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Synthesis and Reactivity of Platinum Group Metal Complexes Featuring the New Pincer-like Bis(phosphino)silyl Ligand [κ^3-(2-Ph$_2$*P*C$_6$H$_4$)$_2$*Si*Me]$^-$ ([PSiP]): Application in the Ruthenium-Mediated Transfer Hydrogenation of Ketones

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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 [κ^3-(2-Ph$_2$PC$_6$H$_4$)$_2$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 ^{i}PrOH 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 [κ^3-(2-Ph$_2$*P*C$_6$H$_4$)$_2$*Si*Me]$^-$ ([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

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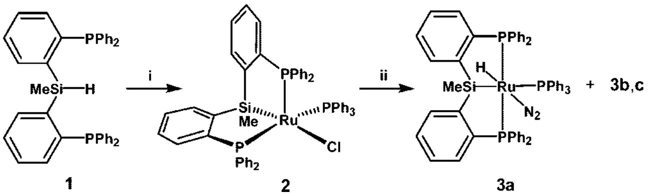
Scheme 1. Synthesis of [PSiP]Ru Chloride (2) and Hydride (3a) Complexes[a]



[a] Reagents: (i) $RuCl_2(PPh_3)_3$, 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-$Ph_2PC_6H_4Br$ with ^{n}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 ^{1}H 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 ($^{3}J_{HH} = 3$ 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 $RuCl_2(PPh_3)_3$ in the presence of Et_3N resulted in quantitative (by ^{31}P NMR) formation of the cyclometalated 16-electron Ru complex **2**, which was isolated in 89% yield (Scheme 1). The X-ray crystal structure of **2**$\cdot(OEt_2)_{1.5}$ (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 = κ^3-Me*Si*($CH_2CH_2CH_2$-*P*$Ph_2)_2$),[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 ^{1}H and ^{31}P NMR spectra of **2** exhibit significant line broadening at 300 K. The $^{31}P\{^{1}H\}$ 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, $^{2}J_{PPcis} = 25$ Hz; 69.9 ppm, dd, $^{2}J_{PPcis} = 27$ Hz, $^{2}J_{PPtrans} = 281$ Hz; 32.4 ppm, dd, $^{2}J_{PPcis} = 24$ Hz, $^{2}J_{PPtrans} = 282$ 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.

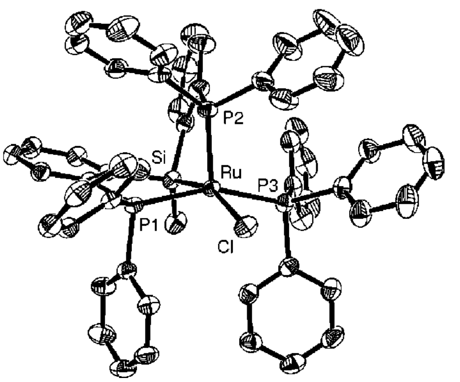


Figure 1. Crystallographically determined structure of **2**$\cdot(OEt_2)_{1.5}$, shown with 50% displacement ellipsoids. All H atoms as well as the diethyl ether solvate have been omitted for clarity. Selected interatomic distances (Å) and angles (deg) for **2**$\cdot(OEt_2)_{1.5}$: Ru−Cl 2.4492(6); 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).

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 ^{1}H NMR resonance at −13.66 ppm (td, $^{2}J_{HP} = 10$ Hz, $^{2}J_{HP} = 27$ Hz) and two ^{31}P NMR resonances in a 2:1 ratio at 64.6 (d, $^{2}J_{PP} = 19$ Hz) and 34.8 (t, $^{2}J_{PP} = 19$ 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-

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(8) Full experimental details, including spectroscopic characterization data for the new compounds reported herein and crystallographic details for **2**$\cdot(OEt_2)_{1.5}$ are provided in the Supporting Information. Selected crystal data for **2**$\cdot(OEt_2)_{1.5}$: triclinic ($P\bar{1}$); $a = 11.2541(9)$ Å; $b = 3.4722(11)$ Å; $c = 17.6235(14)$ Å; $\alpha = 85.0100(11)°$; $\beta = 85.5172(11)°$; $\gamma = 85.8870(11)°$; $V = 2648.1(4)$ Å^3; $Z = 2$; GOF = 1.050; $R_1 = 0.0369$; $wR_2 = 0.0975$.

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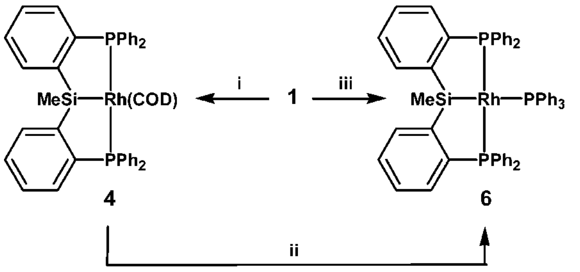
(11) Complex **3b** (300 K, benzene-d_6): Ru−H ^{1}H NMR resonance at −7.18 ppm (br s) and two ^{31}P NMR resonances at 71.0 ppm (d, 2 P, [PSiP], $^{2}J_{PP} = 14$ Hz) and 47.7 ppm (t, 1 P, PPh_3, $^{2}J_{PP} = 14$ Hz). Complex **3c** (300 K, benzene-d_6): Ru−H ^{1}H NMR resonance at −11.04 ppm (br d,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



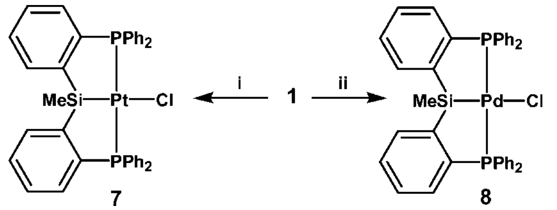
[a] Reagents: (i) (COD)Rh(CH$_2$Ph) (COD = 1,5-cyclooctadiene); (ii) PPh$_3$; (iii) RhCl(PPh$_3$)$_3$, PhCH$_2$K.

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(CH$_2$Ph)[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 ^{31}P{^{1}H} NMR spectrum of **4** (benzene-*d*$_6$) features a doublet at 58.5 ppm ($^{1}J_{\mathrm{PRh}}$ = 140 Hz), consistent with a C_s-symmetric complex in solution. The reaction of **1** with RhCl(PPh$_3$)$_3$ led to quantitative (by ^{31}P NMR) formation of what we tentatively assign as a 1:1 mixture of two isomeric [PSiP]RhHCl(PPh$_3$) species (**5a**,**b**) that each exhibit C_s symmetry in solution.[15] Although Et$_3$N proved incapable of dehydrohalogenating **5a**,**b**, treatment of in situ generated **5a**,**b** with 1 equiv of PhCH$_2$K led to clean formation of [PSiP]RhPPh$_3$ (**6**), which was isolated in 49% yield (Scheme 2). The ^{31}P NMR spectrum of **6** (benzene-*d*$_6$) features two resonances at 58.6 ppm (dd, 2 P, [PSiP], $^{1}J_{\mathrm{PRh}} = 173$ Hz, $^{2}J_{\mathrm{PP}} = 22$ Hz) and 24.9 ppm (dt, 1 P, PPh$_3$, $^{1}J_{\mathrm{PRh}} = 130$ Hz, $^{2}J_{\mathrm{PP}} = 22$ Hz), consistent with C_s symmetry in solution. Complex **6** was also formed cleanly (by ^{31}P NMR) in the reaction of **4** with PPh$_3$ (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 PtCl$_2$(SEt$_2$)$_2$ 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(C$_3$H$_5$)]$_2$ in benzene solution led to precipitation of [PSiP]PdCl as a colorless microcrystalline solid (96% isolated yield). Each complex exhibits a single ^{31}P NMR resonance (chloroform-*d*, for **7**, 51.7 ppm (with Pt satellites, $^{1}J_{\mathrm{PPt}} = 3074$ Hz); for **8**, 46.9 ppm), consistent with C_s symmetry in solution.

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



[a] Reagents: (i) PtCl$_2$(SEt$_2$)$_2$; (ii) 0.5 [PdCl(C$_3$H$_5$)]$_2$.

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^{t}Bu) in ^{i}PrOH at 82 °C under N$_2$. [b] Determined by GC-FID.

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 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(PPh$_3$) (**2**) and [PSiP]RuH(N$_2$)(PPh$_3$) (**3a**) in the transfer hydrogenation of ketones, employing basic ^{i}PrOH 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^{t}Bu 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 ^{i}PrOH, less than 5% conversion was observed in the absence of KO^{t}Bu as base. The preformed Ru hydride complex **3a** was similarly inactive for transfer hydrogenation of cyclohexanone in the absence of added KO^{t}Bu, although 94% conversion was obtained when using 2 mol % KO^{t}Bu 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-Ph$_2$*P*C$_6$H$_4$)$_2$*Si*Me]$^-$ ([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 PhCH$_2$K 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 ^{1}H NMR resonance at −16.66 ppm (m) and two ^{31}P NMR resonances at 59.3 ppm (dd, 2 P, [PSiP], $^{1}J_{\mathrm{RhP}} = 117$ Hz, $^{2}J_{\mathrm{PP}} = 20$ Hz) and 20.3 ppm (dt, 1 P, PPh$_3$, $^{1}J_{\mathrm{RhP}} = 78$ Hz, $^{2}J_{\mathrm{PP}} = 21$ Hz). Complex **5b** (300 K, methylene chloride-*d*$_2$): Rh−H ^{1}H NMR resonance at −18.14 ppm (apparent quart, J = 19 Hz) and two ^{31}P NMR resonances at 50.0 ppm (dd, 2 P, [PSiP], $^{1}J_{\mathrm{RhP}} = 115$ Hz, $^{2}J_{\mathrm{PP}} = 19$ Hz) and 11.5 ppm (dt, 1 P, PPh$_3$, $^{1}J_{\mathrm{RhP}} = 69$ Hz, $^{2}J_{\mathrm{PP}} = 20$ Hz).

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shown to be effective in mediating the transfer hydrogenation of ketones to secondary alcohols, employing basic ^{i}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 **2**$\cdot$(OEt$_2$)$_{1.5}$. (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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