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Template Syntheses of Iron(II) Complexes Containing Chiral P−N−N−P and P−N−N Ligands

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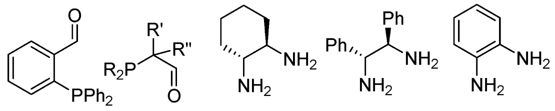
A multicomponent template reaction utilizing an air-stable phosphonium precursor leads initially to the first enantiopure bis-tridentate iron complexes *mer*-$[Fe(P-N-N)_2]^{2+}$ in high yield and then to new tetradentate iron complexes *trans*-$[Fe(MeCN)_2(P-N-N-P)]^{2+}$.

Tetradentate P−N−N−P ligand complexes are important in catalysis. Those based on platinum metals are catalysts for asymmetric transfer hydrogenation,[1–3] direct hydrogenation,[3] kinetic resolution of racemic alcohols,[4] Michael addition,[5] epoxidation and oxidation,[6–9] cyclopropanation,[9,10] and fluorination, both nucleophilic[11] and electrophilic.[12] Those based on iron(II) were recently shown to be catalysts for the asymmetric hydrogenation and transfer hydrogenation of aromatic ketones.[13] This is significant because iron-based catalysts are potentially of lower cost, toxicity, and environmental impact than those of platinum metals.[14,15] The catalyst precursor *trans*-$[Fe(PPh_2C_6H_4CH{=}NC_6H_{10}N{=}CHC_6H_4PPh_2)(MeCN)_2](BF_4)_2$ (**1**) was prepared by the nontemplated route of Scheme 1, starting with (*R*,*R*)-dach (Chart 1) and *o*-diphenylphosphinobenzaldehyde (**2**). While the catalysts displayed good activity, their enantioselectivity needed to be improved.[13] However the types of P−N−N−P ligands that can be prepared are usually derived from phosphinoaldehydes like **3** and its analogues[16] that form six-membered rings M−P−N− with the metal. This report describes how we have overcome this limitation by finding a convenient multicomponent template synthesis of iron complexes with novel P−N−N and P−N−N−P ligands that form five-membered M−P−N− rings starting from an air-stable phosphonium precursor. This method allows the combinatorial synthesis of a large number of related catalyst structures to aid the search for the ones displaying optimum activity and selectivity. Template synthesis[17] is a particularly attractive and efficient method for the synthesis of phosphorus-donor ligands.[18–30]

Scheme 1. Synthetic Routes to P−N−N−P Ligands and Their Complexes with Fe^{2+}

Chart 1. Examples of Phosphino-Aldehyde Precursors and Diamines That Can Be Used in P−N−N−P Ligand and Catalyst Synthesis



2 **3** **(*R*,*R*)-dach** **(*R*,*R*)-dpen** **bn**

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(1) Gao, J.-X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087–1089.

(2) Xing, Y.; Chen, J.-S.; Dong, Z.-R.; Li, Y.-Y.; Gao, J.-X. *Tetrahedron Lett.* **2006**, *47*, 4501–4503.

(3) Rautenstrauch, V.; Hoang-Cong, X.; Churlaud, R.; Abdur-Rashid, K.; Morris, R. H. *Chem.*−*Eur. J.* **2003**, *9*, 4954–4967.

(4) Li, Y. Y.; Zhang, X.-Q.; Dong, Z.-R.; Shen, W.-Y.; Chen, G.; Gao, J.-X. *Org. Lett.* **2006**, *8*, 5565–5567.

(5) Althaus, M.; Bonaccorsi, C.; Mezzetti, A.; Santoro, F. *Organometallics* **2006**, *25*, 3108–3110.

(6) Stoop, R. M.; Mezzetti, A. *Green Chem.* **1999**, 39–41.

(7) Stoop, R. M.; Bachmann, S.; Valentini, M.; Mezzetti, A. *Organometallics* **2000**, *19*, 4117–4126.

(8) Wong, W.-K.; Chen, X.-P.; Chik, T.-W.; Wong, W.-Y.; Guo, J.-P.; Lee, F.-W. *Eur. J. Inorg. Chem.* **2003**, *19*, 3539–3546.

(9) Bonaccorsi, C.; Mezzetti, A. *Curr. Org. Chem.* **2006**, *10*, 225–240.

(10) Bachmann, S.; Furler, M.; Mezzetti, A. *Organometallics* **2001**, *20*, 2102–2108.

(11) Barthazy, P.; Togni, A.; Mezzetti, A. *Organometallics* **2001**, *20*, 3472–3477.

(12) Althaus, M.; Becker, C.; Togni, A.; Mezzetti, A. *Organometallics* **2007**, *26*, 5902–5911.

(13) Sui-Seng, C.; Freutel, F.; Lough, A. J.; Morris, R. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 940–943.

(14) Bart, S. C.; Hawrelak, E. J.; Lobkovsky, E.; Chirik, P. J. *Organometallics* **2005**, *24*, 5518–5527.

(15) Casey, C. P.; Guan, H. *J. Am. Chem. Soc.* **2007**, *129*, 5816–5817.

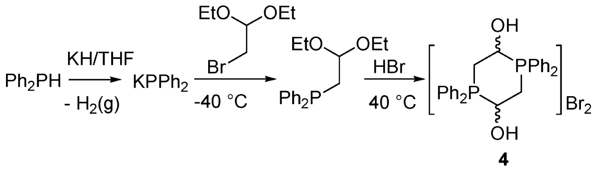
(16) Bonaccorsi, C.; Santoro, F.; Gischig, S.; Mezzetti, A. *Organometallics* **2006**, *25*, 2002–2010.

(17) Busch, D. H.; Stephenson, N. A. *Coord. Chem. Rev.* **1990**, *100*, 119–154.

(22) Edwards, P. G.; Haigh, R.; Li, D. M.; Newman, P. D. *J. Am. Chem. Soc.* **2006**, *128*, 3818–3830.

10.1021/ic800884c CCC: $40.75

Scheme 2. Synthesis of **4**



First, we attempted to synthesize and isolate several compounds with the general structure of **3** shown in Chart 1. Lacking the triaryl structure of **2**, these are air-sensitive and reactive at the phosphorus. These amphoteric bifunctional compounds undergo oligomerization and other undesirable reactions, as indicated by multiple signals in the ^{31}P NMR spectra.

However, the use of the air-stable dimer **4** reported by Matt et al.[31] provided a practical precursor to **3** (R, R′ = H). We improved the overall yield of **4** starting from PPh_2H and $BrCH_2C(OEt)_2H$ to 97% by the use of $KPPh_2$ in the synthesis (Scheme 2). The dimer is produced as a mixture of diastereomers.

The synthesis of P−N−N−P ligands was first attempted by the acid-catalyzed condensation of dimer **4** and different diamines using a Dean−Stark setup (Scheme 1, no template). The ^{31}P NMR spectra taken of the reaction mixtures showed that, under acidic conditions, the dimer is inert to condensation reactions. Under basic conditions and N_2(g), the complete dissociation of the dimer into monomers occurred. However, a byproduct rapidly formed. With the intention of suppressing the reactivity of the phosphorus of **3**, we tried its protection by use of BH_3 without success.[32–34]

Scheme 3. Synthesis of P−N−N−P and P−N−N Iron Complexes

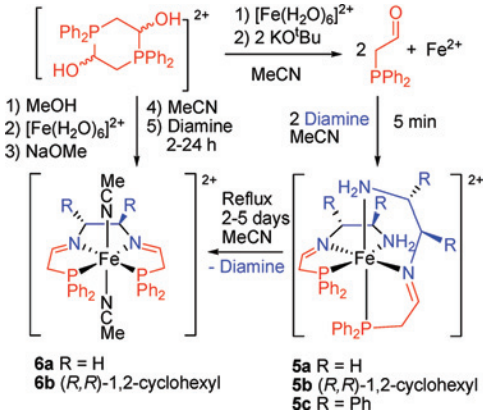


Table 1. Preparation of $[Fe(P-N-N)_2][BPh_4]_2$ (**5a−c**) and *trans*-$[Fe(P-N-N-P)(MeCN)_2][BPh_4]_2$ (**6a,b,d**)

		5[a]		**6**[b]	
	diamine	yield (%)	$^{31}P\{^1H\}$ NMR ppm	yield (%)	$^{31}P\{^1H\}$ NMR ppm
a	en[c]	78[d]	62.9	82[d]	74.0
b	dach	75[e]	60.8	54[f]	74.0
c	dpen	79[d,g]	59.2		
d	bn			86	68.3

[a] The synthesis of the complexes was carried out in MeCN with 2 equiv of KO^{t}Bu and 2 equiv of diamine. [b] The synthesis of complexes was carried out in MeOH with 2 equiv of NaOMe and 1 equiv of diamine. [c] Ethylenediamine. [d] Structure of the BF_4^- salt was confirmed by X-ray diffraction. [e] $[\alpha]_D^{27}$ + 1423° (c 0.22, CH_3CN). [f] $[\alpha]_D^{27}$ + 560° (c 0.24, CH_3CN); the structure of the $FeBr_4^{2-}$ salt was confirmed by X-ray diffraction. [g] $[\alpha]_D^{27}$ + 1087° (c 0.48, CH_3CN).

We then tried a multicomponent template reaction by introducing $[Fe(H_2O)_6][BF_4]_2$ into the reaction mixture (Scheme 1, template route; Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture containing the iron (II) precursor, **4**, and a base in acetonitrile showed the presence of the free monomer of the phosphino-aldehyde and several iron−phosphine complexes with peaks in the 20−45 ppm region. Subsequent addition of the diamine resulted in the instantaneous formation of the new *mer*-bis-tridentate complexes **5a−c** with novel P−N−N ligands as the BF_4^- salts. These were crystallized in low yield as the BF_4^- or $FeBr_4^{2-}$ salts or were converted to the BPh_4^- salts by the addition of $NaBPh_4$ and were isolated in good yield (Table 1).

In each case, a singlet is observed in the $^{31}P\{^1H\}$ NMR spectrum. The singlet for the chiral complexes **5b** and **5c** shows that these complexes form with complete diastereoselectivity at iron. The X-ray crystal structure of **5c** shows that the configuration at iron is *S* (Λ) (Figure 1).[35] These are the first enantiopure *mer*-bis-tridentate complexes of iron. The synthesis of *mer*-bis-tridentate N-glucoside complexes of Ni^{2+} and Zn^{2+} derived from diamines and D-glucosamine is the only other example that uses a template approach to make chiral *mer*-bis-tridentate complexes.[36] This easy templating of P−N−N compounds provides a convenient method for the stereoselective monofunctionalization of diamines.

If the reaction mixture containing the bis-tridentate complex is left in solution overnight, a small amount of the desired tetradentate P−N−N−P complex (**6a**,**b**) forms as indicated by a new singlet in the ^{31}P NMR spectrum. A reflux of the reaction mixture containing the bis-tridentate complex

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(18) Yeo, W.-C.; Chen, S.; Tan, G.-K.; Leung, P.-H. *J. Organomet. Chem.* **2007**, *692*, 2539–2547.
(19) Battle, A. R.; Edwards, P. G.; Haigh, R.; Hibbs, D. E.; Li, D. M.; Liddiard, S. M.; Newman, P. D. *Organometallics* **2007**, *26*, 377–386.
(20) Albers, T.; Edwards, P. G. *Chem. Commun.* **2007**, 858–860.
(21) Edwards, P. G.; Whatton, M. L. *Dalton Trans.* **2006**, 442–450.
(23) Yeo, W.-C.; Tang, L.; Yan, B.; Tee, S.-Y.; Koh, L. L.; Tan, G.-K.; Leung, P.-H. *Organometallics* **2005**, *24*, 5581–5585.
(24) Leung, P.-H. *Acc. Chem. Res.* **2004**, *37*, 169–177.
(25) Bergamini, P.; Bertolasi, V.; Milani, F. *Eur. J. Inorg. Chem.* **2004**, *2004*, 1277–1284.
(26) Price, A. J.; Edwards, P. G. *Chem. Commun.* **2000**, 899–900.
(27) Lebbe, T.; Machnitzki, P.; Stelzer, O.; Sheldrick, W. S. *Tetrahedron* **1999**, *56*, 157–164.
(28) Brauer, D. J.; Gol, F.; Hietkamp, S.; Peters, H.; Sommer, H.; Stelzer, O.; Sheldrick, W. S. *Chem. Ber.* **1986**, *119*, 349–365.
(29) Bartsch, R.; Hietkamp, S.; Morton, S.; Peters, H.; Stelzer, O. *Inorg. Chem.* **1983**, *22*, 3624–3632.
(30) Jeffery, J. C.; Odell, B.; Stevens, N.; Talbot, R. E. *Chem. Commun.* **2000**, 101–102.
(31) Matt, D.; Ziessel, R.; De Cian, A.; Fischer, J. *New J. Chem.* **1996**, *20*, 1257–1263.
(32) Imamoto, T.; Kusumoto, T.; Susuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301–5303.
(33) Imamoto, T.; Oshiki, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244–5252.
(34) Pellon, P. *Tetrahedron Lett.* **1992**, *33*, 4451–4452.
(35) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385−415. (a) For complex **5c** (refer to Figure 1 for the atom numbering), P2 has priority #1, P1 has #2, and N2 (attached to P2) has #3. N2 is found counterclockwise from P1 around the P2−Fe axis. Therefore, the configuration of the complex is **Λ**.
(36) Yano, S.; Inoue, S.; Yasuda, Y.; Tanase, T.; Mikata, Y.; Kakuchi, T.; Tsubomura, T.; Yamasaki, M.; Kinoshita, I.; Doe, M. *J. Chem. Soc., Dalton Trans.* **1999**, 1851.

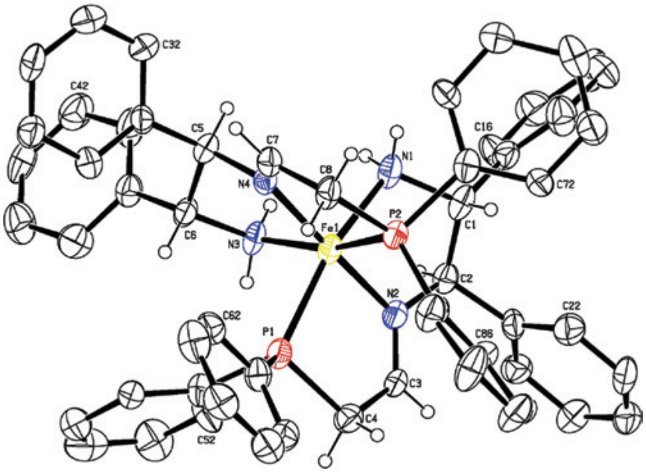

Figure 1. Crystal structure of the dication of complex **5c**.

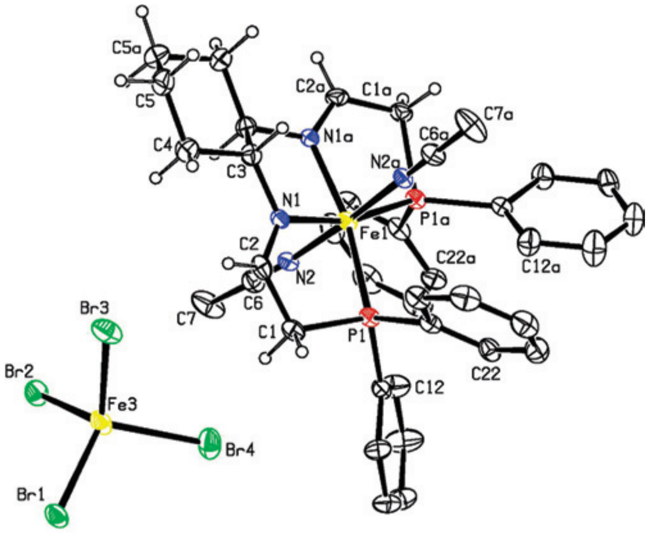

Figure 2. Crystal structure of complex **6b**.

resulted in full conversion of the P−N−N complexes to new P−N−N−P complexes **6a**,**b** along with paramagnetic impurities. The complexes crystallize from these solutions as the BF_4^- or $FeBr_4^{2-}$ salts. The structure of complex **6b** is shown in Figure 2. Although both **6b** and the previously reported complex **1**[13] are both prepared using the same diamine (*R*,*R*)-dach, there is a significant structural difference. Complex **6b** has a P−Fe−P angle of 109.81(8)° that is much wider than the corresponding P−Fe−P angle of 100.24(8)° for complex **1**. This is attributed to the five-, five-, and five-membered chelate rings in **6b** compared to the six-, five-, and six-membered rings in **1**. The structure of **6a** with five-, five-, and five-membered rings has an even wider P−Fe−P angle of 111.84(3)°.

Optimization of the conditions showed that the direct formation of the new complexes **6a**,**b** from **4** can be achieved at room temperature in MeOH with stoichiometric amounts of acetonitrile added (Scheme 3). The complexes were precipitated as the BPh_4^- salts in high yield (Table 1) and characterized by NMR, electrospray ionization mass spectrometry, and elemental analysis.

The formation of the bis-tridentate complex with dach in MeOH occurs instantaneously after the addition of the diamine in CH_3CN to the mixture, similar to the reaction of en. The conversion to the tetradentate complex **6b**, in contrast, occurs much slower than the reactions with en, possibly because dach is more rigid and basic. The template reaction of nonchiral o-phenylenediamine in either acetonitrile or methanol as the solvent gives only the tetradentate P−N−N−P complex *trans*-$[Fe(PPh_2CH_2CH{=}N{-}C_6H_4N{=}CHCH_2PPh_2)(MeCN)_2](BF_4)_2$ **6d**. The extended conjugation of the tetradentate ligand in **6d** likely increases its stability relative to the bis-tridentate complex.

In conclusion, we were able to synthesize in high yield and characterize a series of new enantiopure and nonchiral iron(II) P−N−N and P−N−N−P complexes using the air- and moisture-stable phosphino-aldehyde precursor **4** via a multicomponent template reaction. The applications of these new P−N−N−P iron(II) complexes as catalysts is currently under investigation by our group.

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Supporting Information Available: Experimental preparation of **4**−**6** (PDF) and crystallographic data of **5a**, **5c**, **6a**, and **6b** (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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