Synthesis of P- and S-Functionalized Chiral Imidazolium Salts and Their Rh and Ir Complexes

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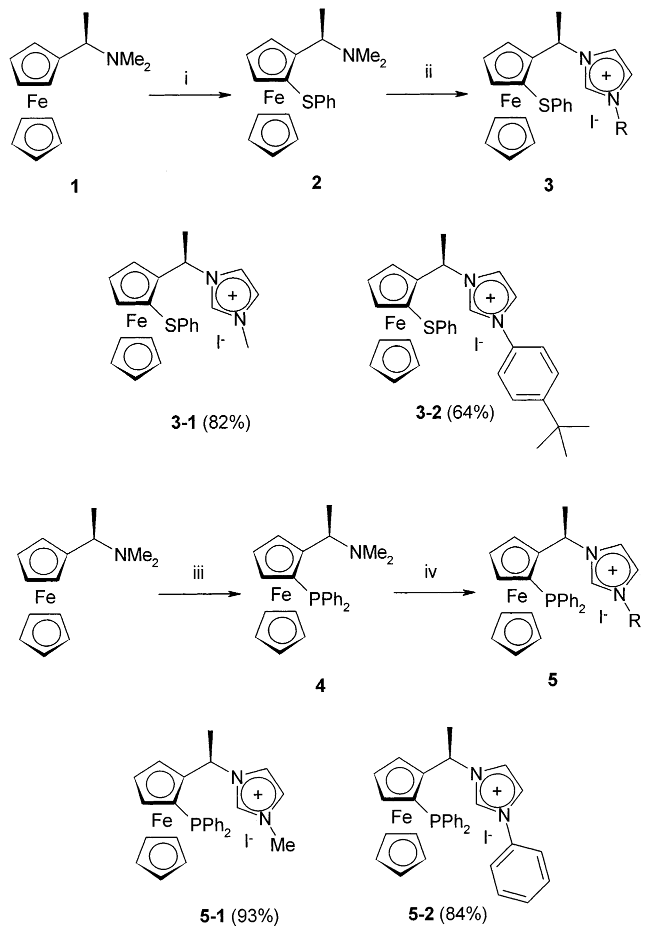
Summary: Chiral imidazolium salts bearing sulfide and phosphine have been synthesized from chiral ferrocenylamine, and their rhodium and iridium complexes have been characterized by an X-ray diffraction study.

Scheme 1[a]



[a] Legend: (i) (a) n-BuLi, ether, (b) PhSSPh; (ii) (a) MeI, CH_2Cl_2, (b) 1-methylimidazole or 1-phenylimidazole, CH_3CN, reflux; (iii) (a) n-BuLi, ether, (b) Ph_2PCl; (iv) (a) 1-methylimidazole or 1-phenylimidazole, AcOH, 60 °C, (b) NaI, EtOH.

Recently, the chemistry of N-heterocyclic carbenes (NHCs) and their transition-metal complexes have received much attention[1] because these carbenes act as efficient ligands in several transition-metal-catalyzed processes. Bidentate or tridentate ligands containing NHC have found widespread use in homogeneous catalysis. Examples include the use of palladium and copper complexes of NHC in combination with pyridine, phosphine, and alkoxide and of CNC and CCC bis(carbene) pincer ligands in C−C coupling reactions.[2,3] It is expected that the introduction of pendant functional groups to a NHC will result in diverse metal complexes and give an opportunity to control the reactivity and stereoselectivity in catalytic reactions. However, chiral complexes containing functional groups and NHC are quite rare[4] and they usually have an N-donor such as pyridine, imine, and oxazoline as a functional group, not phosphine or sulfide. Although the use of transition-metal sulfides as catalysts is quite common, there have been no reports[6] on the preparation of NHCs containing a pendant sulfide. Thus, it would be a challenge to synthesize chiral NHC complexes having sulfide and phosphine and to use them in an asymmetric catalytic reaction. We here communicate a synthesis of functionalized chiral NHC precursors and their use in the synthesis of rhodium and iridium complexes.

For chiral ferrocenylamines such as **1**, it is possible to add a functional group through a diastereoselective ortho lithiation by *n*-BuLi followed by the addition of an electrophile and the dimethylamino group can be substituted by another functional group with retention of configuration. Thus, the ortho lithiation of **1** by *n*-BuLi followed by addition of diphenyl sulfide gave **2**. Subsequent methylation of **2** followed by reaction with 1-methylimidazole gives **3-1** in 82% yield (Scheme 1).

A process similar to the synthesis of **3-1** could not be applied to synthesize **5-1**. Compound **4** was synthesized

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[1] Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290 and references therein.

[2] (a) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741. (b) Arnold, P. L.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2001**, 2340. (c) Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027. (d) Yang, C.; Lee, H. M.; Nolan, S. P. *Org. Lett.* **2001**, *3*, 1511. (e) Danopoulos, A. A.; Winston, S.; Gelbrich, T.; Hursthouse, M. B.; Tooze, R. P. *Chem. Commun.* **2002**, 482.

[3] (a) Gründemann, S.; Albrecht, M.; Loch, J. A.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2001**, *20*, 5485. (b) Tulloch, A. A. D.; Danopoulos, A. A.; Tizzard, G. J.; Coles, S. J.; Hursthouse, M. B.; Hay-Motherwell, R. S.; Motherwell, W. B. *Chem. Commun.* **2001**, 1270. (c) Danopoulos, A. A.; Winston, S.; Motherewell, W. B. *Chem. Commun.* **2002**, 1376.

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[6] Bayon, J. C.; Claver, C.; Masdeu-Bulto, A. M. *Coord. Chem. Rev.* **1999**, *193−195*, 73.

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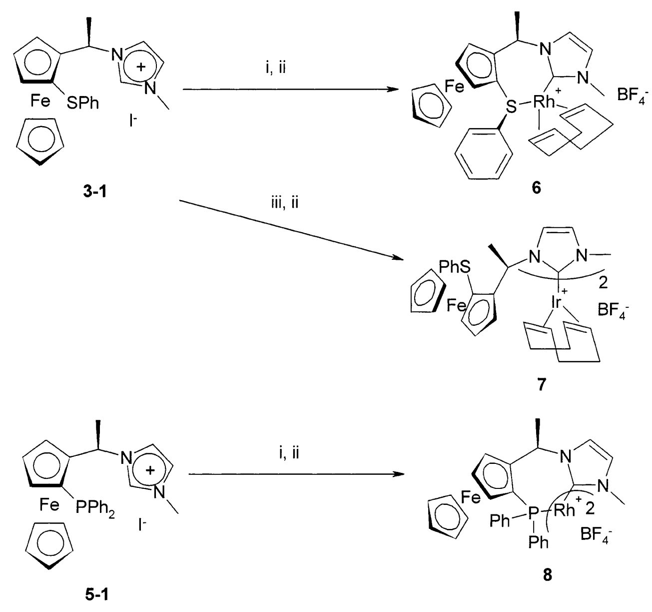
Scheme 2[a]



[a] Legend: (i) t-BuOK, $[Rh(COD)Cl]_2$, 70 °C; (ii) $AgBF_4$, room temperature; (iii) t-BuOK, $[Ir(COD)Cl]_2$, 70 °C.

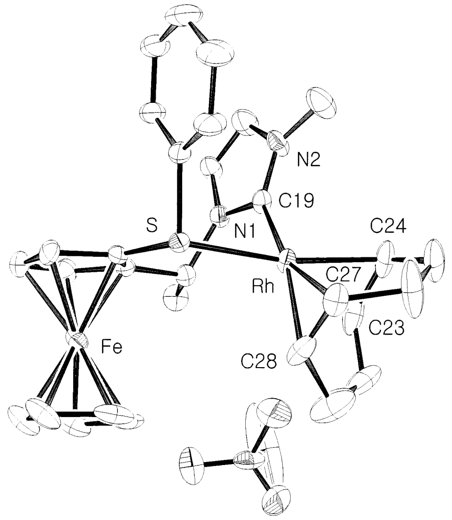


Figure 1. Molecular structure of **6**. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angle (deg): C(19)−Rh = 2.051(7), C(23)−Rh = 2.148(9), C(24)−Rh = 2.137(7), C(27)−Rh = 2.236(8), C(28)−Rh = 2.225(9), S−Rh = 2.394(2); C(19)−Rh−S = 89.0(2).

by the use of chlorodiphenylphosphine instead of diphenyl sulfide. However, because of the methylation of phosphorus, we could not use MeI to generate an ammonium salt as in the synthesis of **3-1**. To introduce an imidazole moiety to **4**, we had to use a modified route. It is known[8] that the substitution reaction of the dimethylamino group with phosphine or pyrazole occurs cleanly in acetic acid. Thus, a slightly modified procedure was applied to the synthesis of **5-1**: an imidazolium salt was generated by the reaction of **4** with 1-methylimidazole in acetic acid, and the anion was changed to iodide by treating with NaI. The yield for the two steps is 93%. The ^{1}H NMR spectra of **3-1** and **5-1** show that one diastereomer exists as the sole product in each solution. The X-ray crystal structures of the rhodium and iridium complexes of **3-1** and **5-1** also show that the configuration of the chiral center is retained even after the substitution reaction. It is possible to modify the ligands by changing added functional groups: i.e., sulfides, phosphines, and imidazoles. Compounds **3-2** and **5-2** were synthesized in 64% and 84% yields, respectively, by the same methods as those of **3-1** and **5-1** using 1-phenylimidazole instead of 1-methylimidazole. Deprotonation of **3-1** with *t*-BuOK followed by a reaction with 0.5 equiv of $[Rh(COD)Cl]_2$ in THF and $AgBF_4$ yielded **6** (43%) (Scheme 2). The X-ray crystal structure of **6** (Figure 1)[9] shows a distorted-square-planar structure with carbene and sulfide ligands in cis positions. The carbene- to-rhodium distance (2.051(7) Å) is within the exepcted range. The distance between rhodium and the COD double bond is slightly longer for the atoms trans to the carbene (2.236(8) and 2.225(9) Å) than to the sulfur (2.148(9) and 2.137(7) Å).[4b] This suggests that the carbene is a stronger donor than the sulfur. As in the synthesis of **6**, compound **7** was synthesized from $[Ir(COD)Cl]_2$ in 21% yield. The ^{1}H NMR spectrum of **7** shows that two carbene ligands and one COD ligand exist in the compound. The X-ray structure of **7** (Figure 2)[10] clearly shows that two carbene ligands and a COD ligand coordinate to the iridium metal center, but the sulfide group does not. The bond distances between the iridium and the carbon atoms of COD suggest that the COD is slightly distorted. As in the synthesis of **6**, compound **8** was prepared by a reaction of $[Rh(COD)Cl]_2$ with **5-1** in 34% yield. The peaks corresponding to COD were not seen in the ^{1}H NMR spectrum of **8**. The X-ray crystal structure of **8** (Figure 3)[11] shows that two carbene ligands coordinate to the rhodium center through C and P in a trans fashion. Thus, the coordination reactivities of the carbene ligands were quite different, depending upon the metal and functional group in the ligand.

Compounds **6**−**8** were tested for their catalytic efficiencies in the hydrogenation of dimethyl itaconate at 50 °C under 10 atm of hydrogen. Disappointingly, **7** and **8** showed no catalytic activities and **6** gave a 44% yield with 18% ee (*R*) after 12 h. Compound **8** is coordinatively saturated, and low catalytic activities were anticipated when it was used as a catalyst. We envisioned

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[7] (a) Hayashi, T. In *Ferrocenes*; Hayashi, T., Togni, A., Eds.; VCH: Weinheim, Germany, 1995; p 105. (b) While we were preparing this paper, Togni et al. reported a C_2-symmetric ferrocenyl carbene having a TMS group in an ortho position using the same methodology: Broggini, D.; Togni, A. *Helv. Chim. Acta* **2002**, *85*, 2518.

[8] Togni, A. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, p 687.

[9] Crystal data for **6** ($C_{30}H_{34}N_2SFeRhBF_4$): orthorhombic, $P2_12_12_1$, $a = 11.870(1)$ Å, $b = 13.595(1)$ Å, $c = 18.772(1)$ Å, $V = 3029.3(4)$ Å^3, $Z = 4$, density 1.535 mg/m^3, θ range for data collection 1.85−27.48°, limiting indices $-15 \leq h \leq 15$, $-17 \leq k \leq 17$, $-24 \leq l \leq 24$, 6592/6592 collected/unique reflections (R(int) = 0.000), goodness of fit on F^2 0.974, final R indices ($I > 2\sigma(I)$) R1 = 0.0480, wR2 = 0.1200.

[10] Crystal data for **7**·2PhCH₃ ($C_{52}H_{56}N_4S_2Fe_2IrBF_4 \cdot 2C_7H_8$): orthorhombic, $P2_12_12_1$, $a = 11.978(1)$ Å, $b = 14.955(1)$ Å, $c = 34.775(1)$ Å, $V = 6229.3(7)$ Å^3, $Z = 4$, density 1.450 mg/m^3, θ range for data collection 3.21−27.49°, limiting indices $-15 \leq h \leq 14$, $-19 \leq k \leq 19$, $-44 \leq l \leq 45$, 12 284/12 284 collected/unique reflections (R(int) = 0.0000), goodness of fit on F^2 0.831, final R indices ($I > 2\sigma(I)$) R1 = 0.0417, wR2 = 0.0747.

[11] Crystal data for **8**·Et₂O ($C_{56}H_{24}N_4P_2Fe_2RhBF_4 \cdot C_4H_{10}O$): monoclinic, $C2$, $a = 16.760(1)$ Å, $b = 13.611(1)$ Å, $c = 12.707(1)$ Å, $\beta = 107.472(1)°$, $V = 2765.0(3)$ Å^3, $Z = 2$, density 1.466 Mg/m^3, θ range for data collection 1.68−27.53°, limiting indices $-21 \leq h \leq 21$, $-17 \leq k \leq 17$, $-16 \leq l \leq 16$, 6193/6193 collected/unique reflections (R(int) = 0.0000), goodness of fit on F^2 = 1.086, final R indices ($I > 2\sigma(I)$) R1 = 0.0352, wR2 = 0.0911.

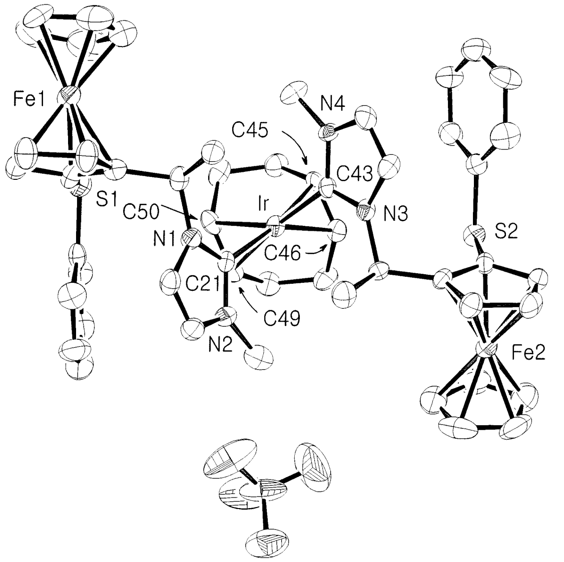

Figure 2. Molecular structure of **7**. The asymmetric unit contains two molecules of toluene. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angle (deg): C(21)−Ir = 2.083(7), C(43)−Ir = 2.084(6), C(45)−Ir = 2.221(6), C(46)−Ir = 2.163(5), C(49)−Ir = 2.252(6), C(50)−Ir = 2.153(5); C(21)−Ir−C(43) = 92.9(2).

that a carbene−phosphine-chelated Rh−COD complex would show a good activity. Thus, to generate a carbene−phosphine-chelated Rh−COD complex, the phosphino-functionalized imidazolium species **5-1** was treated with NaH, filtered, and then reacted with $Rh(COD)_2BF_4$. The in situ generated complex was employed as a catalyst in the hydrogenation of dimethyl itaconate under 4 atm of H_2 and at room temperature. The in situ generated catalyst was highly active. The reaction was completed within 4 h, but the ee was only 13% (*S*).

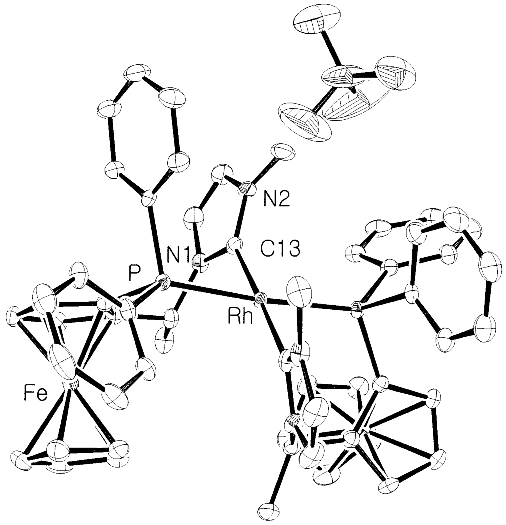

Figure 3. Molecular structure of **8**. The asymmetric unit contains one molecule of diethyl ether. Thermal ellipsoids are shown at 30% probability. Selected bond lengths (Å) and angle (deg): C(13)−Rh = 2.048(4), P−Rh = 2.2935(10); C(13)−Rh−P = 97.24(12).

In conclusion, we synthesized the first chiral imidazolium salts containing sulfide or phosphine and solved the X-ray crystal structures of their rhodium and iridium complexes. Depending upon the functional group of the carbene ligand and the metal, different metal complexes having a different bonding mode were obtained. We are currently exploring the relation between the coordination mode of the carbene ligand and the functional group in the carbene ligand and the metal source, as well as potential applications of our new functionalized chiral metal complexes in asymmetric catalysis.

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Supporting Information Available: Text giving experimental procedures for the synthesis of new compounds and tables giving crystal data, atomic coordinates, and equivalent isotropic displacement parameters for non-hydrogen atoms, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **Fc-6**, **Fc-7**, and **Fc-8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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