Synthesis of an \([(NHC)_2Pd(SiMe_3)_2]\) Complex and Catalytic \(cis\)-Bis(silyl)ations of Alkynes with Unactivated Disilanes**

Melvyn B. Ansell, Debbie E. Roberts, F. Geoffrey N. Cloke, Oscar Navarro,* and John Spencer*

In memory of Mike Lappert
Abstract: The novel complex cis-[(ITMe)₂Pd(SiMe₃)₂] (ITMe = 1,3,4,5-tetramethylimidazol-2-ylidene) has been synthesized by mild oxidative cleavage of Me₃SiSiMe₃ using [(ITMe)₂Pd]. The use of this complex as a catalyst for the cis-bis(silylation) of alkynes using unactivated disilanes is reported.

The transition metal catalyzed activation of disilanes for the synthesis of high-value organosilicon compounds has received significant amount of attention from industry and academia. Applications encompass the formation of silanes, [(ITMe)₂Pd(SiMe₃)₂], which exhibits a very small percent buried volume and a high α-donor character. The conventional synthetic route to 1 was established by Kuhn and co-workers. It involves the formation of the corresponding thione by a ring-forming double condensation of N,N-dimethyl thiourea and acetone, and subsequent reductive desulfurization of the thione using potassium metal, with an overall yield of about 76%. A thorough modification of the synthetic route, including a microwave-mediated cyclization step, allowed us to obtain 1 in 86% overall yield even on a gram scale (Scheme 1).

The second step involved the synthesis of [(ITMe)₂Pd(methallyl)Cl] (2). The synthesis of this complex has not been reported, although unsuccessful attempts were detailed by Cavell and co-workers. The conventional synthetic route to [(NHC)Pd(R-allyl)Cl] species involves the reaction of the corresponding [[Pd(R-allyl)Cl]₂] dimer with a free NHC. We found that reacting [[Pd(methallyl)Cl]₂] with a slight excess of 1 in toluene, initially at −25°C, and then warming to ambient temperature, led to the formation of 2 in 95% yield (Scheme 1).

[(ITMe)₂Pd] (3) has been proposed as the active catalytic species in a number of reactions. The only reported synthesis of 3 was achieved through metal vapor synthesis (MVS). Recently, Fantasia and Nolan used [(NHC)Pd(allyl)Cl] complexes as precursors to easily synthesize a series of [(NHC)Pd] complexes, suggesting that the solvent employed in these reactions (isopropanol) was also a reagent and essential to the mechanism of these transformations. Unfortunately, the application of this methodology to the synthesis of 3 resulted in the precipitation of large quantities

Scheme 1. Synthesis of 1 and 2. 2-Me-THF = 2-methyltetrahydrofuran.
of Pd black. Modifying this procedure by using isopropanol in stoichiometric quantities resulted in the first solution-based synthesis of 3, which was formed as a yellow crystalline precipitate. Its isolation, however, proved difficult because of its limited solubility in toluene, THF, and pyridine, and its instability in alcohols or halogenated solvents. Consequently, the reaction mixture was directly reacted with hexamethyldisilane at room temperature for 18 hours (Scheme 2). cis-[(ITMe)₂Pd(SiMe₃)₂] (4) was collected as an off-white solid in 62% yield.

To our knowledge, the bis(silylation) of disubstituted alkynes using hexamethyldisilane has not been reported. The stoichiometric reaction of 4 with diphenylacetylene at room temperature yielded the corresponding cis-bis(silylated) product 5 (Scheme 4) within 30 hours in quantitative yield (see the Supporting Information). This reaction also resulted in the quantitative formation of the novel complex [(ITMe)₂Pd(PhC≡CPh)] (6), which could be easily isolated after an n-hexane extraction. Compound 6 was fully characterized by NMR spectroscopy and elemental analysis. Single crystals of 6 were obtained from a saturated toluene solution upon cooling to -30 °C and the result of X-ray analysis is depicted in Figure 2, featuring a Y-shaped structure. There is a clear and expected elongation of the C≡C bond and a shortening of the C≡C–C bond when compared to free diphenylacetylene. To the best of our knowledge, this is the first example of an NHC/Pd₀ complex bearing an η²-bound

The reactivity of 4 was then investigated. A solution of 4 in C₆D₆ was heated to 85 °C and resulted in an intense yellow solution in less than 1.5 hours. ¹H NMR analysis showed the formation of hexamethyldisilane and 3 (Scheme 3). The formation of the reductive elimination products was limited to 69% conversion, even upon increasing the temperature and heating time, probably because of the recombination of the two products to form 4.
alkyne. This species can react with an excess of hexamethyldisilane at 50°C for over 5 days, resulting in the formation of 4 and 5 (Scheme 5).

With all this information in hand, we proceeded to the inclusion of all these organometallic species into a catalytic cycle. Diphenylacetylene and hexamethyldisilane were selected as model substrates for the initial optimization of the reaction parameters. To our delight, 100% stereoselective conversion into 5 (yield = 94%) was observed using 1 mol% of 4 (100°C for 24 h in C₆D₆). This reaction is the first reported catalytic synthesis of 5. To test the versatility of 4 towards a range of challenging electronics and sterics surrounding the C≡C bond, a series of internal alkynes and non-activated disilanes were also used as substrates. For instance, the reaction of diphenylacetylene and an excess of PhMe₂SiMe₂Ph yielded compound 7 (Scheme 6). The only synthesis reported for this compound involved the stoichiometric reaction of cis-[(PPh₂Me)₂Pt(SiMe₂Ph)₂] with diphenylacetylene. The novel compounds 8, 9, 10, and 11 were all synthesized as Z isomers from the corresponding unsymmetrical internal acetylenes and excess hexamethyldisilane. Compound 10 was synthesized with greater than 90% conversion into the desired product. However, its isolation from the crude reaction mixture proved troublesome, and after numerous attempts a maximum of 41% of the desired compound was obtained. The reaction of hexamethyldisilane with 1-phenyl-2-trimethylsilylacetylene resulted in the formation of 12 (49% yield), but it required a considerable increase in catalyst loading and reaction time. The only previous reported syntheses of 12 required either the stoichiometric addition of Grignard reagents with acetylenes or the addition of methyl lithium to a silyldisilacyclobutene. The protocol was applied to a terminal alkyn, phenylacetylene, affording compound 13, which was synthesized in a yield comparable to that of the best catalytic protocol in the literature. Unfortunately, the reaction of hexamethyldisilane with 2-heptyne under these reaction conditions gave very low conversion into the desired product (<5%).

The results from the catalytic reactions and the isolation of 4 and 5 prompted us to propose a mechanism for the catalytic cycle, in which 3 is the catalytically active species (Scheme 7). This 14 electron species can oxidatively add hexamethyldisilane, thus yielding 4, followed by a migratory insertion of a silyl group into the acetylene to give the corresponding vinyl-palladium-silyl complex. This complex would be stabilized by a weak interaction between the silicon from the vinylsilyl moiety and the palladium center, thus allowing a stereoselective reductive elimination to yield 5. The coordination of diphenylacetylene to 3 affords 6, which could be considered the resting state of 3.

![Scheme 5](image)

Scheme 5. Reaction of 6 with hexamethyldisilane.

![Scheme 6](image)

Scheme 6. Catalytic bis(silylation) reactions.

![Scheme 7](image)

Scheme 7. Proposed catalytic cycle for the bis(silylation) of internal acetylenes.
In conclusion, we have synthesized the first NHC-bearing complex resulting from the oxidative addition of hexamethyldisilane to a palladium center at room temperature. This complex was used as a precatalyst for the bis(silylation) of electronically and sterically challenging internal acetylenes using non-activated disilanes. A series of novel 1,2-disilylstilbenes were synthesized in high yield and with 100% Z stereoselectivity. Studies on the activity of 4 in this and other catalytic processes are currently ongoing in our laboratories.

Keywords: alkynes · N-heterocyclic carbene · palladium · silicon · synthetic methods

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[29] CCDC 1029150 (4) and 1029151 (6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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