New Concepts in Catalyst Design:

Homogeneous Organometallic Catalysts with Tunable Architectures

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Abstract

This thesis describes the development of homogeneous catalysts containing receptor elements which are capable of participating in reversible bonding interactions with groups bearing complementary functionality. This approach is amenable to combinatorial chemistry, and could facilitate catalyst development processes which are conventionally expensive and time-intensive. To date, the implications of reversible supramolecular interactions in anthropogenic organometallic catalysis are not widely understood.

Simplified pyridyl-borate ligands were prepared to simulate the behaviour of a larger target system composed of a 6,6'-boronic acid-2,2'-bipyridyl unit. Such a framework harnesses the power of reversible covalent bonding between boronic acids and diols. The reactivity of *ortho* and *meta*-pyridyl model ligands was investigated and knowledge gathered as to the hydrolytically unstable nature of the *ortho*-pyridyl borate moiety.

A macrocyclic ligand (**H_4Len**), formed via an *aza*-Michael ring-closing reaction between **N^2,N^6-bis(6-acrylamidopyridin-2-yl)pyridine-2,6-dicarboxamide** (**H_4LacrA**) and ethylenediamine was investigated as an appropriate framework for participation in supramolecular interactions. **N^2,N^6-bis(6-methylpyridin-2-yl)pyridine-2,6-dicarboxamide** (**H_2LMe_2**) was implemented as a model ligand with which to assess the head group ligating properties of the macrocylic ring. Upon deprotonation of **H_2LMe_2** two amidate nitrogens are made available for binding to a metal centre. A series of novel iridium(III) and rhodium(III) complexes of **LMe_2** were prepared and tested for activity in the transfer hydrogenation of acetophenone using isopropanol. Appreciable activity was observed for **$IrCl(py)_2(LMe_2)$** and **$IrCl_3(LMe_2\{H\}_2)$** over the course of 24 hours, with 51 and 96% conversion of acetophenone into 1-phenylethanol respectively. By comparison, the macrocyclic complex, **$(H_4Len)RuCl_2(MeCN)(PPh_3)_2$**, mediated 38% conversion into 1-phenylethanol after 16.5 hours.

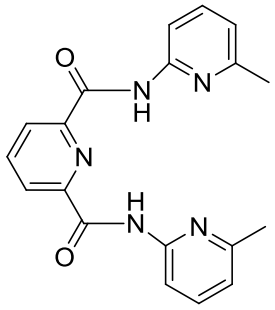
In pursuit of a second macrocyclic system bearing a bisbenzimidazolium tail, a simplified model ligand of **1,1'-(pyridine-2,6-diylbis(methylene))bis(3-methyl-1H-benzo[d]imidazol-3-ium) trifluoromethanesulfonate** (**$[dmp(bzim\{Me\})_2][OTf]_2$**) was prepared. Upon deprotonation with silver(I) oxide base a silver(I) *N*HC (*N*-heterocyclic carbene) was formed. This species was found to be an efficient intermediate by which palladium(II), rhodium(I) and iridium(I) dimethylpyridine bisbenzimidazol-2-ylidene complexes could be reached. Whilst providing a prelude to the target ligand, the rhodium(I) and iridium(I) *N*HCs were also found to be effective catalysts in the hydrosilylation of phenylacetylene using a range of silanes.

With the information gleaned from the model complex studies, the target ligand **$[H_4L(C_2H_4)_2(bzim_2\{macro\})][Br]_2$** was prepared via an *aza*-Michael ring-closing reaction between

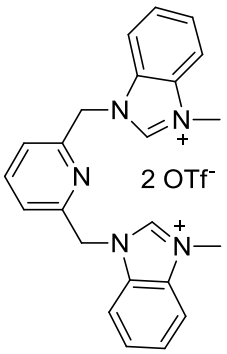
H_4LacrA and **2,6-bis((1H-benzo[d]imidazol-1-yl)methyl)pyridine** (**dmp(bzim)$_2$**)). Subsequent mercuration of the ligand afforded two rare mercury(II) *N*HC complexes **[$H_4L(C_2H_4)_2HgBr_2$((*N*HC)$_2${macro})]$_2$** and **[$H_4L(C_2H_4)_2Hg$((*N*HC)$_2${macro})][$HgBr_4$]**, the latter of which was characterised by an X-ray diffraction study. Both of these materials demonstrated transmetalation to produce the macrocyclic pincer complex **[$H_4L(C_2H_4)_2PdBr$((*N*HC)$_2${macro})][PF_6]**. Preliminary investigations were made into the activity of the macrocyclic palladium pincer *N*HC in the Heck-Mizoroki C-C coupling reaction between bromobenzene and styrene. While conversion into stilbenes after 24 hours was determined to be negligible with the macrocyclic complex alone, the inclusion of additives such as 2-amino-6-methyl pyridine dramatically increased substrate conversion to 84.2 (± 3.0)%. Subsequent analysis provided insight with regard to the nature of the active catalyst.

The novel ligand **[$H_4L(C_2H_4)_2$(bzim$_2${macro})][Br]$_2$** and its *N*HC metal derivatives represent an innovative approach to homogeneous catalyst design which operates in proximity to receptor elements present within the macrocyclic ring.

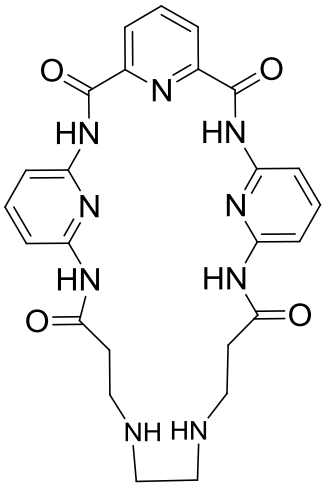
H_2LMe_2



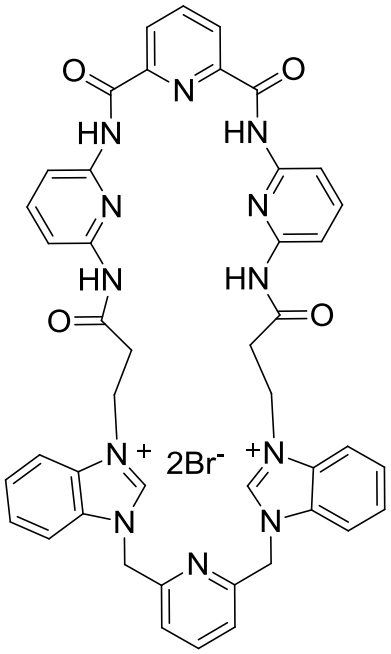
[dmp(bzim{Me})$_2$][OTf]$_2$



H_4Len



[$H_4L(C_2H_4)_2$(bzim$_2${macro})]Br$_2$



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Abbreviations

1D	=	One dimensional
2D	=	Two dimensional
Ad	=	Adamantyl
ADPS	=	Anisotropic Displacement Parameters
BASF	=	Batch scale factors
BDE	=	Bond Dissociation Energy
BINAP	=	2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl
bpy	=	Bipyridine
bpydb	=	Bipyridine diboronic acid
bzim{Me}	=	*N*-methylbenzimidazole
Calc.	=	Calculated
CCDB	=	Cambridge Crystallographic Database
CD	=	Circular dichroism
COD	=	1,5-Cyclooctadiene
COSY	=	Homonuclear correlation spectroscopy
Cp	=	Cyclopentadiene
Cp*	=	Pentamethylcyclopentadienyl
Cy	=	Cyclohexyl
cyclen	=	1,4,7,10-tetraazacyclododecane
d	=	Doublet
DABCO	=	1,4-diazabicyclo[2.2.2]octane
dba	=	Dibenzylacetone
DBU	=	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCM	=	Dichloromethane
DEAM	=	Dihydro-9,10-ethanoanthracene
DELU	=	A restraint to bring the magnitude of the ADPs of neigbouring anisotropic atoms into closer agreement
DEPT 135	=	Distortionless Enhancement by Polarisation Transfer, 135° pulse angle
dft	=	Density Functional Theory
dien	=	Diethylenetriamine
DMAC	=	N,N-Dimethylacetamide
DMAP	=	4-Dimethylaminopyridine
DMF	=	N,N-Dimethylformamide
dmp	=	2,6-Dimethylpyridine
DMSO	=	Dimethylsulfoxide

DMU	=	1,1-Dimethylurea
dvds	=	1,3-Tetramethyl-divinyldisiloxane
E.A.	=	Elemental Analysis
EADP	=	Equal Anisotropic Displacement Parameter
ee	=	Enantiomeric Excess
ESI-MS	=	Electrospray ionisation mass spectrum
FAB-MS	=	Fast Atom Bombardment mass spectrum
HMBC	=	Heteronuclear Multiple Bond Correlation
HSQC	=	Heteronuclear Single Quantum Coherence
IBY	=	Isopropylbenzimidazolidine-2-ylidene)
IPA	=	Isopropyl alcohol
IR	=	Infrared
ISOR	=	A restraint to make an anisotropic atom more isotropic-like
m	=	Multiplet (NMR) / Medium (IR)
macro	=	Macrocyclic
Mes	=	Mesityl
MHMDS	=	Alkali metal (Li or K) Hexamethyldisilazane
MIDA	=	*N*-methyliminodiacetic acid
MS	=	Mass Spectrometry
*N*HC	=	*N*-Heterocyclic Carbene
NMR	=	Nuclear Magnetic Resonance
OAc	=	Acetate
ORTEP	=	Oak Ridge Thermal Ellipsoid Plot
PCy_3	=	Triscyclohexylphosphine
PPh_3	=	Triphenylphosphine
Pr	=	Propyl
q	=	Quaternary
s	=	Singlet
s.d.	=	Standard deviation
SIMU	=	Similar U_{ij}
S/N	=	Signal to noise ratio
t	=	Triplet
terpy	=	Terpyridine
THF	=	Tetrahydrofuran
TMS	=	Tetramethylsilane
TOF	=	Turnover frequency
TON	=	Turnover numbers
TOPSPIN	=	TopSpin NMR software package developed by Bruker
d_4-TSPA	=	3-(trimethylsilyl) 3,3,2,2-tetradeuteropropionic acid Na salt
VT-NMR	=	Variable Temperature Nuclear Magnetic Resonance

Xphos	=	2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl
zgpg	=	Pulse program with a continuous pulse decoupling mode