



Synthesis, structure, and catalytic behavior of a PSiP pincer-type iridium(III) complex

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ABSTRACT

The synthesis and characterization of a novel cyclometalated Iridium(III) complex [IrCl(H)(PSiP)] containing monoanionic, tridentate coordinating PSiP-pincer ligands $[\kappa^3\text{-(2-}^i\text{Bu}_2\text{PC}_6\text{H}_4)_2\text{SiMe}]^-$ ([PSiP]) is reported. Complex (**3**) is one of the few examples of bis(phosphino)silyl(hydrido)iridium(III) complexes structurally characterized by single crystal X-ray analysis. This compound has also been shown to catalyze the transfer hydrogenation of ketones to the corresponding secondary alcohols moderately with 2-propanol as the hydrogen source instead of using molecular dihydrogen gas or hazardous reducing agents (e.g., NaBH_4 and LiAlH_4), and $^i\text{BuOK}$ as the base.

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Cyclometalated phosphine-based “PCP” pincer complexes of the transition-metals have been the subject of intense research since the initial investigations of this type of “PCP” ligands by Shaw et al. [1], owing to the remarkable stoichiometric and catalytic reactivity exhibited by such complexes [2,3]. Recently, significant effort has been devoted to the synthesis of structurally and/or electronically related systems where strategic alterations have been introduced to the pincer ligand architecture, including variation of the central and peripheral donor fragments, as well as the ancillary ligand backbone [4]. However, the “PSiP” pincer-like transition metal complexes have rarely been reported [5]. Although metal–silicon chemistry is well-precedented across the transition series, relatively little attention has been given to the incorporation of silyl donor fragments into the framework of a preformed tridentate and tetradentate ancillary ligand. Silyl ligands have strong σ -donating characters and show a stronger trans influence than do commonly used ligands in transition metal chemistry [6]. Silyl ligands would make an electron-rich metal center and coordinatively unsaturated species by its strong trans-labilizing effect. Therefore, “ancillary” silyl ligands would provide transition metal complexes having unique reactivities useful for catalysis. We have been working on the reaction of chelating disilyl

compounds with group 10 transition metal complexes and obtained a number of unusual complexes bearing chelating silyl ligands [7]. Over the course of the research, we found simple silyl ligands usually have high reactivity and cannot stay on transition metals as “ancillary” ligands. Incorporation of silyl group in a multidentate ligand framework would be a useful strategy to make “ancillary” silyl ligands. There are two types of approaches for this kind of silyl ligands: 1) incorporation of one silyl group at the center of multidentate framework [8], and 2) attachment of two silyl groups in a rigid multidentate framework. The second approach is so far rather limited and the xanthosil ligand by Tobita and co-workers is a representative example [9]. Recently, transition metal complexes bearing other tridentate N_2Si , and S_2Si type ligands as well as tetradentate P_3Si and S_3Si type ligands have also been reported [10].

Hydrogen transfer catalysis is an attractive protocol for the reduction of ketones to alcohols in both academic and industrial research. The use of a hydrogen donor (e.g., 2-propanol) instead of using molecular dihydrogen gas or hazardous reducing agents (e.g., NaBH_4 and LiAlH_4) has a potential advantage in terms of mild reaction conditions and excellent regioselectivity.¹¹ Many pincer-like transition metal complexes of Ru, Ir, and Rh have been found to be active catalysts in (a)symmetric hydrogen transfer reactions of polar groups (e.g., ketones and imines) [11]. In recent years, a number of studies appeared on the successful use of cyclometalated ruthenium(II) complexes containing tridentate, cyclometalated PCP^- , and NCN^- as catalyst precursors in hydrogen transfer reactions [12]. The great interest in the use of *E,C,E*-pincer ligands (*E* = N, P) arises from the remarkable stability of the corresponding metal complexes and the

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possibility to modulate the reactivity of the metal center by fine-tuning and control of the electronic and steric properties of the ligand framework [13].

We are interested in $[(2-(R_2P)C_6H_4)_2MeSi]^-$ ligands ($=PSiP-R$, $R = Cy, ^tBu, ^iPr$), which would have high electron donating property and higher rigidity than do $[(Ph_2P(CH_2)_n)_2MeSi]^-$ ligands [14]. Herein we report the synthesis and structure of a novel cyclometalated iridium (III) complex $[IrCl(H)(PSiP^{tBu})]$ (**3**) containing monoanionic, tridentate coordinating PSiP-pincer ligands $[\kappa^3-(2-^tBu_2PC_6H_4)_2SiMe]^-$ ($[PSiP^{tBu}]$) (Fig. 1), and its catalytic activity in the transfer hydrogenation of ketones with 2-propanol as the hydrogen source and tBuOK as the base. Dialkyl (aliphatic and cyclic), alkyl aryl, and diaryl ketones were all reduced in a moderate yield by this PSiP Ir(III) complex (**3**).

Treatment of the parent tertiary silane, $[PSiP]H$ (**2**) with 0.5 equiv of $[IrCl(COD)]_2$ ($cod = 1,4\text{-cyclooctadiene}$) in dry toluene at $80^\circ C$ resulted in oxidative addition of the Si–H bond to the Iridium (I) center to give a 16-electron Ir(III)–(κ^3 -PSiP) complex in high yields (Scheme 1; isolated yield ca. 90%) [15]. Crystallization of compound (**3**) from benzene afforded X-ray quality single crystals, and its structure was unambiguously confirmed by single-crystal X-ray structure analysis (Fig. 1) [16,17]. To the best of our knowledge, there are only more than 10 examples of bis(phosphino)silyl(hydrido) iridium (III) complexes structurally characterized by single crystal X-ray analysis [14]. Complex (**3**) crystallizes in the monoclinic group $P2_1/c$ (Table 1). The pincer-like title compound contains two stable five-membered cyclometalated rings with the P–Ir–Si angles of $85.92(3)$ and $85.70(4)^\circ$. The Ir atom is coordinated by two P atoms, one Si atom, one Cl atom and one H atom in a distorted square-pyramidal geometry, in which the silyl group occupies the apical coordination site, while the remaining phosphine arms of the $[PSiP]$ ligand, the Cl and H atoms occupy basal sites. The bond distances of Ir1–Si1 and Ir1–Cl1 are 2.2668(9) and 2.3994(8) Å, respectively, which are similar to the other Ir analogue with pincer-like tridentate PSiP ligand, $Ir(H)[SiMe(CH_2CH_2CH_2PPh_2)_2]Cl$ [14]. The two P donor atoms are almost in a *trans* arrangement with a P1–Ir1–P2 angle of $161.99(2)^\circ$, the methyl group on Si1 donor in compound (**3**) is positioned *trans* to hydrido group, and *cis* to Cl, with a Cl(1)–Ir(1)–H(52) angle of $163.0(13)^\circ$. The two phenyl rings are, of course, planar, which are oriented at a dihedral angle of $89.49(2)^\circ$ (Table 2). 1H NMR spectroscopy of compound (**3**) showed the Ir–H signal as triplets with small $^2J(P,H)$ value of 14 Hz at around -23 ppm suggesting a *cis* relationship of the H and the two P atoms.

Based on our synthetic investigations of $[PSiP]$ -ligated metal complexes, we have begun to examine the utility of such species as catalysts in a range of substrate transformations. In particular, we are interested in exploring how the substitution of Si for C in a rigid tridentate ancillary ligand framework influences metal-mediated

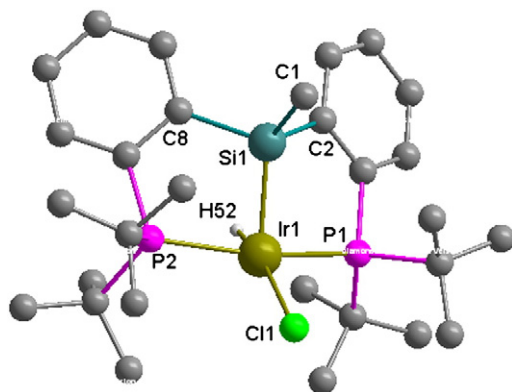
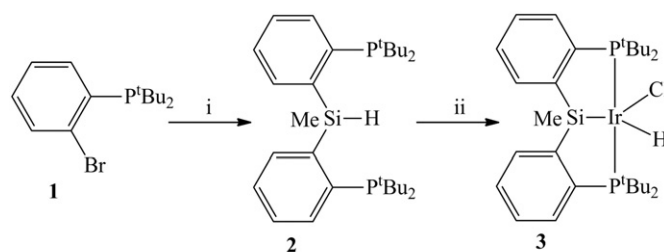


Fig. 1. The structure of **3**, showing the coordination environment of Ir atom. The hydrogen atoms are omitted for clarity.



Reagents: (i) $n\text{-BuLi}$, $\text{CH}_3\text{SiHCl}_2$; (ii) $[IrCl(COD)]_2$.

Scheme 1. Synthetic route of organosilicon complex Ir-(κ^3 -PSiP) (**3**).

reactivity, given the strong electron donating and *trans*-labilizing abilities of Si. Reduction by means of hydrogen-transfer reactions has recently attracted much attention because of its practical simplicity and potential use at ambient pressure. Furthermore, the use of an alternative source of hydrogen may result in different reactivity patterns [18]. Recently, several Ru(II) PCP $^-$, NCN $^-$, CNC $^-$, and CNN $^-$ pincer complexes have been shown to catalyze the transfer hydrogenation of ketones [19], and it has been proposed that the metal–C σ -bond plays an important role in the formation of long-lived, catalytically active species [20]. In this context, we became interested in surveying the catalytic activity of iridium(III) complex $[Ir(H)Cl(PSiP)]$ (**3**) containing monoanionic, tridentate coordinating PSiP-pincer ligand in the transfer hydrogenation of ketones, employing basic iPrOH as the hydrogen source. When employing 0.2 mol% of compound (**3**) with 5 mol% of KO^tBu at $80^\circ C$, moderate conversion to the corresponding secondary alcohols was observed for several ketone substrates, including diaryl, dialkyl, and alkyl/aryl ketones (Scheme 2). Although conditions have not yet been optimised, it is obvious that the activity of compound (**3**) as a catalyst in this reaction is comparable to that observed with phosphinosilyl complexes that feature an aliphatic or benzylic ligand backbone, and we found that reduced conformational rigidity associated with the flexible *o*-tertbutyl backbone of $[PSiP]$ could provide moderate stability and selectivity in metal-mediated substrate transformations and the representative catalytic data obtained in our preliminary survey are summarized in Table 3. The reactions are slow at room

Table 1
Crystal data and structure refinement parameters for **3**.

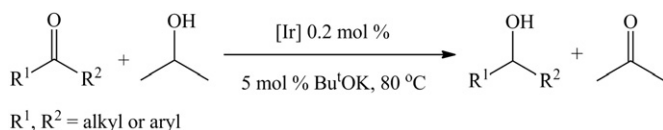
Structure parameters	3
Empirical formula	$C_{29}H_{48}ClIrP_2Si$
fw	714.35
cryst syst	monoclinic
space group	$P2_1/c$
<i>a</i> (Å)	12.291(3)
<i>b</i> (Å)	15.050(2)
<i>c</i> (Å)	16.500(3)
α ($^\circ$)	90.00
β ($^\circ$)	98.57(3)
γ ($^\circ$)	90.00
<i>V</i> (Å ³)	3017.8(11)
<i>Z</i>	4
<i>T</i> (K)	153(2)
<i>F</i> (000)	1440
ρ (g cm ^{−3})	1.572
absorption coefficient (mm ^{−1})	4.675
goodness of fit on <i>F</i> ²	0.941
total no. of data collected	21955
no. of unique data	6935
<i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	$R_1 = 0.0217$ $wR_2 = 0.0435$
<i>R</i> (all data)	$R_1 = 0.0263$ $wR_2 = 0.0441$
largest diff map hole and peak (e Å ^{−3})	0.099 and -0.515
$R1 = \sum F_o - F_c / \sum F_o $; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.	

Table 2
Selected bond lengths and angles for **3**.

Ir(1)–P(1)	2.3251(7)	Ir(1)–P(2)	2.3270(8)
Ir(1)–Cl(1)	2.3994(8)	Ir(1)–Si(1)	2.2668(9)
Si(1)–C(1)	1.886(3)	Si(1)–C(2)	1.898(3)
Si(1)–C(8)	1.897(3)	Ir(1)–H(52)	1.43(3)
C(2)–Si(1)–C(8)	105.04(15)	P(1)–Ir(1)–P(2)	161.99(2)
P(1)–Ir(1)–Cl(1)	99.19(3)	P(2)–Ir(1)–Cl(1)	98.60(3)
C(1)–Si(1)–C(2)	104.63(12)	P(1)–Ir(1)–Si(1)	85.92(3)
P(2)–Ir(1)–Si(1)	85.70(4)	C(1)–Si(1)–Ir(1)	120.62(10)
C(2)–Si(1)–Ir(1)	106.29(9)	Cl(1)–Ir(1)–H(52)	163.0(13)

temperature but proceed at good rates at 80 °C and the catalyst system hydrogenates aliphatic ketones faster than aromatic ones. As is the case for most metal-catalyzed transfer hydrogenation processes conducted in ⁱPrOH, less than 5% conversion was observed in the absence of KO^tBu as base. The preformed Ir complex (**3**) was similarly inactive for transfer hydrogenation of cyclohexanone in the absence of added KO^tBu, although 82% conversion was obtained when using 5 mol% KO^tBu along with 0.2 mol% **3** (entry 6, Table 3). Furthermore, these data show that the stability provided by the chelate ligand, and the potential for electronic/coordination unsaturation are possible reasons for the activity observed. These preliminary results establish [PSiP]Ir complexes as a promising class of precatalysts for transfer hydrogenation. Further mechanistic studies of this reaction, as well as catalytic studies featuring these and other [PSiP] derivatives, are currently in progress.

In this contribution, convenient access to an Ir-(κ³-PSiP) complex with the bulky ligand [κ³-(2-^tBu₂PC₆H₄)₂SiMe][−] has been established from [IrCl(COD)]₂. We report the synthesis and preliminary coordination chemistry studies of the new coordinatively unsaturated group 9 pincer-like complex supported by the bis(phosphino)silyl ligand [κ³-(2-^tBu₂PC₆H₄)₂SiMe][−], as well as a preliminary investigation of the catalytic utility of [PSiP]Ir species in the transfer hydrogenation of ketones. The pincer-like iridium(III) complex (**3**) has been found to display a moderate catalytic activity in the reduction of various ketones to the corresponding alcohols with ⁱPrOH as the hydrogen source and KO^tBu as the promoter. Under these conditions, the Ir–Si σ bond is stable and the [Ir(PSiP)Cl] fragment is preserved. The isolation of free ‘pincer’ type bis(phosphino)silyl ligands has opened new and easy synthetic routes to a variety of complexes with wide scope for functionalisation and catalyst optimisation and tuning. The synthesis of other ‘pincer’ complexes with catalytically important metals using this methodology is under way.



Scheme 2. Transfer Hydrogenation of Ketones.

Table 3
Transfer Hydrogenation of Ketones.

entry	catalyst	substrate	time (h)	conversion (%)
1	3	acetophenone	6	72
2	3	benzophenone	5	70
3	3	p-methyl acetophenone	6.5	69
4	3	2-heptanone	4	78
5	3	cyclopentanone	3	80
6	3	cyclohexanone	3	82

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Appendix A. Supplementary data

CCDC-821325 contains the supplementary crystallographic data for compound (**3**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.inoche.2011.05.018.

References

- [1] C.J. Moulton, B.L. Shaw, Transition metal–carbon bonds .42. complexes of Nickel, Palladium, Platinum, Rhodium and Iridium with tridentate ligand 2,6-bis[(di-*t*-butylphosphino)methyl]phenyl, *J. Chem. Soc. Dalton Trans.* (1976) 1020–1024.
- [2] (a) P. White, M. Brookhart, Iridium bis(phosphinite) p-PCP pincer complexes: Highly active catalysts for the transfer dehydrogenation of alkanes, *J. Am. Chem. Soc.* 126 (2004) 1804–1811; (b) M. Cezrw, K. Zhu, K.B. Renkema, A.S. Goldman, Combined computational and experimental study of substituent effects on the thermodynamics of H-2, CO, arene, and alkane addition to iridium, *J. Am. Chem. Soc.* 124 (2002) 10797–10809; (c) F. Liu, E.B. Pak, A.S. Goldman, Dehydrogenation of n-alkanes catalyzed by iridium “pincer” complexes: Regioselective formation of alpha-olefins, *J. Am. Chem. Soc.* 121 (1999) 4086–4087; (d) M.W. Hanel, W.C. Kaska, M.B. Hall, Thermally stable homogeneous catalysts for alkane dehydrogenation, *Angew. Chem. Int. Ed.* 40 (2001) 3596–3597.
- [3] (a) R. Redon, C. Yung, C.M. Jensen, PdCl(C₆H₅(OPPr₂))(2)–2,6], *Chem. Commun.* (2000) 1619–1620; (b) F. Miyazaki, K. Yamaguchi, M. Shibasaki, The synthesis of a new palladacycle catalyst. Development of a high performance catalyst for Heck reactions, *Tetrahedron Lett.* 40 (1999) 7379–7383; (c) M. Ohff, A. Ohff, D. Milstein, Highly active Pd(II) PCP-type catalysts for the Heck reaction, *J. Am. Chem. Soc.* 119 (1997) 11687–11688.
- [4] (a) L.C. Liang, Metal complexes of chelating diarylamido phosphine ligands, *Coord. Chem. Rev.* 250 (2006) 1152–1177; (b) L.C. Liang, J.M. Lin, C.H. Hung, Nickel(II) complexes of bis(2-diphenylphosphinophenyl)amide, *Organometallics* 22 (2003) 3007–3009; (c) A.M. Winter, K. Eichele, H.G. Mack, W.C. Kaska, Rhodium pincer complexes of 2,2′-bis(diphenylphosphino)diphenylamine, *J. Organomet. Chem.* 682 (2003) 149–154; (d) S.B. Harkins, J.C. Peters, A highly emissive Cu₂N₂ diamond core complex supported by a [PNP](–)ligand, *J. Am. Chem. Soc.* 127 (2005) 2030–2031; (e) B.C. Bailey, E.W. Baum, J.C. Huffman, O.V. Ozerov, Remarkably stable titanium complexes containing terminal alkylidene, phosphinidene, and imide functionalities, *Organometallics* 24 (2005) 1390–1393; (f) W. Weng, C. Guo, B.M. Foxman, Skeletal change in the PNP pincer ligand leads to a highly regioselective alkyne dimerization catalyst, *Chem. Commun.* (2006) 197–199; (g) L. Fan, B.M. Foxman, O.V. Ozerov, N–H cleavage as a route to palladium complexes of a new PNP pincer ligand, *Organometallics* 23 (2004) 326–328.
- [5] (a) M. Stradiotto, K.L. Fudala, T.D. Tilley, Iridium(III) complexes of the new tridentate bis(8-quinolyl)silyl (‘NSiN’) ligand, *Chem. Commun.* (2001) 1200–1201; (b) D.F. MacLean, R. McDonald, M.J. Ferguson, L. Turculet, Room temperature benzene C–H activation by a new [PSiP]Ir pincer complex, *Chem. Commun.* (2008) 5146–5148; (c) S.J. Mitton, R. McDonald, L. Turculet, Nickel and Palladium silyl pincer complexes: unusual structural rearrangements that involve reversible Si–C (sp³) and Si–C(sp²) bond activation, *Angew. Chem. Int. Ed.* 48 (2009) 8568–8571; (d) J. Takaya, N. Iwasawa, Hydrocarboxylation of Allenes with CO₂ Catalyzed by Silyl Pincer-Type Palladium Complex, *J. Am. Chem. Soc.* 130 (2008) 15254–15255; (e) J. Takaya, N. Iwasawa, Bis(o-phosphinophenyl) silane as a Scaffold for Dynamic Behavior of H–Si and C–Si Bonds with Palladium(0), *Organometallics* 28 (2009) 6636–6638; (f) E.E. Korshin, G. Leitus, L.J.W. Shimon, D. Milstein, Silanol-based pincer pt(II) complexes: Synthesis, structure, and unusual reactivity, *Inorg. Chem.* 47 (2008) 7177–7189.
- [6] J. Zhu, Z.Y. Lin, T.B. Marder, Trans influence of boryl ligands and comparison with C, Si, and Sn ligands, *Inorg. Chem.* 44 (2005) 9384–9390.
- [7] (a) Y.H. Li, S. Shimada, (dimethylsilyl)-2-silylbenzene and [(1,2-C₆H₄(SiMe₂)(SiH₂)) Pd(R₂PCH₂CH₂PR₂)], *Organometallics* 29 (2010) 4406–4409; (b) Y.H. Li, S. Shimada, Reaction of 1-(dimethylsilyl)-2-silylbenzene with platinum(0) phosphine complex: Isolation and characterization of the Si-3-Pt-IV-H complex, *J. Organomet. Chem.* 695 (2010) 2057–2061;

- (c) S. Shimada, Y.H. Li, Y.K. Choe, M. Tanaka, M. Bao, T. Uchimar, Multinuclear palladium compounds containing palladium centers ligated by five silicon atoms, *Proc. Natl. Acad. Sci. U. S. A.* 104 (2007) 7758–7763;
- (d) S. Shimada, Y.H. Li, M.L.N. Rao, M. Tanaka, A. (Pt₂Si₂)-Si-III four-membered cycle and a dinuclear platinum complex bridged by a cyclodisiloxane ring, *Organometallics* 25 (2006) 3796–3798.
- [8] M.J. Auburn, S.R. Stobart, (Phosphinoalkyl)silyl complexes. 5. synthesis and reactivity of congeneric chelate-stabilized disilyl complexes of Rhodium(III) and Iridium(III) - chelobis[(diphenylphosphino)ethyl]dimethylsilyl]Rhodium and Iridium, *Inorg. Chem.* 24 (1985) 318–323. (b) F.L. Joslin, S.R. Stobart, Synthesis and structure of a silyl-Rhodium(I) complex - stabilization attributable to multisite anchoring of a silyl fragment, *J. Chem. Soc., Chem. Commun.* (1989) 504–505. (c) F.L. Joslin, S.R. Stobart, (Phosphinoalkyl)silanes. 2. synthesis and spectroscopic properties of the poly(phosphinoalkyl)silanes SiHR[(CH₂)NPR'₂]₂ (R = Me OR Ph N = 2 OR 3 R' = Ph or cyclohexyl) and SiH[(CH₂)NPR'₂]₃ (R = Me OR Ph N = 2, R' = Ph or cyclohexyl N = 3, R' = Ph), *Inorg. Chem.* 32 (1993) 2221–2223. (d) R.A. Gossage, G.D. McInnes, S.R. Stobart, (Phosphinoalkyl)silanes. 3. Poly(o-(diphenylphosphino)benzyl)silanes: Synthesis, spectroscopic properties, and complexation at platinum or iridium, *Inorg. Chem.* 35 (1996) 1729–1730. (e) R.D. Brost, G.C. Bruce, F.L. Joslin, S.R. Stobart, Phosphinoalkylsilyl complexes. 12. Stereochemistry of the tridentate bis(diphenylphosphinopropyl)silyl (biPSi) framework: Complexation that introduces "face discrimination" at coordinatively unsaturated metal centers. X-ray crystal and molecular structures of Pt[SiMe(CH₂CH₂CH₂PPh₂)(2)]Cl, IrH[SiMe(CH₂CH₂CH₂PPh₂)(2)]Cl, and RuH[SiMe(CH₂CH₂CH₂PPh₂)(2)](CO), *Organometallics* 16 (1997) 5669–5680;
- (f) X.B. Zhou, S.R. Stobart, Stereomutation at an octahedral transition-metal center: Energetics of hydride transit between syn and anti faces of the bis(diphenyl phosphinopropyl) (methyl)silyl (biPSi) complex RuH(biPSi)(CO) (2), *Organometallics* 20 (2001) 1898–1900.
- [9] (a) H. Tobita, K. Hasegawa, J.J.G. Minglana, H. Ogino, Extremely facile arene exchange on a ruthenium(II) complex having a novel bis(silyl) chelate ligand (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)(xantsil), *Organometallics* 18 (1999) 2058–2060;
- (b) J.G. Minglana, M. Okazaki, H. Ogino, Coordinatively unsaturated Ru(II) species Ru(xantsil)(CO): A new active catalyst for oligomerization/deoligomerization of HSiMe₂SiMe₃ [xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)], Isolation of a stabilized form of the silyl(silylene) intermediates, *Chem. Lett.* (2002) 406–407;
- (c) H. Tobita, N. Yamahira, M. Okazaki, New hydrosilylation reaction of arylacetylene accompanied by C–H bond activation catalyzed by a xantsil ruthenium complex, *Pure Appl. Chem.* 80 (2008) 1155–1160;
- (d) M. Okazaki, N. Yamahira, J.J.G. Minglana, H. Tobita, Ru(xantsil)(CO)(eta(6)-toluene)]: Synthon for a highly unsaturated ruthenium(II) complex through facile dissociation of the toluene ligand [xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)], *Organometallics* 27 (2008) 918–926.
- [10] (a) M. Stradiotto, K.L. Fudjda, T.D. Tilley, Iridium(III) complexes of the new tridentate bis(8-quinolyl)silyl ('NSiN') ligand, *Chem. Commun.* (2001) 1200–1201;
- (b) A.F. Hill, H. Neumann, J. Wagler, Bis(methimazolyl)silyl Complexes of Ruthenium, *Organometallics* 29 (2010) 1026–1031;
- (c) N.P. Mankad, M.T. Whited, J.C. Peters, Terminal Fe–I–N–2 and Fe–II...H–C interactions supported by tris(phosphino)silyl ligands, *Angew. Chem. Int. Ed.* 46 (2007) 5768–5771;
- (d) M.T. Whited, N.P. Mankad, J.C. Peters, Dinitrogen complexes supported by tris(phosphino)silyl ligands, *Inorg. Chem.* 48 (2009) 2507–2517;
- (e) A. Takaoka, A. Mendiratta, J.C. Peters, E–H bond activation reactions (E = H, C, Si, Ge) at Ruthenium: terminal phosphides, silylenes, and Germynes, *Organometallics* 28 (2009) 3744–3753;
- (f) C. Tsay, N.P. Mankad, J.C. Peters, Four-coordinate, trigonal pyramidal Pt(II) and Pd(II) complexes, *J. Am. Chem. Soc.* 132 (2010) 13975–13977;
- (g) N. Takeda, D. Watanabe, T. Nakamura, M. Unno, Synthesis and complexation of a new tripodal tetradentate ligand, a silyl ligand tethered with three thioether moieties, *Organometallics* 29 (2010) 2839–2841.
- [11] (a) G. Zassinovich, G. Mestroni, S. Gladiali, Asymmetric hydrogen transfer-reactions promoted by homogeneous transition-metal catalysis, *Chem. Rev.* 92 (1992) 1051;
- (b) N. Noyori, S. Hashiguchi, Asymmetric transfer hydrogenation catalyzed by chiral ruthenium complexes, *Acc. Chem. Res.* 30 (1997) 97–102;
- (c) J.E. Backvall, Transition metal hydrides as active intermediates in hydrogen transfer reactions, *J. Organomet. Chem.* 652 (2002) 105–111.
- [12] (a) P. Dani, T. Karlen, R.A. Gossage, S. Gladiali, Hydrogen-transfer catalysis with pincer-aryl ruthenium(II) complexes, *Angew. Chem. Int. Ed.* 39 (2000) 743–744;
- (b) D. Amoroso, A. Jabri, G.P.A. Yap, D.E. Fogg, The first Ru(eta(3)-PCP) complexes of the electron-rich pincer ligand 1,3-bis((dicyclohexylphosphino)methyl)benzene: Structure and mechanism in transfer hydrogenation catalysis, *Organometallics* 23 (2004) 4047–4054;
- (c) S. Medici, M. Gagliardo, P.A. Chase, A.L. Spek, G. van Koten, Novel P-stereogenic PCP pincer-aryl ruthenium(II) complexes and their use in the asymmetric hydrogen transfer reaction of acetophenone, *Helv. Chim. Acta* 88 (2005) 694–705.
- [13] (a) J. Dupont, M. Pfeffer, J. Spencer, Palladacycles-an old organometallic family revisited: new, simple, and efficient catalyst precursors for homogeneous catalysis, *Eur. J. Inorg. Chem.* (2001) 1917–1927;
- (b) M. Albrecht, G. van Koten, Platinum group organometallics based on "Pincer" complexes: Sensors, switches, and catalysts, *Angew. Chem. Int. Ed.* 40 (2001) 3750–3781;
- (c) M.E. van der Boom, D. Milstein, Cyclometalated phosphine-based pincer complexes: Mechanistic insight in catalysis, coordination, and bond activation, *Chem. Rev.* 103 (2003) 1759–1792;
- (d) J.T. Singleton, The uses of pincer complexes in organic synthesis, *Tetrahedron* 59 (2003) 1837–1857.
- [14] R.D. Brost, G.C. Bruce, S.R. Stobart, Phosphinoalkylsilyl complexes. 12. Stereochemistry of the tridentate bis(diphenylphosphinopropyl)silyl (biPSi) framework: Complexation that introduces "face discrimination" at coordinatively unsaturated metal centers. X-ray crystal and molecular structures of Pt[SiMe(CH₂CH₂CH₂PPh₂)(2)]Cl, IrH[SiMe(CH₂CH₂CH₂PPh₂)(2)]Cl, and RuH[SiMe(CH₂CH₂CH₂PPh₂)(2)](CO) (2), *Organometallics* 16 (1997) 5669–5680.
- [15] (a) Preparation of (2-BrC₆H₄)Bu¹P (1): A mixture of Pd(OAc)₂ (4.5 mg, 0.02 mmol), 1,1'-bis(diisopropylphosphino)ferrocene (10 mg, 0.024 mmol) and Cs₂CO₃ (393 mg, 1.2 mmol) in 1,4-dioxane (3 mL) was stirred for 1 h at room temperature under N₂. Then 2-bromo-iodobenzene (284 mg, 1.0 mmol) and ^tBu₂PH (146 mg, 1.0 mmol) (^tBu = tert-butyl) were added by syringe. The mixture was stirred at 80 °C for 3 days, then allowed to cool to room temperature, filtered and concentrated. The crude product was purified by flash column chromatography on silica gel to afford the title compound 1 (150 mg, 50%) as a colorless solid. ¹H NMR (C₆D₆, 499.1 MHz): δ 1.15 (d, 18H, J = 11 Hz), 6.73 (t, 1H, J = 7 Hz), 6.91 (t, 1H, J = 7 Hz), 7.53 (dd, 1H, J = 8 Hz, J = 4 Hz), 7.64 (d, 1H, J = 7 Hz). ³¹P{¹H} NMR (C₆D₆, 202.0 MHz): δ 32.29 (s). Calcd (%) for C₁₄H₂₂PBr: C, 55.83; H, 7.36. Found: C, 56.09; H, 7.47. (b) Preparation of [2-(^tBu₂P)C₆H₄]₂SiHMe ([PSiP]H, 2): n-BuLi (7.2 mL, 1.59 M in hexane, 11.3 mmol) was added dropwise to an Et₂O solution (30 mL) of 2-^tBu₂PCl₂Br (3.40 g, 11.3 mmol) (^tBu = tert-butyl) at –78 °C, resulting in a red-orange colored solution. The resulting solution was allowed to warm to room temperature over the course of 2 h, over the course of which a white precipitate was observed and the solution became yellow-orange in color. Then the mixture was once again cooled to –78 °C and MeHSiCl₂ (0.58 mL, 5.7 mmol) was added via syringe. The resulting pale yellow-orange colored reaction mixture was allowed to warm to room temperature and continue stirring for an additional 14 h at room temperature. Volatiles were then removed under vacuum, and the remaining residue was extracted with benzene (3 × 10 mL). The benzene extracts were filtered through Celite and the benzene was removed in vacuo to afford a viscous, air-sensitive colorless liquid 2 (2.64 g, 95%). ¹H NMR (C₆D₆, 499.1 MHz): δ 0.93 (d, 3H, J = 4 Hz), 1.17 (d, 18H, J = 3 Hz), 1.19 (d, 18H, J = 3 Hz), 6.45 (quasi octet, 1H, J(H,Si) = 216 Hz), 7.13–7.19 (m, 4H), 7.72–7.78 (m, 4H). ³¹P{¹H} NMR (C₆D₆, 202.0 MHz): δ 23.2 (s). ²⁹Si{¹H} NMR (C₆D₆, 99.1 MHz): δ –24.0 (t, J(P,Si) = 22 Hz). Calcd (%) for C₃₇H₅₆P₂Si: C, 75.21; H, 9.55. Found: C, 74.75; H, 9.58. (c) Preparation of [2-(^tBu₂P)C₆H₄]₂SiR(H)ClMe ([PSiP] Ru(H)ClMe, 3): A solution of [2-(^tBu₂P)C₆H₄]₂SiHMe (1.83 g, 3.75 mmol) (^tBu = tert-butyl) in dry toluene (15 mL) was added to a slurry of [IrCl(COD)]₂ (1.27 g, 1.88 mmol) (cod = 1,4-cyclooctadiene) in toluene (10 mL) at room temperature. The resulting wine colored solution was allowed to stir at room temperature for 1 h, and then was heated at 80 °C for 24 h. The volatile components were removed in vacuo, and the residue was washed with hexane (3 × 5 mL) to give the pure product 3 (2.41 g, 90%) as a colorless solid. Colorless crystals suitable for X-ray diffraction were obtained by slow evaporation of a benzene solution (5 mL) of the compound (20 mg) after 2 d. ¹H NMR (C₆D₆, 499.1 MHz): δ –23.7 (t, 1H, J = 14 Hz), 0.84 (s, 3H), 1.39 (t, 18H, J = 7 Hz), 1.55 (t, 18H, J = 7 Hz), 7.03 (t, 2H, J = 8 Hz), 7.15 (t, 2H, J = 7 Hz), 7.66 (br d, 2H, J = 8 Hz), 7.98 (d, 2H, J = 8 Hz). ³¹P{¹H} NMR (C₆D₆, 202.0 MHz): δ 78.59 (s). ²⁹Si{¹H} NMR (C₆D₆, 99.1 MHz): δ 7.56 (s). Calcd (%) for C₂₉H₄₈ClIrP₂Si: C, 48.76; H, 6.77. Found: C, 48.97; H, 6.69. (d) Typical procedure for the catalytic hydrogen-transfer reaction: To a mixture of ketone (2 mmol), the catalyst 3 (0.004 mmol, 2 mL of a stock solution of 3 in ⁱPrOH) and 2 mL of ⁱPrOH was added a solution of KO^tBu (195 μL of a 5 wt % solution in ⁱPrOH, 0.1 mmol) under nitrogen. The resulting brown solution was stirred at room temperature for 10 min. The mixture was then heated at 80 °C. The mixture turned pale yellowish after the reaction was complete. The yields were determined by GC analysis with n-undecane as internal standard, and the identities of the hydrogenation products were confirmed by comparison to authentic samples.
- [16] Crystal data for 3: M = 714.35, monoclinic, P2₁/c, a = 12.291(3) Å, b = 15.050(2) Å, c = 16.500(3) Å, α = 90.00°, β = 98.57(3)°, γ = 90.00°, V = 3017.8(11) Å³, Z = 4, F(000) = 1440, R₁ = 0.0217, wR₂ = 0.0435 [I > 2σ(I)]. Structural data for 3 was collected on a Bruker Smart Apex CCD with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 153 K. The structure was solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.
- [17] (a) G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997;
- (b) G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [18] (a) G. Zassinovich, G. Mestroni, S. Gladiali, Asymmetric hydrogen transfer-reactions promoted by homogeneous transition-metal catalysis, *Chem. Rev.* 92 (1992) 1051–1069;
- (b) N. Noyori, S. Hashiguchi, Asymmetric transfer hydrogenation catalyzed by chiral ruthenium complexes, *Acc. Chem. Res.* 30 (1997) 97–102.
- [19] (a) H.X. Deng, Z.K. Yu, S.Z. Wu, 2,6-Bis(3,5-dimethylpyrazol-1-yl)pyridine: A useful pseudo-N₃ ligand in efficient Ruthenium(II)-catalyzed transfer hydrogenation of ketones, *Organometallics* 24 (2005) 4110–4112;
- (b) G. Zassinovich, G. Mestroni, S. Gladiali, Asymmetric hydrogen transfer-reactions promoted by homogeneous transition-metal catalysis, *Chem. Rev.* 92 (1992) 1051–1069;
- (c) W. Baratta, G. Chelucci, S. Gladiali, E. Zangrando, P. Rigo, Ruthenium(II) terdentate CNN complexes: Superlative catalysts for the hydrogen-transfer

- reduction of ketones by reversible insertion of a carbonyl group into the Ru–H bond, *Angew. Chem. Int. Ed.* 44 (2005) 6214–6219;
- (d) V. Cadierno, P. Crochet, J. Gimeno, Efficient transfer hydrogenation of ketones catalyzed by the bis(isocyanide)-ruthenium(II) complexes *trans*, *cis*, *cis*-[RuX₂(CNR)(2)(dppf)] (X = Cl, Br; dppf = 1,1'-bis(diphenylphosphino)ferrocene): Isolation of active mono- and dihydride intermediates, *Organometallics* 23 (2004) 4836–4845;
- (e) P. Brandt, P. Roth, P.G. Andersson, Origin of enantioselectivity in the Ru(arene)(amino alcohol)-catalyzed transfer hydrogenation of ketones, *J. Org. Chem.* 69 (2004) 4885–4890.
- [20] (a) D. Amoroso, A. Jabri, D.E. Fogg, The first Ru(eta(3)-PCP) complexes of the electron-rich pincer ligand 1,3-bis((dicyclohexylphosphino)methyl)benzene: Structure and mechanism in transfer hydrogenation catalysis, *Organometallics* 23 (2004) 4047–4054;
- (b) A.A. Danopoulos, S. Winston, W.B. Motherwell, Stable N-functionalised 'pincer' bis carbene ligands and their ruthenium complexes; synthesis and catalytic studies, *Chem. Commun.* (2002) 1376–1377;
- (c) W. Baratta, G. Chelucci, S. Gladiali, P. Rigo, Ruthenium(II) terdentate CNN complexes: Superlative catalysts for the hydrogen-transfer reduction of ketones by reversible insertion of a carbonyl group into the Ru–H bond, *Angew. Chem. Int. Ed.* 44 (2005) 6214–6219.