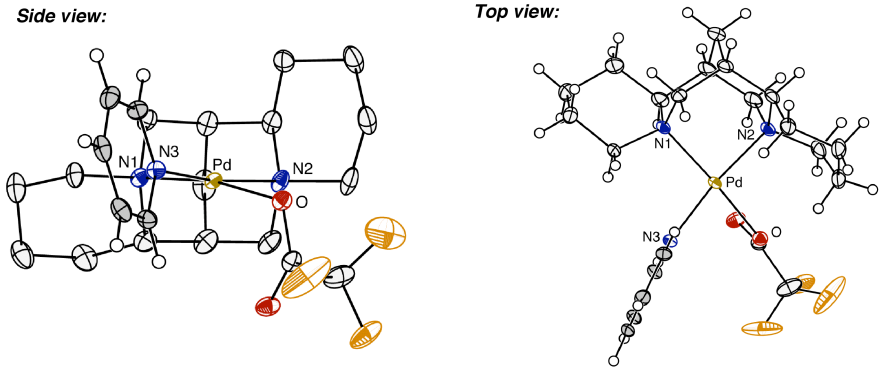
APPENDIX 5

*X-ray Crystallographic Data for (sp)Pd(pyridine)TFA$^+$SbF$_6^-$ (**312**)*

*Figure A5.1 (sp)Pd(pyridine)TFA$^+$SbF$_6^-$ (**312**).*[1,2]



Selected bond lengths (Å) and angles (°)			
Pd–N1	2.0875(16)	N1–Pd–N2	88.68(6)°
Pd–N2	2.0750(16)	N3–Pd–O	81.60(6)°
Pd–N3	2.0484(15)	N2–Pd–N3	171.30(7)°
Pd–O	2.0626(14)	N1–Pd–O	170.01(6)°
		N1–Pd–N3	97.30(6)°
		N2–Pd–O	93.59(6)°
		Σ∠	700.48°



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[1] (a) The numbering in Figure A5.1 differs from that in the crystallographic report. (b) The SbF_6 anion in both views and the hydrogens of the (–)-sparteine backbone in the side view are not shown.

[2] The crystallographic data have been deposited at the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 243028.

*Crystal data and structure refinement for **312** (CCDC 243028).*

Empirical formula	$[C_{22}H_{31}F_3N_3O_2Pd]^+[SbF_6]^- \_CH_2Cl_2$
Formula weight	811.11
Crystallization solvent	Dichloromethane/pentane
Crystal habit	Lozenge
Crystal size	0.37 x 0.32 x 0.23 mm^3
Crystal color	Yellow

Data collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data collection temperature	100(2) K
θ range for 81920 reflections used in lattice determination	2.42 to 46.04°
Unit cell dimensions	a = 18.2445(5) Å b = 21.4289(6) Å c = 7.1398(2) Å
Volume	2791.37(13) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12$
Density (calculated)	1.930 Mg/m^3
F(000)	1596
Data collection program	Bruker SMART v5.054
θ range for data collection	1.90 to 46.49°
Completeness to θ = 46.49°	97.7 %
Index ranges	$-35 \le h \le 36$, $-43 \le k \le 30$, $-14 \le l \le 14$
Data collection scan type	ω scans at 3 ϕ settings of 2θ=-28° and 2 of 2θ=-68°
Data reduction program	Bruker SAINT v6.45
Reflections collected	55475
Independent reflections	23781 [R_{int}= 0.0648]
Absorption coefficient	1.795 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.6830 and 0.5564

Structure solution and refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	23781 / 0 / 362
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.270
Final R indices [I>2σ(I), 19622 reflections]	R1 = 0.0421, *w*R2 = 0.0757
R indices (all data)	R1 = 0.0531, *w*R2 = 0.0774
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(Fo^2)$
Max shift/error	0.004
Average shift/error	0.000

Absolute structure parameter	-0.035(11)
Largest diff. peak and hole	2.165 and -2.611 e.Å^{-3}

Special refinement details

The final electron density Fourier map contains peaks near the metal centers and near the disordered dichloromethane included in the model as a solvent of crystallization. Absorption correction did not improve the quality of the model or the Fourier map and therefore was not used for the final model.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

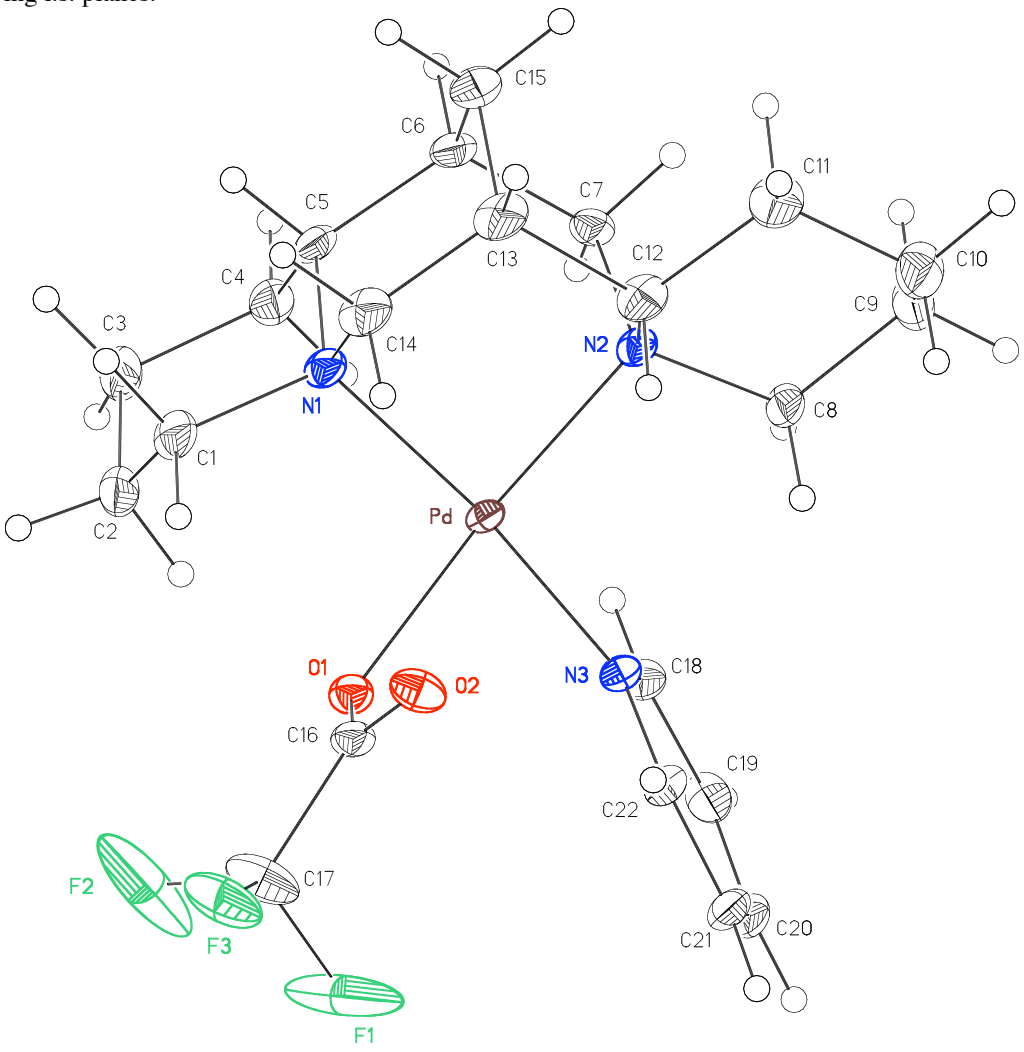


*Figure A5.2 Molecule of **312**.*

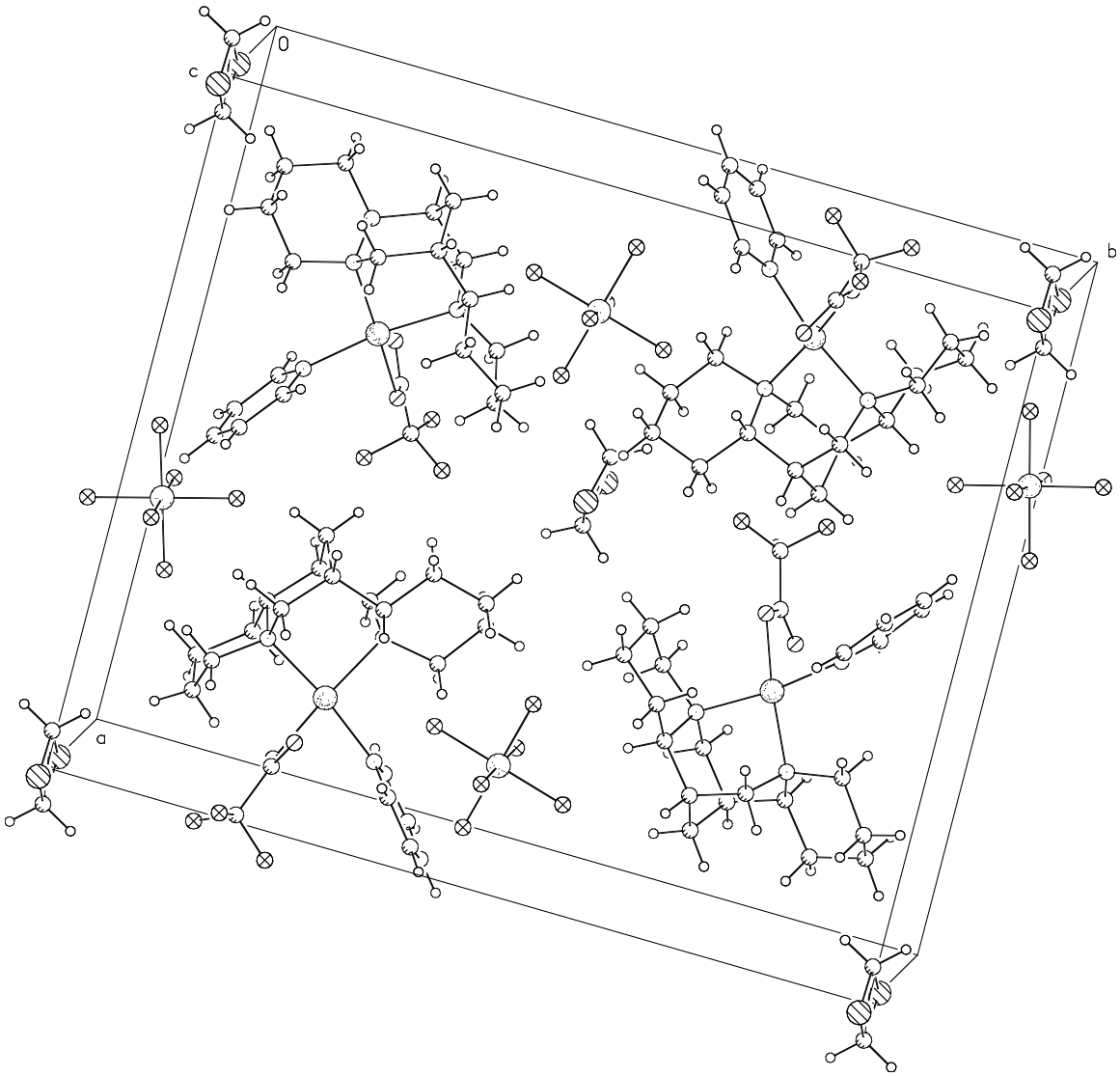


*Figure A5.3 Unit cell contents of **312**.*

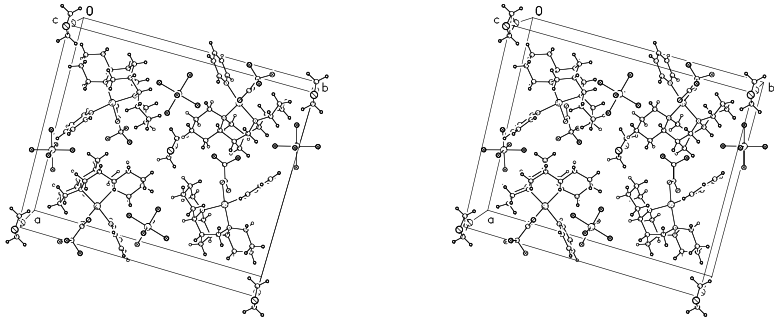


*Figure A.5.4. Stereo view of unit cell contents of **312**.*

*Table A5.1 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **312** (CCDC 243028). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.*

	x	y	z	U_{eq}	Occ
Pd		1638(1)	7238(1)	5554(1)	11(1)
F(1)		-428(1)	7274(1)	9652(3)	66(1)
F(2)		-239(1)	8226(1)	8933(3)	79(1)
F(3)		190(1)	7852(1)	11513(2)	35(1)
O(1)		735(1)	7593(1)	6925(2)	16(1)
O(2)		1263(1)	7285(1)	9630(2)	20(1)
N(1)		2242(1)	8052(1)	5870(2)	16(1)
N(2)		2587(1)	6796(1)	4601(2)	14(1)
N(3)		926(1)	6518(1)	5048(2)	13(1)
C(1)		1788(1)	8596(1)	6539(3)	24(1)
C(2)		1199(1)	8787(1)	5141(4)	26(1)
C(3)		1522(2)	8927(1)	3224(4)	27(1)
C(4)		2005(1)	8384(1)	2584(3)	21(1)
C(5)		2591(1)	8246(1)	4027(3)	19(1)
C(6)		3175(1)	7778(1)	3389(3)	20(1)
C(7)		2892(1)	7126(1)	2931(3)	17(1)
C(8)		2407(1)	6126(1)	4098(3)	18(1)
C(9)		3071(1)	5704(1)	3804(4)	26(1)
C(10)		3529(1)	5689(1)	5584(4)	27(1)
C(11)		3766(1)	6350(1)	6063(4)	26(1)
C(12)		3108(1)	6803(1)	6271(3)	20(1)
C(13)		3395(1)	7470(1)	6642(3)	22(1)
C(14)		2815(1)	7925(1)	7327(3)	22(1)
C(15)		3769(1)	7731(1)	4910(4)	26(1)
C(16)		776(1)	7516(1)	8692(3)	16(1)
C(17)		76(1)	7733(1)	9712(3)	31(1)
C(18)		654(1)	6442(1)	3306(3)	16(1)
C(19)		71(1)	6052(1)	2941(3)	20(1)
C(20)		-259(1)	5735(1)	4430(4)	19(1)
C(21)		20(1)	5810(1)	6210(3)	19(1)
C(22)		621(1)	6199(1)	6470(3)	16(1)
Sb(1)		3246(1)	9900(1)	256(1)	13(1)
F(4)		3338(1)	9932(1)	-2366(2)	26(1)
F(5)		2972(1)	10743(1)	328(2)	29(1)
F(6)		3163(1)	9857(1)	2874(2)	29(1)
F(7)		3520(1)	9054(1)	215(2)	30(1)
F(8)		2262(1)	9675(1)	-29(2)	28(1)
F(9)		4232(1)	10130(1)	474(2)	29(1)
C(31)		4489(3)	5056(4)	118(9)	58(2)
Cl(1)		5000	5000	2262(2)	119(1)
Cl(2)		5000	5000	-1740(2)	91(1)

*Table A5.2 Selected bond lengths [Å] and angles [°] for **312** (CCDC 243028).*

Pd-N(3)	2.0484(15)	N(3)-Pd-O(1)	81.60(6)
Pd-O(1)	2.0626(14)	N(3)-Pd-N(1)	171.30(7)
Pd-N(1)	2.0750(16)	O(1)-Pd-N(1)	93.59(6)
Pd-N(2)	2.0875(16)	N(3)-Pd-N(2)	97.30(6)
		O(1)-Pd-N(2)	170.01(6)
		N(1)-Pd-N(2)	88.68(6)

*Table A5.3 Bond lengths [Å] and angles [°] for**312** (CCDC 243028).*

Pd-N(3)	2.0484(15)	Sb(1)-F(6)	1.8782(13)
Pd-O(1)	2.0626(14)	Sb(1)-F(7)	1.8800(12)
Pd-N(1)	2.0750(16)	Sb(1)-F(4)	1.8801(12)
Pd-N(2)	2.0875(16)	C(31)-Cl(2)	1.626(6)
F(1)-C(17)	1.347(3)	C(31)-Cl(1)	1.797(7)
F(2)-C(17)	1.325(3)	C(31)-C(31)#1	1.881(11)
F(3)-C(17)	1.327(3)	Cl(1)-C(31)#1	1.797(7)
O(1)-C(16)	1.275(3)	Cl(2)-C(31)#1	1.626(6)
O(2)-C(16)	1.218(3)		
N(1)-C(14)	1.500(3)	N(3)-Pd-O(1)	81.60(6)
N(1)-C(1)	1.507(3)	N(3)-Pd-N(1)	171.30(7)
N(1)-C(5)	1.521(3)	O(1)-Pd-N(1)	93.59(6)
N(2)-C(7)	1.494(3)	N(3)-Pd-N(2)	97.30(6)
N(2)-C(8)	1.515(2)	O(1)-Pd-N(2)	170.01(6)
N(2)-C(12)	1.525(3)	N(1)-Pd-N(2)	88.68(6)
N(3)-C(22)	1.346(2)	C(16)-O(1)-Pd	112.00(13)
N(3)-C(18)	1.349(3)	C(14)-N(1)-C(1)	107.63(17)
C(1)-C(2)	1.523(4)	C(14)-N(1)-C(5)	110.94(16)
C(2)-C(3)	1.520(4)	C(1)-N(1)-C(5)	107.00(16)
C(3)-C(4)	1.529(3)	C(14)-N(1)-Pd	107.09(13)
C(4)-C(5)	1.514(3)	C(1)-N(1)-Pd	113.16(13)
C(5)-C(6)	1.534(3)	C(5)-N(1)-Pd	111.01(12)
C(6)-C(7)	1.524(3)	C(7)-N(2)-C(8)	109.88(16)
C(6)-C(15)	1.537(3)	C(7)-N(2)-C(12)	112.82(15)
C(8)-C(9)	1.525(3)	C(8)-N(2)-C(12)	109.25(15)
C(9)-C(10)	1.521(4)	C(7)-N(2)-Pd	110.70(12)
C(10)-C(11)	1.519(3)	C(8)-N(2)-Pd	109.13(11)
C(11)-C(12)	1.552(3)	C(12)-N(2)-Pd	104.92(12)
C(12)-C(13)	1.546(3)	C(22)-N(3)-C(18)	118.78(16)
C(13)-C(15)	1.518(3)	C(22)-N(3)-Pd	120.87(13)
C(13)-C(14)	1.521(3)	C(18)-N(3)-Pd	119.15(13)
C(16)-C(17)	1.543(3)	N(1)-C(1)-C(2)	112.85(18)
C(18)-C(19)	1.377(3)	C(3)-C(2)-C(1)	111.7(2)
C(19)-C(20)	1.398(3)	C(2)-C(3)-C(4)	110.06(19)
C(20)-C(21)	1.378(3)	C(5)-C(4)-C(3)	110.5(2)
C(21)-C(22)	1.389(3)	C(4)-C(5)-N(1)	110.25(17)
Sb(1)-F(8)	1.8705(13)	C(4)-C(5)-C(6)	114.59(19)
Sb(1)-F(9)	1.8722(13)	N(1)-C(5)-C(6)	111.65(17)
Sb(1)-F(5)	1.8769(12)	C(7)-C(6)-C(5)	115.33(16)

C(7)-C(6)-C(15)	109.32(18)	C(18)-C(19)-C(20)	118.9(2)
C(5)-C(6)-C(15)	108.79(18)	C(21)-C(20)-C(19)	119.06(18)
N(2)-C(7)-C(6)	112.90(16)	C(20)-C(21)-C(22)	119.0(2)
N(2)-C(8)-C(9)	114.99(16)	N(3)-C(22)-C(21)	122.09(19)
C(10)-C(9)-C(8)	109.5(2)	F(8)-Sb(1)-F(9)	178.51(7)
C(11)-C(10)-C(9)	109.04(19)	F(8)-Sb(1)-F(5)	89.73(6)
C(10)-C(11)-C(12)	112.54(18)	F(9)-Sb(1)-F(5)	90.00(6)
N(2)-C(12)-C(13)	110.76(17)	F(8)-Sb(1)-F(6)	91.03(7)
N(2)-C(12)-C(11)	113.66(18)	F(9)-Sb(1)-F(6)	90.44(7)
C(13)-C(12)-C(11)	109.41(17)	F(5)-Sb(1)-F(6)	89.86(7)
C(15)-C(13)-C(14)	109.8(2)	F(8)-Sb(1)-F(7)	90.31(6)
C(15)-C(13)-C(12)	110.70(19)	F(9)-Sb(1)-F(7)	89.98(7)
C(14)-C(13)-C(12)	114.36(18)	F(5)-Sb(1)-F(7)	179.28(8)
N(1)-C(14)-C(13)	112.22(18)	F(6)-Sb(1)-F(7)	89.42(7)
C(13)-C(15)-C(6)	106.48(16)	F(8)-Sb(1)-F(4)	89.23(7)
O(2)-C(16)-O(1)	129.79(19)	F(9)-Sb(1)-F(4)	89.31(7)
O(2)-C(16)-C(17)	117.89(19)	F(5)-Sb(1)-F(4)	90.93(7)
O(1)-C(16)-C(17)	112.27(19)	F(6)-Sb(1)-F(4)	179.17(7)
F(2)-C(17)-F(3)	108.8(2)	F(7)-Sb(1)-F(4)	89.79(7)
F(2)-C(17)-F(1)	105.9(2)	Cl(2)-C(31)-Cl(1)	113.1(3)
F(3)-C(17)-F(1)	106.2(2)	Cl(2)-C(31)-C(31)#1	54.7(2)
F(2)-C(17)-C(16)	113.7(2)	Cl(1)-C(31)-C(31)#1	58.44(18)
F(3)-C(17)-C(16)	112.62(19)	C(31)-Cl(1)-C(31)#1	63.1(4)
F(1)-C(17)-C(16)	109.2(2)	C(31)#1-Cl(2)-C(31)	70.7(4)
N(3)-C(18)-C(19)	122.1(2)		

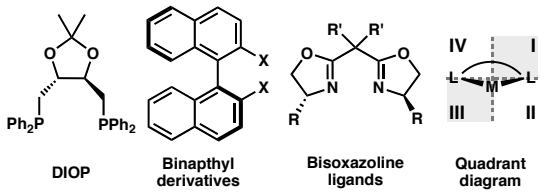
Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,z

APPENDIX 6

Understanding Asymmetric Induction by C_1 Symmetric Ligands

Catalytic asymmetric synthesis continues to emerge as one of the most important areas in organic chemistry. Several of the most useful catalysts are transition metals that induce asymmetry via a bidentate chiral ligand.[1] Thus, efforts have often focused on discovering ligands more capable of imparting enantioselectivity. Since the introduction of the DIOP ligand by Kagan in 1972,[2] C_2 symmetry has been a dominant guiding force in the design of improved systems. In this respect a C_2 symmetric scaffold offers distinct advantages: the presence of a symmetry axis reduces the number of competing diastereomeric reaction pathways, enables a straightforward analysis of substrate-catalyst interactions, and simplifies mechanistic and structural studies.[3] The chiral scaffold can be modeled by a quadrant diagram of the ligand–metal complex, in which quadrants I and III (or II and IV) are equivalently hindered (Figure A6.1). These advantages have led to the development of seminal classes of chiral ligands such as bisphosphines, binapthyl derivatives,[4] and the bisoxazolines.[5]

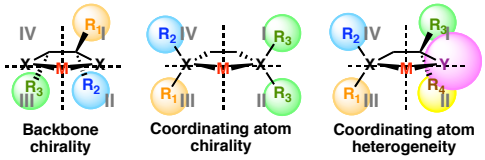
Figure A6.1 Common C_2 symmetric ligand scaffolds.



While C_2 symmetric ligands have led to remarkable levels of enantioselectivity, their conceptual appeal has perhaps resulted in the neglect of other, more complicated scaffolds, such as those with C_1-symmetry.[6] Further, C_2 symmetric ligands are not necessarily inherently more selective for all processes. Efforts towards developing models or understanding general trends for C_1 symmetric systems could help accelerate the discovery of useful ligands. To this end, recent developments in asymmetric synthesis using bidentate C_1 symmetric ligands will be discussed.[7]

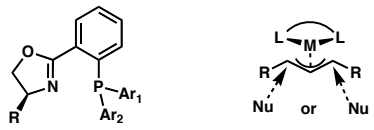
Rather than presenting two equivalent chiral sites on a metal catalyst, as in the case of C_2 symmetric ligands, C_1 symmetric ligands ideally constrain reactivity to a single site by one or a combination of controlling factors. These factors include steric control by chirality in the backbone, steric control by chirality at the coordinating atom, and electronic differentiation of the coordinating atoms (Figure A6.2). Other achiral ligands at the metal center may also influence the effect of these factors. In terms of a quadrant diagram, a C_1 symmetric framework containing any of these chiral elements can render one of the quadrants unique in order to produce single-site reactivity. The following brief review of recent examples of catalysts featuring C_1 symmetric ligands for a variety of reactions highlights these aspects.

Figure A6.2 Possible controlling factors for C_1 symmetric ligands.



The most well-developed class[8] of C_1 symmetric ligands for asymmetric catalysis are the phosphinooxazolines, the so-called "Pfaltz ligands" (Figure 6.3). These ligands were originally developed for palladium catalyzed allylic alkylation reactions, [9,10] the enantioselectivity of which depends upon the regioselectivity of nucleophilic attack at the allylic terminus (Figure A6.3). While high enantioselectivities were observed with C_2 symmetric bisoxazolines, it was thought that changing one of the coordinating atoms could further *electronically* differentiate the termini and lead to more selective systems.

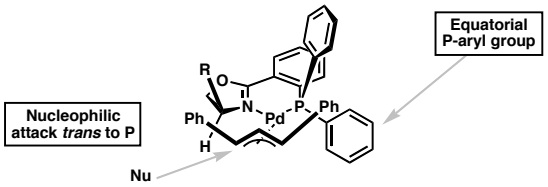
Figure A6.3 Phosphinooxazoline, or Pfaltz, ligand; nucleophilic attack at either allylic terminus.



This strategy was successfully borne out with the phosphinooxazoline framework (Figure A6.4). Steric interaction between the equatorial P-aryl group and the allylic substituent controls the facial orientation of the substrate. Because of the greater π-backbonding capability of P compared to N (i.e., the *trans* influence), the allylic C atom *trans* to P is attacked preferentially and results in single-site reactivity. Increasing the bulk of the R group torques the chelate ring so that the interaction between the equatorial P-aryl group and the allyl moiety is reinforced.[11] The Pfaltz ligands thus incorporate the controlling factors of backbone chirality and coordinating atom heterogeneity to govern

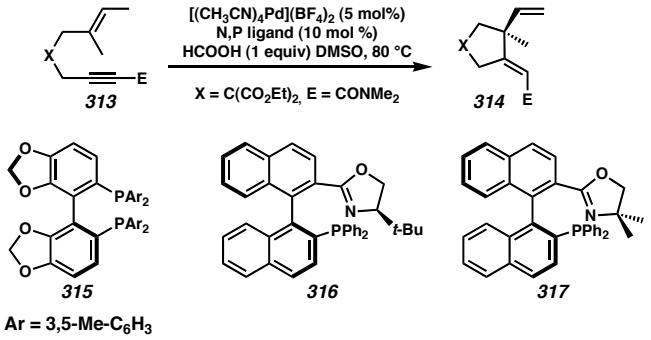
the reactive geometry. This system has been extended to several other enantioselective processes, and is easily tailored to a given reaction.[9]

Figure A6.4 Model for asymmetric induction with the phosphinooxazole ligand framework.



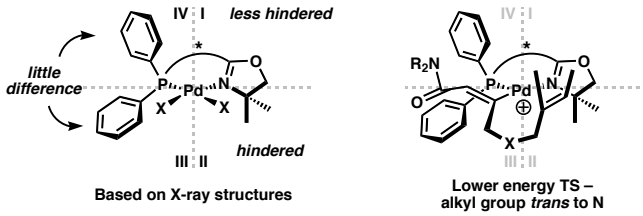
More recently, Mikami and coworkers have employed a related C_1 symmetric N/P ligand in a palladium catalyzed enyne cyclization.[12] Enantioselectivities were higher than those observed with a C_2 symmetric ligand (**3**, Scheme A6.1), and selectivity was correlated to the degree of substitution on the oxazoline ring (**4** and **5**, Scheme 1).[13] Based on crystallographic data and transition-state calculations, the authors propose a model for asymmetric induction. As with the Pfaltz ligands, the electronic difference in coordinating atoms (P vs. N) controls geometry, in this case, of the palladium alkyl intermediate. The chirality of the binaphthyl backbone is farther removed from the reacting center than in the Pfaltz ligands, but still serves to enforce single-site reactivity, with substrate steric bulk occupying open quadrant I (Figure A6.5).

Scheme A6.1



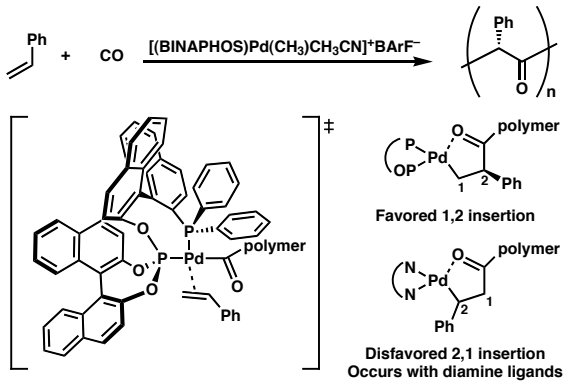
Entry	Ligand	Time (h)	% Yield	%ee
1	*3*	3	>99	6
2	*4*	24	42	81
3	*5*	3	>99	95

Figure A6.5 Mikami's model of asymmetric induction.



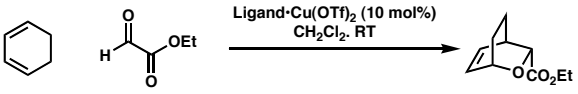
Unlike the preceding two systems in which electronic differentiation played a large role in controlling asymmetry, Nozaki and Matsubara's C_1 symmetric phosphine-phosphite ligand (BINAPHOS) for palladium catalyzed asymmetric alternating copolymerization exerts only steric control via backbone chirality.[14] With conventional C_2 symmetric diamine ligands, the copolymerization of styrene and carbon monoxide occurs with exclusive 2,1 insertion of styrene (Scheme A6.2). Although the coordinating atoms have different electronic properties,[15] the authors found that steric interaction alone between BINAPHOS and the growing polymer chain was responsible for the unusual 1,2 insertion to produce stereoregular polymer.

Scheme A6.2

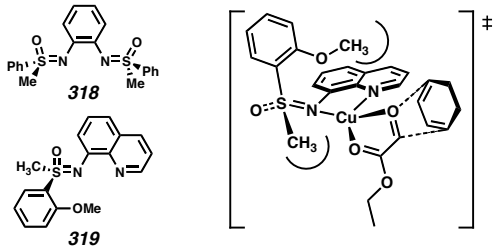


In some cases, while C_2-symmetry results in high enantioselectivity, a successful C_1 symmetric variant of the ligand can be just as effective and easier to obtain. In 2003 Bolm and coworkers reported a C_1 symmetric monosulfoximine ligand for an enantioselective Cu-catalyzed hetero Diels-Alder reaction that meets these criteria.[16] A distorted, non symmetric square-pyramidal geometry at Cu had been determined for the C_2 symmetric variant (**318**, Scheme A6.3), which rendered the two coordinating atoms of the ligand nonequivalent, unlike in a typical symmetric case.[17] This led the authors to hypothesize that a ligand of reduced symmetry (i.e., **319**) could be similarly selective. Based on crystallographic data, the coordination geometry at Cu combined with the steric influences of the ligand backbone (including a chiral environment at S) determines the enantioselectivity of the hetero Diels-Alder reaction. To avoid interaction with the aryl methoxy group, the glyoxalate coordinates so that the ethoxy moiety is below the plane of the quinoline (Scheme A6.3). Cyclohexadiene is then restricted to one face of attack by shielding of the other face with the sulfur methyl. Again it is evident that multiple elements of the C_1 symmetric ligand-metal interaction collaborate to enforce a single reactive geometry.

Scheme A6.3

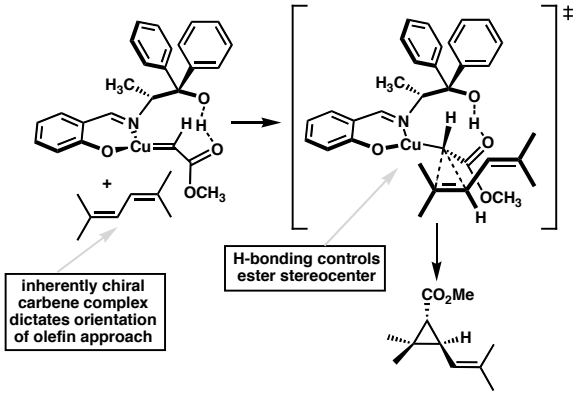


Entry	Ligand	% Yield	%ee	*endo:exo*	
1	***318***	62	99	99:1	
2	***319***	98	91	98:2	
3	***319***	65	96	99:1	*with $Cu(ClO_4)_2$ @ -10 °C*



A detailed study of another Cu system highlights complex metal-ligand cooperativity. The Aratani process[18] for asymmetric cyclopropanation is historically and industrially important, but represents another non-obvious C_1 symmetric system that was not well-understood. Recently, Suenobu and Nakamura undertook to elucidate a model for the cyclopropanation of dimethyl hexanediamine by methyldiazoacetate in the presence of a chiral Cu salicylaldimine catalyst using chemical data and computational methods.[19] The authors conclude that the reactive carbene intermediate (Figure A6.6) is intrinsically chiral (excluding the ligand stereocenter), and that intramolecular hydrogen bonding transmits the chirality of the ligand side chain to the geometry of the ester stereocenter. The intricacies of C_1 symmetric ligand-metal-substrate interactions are vastly different than the global chiral environment created by C_2 symmetric ligands.

Figure A6.6 Intricacies of cyclopropanation directed by a C_1 symmetric ligand in the Aratani process.

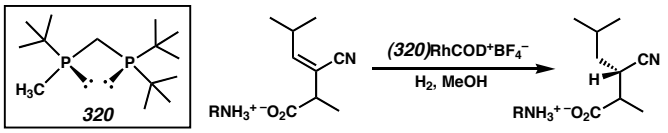


Still other C_1 symmetric ligands rely on the chirogenicity of coordinating metal atoms for asymmetric induction. Such ligands offer the potential advantage of having the chirality closer to the metal center, rather than removed in the backbone.[20] This controlling factor has been exploited in highly selective catalysts for Rh-catalyzed hydrogenation. Ohashi and coworkers synthesized a variety of P-chirogenic bis(phosphino)ethanes (Figure A6.7) that provided up to 99% ee for the hydrogenation of α-amino acid derivatives, and up to 71% ee for β-amino acid derivatives.[21] Hoge and coworkers have synthesized a similar, but simpler P-chirogenic ligand (**320**, Scheme A6.4) that displays >99% ee for α-amino acids, and can be used at substrate:catalyst loadings of 27000:1 under lower hydrogen pressures, conditions that compare favorably to C_2 symmetric (*R*,*R*)-Me-DuPhos (Scheme A6.4).[22] While models for asymmetric induction have not yet been developed, these ligands likely function by enforcing a single site of reactivity through the P-chirogenic centers.

Figure A6.7 Ohashi's P-chirogenic ligands.

R_1 = Ad, *t*Bu, or Cy
R_2 = *t*Bu, Cy, *i*Pr, Me, or Ph
R_3 = Me, Cy or Ph

Scheme A6.4



Entry	Ligand	Substrate conc (%)	S/C	H_2 psi	time	%ee
1	*320*	6	100	45	< 15 min	99
2	*(R,R)-Me-DuPhos*	6	100	90	< 15 min	95
3	*(R,R)-Me-DuPhos*	10	2700	45	4 h	97
4	*320*	20	27000	50	40 h	98

Another C_1 symmetric ligand that exploits both backbone chirality as well as coordinating-atom chirogenicity is the ubiquitous natural product (–)-sparteine (**22**). Refer to Chapter 4 and Appendix 7 of this thesisfor a description of a model that explains the stereoinduction by **22** in an oxidative kinetic resolution of secondary alcohols, as well as for further discussions of this ligand.

Although C_2 symmetric ligands remain dominant, it is clear from a consideration of recent examples that C_1 symmetric ligands at least deserve appreciation. While for some asymmetric processes C_1 symmetric ligands can be as selective as their C_2 symmetric counterparts, other processes appear to require C_1-symmetry for high enantiocontrol. The variety of motifs and interplay of controlling factors in C_1 symmetric ligands suggest that many new and successful frameworks await discovery. Neglect of these systems by virtue of their lower symmetry and greater complexity should not be allowed to slow this discovery.

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[5] For a review, see: Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron:Asymmetry* **1998**, *9*, 1.

[6] C_1 symmetric molecules possess no symmetry elements beyond the identity element.

[7] C_1 symmetric monodentate ligands will not be covered here, although they comprise another important class of chiral ligands.

[8] Also well-developed are C_1 symmetric *ansa*-metallocene ligands, which have played an important role in the development of early-metal propene polymerization catalysts but will not be discussed here; for a review, see: Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

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APPENDIX 7

Notebook Cross-Reference

The following notebook cross-reference has been included to facilitate access to the original spectroscopic data obtained for the compounds presented in this thesis. For each compound, both hard copy and electronic characterization folders have been created that contain the original ^{1}H NMR, ^{13}C NMR, ^{2}H NMR, ^{19}F NMR, and IR spectra. All notebooks and spectroscopic data are stored in the Stoltz group archives.

Table A7.1 Compounds appearing in Chapter 2.

Compound	^{1}H NMR	^{13}C NMR	IR
26	RMT-IV-071	RMT-IV-071	RMT-IV-071
27	RMT-IV-065	RMT-IV-065	RMT-IV-065
28	RMT-XIV-049	RMT-XIV-049	RMT-XIV-049
29	RMT-XIV-153	RMT-XIV-153	RMT-XIV-153
45	RMT-IV-149	RMT-IV-149	RMT-IV-149
47	RMT-IV-195	RMT-IV-195	RMT-IV-195
80	RMT-V-289	RMT-V-289	RMT-V-289
81	RMT-VI-063	RMT-VI-063	RMT-VI-063
82	RMT-V-085	RMT-V-085	RMT-V-085
83	RMT-V-103	RMT-V-103	RMT-V-103
84	RMT-IV-159	RMT-IV-159	RMT-IV-159
85	RMT-IV-181	RMT-IV-181	RMT-IV-181
86	RMT-VI-245	RMT-VI-245	RMT-VI-245
87	RMT-VI-247	RMT-VI-247	RMT-VI-247
88	RMT-IV-165	RMT-IV-165	RMT-IV-165
89	RMT-IV-189	RMT-IV-189	RMT-IV-189

90	RMT-IV-251	RMT-IV-251	RMT-IV-251
91	RMT-VI-067	RMT-VI-067	RMT-IV-277
92	RMT-V-181	RMT-V-181	RMT-V-181
93	RMT-V-183	RMT-V-183	RMT-V-183
94	RMT-V-265	RMT-V-265	RMT-V-265
95	RMT-VI-097	RMT-VI-097	RMT-VI-097
96	RMT-V-191	RMT-V-191	RMT-V-191
97	RMT-V-239	RMT-V-239	RMT-V-239
98	RMT-I-051	RMT-I-051	RMT-I-051
99	RMT-IV-073	RMT-IV-073	RMT-IV-073
100	RMT-XIV-049	RMT-XIV-049	RMT-XIV-049
101	RMT-VI-139	RMT-VI-139	RMT-VI-139
102	RMT-VI-143	RMT-VI-143	RMT-VI-143
104	RMT-VI-165	RMT-VI-165	RMT-VI-165
107	RMT-XIV-181	RMT-XIV-181	RMT-XIV-181
109	YKR-I-295	YKR-I-295	YKR-I-295
110	YKR-II-031	YKR-II-031	YKR-II-031
111	YKR-II-097	YKR-II-097	YKR-II-097
112	YKR-II-051	YKR-II-051	YKR-II-051
113	YKR-II-099	YKR-II-099	YKR-II-099
114	YKR-II-137	YKR-II-137	YKR-II-137
115	YKR-III-027	YKR-III-027	YKR-III-027
116a	YKR-III-089a	YKR-III-089a	YKR-III-089a
116b	YKR-III-089b	YKR-III-089b	YKR-III-089b
117	YKR-III-255	YKR-III-255	YKR-III-255
118	YKR-IV-037	YKR-IV-037	YKR-IV-123
134	RMT-IV-291	RMT-IV-265	
135	RMT-VI-173	RMT-VI-173	RMT-VI-173
144	RMT-X-229	RMT-X-229	
145	RMT-VIII-191	RMT-VIII-191	
146	RMT-VIII-133	RMT-VIII-133	
147	RMT-VIII-111	RMT-VIII-111	
148	RMT-VII-057	RMT-VII-057	
151	RMT-IX-291	RMT-IX-291	
152	RMT-IX-293	RMT-IX-293	
153	RMT-VII-047	RMT-VII-047	
154	RMT-VII-045	RMT-VII-045	

Table A7.2 Compounds Appearing in Chapter 3.

Compound	^{1}H NMR	^{13}C NMR	IR(°) or ^{2}H NMR(*)
***cis*-*d*-210**	RMT-XIV-209	RMT-XIV-209	RMT-XIV-209*
***trans*-3-*d*-212**	RMT-XIII-215	RMT-XIII-215	RMT-XIII-215*
***cis*-3-*d*-212**	RMT-XIII-187	RMT-XIII-187	RMT-XIII-187*
212	RMT-XIII-179	RMT-XIII-179	RMT-XIII-179°
3-*d*-213	RMT-XIII-231	RMT-XIII-231	RMT-XIII-231*
213	RMT-XIII-279	RMT-XIII-279	RMT-XIII-279°
3-*d*-214	RMT-XIII-231	RMT-XIII-231	RMT-XIII-231*
***cis*-2-*d*-214**	RMT-XIII-233	RMT-XIII-233	RMT-XIII-233*
214	RMT-XIV-037	RMT-XIV-037	RMT-XIV-037°
***trans*-3-*d*-233**	RMT-XIV-035	RMT-XIV-035	RMT-XIV-035°*
***cis*-3-*d*-233**	RMT-XIII-303	RMT-XIII-303	RMT-XIII-303°*
233	RMT-XIV-045	RMT-XIV-045	RMT-XIV-045°
***trans*-3-*d*-242**	RMT-XIV-151	RMT-XIV-151	RMT-XIV-151°*
***cis*-3-*d*-242**	RMT-XIV-141	RMT-XIV-141	RMT-XIV-133°
243	RMT-XIV-157	RMT-XIV-157	RMT-XIV-157°
3-*d*-243	RMT-XIV-143	RMT-XIV-149	RMT-XIV-149*

Table A7.3 Compounds Appearing in Chapter 4.

Compound	^{1}H NMR	^{13}C NMR	IR(°) or ^{19}F NMR(*)
255	RMT-IX-035	RMT-IX-035	RMT-IX-035°
256	RMT-XIV-245	RMT-XIV-245	RMT-XIV-245°
257	RMT-XV-057	RMT-XV-057	
260/261	RMT-VIII-217	RMT-VIII-217	
265	RMT-XV-051	RMT-VIII-051	
271	RMT-IX-033	RMT-IX-033	RMT-IX-033*
274	RMT-IX-055	RMT-IX-055	RMT-IX-055*
288	RMT-XIV-291	RMT-XIV-291	
289	RMT-VIII-303	RMT-VIII-303	
290	RMT-XIV-279	RMT-XIV-279	
293	RMT-VIII-243	RMT-VIII-243	RMT-VIII-243°

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SUBJECT INDEX

About the Author

Raissa M. Trend was born on October 16th, 1975, in Madison, Wisconsin and spent her childhood enjoying many cold winters in St. Paul, Minnesota. Her younger sister Alice and parents John and Beth make up her immediate family. Her first chemistry class was at Webster Elementary School, where she also played French horn in the school band and went on tour to Winnipeg. As a diversion from high school, she tried to introduce the harpsichord to a rock band, and started a small, short-lived 7" record company in the heyday of the early 1990s.

In 1994, Raissa moved to the University of Chicago where she became an incontrovertible multidisciplinarian and pursued such topics as neurobiology, films of the Weimar era, late 19th century American literature, and French sociology. She was president of a classic film society, and spent her junior year in Berlin, Germany, where she acquired a fondness for beer and sausages. Raissa graduated in 1998 with a BA in English literature after reading too much Henry James, and took a job at a small human resources consulting firm.

Disenchanted with office work and faced with the lack of obvious career paths afforded by an English degree, Raissa decided to return to school with the hopes that chemistry might prove a more promising field for her. As luck would have it she was able to enroll at the University of Wisconsin–Madison, where she enjoyed hanging out on the Union Terrace, ballroom dancing, and attending Badger hockey games. The chemistry thing worked out, and while doing research in the labs of Prof. Chuck Casey, Raissa decided to go for the gusto and apply to grad school.

In August 2001 Raissa left behind the snows and summers of the Midwest to attend graduate school at the California Institute of Technology in the labs of Prof. Brian M. Stoltz. She has taken great pleasure in the gastronomic delights, interesting terrain, crazy urban sprawl, and bird watching opportunities that Pasadena and LA county have to offer. Raissa will receive her Ph.D. in 2006 for her work on the mechanistic aspects and stereoselectivity of palladium-catalyzed oxidation reactions. Never to be one to settle down, her next adventure will take place in Lausanne, Switzerland, where she will begin postdoctoral studies in biophysical chemistry under the direction of Prof. Horst Vogel in June 2006.