

Synthesis and Reactivity of Platinum Group Metal Complexes Featuring the New Pincer-like Bis(phosphino)silyl Ligand $[\kappa^3\text{-(2-Ph}_2\text{PC}_6\text{H}_4)_2\text{SiMe}]^-$ ([PSiP]): Application in the Ruthenium-Mediated Transfer Hydrogenation of Ketones

Morgan C. MacInnis,^{†,‡} Darren F. MacLean,^{†,‡} Rylan J. Lundgren,^{†,‡} Robert McDonald,[§] and Laura Turculet^{*,‡}

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3, and
X-Ray Crystallography Laboratory, Department of Chemistry, University of Alberta,
Edmonton, Alberta, Canada T6G 2G2

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Summary: The synthesis of coordinatively unsaturated Ru, Rh, Pd, and Pt complexes supported by the new pincer-like bis(phosphino)silyl ligand $[\kappa^3\text{-(2-Ph}_2\text{PC}_6\text{H}_4)_2\text{SiMe}]^-$ ([PSiP]) is described. In the first application of silyl pincer-type complexes in transfer hydrogenation catalysis, [PSiP]Ru species were shown to be effective in mediating the reduction of ketones employing basic ¹PrOH as the hydrogen source.

Cyclometalated phosphine-based “PCP” pincer complexes of the platinum group metals have been the subject of intense research in recent years, owing to the remarkable stoichiometric and catalytic reactivity exhibited by such complexes.¹ With the goal of discovering new metal-mediated reactivity patterns and extending the versatility of metal pincer chemistry, 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.^{1b,c,2} In this context, we are interested in the synthesis and study of pincer-like metal complexes supported by new tridentate ancillary ligands featuring formally anionic heavier main group element donors, in

anticipation that such novel ligand architectures will impart unique physical and reactivity properties to the ensuing complexes.

In this contribution, we report the synthesis and preliminary coordination chemistry studies of the new pincer-like bis(phosphino)silyl ligand $[\kappa^3\text{-(2-Ph}_2\text{PC}_6\text{H}_4)_2\text{SiMe}]^-$ ([PSiP]). Although metal–silicon chemistry is well-precedented across the transition series,³ relatively little attention has been given to the incorporation of silyl donor fragments into the framework of a preformed tridentate ancillary ligand.⁴ A notable exception is the work of Stobart and co-workers,⁵ who have reported late transition metal complexes featuring bi-, tri-, and tetradentate phosphinosilyl ligands. In addition, Tilley and co-workers have recently reported Rh and Ir complexes featuring a rigid, tridentate NSiN ligand framework.⁶ While it has been proposed that the incorporation of strongly electron donating and *trans*-labilizing silyl groups into such multidentate ligand architectures may promote the formation of coordinatively unsaturated complexes that exhibit enhanced reactivity properties, the catalytic utility of metal complexes supported by such ancillary ligands has not been widely demonstrated.^{6c,7} Herein we report the synthesis and characterization of coordinatively unsaturated Ru, Rh, Pd, and Pt complexes featuring [PSiP], as well as a preliminary investigation of the catalytic utility of [PSiP]Ru species in the transfer hydrogenation of ketones. In contrast to the phosphinosilyl complexes previously reported by Stobart and co-workers that feature an aliphatic or benzylic ligand backbone, we anticipated that the reduced conformational flexibility and lack of β -hydrogens associated with the rigid *o*-phenylene backbone

* To whom correspondence should be addressed. Tel: 1-902-494-6414. Fax: 1-902-494-1310. E-mail: laura.turculet@dal.ca.

[†] These authors contributed equally to this work.

[‡] Dalhousie University.

[§] University of Alberta.

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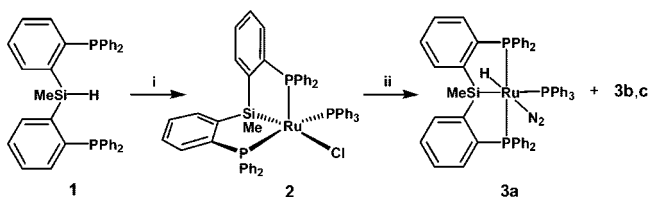
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Scheme 1. Synthesis of [PSiP]Ru Chloride (2) and Hydride (3a) Complexes^a



^a Reagents: (i) $\text{RuCl}_2(\text{PPh}_3)_3$, Et_3N ; (ii) LiEt_3BH .

of [PSiP] could provide enhanced stability and selectivity in metal-mediated substrate transformations.

The parent tertiary silane, [PSiP]H (1), was obtained by lithiation of 2- $\text{Ph}_2\text{PC}_6\text{H}_4\text{Br}$ with $^n\text{BuLi}$, followed by in situ treatment with 0.5 equiv of MeSiHCl_2 .⁸ Isolated 1 was obtained as a peach-colored solid in 90% yield. The ^1H NMR spectrum of 1 (benzene- d_6) features a multiplet at 6.03 ppm corresponding to the Si-H, as well as a doublet at 0.81 ppm ($^3J_{\text{HH}} = 3$ Hz) corresponding to the silyl methyl substituent. The ^{31}P NMR resonance of 1 is found at -10.9 ppm, while the ^{29}Si NMR resonance occurs at -23.2 ppm (benzene- d_6).

Treatment of 1 with $\text{RuCl}_2(\text{PPh}_3)_3$ in the presence of Et_3N resulted in quantitative (by ^{31}P NMR) formation of the cyclo-metalated 16-electron Ru complex 2, which was isolated in 89% yield (Scheme 1). The X-ray crystal structure of $2 \cdot (\text{OEt}_2)_{1.5}$ (Figure 1) confirms the formation of a five-coordinate *fac*-[PSiP] complex with distorted square-pyramidal geometry at Ru,⁸ in which a phosphine arm of the [PSiP] ligand occupies the apical coordination site, while the remaining phosphine arm and the silyl group occupy basal sites. The Si donor in 2 is positioned *trans* to Cl, with a Ru-Si distance of 2.3361(6) Å. These structural features differ somewhat from those of the related complex (biPSi)RuCl(CO) (biPSi = $\kappa^3\text{-MeSi}(\text{CH}_2\text{CH}_2\text{CH}_2\text{-PPh}_2)_2$),⁹ which features the biPSi ligand in a *mer*-type configuration with Si positioned *trans* to the vacant coordination site (Ru-Si, 2.339(5) Å). While the acute P2-Ru-Si angle of 79.23(2)° in 2 may arise due to the geometric constraints of the rigid [PSiP] ligand (P1-Ru-Si, 81.53(2)°), it is also feasible that the structure of 2 might be influenced by previously described electronic effects involving the distortion of five-coordinate d^6 complexes.¹⁰ Such distortion results in a "Y-shaped" molecular geometry in which a ligand with poor σ -donor but good π -donor properties (such as Cl^-) is positioned opposite the acute angle of the "Y". However, in the case of 2 the chloride ligand is positioned significantly closer to P2 than to Si (Cl-Ru-P2, 119.66(2)°; Cl-Ru-Si, 160.41(2)°), such that the complex is better represented as square pyramidal, with the arrangement of Si, Cl, and P2 described by a distorted T-shape.^{10c}

In methylene chloride- d_2 solution, both the ^1H and ^{31}P NMR spectra of 2 exhibit significant line broadening at 300 K. The

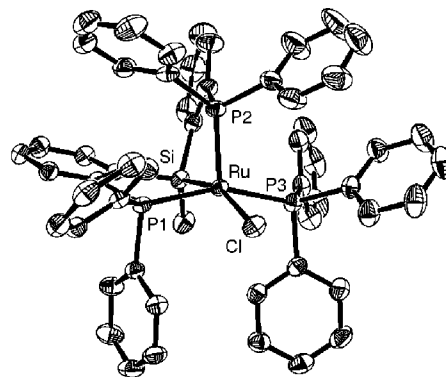


Figure 1. Crystallographically determined structure of $2 \cdot (\text{OEt}_2)_{1.5}$, shown with 50% displacement ellipsoids. All H atoms as well as the diethyl ether solvate have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) for $2 \cdot (\text{OEt}_2)_{1.5}$: Ru-Cl 2.4492(6); Ru-P1 2.3040(6); Ru-P2 2.2093(6); Ru-P3 2.3891(6); Ru-Si 2.3361(6); Cl-Ru-P1 89.26(2); Cl-Ru-P2 119.66(2); Cl-Ru-P3 87.42(2); Cl-Ru-Si 160.41(2); P1-Ru-P3 156.79(2); P1-Ru-Si 81.53(2); P2-Ru-Si 79.23(2); P3-Ru-Si 94.24(2).

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 2 (300 K, 202.5 MHz) features three resonances in a 1:1:1 ratio, consisting of a broad singlet at 96.8 ppm, a broad doublet at 67.1 ppm ($J = 289$ Hz), and a doublet at 29.1 ppm ($J = 258$ Hz). Upon cooling of the solution to 223 K, the ^{31}P NMR resonances (101.3 MHz) sharpen significantly, revealing further PP coupling (98.5 ppm, apparent t, $^2J_{\text{PPcis}} = 25$ Hz; 69.9 ppm, dd, $^2J_{\text{PPcis}} = 27$ Hz, $^2J_{\text{PPtrans}} = 281$ Hz; 32.4 ppm, dd, $^2J_{\text{PPcis}} = 24$ Hz, $^2J_{\text{PPtrans}} = 282$ Hz). No further decoalescence phenomena are observed at temperatures below 223 K. The resonances observed at low temperature in the ^{31}P NMR spectrum of 2 are consistent with the structure observed in the solid state, where the three phosphine donors are arranged in a T-type configuration. These temperature-dependent NMR line shape changes may arise due to intramolecular rearrangement processes (e.g., pseudorotation) and/or Ru-P dissociation.

Complex 2 reacted with LiEt_3BH to form a mixture of three Ru hydride species (3a-c) that each exhibit C_s symmetry in solution (^{31}P NMR). In benzene- d_6 solution, the major hydride product (3a) features a Ru-H ^1H NMR resonance at -13.66 ppm (td, $^2J_{\text{HP}} = 10$ Hz, $^2J_{\text{HP}} = 27$ Hz) and two ^{31}P NMR resonances in a 2:1 ratio at 64.6 (d, $^2J_{\text{PP}} = 19$ Hz) and 34.8 (t, $^2J_{\text{PP}} = 19$ Hz) ppm, corresponding to the [PSiP] and PPh_3 ligands, respectively.¹¹ The ratio of 3a:b:c observed in situ was approximately 2:1:1, and heating of the mixture (20 h, 70 °C, benzene- d_6) did not change the observed ratio of these three Ru-H species. In a preparative scale reaction of 2 with LiEt_3BH , 3a was readily isolated in 64% yield by washing of the crude product (which also contained 3b and 3c) with diethyl ether.¹² On the basis of spectroscopic and microanalytical data, complex 3a is assigned as a dinitrogen adduct of the type [PSiP]RuH(N_2)(PPh_3) (Scheme 1). Facile formation of dinitro-

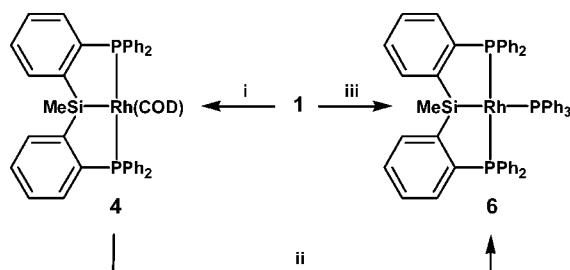
(8) Full experimental details, including spectroscopic characterization data for the new compounds reported herein and crystallographic details for $2 \cdot (\text{OEt}_2)_{1.5}$ are provided in the Supporting Information. Selected crystal data for $2 \cdot (\text{OEt}_2)_{1.5}$: triclinic ($P\bar{1}$); $a = 11.2541(9)$ Å; $b = 3.4722(11)$ Å; $c = 17.6235(14)$ Å; $\alpha = 85.0100(11)^\circ$; $\beta = 85.5172(11)^\circ$; $\gamma = 85.8870(11)^\circ$; $V = 2648.1(4)$ Å³; $Z = 2$; GOF = 1.050; $R_1 = 0.0369$; $wR_2 = 0.0975$.

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(11) Complex 3b (300 K, benzene- d_6): Ru-H ^1H NMR resonance at -7.18 ppm (br s) and two ^{31}P NMR resonances at 71.0 ppm (d, 2 P, [PSiP], $^2J_{\text{PP}} = 14$ Hz) and 47.7 ppm (t, 1 P, PPh_3 , $^2J_{\text{PP}} = 14$ Hz). Complex 3c (300 K, benzene- d_6): Ru-H ^1H NMR resonance at -11.04 ppm (br d, $J \approx 140$ Hz), and two ^{31}P NMR resonances at 71.3 ppm (br, 2 P, [PSiP]) and 54.7 ppm (t, 1 P, PPh_3 , $^2J_{\text{PP}} = 16$ Hz).

(12) We attribute the 64% isolated yield of 3a to the conversion of 3b and/or 3c to 3a upon workup. Efforts to definitively identify 3b and 3c are ongoing.

Scheme 2. Synthesis of [PSiP]Rh Complexes^a

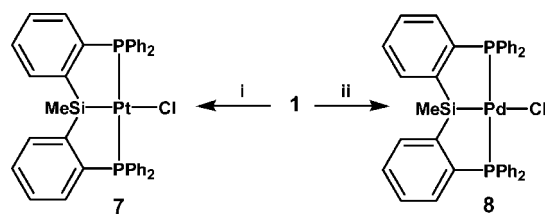
^a Reagents: (i) (COD)Rh(CH₂Ph) (COD = 1,5-cyclooctadiene); (ii) PPh₃; (iii) RhCl(PPh₃)₃, PhCH₂K.

gen adducts has been reported in related [PCP]Ru and [PNP]Ru pincer chemistry.¹³

In an effort to explore further the coordination chemistry of [PSiP], we also pursued the synthesis of group 9 and 10 complexes featuring this new tridentate ligand. The treatment of **1** with (COD)Rh(CH₂Ph)¹⁴ in THF solution at room temperature led to the formation of [PSiP]Rh(COD) (**4**), which was isolated in 49% yield (Scheme 2). The ³¹P{¹H} NMR spectrum of **4** (benzene-*d*₆) features a doublet at 58.5 ppm (¹J_{PRh} = 140 Hz), consistent with a C_s-symmetric complex in solution. The reaction of **1** with RhCl(PPh₃)₃ led to quantitative (by ³¹P NMR) formation of what we tentatively assign as a 1:1 mixture of two isomeric [PSiP]RhHCl(PPh₃) species (**5a,b**) that each exhibit C_s symmetry in solution.¹⁵ Although Et₃N proved incapable of dehydrohalogenating **5a,b**, treatment of in situ generated **5a,b** with 1 equiv of PhCH₂K led to clean formation of [PSiP]RhPPh₃ (**6**), which was isolated in 49% yield (Scheme 2). The ³¹P NMR spectrum of **6** (benzene-*d*₆) features two resonances at 58.6 ppm (dd, 2 P, [PSiP], ¹J_{PRh} = 173 Hz, ²J_{PP} = 22 Hz) and 24.9 ppm (dt, 1 P, PPh₃, ¹J_{PRh} = 130 Hz, ²J_{PP} = 22 Hz), consistent with C_s symmetry in solution. Complex **6** was also formed cleanly (by ³¹P NMR) in the reaction of **4** with PPh₃ (Scheme 2).

Group 10 [PSiP] complexes were readily synthesized by treatment of **1** with an appropriate Pt or Pd starting material (Scheme 3). Thus, the reaction of **1** with 1 equiv of PtCl₂(SEt₂)₂ in benzene solution resulted in the precipitation of [PSiP]PtCl (**7**) as a colorless microcrystalline solid (95% isolated yield). Similarly, treatment of **1** with 0.5 equiv of [PdCl(C₃H₅)₂] in benzene solution led to precipitation of [PSiP]PdCl as a colorless microcrystalline solid (96% isolated yield). Each complex exhibits a single ³¹P NMR resonance (chloroform-*d*, for **7**, 51.7 ppm (with Pt satellites, ¹J_{PPt} = 3074 Hz); for **8**, 46.9 ppm), consistent with C_s symmetry in solution.

Building 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

Scheme 3. Synthesis of [PSiP]PtCl (**7**) and [PSiP]PdCl (**8**)^a

^a Reagents: (i) PtCl₂(SEt₂)₂; (ii) 0.5 [PdCl(C₃H₅)₂].

Table 1. Transfer Hydrogenation of Ketones^a

entry	catalyst	substrate	time (h)	conv (%) ^b
1	2	acetophenone	6	96
2	2	benzophenone	6	92
3	2	2-heptanone	4.5	99
4	2	cyclopentanone	3	>99
5	2	cyclohexanone	3	>99
6	3a	cyclohexanone	3	94

^a Reactions were performed on a 1 mL scale (0.1 M ketone, 0.2 mol % Ru, 2 mol % KO^tBu) in ¹PrOH at 82 °C under N₂. ^b Determined by GC-FID.

of Si for C in a rigid tridentate ancillary ligand framework influences metal-mediated reactivity, given the strong electron-donating and *trans*-labilizing abilities of Si. Previous work has established that Ru(II) PCP-, NCN-, CNC-, and CNN-pincer complexes are effective catalysts for the transfer hydrogenation of ketones, and it has been proposed that the Ru–C σ-bond plays an important role in the formation of long-lived, catalytically active species.^{13b,16} In this context, we became interested in surveying the catalytic activity of [PSiP]RuCl(PPh₃) (**2**) and [PSiP]RuH(N₂)(PPh₃) (**3a**) in the transfer hydrogenation of ketones, employing basic ¹PrOH as the hydrogen source; the results obtained in our preliminary survey are summarized in Table 1. Although the conditions have not yet been optimized, the activity of **2** as a precatalyst in this reaction is comparable to that of related Ru pincer catalysts that lack an NH functionality.^{13b,16} When employing 0.2 mol % of **2** with 2 mol % of KO^tBu at 82 °C, high conversion to the corresponding secondary alcohols was observed for several ketone substrates, including diaryl, dialkyl, and alkyl/aryl ketones. As is the case for most metal-catalyzed transfer hydrogenation processes conducted in ¹PrOH, less than 5% conversion was observed in the absence of KO^tBu as base. The preformed Ru hydride complex **3a** was similarly inactive for transfer hydrogenation of cyclohexanone in the absence of added KO^tBu, although 94% conversion was obtained when using 2 mol % KO^tBu along with 0.2 mol % **3a** (entry 6, Table 1). These preliminary results establish [PSiP]Ru 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 summary, the facile synthesis of platinum group metal complexes supported by the versatile new pincer-like bis(phosphino)silyl ligand [*κ*³-(2-Ph₂PC₆H₄)₂SiMe][−] ([PSiP]) has been described. In one of the first applications of silyl pincer-type complexes in catalysis to be documented in the academic literature, both chloro- and hydrido-[PSiP]Ru species were

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(14) Generated in situ from 0.5 [Rh(COD)Cl]₂ and PhCH₂K in THF (COD = 1,5-cyclooctadiene). See: Fryzuk, M. D.; McConville, D. H.; Rettig, S. J. *J. Organomet. Chem.* **1993**, *445*, 245.

(15) Complex **5a** (300 K, methylene chloride-*d*₂): Rh–H ¹H NMR resonance at −16.66 ppm (m) and two ³¹P NMR resonances at 59.3 ppm (dd, 2 P, [PSiP], ¹J_{RhP} = 117 Hz, ²J_{PP} = 20 Hz) and 20.3 ppm (dt, 1 P, PPh₃, ¹J_{RhP} = 78 Hz, ²J_{PP} = 21 Hz). Complex **5b** (300 K, methylene chloride-*d*₂): Rh–H ¹H NMR resonance at −18.14 ppm (apparent quart, *J* = 19 Hz) and two ³¹P NMR resonances at 50.0 ppm (dd, 2 P, [PSiP], ¹J_{RhP} = 115 Hz, ²J_{PP} = 19 Hz) and 11.5 ppm (dt, 1 P, PPh₃, ¹J_{RhP} = 69 Hz, ²J_{PP} = 20 Hz).

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shown to be effective in mediating the transfer hydrogenation of ketones to secondary alcohols, employing basic $^i\text{PrOH}$ as the hydrogen source. These preliminary studies establish [PSiP]-ligated platinum group metal complexes as promising candidates for further catalytic studies.

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Supporting Information Available: Experimental details and characterization data, including crystallographic data for $\mathbf{2} \cdot (\text{OEt}_2)_{1.5}$ (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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