Triphenylsilane

$\boxed{Ph_3SiH}$

[789-25-3] $C_{18}H_{16}Si$ (MW 260.43)
InChI = 1/C18H16Si/c1-4-10-16(11-5-1)19(17-12-6-2-7-13-17)18-14-8-3-9-15-18/h1-15,19H
InChIKey = AKQNYQDSIDKVJZ-UHFFFAOYAL

(reducing agent for esters, xanthates, and polychloroalkanes; protecting group for alcohols)

Physical Data: mp 47 °C; bp 152 °C/2 mmHg.
Solubility: sol most organic solvents.
Form Supplied in: white solid; commercially available.
Handling, Storage, and Precautions: this reagent is stable in air. Because the toxicogical properties are unknown, it should be handled in a well-ventilated fume hood. Contact with the eyes and skin should be avoided.

Original Commentary

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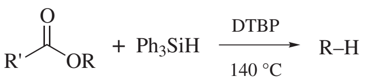
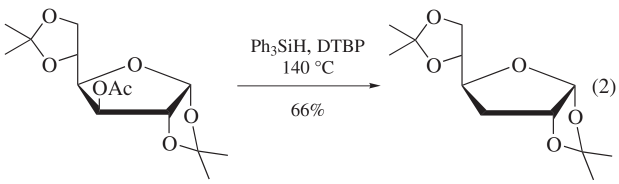
Deoxygenations. Ph_3SiH is a useful reducing reagent under radical conditions. Esters are reduced to hydrocarbons at 140 °C by Ph_3SiH in the presence of a radical generator, ***1,1-Di-tert-butyl Peroxide*** (DTBP) (eq 1).[1]



(1)

The best results are obtained with acetate esters compared with other esters, such as isobutyrate, pivalate, or benzoate. Acetates derived from primary, secondary, and tertiary alcohols are all reduced in high yield. Other silanes such as tripropylsilane and diphenylmethylsilane are not as effective, and other radical generators such as AIBN and dibenzoyl peroxide are not suitable for the deoxygenations.

This reaction can be applied to deoxygenation of carbohydrates. Thus both *O*-acetylfuranoses and -pyranoses can be converted to the corresponding deoxy sugars (eqs 2 and 3).[2]



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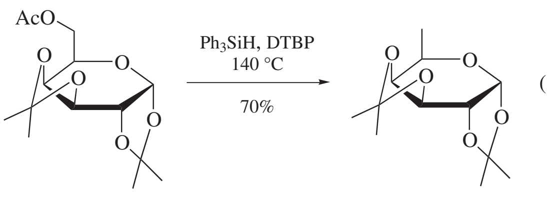
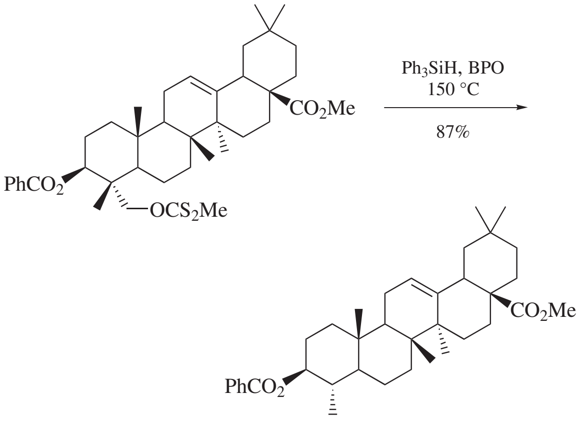


(3)

Xanthates (eq 4)[3] and perhaloalkanes[4] are also reduced by Ph_3SiH.

Ph_3SiH in combination with ***Trifluoroacetic Acid*** has been used for ionic deoxygenation of tertiary alcohols (eq 5).[5]

Protecting Group. Triphenylsilane is used in certain cases for the preparation of triphenylsilyl ethers, which serve as alcohol protecting groups.[6] The triphenylsilyl group is considerably more stable (about 400 times) than the TMS group toward acidic hydrolysis.[7]



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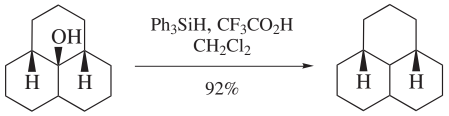

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First Update

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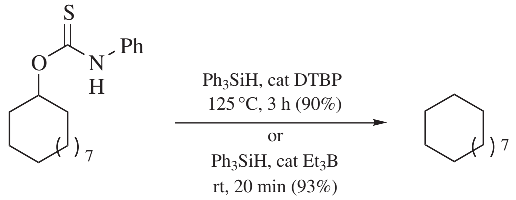
Introduction. In the years following the original EROS article on triphenylsilane, many new and improved uses of this reagent as a reducing agent for a variety of functional groups have appeared in the literature. Perhaps most prevalent among these recent studies have been investigations of triphenylsilane as a reagent for the transition metal-mediated hydrosilylation of alkenes, alkynes, and carbonyls. This update shall discuss these new findings, paying particular attention to instances where triphenylsilane is unique among other silanes for such functional group transformations.

Deoxygenations. Deoxygenations using Ph_3SiH and a radical initiator (i.e., DTBP) were shown in the previous EROS article to proceed for esters, xanthates, and perhaloalkanes (eqs 1–4) at elevated temperatures (~140 °C) in moderate yields. It has since been shown that DTBP-initiated deoxygenations of *N*-phenylthioxocarbamate-derived aliphatic alcohols can be achieved in excellent yield. Moreover, Et_3B facilitates silane reductions at lower temperatures, and thus the identical deoxygenation was achieved in 20 min at rt (eq 6).[8,9] This procedure has been extended to a variety of xanthates and thiocarbonates using Ph_3SiH and AIBN.[10] Likewise, decarbonylative reductions of a 2-pyridylmethyl ester can be achieved with $Ru_3(CO)_{12}$ and Ph_3SiH as the hydrogenation reagent (eq 7).[11]



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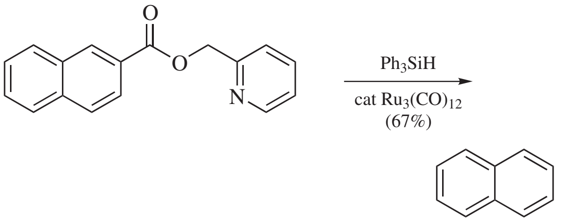

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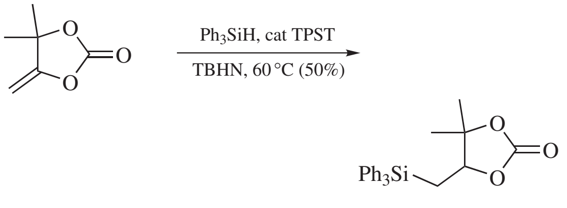
Hydrosilylations.[12] The addition of a triorganosilane across multiple bonds can be aided by a number of catalysts. The most commonly used triorganosilane is triethylsilane and the reader in referred to the EROS articles on Et_3SiH (see triethylsilane) for a more in depth analysis of the various catalyst systems employed for hydrosilylation reactions. This update shall detail some advancements not discussed in the aforementioned article and areas in which Ph_3SiH has proven to be a more (or less) appropriate triorganosilane. One general advantage of Ph_3SiH and other arylsilanes in C–Si bond forming reactions is the opportunity for subsequent Tamao–Fleming oxidation to afford the corresponding alcohols.[13]

Alkenes.

Radical Chain Hydrosilylations. Thiols such as *tert*-dodecanethiol have been shown to catalyze the radical-chain addition of Ph_3SiH to terminal alkenes when initiated by di-*tert*-butyl hyponitrite (TBHN).[14] Slow catalyst addition was necessary to afford the product in good yield with Ph_3SiH, whereas methyl thioglycolate (MeO_2CCH_2SH) and triphenylsilanethiol (TPST) have been shown to be more effective catalysts, therefore, negating contrrolled thiol addition, especially with the use of triphenylsilane as opposed to other trialkylsilanes (eq 8). These products were formed as a racemic mixture but carbohydrate-derived homochiral thiol catalysts may be used to achieve enantioselective (76% ee) additions (eq 9).[15]



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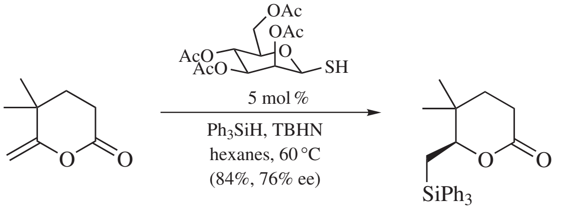

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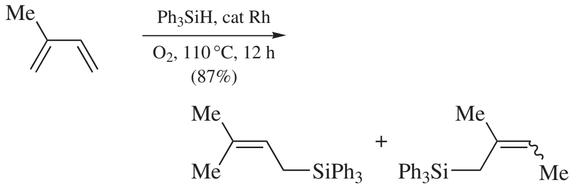
Metal-catalyzed Hydrosilylations. Various metals, particularly Pd, Pt, and Rh, have also been shown to catalyze alkene hydrosilylations.[16] The 1,4-addition of Ph_3SiH across 1,3-dienes can give rise to up to four different allylic silane isomers (eq 10).[17] Oxygen has been shown to have an affect on the regioselectivity, favoring the formation of the "head-product" (compound **II**). When *E*- or *Z*-isomers were possible, only the *Z*-isomer was observed. With silanes other than Ph_3SiH, reaction under an inert atmosphere favors the "tail-product" (compound **I**), but with Ph_3SiH a mixture of products was observed.[17] *N*-Hydroxyphthalimide (NHPI)catalyzed coupling of alkenes with Ph_3SiH and Co(II)-catalyst in O_2 provides the hydroxysilylation product at rt (eq 11).[18] In contrast, use of Et_3SiH required a reaction temperature of 60 °C to afford the hydroxysilylation product and even then lower yields were observed. Disparate reactivity between Ph_3SiH and Et_3SiH has also been noted during the hydrosilylation of vinylcyclopropanes, where the former reagent allows reaction *without* opening of the cyclopropane.[19]



I (tail-product) *E/Z*-**II** (head-product)

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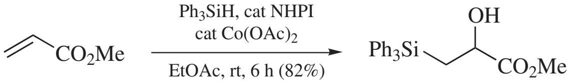

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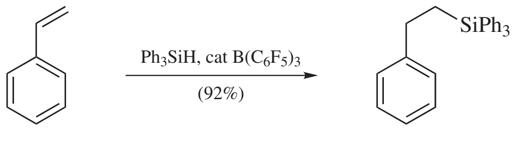
Lewis Acid-assisted Hydrosilylations. To date the only Lewis acid-mediated hydrosilylation utilizing arylsilanes has been achieved with assistance from $B(C_6F_5)_3$ (eq 12).[20]



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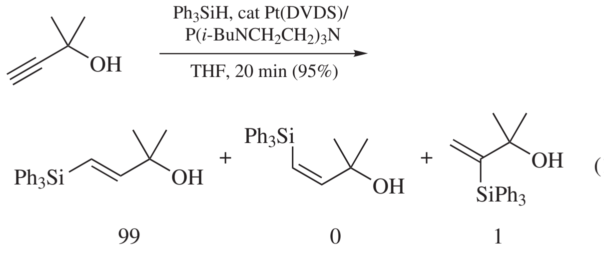
Alkynes.

Metal-catalyzed Hydrosilylations. Many factors such as the type of catalyst employed, substrate, hydrosilylating agent, and solvent can impact the ability of these reactions to afford the β-(*E*)-, β-(*Z*)-, and α-substituted vinylsilanes preferentially. High selectivity for the β-(*E*)-vinylsilane can be achieved through the use of Pt(DVDS)/P(*i*-$BuNCH_2CH_2)_3N$ (DVDS = [(H_2C=CH)

$Me_2Si]_2O$) and exhibits high functional group tolerance including ethers, halides, cyano groups, esters, and alcohols (eq 13).[21] Notably, free amines do not require protection to avoid alkyne polymerization as is needed with cationic $[Rh(COD)_2]BF_4$ catalysis.[22] β-(*E*)-Vinylsilanes have also been selectively achieved through utilization of various Pt[23,24] (via photoactivation), Pd,[25] and Ir[26] catalysts.



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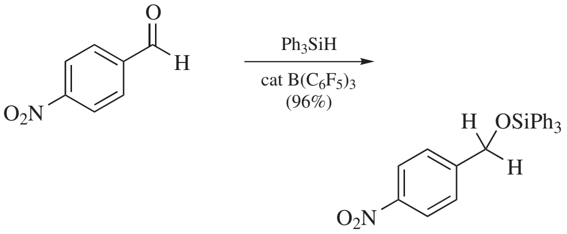
Neutral Rh catalysts allow access to the β-(*Z*)-vinylsilanes.[27] Ru[28] and Rh[29] *N*-heterocyclic carbenes and $EtAlCl_2$ [30] Lewis acid catalysis have also shown β-(*Z*) selectivity. α-Substituted vinylsilanes can be obtained when Ru carbene complexes are used.[31]

Hydrosilylation of carbonyls with Ph_3SiH can provide direct access to the corresponding triphenylsilyl ethers via a Rh[29,32] complex. Side products of silyl enol ethers and alcohols are occasionally observed. Aromatic aldehydes, ketones, and esters are hydrosilylated by a borane[33,34] catalyst (eq 14). Thioketones and imines may also be hydrosilylated to the corresponding heteroatom-silylated products using $B(C_6F_5)_3$[35] or an ytterbium[36] catalyst, respectively. α,β-Unsaturated carbonyls have been selectively converted to their triphenylsilyl enol ethers upon treatment with Ph_3SiH and Karstedt's catalyst.[37] It should be noted that triethylsilane has been more widely studied for the hydrosilylation of carbonyls, and it would appear that some, but certainly not all, of the methods used for that reagent can be successfully applied to Ph_3SiH.



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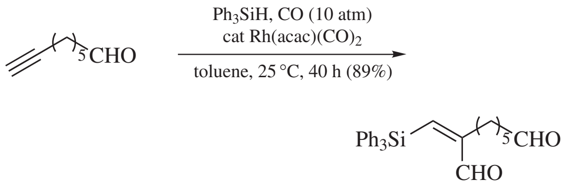
Silylformylation of alkynals with Ph_3SiH proceeds in a *syn*-selective fashion upon treatment with $Rh(acac)(CO)_2$ under 10 atm of CO (eq 15).[38] Ph_3SiH has proven to be a more efficient silane as compared with Et_3SiH although longer reaction times are required. The Pd-catalyzed carbocyclization of tetraenes proceeds rapidly with Ph_3SiH, exhibiting similar reactivity to Et_3SiH (eq 16).[39] Tandem hydrosilylation-intramolecular aldol rections afforded substituted cycloalkanols in 42% yield with 1.5:1 *cis*: *trans* ratio (eq 17).[40] Here, Et_3SiH appears to be a more efficient silane, affording the requisite product in 81% yield and higher *cis*-selectivity (3:1).



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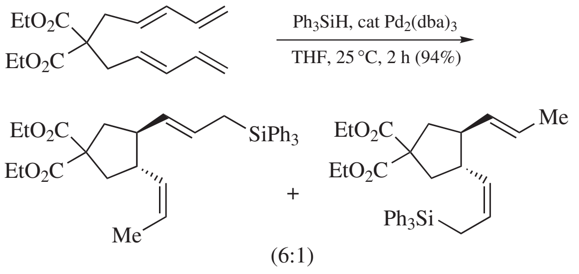

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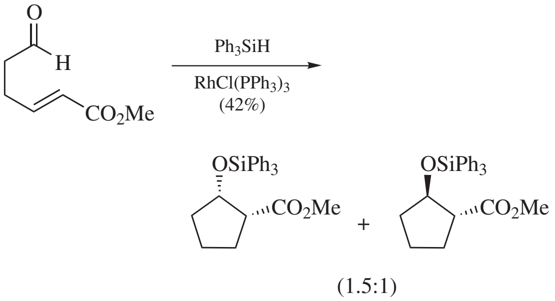

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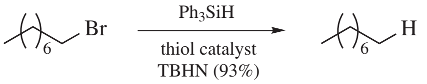
Reductions.

Heteroatom Reductions. Treatment of alkyl halides with a thiol-Ph_3SiH couple promotes dehalogenation (eq 18).[41] A defluorination using catalytic Os-hydrides as the hydride donor and stoichiometric Ph_3SiH to regenerate the Os-hydride has been achieved.[42] Reductions of 1° alcohols to the corresponding deoxygenated products proceed after treatment with catalytic $B(C_6F_5)_3$ and 3 equiv of silane. When 2° and 3° alcohols are used, the triphenylsilyl ethers are obtained. Ph_2CHOH and Ph_3COH afforded the deoxygenated products with only 1.1 equiv of silane. The authors reported the results for the reaction with Et_3SiH and stated that Ph_3SiH produced similar results.[43]



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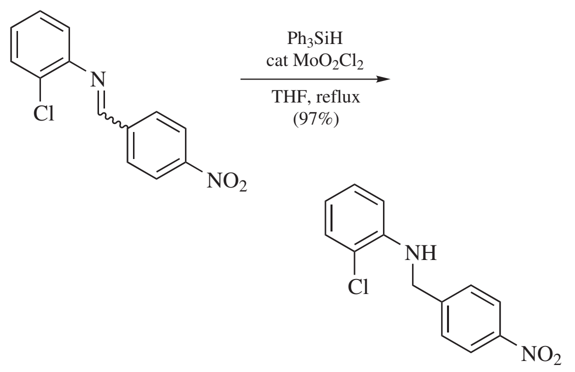
Multiple Bond Reductions. Imines bearing aryl substitution on C and N may be reduced upon treatment with Ph_3SiH and MoO_2Cl_2 (eq 19).[44] Best results were obtained when electron withdrawing substituents were present on the aryl rings.



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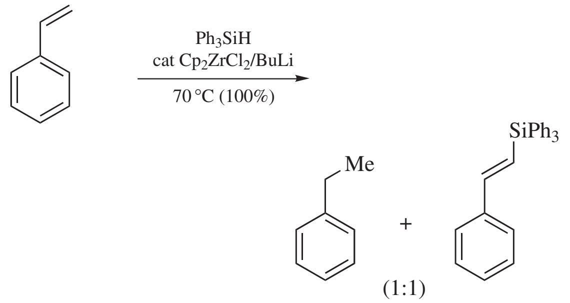
Alkene Hydrogenations. Treatment of olefins with Zr catalysts effected their saturation in 50% yield along with 50% dehydrogenative silylation as calculated by GC (eq 20).[45] Ru carbene complexes also afforded the reduced product in the presence of Ph_3SiH. Reduction of an olefin via radical-chain reductive carboxyalkylation proceeded with Ph_3SiH and a homochiral thiol catalyst upon TBHN initiation (eq 21).[46] The olefin of vinylstannanes could be reduced without any protodestannylated product produced (eq 22).[47]



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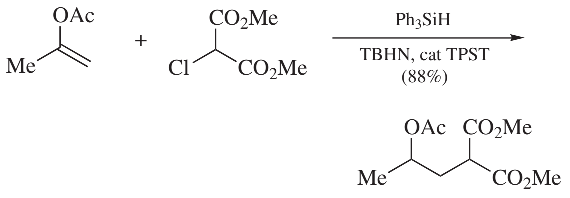

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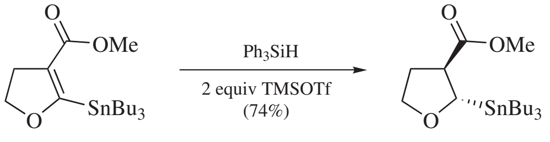

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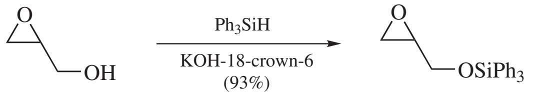
Silylations.

Si–O Bond Forming Reactions.

Alcoholysis. One route to silyl-protected alcohols is by dehydrogenative silylation in the presence of triorganosilanes. Conversion of alcohols to the corresponding triphenylsilyl ethers have been mediated by transition metal catalysts including Pd,[48] Cu,[49,50] and Au[51] in excellent yields. These catalysts exhibit high selectivity and functional group tolerance. A wide range of functionalized 1°, 2°, and 3° alcohols (alkenes, alkynes, halides, cyanos, ketones, and esters) and functionalized phenols were silylated upon treatment with catalytic $B(C_6F_5)_3$ and Ph_3SiH in excellent yields.[52] KOH/18-crown-6 can serve as a simple and economical combination for the silylation of 1° and 2° alcohols. For this method, phenylhydrosilanes, such as Ph_3SiH, were superior to Me_3SiH (eq 23).[53]



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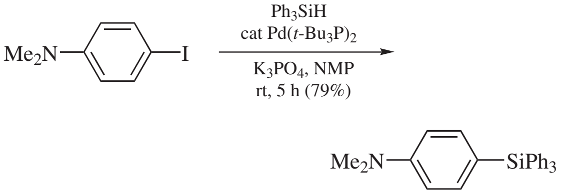
Si–C Bond Forming Reactions.

Halogen/Si Exchange. Aryl- and vinyl iodides have been treated with $Pd(t\text{-}Bu_3P)_2$[54] (eq 24) and $Pd_2(dba)_3{\cdot}CHCl_3$,[55] respectively, to afford the triphenylsilyl-transferred products in moderate to excellent yields.



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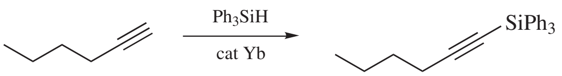
Dehydrogenative Silylation. Ytterbium–imine complexes have catalyzed the dehydrogenative silylation of terminal alkynes (eq 25).[56]



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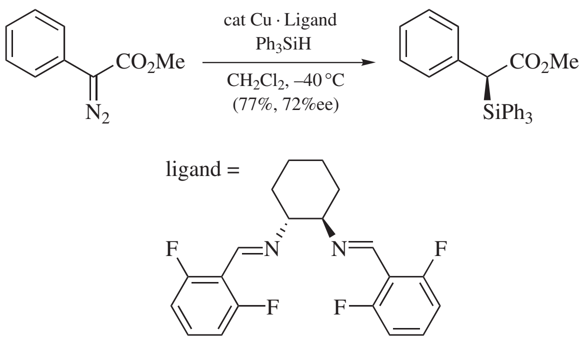
Carbene Insertion. Carbenoid insertion into silanes of various metals including Cu[57] (eq 26), Rh[58,59] (derived from diazoesters), and Cr[60,61] carbenoids can proceed in good to excellent yields. When chiral ligands on the metal or chiral auxiliaries (eq 27)[61] were implemented, good to excellent diastereocontrol was possible (46:1 dr).



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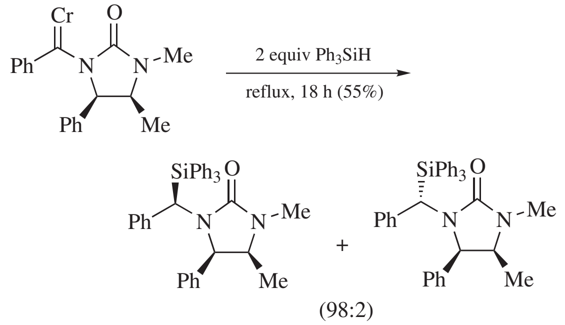

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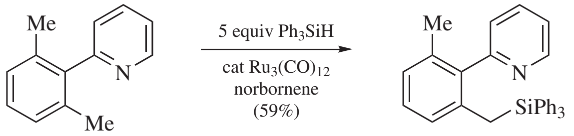
Via Benzylic C–H Activation. Silylation by nitrogen atom-directed activation of benzylic sp^3 C–H bonds has been reported employing triphenylsilane, catalytic Ru$_3$(CO)$_{12}$, and norbornene as a hydrogen acceptor (eq 28). No bissilylation products were detected with Ph$_3$SiH, as opposed to with Et$_3$SiH, where the disilylated product was major.[62]



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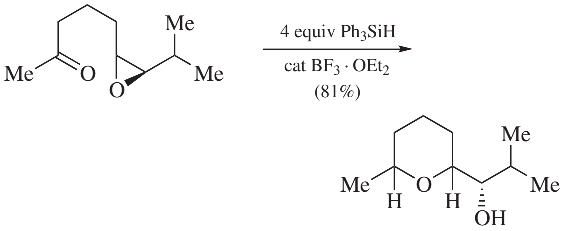
Miscellaneous.

Cyclizations. Lewis acid-catalyzed cyclizations of epoxy ketones with Ph$_3$SiH may afford cyclic ketals and substituted tetrahydrofuran or pyran rings depending on the Lewis acid and substrate (eq 29).[63]



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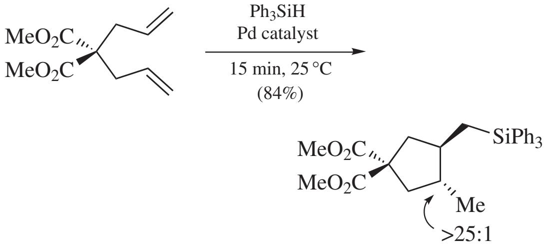
An asymmetric cyclization/hydrosilylation of a ω-formyl-1,3-diene has been catalyzed by Ni(0) in the presence of Ph$_3$SiH to afford the five-membered carbocycle. The same reaction with other silanes has been applied to the construction of six-membered carbocycles and pyrrolidines. However, the operative mechanism has been shown to be silane dependent and thus care should be taken before extrapolating those results to any proposed reaction schemes with Ph$_3$SiH.[64] Rh-catalyzed cyclization/hydrosilylation of enynes with Ph$_3$SiH afforded the silylcarbocyclization product, but for these reactions other silanes [e.g., Me$_2$PhSiH, (MeO)$_3$SiH, etc.] provided better results.[65] Cyclization/hydrosilylation of 1,6-dienes with Ph$_3$SiH have been demonstrated with a cationic Pd-catalyst (eq 30).[66]



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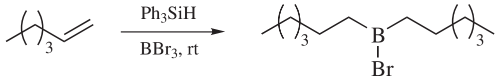
Hydroborations. Ph$_3$SiH can convert tri- and dihaloboranes to the corresponding di- and monohaloboranes, which can then be used in the in situ hydroboration of alkenes and alkynes. Notably, these reactions may be run from −78 °C to rt, thereby negating the usual need for elevated temperatures (∼100 °C) (eq 31).[67] Oxygen functionalities were typically not tolerated by this method.



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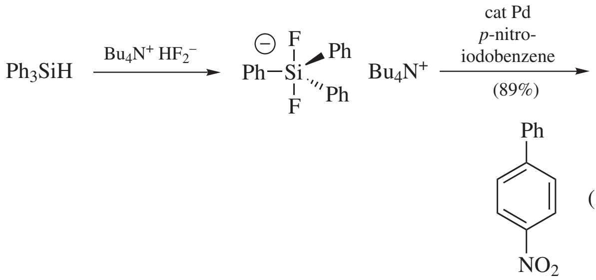
Cross-coupling Reactions. Triphenyl(difluoro)silicates arise from the reaction of Ph$_3$SiH and quaternary onium hydrogendifluoride. These species can then be subject to cross-coupling phenylation reactions under Pd-catalysis. Usefully, no homocoupled product formation was observed under these conditions (eq 32).[68]



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Related Reagents. 1,4-Bis(diphenylhydrosilyl)benzene; Triethylsilane Acid.

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