Formation of Chlorosilyl Pincer-Type Rhodium Complexes by Multiple Si−H Activations of Bis(phosphine)/Dihydrosilyl Ligands

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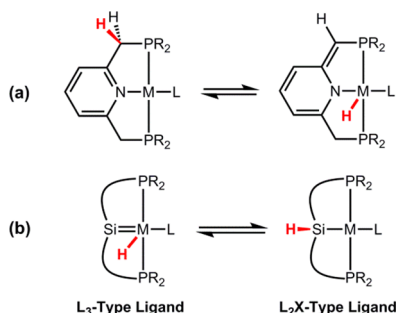
Ⓢ *Supporting Information*

ABSTRACT: The synthesis and metalation of two bis(phosphine)/dihydrosilyl ligands at rhodium(I) sources is reported. Irrespective of the substitution at silicon (diaryl versus diamino), multiple Si−H activations and chloride migration afford tridentate bis(phosphine)/chlorosilyl complexes of Rh(I). For the diarylsilyl ligand, reaction with a cationic rhodium(I) triflate precursor gives the analogous triflatosilyl complex. The [P_2Si]H_2 proligands and their Rh complexes provide distinct opportunities for exploring metal/silicon cooperative reactivity.
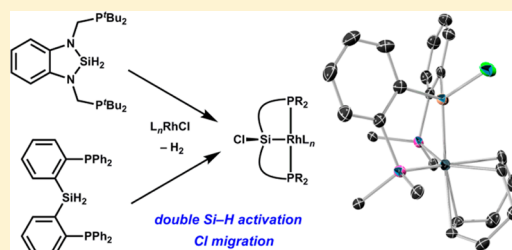
The preparation of molecular systems containing complementary sites capable of activating substrates in a cooperative fashion has facilitated the discovery of a number of unusual transformations.[1] Main-group "frustrated Lewis pairs" (FLPs) containing acidic and basic sites that are sterically prevented from quenching provide one recent example of such a system.[2] Another relevant, though somewhat different, example comes from Milstein's laboratory, which has shown that lutidine-based PNP pincers can serve as hydride shuttles to open coordination sites and facilitate proton management at metal centers during catalysis (Scheme 1a).[3] In both cases, a particular arrangement of
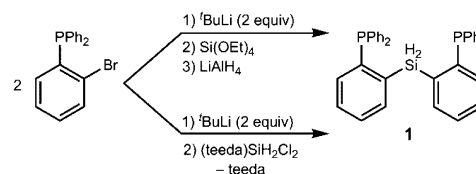
Scheme 1

complementary sites allows new modes of substrate activation and opens reactivity pathways that would otherwise be kinetically inaccessible.

Our laboratory has developed an interest in utilizing main-group elements for cooperative small-molecule activation and catalysis involving late transition metals.[4] In one scheme, we have envisioned late-metal systems supported by pincer-type ligands containing an electropositive central donor that can open cooperative FLP-type pathways in combination with an electron-

rich metal center (Scheme 1b).[5] Like lutidine- and picoline-based pincers, ligands with a central silylene donor could serve as hydride shuttles, alternating between formally L_3- and L_2X-type ligands. Here we report the synthesis of bis(phosphine) diaryl- and diaminodihydrosilyl ligands and their reactivity with Rh(I) sources. Though formally related to other silicon-based pincers, these P_2Si ligands exhibit distinct reactivity, undergoing double Si−H activation with H_2 loss and halide migration at Rh(I) centers, showing that dihydrosilyl pincer ligands can serve as masked silylene equivalents and providing new possibilities for Rh/Si cooperative reactivity.

(P_2^{Ar}Si)H_2 Ligand Synthesis and Reactivity. Inspired by results from the laboratories of Turculet[6] and Iwasawa[7] regarding the use of methyldiarylsilyl PSiP pincers as well as Ozerov's success utilizing diarylamido PNP pincer ligands[8] and Piers's use of diarylcarbyl/carbene PCP ligands,[9] we initially targeted a diaryldihydrosilyl ligand precursor (**1**) akin to what has been reported by Milstein (Scheme 2).[10] Ligand **1** could be prepared most reproducibly by reaction of an in situ generated *o*-phosphinoaryllithium with tetraethyl orthosilicate followed by reduction with $LiAlH_4$ (Scheme 2, top pathway).[11] We also found that (teeda)SiH_2Cl_2[12] served as a suitable source of dichlorosilane (teeda = *N,N,N',N'*-tetraethylethylenediamine),

Scheme 2

allowing clean disubstitution at silicon without the need for subsequent reduction (Scheme 2, bottom pathway). Both methods afforded the desired ligand **1** in reasonable yield (>60%). The crystal structure of ligand 1 is provided in the Supporting Information.

We expected that reaction of **1** with a low-valent late-metal precursor such as $[Rh(cod)Cl]_2$ would result in oxidative addition of one Si−H bond with loss of 1,5-cyclooctadiene (cod), similar to the methylated version of **1**.[13] However, reaction of **1** with $[Rh(cod)Cl]_2$ in acetonitrile led to a single major C_s-symmetric product (**2-cod**) with a bound cod ligand and no metal or silyl hydrides. The poor solubility of **2-cod** in acetonitrile allowed pure crystalline material to be obtained when the initial reaction mixture was left unperturbed overnight at ambient temperature. Single-crystal X-ray diffraction revealed a species with a tridentate, facially coordinated bis(phosphine)/chlorosilyl ligand and a bidentate cod ligand (Figure 1). The complex adopts an approximately trigonal bipyramidal geometry with apical silyl and olefin ligands.
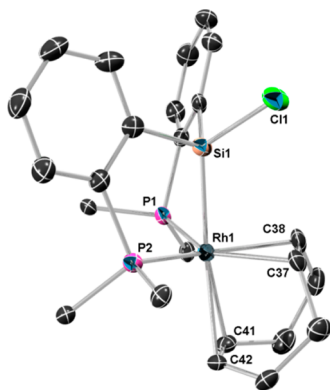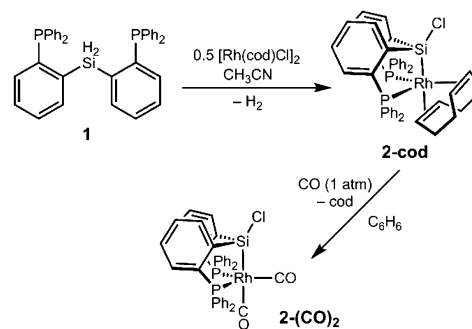
Figure 1. Solid-state structure of $(^{Ph}P_2^{Ar}SiCl)Rh(cod)$ (**2-cod**) with thermal ellipsoids at the 50% probability level and hydrogen atoms and phosphine phenyl substituents (except for *ipso* carbons) omitted for clarity. Selected bond lengths (Å): Rh1−Si1, 2.2791(9); Rh1−P1, 2.3639(8); Rh1−P2, 2.3134(8); Si1−Cl1, 2.1188(11).

Solvent plays an important, though currently undetermined, role in the formation and degradation of **2-cod**. Attempted metalation of the $(^{Ph}P_2^{Ar}Si)H_2$ ligand in solvents other than acetonitrile (e.g., benzene and dichloromethane) led to the formation of numerous products from which **2-cod** could not be cleanly isolated. Furthermore, though **2-cod** could be prepared by reaction in acetonitrile, it was unstable for prolonged periods under these conditions. We suspect that both the formation and decomposition of **2-cod** rely on the lability of the cod ligand, requiring either partial or total dissociation in order to metalate ligand **1** and lose H_2. Such a process is facilitated in the presence of donor solvents such as acetonitrile, where **2-cod** and the intermediates in its formation may be in equilibrium with mono- or bis(acetonitrile) adducts.

Further evidence for the lability of the cod ligand in **2-cod** was provided by the reaction of **2-cod** with carbon monoxide (Scheme 3). When a sample of **2-cod** in benzene was exposed to excess CO (1 atm), slow conversion (17 h) to a new C_s-symmetric product was observed along with release of cod. The presence of two carbonyl ligands was suggested by ^{13}C NMR spectroscopy (δ 200.9 (dt, $^1J_{RhC}$ = 70 Hz, $^2J_{PC}$ = 26 Hz), 198.0 (dt, $^1J_{RhC}$ = 49 Hz, $^2J_{PC}$ = 14 Hz)) and IR spectroscopy (ν_{CO} 1974, 2025 cm^{-1}). The identity of the new complex as

Scheme 3

$(^{Ph}P_2^{Ar}SiCl)Rh(CO)_2$ (**2-(CO)$_2$**) was confirmed by single-crystal X-ray diffraction (Figure 2). The slow conversion of **2-**
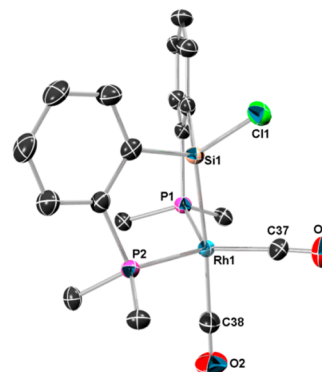
Figure 2. Solid-state structure of $(^{Ph}P_2^{Ar}SiCl)Rh(CO)_2$ (**2-(CO)$_2$**) with thermal ellipsoids at the 50% probability level and hydrogen atoms and phosphine phenyl substituents (except for *ipso* carbons) omitted for clarity. Selected bond lengths (Å): Rh1−Si1, 2.3375(4); Rh1−P1, 2.3467(4); Rh1−P2, 2.3267(3); Si1−Cl1, 2.1122(3); Rh1−C37, 1.9119(3); Rh1−C38, 1.9397(3).

cod to **2-(CO)$_2$** without any observed intermediates suggests that the first CO substitution is slow and likely irreversible, followed by a fast second substitution to afford **2-(CO)$_2$**.

The geometric parameters of **2-(CO)$_2$** are similar to those of **2-cod**, though the Rh−Si bond is ca. 0.06 Å longer in **2-(CO)$_2$**, likely due to the competing trans influences of the apical CO and silyl ligands. For the same reason, the axial Rh−CO bond is ca. 0.03 Å longer than the equatorial Rh−CO bond. Weakening of the Rh−Si bond upon substitution of CO for cod is supported by a decrease in the one-bond Si−Rh coupling constant from 38 to 23 Hz, as observed by ^{29}Si NMR spectroscopy.

The formation of **2-cod** from ligand **1** and $[Rh(cod)Cl]_2$ supports the feasibility of a scheme invoking reversible migrations of X-type ligands to and from silicon, as shown in Scheme 1b, since the polydentate silyl ligand can engage in an efficient halide abstraction from Rh without dissociation. Redistribution of silicon substituents at transition metals leading to chlorosilyl complexes is known.[14] A particularly relevant example comes from the work of Osakada et al. on the reactions of diarylsilanes with $[Rh(PMe_3)_4]Cl$,[14a] where the formation of a chlorosilylrhodium(III) dihydride complex was observed to proceed via consecutive Si−H oxidative addition, Si−Cl reductive elimination, and Si−H oxidative addition.

By analogy with Osakada's work, we currently favor a mechanistic proposal where Si−H oxidative addition to the Rh(I) precursor is followed by Si−Cl reductive elimination and

then Si−H oxidative addition and H_2 elimination (or σ-complex-assisted metathesis where the η^2-Si−H adduct produces an η^2-H_2 complex without oxidative addition).[15] It is also possible to invoke a silylene intermediate in the formation of **2-cod**, where Si−H oxidative addition would be followed either by a second oxidative addition or a 1,2-elimination of H_2 to form an electrophilic silylene followed by 1,2-migration of chloride. Silylenes have been invoked as intermediates in related formations of silicon−heteroatom bonds,[14c,16] but we currently do not have sufficient evidence to distinguish between the mechanisms.

The formation of a chlorosilyl pincer-type complex from a rhodium(I) chloride precursor suggested that differentially substituted silyl pincers could be obtained by double Si−H activation and H_2 elimination with Rh(I) precursors containing other halides or pseudohalides. In fact, reaction of **1** with $[Rh(nbd)_2][OTf]$ (nbd = norbornadiene) in dichloromethane quantitatively affords the corresponding triflatosilyl complex ($^{Ph}P_2{}^{Ar}SiOTf$)Rh(nbd) (**3**; Scheme 4). Though no intermediates are observable, **3** likely forms by triflate trapping of a cationic silylene intermediate.

Scheme 4
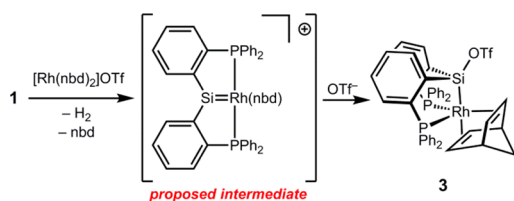
Though decomposition of **3** during attempted crystallization prevented structural characterization, multinuclear NMR experiments confirmed that it is the structural relative of **2-cod**. Triflate substituents on silyl ligands are known to form weak bonds with silicon, in some cases leading to an equilibrium between triflatosilyl and cationic silylene complexes.[17] In this case, substitution of triflate for chloride leads to a ca. 20 ppm downfield shift of the ^{29}Si NMR signal for **3** relative to **2-cod** (98 ppm versus 79 ppm), with a concomitant increase in one-bond rhodium−silicon coupling from 38 to 48 Hz.

Chlorosilyl and triflatosilyl complexes are often readily functionalized with various nucleophiles[18] and are known to serve as precursors to silylenes via chloride or triflate abstraction.[19] Studies to these ends are currently underway in our laboratory.

($P_2{}^NSi$)H_2 Ligand Synthesis and Reactivity. Given the propensity of ligand **1** to abstract chloride from rhodium, we wondered whether attachment of π-donating nitrogen groups might render a pincer-type silylene complex accessible by making silicon less electrophilic. Although no examples have been reported of double Si−H activation to make N-heterocyclic silylene (NHSi) ligands, results from Berry's laboratory[20] regarding NHSi formation by combined Si−Cl/Si−H activation suggested that a diamino(dihydro)silane might serve as a suitable precursor for a metal/NHSi complex.

Inspired by related syntheses of PBP boryl pincer ligands by Nozaki,[21] we targeted ($P_2{}^NSi$)H_2 ligands such as **4**,[22] which required an appropriate silicon electrophile for installing the two Si−N linkages. Although $SiCl_4$ gave complicated mixtures of products, we found that (teeda)SiH_2Cl_2[12] reacts cleanly with the appropriate bis(phosphine) diamine to form ($^{tBu}P^NSi$)H_2 (**4**)

quickly and quantitatively (eq 1). A convenient feature of (teeda)SiH_2Cl_2 for this reaction is that the coordinated diamine
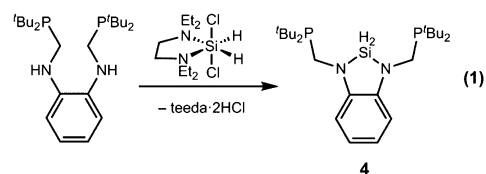
serves as an internal base that receives the 2 equiv of HCl generated during the reaction.

In spite of the reduced electrophilicity at silicon, ligand **4** reacts with Rh(I) precursors in a manner similar to diaryl-substituted **1**. For instance, mixing **4** with $Rh(Cl)(PPh_3)_2(CO)$ in THF followed by modest heating (50 °C, 12 h) leads to the generation of chlorosilyl complex **5** along with H_2 (1 equiv) and PPh_3 (2 equiv) without observable intermediates (Figure 3).[23] Complex
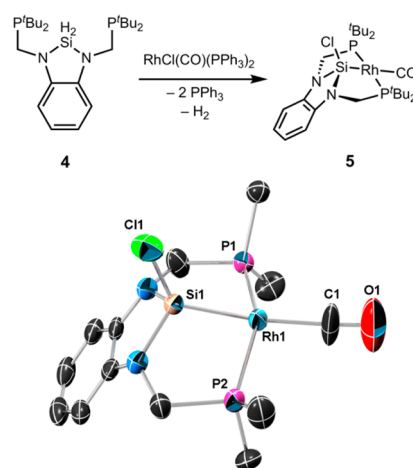
Figure 3. Reaction of ligand **4** and $RhCl(CO)(PPh_3)_2$ to give chlorosilyl complex **5** and the solid-state structure of **5** with thermal ellipsoids at the 50% probability level and hydrogen atoms and phosphine *tert*-butyl substituents (except quaternary carbons attached to phosphorus) omitted for clarity. Selected bond lengths (Å): Rh1−Si1, 2.2696(12); Rh1−C1, 1.907(7); Rh1−P1, 2.3283(13); Rh1−P2, 2.3233(13); Si1−Cl1, 2.0942(15); C1−O1, 1.114(9).

5 adopts an approximately square planar geometry, with the phosphine donors pulled slightly down and away from the plane. The Rh−Si, Rh−P, and Si−Cl bond lengths in **5** are similar to those in **2-cod** and **2-(CO)$_2$**. Complex **5** also exhibits a single intense infrared stretch for the CO ligand (1966 cm^{-1}).

Complex **5** may be formed either by a series of oxidative addition (Si−H) and reductive elimination (Si−Cl) reactions or by initial Si−H oxidative addition followed by 1,2-elimination of H_2 and 1,2-chloride migration to afford the observed product. The second mechanism, which would invoke an N-heterocyclic silylene intermediate, is consistent with other studies indicating that free N-heterocyclic silylenes will insert into Pd−Cl,[24] Pt−Cl,[25] and Cu−O[26] bonds to afford N-heterocyclic silyl species such as **5**. Experiments are underway to determine whether X-type-ligand migration can be prevented by substitution of chloride with a bulky alkyl or aryl ligand.

Conclusions. Complexes **2**, **3**, and **5** serve as the first examples of pincer-type complexes employing central chlorosilyl and triflatosilyl donors and are unusual examples of polydentate ligands incorporating halo- and pseudohalosilyl donors.[27] These

studies provide preliminary evidence for a cooperative role that silicon and other electropositive main-group elements may play in reactions with electron-rich late transition metals.[1g,i,28] Thus, the proligands **1** and **4** and their resulting Rh complexes offer distinct routes to systems for possible applications in M/Si cooperative reactivity. Ongoing investigations in our laboratory will focus on the use of complexes such as **2**, **3**, and **5** as precursors to pincer-type silylene complexes as well as modification of the Si−Cl and Si−OTf linkages.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving detailed experimental procedures and characterization data, including NMR spectra, for all reported complexes, a table giving crystallographic parameters, and CIF files giving crystallographic data for complexes **1**, **2-cod**, **2-(CO)₂**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interests.

■ ACKNOWLEDGMENTS

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(23) Complex **5** generally formed and cocrystallized with small quantities (<5%) of a chemically similar impurity that has not yet been identified. Because removal of this side product by recrystallization or other methods was not typically feasible, we have not yet been able to obtain analytically pure material but provide full characterization for **5** in the Supporting Information.
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