

## Abstracts

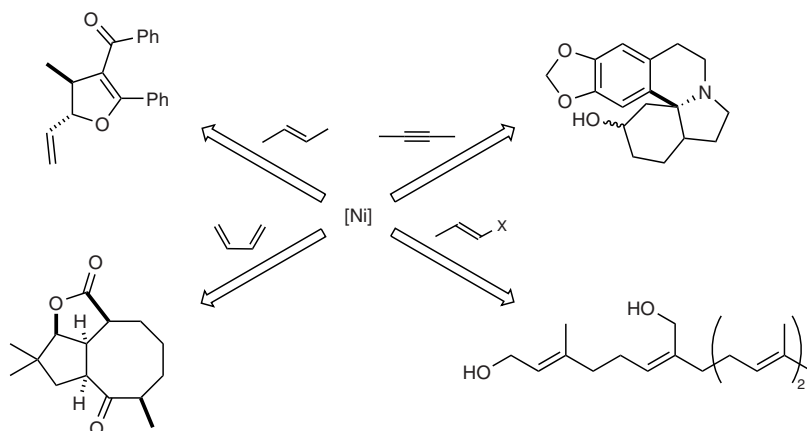
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## 1.1.5 Organometallic Complexes of Nickel

R. M. Stolley and J. Louie

This chapter is an update to the earlier *Science of Synthesis* contribution describing the organometallic complexes of nickel. This update highlights the applications of organometallic complexes of nickel, building on the general trends of organonickel chemistry described in the previous contribution. Within this update, particular emphasis is placed on nickel-mediated oxidative and reductive coupling reactions, carbon–heteroatom bond-forming reactions, annulation, and strong-bond activation reactions. This update focuses mainly on literature from 2003 to 2012.



**Keywords:** nickel · reductive coupling · oxidative coupling · heterocoupling · oxidative addition · homocoupling · cyclization · carbon–heteroatom bonds · allylic · alkyne · 1,3-dienes · C–H bond activation · insertion · isomerization · carboxylation

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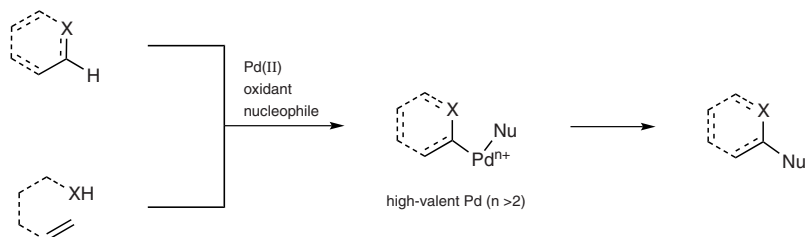
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1.2.6

**High-Valent Palladium in Catalysis***P. Chen, G. Liu, K. M. Engle, and J.-Q. Yu*

This chapter documents recent studies of palladium-catalyzed organic transformations in which a high-valent palladium intermediate is involved in the formation of a new chemical bond. The interest in these reactions has focused mainly on C–H activation and the difunctionalization of alkenes.



**Keywords:** high-valent palladium complexes · C–H activation · alkenes · difunctionalization · oxidation · reductive elimination

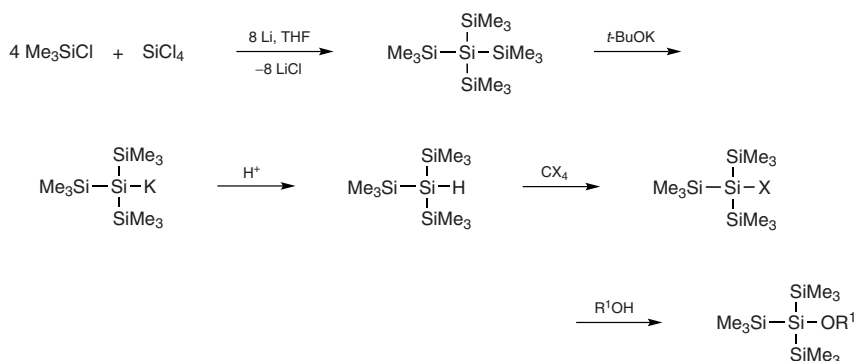
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4.4.5

**Product Subclass 5: Disilanes and Oligosilanes***C. Marschner and J. Baumgartner*

This chapter is a revision of the earlier *Science of Synthesis* contribution describing methods for the preparation and synthetic use of disilanes. This update is extended by coverage of synthetically useful oligosilanes.



**Keywords:** silicon compounds · disilanes · oligosilanes · silylation · protecting groups · radicals · Si–Si bonds · Si–C bonds

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4.4.9

**Product Subclass 9: Silyl Zinc Reagents***A. Durand, I. Hemeon, and R. D. Singer*

This chapter is a revision of the contribution on silyl zinc reagents published in 2001, which describes the preparation and application of triorganosilyl zinc compounds. Homo silyl zinc reagents, such as bis(triphenylsilyl)zinc(II) [(Ph<sub>3</sub>Si)<sub>2</sub>Zn] and lithium tris[dimethyl(phenyl)silyl]zincate [(PhMe<sub>2</sub>Si)<sub>3</sub>ZnLi], as well as hetero or mixed silyl zinc reagents, such as lithium [dimethyl(phenyl)silyl]dimethylzincate [(PhMe<sub>2</sub>Si)ZnMe<sub>2</sub>Li] and (biphenyl-

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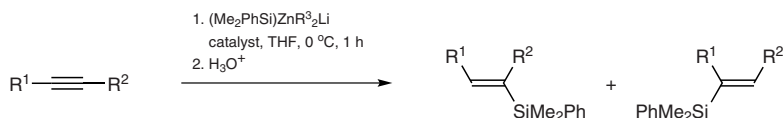
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2,2'-diolato(*tert*-butyl)[dimethyl(phenyl)silyl]zincates  $\{M_2Zn(t-Bu)[(2-OC_6H_4)_2](SiMe_2Ph)\}$ ;  $M = Li, MgCl$ , are prepared with relative ease and are utilized in a variety of synthetic applications. These reagents react under a variety of conditions with unsaturated organic substrates to afford synthetically useful triorganosilylated species.



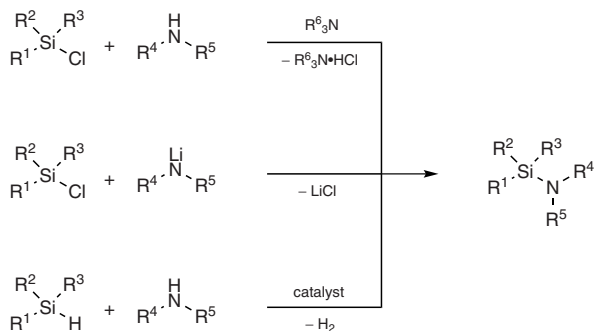
**Keywords:** bis(triorganosilyl)zincs · dialkyl(triorganosilyl)zincates · dianionic silylzincates · catalysis · vinylsilanes · 3-(triorganosilyl) ketones · allylsilanes

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4.4.21.13 **Silylamines***A. Kawachi*

This review, which updates the original Section 4.4.21, published in 2001, discusses the preparation of silylamines bearing dicoordinate, tricoordinate, tetracoordinate, and pentacoordinate silicon centers. Reaction of chlorosilanes with primary or secondary amines is one of the most conventional methods for the syntheses of these compounds. Reactions of halosilanes with lithium amides, lithium  $\beta$ -diketiminates, and other metalated nitrogen species are also useful. A more recent advance is the dehydrogenative condensation of hydrosilanes with primary or secondary amines using transition-metal or Lewis acid catalysts.



**Keywords:** silylamines · halosilanes · hydrosilanes · amines · diamines · amino alcohols · amides · dehydrogenative condensation · dehydrochlorination · transition-metal-catalyzed reactions

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4.4.22 **Product Subclass 22: Silyl Phosphines***M. Hayashi*

This chapter is a revision of the earlier *Science of Synthesis* contribution, published in 2001, describing methods for the synthesis of silyl phosphines and their applications in organic synthesis. In contrast to the earlier contribution, in which the applications of silyl phosphines were described only very briefly, in this revision the applications of silyl phosphines are classified and summarized and include recent improvements, especially with regard to P—C bond formation.

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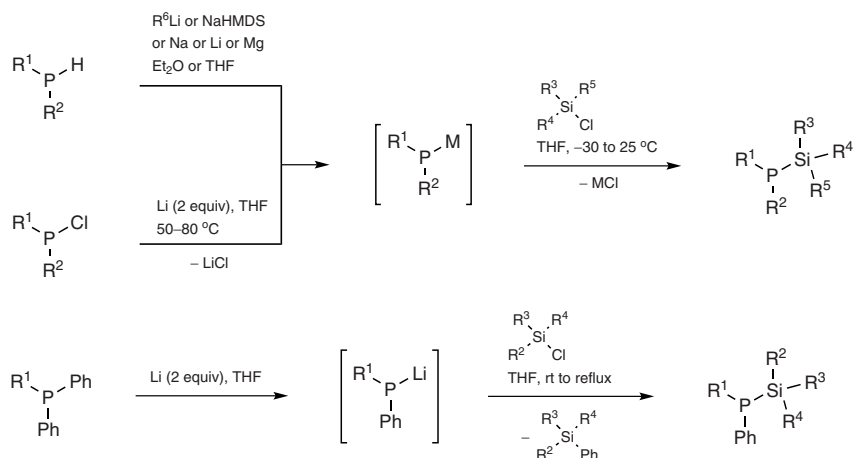
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**Keywords:** silyl phosphines · phosphines · phosphorus compounds · phosphaaalkenes · phosphaaalkynes · phosphorus heterocycles · silyl ethers

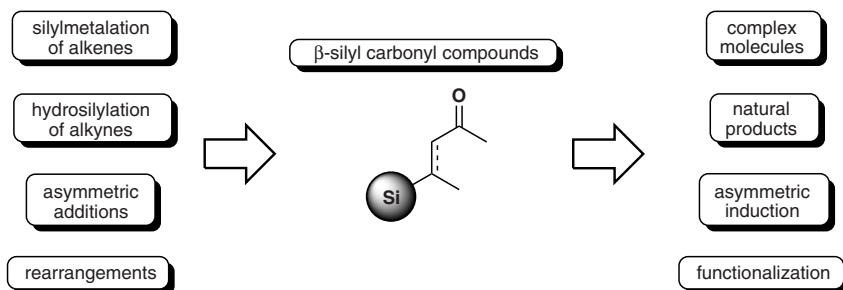
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#### 4.4.41.8 $\beta$ -Silyl Carbonyl Compounds

*F. Nahra and O. Riant*

$\beta$ -Silyl carbonyl or carboxy compounds are attractive synthetic intermediates. They are important building blocks for various synthetic transformations, thus allowing the construction of more complex molecules. The position of the silyl group far from the carbonyl group allows for numerous transformations on the latter, giving access in some cases to complex natural products. Moreover, the installation of the silyl group on these intermediates in an enantioselective manner has been the subject of numerous investigations, mainly due to its subsequent influence on the adjacent addition of other groups. Finally, the possibility of converting these silyl groups into various other functional groups renders these intermediates valuable tools in the organic chemist's arsenal.



**Keywords:**  $\beta$ -silyl carbonyl · silylmetalation · hydrosilylation · silyl migration · asymmetric addition

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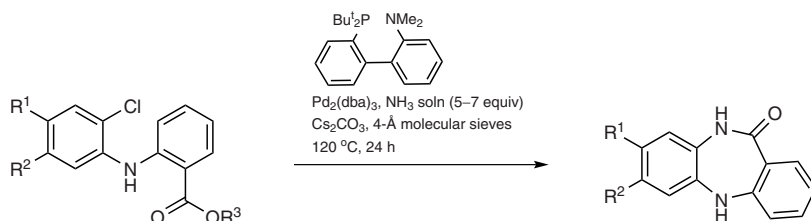
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17.5.4 **Seven-Membered Heterenes with Two or More Heteroatoms**

J. Zhang

This update deals with important general methods for the synthesis of diazepines, benzodiazepines, and dibenzodiazepines that have not been discussed in the earlier *Science of Synthesis* Section 17.5 or in *Houben–Weyl*, Vol. E 9d. Literature published up to 2011 is reviewed.



**Keywords:** diazepines · benzodiazepines · dibenzodiazepines · diazepinones · ring closure · condensation reactions · copper-catalyzed cyclization · palladium-catalyzed cyclization

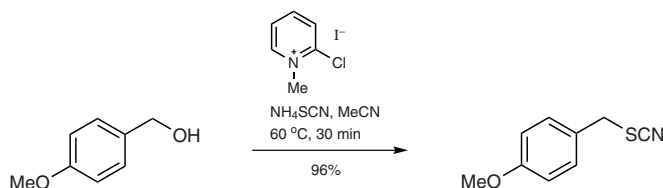
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18.1.7 **Cyanogen Halides, Cyanates and Their Sulfur, Selenium, and Tellurium Analogues, Sulfinyl and Sulfonyl Cyanides, Cyanamides, and Phosphaalkynes**

J. Podlech

This chapter is an update to the earlier *Science of Synthesis* contribution on the preparation of cyanogen halides, cyanates, thiocyanates, sulfonyl cyanides, and cyanamides, as well as their application in organic synthesis. It focuses on the literature published in the period 2003–2012.



**Keywords:** cyanogen halides · thiocyanates · sulfonyl cyanides · cyanamides · cyanation · thiocyanation

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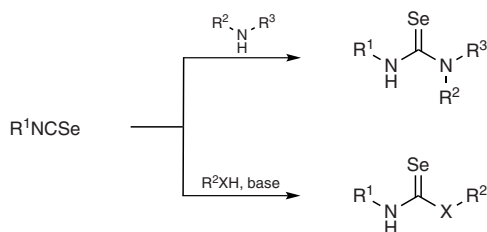
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18.11.10 **Seleno- and Tellurocarbonyl Acids and Derivatives**

K. Shimada

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of seleno- and tellurocarbonyl acids and their derivatives. It focuses on the literature published in the period 2002–2012.



X = O, S

**Keywords:** bis(dimethylaluminum) selenide · *N,N*-dialkylcyanamides · *N,N*-dimethylselenocarbamoyl chloride · elemental selenium · isoselenocyanates · potassium selenocyanate · selenocarbamates · selenosemicarbazides · selenosemicarbazones · selenoureas · sodium hydroselenide · Viehe's salt

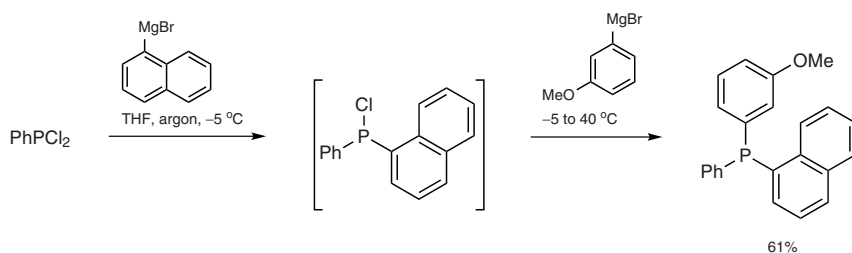
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31.42 **Product Class 42: Arylphosphines and Derivatives**

M. Stankevič and K. M. Pietrusiewicz

This manuscript is a revision of the earlier *Science of Synthesis* contribution describing methods for the synthesis of arylphosphines. Classical routes to arylphosphines involve the formation of the required C–P bonds from P-electrophilic, P-nucleophilic, and P-radical precursors. Newer methods are based on hydrophosphination and coupling processes catalyzed by transition-metal complexes. Methods involving reductions and decomplexations of tetracoordinate phosphorus precursors and modifications of the carbon skeleton in existing arylphosphines are also included.



**Keywords:** aryl compounds · C–P bonds · coupling reactions · deoxygenation · desulfurization · nucleophilic substitution · nucleophilic addition · phosphines · phosphorus compounds · radical addition · transition metals

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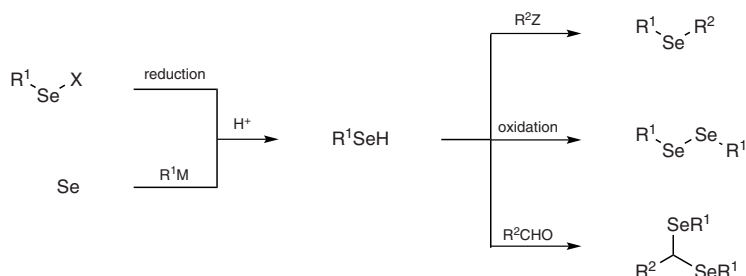
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## 39.18.2 Alkaneselenols

C. Santi

This chapter is an update to the earlier *Science of Synthesis* contribution describing methods for the synthesis of alkaneselenols. It focuses on the literature published in the period 2001–2012; some applications of alkaneselenols in organic synthesis are also discussed.



**Keywords:** selenium · selenides · diselenides · nucleophilic substitution · diselenoacetals · conjugate addition · reduction

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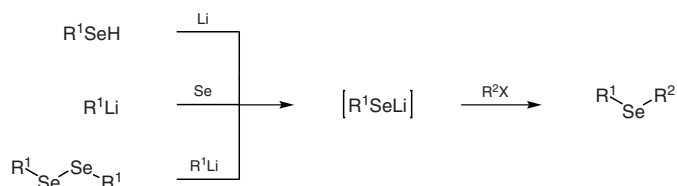
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## 39.19.1.2 Alkaneselenolates of Group 1, 2, and 13–15 Metals

C. Santi

This chapter is an update to the earlier *Science of Synthesis* contribution describing the preparation of acyclic alkaneselenolates of metals in groups 1, 2, and 13–15. It focuses on the literature published in the period 2001–2012, and some aspects of the reactivity of these compounds are also described.

Alkaneselenolates are usually prepared *in situ* under inert conditions and are immediately used for subsequent reactions, most typically nucleophilic substitutions.



**Keywords:** selenium · lithium · sodium · nucleophilic substitution · enolates · Grignard reagents

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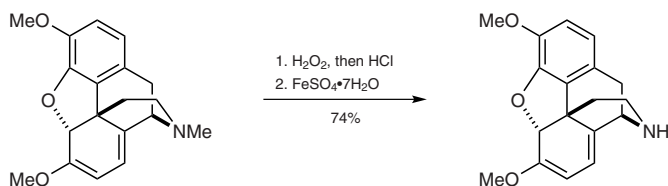
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40.1.1.5.4.5 **Substitution on the Amine Nitrogen***P. J. Scammells*

This chapter is an update to the earlier *Science of Synthesis* contribution that describes methods for the dealkylation and substitution of amines. It focuses on the literature published up to early 2012.



**Keywords:** alkylation · amination · amine *N*-oxides · amines · dealkylation · C–N bond cleavage · C–N bond formation