Platinum Catalysed Regioselective *ortho*-Silylation of Benzylideneamines *via* Intramolecular C–H Activation

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The Pt–P(OCH$_2$)$_3$CEt complex catalyses the *ortho*-silylation of benzylideneamines with disilanes *via* intramolecular C–H activation; both mono- and bis-silylated products are obtained.

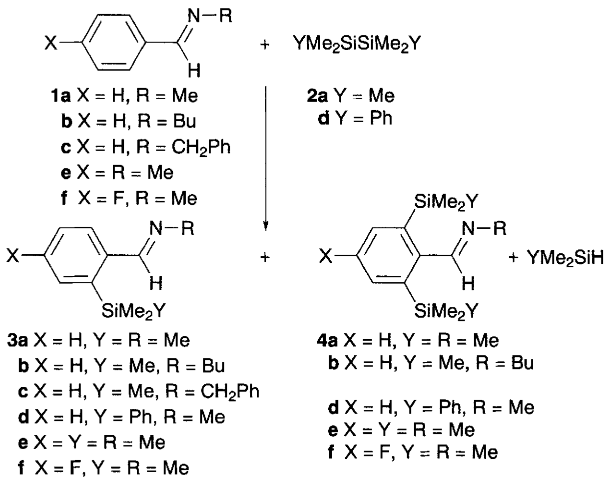
A plethora of stoichiometric reactions involving C–H cleavage have appeared in the literature;[1] examples of intramolecular C–H activation are particularly abundant. However, for this method to be synthetically useful, systems have to be devised where the metal is used as a catalyst. A major problem with such a design is the regeneration of the metal into an oxidation state which will allow it to be efficient towards C–H cleavage. There are very few examples[2] where catalytic reactions have been developed with any real success; yields, turnovers and selectivity are generally low. Notable exceptions include the recent work of Murai *et al.*[3] and Kim *et al.*[4] involving the coupling of aromatic C–H and alkenes.

Organosilicon compounds have proved to be useful reagents in organic synthesis and as precursors to silicon-containing polymers.[5] We previously reported the direct silylation of arenes, *via* catalytic C–H activation, using RhCl(CO)(PMe$_3$)$_2$ under irradiation[6] and the platinum catalysed coupling of aryl C–H bonds with *o*-bis(dimethylsilyl)benzene.[7] Ishikawa has also reported the coupling of silanes with C–H bonds.[8] In the course of our work on the double silylation of unsaturated carbon–heteroatom bonds, we discovered the $\frac{1}{2}$ Pt$_2$(dibenzylideneacetone)$_3$–$\frac{2}{3}$P(OCH$_2$)$_3$CEt system-catalysed regioselective *ortho*-silylation of aromatic imines with disilanes.

In a typical reaction *N*-benzylidenemethylamine **1a** (0.5 mmol), hexamethyldisilane **2a** (0.5 mmol), Pt catalyst (0.01 mmol) and toluene (0.1 ml) were heated at 160 °C for 120 h in a sealed tube, giving *N*-(2-trimethylsilylbenzylidene)methylamine **3a** in 38% yield and *N*-[2,6-bis(trimethylsilyl)benzylidene]methylamine **4a** in 54% yield (Scheme 1).† When the reaction was performed in a sealed NMR tube, ^{1}H NMR analysis indicated a small amount of dissolved trimethylsilane (δ 0.02, d, $^3J_{HH}$ 3.6 Hz) formed as a co-product.‡ Selectivity for the mono-silylated imine could be enhanced by employing an excess of **1a**, and conversely a higher yield of the bis-silylated imine was achieved with excess **2a**, Table 1.

In relation to the mechanistic investigations (*vide infra*), reactions were also performed with *para*-substituted imines. If the reaction is considered in terms of electrophilic C–H activation, the results appear unusual; electron-donating substituents retarded the reaction, whereas electron-withdrawing groups accelerated it to give nearly 90% combined yield of the mono- and bis-silylated products under identical conditions. The reaction also proceeded with other aldimines, *N*-benzylidenebutylamine **1b** giving the mono-silylated and bis-silylated products in 19% and 3% yields, respectively (160 °C, 120 h). GC and GC–MS analyses indicated that the mono-silylated product was formed in about 3% yield when *N*-benzylidenebenzylamine **1c** was employed under the same conditions. In the reaction between 1,2-diphenyl-1,1,2,2-tetramethyldisilane **2d** and **1a**, the *ortho*-silylated product was formed in 15% yield. GC analysis indicated that an equimolar amount of phenyldimethylsilane was produced;‡ products arising from redistributions§ were also observed. Only a slight trace of the bis-silylated product was detected by GC–MS. The lower yields in the reactions involving **1b**, **c** and **2d** can presumably be attributed to steric hindrance.

The oxidative addition of disilanes to Pt^0 yielding bis(silyl)platinum species and the high catalytic activity of the $\frac{1}{2}$ Pt$_2$(dba)$_3$–$\frac{2}{3}$ P(OCH$_2$)$_3$CEt system have been demonstrated.[9] Accordingly, one can imagine a mechanism that involves *ortho*-metallation of an imine with a Pt(SiMe$_3$)$_2$ species, reductive elimination of a hydrosilane and further reductive elimination of a silylated imine, as depicted in Scheme 2. The *ortho*-metallation of aromatic imines with Pt^{II} is well documented. In the closely related stoichiometric reactions reported by

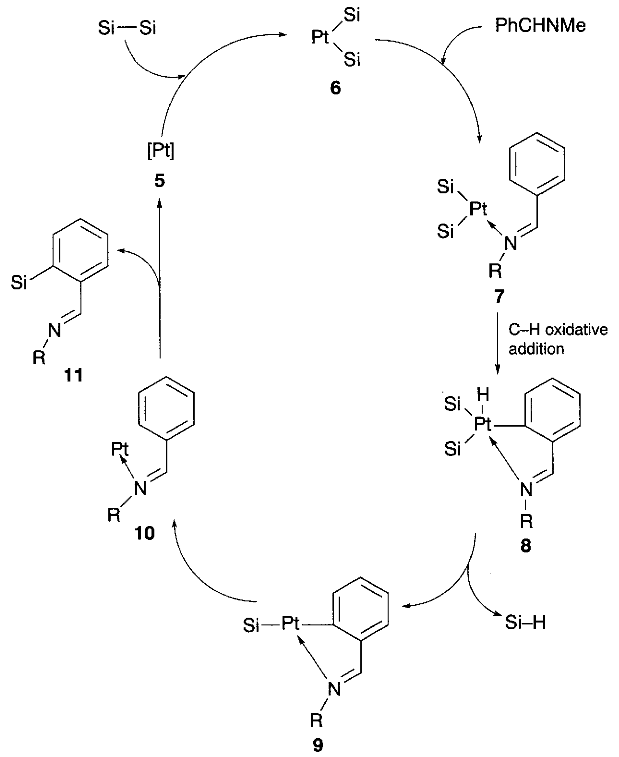


Scheme 1 *Reagents and conditions*: $\frac{1}{2}$ Pt$_2$(dta)$_3$–$\frac{2}{3}$ P(OCH$_2$)$_3$CEt, 160 °C

Table 1 Platinum catalysed *ortho*-silylation of benzylideneamines at 160 °C

Imine	Disilane	Imine : Disilane	Conversion (%)	*t*/h	Yield[a] (%) 3	4
1a (X = H, R = Me)	**2a** (Y = Me)	1 : 1	65	120	**3a** 38	**4a** 27[b]
1a	**2a**	4 : 1	25	120	**3a** 82[c]	**4a** 9[c]
1a	**2a**	1 : 4	75	120	**3a** 23	**4a** 52
1b (X = H, R = Bu^n)	**2a**	1 : 1	23	120	**3b** 19	**4b** 3
1c (X = H, R = CH$_2$Ph)	**2a**	1 : 1	3	120	**3c** 3	—
1a	**2d** (Y = Ph)	1 : 1	15	120	**3d** 15[d]	**4d** trace
1a	**2a**	1 : 2	69	20	**3a** 31	**4a** 38
1e (X = Me, R = Me)	**2a**	1 : 2	54	20	**3e** 29	**4e** 20
1f (X = F, R = Me)	**2a**	1 : 2	90	20	**3f** 23	**4f** 66

[a] Unless stated differently yields are based on amount of imine charged. [b] Yield 54% based on disilane charged. [c] Yields based on disilane charged. [d] GC and GC–MS analysis indicated an equimolar amount (15%) of PhMe$_2$SiH was produced.



Scheme 2 Phosphine ligands that may be bound to platinum are omitted

Puddephatt and Crespo *et al.*,[10] Pt^{II}Me$_2$ sulfide complexes react with aromatic imines *via* Pt^{IV} species to give *ortho*-metallated Pt^{II}Me complexes with extrusion of a methane molecule. The proposed transformations of complexes **6** ⟶ **7** ⟶ **8** ⟶ **9** are in full agreement with these precedents.

The only puzzling observation that merits further consideration is the unusual *para*-substituent effect. There are two possibilities for *ortho* C–H activation: electrophilic substitution by an electron deficient platinum and oxidative addition of the C–H bond to an electron rich metal centre. Generally, aromatic C–H activation with Pt^{II} species has been assumed to involve electrophilic substitution.[1] Numerous examples[1,11] indicate that this supposition is reasonable for species like $[PtCl_4]^{2-}$, as the platinum is considerably electron deficient. This however, is not true for a Pt^{II}(SiMe$_3$)$_2$–phosphine species, where the silyl groups are electron donating in nature. The platinum centre is envisioned to be much more electron rich than the formal valence state suggests. Accordingly the seemingly unusual substituent effect in the present catalysis can be attributed to oxidative addition with an electron rich metal centre being a crucial step, rather than the electrophilic attack of a 'high valent' species.¶ Similar arguments are found in recent publications on calculations of Pt–Si species[12] and on intermolecular aromatic C–H bond activation with Ta–Si complexes.[13] In our own recent work, it seemed apparent that a bis(silyl)platinum species was reacting as an electron rich system in the coupling of aryl C–H with *o*-bis(dimethylsilyl)benzene.[7]

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Footnotes

† Yields were determined by GC analysis with decane as an internal standard, and are based on the amount of disilane added. The compounds were isolated by kugelrohr distillation.

Selected data for **3a**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.34 (s,9H, Si*Me*$_3$), 3.52 (d, $^4J_{HH}$ 1.4 Hz, 3H, N*Me*), 7.35–7.44 (m, 2H, aromatic), 7.56–7.60 (m, 1H, aromatic), 7.85–7.91 (m, 1H, aromatic), 8.57 (d, $^4J_{HH}$ 1.4 Hz, C*H*=N); ^{13}C NMR (75 MHz, CDCl$_3$) δ 0.9 (3C, Si*Me*$_3$), 48.1 (N*Me*), 127.3 129.3 (2C), 134.7, 140 (*ipso*-C), 141.6 (*ipso*-C), 162.9 (*C*=N); ^{29}Si NMR (59.6 MHz, CDCl$_3$) δ −4.77; IR (neat) ν/cm^{-1} 2956, 2886, 1665, 1649, 1253, 841.

For **4a**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.29 (s, 18H, 2Si*Me*$_3$), 3.49 (d, $^4J_{HH}$ 1.5 Hz, 3H, N*Me*), 7.36 (t, 1H, aromatic), 7.62 (d, 2H, aromatic), 8.68 (q, $^4J_{HH}$ 1.5 Hz, 1H, C*H*=N); ^{13}C NMR (75 MHz, CDCl$_3$) δ 1.25 (6C, Si*Me*$_3$), 47.0 (N*Me*), 127.6, 135.8 (2C), 139.3 (2 *ipso*-C), 148.0 (*ipso*-C), 164.3 (C=N); ^{29}Si NMR (59.6 MHz, CDCl$_3$) δ −5.3; IR (KBr disk) ν/cm^{-1} 2960, 2902, 1661, 1251, 874, 835.

‡ Hydrosilylation products could not be detected. Hence, the extruded hydrosilane does not play a further role in the catalytic cycle. In a separate experiment, **1a** was treated with phenyldimethylsilane in the presence of the same catalyst system; **1a** was completely recovered after heating at 160 °C for 48 h.

§ GC–MS analysis suggested the formation of Ph$_2$SiMe$_2$ *m*/*z* 212 (M$^+$), PhSiMe$_3$ *m*/*z* 150 (M$^+$) and PhMe$_2$SiSiMePh$_2$ *m*/*z* 332 (M$^+$).

¶ The seemingly unusual substituent effect may be associated with other steps being rate-determining: proton loss after the electrophilic attack of platinum, or the reductive elimination **8**⟶**9**, for example. We thank the reviewer for the comment.

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