the measurements. The polarization measurements were conducted by applying a constant current (1 μA) between the two RuO_2 electrodes. The voltage was measured as a function of time at 700 °C. RuO_2 electrodes were utilized when the atmosphere contained Cl_2 because this would react with Pt electrodes. DC conductivity determination was based on the voltage, applied current, RuO_2 electrode surface area, and pellet thickness. Details of similar experiments are described elsewhere.[7]

The relative density and the Vickers hardness of the pellets were measured by a Micromeritics (AccuPyc 1330) porosimeter and a Shimadzu Micro Hardness Tester (HMV-2).

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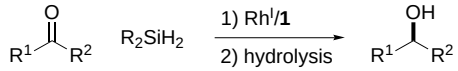
Application of a New Family of P,N Ligands to the Highly Enantioselective Hydrosilylation of Aryl Alkyl and Dialkyl Ketones**

Beata Tao and Gregory C. Fu*

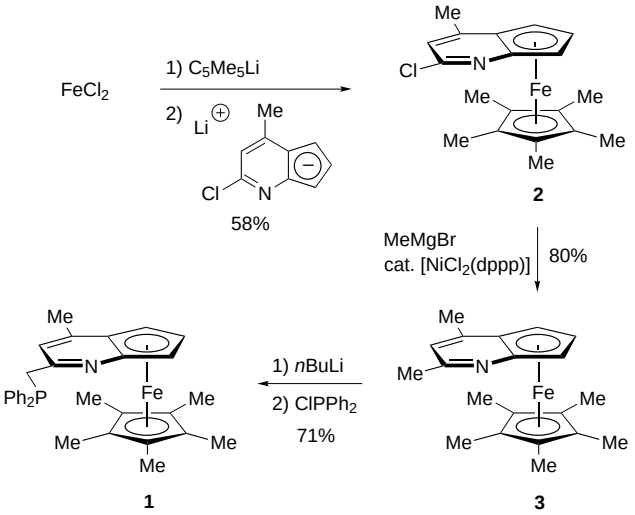
Due in large part to the utility of enantiomerically enriched alcohols and their selectively O-protected derivatives, considerable energy has been devoted to the search for efficient catalysts for the asymmetric hydrosilylation of ketones.[1] Very good enantioselectivities have been obtained for many aryl alkyl ketones, but for dialkyl ketones they are generally more modest. Seminal discoveries have resulted from these efforts, including the development of pybox, the first highly effective bis(oxazoline)-based ligand.[2,3]

During the past few years, we have been pursuing the design and development of new chiral ligands that are based on "planar-chiral" heterocycles,[4] and for several metal-catalyzed processes we have demonstrated that this family of ligands can provide enantioselectivity superior to the best methods that had previously been reported.[5] Here we describe the synthesis of a new planar-chiral P,N ligand, and we establish its exceptional efficiency in rhodium-catalyzed asymmetric hydrosilylations of aryl alkyl ketones and dialkyl ketones [Eq. (1)].



(1)

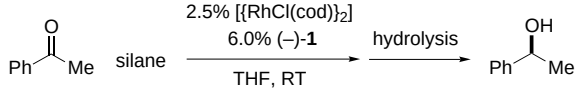
The synthesis of planar-chiral ligand **1** is illustrated in Scheme 1.[6] Treatment of $FeCl_2$ with C_5Me_5Li and then 2-chloro-4-methyl-7*H*-cyclopenta[b]pyridinyllithium affords ferrocene derivative **2**.[7] Kumada coupling of **2** with MeMgBr furnishes **3**, which is lithiated and then quenched with $ClPPh_2$ to provide ligand **1**, the enantiomers of which are readily resolved by chiral HPLC. We have determined the absolute configuration of (−)-**1** by X-ray crystallography.



Scheme 1. Synthesis of planar-chiral P,N ligand **1** (only (+)-**1** is depicted). dppp = 1,3-bis(diphenylphosphanyl)propane.

For an initial investigation of the utility of ligand **1**, we chose to focus on the rhodium-catalyzed asymmetric hydrosilylation of ketones. Specifically, we examined the reduction of acetophenone, and we discovered that the level of enantioselectivity is highly dependent on the choice of silane (Table 1). Thus, monoalkyl- and monoaryl silanes (entries 1 and 2), as well as dialkyl silanes (entry 3), furnish disappoint-

Table 1. Hydrosilylation of acetophenone catalyzed by Rh[I]/(−)-**1**: enantioselectivity as a function of the silane.



Entry	Silane	*ee* [%][a]
1	*n*-octylSiH$_3$	3
2	PhSiH$_3$	8
3	Et$_2$SiH$_2$	1
4	PhMeSiH$_2$	66
5	Ph$_2$SiH$_2$	80
6	*o*-TolPhSiH$_2$[b]	95
7	*o*-Tol$_2$SiH$_2$[b]	92
8	MesPhSiH$_2$[c]	98
9	Mes$_2$SiH$_2$[c]	(no reaction)

[a] Average of two runs. [b] Tol = tolyl. [c] Mes = Mesityl.

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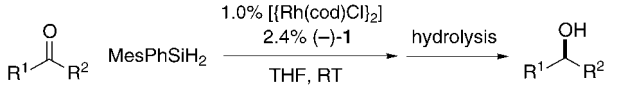
ing stereoselectivity (< 10% *ee*). In contrast, an aryl alkyl silane ($PhMeSiH_2$) provides moderate enantioselectivity (66% *ee*; entry 4), and diaryl silanes afford very good enantioselectivity (entries 5–8). Generally, as the steric demand of the aromatic group increases, the enantiomeric excess increases, reaching 98% in the case of $MesPhSiH_2$.[8] However, if the silane is extremely bulky, no hydrosilylation is observed under these conditions (entry 9).

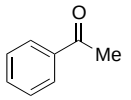
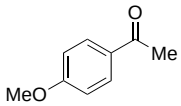
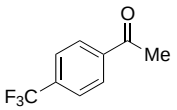
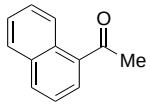
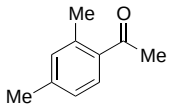
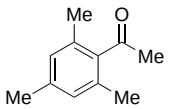
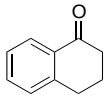
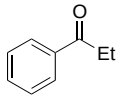
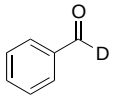
In the optimization study documented in Table 1, we employed a catalyst loading of 5%, but we subsequently determined that these asymmetric hydrosilylations proceed at a convenient rate with just 2% rhodium to afford the reduction of an array of aryl alkyl ketones with excellent enantioselectivity and yield (Table 2).[9] Thus, acetophenone is hydrosilylated cleanly in high enantioselectivity (entry 1), as are electronically varied derivatives (entries 2 and 3). Sterically demanding aryl methyl ketones are also reduced with exceptional stereoselectivity and yield (entries 4–6). If the alkyl group of the aryl alkyl ketone is larger than a methyl group, these rhodium-catalyzed hydrosilylations proceed rather slowly, albeit still with excellent enantioselectivity (3 days at room temperature; entries 7 and 8).[10] An aldehyde, [1-D]benzaldehyde, can also be reduced in high enantioselectivity (entry 9).[11–13]

We have also applied planar-chiral ligand **1** to catalytic asymmetric reductions of dialkyl ketones, which are typically more challenging substrates than aryl alkyl ketones.[14,15] For this class of compounds, *o*-Tol_2SiH_2[16] has provided the best stereoselectivity and the broadest scope among the silanes that we have surveyed. Thus, adamantyl methyl ketone is reduced in 96% *ee* and 92% yield (Table 3, entry 1). More challenging cyclohexyl methyl ketone is also hydrosilylated with excellent enantioselectivity (entry 2). Rh/**1** can even effect reductions of *n*-alkyl methyl ketones, a quite formidable family of substrates, with good asymmetric induction (entries 3 and 4). Interestingly, the *ee* values provided in Table 3 are comparable to or even better than the best that can be obtained through enantioselective hydrogenation of dialkyl ketones.[17]

In summary, we have designed a new class of planar-chiral ligands, and we have applied one member to the catalytic asymmetric hydrosilylation of ketones. For a broad spectrum of substrates—aryl alkyl ketones as well as dialkyl ketones—a single catalyst system, Rh/**1**, furnishes consistently excellent enantioselectivities and yields. In terms of both scope and stereoselectivity, this method compares favorably with previously described catalysts for this process. Future work will explore optimization of the ligand design (e.g., variation of the cyclopentadienyl ring and of the phosphanyl group) and the application of this new family of chiral ligands to a range of interesting reactions.

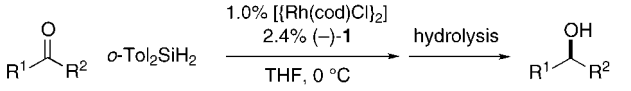
Table 2. Catalytic asymmetric hydrosilylation of aryl alkyl ketones.

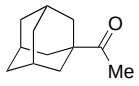
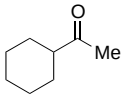
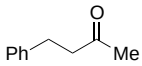
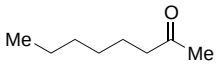


Entry	Ketone	*ee* [%][a]	Yield [%][a]
1		98	94
2		97	97
3		96	88
4		99	97
5		95	97
6		98	99
7		98	95
8		98	96
9		95[b]	74

[a] Average of two runs. [b] (*R*)-[α-D]Benzyl alcohol is generated preferentially.

Table 3. Catalytic asymmetric hydrosilylation of dialkyl ketones.



Entry	Ketone	*ee* [%][a]	Yield [%][a]
1		96	92
2		94	91
3		82	98
4[b]		72	81

[a] Average of two runs. [b] Reaction carried out at −20 °C.

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[6] For a review of the use of phosphanyl–pyridyl ligands, see: P. Espinet, K. Soulantica, *Coord. Chem. Rev.* **1999**, *193*–195, 499 – 556.
[7] R. Rios, J. Liang, M. M.-C. Lo, G. C. Fu, *Chem. Commun.* **2000**, 377 – 378.
[8] $MesPhSiH_2$ can be synthesized in one step by treating Ph_2SiH_2 with TfOH and MesMgBr.
[9] Notes: a) Comparable enantioselectivity is observed in THF, Et_2O, toluene, and CCl_4; b) a small enhancement in enantioselectivity is obtained at lower temperature; c) the stereoselectivity does not appear to be dependent on the concentration.
[10] In the case of isopropyl phenyl ketone, we observe good enantioselectivity (86 % *ee*), but a very slow reaction rate (14 % conversion after 5 days with a 5 % catalyst loading).
[11] The modest yield is due to the volatility of the product.
[12] For leading references to uses of enantiopure [α-D]benzyl alcohol, see: a) I. Sato, D. Omiya, T. Saito, K. Soai, *J. Am. Chem. Soc.* **2000**, *122*, 11739 – 11740; b) I. Yamada, R. Noyori, *Org. Lett.* **2000**, *2*, 3425 – 3427.
[13] For an unsymmetrical disubstituted silane such as $MesPhSiH_2$, there is the potential for differentiation by the chiral catalyst of the two enantiotopic Si–H bonds. We have established that Rh/**1** can in fact efficiently distinguish between the two; thus, for the reaction of $MesPhSiH_2$ with acetone, $MesPhSiH(OCHMe_2)$ is generated in 97 % *ee*. For leading references to the synthesis and applications of "Si-chiral" silanes, see: T. H. Chan, D. Wang, *Chem. Rev.* **1992**, *92*, 995 – 1006.
[14] For examples of asymmetric hydrosilylation catalysts that are effective for aryl alkyl ketones but relatively ineffective for dialkyl ketones, see: a) H. Mimoun, J. Yves de Saint Laumer, L. Giannini, R. Scopelliti, C. Floriani, *J. Am. Chem. Soc.* **1999**, *121*, 6158 – 6166; b) J. Yun, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 5640 – 5644.
[15] Until now, taking into account both scope and enantioselectivity, the best catalysts for asymmetric hydrosilylations of dialkyl ketones were rhodium complexes of Ito's TRAP family of ligands: a) R. Kuwano, T. Uemura, M. Saitoh, Y. Ito, *Tetrahedron Lett.* **1999**, *40*, 1327 – 1330; b) R. Kuwano, M. Sawamura, J. Shirai, M. Takahashi, Y. Ito, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 485 – 496. The Rh/TRAP catalysts provide good, but not exceptionally high, enantioselectivities for hydrosilylations of aryl alkyl ketones. See also: D. K. Heldmann, D. Seebach, *Helv. Chim. Acta* **1999**, *82*, 1096 – 1110; Y. Nishibayashi, K. Segawa, K. Ohe, S. Uemura, *Organometallics* **1995**, *14*, 5486 – 5487.
[16] *o*-Tol_2SiH_2 can be synthesized in one step by treating $HSiCl_3$ with *o*-TolMgBr and $LiAlH_4$.
[17] Dialkyl ketones have proved to be very challenging substrates for asymmetric hydrogenation catalysts. a) For overviews, see: T. Ohkuma, R. Noyori in *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, New York, **1999**, chap. 6.1; V. Fehring, R. Selke, *Angew. Chem.* **1998**, *110*, 1927 – 1930; *Angew. Chem. Int. Ed.* **1998**, *37*, 1827 – 1830; b) Q. Jiang, Y. Jiang, D. Xiao, P. Cao, X. Zhang, *Angew. Chem.* **1998**, *110*, 1203 – 1207; *Angew. Chem. Int. Ed.* **1998**, *37*, 1100 – 1103.

Design Optimization of 1,3-Diphospha-2,4-diboretane Diradicals**

Mark Seierstad, Christopher R. Kinsinger, and Christopher J. Cramer*

Diradicals may be defined as molecules having an even number of electrons and a narrow separation between their highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively).[1–4] Degeneracy of these orbitals is also a possibility. Diradicals share a number of characteristic features associated with having frontier MO energies that are similar. They tend, for instance, to exhibit relatively small energy splittings between their lowest energy singlet and triplet states (ΔE_{S-T}) and between their lowest energy and first excited singlet states, where the latter splitting is associated with a long-wavelength absorption in the ultraviolet/visible (UV/Vis) spectrum of the lower energy state.

A large number of organic diradicals are known, although they are almost exclusively characterized as reactive intermediates. Typical single-center diradicals include carbenes,[5–9] nitrenes,[5,10–13] and nitrenium ions,[14–16] and well known multicenter diradicals include didehydroarenes[5,17–20] (e.g., benzynes) and non-Kekulé hydrocarbons like trimethylenemethane[21–24] and tetramethyleneethane.[21,25–27] An example of a diradical system that has been known since the pioneering work of Huckel in the 1930s is a high-symmetry "antiaromatic" cycloarene having $4n$ electrons and $4n$ ring atoms. All-carbon examples such as cyclobutadiene and cyclooctatetraene, however, are well known to lift the degeneracy of their frontier orbitals by distorting from D_{nh} structures to geometries belonging to lower symmetry point groups (although this by no means precludes their possible continuing description as diradicals).[1,28,29] A key to success, then, in the design of any diradical, is to engineer the molecular and electronic structure in such a way that the frontier orbital separation remains as small as possible.[30–32]

Recently, Scheschkewitz et al.[33] reported that the reaction of lithium diisopropylphosphide with 1,2-di-*tert*-butyl-1,2-dichlorodiborane provided an isolable 1,3-diphospha-2,4-diboretane product **1d** (Scheme 1) having a long-wavelength UV absorption (446 nm) consistent with it having substantial diradical character, in spite of its thermal stability. Such character is easily inferred from consideration of the simplest resonance structure that may be drawn for **1d**, which places positive charges on the P atoms and a negative charge and one formally unpaired electron on each of the B atoms (Scheme 1).

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