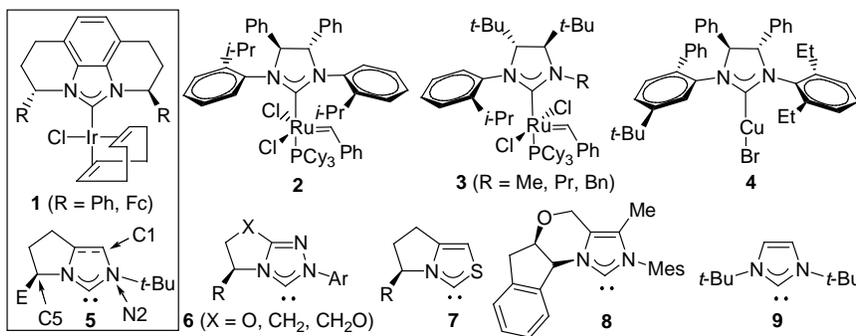
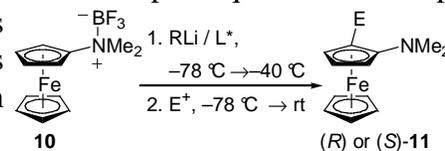


Our research program is focused on designing new chiral reagents and catalysts for applications in asymmetric synthesis. The targets have structural features that are expected to provide complementary reactivity and/or improvements in stereoselectivity over known reagents, but have been difficult or impractical to make in the past. Our intention is to develop viable routes to these materials to allow their systematic evaluation as catalysts. To this end, we have developed a route to benzannulated *N*-heterocyclic carbene (NHC) ligands as in **1**,¹ derived from phenanthrolines and similar to the Grubbs complex **2**,² but in which the positions of the stereogenic centers were switched to influence more directly the chiral environment near the metal.

More recently, we have devised asymmetric syntheses of C_1 -symmetric pyrroloimidazol(in)ylidene NHCs of type **5**,³ which also have proximal chiral centers (C5) in a ring. This development is significant for several reasons: (1) There is a lack of previous examples of these reagents because they are challenging to prepare, as illustrated by Bode's 8-step synthesis of the related compound **8**.⁴ (2) As nucleophilic catalysts, **5** will lead to different products over common reagents **6** and **7**⁵ due to electronic differences.^{4,6} (3) The use of C_1 -symmetric "Grubbs-like" NHCs (e.g. in **3**⁷ and **4**⁸) in enantioselective transition-metal-catalyzed reactions is increasing. (4) Most current versions of NHCs **5** have *N*-*t*-Bu groups. Because **9** forms a "Frustrated" Lewis Pair (FLP) with $B(C_6F_5)_3$ that activates small molecules such as H_2 ,⁹ bulky derivatives of **5** are excellent chiral NHCs to investigate in this young field of chemistry, which may reduce the need for precious metal catalysts in the future.¹⁰



We are also currently developing an enantioselective synthesis of planar chiral aminoferrocenes of type **11** in which nitrogen is directly attached to the cyclopentadienyl (Cp) ring. This class of compounds is not easily accessible so there has been little in-depth exploration of enantiopure aminoferrocene ligands.¹¹ Our unique approach to their preparation starts with aminoferrocenes, whose complexes with BF_3 (**10**) undergo enantioselective lithiation–electrophile quench on the Cp ring to give products of considerable structural diversity. This method, under patent protection in the U.S. and Canada, has yielded aminoferrocenes with unusual substitution patterns, such as aminophosphines **11** ($E = PR_2$).^{12,13}



¹ Metallinos, C.; Du, X. *Organometallics* **2009**, *28*, 1233.

² Grubbs R. H. et al. *Org. Lett.* **2001**, *3*, 3225.

³ Metallinos, C.; Xu, S. *Org. Lett.* **2009**, *11*, in press.

⁴ Bode, J. W. et al. *Org. Lett.* **2008**, *10*, 957.

⁵ (a) Rovis, T. *Chem. Lett.* **2008**, *37*, 2. (b) Enders, D. et al. *Chem. Rev.* **2007**, *107*, 5606. (c) Christmann, M.; *Angew. Chem. Int. Ed.* **2005**, *44*, 2632.

⁶ Bode, J. W. et al. *Org. Lett.* **2009**, *11*, 677.

⁷ Collins, S. K. et al. *Adv. Synth. Catal.* **2009**, *351*, 1826 and *Organometallics* **2007**, *26*, 2945.

⁸ Hoveyda, A. H. et al. *J. Org. Chem.* **2009**, *74*, 4455.

⁹ Stephan, D. W. et al. *Angew. Chem. Int. Ed.* **2008**, *47*, 7433.

¹⁰ Stephan, D. W. *Dalton Trans.* **2009**, 3129.

¹¹ (a) Carretero, J. C. et al. *J. Org. Chem.* **2002**, *67*, 1346. (b) Togni, A. et al. *Eur. J. Inorg. Chem.* **2005**, 347. (c) Togni, A. et al. *Organometallics* **2006**, *25*, 622.

¹² Metallinos, C.; Zaifman, J.; Dodge, L. *Org. Lett.* **2008**, *10*, 3527.

¹³ Metallinos, C. et al. *Organometallics* **2009**, *28*, 4534.