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A Practical Reversed-Polarity Alternative to Organocuprate Conjugate Addition Chemistry. Halocarbon Coupling Reactions of Enal- and Enone-Derived Allylnickel Reagents

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Abstract: A direct method for the conversion of conjugated enals and enones into [1-[(trialkylsilyl)oxy]allyl]nickel(II) chloride complexes is described. Reaction of $R^1CH{=}CR^2CHO$ (R^1 = H, Me, Ph; R^2 = H and R^1 = H; R^2 = Me) with $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) and $ClSiMe_2R^3$ (R^3 = Me or *t*-Bu) affords bis[[1,2,3-η^3-1-[(trialkylsilyl)oxy]-2-propenyl](μ-chloro)nickel(II)] complexes **1a–f** as burgundy-red crystalline solids in high to excellent yields (86–98%). The X-ray crystal structure of **1c** confirms the η^3-bonding mode for the allyl ligand and provides evidence of significant overlap of oxygen lone pair electron density with the allyl π-system. Reaction of 3-buten-2-one with $Ni(COD)_2$ and Me_3SiCl similarly affords bis[[1,2,3-η^3-1-methyl-1-[(trimethylsilyl)oxy]-2-propenyl](μ-chloro)nickel(II)] (**1g**) in 72% yield, while the corresponding 2-cyclopentenone reaction fails, giving rise to a nickel metal mirror. The latter reaction does, however, succeed when conducted in the presence of pyridine, giving bis(pyridine)(chloro)[1,2,3-η^3-1-[(*tert*-butyldimethylsilyl)oxy]-2-cyclopentenyl]nickel(II) complex (**1h**) in 95% yield. Irradiation of **1e** (R^1 = R^2 = H; R^3 = *t*-Bu) in the presence of 2-iodopropane affords *tert*-butyldimethylsilyl (*E*)-enol ether **2a** in 78% yield (*E*:*Z* = 10:1). Similar results are observed with [1-[(trialkylsilyl)oxy]allyl]nickel(II) chloride complexes generated in situ from propenal, 2-methylpropenal, 2-butenal, 2-methyl-2-butenal, hexenal, and 3-buten-2-one, in coupling reactions with 1-iodobutane, 2-iodopropane, 1-bromoethene, 2-bromopropene, bromobenzene, *o*-bromobenzaldehyde, and isobutyryl chloride, affording the corresponding silyl (*E*)-enol ethers in 60–78% isolated, purified yield, based on $Ni(1,5\text{-}COD)_2$. High C(3) regioselectivities (>20:1) are observed for all of the C(3)-unsubstituted enals, while lower regioselectivities, in the range of 4–6:1 before purification, are observed for the C(3)-substituted enals; regioisomerically pure materials are obtained upon chromatography. Moderate to high *E*:*Z* stereoselectivities (*E*:*Z* = 4–15:1 before purification; *E*:*Z* = 20–50:1 after chromatography) are observed in all cases, save the reaction of isobutyryl chloride with **1e** and the reaction of the 3-buten-2-one-derived allylnickel complex with 2-bromopropene, both of which give 1:1 *E*:*Z* ratios. In a more convenient, economical, and general variant, $Ni(COD)_2$ is generated in situ via the sodium metal reduction of $NiCl_2(pyridine)_4$ (in turn prepared from $NiCl_2(H_2O)_6$) in the presence of cyclooctadiene and reacted with the enal or enone in the presence of $ClSiMe_2R^3$ to afford the [1-[(trialkylsilyl)oxy]allyl](chloro)(pyridine)nickel(II) complex, which is treated with the halocarbon and irradiated to afford the usual silyl enol ether products. Yields of 63–84%, based on enal or enone, were observed in reactions with propenal, (*E*)-2-hexenal, 2-cyclopentenone, and 2-cyclohexenone in reactions with bromoethene, bromobenzene, and 1-iodobutane using this procedure.

Introduction

The coupling of halocarbons with α,β-unsaturated aldehydes and ketones is normally achieved via transition metal mediated conjugate addition chemistry[1] and usually entails initial conversion of the halocarbon electrophile into an organolithium or other organo(main group) reagent, followed by reaction with the transition metal and lastly the enal or enone electrophile. We report herein a simple, inexpensive, and general, reversed-polarity[2,3] approach, wherein it is the enal or enone that is converted into an organometallic nucleophile and the halocarbon electrophile that is added last, a distinction that holds out the possibility of higher and/or complementary chemoselectivities (vide infra). The products are silyl enol ethers, useful as starting materials for aldol[4] and enolate alkylation[5] chemistry.

Allylnickel Complex Synthesis. Our approach is based, firstly, on the established utility of allylnickel reagents in halocarbon coupling reactions[6,7] and, secondly, on the propensity of nickel(0) complexes of conjugated enals and enones to react with oxophilic metal or metalloid halides to afford [1-(metallo-/metalloidooxy)allyl]nickel(II) halide derivatives, first exemplified by the reaction of bis(acrolein)nickel(0) with HBr to afford (1-hydroxyallyl)nickel(II) bromide.[8,9] Following the latter precedent, the reaction of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene), conveniently and inexpensively available via the $^iBu_2AlH$ reduction of (technical grade) $Ni(acac)_2$ in the presence of COD,[10] with conjugated enals and chlorotrialkylsilanes was investigated.[11] A bright red precipitate, presumed to be a mono- or bis(enal)nickel(0) complex,[12] is initially formed upon mixing the enal and $Ni(COD)_2$; this rapidly redissolves upon addition of the chlorotrialkylsilane reagent to give a deep burgundy-red solution.[13] Subsequent concentration and recrystallization of the residue

Table I. [1-[(Trialkylsilyl)oxy]allyl]nickel(II) Chloride Complexes[a]

entry	compd	R^1	R^2	R^3	% yield[b]
1	**1a**	H	H	Me	86
2	**1b**	H	Me	Me	98
3	**1c**	Me	H	Me	90
4	**1d**	Ph	H	Me	87
5	**1e**	H	H	*t*-Bu	87
6	**1f**	Me	H	*t*-Bu	98

[a] *syn*-$OSiMe_2R^3$:*anti*-$OSiMe_2R^3$ ≥ 20 in benzene. [b] Isolated yield of purified product.

[†] Northwestern University.

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[1] (a) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley-Interscience: New York, 1980. (b) Corey, E. J.; Hannon, F. J.; Boaz, N. W. *Tetrahedron* **1989**, *45*, 545. (c) Horiguchi, Y.; Komatsu, M.; Kuwajima, I. *Tetrahedron Lett.* **1989**, *30*, 7087. (d) Loots, M. J.; Schwartz, J. *J. Am. Chem. Soc.* **1977**, *99*, 8045. (e) Loots, M. J.; Schwartz, J. *Tetrahedron Lett.* **1978**, 4381. (f) Bagnell, L.; Jeffrey, E. A.; Mole, T. *Aust. J. Chem.* **1975**, *28*, 801. (g) Hansen, R. T.; Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2244. (h) Soai, K.; Hayasaka, T.; Ugajin, S. *J. Chem. Soc., Chem. Commun.* **1989**, 517. (i) Ito, K.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1987**, 2103. (j) Ito, K.; Nakanishi, S.; Otsuji, Y. *Chem. Lett.* **1988**, 473.

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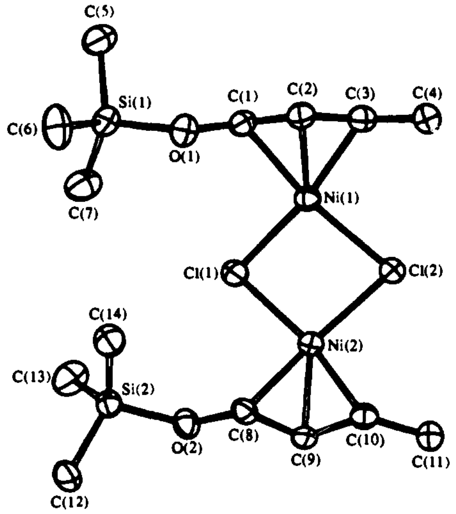
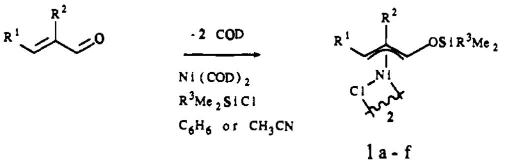


Figure 1. ORTEP diagram of the X-ray crystal structure of **1c**. Selected distances and angles: d[C(1)–O(1)] = 1.368 (5) Å; d[Ni(1)–C(1)] = 2.043 (4) Å; d[Ni(1)–C(3)] = 2.002 (4) Å; ∠C(1)–O(1)–Si(1) = 128.0 (2)°.

afford high yields of [1-[(trialkylsilyl)oxy]allyl]nickel chloride dimers **1a–f** as burgundy-red, crystalline solids (eq 1, Table I).



(1)

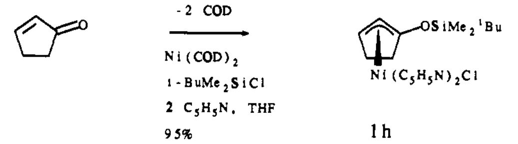
The X-ray crystal structure of **1c**[14] (Figure 1) confirms the η^3-bonding mode for the allyl ligand and further indicates that there is significant overlap of oxygen lone pair electron density with the allyl π-system: The O(1)–C(1) bond distance is only 1.368(5) Å, the C(1)–O(1)–Si(1) bond angle is 128.0 (2)°, the three allyl carbons, O(1), and Si(1) are all coplanar, and the allyl C(1) terminus is 0.043(4) Å further from the metal than the allyl C(3) terminus. This asymmetry *may* be related, by a least motion argument, to the C(3) regioselectivity of the halocarbon coupling chemistry (vide infra).

Table II. Halocarbon Coupling Reaction Products

entry	R¹	R²	RX	pdt	*E*:*Z*[a]	% yield
1	H	H	^{i}PrI	**2a**	>40:1 (10:1)	68[b]
2	H	H	^{n}BuI	**2b**	>25:1 (10:1)	76[b]
3	H	H	H_2CCHBr	**2c**	>20:1 (7:1)	78[b]
4	H	Me	H_2CCHBr	**2d**	>40:1 (8:1)	74[b]
5	H	H	$H_2CCMeBr$	**2e**	>30:1 (10:1)	71,[b] 84[c]
6	H	H	PhBr	**2f**	>20:1 (8:1)	70[b,c]
7	H	H	*o*-BrC_6H_4CHO	**2g**	>40:1 (4:1)	69[b]
8	H	H	^{i}PrC(O)Cl	**2h**	1:1 (1:1)	60[b]
9	Me	H	PhBr	**2i**	>50:1 (6:1)	65[b,d,e]
10	^{n}Pr	H	$H_2CCMeBr$	**2j**	>20:1 (5:1)	63[b–d,f]
11	Me	Me	PhBr	**2k**	>50:1 (10:1)	70[b,d,e]
12	Me	H	H_2CCHBr	**2l**	>40:1 (17:1)	83[d,g,h]
13	3-buten-2-one		$H_2CCMeBr$	**2m**	*i* (1:1)	63[c,i]
14	2-cyclopentenone		H_2CCHBr	**2n**		73[c]
15	2-cyclopentenone		^{n}BuI	**2o**		71[c,i]
16	2-cyclopentenone		PhBr	**2p**		82[c,i]
17	2-cyclohexenone		H_2CCHBr	**2r**		63[i]

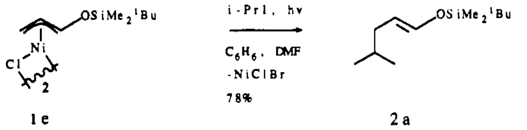
[a] *E*:*Z* ratio after chromatography; *E*:*Z* ratio of crude product in parentheses. [b] Method A (c.f. eq 4); yield based on Ni(COD)$_2$). [c] Method B (c.f. eq 6) R^3 = Me unless otherwise noted; yield based on enal or enone. [d] Yield of isolated, purified C(3)-coupling product only. [e] Crude product was a 6:1 mixture of C(3)- to C(1)-coupling products. [f] Crude product was a 4:1 mixture of C(3)- to C(1)-coupling products. [g] Reaction proceeded without irradiation and was complete after 35 min in the dark. [h] Prepared from isolated **1f**. [i] R^3 = Me; product isolated as the corresponding ketone after MeOH/K$_2$CO$_3$ hydrolysis.

Although standard reaction conditions (C_6H_6, 25 °C) fail for methyl vinyl ketone, reaction at 0 °C in diethyl ether was found to give [1-methyl-1-[(trimethylsilyl)oxy]allyl]nickel(II) chloride dimer **1g**, isolated in 72% yield as a thermally unstable, orange crystalline solid. (^{1}H NMR spectroscopy of **1g** in C_6D_6 shows the presence of a 3:1 mixture of two isomers, tentatively assigned as *syn*-OSiMe$_3$-**1g** and *anti*-OSiMe$_3$-**1g**, respectively.) In contrast, reaction of 2-cyclopentenone with Ni(COD)$_2$ and Me$_3$SiCl under similar conditions (Et$_2$O, 0 °C) gave little or none of the desired product, and instead resulted in rapid formation of a nickel metal mirror. Reasoning that a more electron rich nickel(0) derivative would tend to bind the enone more tightly and accelerate O silylation by increasing the electron density on oxygen, the effect of added pyridine was examined and found to result in the clean formation of crystalline pyridine adduct **1h** (eq 2).[15]



(2)

Halocarbon Coupling Reactions. As expected from the aforementioned precedents,[3,6,7] [1-[(trialkylsilyl)oxy]allyl]nickel(II) halide complexes react with a variety of halocarbons to afford the corresponding silyl enol ethers, as exemplified by the reaction of **1e** with 2-iodopropane (eq 3).



(3)

Inasmuch as early research showed that there was little to be gained from isolating the allylnickel reagents prior to halocarbon coupling, the scope of these reactions has been explored by using one-pot reaction procedures, wherein the allylnickel derivative is generated in situ, typically on a 5-g scale, and reacted without

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(9) The reactions of BBNBr and Cp$_2$ZrCl$_2$ with 2-butenal and Ni(COD)$_2$ give rise to analogous [1-(boronoxy)- and [1-(zirconoxy)allyl]nickel(II) halide complexes. Ward, Y. D.; Mackenzie, P. B. Unpublished results.

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(11) Chlorotrimethylsilane-modified dialkylcuprate conjugate additions[1b,c] have been proposed[1b] to proceed via analogous [1-[(trimethylsilyl)oxy]allyl]copper intermediates.

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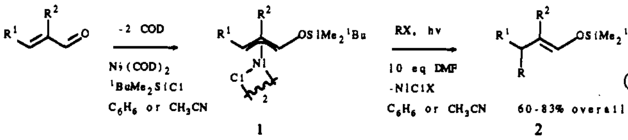
(13) Similar results are observed if the order of addition is changed such that a mixture of the enal, chlorotrialkylsilane, and silyl ketene acetal is added *to* the Ni(COD)$_2$.

(14) Crystals of **1c** suitable for X-ray diffraction were obtained by slow crystallization from ether/pentane at −25 °C. The structure was solved by direct methods (SIR) and refined by using TEXSAN 5.0. Full-matrix least-squares refinement yielded $R(F) = 0.031$ and $R_w(F) = 0.041$ for 2996 absorption-corrected reflections with $I > 3\sigma(I)$ measured on an Enraf-Nonius CAD4 diffractometer at −120 °C up to $2\theta = 50°$ (Mo Kα radiation, λ = 0.710 69 Å). Crystal data: $C_{14}H_{30}Cl_2Ni_2O_2Si_2$, m_T = 474.87; monoclinic, $P2_1/c$ (No. 14); a = 11.257 (2) Å; b = 10.627 (2) Å; c = 18.138 (4) Å; β = 94.05 (2)°; V = 2164 (1) Å^3; Z = 4, d_{calcd} = 1.46 g cm^{-3}.

(15) Studies of the effect of added pyridine on the ^{1}H NMR spectra of **1e** in THF-d_8 show that the major species in solution is the mono(pyridine) complex. Johnson, J. R.; Mackenzie, P. B. Unpublished results.

purification. Two protocols have been explored. The first to be developed (method A) involved reaction of $Ni(COD)_2$ (prepared via diisobutylaluminum hydride reduction of technical grade bis(acetylacetonate)nickel(II) in the presence of cyclooctadiene) with a mixture of the enal and *tert*-butyldimethylsilyl chloride to afford the allylnickel complex, which was then treated with the halocarbon and exposed to sunlight or irradiated with a sunlamp to achieve coupling (eq 4, Table II).

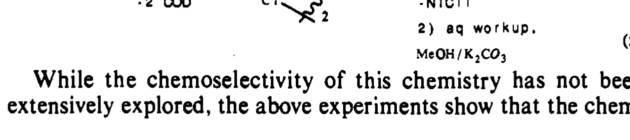


(4)

In accord with previous studies that showed that a coordinating cosolvent is required in similar halocarbon coupling reactions with allylnickel(II) halide[6,7] and (1-alkoxyallyl)nickel(II) chloride[3] complexes, the reactions were conducted in the presence of 10 equiv of dimethylformamide. The progress of the reaction was followed by monitoring the disappearance of the burgundy-red color of the [1-[(*tert*-butyldimethylsilyl)oxy]allyl]nickel starting material and the appearance of a green or brown-green precipitate of the nickel(II) dihalide coproduct, the supernatant becoming essentially colorless. The *tert*-butyldimethylsily enol ether products were recovered by buffered aqueous extraction and purified by chromatography and/or distillation to afford **2a–l** in 60–83% nonoptimized yield, based on $Ni(COD)_2$ (the most expensive reagent in this procedure). Crude yields were typically on the order of 80–90%.

With this method, successful reactions were observed with aryl bromide, alkenyl bromide, primary and secondary alkyl iodides, and isobutyryl chloride (Table II). Although initial experiments employed excess enal, t-$BuMe_2SiCl$, and halocarbon, later experiments showed that excess enal and t-$BuMe_2SiCl$ had no effect. Excess halocarbon (3–10 equiv) was usually employed in order to minimize reaction time; reactions with smaller excesses (e.g., 1.1 equiv) proceed equally well but are correspondingly slower. Complexes derived from the C(3)-unsubstituted enals 2-propenal and 2-methylpropenal were found to react with essentially complete C(3) regioselectivity (>20:1). The isobutyryl chloride, alkenyl bromide, and *o*-bromobenzaldehyde reactions with these complexes are rapid and generally complete within 0–30 min of irradiation; the aryl bromide and alkyl iodide reactions are slower and typically require 4–14 h of irradiation to achieve complete reaction. Complexes derived from the C(3)-substituted enals 2-butenal, 2-methyl-2-butenal, and 2-hexenal were generally found to react more slowly and generate small amounts of nickel metal, but still gave good yields and moderate C(3) regioselectivities, (crude C(3):C(1) coupling ratio 4–6:1, Table II, entries 9–12). With the exception of the reactions giving rise to **2h** and **2m**, which were found to be completely nonstereoselective (*E*:*Z* = 1:1), moderate to high *E*:*Z* ratios (4–17:1 before purification; >20:1 after chromatography) were generally observed. (In the case of the monosubstituted enol ethers, the *E* and *Z* isomers give rise to well-separated C(1)H NMR signals with different coupling constants. In the case of the disubstituted enol ethers **2d** and **2k**, the coupling constants are similar for the *E* and *Z* isomers, but ^1H NOE experiments with **2d** indicate that *E* isomer is still the major product.)

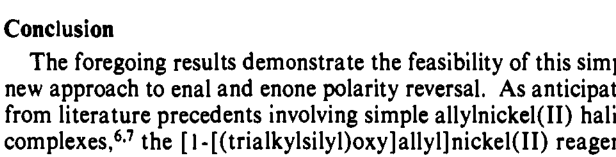
In contrast to the C(3) regioselectivity of the C(3)-alkyl-substituted enal reactions, the corresponding 3-phenylpropenal reaction was found to be highly C(1) regioselective (>20:1, eq 5), a change we tentatively attribute to the electronic effect of the 3-phenyl substituent, which presumably favors C(1) attack so the phenyl group can remain conjugated in the product.



(5)

While the chemoselectivity of this chemistry has not been extensively explored, the above experiments show that the chemistry can tolerate conjugated enal, enol ether, aromatic aldehyde, nitrile, amide, and styryl groups. The intermediate 1-allylnickel chloride is oxygen-sensitive, but is generated and reacted in situ, so that this is not a major concern. If necessary, water and other Bronsted acid impurities can be scavenged through the addition of (commercially available) $Me_2C{=}C(OMe)(OSiMe_3)$. This is especially convenient in the case of readily polymerizable enals such as propenal and 2-methylpropenal, which are stabilized with 3% water but need not be dried prior to use with this procedure.

Although useful for a variety of aldehydes and methyl vinyl ketone, the above method does not work for more substituted ketones such as 2-cyclopentenone and 2-cyclohexenone, which require a donor ligand such as pyridine for allylnickel complex formation (vide supra). Given the latter requirement, and wanting to explore in situ methods for generating $Ni(COD)_2$, we were prompted to examine the possibility that the method of Ohta et al.,[16] sodium metal reduction of $NiCl_2(pyridine)_4$ in the presence of cyclooctadiene in THF at 0 °C, would be compatible with subsequent enal and enone chemistry. The pursuit of this possibility led to the development of a second, more convenient and economical procedure (method B), wherein both enals and enones can be converted to the corresponding silyl enol ethers in 63–84% nonoptimized yield (based on enal or enone) starting from $NiCl_2(pyridine)_4$, in turn readily prepared from inexpensive $NiCl_2(H_2O)_6$ (eq 6, Table II).



(6)

With this procedure, successful reactions were observed with complexes derived from propenal, (*E*)-2-hexenal, 2-cyclopentenone, and 2-cyclohexenone in coupling reactions with 1-iodobutane, bromoethene, and bromobenzene, using both t-$BuMe_2SiCl$ and Me_3SiCl (the products of the latter reactions being isolated as the corresponding ketones after hydrolysis with $MeOH/K_2CO_3$). As before, the silyl enol ether products were recovered by aqueous extraction, which removes all but the cyclooctadiene and any excess, nonvolatile halocarbon, followed by chromatography or distillation to isolate pure material.

Conclusion

The foregoing results demonstrate the feasibility of this simple new approach to enal and enone polarity reversal. As anticipated from literature precedents involving simple allylnickel(II) halide complexes,[6,7] the [1-[(trialkylsilyl)oxy]allyl]nickel(II) reagents exhibit a promisingly high level of chemoselectivity. In the case of method B, these reactions are already competitive with organocuprate chemistry in terms of cost and convenience, and give respectable yields that are expected to improve upon optimization. The mechanism of these reactions has not been addressed, but is *tentatively* assumed to be similar to the nickel(I)/nickel(III) radical chain mechanism proposed by Hegedus et al.[7] to describe the reactions of simple allylnickel halides with halocarbons. Studies designed to elucidate the mechanism are in progress, as are further explorations of the scope and chemoselectivity.

Experimental Section

A. General Methods. All manipulations were conducted in a nitrogen atmosphere drybox or on a dual-manifold Schlenk line by using purified, deoxygenated solvents and standard inert atmosphere techniques, unless otherwise stated. NMR spectra were recorded on a Varian XLA-400 Spectrometer (400 MHz for ^1H NMR; 101 MHz for ^{13}C NMR). ^1H NMR chemical shifts are reported in parts per million downfield from tetramethylsilane but were measured relative to residual ^1H solvent resonances (C_6HD_5 at 7.15 ppm; $CHCl_3$ at 7.26 ppm). ^{13}C NMR chemical shifts are reported in parts per million downfield from tetramethylsilane but were referenced to benzene-d^6 at 124.0 ppm or chloroform-*d* solvent at 77.0 ppm. Mass spectra were obtained on a VG high-resolution mass spectrometer, Model 70-250SE. Elemental analyses

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were performed by G.D. Searle Research and Development, Skokie, IL, Oneida Research Services, Inc., Whitesboro, NY 13492, or Galbraith Laboratories, Inc., Knoxville, TN 37950.

Acetonitrile, acetonitrile-d^3, dichloromethane, chloroform-*d* and *N*,*N*-dimethylformamide (DMF) were distilled from calcium hydride and stored under nitrogen. Benzene, benzene-d^6, diethyl ether, tetrahydrofuran, and pentane were vacuum transferred from sodium benzophenone ketyl and stored under nitrogen. Gravity column chromatography employed Aldrich (70–270 mesh) silica gel. The following reagents were used as received or as otherwise noted: chlorotrimethylsilane (Aldrich, distilled from quinoline), methyl trimethylsilyl dimethylketene acetal (Aldrich, degassed), propenal (Aldrich, degassed), 2-methylpropenal (Aldrich, degassed), (*E*)-2-butenal (Aldrich, degassed), cinnamaldehyde (Aldrich), and *tert*-butyldimethylsilyl chloride (Aldrich). Bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) was prepared according to literature procedure.[10]

B. [1-[(Trialkylsilyl)oxy]allyl]nickel Complexes. Typical Procedure for the Preparation of Complexes 1a–f. Preparation of Bis[(μ-chloro)-[1,2,3-η^3-1-[(trimethylsilyl)oxy]-2-propen-1-yl]nickel(II)] (1a). In the drybox, a 50-mL Schlenk tube was charged with $Ni(COD)_2$ (500 mg, 1.82 mmol, 1.00 equiv), equipped with a stir bar, and sealed with a septum. On the line, a solution of propenal (244 μL, 3.64 mmol, 2.00 equiv) in benzene (8 mL) in a 25-mL Schlenk vessel was treated with $(MeO)(Me_3SiO)CCMe_2$ (185 μL, 0.909 mmol, 0.500 equiv; added as a proton-scavenging reagent), stirred for 5 min and then transferred by cannula onto the $Ni(COD)_2$. The resultant purple-red slurry was stirred for 10 min and then treated with Me_3SiCl (462 μL, 3.64 mmol, 2.00 equiv) to afford a deep red solution. After 45 min, the volatiles were removed at 0.1 mmHg to obtain an orange-red powder. This was extracted with pentane (20 mL) through a filter paper tipped cannula. The clear red filtrate was concentrated under vacuum to ca. 5 mL volume and then cooled to −20 °C for 24 h to induce crystallization. The precipitate was isolated by removal of the supernatant through a filter paper tipped cannula while maintaining the mixture at −20 °C and washed with pentane (2 × 3 mL) to yield **1a** (0.349 g, 86%) as a burgundy-red crystalline solid: 400-MHz ^1H NMR (CD_3CN) δ 5.61 (1 H, d, $J = 9.6$ Hz), 5.22 (1 H, ddd, $J = 12.4, 9.6, 6.2$ Hz), 2.47 (1 H, d, $J = 6.2$ Hz), 1.30 (1 H, d, $J = 12.4$ Hz), 0.21 (9 H, s); 101-MHz NMR (C_6D_6) δ 103.0, 92.1, 37.6, −0.17; MS (70 eV) (isotopomeric intensity) *m/z* 450 (26.6 calcd, 15.6 obsd), 449 (17.1 calcd, 10.8 obsd), 448 (65.8 calcd, 54.8 obsd), 447 (25.3 calcd, 12.9 obsd), 446 (100.0 calcd, 100.0 obsd), 445 (15.7 calcd, 10.8), 444 (66.7 calcd, 58.1 obsd). Anal. Calcd for $C_{12}H_{26}Cl_2Ni_2O_2Si_2$: C, 32.26; H, 5.86. Found: C, 32.44; H, 5.57.

Bis[(μ-chloro)[1,2,3-η^3-2-methyl-1-[(trimethylsilyl)oxy]-2-propenyl]-nickel(II)] (1b): 400-MHz ^1H NMR (C_6D_6) δ 4.95 (1 H, s), 2.32 (1 H, s), 2.17 (3 H, s), 0.97 (1 H, s), 0.15 (9 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 103.9, 99.5, 41.4, 16.2, −0.10; MS (70 eV) (isotopomeric intensity) *m/z* 482 (1.8 calcd, 2.7 obsd), 481 (2.1 calcd, 3.2 obsd), 480 (7.9 calcd, 8.6 obsd), 479 (7.4 calcd, 7.5 obsd), 478 (26.9 calcd, 26.7 obsd), 477 (18.6 calcd, 20.3 obsd), 476 (66.2 calcd, 65.8 obsd), 475 (27.4 calcd, 31.0 obsd), 474 (100.0 calcd, 100.0 obsd), 473 (17.2 calcd, 18.2 obsd), 472 (66.4 calcd, 70.1 obsd). Anal. Calcd for $C_{14}H_{30}Cl_2Ni_2O_2Si_2$: C, 35.41; H, 6.37. Found: C, 35.02; H, 6.46.

Bis[(μ-chloro)[1,2,3-η^3-1-[(trimethylsilyl)oxy]-2-butenyl]nickel(II)] (1c): 400-MHz ^1H NMR (CD_3CN) δ 5.39 (1 H, d, $J = 9.2$ Hz), 5.09 (1 H, dd, $J = 12.2, 9.2$ Hz), 2.13 (1 H, dq, $J = 12.2, 6.0$ Hz), 0.74 (3 H, d, $J = 6.0$ Hz), 0.20 (9 H, s); 101-MHz ^{13}C NMR (CD_3CN) δ 102.1, 98.3, 55.9, 16.7, −0.33; MS (70 eV) (isotopomeric intensity) *m/z* 478 (26.9 calcd, 29.8 obsd), 477 (18.6 calcd, 18.1 obsd), 476 (66.2 calcd, 60.6 obsd), 475 (27.4 calcd, 29.3 obsd), 474 (100.0 calcd, 100.0 obsd), 473 (17.2 calcd, 14.9 obsd), 472 (66.4 calcd, 73.4 obsd). Anal. Calcd for $C_{14}H_{30}Cl_2Ni_2O_2Si_2$: C, 35.41; H, 6.37. Found: C, 35.45; H, 6.11.

Bis[(μ-chloro)[1,2,3-η^3-1-[(trimethylsilyl)oxy]-3-phenyl-2-propenyl]-nickel(II)] (1d): 400-MHz ^1H NMR (CD_3CN) δ 7.66–7.21 (5 H, m), 5.83 (1 H, d, $J = 9.2$ Hz), 5.74 (1 H, dd, $J = 11.6, 9.2$ Hz), 2.91 (1 H, d, $J = 11.6$ Hz), 0.26 (9 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 141.1, 129.3, 129.2, 126.2, 101.2, 89.0, 53.8, −0.16. Anal. Calcd for $C_{24}H_{34}Cl_2Ni_2O_2Si_2$: C, 48.12; H, 5.72. Found: C, 48.47; H, 5.41.

Bis[(μ-chloro)[1,2,3-η^3-1-[(*tert*-butyldimethylsilyl)oxy]-2-propenyl]-nickel(II)] (1e): (prepared as per **1a** but by using CH_3CN as the reaction solvent) 400-MHz ^1H NMR (C_6D_6) δ 5.09 (1 H, d, $J = 9.6$ Hz), 4.95 (1 H, ddd, $J = 12.0, 9.6, 6.4$ Hz), 2.27 (1 H, d, $J = 6.4$ Hz), 0.90 (1 H, d, $J = 12.0$ Hz), 0.87 (9 H, s), 0.22 (3 H, s), 0.14 (3 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 103.3, 92.2, 37.6, 25.6, 18.1, −4.3, −5.7. Anal. Calcd for $C_{18}H_{38}Cl_2Ni_2O_2Si_2$: C, 40.72; H, 7.21. Found: C, 40.71; H, 7.16.

Bis[(μ-chloro)[1,2,3-η^3-1-[(*tert*-butyldimethylsilyl)oxy]-2-butenyl]-nickel(II)] (1f): (prepared as per **1a** but by using CH_3CN as the reaction solvent) 400-MHz ^1H NMR (C_6D_6) δ 4.879 (1 H, m), 4.876 (1 H, d, $J = 3.6$ Hz), 1.764 (1 H, dq, $J = 11.6, 6.4$ Hz), 0.904 (9 H, s), 0.533 (3 H, d, $J = 6.4$ Hz), 0.251 (3 H, s), 0.160 (3 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 98.34, 95.99, 53.59, 25.71, 18.19, 16.73, −4.27, −5.64; MS (70 eV) (isotopomeric intensity) *m/z* 556 (65.59 calcd, 66.66 obsd), 557 (21.36 calcd, 18.52 obsd), 558 (100.00 calcd, 100.00 obsd), 559 (33.77 calcd, 33.33 obsd), 560 (67.35 calcd, 66.66 obsd), 561 (22.77 calcd, 25.93 obsd), 562 (27.91 calcd, 25.93 obsd), 564 (8.35 calcd, 7.41 obsd). Anal. Calcd for $C_{10}H_{21}OClNiSi$: C, 42.97; H, 7.57. Found: C, 42.86; H, 7.41.

Bis[(μ-chloro)[2,3,4-η^3-2-[(trimethylsilyl)oxy]-3-buten-2-yl]nickel(II)] (1g): (prepared as per **1a** but by using Et_2O as the reaction solvent and a reaction temperature of 0 °C) 400-MHz ^1H NMR (C_6D_6) 4.702 (1 H, dd, $J = 13.0, 7.0$ Hz), 2.381 (1 H, d, $J = 7.0$ Hz), 1.188 (1 H, d, $J = 13.0$ Hz), 1.137 (3 H, s), 0.224 (9 H, s); 101-MHz ^{13}C NMR (C_6D_6) 115.26, 89.09, 36.64, 22.14, 1.14; MS (70 eV) (isotopomeric intensity) *m/z* 472 (66.43 calcd, 68.32 obsd), 473 (17.17 calcd, 13.26 obsd), 474 (100.00 calcd, 100.00 obsd), 475 (27.44 calcd, 25.97 obsd), 476 (66.18 calcd, 64.64 obsd), 477 (18.85 calcd, 15.65 obsd), 478 (26.89 calcd, 26.89 obsd), 480 (7.91 calcd, 7.36 obsd). (Elemental analysis was precluded by thermal instability of the solid at 25 °C.)

Bis(pyridine)(chloro)[1,2,3-η^3-1-[(*tert*-butyldimethylsilyl)oxy]-2-cyclopentyl]nickel(II) (1h). In a 100-mL Schlenk tube containing a magnetic stirring bar, solid $Ni(COD)_2$ (0.500 g, 1.00 equiv, 1.82 mmol) was sequentially treated with a solution of 2-cyclopentenone (0.152 mL, 1.82 mmol, 1.00 equiv) and pyridine (0.294 mL, 3.64 mmol, 2.00 equiv) in THF (4 mL), followed by *t*-$BuMe_2SiCl$ (0.274 g, 1.82 mmol, 1.00 equiv) to afford a deep red solution. Removal of the volatiles at 0.1 mmHg and crystallization from a mixture of Et_2O (4 mL) and pentane (6 mL) gave the crude product as an orange crystalline solid, isolated by removal of the supernatant through a filter paper tipped cannula. Recrystallization (Et_2O/pentane, $(Me_3)_2N$-treated glassware) gave pure **1h** (0.775 g, 95%). In solution, pyridine exchange occurs at a rate comparable to the NMR time scale at 25 °C and results in the near complete loss of ^1H and ^{13}C signals for the pyridine ligand:[15] 400-MHz ^1H NMR (CD_3CN) δ 5.45 (1 H, d, $J = 3.2$ Hz), 3.20 (1 H, m), 2.07 (1 H, ddd, $J = 17.6, 8.0, 3.6$ Hz), 1.71 (1 H, dd, $J = 16.0, 7.6$ Hz), 0.94 (1 H, m), 0.80 (9 H, s), 0.58 (1 H, m), 0.10 (3 H, s), 0.001 (3 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 151.2, 118.5, 84.7, 56.7, 33.7, 28.5, 25.7, 18.1, −4.1, −4.6. Anal. Calcd for $C_{21}H_{31}ClOSiN_2Ni$: C, 56.09; H, 6.95; N, 6.23. Found: C, 56.16; H, 6.79; N, 6.28.

C. Halocarbon Coupling Reactions. Silyl enol ethers **2m** and **2o–p** (Table II) were not isolated as such, but were rather hydrolyzed by treatment with $MeOH/K_2CO_3$ to afford the corresponding known ketones 5-methyl-5-hexen-2-one,[17] 3-butylcyclopentanone,[18] 3-phenylcyclopentanone,[19] and 3-ethenylcyclohexanone.[20]

Method A. Typical Procedure for the One-Pot Conversion of an Enal to the Corresponding [1-(*tert*-Butyldimethylsilyl)oxy]allyl]nickel Chloride Complex and Subsequent Halocarbon Coupling. Preparation of *tert*-Butyldimethyl[((*E*)-4-methyl-1-pentenyl)oxy]silane (2a) from Propenal, *tert*-Butylchlorodimethylsilane and 2-Iodopropane. A 100-mL Schlenk tube, equipped with a magnetic stir bar, was sequentially charged with *t*-$BuMe_2SiCl$ (3.56 g, 23.6 mmol, 1.30 equiv), acetonitrile (30 mL), $(MeO)(Me_3SiO)CCMe_2$ (3.69 mL, 18.2 mmol, 1.00 equiv; added as a proton-scavenging reagent), and propenal (2.43 mL, 36.4 mmol, 2.00 equiv). The mixture was stirred for 5 min, during which time nitrogen was bubbled through the solution, and then transferred via cannula into a 100-mL Schlenk tube containing $Ni(COD)_2$ (5.00 g, 18.2 mmol, 1.00 equiv) and a spinning stir bar, with an acetonitrile wash (5 mL) to complete the transfer. The resultant deep burgundy-red solution was stirred for 1 h and then concentrated under reduced pressure (0.01 mmHg) for 14 h to afford crude **1e** as a dark red solid contaminated with 1,5-cyclooctadiene. This was dissolved in acetonitrile (30 mL) and sequentially treated with $(MeO)(Me_3SiO)CCMe_2$ (0.10 mL, 0.49 mmol, 0.03 equiv), DMF (14.1 mL, 182 mmol, 10.0 equiv), and 2-iodopropane (14.1 mL, 181 mmol, 10.0 equiv). The resultant burgundy-red solution was stirred for 5 min and then irradiated with sunlight or a 275-W GE Model RSW sunlamp until the burgundy-red color of the allylnickel complex had been completely discharged (ca. 12 h), during which time a brown-green crystalline precipitate was deposited and the supernatant became light blue-green or nearly colorless (depending on the completeness of the precipitation). The supernatant was transferred via cannula into a round-bottom flask containing pentane, and the cloudy mixture was stirred for 30 min to complete precipitation of the nickel dihalide coproduct. The supernatant was then transferred through a filter paper tipped cannula onto a stirred aqueous buffer (150 mL of a pH 7 $KH_2PO_4/NaOH/H_2O$ solution). (An emulsion tends to form at this

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stage if most of the nickel dihalide has not been removed through the prescribed procedure.) The pentane layer was separated, washed with water (3 × 20 mL), dried over $MgSO_4$, and concentrated under reduced pressure (15 mmHg) to afford crude **2a** (E:Z = 10:1) as a clear, yellow oil, contaminated by 1,5-cyclooctadiene and 2-iodopropane. Column chromatography (SiO_2, 343 g, 98:2 hexane/EtOAc) afforded pure **2a** (2.64 g, 68%; bp 76 °C at 15 mmHg; E:Z > 40:1): 400-MHz ^1H NMR ($CDCl_3$) δ 6.19 (1 H, dt, J = 12.0, 1.2 Hz), 4.98 (1 H, dt, J = 12.0, 8.0 Hz), 1.76 (2 H, ddd, J = 8.0, 6.8, 1.2 Hz), 1.53 (1 H, heptet, J = 6.8 Hz), 0.92 (9 H, s), 0.86 (6 H, d, J = 6.8 Hz), 0.13 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 140.7, 110.2, 36.6, 28.9, 25.8, 22.2, 18.4, −5.2; HRMS for $C_{12}H_{26}OSi$, calcd 214.1752, found 214.1737. Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 67.37; H, 12.23.

Reaction of Isolated 1e with 2-Iodopropane To Afford 2a. **1e** (0.250 g, 0.942 mmol, 1.00 equiv) was dissolved in benzene (10 mL) and sequentially treated with $(MeO)(Me_3SiO)CCMe_2$ (191 μL, 0.942 mmol, 1.00 equiv), 2-iodopropane (470 μL, 4.71 mmol, 5.00 equiv), and DMF (729 μL, 9.42 mmol, 10.0 equiv). Irradiation (GE sunlamp, 275 W Model RSW) for 14 h at 10 °C caused the initially burgundy-red solution to become almost colorless and deposit a mixture of brown and green crystals. Workup and chromatography as above gave **2a** (157 mg, 78%).

Reaction of Isolated 1f with Bromoethene To Afford *tert*-Butyldimethyl[((*E*)-3-methyl-1,4-pentadienyl)oxy]silane (2l). **1f** (0.500 g, 1.73 mmol, 1.00 equiv) was dissolved in acetonitrile (5 mL) and sequentially treated with $(MeO)(Me_3SiO)CCMe_2$ (0.035 mL, 0.172 mmol, 0.100 equiv), DMF (0.665 mL, 8.60 mmol, 5.00 equiv), and bromoethene (0.365 mL, 5.17 mmol, 3.00 equiv) in the absence of light. After 35 min in the dark, the burgundy-red color of **1f** was completely discharged and replaced by an emerald-green supernatant and a green-blue precipitate of crystalline nickel dihalide. Workup and chromatography (SiO_2, 180 g, 98:2 hexane/EtOAc) as above gave **2l** (0.303 g, 83%; E:Z > 40:1 after purification, crude E:Z = 17:1) as a clear, colorless oil: 400-MHz ^1H NMR (C_6D_6) δ 6.30 (1 H, dd, J = 12.0, 1.0 Hz), 5.79 (1 H, ddd, J = 17.2, 10.3, 6.2 Hz), 5.13 (1 H, dd, J = 12.0, 4.0 Hz), 5.03 (1 H, d, J = 17.2 Hz), 4.93 (1 H, d, J = 10.2 Hz), 2.71 (1 H, m), 1.04 (3 H, d, J = 6.9 Hz), 0.93 (9 H, s), 0.06 (6 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 143.9, 140.3, 115.9, 112.5, 36.5, 25.8, 21.2, 18.4, −5.2; HRMS for $C_{12}H_{24}OSi$, calcd 212.1596, found 212.1589. Anal. Calcd $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.63; H, 11.03.

Method B. Typical One-Pot Procedure Starting from $NiCl_2(C_5H_5N)_4$. Preparation of *tert*-Butyldimethyl-[(3-ethenyl-1-cyclopentenyl)oxy]silane (2n) from 2-Cyclopentenone, *tert*-Butylchlorodimethylsilane and Bromoethene. A 100-mL Schlenk tube equipped with a magnetic stir bar and rubber septum was charged with $NiCl_2(pyridine)_4$ (10.0 g, 22.4 mmol, 1.00 equiv) and evacuated and refilled with N_2 twice to establish an inert atmosphere. THF (40 mL) was added, followed by cyclooctadiene (8.20 mL, 67.2 mmol, 3.00 equiv), and the resultant mixture cooled to 0 °C. A second 100-mL Schlenk tube containing sodium metal strips (1.03 g, 44.8 mmol, 2.00 equiv; each ca. 2 cm × 0.4 cm × 0.1 cm) was connected to this flask with a flexible adaptor (available from Aldrich) under a rapid flow of N_2 (an inert atmosphere having previously been established in the second Schlenk tube and adaptor by capping the free end of the adaptor and evacuating and refilling with N_2). The sodium strips were then transferred to the stirred 0–5 °C reaction mixture in four portions over 1.5 h to give, after an additional 40 min at 0–5 °C, a very dark brown (but not black) supernatant, a small amount of precipitated yellow $Ni(COD)_2$, and no apparent blue $NiCl_2(pyridine)_4$. This was treated with a solution of 2-cyclopentenone (1.88 mL, 22.4 mmol, 1.00 equiv) and t-$BuMe_2SiCl$ (3.38 g, 22.4 mmol, 1.00 equiv) in THF (15 mL) and stirred at 25 °C for 30 min to afford an orange mixture. A solution of bromoethene (4.74 mL, 67.2 mmol, 3.00 equiv) in THF (5 mL) was added via cannula, and the mixture was irradiated at 10 °C with a GE Model RSW sunlamp for 12.5 h to afford an olive-green precipitate and a light brown supernatant. The mixture was poured into a 2000-mL separatory funnel containing pentane (400 mL) and aqueous buffer (400 mL of KH_2PO_4/NaOH, pH 7) and shaken to give an emulsion that was filtered with suction through Celite to achieve separation. The organic phase was washed with water (3 × 300 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure (15 mmHg) to afford a mixture of **2n** and cyclooctadiene. Distillation through a 20-cm Vigreux column under reduced pressure afforded **2n** as a clear, colorless oil (3.62 g, 72%; bp 80–82 °C at 3 mmHg): 400-MHz ^1H NMR ($CDCl_3$) δ 5.78 (1 H, ddd, J = 7.6, 10.0, 17.1 Hz), 4.97 (1 H, ddd, J = 17.1, 2.0, 1.2 Hz), 4.86 (1 H, ddd, J = 10.0, 0.8, 2.0 Hz), 4.56 (1 H, m), 3.24 (1 H, m), 2.27 (2 H, m), 2.10 (1 H, m), 1.57 (1 H, m), 0.93 (9 H, s), 0.17 (6 H, s); 101-MHz ^{13}C NMR ($CDCl_3$) δ 156.1, 143.8, 111.9, 105.4, 45.9, 33.2, 28.8, 25.7, 18.1, −4.7. Anal. Calcd for $C_{13}H_{24}OSi$: C, 69.58; H, 10.78. Found: C, 69.87; H, 11.21.

***tert*-Butyldimethyl((*E*)-1-heptenyloxy)silane (2b).** Reaction of $Ni(COD)_2$ (5.00 g, 18.2 mmol, 1.00 equiv), propenal (2.43 mL, 36.4 mmol, 2.00 equiv), t-$BuMe_2SiCl$ (3.56 g, 23.6 mmol, 1.30 equiv), and 1-iodobutane (4.14 mL, 36.4 mmol, 2.00 equiv) as per method A afforded, after chromatography (SiO_2, 369 g, 98:2 hexane/EtOAc), **2b** (3.16 g, 76%; E:Z > 25:1 after purification, crude E:Z = 10:1) as a clear, colorless oil (bp 104 °C at 11 mmHg): 400-MHz ^1H NMR (C_6D_6) δ 6.32 (1 H, dt, J = 12.0, 1.2 Hz), 5.18 (1 H, dt, J = 12.0, 7.6 Hz), 1.88 (2 H, dt, J = 7.6, 1.2 Hz), 1.30–1.05 (6 H, br m), 0.779 (3 H, t, J = 7.0 Hz), 0.95 (9 H, s), 0.08 (6 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 140.5, 111.8, 31.6, 30.6, 27.7, 25.9, 22.9, 18.5, 14.3, −5.1; HRMS for $C_{13}H_{28}OSi$, calcd 228.1909, found 228.1909. Anal. Calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35. Found: C, 68.24; H, 12.43.

***tert*-Butyldimethyl((*E*)-1,4-pentadienyloxy)silane (2c).** Reaction of $Ni(COD)_2$ (5.00 g, 18.2 mmol, 1.00 equiv), propenal (2.43 mL, 36.4 mmol, 2.00 equiv), t-$BuMe_2SiCl$ (3.56 g, 23.6 mmol, 1.30 equiv), and vinyl bromide (4.14 mL, 36.4 mmol, 2.00 equiv) as per method A afforded, after chromatography (SiO_2, 309 g, 98:2 hexane/EtOAc), **2c** (2.79 g, 78%; E:Z > 20:1 after purification, crude E:Z = 7:1) as a clear, colorless oil: 400-MHz ^1H NMR ($CDCl_3$) δ 6.24 (1 H, dt, J = 11.9, 1.3 Hz), 5.81 (1 H, ddt, J = 17.1, 10.1, 6.1 Hz), 5.03 (1 H, ddt, J = 17.2, 1.8, 1.8 Hz), 5.00 (1 H, dt, J = 11.9, 7.2 Hz), 4.96 (1 H, ddt, J = 10.1, 1.8, 1.8 Hz), 2.64 (2 H, dddt, J = 6.7, 6.6, 1.4, 1.4 Hz), 0.92 (9 H, s), 0.13 (6 H, s); 101-MHz ^{13}C ($CDCl_3$) δ 141.2, 137.4, 114.4, 108.9, 31.5, 25.7, 18.3, −5.2; HRMS for $C_{11}H_{22}OSi$, calcd 198.1440, found 198.1436. Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.51; H, 11.19.

***tert*-Butyldimethyl[((*E*)-2-methyl-1,4-pentadienyl)oxy]silane (2d).** Reaction of $Ni(COD)_2$ (5.00 g, 18.2 mmol, 1.00 equiv), 2-methylpropenal (3.01 mL, 36.4 mmol, 2.00 equiv), t-$BuMe_2SiCl$ (3.56 g, 23.6 mmol, 1.30 equiv), and vinyl bromide (4.14 mL, 36.4 mmol, 2.00 equiv) as per **2a** afforded, after chromatography (SiO_2, 307 g, 98:2 hexane/EtOAc), **2d** (2.85 g, 74%; E:Z > 40:1 after purification, crude E:Z = 8:1) as a clear, colorless oil: 400-MHz ^1H NMR ($CDCl_3$) δ 6.09 (1 H, d, J = 1.6 Hz), 5.74 (1 H, ddt, J = 17.0, 9.8, 6.8 Hz), 5.03 (1 H, dd, J = 17.0, 1.6 Hz), 4.98 (1 H, dd, J = 9.8, 1.6 Hz), 2.60 (2 H, d, J = 6.8 Hz), 1.57 (3 H, d, J = 1.6 Hz), 0.92 (9 H, s), 0.12 (6 H, s); 101-MHz ^{13}C ($CDCl_3$) δ 137.4, 134.9, 115.7, 115.2, 38.3, 25.7, 18.3, 12.8, −5.3; HRMS for $C_{12}H_{24}OSi$, calcd 212.1596, found 212.1607. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.63; H, 11.01. NMR NOE results ($CDCl_3$) are the following: Irradiation of the pentadienyloxy C(1)H at 6.09 ppm resulted in a 3% enhancement of the pentadienyloxy C(3)H resonance at 2.60 ppm. No enhancement of the pentadienyloxy C(2) methyl group protons at 1.57 ppm was observed. The enol ether is therefore inferred to have the E configuration.

***tert*-Butyldimethyl[((*E*)-4-methyl-1,4-pentadienyl)oxy]silane (2e).** Reaction of $NiCl_2(pyridine)_4$ (5.00 g, 11.2 mmol, 1.00 equiv), sodium (515 mg, 22.4 mmol, 2.00 equiv), 1,5-cyclooctadiene (4.12 mL, 33.6 mmol, 3.00 equiv), propenal (748 μL, 11.2 mmol, 1.00 equiv), t-$BuMe_2SiCl$ (1.69 g, 11.2 mmol, 1.00 equiv), $(MeO)(Me_3SiO)CCMe_2$ (228 μL, 1.12 mmol, 0.100 equiv), and 2-bromopropene (3.00 mL, 33.6 mmol, 3.00 equiv) as per method B afforded, after chromatography (450 g SiO_2, 98:2 hexane/EtOAc), **2e** (1.99 g, 84%; E:Z > 30:1 after purification, crude E:Z = 10:1) as a clear, colorless oil (bp 77 °C at 7 mmHg): 400-MHz ^1H NMR (C_6D_6) δ 6.27 (1 H, dd, J = 12.0, 1.2 Hz), 5.19 (1 H, dt, J = 12.0, 7.6 Hz), 4.85 (1 H, br s), 4.78 (1 H, br s), 2.53 (2 H, d, J = 7.6 Hz), 1.64 (3 H, s), 0.93 (9 H, s), 0.06 (6 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 145.5, 141.9, 110.5, 109.3, 36.1, 25.8, 22.3, 18.4, −5.1; HRMS for $C_{12}H_{24}OSi$, calcd 212.1596, found 212.1599. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.80; H, 11.39. Found: C, 67.42; H, 11.39.

***tert*-Butyldimethyl[((*E*)-3-phenyl-1-propenyl)oxy]silane (2f).** Reaction of $NiCl_2(pyridine)_4$ (5.00 g, 11.2 mmol, 1.00 equiv), sodium (515 mg, 22.4 mmol, 2.00 equiv), 1,5-cyclooctadiene (4.12 mL, 33.6 mmol, 3.00 equiv), propenal (748 μL, 11.2 mmol, 1.00 equiv), t-$BuMe_2SiCl$ (1.69 g, 11.2 mmol, 1.00 equiv), and bromobenzene (3.40 mL, 33.6 mmol, 3.00 equiv) as per method B afforded, after chromatography (600 g SiO_2, 98:2 hexane/EtOAc), **2f** (1.94 g, 70%; E:Z > 30:1 after purification, crude E:Z = 10:1) as a clear, colorless oil: 400-MHz ^1H NMR (C_6D_6) δ 7.13 (5 H, m), 6.30 (1 H, dt, J = 11.6, 1.6 Hz), 5.29 (1 H, dt, J = 11.6, 7.6 Hz), 3.12 (2 H, d, J = 7.6, 1.6 Hz), 0.92 (9 H, s), 0.05 (6 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 141.8, 141.7, 128.6, 128.6, 126.2, 110.6, 25.80, 18.4, −5.1; HRMS for $C_{15}H_{24}OSi$, calcd 248.1596, found 248.1598. Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74. Found: C, 72.73; H, 9.79.

***tert*-Butyldimethyl[[(*E*)-3-(2-formylphenyl)-1-propenyl]oxy]silane (2g).** Reaction of $Ni(COD)_2$ (5.00 g, 18.2 mmol, 1.00 equiv), propenal (2.43 mL, 36.4 mmol, 2.00 equiv), t-$BuMe_2SiCl$ (3.56 g, 23.6 mmol, 1.30 equiv), and o-bromobenzaldehyde (2.55 mL, 21.8 mmol, 1.20 equiv) as per method A afforded, after chromatography (SiO_2, 483 g, 98:2 hexane/EtOAc), pure **2g** (3.48 g, 69%; E:Z > 40:1 after purification, crude E:Z = 4:1) as a clear, colorless oil: 400-MHz ^1H NMR (C_6D_6) δ 10.02

(1 H, s), 6.97 (4 H, br m), 6.31 (1 H, d, *J* = 12.0, 1.0 Hz), 5.26 (1 H, dt, *J* = 12.0, 7.2 Hz), 3.52 (2 H, d, *J* = 7.2 Hz), 0.90 (9 H, s), 0.03 (6 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 191.8, 144.0, 142.3, 134.3, 133.5, 132.4, 130.4, 126.6, 110.2, 30.6, 25.8, 18.4, −5.2; HRMS for $C_{16}H_{24}O_2Si$, calcd 276.1546, found 276.1533. Anal. Calcd for $C_{16}H_{24}O_2Si$: C, 69.52; H, 8.75. Found: C, 69.15; H, 8.49.

(*E*)- and (*Z*)-2-Methyl-6-[(*tert*-butyldimethylsilyl)oxy]-5-hexen-3-one (2h). Reaction of Ni(COD)$_2$ (5.00 g, 18.2 mmol, 1.00 equiv), propenal (2.43 mL, 36.4 mmol, 2.00 equiv), *t*-BuMe$_2$SiCl (3.65 g, 23.6 mmol, 1.30 equiv), and isobutryl chloride (2.29 mL, 21.9 mmol, 1.00 equiv) according to method A afforded, after distillation (bp 65 °C at 2 mmHg), **2h** (3.03 g, 60%; *E*:*Z* = 1:1 before and after purification) as a clear yellow oil. Chromatography (254 g SiO$_2$, 98:2 hexane/EtOAc) separated *E* and *Z* isomers: 400-MHz ^{1}H NMR (C_6D_6) for (*Z*)-**2h** δ 6.17 (1 H, dd, *J* = 5.8, 1.5 Hz), 4.84 (1 H, dt, *J* = 7.0, 5.8 Hz), 3.22 (2 H, dd, *J* = 7.0, 1.5 Hz), 2.36 (1 H, septet, *J* = 6.9 Hz), 0.95 (6 H, dd, *J* = 6.9, 0.72 Hz), 0.89 (9 H, s), −0.01 (6 H, s); 400-MHz ^{1}H NMR (C_6D_6) for (*E*)-**2h** δ 6.24 (1 H, dt, *J* = 12.0, 1.4 Hz), 5.28 (1 H, dt, *J* = 12.0, 7.4 Hz), 2.70 (2 H, dd, *J* = 7.4, 1.3 Hz), 2.24 (1 H, septet, *J* = 7.0 Hz), 0.88 (6 H, d, *J* = 7.0 Hz), 0.92 (9 H, s), 0.06 (6 H, s); 101-MHz ^{13}C NMR ($CDCl_3$) (*E*)-**2h** δ 213.3, 140.8, 101.9, 40.0, 36.0, 25.5, 18.3, 18.2, −5.4, HRMS for $C_{12}H_{23}OSi$, calcd 227.1467, found 227.1475.

***tert*-Butyldimethyl[((*E*)-3-phenyl-1-butenyl)oxy]silane (2i).** Reaction of Ni(COD)$_2$ (5.00 g, 18.2 mmol, 1.00 equiv), 2-butenal (3.01 mL, 36.4 mmol, 2.00 equiv), *t*-BuMe$_2$SiCl (3.56 g, 23.6 mmol, 1.30 equiv), and bromobenzene (5.74 mL, 54.5 mmol, 3.00 equiv) as per method A afforded, after chromatography (424 g SiO$_2$, 98:2 hexane/EtOAc), **2i** (3.11 g, 65%; *E*:*Z* > 50:1 after purification, crude *E*:*Z* = 6:1; crude C(3):C(1) coupling product ratio 6:1) as a clear, colorless oil: 400-MHz ^{1}H NMR (C_6D_6) δ 7.08 (5 H, br m), 6.30 (1 H, dd, *J* = 12.0, 1.0 Hz), 5.35 (1 H, dd, *J* = 12.0, 8.0 Hz), 3.26 (1 H, dqd, *J* = 8.0, 7.0, 1.0 Hz), 1.24 (3 H, d, *J* = 7.0 Hz), 0.91 (9 H, s), 0.03 (6 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 147.1, 140.1, 128.6, 127.3, 126.2, 117.4, 38.5, 25.8, 22.8, 18.4, −5.1; HRMS for $C_{16}H_{26}OSi$, calcd 262.1753, found 262.1743. Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98. Found: C, 72.93; H, 10.25.

***tert*-Butyl[[(*E*)-3-(1-methylethenyl)-1-hexenyl]oxy]dimethylsilane (2j).** Reaction of NiCl$_2$(pyridine)$_4$ (5.00 g, 11.2 mmol, 1.00 equiv), sodium (515 mg, 22.4 mmol, 2.00 equiv), 1,5-cyclooctadiene (4.12 mL, 33.6 mmol, 3.00 equiv), (*E*)-2-hexenal (1.30 mL, 11.2 mmol, 1.00 equiv), *t*-BuMe$_2$SiCl (1.69 g, 11.2 mmol, 1.00 equiv), and 2-bromopropene (2.98 mL, 33.6 mmol, 3.00 equiv) as per method B (using, however, a 450-W medium-pressure Hg lamp instead of the usual sunlamp and an irradiation time of 24 h) afforded, after chromatography (500 g SiO$_2$, 98:2 hexane/EtOAc), **2j** (1.69 g, 63%; *E*:*Z* > 50:1 after purification, crude *E*:*Z* = 17:1) as a clear, colorless oil: 400-MHz ^{1}H NMR (C_6D_6) δ 6.32 (1 H, dd, *J* = 12.0, 0.76 Hz), 5.11 (1 H, dd, *J* = 12 Hz, 9.2 Hz), 4.81 (2 H, 2 br s), 2.55 (1 H, m), 1.65 (3 H, s), 1.50–1.20 (4 H, br m), 0.86 (3 H, t, *J* = 7 Hz), 0.94 (9 H, s), 0.07 (6 H, s); 101-MHz ^{13}C NMR (C_6D_6) δ 151.27, 148.93, 140.84, 114.82, 109.86, 45.81, 36.15, 25.83, 20.96, 20.12, 18.43, 14.20, −5.12; HRMS for $C_{15}H_{30}OSi$, calcd 254.2050, found 254.2050. Anal. Calcd for $C_{15}H_{30}OSi$: C, 70.80; H, 11.88. Found: C, 70.86; H, 11.59.

***tert*-Butyldimethyl[((*E*)-2-methyl-3-phenyl-1-butenyl)oxy]silane (2k).** Reaction of Ni(COD)$_2$ (1.00 g, 3.64 mmol, 1.00 equiv), 2-methylbutenal (612 μL, 7.28 mmol, 2.00 equiv), *t*-BuMe$_2$SiCl (713 mg, 4.73 mmol, 1.30 equiv), and bromobenzene (1.15 mL, 10.9 mmol, 3.00 equiv) as per method A afforded, after chromatography (SiO$_2$, 83 g, 98:2 hexane/EtOAc), **2k** (713 mg, 70%; *E*:*Z* > 50:1 after purification, crude *E*:*Z* = 10:1; crude C(3):C(1) coupling product ratio 4:1) as a clear, colorless oil: 400-MHz ^{1}H NMR (C_6D_6) δ 7.14 (5 H, br m), 6.33 (1 H, t, *J* = 1.4 Hz), 3.27 (1 H, q, *J* = 7.0 Hz), 1.60 (3 H, d, *J* = 1.4 Hz), 1.30 (3 H, d, *J* = 7.0 Hz); ^{13}C NMR (C_6D_6) δ 145.6, 135.0, 128.5, 127.7, 126.2, 43.2, 25.9, 19.4, 18.4, 11.3, −5.2. HRMS for $C_{17}H_{28}OSi$, calcd 276.1909, found 276.1912. Anal. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.60; H, 10.04.

4-Phenyl-3-buten-2-ol. **1d** (40 mg, 0.13 mmol, 1.0 equiv) and methyl iodide (25 μL, 0.40 mmol, 3.0 equiv) were reacted according to the procedure given above for the reaction of **1e** with 2-iodopropane to afford, after aqueous workup and desilylation (MeOH/K_2CO_3), the title compound as a clear, colorless oil (21 mg, 72%), identified by comparison of its ^{1}H NMR spectrum with that previously reported.[21]

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Supplementary Material Available: Crystallographic details for **1c**, including ORTEP diagrams and tables of atomic coordinates, thermal parameters, bond angles, bond lengths, and least-squares planes (8 pages); a table of calculated and observed structure factors (21 pages). Ordering information is given on any current masthead page.

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