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'Hemilabile' silyl pincer ligation: platinum group PSiN complexes and triple C–H activation to form a (PSiC)Ru carbene complex†

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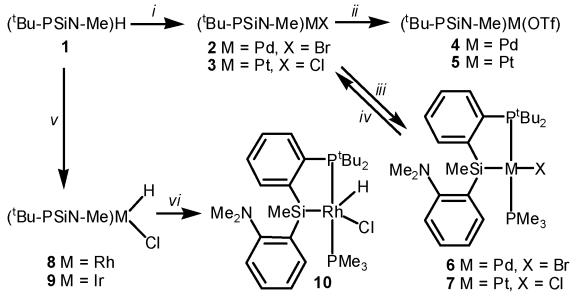
The first example of PSiN mixed-donor silyl pincer ligation is described. Studies involving platinum group metal complexes of [(2-^{t}Bu$_2$*P*C$_6$H$_4$)(2-Me$_2$*N*C$_6$H$_4$)*Si*Me]$^-$ (^{t}Bu-PSiN-Me) confirmed that the ligand amino donor is labile. Within the coordination sphere of Ru, ^{t}Bu-PSiN-Me is transformed into a PSiC ligand *via* multiple C-H bond activation events.

Transition metal pincer complexes supported by LXL-type (L = neutral donor, X = anionic donor) ligands are of substantial interest due to the remarkable stoichiometric and catalytic reactivity exhibited by such complexes.[1] While PCP, NCN, and PNP pincer ligation has been widely explored in this context, significant effort has also been devoted to the development of alternative pincer architectures.[1,2] In this regard, there has been increased interest in the chemistry of pincer complexes supported by PCN or PNN ligands that contain both hard (N) and soft (P) neutral donors.[3] Upon complexation to electron-rich late metal centers, such ligands have been shown to exhibit hemilabile[4] coordination involving the L-donors due to the more labile amine donor, which has been demonstrated to lead to unique reactivity.[3]

We have recently reported on the synthesis and reactivity of complexes featuring bis(phosphino)silyl ligation of the type [κ^3-(2-R$_2$*P*C$_6$H$_4$)$_2$*Si*Me]$^-$ (R-PSiP),[5,6] including rare examples of trigonal pyramidal Ru complexes,[5a] Ir species that undergo C–H and N–H bond activation,[5b,c] and Group 10 complexes that undergo reversible sp^2–sp^3 and sp^3-sp^3 C–Si bond cleavage.[5d] Our group, as well as that of Iwasawa, has also demonstrated the catalytic utility of PSiP ligation, including examples of ketone transfer hydrogenation,[5e] dehydrogenative borylation of alkenes,[6a] and hydrocarboxylation of alkenes[6b] and allenes.[6c] The synthesis and reactivity of NSiN pincer species has also been investigated.[7] However, no previous example of PSiN pincer ligation has been reported. Given the unique reactivity properties and catalytic utility of PSiP and NSiN pincer species, we viewed hemilabile PSiN-ligated complexes as being attractive targets of inquiry. We report herein on the establishment of PSiN ligation, including the synthesis of Ru, Rh, Ir, Pd and Pt complexes derived from the new PSiN silyl pincer precursor [(2-^{t}Bu$_2$*P*C$_6$H$_4$)(2-Me$_2$*N*C$_6$H$_4$)*Si*Me]H (^{t}Bu-PSiN-Me)H). Our preliminary studies confirm that the amino donor of the ^{t}Bu-PSiN-Me ligand is indeed labile. Furthermore, we disclose herein that within the coordination sphere of Ru, the ^{t}Bu-PSiN-Me ligand is transformed into a PSiC ligand by a process involving multiple C–H bond activation events.

Our synthetic strategy for the preparation of PSiN-type ligands involved the synthesis of [2-(NMe$_2$)C$_6$H$_4$]SiMeHCl, which was achieved by the reaction of [2-(NMe$_2$)C$_6$H$_4$]MgBr with excess MeSiHCl$_2$. The tertiary silane (^{t}Bu–PSiN–Me)H (**1**) was prepared in 78% yield by the reaction of [2-(NMe$_2$)C$_6$H$_4$]-SiMeHCl with 2-(^{t}Bu$_2$P)C$_6$H$_4$Li.

Group 10 complexes of the type (^{t}Bu–PSiN–Me)MX (**2**, M = Pd, X = Br; **3**, M = Pt, X = Cl) were prepared by the reaction of **1** with either PdBr$_2$ or (COD)PtCl$_2$ (COD = 1,5-cyclooctadiene) in the presence of Et$_3$N (Scheme 1). The room temperature ^{1}H NMR (benzene-d_6) spectra of **2** and **3** each feature a broad singlet corresponding to the ligand N*Me*$_2$ protons (**2**: 3.17 ppm; **3**: 3.22 ppm). At low temperature, this resonance decoalesces (toluene-d_8, 218 K: for **2**, 3.30 and 3.05 ppm; for **3**, 3.29 and 3.01 ppm), which is indicative of inequivalent N*Me* groups in square planar complexes of the type κ^3-(^{t}Bu-*PSiN*-Me)MX. These lineshape changes are consistent with a dynamic process involving decomplexation of the amine arm and inversion and



Scheme 1 Synthesis of Group 9 and 10 ^{t}Bu-PSiN-Me complexes. (i) for M = Pd, PdBr$_2$; for M = Pt, (COD)PtCl$_2$ (COD = 1,5-cyclooctadiene); Et$_3$N; (ii) AgOTf; (iii) PMe$_3$; (iv) M = Pd, BPh$_3$; (v) 0.5 [(COD)MCl]$_2$; (vi) PMe$_3$.

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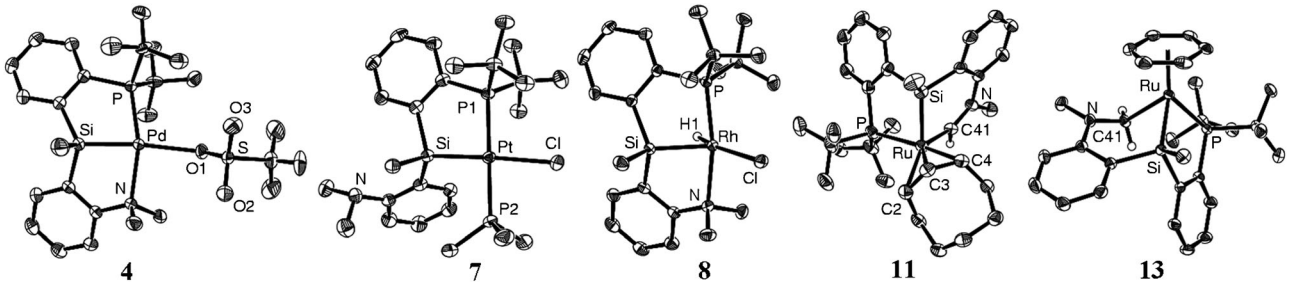


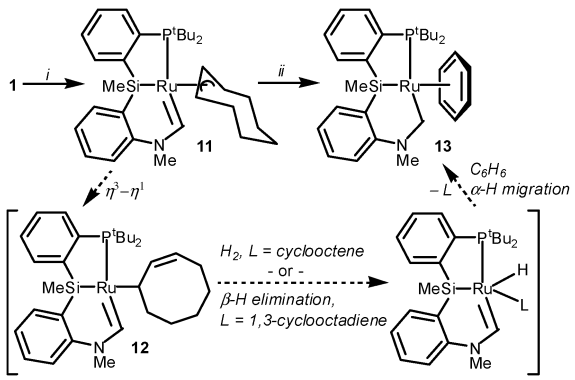
Fig. 1 ORTEP diagrams for **4**·0.5C_6H_6, **7**, **8**, **11**, and **13** shown with 50% ellipsoids. Solvate molecules and selected H-atoms have been omitted for clarity. Bond lengths (Å) and angles (°) for **4**·0.5C_6H_6: Pd-P 2.2731(4), Pd-Si 2.2336(4), Pd-N 2.2345(12), Pd-O1 2.3518(11), P-Pd-N 157.86(4), Si-Pd-O1 168.92(3); for **7**: Pt-P1 2.3188(8), Pt-P2 2.3026(8), Pt-Si 2.3077(9), Pt-Cl 2.4846(8), Cl-Pt-Si 176.86(3), P1-Pt-P2 179.36(3); for **8**: Rh-Si 2.2175(4), Rh-P 2.2421(4), Rh-N 2.2349(12), Rh-Cl 2.4365(4), P-Rh-N 163.70(3), Si-Rh-H1 67.4(9), Cl-Rh-Si 132.103(14); for **11**: Ru-Si 2.2461(5), Ru-P 2.3698(4), Ru-C41 1.9101(15), N-C41 1.353(2), Ru-C2 2.2752(16), Ru-C3 2.1737(15), Ru-C4 2.2115(16), P-Ru-C41 97.47(5); for **13**: Ru-P 2.3458(4), Ru-Si 2.3322(4), Ru-C41 2.1558(13), N-C41 1.4653(18), P-Ru-Si 83.001(13), P-Ru-C41 88.42(4). Si-Ru-C41 74.16(4).

rotation at N, which renders the N*Me* groups equivalent at elevated temperatures ($\Delta G^{\ddagger}$ = 12 kcal mol^{-1} for **2**; $\Delta G^{\ddagger}$ = 13 kcal mol^{-1} for **3**). This phenomenon highlights the labile coordination of the amino donor of the ^{t}Bu-PSiN-Me ligand. Treatment of **2** and **3** with AgOTf led to the formation of (^{t}Bu-PSiN-Me)M(OTf) (M = Pd, **4**; M = Pt, **5**) species. The structure of **4** was confirmed by X-ray diffraction analysis (Fig. 1) and indicates approximate square planar geometry at Pd, with *trans*-disposed phosphino and amino donors. The Pd-Si distance of 2.2336(4) Å is short and falls outside the range characteristic of Pd–Si bond distances (2.26–2.64 Å).[8] As well, the Pd–O distance of 2.3518(11) Å is longer than the Pd–O distance in [κ^3-(2-$Me_2NC_6H_4)_2N$]PdOTf (2.1067(16) Å),[9] which highlights the strong *trans* influence of the silyl donor in **4**.

Treatment of **2** and **3** with PMe_3 led to selective decomplexation of the amine arm of the PSiN ligand and the formation of κ^2-(^{t}Bu-*PSi*N-Me)MX(PMe_3) (**6**, M = Pd, X = Br; **7**, M = Pt, X = Cl; Scheme 1). The ^{1}H NMR spectra of **6** and **7** each feature a sharp singlet resonance corresponding to the six equivalent NMe_2 protons of the uncoordinated amino ligand arm. The coordination of PMe_3 to the metal center was confirmed by use of ^{31}P NMR spectroscopy. The solid state structure of **7** (Fig. 1) indicates approximate square planar geometry at Pt, with the PMe_3 ligand coordinated *trans* to the phosphino ligand arm. Treatment of complex **6** with an equivalent of BPh_3 in benzene led to precipitation of Ph_3BPMe_3[10] and quantitative regeneration of **2** (Scheme 1). This sequence of reactions involving complexation of PMe_3 to **2** to form **6** followed by reformation of **2** upon reaction with BPh_3 further illustrates the hemilabile character of ^{t}Bu–PSiN–Me ligation.

In an effort to extend the coordination chemistry of ^{t}Bu–PSiN–Me ligation to Group 9 metals, complexes of the type (^{t}Bu-PSiN-Me)M(H)Cl (M = Rh, **8**; M = Ir, **9**) were prepared by the reaction of **1** with [(COD)MCl]$_2$. The room temperature ^{1}H NMR (benzene-d_6) spectra of **8** and **9** each feature two resonances corresponding to inequivalent N*Me* groups (for **8**: 3.06 and 2.96 ppm; for **9**: 3.17 and 2.94 ppm), consistent with coordination of the amine ligand arm to the metal center. Single-crystal X-ray diffraction analysis (Fig. 1 and S1†) established that complexes **8** and **9** both exhibit distorted square based pyramidal geometry with Si in the apical site. These structures are similar to those observed for (Cy-PSiP)M(H)Cl complexes, and feature acute Si–M–H angles (for M = Rh, 67.4(9)°; for M = Ir, 71.0(12)°) as was previously observed for the analogous Cy–PSiP ligated species (for M = Rh, 65.8(12)°; for M = Ir, 68.7(18)°).[5b] Treatment of **8** with PMe_3 led to the quantitative formation of κ^2-(^{t}Bu-*PSi*N-Me)Rh(H)(Cl)(PMe_3) (**10**), in keeping with the hemilabile character of ^{t}Bu-PSiN-Me. The solid state structure of **10** was confirmed using single-crystal X-ray diffraction analysis (Fig. S2†). No reaction was observed upon treatment of **10** with BPh_3.

Attempts to prepare (^{t}Bu-PSiN-Me)Ru complexes by the reaction of **1** with Ru^{II} starting materials such as $(PPh_3)_3RuCl_2$ and [(*p*-cymene)$RuCl_2]_2$ in the presence of Et_3N were largely unsuccessful, typically leading to the formation of multiple intractable products (^{31}P NMR). Conversely, heating **1** with one equiv. of (COD)Ru(2-methylallyl)$_2$ for 18 h at 85 °C (THF) led to the quantitative (^{31}P NMR) formation of a single new product (**11**). However, the NMR features of isolated **11** are not consistent with the formation of a (^{t}Bu-PSiN-Me)Ru(2-methylallyl) complex. Rather, the ^{1}H and ^{13}C NMR spectra of **11** indicate surprisingly the formation of a cyclooctenyl (PSiC)Ru carbene complex resulting from C–H bond activation of an N*Me* group in the ^{t}Bu-PSiN-Me ligand and of the 1,5-cyclooctadiene, respectively (Scheme 2). The Ru=CH_2 unit exhibits diagnostic ^{13}C and ^{1}H NMR resonances (benzene-d_6) at 250.8 and 13.11 ppm, respectively. The ^{1}H NMR spectrum of **11** also revealed the presence of only one N*Me* group (2.82 ppm, s, 3H), which is consistent with the proposed formulation of **11**. The structure of **11** was confirmed by X-ray diffraction analysis (Fig. 1).



Scheme 2 Synthesis of (PSiC)Ru complexes. (i) (COD)Ru(2-methylallyl)$_2$; (ii) 1 atm H_2, 75 °C, 3 days *or* 110 °C, 10 days, both in C_6H_6.

The geometry at Ru is distorted square-pyramidal with Si in the apical site. The Ru–C41 distance of 1.9101(15) Å is consistent with related Ru carbene complexes.[11a,b] The short N–C41 bond distance of 1.353(2) Å (*cf.* N–C42 = 1.468(2) Å) and planar environment at N are indicative of π-bonding between nitrogen and C41.

Remarkably, the formation of **11** requires three C–H bond activation steps, as well as Si–H bond activation at a single Ru center. We propose that the formation of the carbene fragment may occur *via* C–H bond activation of the Ru-bound NMe_2 ligand arm in a putative κ^3-(^{t}Bu-*PSiN*-Me)Ru(η^1-2-methylallyl)(COD) intermediate to form a cyclometalated species, which undergoes α–H elimination to form the carbene complex (Scheme S1†). Double C–H bond activation of a Me group by a Ru^{II} center to generate a carbene complex has been reported,[11,12] and analogous mechanisms have been proposed.[11,12] Complex **11** is the first reported example of a PSiC ligated metal species.

We envisioned that **11** could serve as a source of the 14-electron species **12** upon undergoing an η^3 to η^1 rearrangement of the cyclooctenyl ligand (Scheme 2). Indeed, the reaction of a benzene solution of **11** with an atmosphere of H_2 resulted in the formation of the η^6-benzene Ru^{II} alkyl complex **13** with concomitant formation of cyclooctene (Scheme 2). The ^{1}H NMR spectrum of **13** (benzene-d_6) no longer features a downfield-shifted carbenic resonance; rather, diastereotopic Ru-CH_2N protons are observed as multiplets at 4.58 and 1.92 ppm. The solid state structure of **13** was confirmed by X-ray diffraction analysis (Fig. 1). The Ru–C41 distance of 2.156(1) Å is consistent with a Ru–C single bond, while the N–C41 bond length of 1.465(2) Å is indicative of a N–C single bond.

We propose that the formation of **13** occurs *via* the net reaction of **12** with H_2 to form a cyclooctene hydride Ru species, which liberates cyclooctene in benzene solution to form a benzene adduct (Scheme 2). Subsequent α–H migration from Ru to the carbenic carbon leads to the formation of **13**. Interestingly, **13** can also be synthesized by simply heating a benzene solution of **11** at 110 °C for ten days. The mechanism for the formation of **13** in the absence of H_2 likely involves *β*–H elimination in **12** to form a 1,3-cyclooctadiene hydride Ru species, which subsequently liberates cyclooctadiene to form a benzene adduct (Scheme 2).

In summary, the synthesis of the first examples of PSiN-ligated platinum group pincer complexes has been provided. The amino donor of the ^{t}Bu-PSiN-Me ligand is labile and is displaced from the metal coordination sphere by a better donor, such as PMe_3, to form κ^2-(^{t}Bu-*PSi*N-Me) species. The pincer structure is reformed upon abstraction of PMe_3 from the metal center. This reversible coordination of the amine pincer arm is anticipated to render PSiN-ligated complexes responsive to the changing electronic and coordinative requirements at a metal center that arise during substrate transformations, and may provide access to new and/or enhanced reactivity. We are currently exploring the influence of this hemilability on the catalytic behavior of PSiN-ligated complexes and this will be the topic of future reports. We also observed that within the coordination sphere of Ru, **1** is transformed into a PSiC ligand in a process requiring overall three C–H bond activation steps, as well as Si-H bond activation, at a single metal center. This represents the first reported example of PSiC ligation, which also promises to provide access to reactive late metal species. The reactivity of such PSiC-ligated Ru complexes with E–H bonds is currently under investigation.

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