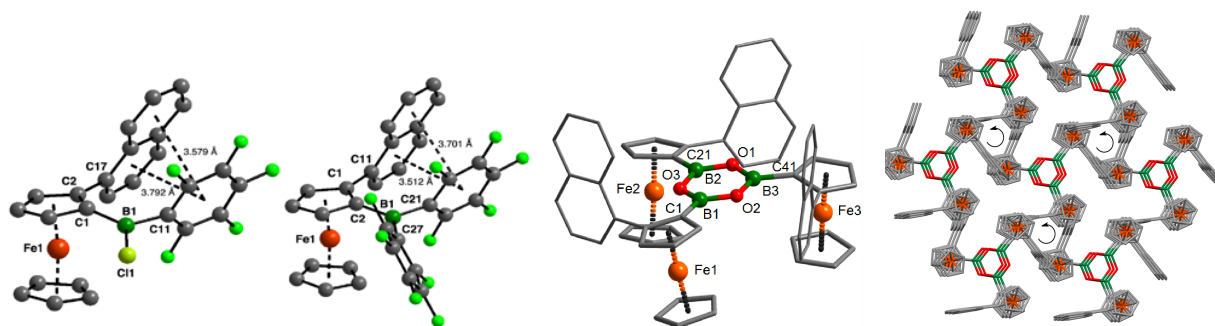
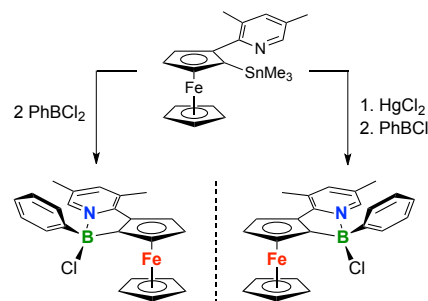


Project F: Ferrocene-Based Chiral Lewis Acids, Lewis Bases, and Lewis Pairs

1) Ferrocene-Based Planar Chiral Lewis Acids. We developed the first examples of highly Lewis acidic planar-chiral naphthylferrocenylborane Lewis acids. The fluorinated boranes were obtained with high selectivity via a series of organometallic substitution reactions. The structures were confirmed by single-crystal X-ray diffraction (shown) and the steric effect around the boron center was examined by variable temperature ^{19}F NMR spectroscopy, suggesting that the naphthylferrocene framework provides a rigid chiral environment for the borane moiety. These compounds are structurally closely related to the important class of chiral binaphthyl species, which have found abundant use in catalysis. We also prepared the corresponding boronic acid derivative and its anhydride, the naphthylferrocenyl boroxine. The boroxine adopts, both in solution and the solid state, an interesting C_3 -symmetric arrangement, in which all three ferrocenyl moieties are positioned on one side of the boroxine ring system, while the naphthyl-substituents point into the other direction. Supramolecular interactions in the solid state result in a highly unusual triple-helical structure and the formation of large cavities that are occupied by solvent molecules. The presence of three redox-active ferrocenyl moieties that are in close vicinity leads to three well-separated waves in the cyclic voltammogram with significant redox-splitting; they are shifted to lower potentials upon addition of DMAP as a Lewis base.



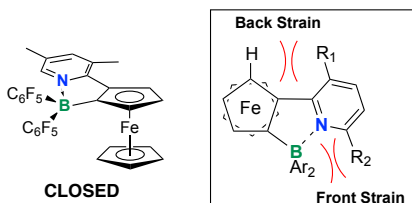
In an effort at developing new routes to planar chiral Lewis pairs, the borylation of enantiomerically pure stannylated and mercurated pyridylferrocenes with PhBCl_2 was investigated. In both cases, clean conversion to 2-(chlorophenylboryl)-1-(3,5-dimethylpyrid-2-yl)ferrocene, a novel boron-nitrogen heterocycle, was observed. The structures of the products were confirmed by multinuclear and 2D NOESY NMR, high resolution MS, and single crystal X-ray diffraction analysis. However, while all NMR data proved to be identical, the single crystal X-ray structures revealed retention of stereochemistry for the mercury precursor, but inversion of stereochemistry for the organotin precursor. The opposite chirality of the products was further confirmed by chiral HPLC analyses and optical rotation measurements. These results imply that the reaction of PhBCl_2 with 1-mercurio-2-(3,5-dimethylpyrid-2-yl)ferrocene proceeded as expected via an *ipso*-borodemercuration process, whereas a stereoselective rearrangement occurred in the reaction with 1-stannyl-2-(3,5-dimethylpyrid-2-yl)ferrocene. A mechanism is proposed, in which the Lewis basic pyridyl group in the stannylferrocene precursor acts as an *ortho*-directing group that facilitates highly selective attack of the boryl species at the adjacent C-H position. Subsequent proton migration and elimination of Me_3SnCl result in a single isomer of the product with inverted stereochemistry. The mechanistic studies also suggest the involvement of a borenium cation as strong electrophile that rapidly attacks the Cp ring even at -78°C .



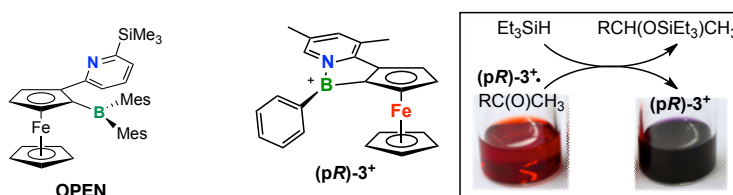
Taking advantage of this new methodology, we set out to construct new planar chiral Lewis pairs that feature substituted pyridyl groups as the base and electron-deficient bis(pentafluorophenyl)boryl and bulky dimesitylboryl groups as the acid. Despite the steric effects of the methyl groups on pyridine a strong B-N bond formed, which remains intact even under strongly acidic conditions. A bulky trimethylsilyl group was

then incorporated in the *ortho* position of the pyridine ring to further increase the steric congestion and thus to weaken the B-N interaction. The derivative with a bis(pentafluorophenyl)boryl acceptor formed a labile B-N bond, which opened at elevated temperature according to EXSY spectroscopy data and reacted with a water molecule to a ring-opened pyridinium borate. In contrast, the dimesitylboryl derivative adopted an open conformation in which the entire pyridyl group was flipped to release steric repulsion.

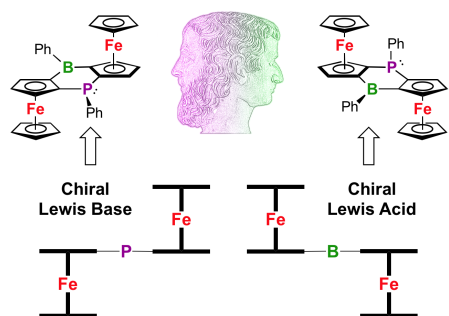
Switchable Lewis Pairs



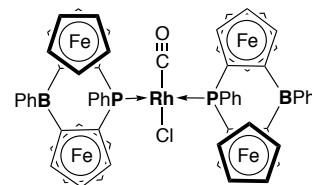
Borenium Catalyst for Hydrosilylation



Using this unique molecular scaffold we synthesized the corresponding planar-chiral borenium cation, **(pR)-3⁺**, as a new powerful Lewis acid catalyst. A competition study showed that the Lewis acidity is almost as high as that of the widely used *tris*(pentafluorophenyl)borane and the affinity towards anions such as Cl⁻ is even stronger. The borenium species not only binds to Lewis basic substrates such as ketones and THF, but also activates the Si-H bond of silanes such as Et₃SiH. This unique Lewis acid was tested as a catalyst for the hydrosilylation of ketones with excellent conversion but moderate enantiomeric excess.

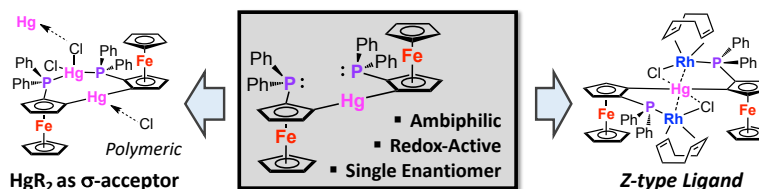


We recently introduced a new class of Janus-like ambiphilic phosphaborin ligands. The rigid diferrocene backbone in these heterocycles creates an unprecedented chiral environment as demonstrated by multinuclear NMR and single-crystal X-ray studies. We emphasize that these ligands display no central chirality at P, but the chiral environment is determined solely by the orientation of the ferrocene “paddles”. The phosphaborin is not only redox-active but also responsive to the presence of fluoride anions. Binding of F⁻ to B in the



corresponding Vaska-type Rh complex shifts $\nu(\text{CO})$ from 1967 to 1948 cm⁻¹, a value that is approaching that for the highly electron-rich alkylphosphine PCy₃. Given the importance of phosphines in a large array of catalytic processes we envision broad utility of this new class of rigid, chiral, and stimuli-responsive ligands in catalysis.

Finally, we have developed a new class of ambiphilic ferrocene-based chelate ligands. Reaction between 1,2-Fc(PPh₂)(SnMe₃) and HgCl₂ is accompanied by spontaneous disproportionation to give a novel diphosphine chelate ligand with a wide and flexible bite angle and unique stereochemical environment. Its HgCl₂ complex shows unprecedented Hg-Cl→HgR₂ interactions that give rise to a polymeric structure, whereas ambiphilic behavior with short Rh⋯Hg contacts is found for a Rh(I) complex by X-ray analysis and further examined by theoretical calculations. Thorough mechanistic studies have been performed on the formation of the diferrocenylmercury chelate ligand.



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