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Selective Cobalt-Catalyzed Reduction of Terminal Alkenes and Alkynes Using $(\text{EtO})_2\text{Si}(\text{Me})\text{H}$ as a Stoichiometric Reductant

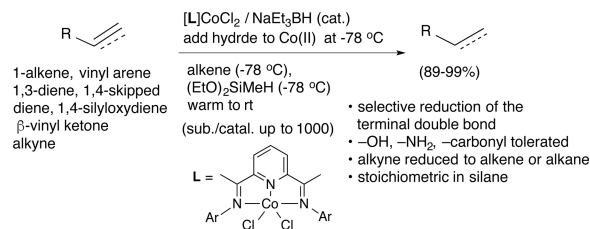
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Abstract

While attempting to effect Co-catalyzed hydrosilylation of β -vinyl trimethylsilyl enol ethers we discovered that depending on the silane, solvent and the method of generation of the reduced cobalt catalyst, a highly efficient and selective reduction or hydrosilylation of an alkene can be achieved. This paper deals with this reduction reaction, which has not been reported before in spite of the huge research activity in this area. The reaction, which uses an air-stable [2,6-di(aryliminoyl)pyridine]CoCl₂ activated by 2 equivalents of NaEt₃BH as a catalyst (0.001–0.05 equiv) and $(\text{EtO})_2\text{SiMeH}$ as the hydrogen source, is best run at ambient temperature in toluene and is highly selective for the reduction of simple unsubstituted 1-alkenes and the terminal double bonds in 1,3- and 1,4-dienes, β -vinyl ketones and silyloxy dienes. The reaction is tolerant of various functional groups such as a bromide, alcohol, amine, carbonyl, and di or trisubstituted double bonds, and water. Highly selective reduction of a terminal alkyne to either an alkene or alkane can be accomplished by using stoichiometric amounts of the silane. Preliminary mechanistic studies indicate that the reaction is stoichiometric in the silane and both hydrogens in the product come from the silane.

Graphical Abstract



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ASSOCIATED CONTENT

Supporting Information

Experimental procedures for the scouting experiments, syntheses and isolation of the hydrogenation products. Spectroscopic and gas chromatographic data showing compositions of products under various reaction conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>

The authors declare no financial interest.

Keywords

cobalt catalysis; selective hydrogenation; hydrosilylation; ligand effects; dienes; hydrogenation

Introduction

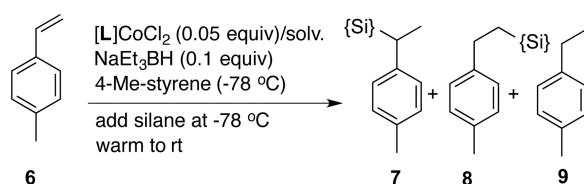
We recently reported a general procedure for a catalytic enantioselective synthesis of trialkylsilyl enol ethers (**2**) bearing a vinyl group on a chiral β -carbon center via hydrovinylation of 2-silyloxy-1,3-dienes (**1**) (Scheme 1).¹ Further synthetic value of these functionalized enolates could be realized from their subsequent chemo-, regio- and stereoselective reactions. In this regard, a class of reactions that would lead to many different useful intermediates is the selective hydrofunctionalization² of the terminal alkene in a product like **2** *without affecting the silyl enol ether moiety*, which in turn can be used for subsequent reactions with electrophiles. We found³ that one version of a cobalt-catalyzed hydrosilylation is such a reaction that can be accomplished with varying degree of success by the proper choice of the catalyst, reducing agent, solvent and an appropriate silane to give **3** in high yield and selectivity.⁴ During these investigations, we also discovered that $(\text{EtO})_2\text{Si}(\text{Me})\text{H}$ as a unique reagent capable of affecting an exceptionally selective reduction of the terminal alkene in **2** to give the silyl enol ether product **4**. Thus a combination of this silane, an in situ generated Co(I)-2,6-di(aryliminoyl)pyridine [Co(I)-(PDI)] catalyst and toluene as a solvent was found to be critical for the success of this reaction, which is distinctly different from the atom-transfer hydrogenations recently reported by Shenvi^{5,6} and Herzon.^{7,8} They carried out such reactions under oxidative conditions similar to the classical Mukaiyama protocol,⁹ which involves the use of stoichiometric amounts of an oxidant (e. g., *t*-butyl hydroperoxide) in addition to the silane. Attendant problems of such a protocol for oxidatively sensitive substrates we are interested in (e.g., **2**) are obvious. Classical hydrogenation reactions using Rh, Ir and Co catalysts failed to deliver **4** (vide infra). Other reactions that involve hydrogen atom transfer steps under neither oxidizing nor reducing conditions lead to isomerization reactions, not simple reductions.^{10,11} The highly selective reactions reported in this paper have selectivities that are *distinctly different* from several cobalt and iron-catalyzed hydrogenation reactions reported recently.¹² We have since found that this reaction has wide scope beyond the originally intended substrates, including for semi-reduction terminal alkynes. While the use of stoichiometric amount of a silane is a minor detraction from an atom economy perspective, an operationally simple, highly efficient (typically 90–100% yield), selective and catalytic (up to 0.001 equiv of cobalt) hydrogenation protocol that *does not involve the use hydrogen gas or pressure reactors* does have some attraction for lab-scale preparations. Here we provide the details of these studies.

Results and Discussion

Our investigations started with an examination of the reactions of various silanes with a prototypical substrate, 4-methylstyrene. In initial scouting of a series of 1,*n*-*bis*-diphenylphosphinoalkanes ($n = 1-4$) and bisimine Co(II)-complexes (Figure 1) we identified the 2,6-diaryliminopyridine (PDI) ligands (**5a-d**),¹³ in particular the 2,6-diisopropyl derivative (**5a**) to be the most optimum ligand for these reactions. A quick survey of most

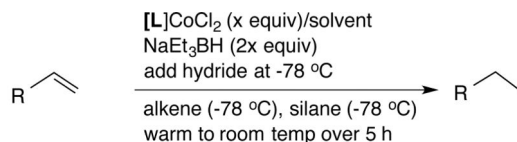
commonly used activators (trimethyl aluminum, MeLi, EtMgBr, *n*-BuLi, and NaEt₃BH) confirmed that NaEt₃BH¹⁴ at -78 °C is the best reagent for reduction of the [PDI]CoCl₂ complex for our purpose.¹⁵ Reactions of various commercially available silanes with 4-methylstyrene using a combination of [Pr-PDI]CoCl₂ (**5a**) and NaEt₃BH as a catalyst are shown in Eq 1 and Table 1. In a typical procedure, the Co-complex (0.001–0.05 equiv) and the alkene (1 equiv) are dissolved in the appropriate solvent under argon and the mixture is cooled to -78 °C. To this solution is added a toluene solution of NaEt₃BH (0.002–0.1 equiv) followed by the silane (1.0–1.1 equiv). The mixture is slowly warmed to rt while monitoring the reaction by gas chromatography (GC) and GC-mass spectrometry. After the completion of the reaction, the mixture is passed over a pad of silica using hexane as an eluent to remove ligand residues and the insoluble silicon-containing byproducts (as determined by MALDI) and the combined fractions are concentrated and analyzed by GC and NMR spectroscopy. Chromatograms of products from several preparative runs are included in the Supporting Information.

A careful examination of the data in Table 1 suggests that two kinds of products can be obtained in preparatively useful yields. Thus a primary silane, PhSiH₃ gives an excellent yield of the linear silane **8** (entry 1). The same product is obtained as the major component in reactions with secondary silanes such as Et₂SiH₂, MePhSiH₂ and Ph₂SiH₂ (entries 2, 6 and 7). Unlike the exquisitely selective PhSiH₃, these reagents also yield varying amounts of a branched hydrosilylation product (**7**) and a reduction product (**9**). Tertiary silanes such as Ph₃SiH, Cl₃SiH, Et₃SiH, (EtO)₃SiH and (TMSO)₂Si(Me)H are much less reactive and the starting 4-methylstyrene remains mostly unreacted for several hours at room temperature. In sharp contrast, another tertiary silane, (EtO)₂SiMeH, is a remarkable reagent giving nearly quantitative yield of a reduction product **9** (entry 10). An examination of the solvent effect reveals that while hexane and chlorinated solvents such as CH₂Cl₂ and ClCH₂CH₂Cl are unsatisfactory, THF and diethyl ether lead to acceptable yields. In a parallel run using these solvents, the best solvent for the reaction was identified as toluene, where a quantitative yield of the reduction product, **9**, uncontaminated by the starting material (**6**) or hydrosilylation product (**8**) was observed (entry 10).



(1)

The highly selective silane-mediated reduction of the terminal alkene is a broadly useful reaction with applications in varied class of substrates. The optimized procedure for the reaction is shown in Eq 2 and the full scope of the reaction is illustrated by the examples shown in Figure 3.

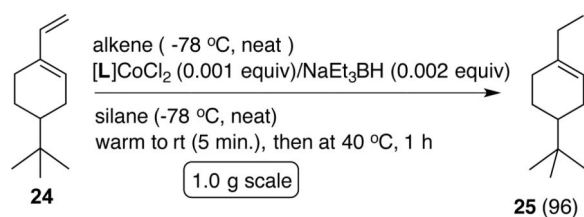


functionalized 1-alkenes,
vinyl arenes, 1,3-diene,
1,4-skipped diene,
1,4-silyloxydiene, β -vinyl ketone

selective reduction of
the terminal double bond

(2)

As expected from the scouting studies, vinyl arenes (**10–14**) undergo exceptionally clean reduction to the corresponding saturated compounds. Particularly noteworthy is the retention of bromine in the aromatic ring in the example **10c** which suggest the absence of Co(0) intermediates.¹⁶ 3-Arylbutenes are a class of compounds especially prone to isomerization^{17–19} of the double bond under reactions that generate metal-hydrides to give products in which the double bond is in conjugation with the aryl ring. Reductions of 3-arylbutenes (**17a, b** and **18**) proceed with no rearrangement to more stable conjugated products, precluding hydrogen-atom transfer processes, the likes of which are involved in the 1-alkene to 2-alkene isomerization catalyzed by Co-salen complexes reported by Shenvi.¹⁰ Terminal alkenes bearing carbonyl (**19**), Br (**20**), OH (**21**), NH₂ (**22**) and epoxy (**23**) functionality are reduced in nearly quantitative yields. The products are isolated by simple filtration of the crude product through silica to remove what appears to be silicon-containing polymeric materials and residues from the catalyst.¹⁵ These reactions are easily scaled up without loss of yield or selectivity and several examples run on preparative scales are included in the Supporting Information.

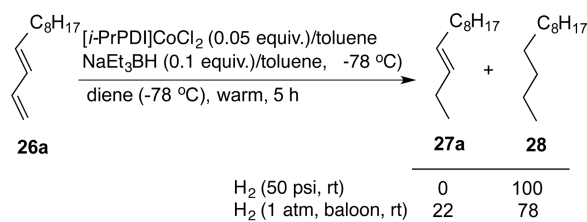


(3a)



(3b)

The most significant finding in this study is the highly selective reduction of the terminal double bond in 1,3-dienes. Two examples illustrated in Eq 3a and 3b. The selectivity in the reduction of the terminal double bond in the 1,3- (**26a–c**) and a 1,4-dienes (**30** and **31**, Figure 4) in the presence of the additional disubstituted double bond is unprecedented. Attempted hydrogenation of the diene **26a** using a Co(PDI)-catalyst under hydrogenation conditions^{12g} using hydrogen as the stoichiometric reductant gives complete reduction of both bonds at 50 psi (Eq 4). Even at 1 atmosphere hydrogen, competitive reduction ensues giving a mixture of reduction products **27a** and **28** (Eq 4). Likewise, selective hydrogenation by cobalt (II)-complexes of bis[2-(dicyclohexylphosphino)ethyl]-amine also lack this selectivity between a mono- and disubstituted alkenes.²⁰



(4)

These reduction reactions can be accomplished in neat substrate using as little as 0.001 equiv (substrate/catalyst = 1000) of the catalyst. Examples of products from selective reduction of the terminal double bond in several 1,3- and 1,4- are shown in Figure 4. As indicated by gas chromatographic analysis of the crude products,¹⁵ these reactions are exceptionally clean and gave >90% isolated yields of the products. The less than quantitative yield of the products is a reflection of the volatility of the hydrocarbon products.

Returning to the highly sensitive β -vinyl silyl enolate derivatives (Scheme 1), we find that all attempts to reduce the terminal double bond in **32** (Scheme 2) via standard hydrogenation conditions using either the Wilkinson's catalyst (Ph_3P)₃RhCl or Crabtree's catalyst [(COD)Ir(Py)(PCy₃)]⁺ [PF₆]⁻ gave a mixture of products including the ketone (Scheme 2). Well-known Co-hydrogenation catalysts^{12g} also gave the ketone product **19**. A heterogeneous catalyst, Pd(OH)₂/carbon (Pearlman's catalyst) leads to the same result, but in much poorer yields (Scheme 2). In sharp contrast, the (EtO)₂SiMeH effects highly selective reduction of the terminal alkene in **32** giving excellent yield of the silyl enol ether **33**. A related derivative **34** also underwent the reaction with no complications. The enantiomeric purity of the starting materials is not affected under these conditions, as revealed by chiral stationary phase gas chromatographic analysis of the products, where base-line separation of the starting materials (**32** and **34**) and products (**33** and **35**) can be observed.

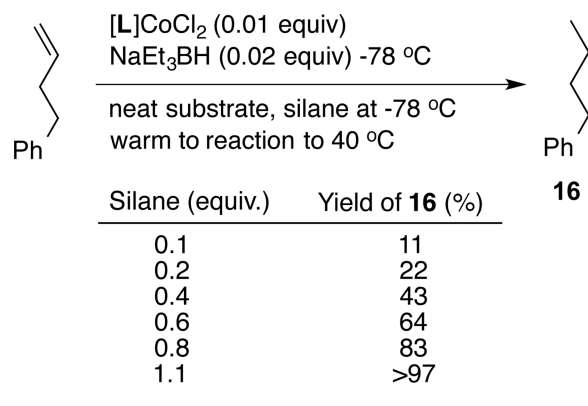
The new reduction protocol is applicable for the reduction of terminal alkynes either to the 1-alkene, or, to the completely reduced alkanes based on the stoichiometry of the silane used (Scheme 3). For example, using 1 equivalent of (EtO)₂Si(Me)H and 0.01 equivalent of the catalyst a variety of terminal alkynes **36a–d** are selectively reduced to 1-alkene **37a–d**. Under the same conditions except using 2 equiv of the silane and slightly longer reaction

times the alkanes **38a–d** are formed in excellent yields. The rate of the second reduction (of the alkene to the alkanes) is slow enough to enable the isolation the intermediate alkene in excellent yields. As illustrated by the examples shown in the Scheme 3, the reaction is compatible with a variety of functional groups.

In a mechanistically relevant experiment, the two steps can be performed back-to-back *in a single flask*, first by adding 1 equivalent of the silane to a mixture of the alkyne and 0.01 equiv of the catalyst, fully characterizing the intermediate alkene, and then adding a second equivalent of the silane (*no additional catalyst*) and, isolating the saturated product (Scheme 4).¹⁵ There is no reduction of yields of the final products (**38a–d**) as compared to the single step operation described in Scheme 3.

Finally under a variety of conditions the following substrates (Figure 5) failed to react, leaving behind unreacted starting materials even after prolonged reaction times.

Mechanism of the (EtO)₂Si(Me)H-mediated reduction, in particular the origin of the two hydrogens has not been ascertained with certainty primarily because of the difficulties in preparing the completely deuterated silane, which would involve the use specialized equipment and prohibitively expensive chemistry. But the following experiments provide strong circumstantial evidence to suggest that both hydrogens come from the silane. (i) Reduction of 4-phenyl-1-butene performed with 0.001 equivalent of the catalyst in either toluene-d₈ or THF-d₈, which are the best solvents for the reaction, show 0% incorporation of deuterium in the products (high resolution ¹H NMR and mass spectrometry). (ii) No byproducts derived from THF or toluene are detectable by GC or GC-MS. (iii) The presence of excess D₂O has no effect on the product composition, nor does added activated 4 Å sieves inhibit the reaction. These experiments rule out the unlikely role of any adventitious water as the source of hydrogen in these reactions. (iv) We have carried out a series of experiments in which the stoichiometry of the silane was varied and the yield of the reduction product determined from preparatively meaningful scale of 200 mg (1.51 mmol) of 4-phenylbutene. The results shown in Eq 5 and associated Table below confirm that the extent of conversion to the product is within experimental error of what would be expected in a reaction that is stoichiometric in the silane. These experiments suggest the possibility that the silane is the sole source of hydrogen. The ultimate fate of the silane reagent is currently not known, even though a white gelatinous material isolated upon evaporation of the solvents at the end of the reaction suggests oligomeric silyl compounds as determined by mass spectrometry (MALDI). Fortunately the formation of this material (siloxane polymer?), which is easily removed by filtration through silica gel, also makes the isolation of the products exceptionally easy.



(5)

Based on the available evidence we suggest a mechanism shown in Scheme 5. Reduction of the (PDI)CoCl₂ complex **5a** with two equivalents of NaBEt₃H can be expected to give a Co(I)-H intermediate (**40**).¹⁴ Reduced ClCo(^{*i*}PrPDI)²¹ in itself or in the presence of Et₃B does not catalyze the reaction. However, reduced ClCo(^{*i*}PrPDI) in the presence of 1 equiv of NaBEt₃H is an effective catalyst for the reaction. Viability of a metal hydride in the initial step in hydrogenation of an alkene has been established before.^{12g} Intermediacy of the metal hydride (**40**) might also explain why chlorinated solvents such as CH₂Cl₂ are ineffective for the reaction, since LCo(I)-hydride can be presumed to react with a chlorinated solvent under these conditions.²⁰ Insertion of the alkene into the Co-H bond gives a primary Co-alkyl complex (**42**), which upon reaction with the silane could give the product **43**. The reactivity of **42** with different silanes might account for the dramatic difference in hydrogenation vs hydrosilylation activity depending on the silane structures. For example, the exclusive hydrosilylation activity seen with PhSiH₃ [e.g., formation of **46** [(R = *p*-tolyl), Table 1, entry 1] maybe explained by a σ-bond metathesis of the C-Co bond in **42** with this reagent giving the hydrosilylation product (**46**), rather than the hydrogenation product (**43**) seen when (EtO)₂SiMeH is employed. Finally, careful monitoring of the reaction from very early stages of provide no indication that the silane undergoes metathesis reactions producing any other polyhydrides.²²

In conclusion, we describe a new, experimentally simple protocol for a highly selective reduction of mono-substituted alkenes including those in 1,3- and 1,4-dienes using (EtO)₂Si(Me)H as a stoichiometric reducing agent. The reaction is carried out in the presence of catalytic amounts of a readily available air-stable [2,6-di(arylaminoyl)pyridine]-CoCl₂ and NaEt₃BH. Substrates carrying alcohols, bromides, amines, carbonyl groups or other di- and tri-substituted alkenes are tolerated. Terminal alkynes are reduced to 1-alkenes or to the corresponding alkanes depending on the amount of silane used. The reaction is highly dependent on the silane and the solvent, with (EtO)₂Si(Me)H and toluene giving nearly quantitative yields of the expected products. Preliminary mechanistic studies indicate that the reaction is stoichiometric in the silane and both hydrogens in the product come from the silane.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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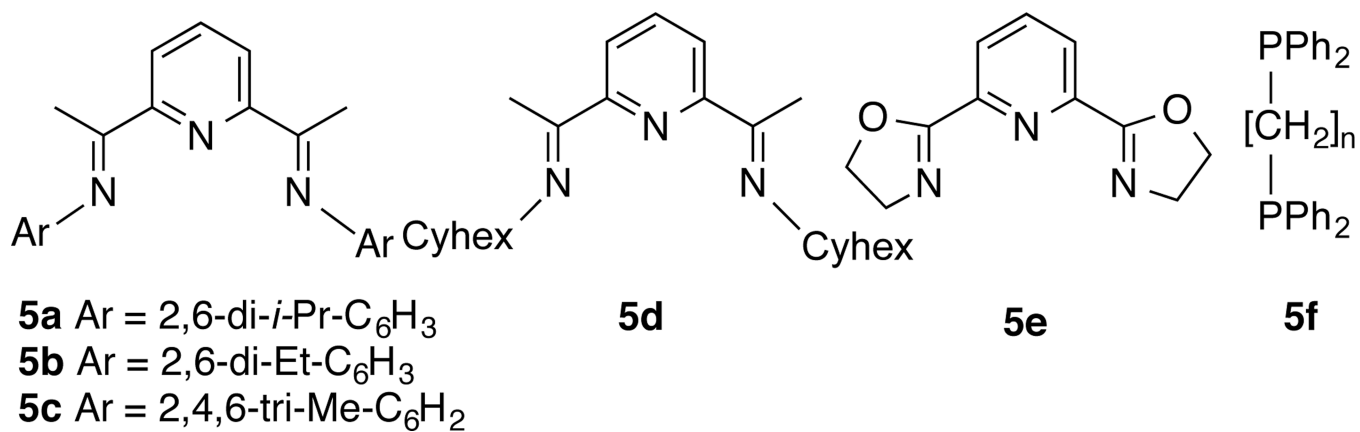
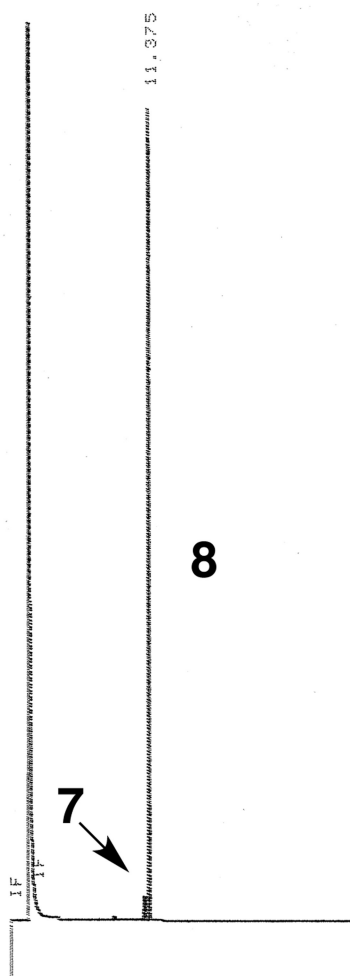


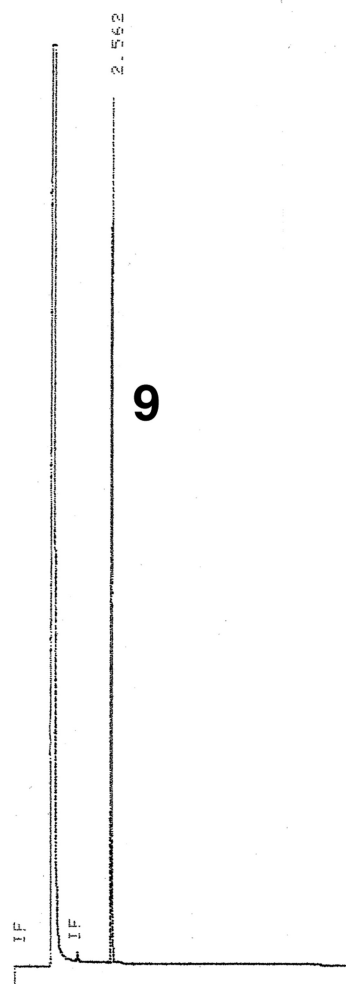
Figure 1.
Ligands (L) in Pre-catalyst [L]CoCl₂ Used for Hydrosilylation/Reduction

(Table 1, entry 1)



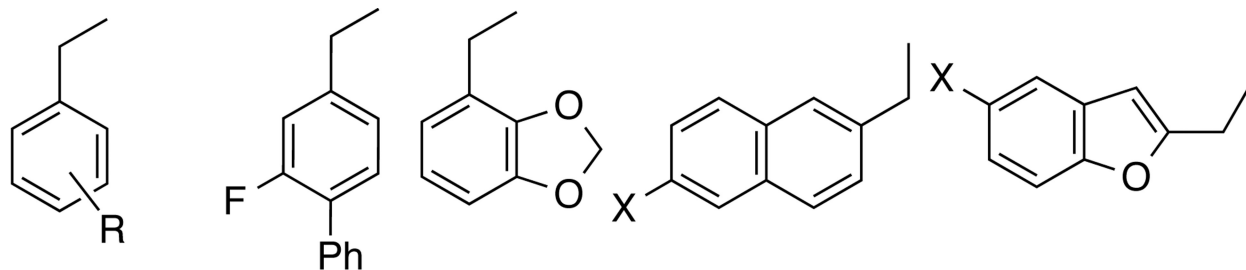
(Reaction with PhSiH_3 :
100% hydrosilylation
0% reduction)

(Table 1, entry 10)

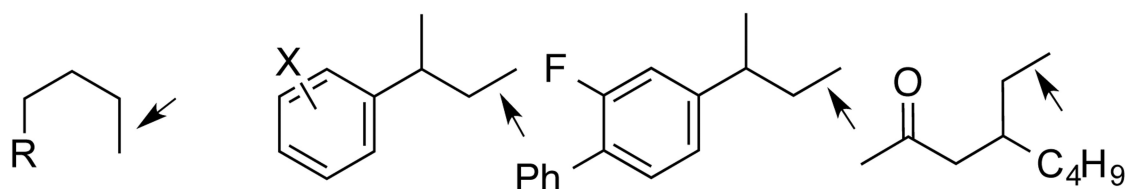


(Reaction with $(\text{EtO})_2\text{Si}(\text{Me})\text{H}$:
100% reduction
0% hydrosilylation)

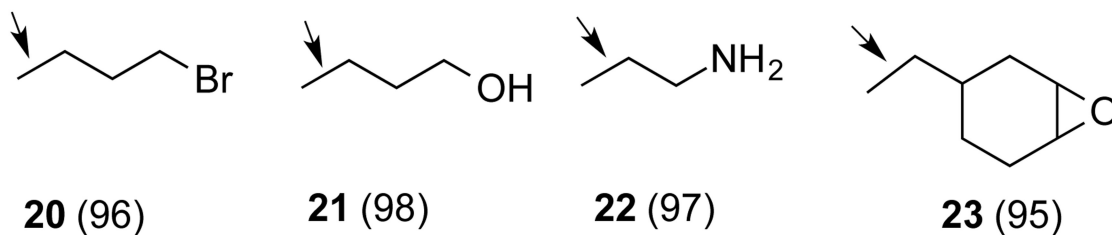
Figure 2.
GC Traces of Crude Products Showing Uncommon Selectivity with Two Different Silanes



10a R = 4-Me (97) **11** (96) **12** (98) **13** X = OMe (99) **14** X = OMe (89)
10b R = 3-OPh (94)
10c R = 3-Br (92)



15 R = C₆H₁₃ (97) **17a** X = 3-Cl (91) **18** (96) **19** (99)
16 R = Ph (96) **17b** X = 4-*i*-Bu (93)



20 (96) **21** (98) **22** (97) **23** (95)

Figure 3. Cobalt-Catalyzed Selective Reduction of Terminal Alkenes Mediated by Stoichiometric (EtO)₂Si(Me)H (isolated yields in bracket). Arrow Shows the Position of Reduction. See Eq 2 and Supporting Information for Details.

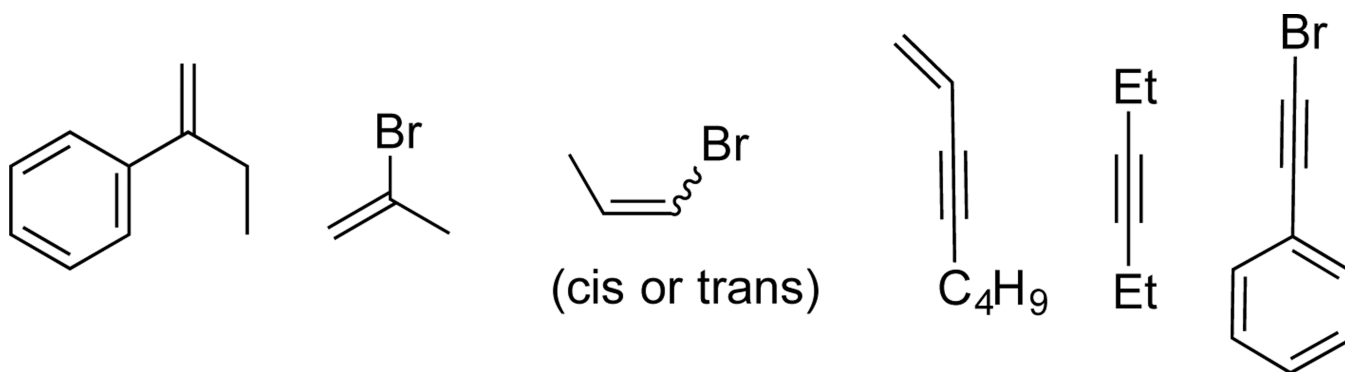
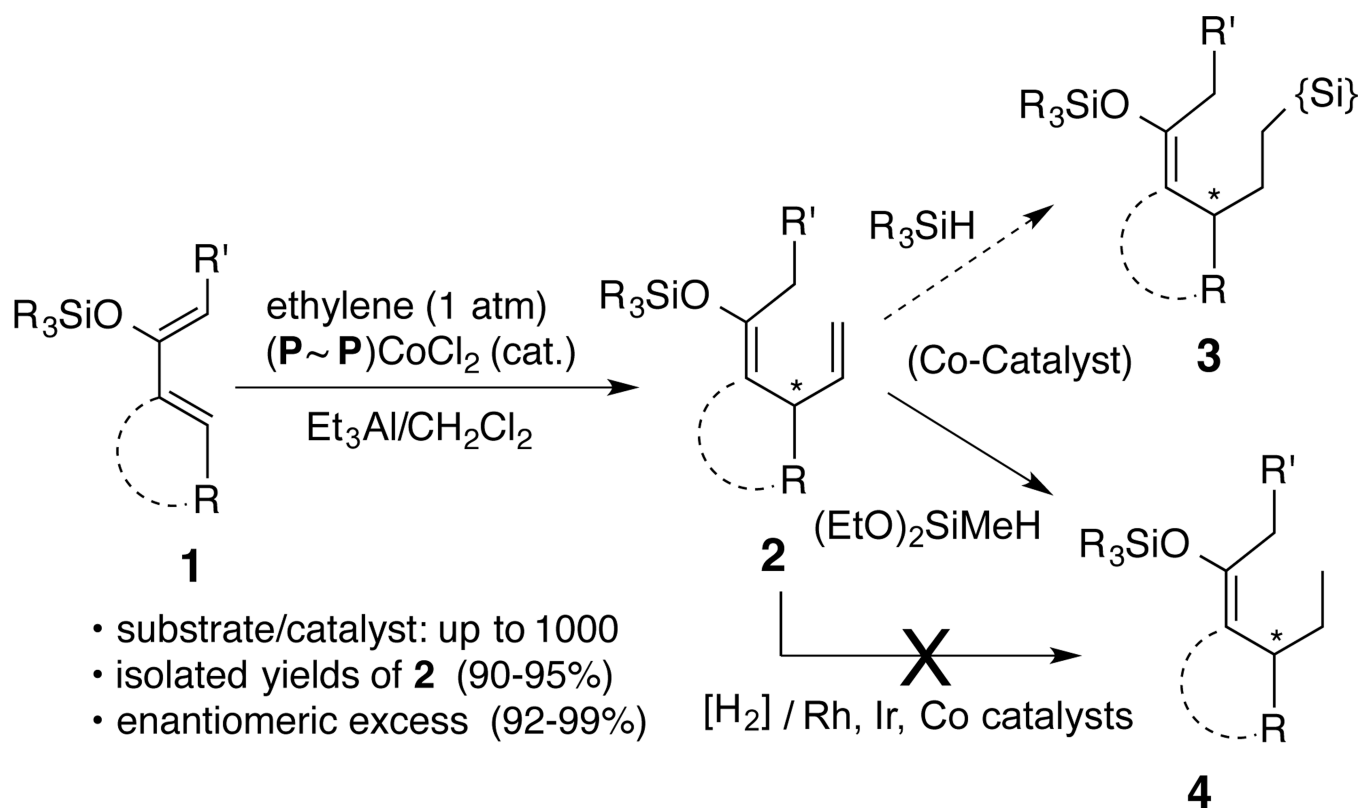
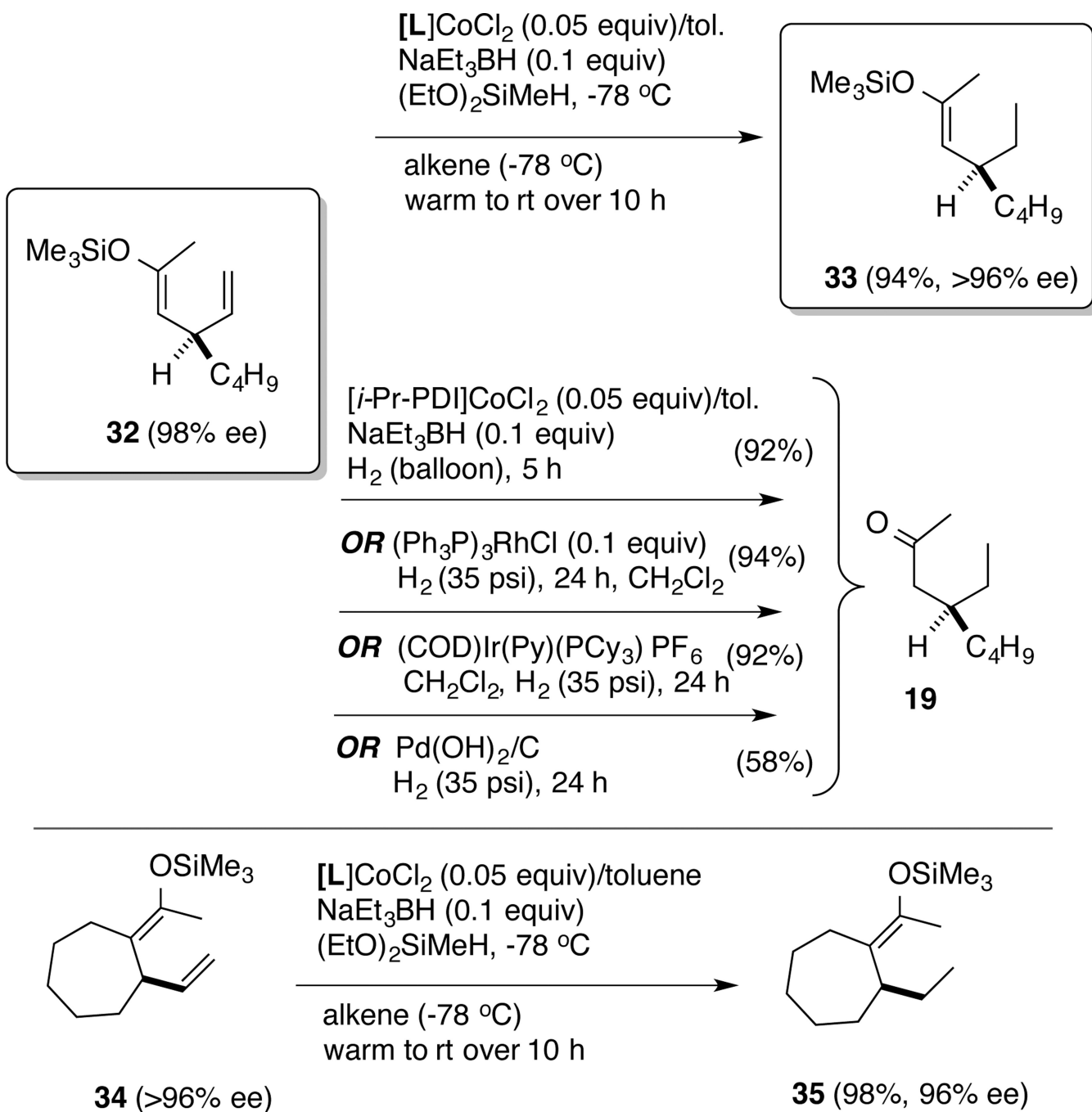


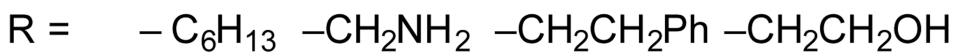
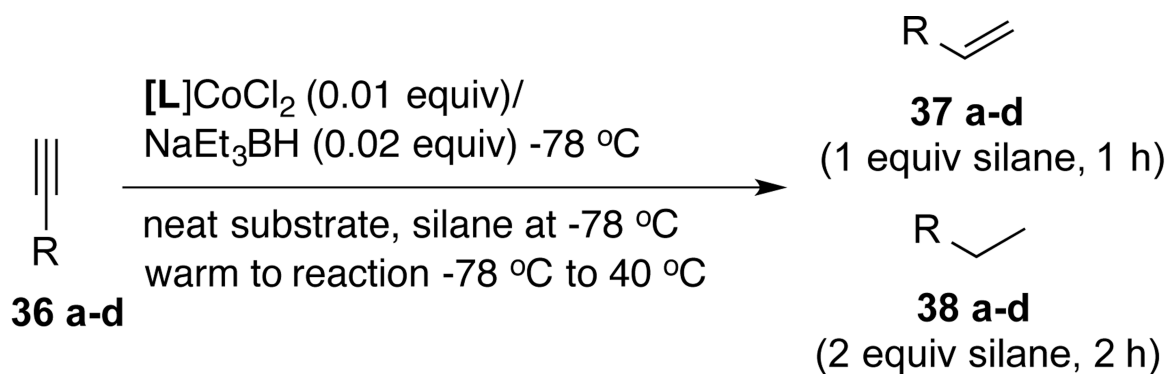
Figure 5.
Unreactive Substrates



Scheme 1.
Chemoselective Hydrosilylation and Reduction of Silyloxy-1,4-dienes.

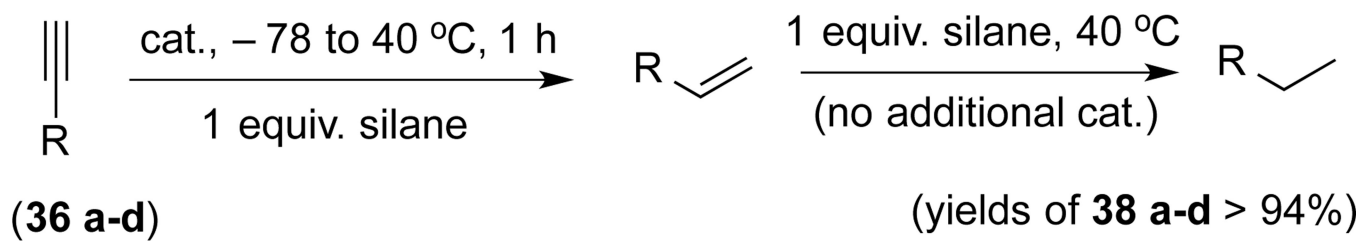


Scheme 2.
Chemoselective Reduction of Siloxy-1,4-Dienes

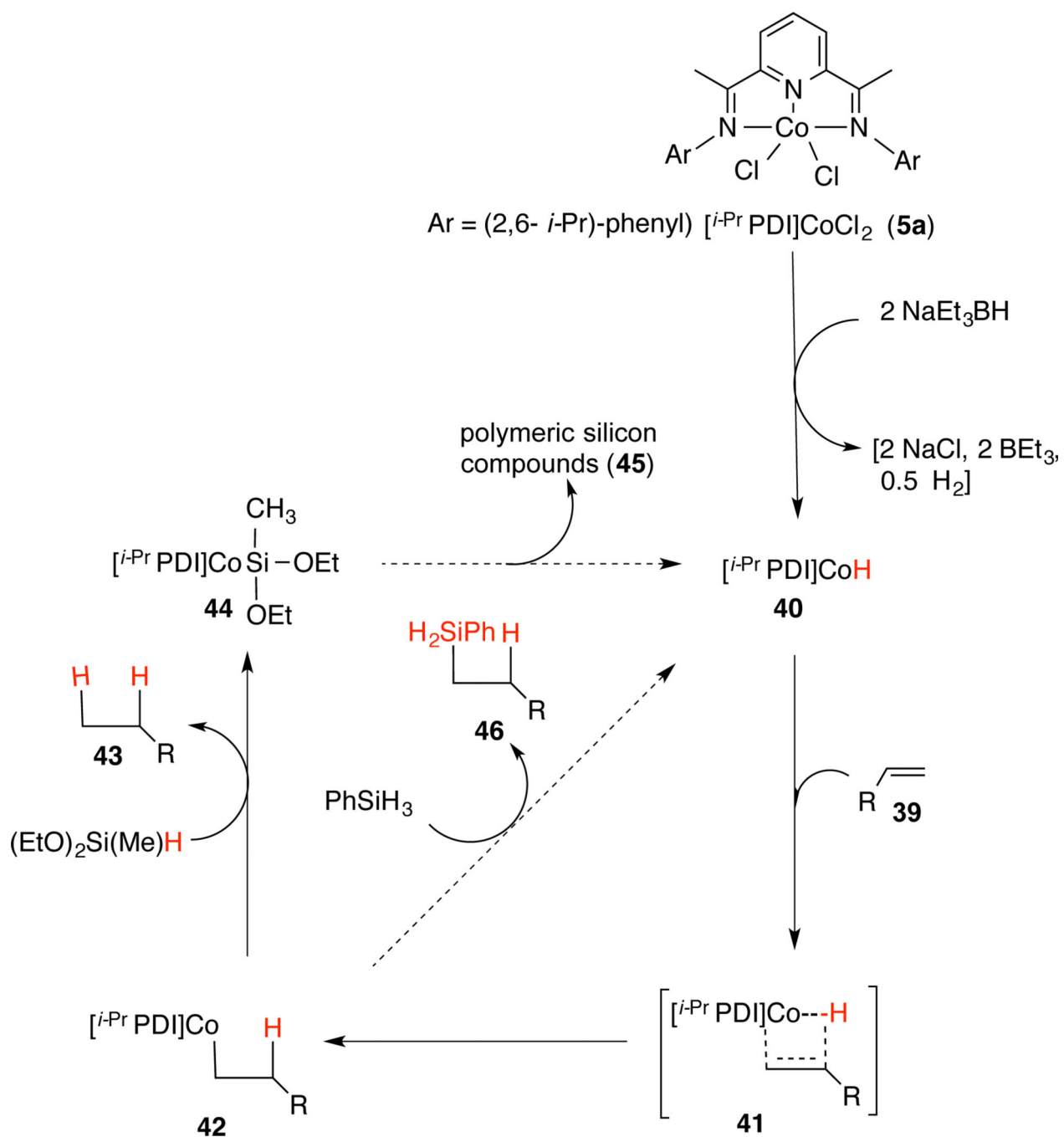


1 equiv. silane, 1 h (37 a-d)	95	96	94	97
2 equiv. silane, 2 h (38 a-d)	95	93	97	96

Scheme 3.
 Selective Reduction of Alkynes

**Scheme 4.**

Sequential Reduction of Alkyne Controlled by Stoichiometry of the Silane



Scheme 5.
Plausible Mechanism of Silane-Mediated Hydrogenation/Hydrosilylation

Table 1

Effect of Silane, Solvents on the Co-Catalyzed Reactions of 4-Methylstyrene^a

entry	silane	solvent time (h)	products					
			6	7	8	9		
1	PhSiH ₃	tol/5	0	2	98	0		
2	Et ₂ SiH ₂	tol/12	0	2	78	17		
3	Ph ₃ SiH	tol/12	88	0	0	12		
4	Cl ₃ SiH	tol/12	87	0	0	13		
5	Et ₃ SiH	tol/12	64	0	0	36		
6	MePhSiH ₂	tol/12	0	2	83	9		
7	Ph ₂ SiH ₂	tol/12	4	2	50	0		
8	(EtO) ₃ SiH	tol/12	52	0	0	47 ^b		
9	(TMSO) ₂ SiMeH	tol/5	53	0	0	47 ^b		
10	(EtO) ₂ SiMeH	tol/5	0	0	0	100 ^b		
11	(EtO) ₂ SiMeH	dcm/5	96	0	0	4		
12	(EtO) ₂ SiMeH	THF/12	13	0	0	87		
13	(EtO) ₂ SiMeH	hex/12	88	0	0	12		
14	(EtO) ₂ SiMeH	ether/12	10	0	0	90		
15	(EtO) ₂ SiMeH	dce/12	91	0	0	9		
16	(EtO) ₂ SiMeH	C ₆ H ₆ /12	20	0	0	80		

^aSee Supporting Information for details. Ratios of products determined by GC.^bNo other products detected by GC or NMR.

tol. toluene; dcm dichloromethane; hex hexane; dce dichloroethane.