Crossover Experiment of Zwitterion 14 with 18. An NMR sample containing zwitterion **14** (22 mg, 0.035 mmol) and imidate **18** (10 mg, 0.036 mmol) in 0.7 mL of $CDCl_3$ was prepared. After 2.5 h at room temperature, no metallacycle **21** could be detected by ^1H NMR.

Crossover Experiment of Zwitterion 15 with 17. An NMR sample containing zwitterion **15** (12 mg, 0.017 mmol) and imidate **17** (6 mg, 0.028 mmol) in 0.7 mL of $CDCl_3$ was prepared. After 2.5 h at room temperature, no metallacycle **23** could be detected by ^1H NMR.

Reaction of $(CO)_5W(THF)$ with Diaziridine 20. The $(CO)_5W(THF)$ was prepared by photolyzing a degassed (by two freeze-pump-thaw cycles) solution containing $W(CO)_6$ (400 mg, 1.14 mmol) in 10 mL of THF. After 13 h of photolysis the solution was degassed again (by two freeze-pump-thaw cycles) and photolyzed for an additional 24 h. About one-fifth of the solution was used, and the solvent was removed in vacuo at 0 °C to yield a yellow solid, which was dissolved in hexane.

A mixture of diaziridine **20** and imidate **17** was prepared by dissolving zwitterion **14** (43 mg, 0.07 mmol) in 2 mL of CH_3CN. After 1 h the imidate and diaziridine mixture was extracted from the CH_3CN with 3 × 3 mL of hexane. The solvent was removed in vacuo and the residue was washed with hexane. The solvent from the washings was removed and the residue dissolved in C_6H_6. The hexane solution of $(CO)_5W$-(THF) was added dropwise to the mixture of the diaziridine and imidate in C_6H_6, and the solution turned from yellow to dark reddish brown. The solution was left to stir for 15 min. After the solvent was removed, ^1H NMR showed that all the imidate had been coordinated to $(CO)_5W$ and metallacycle **23** was formed in 11.5% yield.

Decomposition of Zwitterion 14 in THF. A sample of **14** (25 mg, 0.040 mmol) was dissolved in 1 mL of THF. After 2 h at room temperature, the solution had turned dark red and the removal of the solvent in vacuo yielded a dark red oil. Analysis of this oil by ^1H NMR revealed a complex mixture with the following composition: diaziridine **20** (25%), imidate **17** (20%), zwitterion **24** (20%), metallacycle **23** (16%), coordinated imidate **26** (11%), and unreacted zwitterion **14** (6%).

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Nickel-Catalyzed, Chlorotrialkylsilane-Assisted Conjugate Addition of Alkenyltributyltin Reagents to α,β-Unsaturated Aldehydes. Evidence for a [1-((Trialkylsilyl)oxy)allyl]nickel(II) Mechanism

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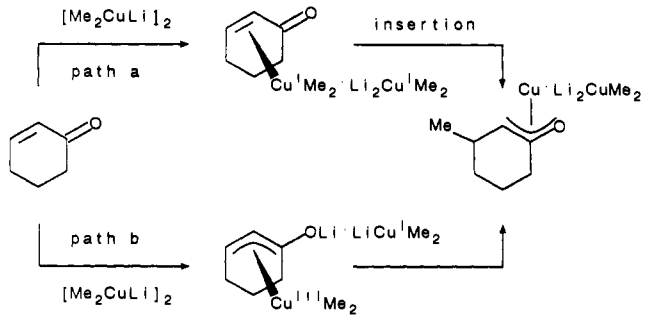
Abstract: α,β-Unsaturated aldehydes $R^1CH{=}CR^2CHO$ (R^1 = H, Me, *n*-Pr; R^2 = H, Me) react with ethenyl-, (1-ethoxyethenyl)-, (2-phenylethenyl)-, and 1-propenyltrialkyltin reagents and chlorotrialkylsilanes (Me_3SiCl or *t*-$BuMe_2SiCl$) in the presence of $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) or 1-((trialkylsilyl)oxy)allylnickel(II) chloride catalyst precursors to afford the corresponding trialkylsilyl (*E*)-enol ethers in 48-79% yield. High C(3)-regioselectivities (≥15:1 crude, ≥50:1 purified) are observed when R^1 = H; moderate C(3)-regioselectivities (2-12:1 crude, 2->50:1 purified) are observed when R^1 = Me or *n*-Pr. High (*E*)-enol ether selectivities (5->19:1 crude, 10->50:1 purified) are observed in all cases save the addition of (1-ethoxyethenyl)tributyltin to 2-propenal, for which case a 2:1 *E*/*Z* ratio is observed. Stoichiometric model reaction and kinetic studies strongly support a Ni(0)/Ni(II) mechanism involving 1-((trialkylsilyl)oxy)allylnickel(II) intermediates and turnover-limiting alkenyl group transmetalation.

Introduction

Although frequently employed in synthesis, transition-metal-catalyzed conjugate addition reactions are mechanistically ill-defined.[1] Important issues such as the extent of electron transfer from the metal to the α,β-unsaturated carbonyl compound[1b,e] and the oxidation state and coordination number of the metal remain to be resolved,[1g,h] so that it is unclear, for example, whether organocuprate conjugate addition reactions are best thought of as redox-neutral alkene insertion reactions (Scheme I, path a) or as oxidative addition/reductive elimination reactions involving [1-(metalloxy)allyl]copper(III)[1d] intermediates (Scheme I, path b). A similar dichotomy exists for Me_3SiCl-modified organocuprate conjugate addition reactions[1d,f] and for related nickel- and palladium-catalyzed conjugate additions of organoaluminum,[2,3] organozirconium,[4] and organozinc[5] reagents to enones, all of which

Scheme I



(1) (a) Kharasch, M. S.; Tawney, P. O. *J. Am. Chem. Soc.* **1941**, *63*, 2308. (b) House, H. O.; Respess, W. L.; Whitesides, G. M. *J. Org. Chem.* **1966**, *31*, 3128. (c) Posner, G. H. *An Introduction to Synthesis Using Organocopper Reagents*; Wiley-Interscience: New York, 1980. (d) Corey, E. J.; Hannon, F. J.; Boaz, N. W. *Tetrahedron* **1989**, *45*, 545. (e) Bertz, S. H.; Smith, R. A. *J. Am. Chem. Soc.* **1989**, *111*, 8276. (f) Matsuzawa, S.; Horiguchi, Y.; Nakamura, E.; Kuwajima, I. *Tetrahedron* **1989**, *45*, 349. (g) Bertz, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 4031. (h) Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *J. Am. Chem. Soc.* **1990**, *112*, 4032.

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Table I. Nickel-Catalyzed Conjugate Addition Reaction Products (Cf. Equation 3)[a]

entry	R	R^1	R^2	time,[b] h	pdt	*E*/*Z*[c]	C(3):C(1)[d]	% yield[e]
1	H_2C=CH[f]	H	H	44	**2a**	>50:1 (>19:1)	>50:1 (>50:1)	75, 62,[g] 60[h]
2	H_2C=CH[f]	H	Me	72	**2b**	>50:1 (>19:1)	>50:1 (>50:1)	69
3	H_2C=CH	Me	H	50	**2c**	>50:1 (>19:1)	>50:1 (12:1)	72
4	H_2C=CH	Me	Me	71	**2d**	>50:1 (>19:1)	>50:1 (5:1)	56
5	H_2C=CH	*n*-Pr	H	53	**2e**	>50:1 (>19:1)	6:1 (9:1)	79
6	PhHC=CH[f,i,j]	H	H	65	**2f**	>50:1 (>19:1)	>50:1 (15:1)	60
7	PhHC=CH[j]	Me	H	72	**2g**	19:1 (19:1)	19:1 (3:1)	63
8	PhHC=CH[j]	Me	Me	66	**2h**	19:1 (10:1)	2:1 (2:1)	53
9	PhHC=CH[j]	*n*-Pr	H	66	**2i**	15:1 (20:1)	2:1 (2:1)	48
10	$H_3CC(O)$[f,k]	H	H	36	**2j**	2:1 (2:1)	>50:1 (>50:1)	55
11	$H_3CC(O)$[f,k]	H	Me	36	**2k**	>50:1 (6:1)	>50:1 (>50:1)	52
12	$H_3CC(O)$[k,l]	Me	H	48	**2l**	15:1 (5:1)	>50:1 (5:1)	50[m]
13	CH_3HC=CH[i,n]	Me	H	96	**2m**	10:1 (6:1)	10:1 (≥5:1)	66[m]

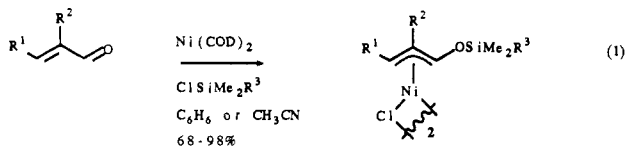
[a] All reactions were conducted in DMF at 25 °C with 10 mol % $Ni(COD)_2$, unless otherwise noted. [b] Nonoptimized reaction time. [c] *E*:*Z* ratio of isolated, purified product; *E*:*Z* ratio of crude product in parentheses. [d] Regioisomer ratio of isolated, purified product; regioisomer ratio of crude product in parentheses. [e] Yield, based on organotin reagent, of isolated, purified product. [f] Reaction conducted in CH_2Cl_2. [g] Reaction catalyzed by 20 mol % $Ni(COD)_2$ generated in situ. [h] Reaction catalyzed by 10 mol % **1a**. [i] Reaction catalyzed by 20 mol % $Ni(COD)_2$. [j] Reaction conducted with 10:1 *E*:*Z* mixture of (2-phenylethenyl)tributylin. [k] Product of H_2C=C(OEt)$SnBu_3$ conjugate addition and subsequent hydrolysis of the ethoxyvinyl group upon SiO_2 chromatography. [l] Reaction conducted in CH_3CN with 1.5 equiv organotin reagent. [m] Yield based on 2-butenal. [n] 2 equiv of a 1:3 mixture of (*E*)- and (*Z*)-1-propenyltributyltin reagents employed; 2:1 mixture of (1*E*,4*E*)- and (1*E*,4*Z*)-hexadienyloxysilanes obtained.

could be proposed to proceed either via enone insertion or via oxidative addition to afford a d^8 1-(metallo)- or 1-(silyloxy)allylmetal intermediate, followed by reductive elimination.

As an outgrowth of research into nickel-mediated methods for enal and enone polarity reversal,[6] we have recently developed a new, nickel-catalyzed, chlorotrialkylsilane-assisted method for the conjugate addition of alkenyltin reagents to enals. We describe herein the scope and limitations of this method, which promises to complement existing methods by virtue of the mildness of the reaction conditions and the high chemoselectivity generally associated with the use of organotin "nucleophiles",[7] and present the results of kinetic studies and stoichiometric model reaction chemistry which strongly support a 1-((trialkylsilyl)oxy)allylnickel(II) mechanism for these reactions.

Background and Scope

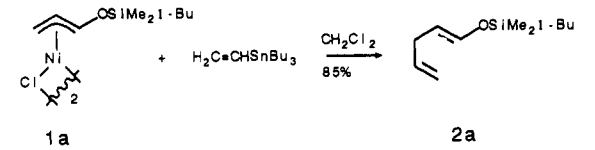
The preparation of bis[(μ-chloro){1-((trialkylsilyl)oxy)allyl}nickel(II)] complexes **1a–c** by reaction of 2-propenal or 2-butenal with $Ni(COD)_2$ (COD = 1,5-cyclooctadiene) and chlorotrialkylsilane (eq 1) has been described previously,[6] as has the X-ray crystal structure of **1c**.[6] The intermediacy of (enal)nickel(0) complexes in these reactions is indicated by the observation of an insoluble, brick-red precipitate upon mixing the enal with the $Ni(COD)_2$ and the subsequent dissolution of the latter upon addition of chlorotrialkylsilane.



(1)

1a: R^1=H; R^2=H; R^3=t-Bu
1b: R^1=Me; R^2=H; R^3=t-Bu
1c: R^1=Me; R^2=H; R^3=Me
1d: R^1=Me; R^2=Me; R^3=t-Bu

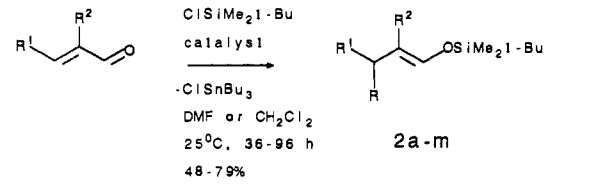
Although originally of interest for their utility as reversed polarity reagents in coupling reactions with halocarbon *electrophiles*,[6] a variety of literature precedents[3-5,7-9] suggested that these complexes might also undergo coupling reactions with organotin *nucleophiles*. In the event, reaction of **1a** with ethenyltributyltin afforded a high yield of the corresponding trialkylsilyl (*E*)-enol ether **2a**, accompanied by a flocculent black precipitate and a nickel metal mirror (eq 2).



(2)

1a 2a

Since nickel(0) is consumed in making **1a** from 2-propenal and regenerated in forming **2a**, the success of this *stoichiometric* chemistry implied that *catalytic* conjugate addition could be achieved, a possibility subsequently realized with the observation of successful nickel-catalyzed reactions of 2-propenal, 2-methyl-2-propenal, 2-butenal, 2-methyl-2-butenal, and 2-hexenal with alkenyltributyltin reagents and *t*-$BuMe_2SiCl$ (eq 3, Table I).



(3)

Both $Ni(COD)_2$ and **1a** were found to be effective catalyst precursors and gave essentially identical results; a control reaction with 2-propenal, ethenyltributyltin, and *t*-$BuMe_2SiCl$ showed no reaction in the absence of catalyst. $Ni(COD)_2$ generated in situ by reaction of 2 equiv of *i*-Bu_2AlH with 1 equiv of $Ni(acac)_2$ in THF was also found to be an effective catalyst.[4,10] Suitable solvents for reaction of the *C(3)-unsubstituted* enals 2-propenal and 2-methyl-2-propenal were found to include benzene, dichloromethane, and tetrahydrofuran, but not dimethylformamide, which resulted in lower yields and the appearance of the enal-derived homocoupling product *t*-$BuMe_2SiOCH$=$CRCH_2$-CH_2CR=$CHOSiMe_2$-*t*-Bu (R = H, Me). In the case of the C(3)-substituted enals 2-butenal, 2-methyl-2-butenal, and 2-hexenal, no reaction was observed in benzene, dichloromethane, or tetrahydrofuran and the more coordinating solvent dimethylformamide was required for successful reaction. Buffered aqueous workup and subsequent silica gel chromatography afforded *tert*-butyldimethylsilyl enol ethers **2a–m**, in 48–79% yield (the 1-ethoxyvinyl groups of **2j–l** undergoing hydrolysis to methyl keto groups upon silica gel chromatography). Ethenyl, 1-eth-

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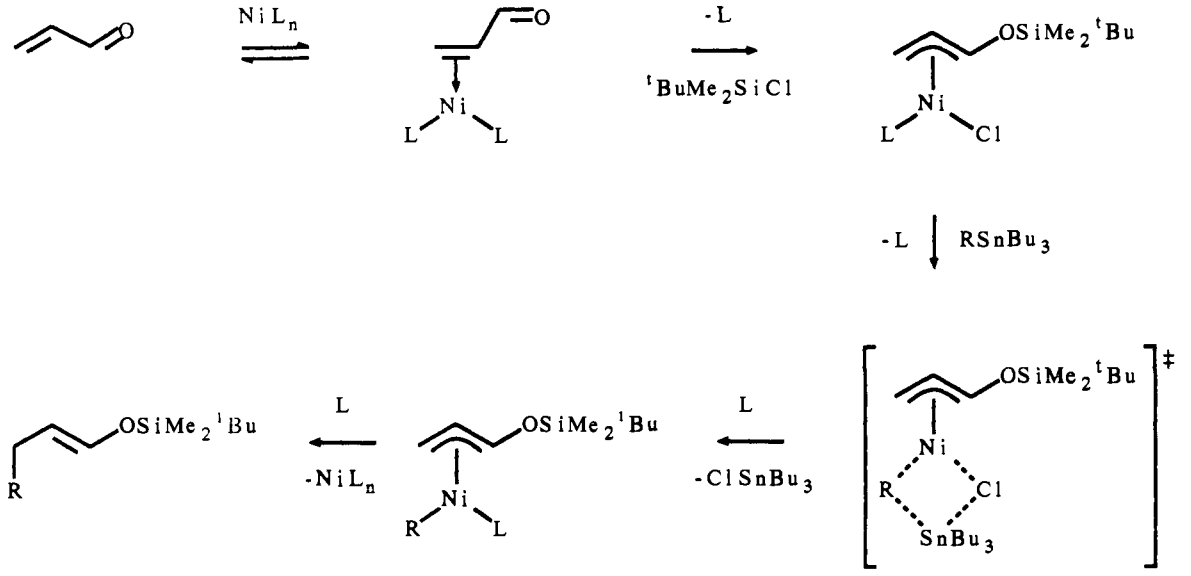
Scheme II



oxyethenyl, 2-phenylethenyl-, and 1-propenyltributyltin reagents were found to react; phenyltrimethyltin was unreactive, both in an attempted catalytic reaction with 2-propenal in benzene and in an attempted stoichiometric coupling reaction with **1a** at 60 °C in benzene. Zero or low and poorly reproducible yields were observed with unsaturated ketones.

High C(3)-regioselectivities (≥15:1 before chromatography) were observed in the case of the C(3)-unsubstituted enals, while the C(3)-subsituted enals gave rise to more moderate C(3)-regioselectivities, in the range of 2–12:1 before chromatography and 2–>50:1 after chromatography. High (*E*)-selectivities (5–>19:1 before chromatography, 10–>50:1 after chromatography) were observed in all cases save the reaction of 2-propenal with (1-ethoxyethenyl)tributyltin, for which a 2:1 *E*/*Z* ratio was observed.

Mechanism

The foregoing results are consistent with a nickel(0)/nickel(II) catalytic cycle (Scheme II, L = solvent, ethenyltrialkyltin, enal or enol ether) wherein a weakly ligated nickel(0) catalyst reacts with the enal and chlorotrialkylsilane to afford a {1-((trialkylsilyl)oxy)allyl}(chloro)nickel(II) intermediate, followed by turnover-limiting transmetalation of the alkenyl group from tin to nickel to give an unstable (alkenyl){1-((trialkylsilyl)oxy)allyl}-nickel(II) intermediate which rapidly decomposes to afford the observed organic product and regenerate the nickel(0) catalyst.

Supporting observations include the following. (1) Both Ni(COD)$_2$ and **1a** are suitable catalyst precursors and give similar results, not involving any induction period. (2) The reaction of nickel(0) with 2-propenal and *t*-BuMe$_2$SiCl to afford **1a**, and the reaction of **1a** with 1-ethenyltributyltin, have both been modeled by high-yielding stoichiometric reactions (eqs 1 and 2) which display qualitatively appropriate rates. (3) The Ni(COD)$_2$-catalyzed reaction of 2-butenal with ethenyltributyltin in DMF-d_7 was followed by ^{1}H NMR and found to be first order in Ni(COD)$_2$, first order in ethenyltributyltin, zero order in 2-butenal, and zero order in *t*-BuMe$_2$SiCl (Figure 1), fitting the expression d[product]/dt = k_{cat}[Ni][ethenyltributyltin], with k_{cat} = 0.039 ∓ 0.004 L mol^{-1} min^{-1}. (4) The putative intermediate **1b** is the only nickel-containing species apparent in the latter spectra and is present at a level roughly comparable to the initial catalyst concentration. (5) When **1b** is used as the catalyst precursor for the reaction of 2-methyl-2-butenal with ethenyltributyltin, the rate of disappearance of **1b** is equal to the rate of appearance of **1d**, fitting the expression −d[**1b**]/dt = k_{app}[**1b**] with k_{app} = 0.0085 min^{-1}. Making the crude approximation of an invariant [ethenyltributyltin] (which actually decreased by ca. 25% over the interval examined) and assuming that −d[**1b**]/dt = k_{sto}[**1b**][ethenyltributyltin], then k_{sto} = k_{app}/[ethenyltributyltin] = 0.03 ∓ 0.01 L mol^{-1} min^{-1}, in satisfactory agreement with k_{cat} given the aforementioned assumption and small data set (five points, see Experimental Section). (6) Ni(COD)$_2$ catalysis of the reaction of 2-butenal with ethenyltributyltin in DMF-d_7 is completely inhibited by triphenylphosphine (5 equiv/equiv of Ni(COD)$_2$).

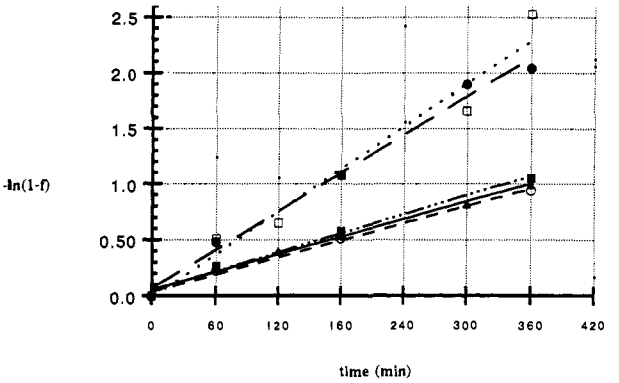


Figure 1. Graphs of −ln (1 − f), where f is the fraction of product, as a function of time in DMF-d_7 at 25 °C: (a) under standard conditions (▲ data points, [2-butenal]$_0$ = [ethenyltributyltin]$_0$ = [*t*-BuMe$_2$SiCl]$_0$ = 0.34 M, [Ni(COD)$_2$] = 0.073 M), (b) with twice as much chlorotrialkylsilane ([*t*-BuMe$_2$SiCl]$_0$ = 0.68 M, ○ data points), (c) with twice as much 2-butenal ([2-butenal]$_0$ = 0.68 M), ■ data points), (d) with twice as much organotin reagent [ethenyltributyltin]$_0$ = 0.67 M, □ data points); (e) with twice as much catalyst ([Ni(COD)$_2$]$_0$ = 0.14 M, ● data points).

With regard to the possible involvement of Ni(I) and/or Ni(III) intermediates[11] in these reactions, it is evident that any such species would have to be present in very low concentration given the sharpness of the ^{1}H NMR spectra observed in the aforementioned kinetics experiments. More definitive evidence was sought and obtained through ESR studies which showed that a frozen sample of a catalytic reaction mixture containing Ni(COD)$_2$, 2-butenal, *t*-BuMe$_2$SiCl, and ethenyltributyltin in DMF gave no ESR signal. In a similar vein, NiCl$_2$ was found to be unreactive with mixtures of 2-butenal, chlorotrialkylsilane, and ethenyltributyltin in DMF, suggesting that enal insertion into an ethenylnickel(II) intermediate does not constitute a viable alternative to the proposed mechanism.

Conclusion

The above data provide strong support for the proposed 1-((trialkylsilyl)oxy)allylnickel(II) mechanism and strongly disfavor any Ni(I)/Ni(III) or Ni(II) insertion mechanism. Experiments

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designed to probe the generality of this mechanism with other catalysts, organometallic nucleophiles, and oxophiles are in progress.[12] From a synthetic perspective, the reactions reported herein are notable for the mildness of the reaction conditions and the possibility that, like other late metal-catalyzed organotin reagent coupling reactions, they will prove to be highly chemoselective and useful in the synthesis of functionally complex molecules.

Experimental Section

A. General Methods. All reactions were carried out in a nitrogen atmosphere drybox or on a dual-manifold Schlenk line using purified, deoxygenated solvents and standard inert atmosphere techniques, unless otherwise noted. NMR spectra were recorded on a Varian XLA-400 spectrometer (400 MHz for ^{1}H NMR; 101 MHz for ^{13}C NMR) or on a Varian Gemini-300 spectrometer (300 MHz for ^{1}H NMR; 75 MHz for ^{13}C NMR). ^{1}H NMR chemical shifts are reported in parts per million downfield from tetramethylsilane but were measured relative to residual ^{1}H solvent resonances (C_6HD_5 at 7.15 ppm; $CHCl_3$ at 7.26 ppm; DMF-d_7 at 8.01 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 were performed by G. D. Searle Research and Development, Skokie, IL, or by Oneida Research Services, Inc., Whitesboro, NY, or by Galbraith Laboratories, Inc., Knoxville, TN. Acetonitrile, acetonitrile-d_3, dichloromethane, and chloroform-d were distilled from calcium hydride and stored under nitrogen. *N*,*N*-Dimethylformamide (DMF) and DMF-d_7 were distilled first from barium oxide and then from calcium hydride and stored under nitrogen. Benzene, benzene-d_6, diethyl ether, tetrahydrofuran, hexane, pentane, and toluene 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); 2-propenal (Aldrich, degassed); 2-methyl-2-propenal (Aldrich, degassed); (*E*)-2-butenal (Aldrich, degassed); *tert*-butyldimethylsilyl chloride (Aldrich); ethenyltributyltin (Aldrich, degassed); (1-ethoxyethenyl)tributyltin (Aldrich, degassed); bis(acetylacetonate)nickel(II) (Aldrich, technical grade, 90%); diisobutylaluminum hydride (Aldrich, 1.0 M solution in tetrahydrofuran); 1,5-cyclooctadiene (Aldrich, redistilled grade, degassed and stored under nitrogen).

The following compounds were prepared by literature procedures: bis(1,5-cyclooctadiene)nickel(0),[10] bis[(μ-chloro){(1-trialkylsilyloxy)allyl}nickel(II)] complexes **1a–c**,[6] phenyltrimethyltin,[13] (*E*)-(2-phenylethenyl)tributyltin (*E*:*Z* = 10:1),[14] (*Z*,*E*)-1-propenyltributyltin (*Z*:*E* = 3:1).[15]

B. Preparation of Bis[(μ-chloro){1-((*tert*-butyldimethylsilyl)oxy)-2-methyl-2-butenyl}nickel(II)] (1d). Reaction of Ni(COD)$_2$, 2-methyl-2-butenal, and *tert*-butyldimethylsilyl chloride according to published procedure[6] gave **1d** in 68% recrystallized yield. 300-MHz ^{1}H NMR (CD_3CN) δ 5.25 (1 H, s), 2.13 (3 H, s), 2.08 (1 H, q, *J* = 6.5 Hz), 0.89 (9 H, s), 0.71 (3 H, d, *J* = 6.5 Hz), 0.19 (3 H, s), 0.15 (3 H, s); (DMF-d_7) δ (coupling not resolved) 4.91 (1 H, s), 2.15 (3 H, s), 1.78 (1 H, br s), 0.83 (9 H, s), 0.46, (3 H, br s), 0.14 (3 H, s), 0.07 (3 H, s). 101-MHz ^{13}C NMR (CD_3CN) δ 108.0, 11.5, 56.9, 25.8, 18.7, 13.3, 12.0, −4.5, −5.6. Anal. Calcd for $C_{22}H_{46}Cl_2Ni_2O_2Si_2$: C, 45.01; H, 7.90. Found: C, 44.76; H, 7.69.

C. Stoichiometric Reaction of 1a with Ethenyltributyltin To Afford *tert*-Butyldimethyl[(*E*)-1,4-pentadienyloxy]silane (2a). A 25-mL Schlenk flask equipped with a stir bar was sequentially charged with 1-ethenyltributyltin (875 μL, 2.99 mmol), (MeO)(Me$_3$SiO)CCMe$_2$ (57.0 μL, 0.281 mmol, added as a proton-scavenging reagent), CH_2Cl_2 (3.0 mL), and **1a** (750 mg, 2.83 mmol), resulting in a black mixture. After the mixture was stirred for 2.5 h, the solvent was removed under reduced pressure (15 mmHg) and residue extracted with pentane (3 × 20 mL), the extracts being removed via a filter-paper-tipped cannula. The combined extracts were washed with aqueous buffer (2 × 25 mL of a pH 7, 0.1 M KH_2PO_4/NaOH/H_2O solution), dried ($MgSO_4$), filtered, and concentrated under reduced pressure (15 mmHg) to afford an oil (*E*:*Z* = 24:1) which was chromatographed (SiO_2, 100 g, hexane/Et_2O 97:3) to obtain **2a** (474 mg, 85%, *E*:*Z* > 50:1 by ^{1}H NMR analysis) as a clear, colorless oil. 400-MHz ^{1}H 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, dq, *J* = 17.2, 1.8 Hz), 5.00 (1 H, dt, *J* = 11.9, 7.2 Hz), 4.96 (1 H, dq, *J* = 10.1, 1.8 Hz), 2.64 (2 H, ddq, *J* = 6.7, 6.6, 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. High-resolution mass spectrometry (HRMS) calcd for $C_{11}H_{22}OSi$, 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.

***D. Catalytic Reactions. Typical Procedure. Preparation of tert*-Butyldimethyl[(*E*)-1,4-pentadienyloxy]silane (2a). Using Ni(COD)$_2$ as the Catalyst Precursor.** A 25-mL Schlenk tube equipped with a stir bar was sequentially charged with 2-propenal (74.0 μL, 1.11 mmol), (MeO)(Me$_3$SiO)CCMe$_2$ (30.0 mg, 0.148 mmol), *t*-BuMe$_2$SiCl (168 mg, 1.12 mmol), and CH_2Cl_2 (1.5 mL). The solution was stirred for 5 min, treated with Ni(COD)$_2$ (27 mg, 0.098 mmol), stirred for an additional 5 min, and then treated with ethenyltributyltin (293 μL, 1.00 mmol) to give a clear red solution. This was stirred at 25 °C for 48 h, near the end of which time the mixture turned black and deposited a nickel metal precipitate. The mixture was diluted with pentane (25 mL) and washed with aqueous buffer (2 × 25 mL of a pH 7, 0.1 M KH_2PO_4/NaOH/H_2O solution), organic layer was separated, and the product was dried ($MgSO_4$), filtered, and concentrated under reduced pressure (15 mmHg) to afford an oil (*E*:*Z* = 19:1) which was chromatographed (SiO_2, 35 g, hexane/EtOAc (98:2)) to obtain pure **2a** (149 mg, 75%, *E*:*Z* >50:1 by ^{1}H NMR analysis) as a clear, colorless oil.

Using 1a as the Catalyst Precursor. 2-Propenal (1.22 mL, 18.3 mmol), (MeO)(Me$_3$SiO)CCMe$_2$ (0.690 mL, 3.40 mmol), *t*-BuMe$_2$SiCl (3.44 g, 22.8 mmol), and ethenyltributyltin (5.60 mL, 19.2 mmol) in CH_2Cl_2 (28 mL) were reacted for 44 h according to the typical procedure given above using **1a** (0.509 g, 1.92 mmol) in place of Ni(COD)$_2$ as the catalyst precursor to afford, after buffered aqueous workup and distillation, **2a** (2.28 g, 60%, bp 85–86 °C at 15 mmHg).

***tert*-Butyldimethyl[((*E*)-2-methyl-1,4-pentadienyl)oxy]silane (2b).** 2-Methyl-2-propenal (87.0 μL, 1.05 mmol), *t*-BuMe$_2$SiCl (208 mg, 1.38 mmol), ethenyltributyltin (292 μL, 1.00 mmol), and Ni(COD)$_2$ (28 mg, 0.10 mmol) in 1.50 mL of CH_2Cl_2 were reacted for 72 h as per **2a** to afford, after chromatography (SiO_2, 50 g, hexane/Et_2O 98:2), **2b** as a clear, colorless oil (147 mg, 69%, *E*:*Z* > 50:1 (crude *E*:*Z* = 19:1) by ^{1}H NMR analysis). 400-MHz ^{1}H 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 calcd for $C_{12}H_{24}OSi$, 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. ^{1}H NMR NOE ($CDCl_3$): Irradiation of the pentadienyloxy C(1)H at 6.09 ppm resulted in a 3% enhancement of the pentadienyloxy C(3)H resonance at δ 2.60 ppm. No enhancement of the pentadienyloxy C(2) methyl group protons at δ 1.57 ppm was observed. The enol ether was therefore inferred to have the (*E*) configuration.

***tert*-Butyldimethyl[((1*E*)-3-methyl-1,4-pentadienyl)oxy]silane (2c).** 2-Butenal (44.0 μL, 0.531 mmol), (MeO)(Me$_3$SiO)CCMe$_2$ (100 μL, 0.492 mmol), *t*-BuMe$_2$SiCl (76 mg, 0.504 mmol), ethenyltributyltin (146 μL, 0.500 mmol), and Ni(COD)$_2$ (15 mg, 0.054 mmol) in DMF (1.5 mL) were reacted for 50 h as per **2a** to afford, after chromatography (SiO_2, 30 g, gradient, 200 mL of hexane then 97:3 hexane/Et_2O), **2c** (76 mg, 72%; *E*:*Z* >50:1 by ^{1}H NMR analysis; crude *E*:*Z* = 19:1; C(3):C(1) = 12:1) as a clear, colorless oil. 400-MHz ^{1}H NMR ($CDCl_3$) δ 6.23 (1 H, d, *J* = 12.0 Hz), 5.79 (1 H, ddd, *J* = 16.8, 10.4, 6.0 Hz), 4.98 (1 H, dd, *J* = 17.4, 1.4 Hz), 4.95 (1 H, dd, *J* = 12.0, 7.6 Hz), 4.91 (1 H, dd, *J* = 10.3, 1.4 Hz), 2.79–2.74 (1 H, m), 1.07 (3 H, d, *J* = 6.8 Hz), 0.92 (9 H, s), 0.13 (6 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 143.7, 139.9, 115.7, 112.3, 36.0, 25.7, 20.9, 18.4, −5.2. HRMS calcd for $C_{12}H_{24}OSi$, 212.1596; found, 212.1589. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.63; H, 11.03.

***tert*-Butyldimethyl[((*E*)-2,3-dimethyl-1,4-pentadienyl)oxy]silane (2d).** 2-Methyl-2-butenal (102 μL, 1.06 mmol), *t*-BuMe$_2$SiCl (152 mg, 1.01 mmol), ethenyltributyltin (292 μL, 1.00 mmol), and Ni(COD)$_2$ (28 mg, 0.10 mmol) in DMF (3.0 mL) were reacted for 71 h as per **2c** to afford, after chromatography (SiO_2, 55 g, gradient, 300 mL of hexane followed by 97:3 hexane/Et_2O, then SiO_2, 20 g, gradient, 150 mL of hexane followed by 98:2 hexane/Et_2O), pure **2d** as a clear, colorless oil (127 mg, 56%, *E*:*Z* > 50:1, C(3):C(1) coupling ratio >50:1 by ^{1}H NMR analysis, crude *E*:*Z* = 19:1, crude C(3):C(1) coupling ratio 5:1). **2d** 400-MHz ^{1}H

(12) With regard to the possibility that a similar mechanism is operative in the nickel-catalyzed conjugate addition of Cp_2ZrCl(alkenyl) reagents to enones, we note that preliminary experiments have shown that 2-butenal, Ni(COD)$_2$, and Cp_2ZrCl_2 react to give the corresponding bis[(μ-chloro){(1-bis(cyclopentadienyl)(chloro)zirconoxy)-1-butenyl}nickel(II)] complex and that **1a** reacts with Cp_2ZrCl(CH=CH-*n*-Bu) to afford corresponding silyl enol ether, *n*-BuCH=CHCH$_2$CH=CHOSi-*t*-BuMe$_2$.[12a] (a) Ward, Y. D.; Grisso, B. A.; Mackenzie, P. B. Unpublished results.

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NMR ($CDCl_3$) δ 6.14 (1 H, s), 5.77 (1 H, ddd, J = 17.2, 10.4, 6.0 Hz), 4.98 (1 H, dd, J = 10.4, 1.6 Hz), 4.98 (1 H, dd, J = 18.4, 1.6 Hz), 2.72 (1 H, pentet, J = 6.8 Hz), 1.52 (3 H, J = 1.2 Hz), 1.09 (3 H, d, J = 6.8 Hz), 0.92 (9 H, s), 0.12 (6 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 142.9, 134.3, 120.6, 112.8, 40.8, 25.7, 18.3, 18.0, 10.2, −5.3. Anal. Calcd for $C_{13}H_{26}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 68.92; H, 11.79. C(1)-coupling product *tert*-butyldimethyl[((*E*)-1-ethenyl-2-methyl-2-butenyl)oxy]silane (12 mg, 5%, *E*:*Z* >50:1 by ^1H NMR analysis): 400-MHz ^1H NMR ($CDCl_3$) δ 5.75 (1 H, ddd, J = 15.6, 10.4, 5,2 Hz), 5.47 (1 H, q, J = 6.8 Hz), 5.23 (1 H, dd, J = 17.2, 1.6 Hz), 5.04 (1 H, dd, J = 10.4, 1.6 Hz), 4.46 (1 H, d, J = 4.8 Hz), 1.60 (3 H, d, J = 6.8 Hz), 1.52 (3 H, d, J = 1.2 Hz), 0.89 (9 H, s), 0.04 (3 H, s), 0.02 (3 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 140.51, 137.30, 119.55, 113.44, 78.86, 25.84, 18.33, 13.08, 11.19, −4.90. HRMS calcd for $C_{13}H_{26}OSi$, 226.1753; found, 226.1708. HRMS calcd for $C_{13}H_{25}OSi$ (M − H), 225.1675; found, 225.1672.

***tert*-Butyldimethyl[((*E*)-3-ethenyl-1-pentenyl)oxy]silane (2e).** 2-Hexenal (122 μL, 1.05 mmol), *t*-$BuMe_2SiCl$ (151 mg, 1.00 mmol), ethenyltributyltin (292 μL, 1.00 mmol), and $Ni(COD)_2$ (28 mg, 0.10 mmol) in DMF (3.50 mL) were reacted for 53 h as per **2c** to afford, after chromatography (SiO_2, 50 g, gradient, 200 mL of hexane followed by 97:3 hexane/Et_2O), an otherwise pure mixture of **2e** and the corresponding C(1)-coupling product (189 mg, 79%, *E*:*Z* >50:1; C(3):C(1) = 6:1 by ^1H NMR analysis; crude *E*:*Z* = 19:1, C(3):C(1) = 9:1). Further chromatography (SiO_2, 30 g, gradient, 170 mL of hexane followed by 98:2 hexane/Et_2O) gave pure **2e** as a clear, colorless oil (131 mg, 55%, *E*:*Z* >50:1 by ^1H NMR analysis). 400-MHz ^1H NMR ($CDCl_3$) δ 6.20 (1 H, d, J = 12.0 Hz), 5.72 (1 H, ddd, J = 17.2, 10.0, 7.2 Hz), 4.97 (1 H, dd, J = 17.6, 1.6 Hz), 4.93 (1 H, dd, J = 10.0, 1.6 Hz), 4.88 (1 H, dd, J = 12.0, 8.8 Hz), 2.61–2.54 (1 H, m), 1.40–1.25 (4 H, m), 0.92 (9 H, s), 0.13 (6 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 142.8, 140.3, 114.4, 113.0, 41.8, 37.6, 25.7, 20.2, 18.4, 14.0, −5.2. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74. Found: C, 70.06; H, 11.98.

***tert*-Butyldimethyl[((1*E*,4*E*)-5-phenyl-1,4-pentadienyl)oxy]silane (2f).** 2-Propenal (37.0 μL, 0.554 mmol), *t*-$BuMe_2SiCl$ (76.0 mg, 0.504 mmol), ((*E*)-2-phenylethenyl)tributyltin (*E*:*Z* = 10:1, 195 mg, 0.496 mmol) and $Ni(COD)_2$ (28 mg, 0.10 mmol) in DMF (3.0 mL) were reacted for 65 h as per **2c** to afford, after chromatography (SiO_2, 30 g, gradient, 170 mL of hexane followed by 98:2 hexane/Et_2O), **2f** (82.5 mg, 60%, *E*:*Z* >50:1 by ^1H NMR analysis; crude *E*:*Z* = 19:1, crude C(3):C(1) = 15:1) as a clear, colorless oil. 400-MHz ^1H NMR ($CDCl_3$) δ 7.35–7.18 (5 H, m), 6.39 (1 H, d, J = 16.0 Hz), 6.31 (1 H, dd, J = 12.0, 1.6 Hz), 6.19 (1 H, dt, 16.0, 6.4 Hz), 5.06 (1 H, dt, J = 12.0, 7.2 Hz), 2.80 (2 H, dd, J = 7.6, 7.2 Hz), 0.93 (9 H, s), 0.15 (6 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 141.4, 137.7, 129.9, 129.8, 128.4, 126.9, 126.0, 108.9, 30.7, 25.7, 18.3, −5.2. HRMS calcd for $C_{17}H_{26}OSi$, 274.1753; found, 274.1743.

***tert*-Butyldimethyl[((1*E*,4*E*)-3-methyl-5-phenyl-1,4-pentadienyl)oxy]silane (2g).** 2-Butenal (90.0 μL, 1.09 mmol), *t*-$BuMe_2SiCl$ (151 mg, 1.00 mmol), ((*E*)-2-phenylethenyl)tributyltin (*E*:*Z* = 10:1; 395 mg, 1.00 mmol), and $Ni(COD)_2$ (28 mg, 0.10 mmol) in DMF (3.00 mL) were reacted for 72 h as per **2c** to afford, after chromatography (SiO_2, 55 g, gradient, 300 mL of hexane followed by 97:3 hexane/Et_2O), pure **2g** (135 mg, 47%, *E*:*Z* >50:1 by ^1H NMR analysis) as a clear, colorless oil, along with several otherwise pure mixed fractions containing **2g** and the corresponding C(1)-coupling product (combined total, pure and mixed fractions, 183 mg, 63%, *E*:*Z* = 19:1, C(3):C(1) = 19:1 by ^1H NMR analysis; crude *E*:*Z* = 19:1, C(3):C(1) = 3:1). **2g** 400-MHz ^1H NMR ($CDCl_3$) δ 7.37–7.16 (5 H, m), 6.36 (1 H, d, J = 15.6 Hz), 6.30 (1 H, dd, J = 12.0, 1.2 Hz), 6.18 (1 H, dd, 16.0, 6.4 Hz), 5.04 (1 H, dd, J = 12.0, 8.0 Hz), 2.98–2.92 (1 H, m), 1.18 (3 H, d, J = 6.8 Hz), 0.94 (9 H, s), 0.16 (6 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 140.1, 137.7, 135.7, 128.4, 127.8, 126.8, 126.0, 115.7, 35.5, 25.7, 21.4, 18.4, −5.2. HRMS calcd for $C_{18}H_{28}OSi$, 288.1909; found, 288.1916.

***tert*-Butyldimethyl[((1*E*,4*E*)-3,4-dimethyl-5-phenyl-1,4-pentadienyl)oxy]silane (2h).** 2-Methyl-2-butenal (102 μL, 1.06 mmol), *t*-$BuMe_2SiCl$ (152 mg, 1.01 mmol), ((*E*)-2-phenylethenyl)tributyltin (*E*:*Z* = 10:1, 393 mg, 1.00 mmol), and $Ni(COD)_2$ (28 mg, 0.10 mmol) in DMF (3.00 mL) were reacted for 66 h as per **2c** to afford, after chromatography (SiO_2, 50 g, gradient, 300 mL of hexane followed by 98:2 hexane/Et_2O), pure **2h** (50 mg, 17%, *E*:*Z* >50:1 by ^1H NMR analysis) as a clear, colorless oil, along with several otherwise pure mixed fractions containing **2h** and the corresponding C(1)-coupling product (combined total, pure and mixed fractions, 160 mg, 53%, *E*:*Z* >19:1, C(3):C(1) = 7:1 by ^1H NMR analysis; crude *E*:*Z* = 10:1, C(3):C(1) = 2:1). 400-MHz ^1H NMR ($CDCl_3$) δ 7.36–7.19 (5 H, m), 6.35 (1 H, d, J = 16.4 Hz), 6.21 (1 H, s), 6.18 (1 H, dd, J = 16.0, 6.4 Hz), 2.90 (1 H, dq, J = 6.8, 6.4 Hz), 1.58 (3 H, d, J = 1.2 Hz), 1.20 (3 H, d, J = 6.8 Hz), 0.94 (9 H, s), 0.14 (6 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 137.8, 135.0, 134.5, 128.4, 128.4, 126.8, 126.0, 120.7, 40.3, 25.7, 18.6, 18.2, −5.3. HRMS calcd for $C_{19}H_{30}OSi$, 302.2066; found, 302.2060.

***tert*-Butyldimethyl[((1*E*)-3-[(*E*)-2-phenylethenyl]-1-hexenyl)oxy]silane (2i).** 2-Hexenal (122 μL, 1.05 mmol), *t*-$BuMe_2SiCl$ (152 mg, 1.01 mmol), ((*E*)-2-phenylethenyl)tributyltin (*E*:*Z* = 10:1; 393 mg, 1.00 mmol), and $Ni(COD)_2$ (28 mg, 0.10 mmol) in DMF (3.00 mL) were reacted for 66 h as per **2c** to afford, after chromatography (SiO_2, 52 g, gradient, 300 mL hexane followed by 98:2 hexane:Et_2O), an otherwise pure mixture of **2i** and the corresponding C(1)-coupling product (153 mg, 48%, E:Z = 20:1, C(3):C(1) = 15:1 by ^1H NMR analysis; crude E:Z = 15:1, C(3):C(1) = 2:1) as a clear, colorless oil. (*E*)-**2i** 400-MHz ^1H NMR ($CDCl_3$) δ 7.40–7.18 (5 H, m), 6.37 (1 H, d, J = 16.0 Hz), 6.29 (1 H, dd, J = 12.0, 0.8 Hz), 6.15 (1 H, dd, J = 16.0, 6.8 Hz), 4.985 (1 H, dd, J = 12.0, 8.8 Hz), 2.81–2.74 (1 H, m), 1.49–1.35 (4 H, m), 0.95 (9 H, s), 0.94 (3 H, t, J = 7.2 Hz), 0.17 (6 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 140.5, 137.8, 134.7, 128.5, 128.4, 126.8, 126.0, 114.4, 41.1, 38.0, 25.7, 20.4, 18.4, 14.0, −5.2. HRMS calcd for $C_{20}H_{32}OSi$, 316.2222; found, 316.2232. A small amount of (*Z*)-**2i** (7.9 mg, 3%, *Z*:*E* >50:1 by ^1H NMR analysis) was also recovered from chromatography. (*Z*)-**2i** 400-MHz ^1H NMR ($CDCl_3$) δ 7.41–7.15 (5 H, m), 6.36 (1 H, d, J = 15.6 Hz), 6.24 (1 H, d, J = 6.0 Hz), 6.13 (1 H, dd, J = 15.6, 7.6 Hz), 4.39 (1 H, dd, J = 9.2, 5.6 Hz), 3.48–3.40 (1 H, m), 1.48–1.26 (4 H, m), 0.93 (9 H, s), 0.91 (3 H, t, J = 6.0 Hz), 0.13 (3 H, s), 0.12 (3 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 138.5, 138.1, 134.5, 128.4, 128.1, 126.6, 126.0, 112.8, 37.8, 37.3, 25.6, 20.4, 18.2, 14.1, −5.3, −5.4. Anal. Calcd for $C_{20}H_{32}OSi$: C, 75.88; H, 10.19. Found: C, 75.73; H, 10.26.

***tert*-Butyldimethyl[((*E*,*Z*)-4-oxo-1-pentenyl)oxy]silane (2j).** 2-Propenal (155 μL, 2.32 mmol), *t*-$BuMe_2SiCl$ (404 mg, 2.68 mmol), $(MeO)(Me_3SiO)CCMe_2$ (80 μL, 0.39 mmol), (1-ethoxyethenyl)tributyltin (676 μL, 2.00 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) in CH_2Cl_2 (3.50 mL) were reacted for 36 h as per **2a** to afford crude *tert*-butyldimethyl[((*E*,*Z*)-4-ethoxy-1,4-pentadienyl)oxy]silane (*E*:*Z* = 2:1). Chromatography (SiO_2, 100 g, hexane/Et_2O (97:3)) resulted in hydrolysis of the ethoxyvinyl group and gave **2j** (234 mg, 55%, *E*:*Z* = 2:1) as a clear, colorless oil. Further chromatography as above gave small amounts of the pure (*E*) and (*Z*) isomers. (*E*)-**2j** 400-MHz ^1H NMR ($CDCl_3$) δ 6.31 (1 H, dt, J = 12.0, 1.3 Hz), 5.07 (1 H, dt, J = 12.0, 7.6 Hz), 2.97 (2 H, d, J = 7.7 Hz), 2.15 (3 H, s), 0.92 (9 H, s), 0.14 (6 H, s). (*E*)-**2j** 101-MHz ^{13}C ($CDCl_3$) δ 207.8, 143.5, 103.3, 42.6, 28.9, 25.6, 18.3, −5.3. (*Z*)-**2j** 400-MHz ^1H NMR ($CDCl_3$) δ 6.348 (1 H, dt, J = 5.8, 1.4 Hz), 4.642 (1 H, td, J = 7.2, 5.8 Hz), 3.203 (2 H, dd, J = 7.2, 1.2 Hz), 2.162 (3 H, s), 0.926 (9 H, s), 0.144 (6 H, s). (*Z*)-**2j** 101-MHz ^{13}C ($CDCl_3$) δ 207.8, 141.1, 101.5, 39.3, 29.2, 25.6, 18.2, −5.4. HRMS calcd for $C_{11}H_{21}O_2Si$ (M − H), 213.1311; found, 213.1306.

***tert*-Butyldimethyl[((*E*)-2-methyl-4-oxo-1-pentenyl)oxy]silane (2k).** 2-Methyl-2-propenal (182 μL, 2.20 mmol), *t*-$BuMe_2SiCl$ (411 mg, 2.73 mmol), $(MeO)(Me_3SiO)CCMe_2$ (40 μL, 0.20 mmol), (1-ethoxyethenyl)tributyltin (670 μL, 1.98 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) in CH_2Cl_2 (3.50 mL) were reacted for 36 h as per **2a** to afford crude *tert*-butyldimethyl[((*E*)-4-ethoxy-2-methyl-1,4-pentadienyl)oxy]-silane (*E*:*Z* = 6:1). Chromatography (SiO_2, 100 g, hexane/Et_2O (90:10) resulted in hydrolysis of the ethoxyvinyl group and gave pure **2k** (237 mg, 52%, *E*:*Z* >50:1 by ^1H NMR analysis) as a clear, colorless oil. 400-MHz ^1H NMR ($CDCl_3$) δ 6.19 (1 H, q, J = 1.2 Hz), 2.90 (2 H, s), 2.12 (3 H, s), 1.60 (3 H, d, J = 1.6 Hz), 0.93 (9 H, s), 0.14 (6 H, s). 101-MHz ^{13}C ($CDCl_3$) δ 208.3, 137.8, 111.2, 49.1, 28.5, 25.6, 18.2, 13.1, −5.3. HRMS calcd for $C_{12}H_{24}O_2Si$, 228.1546; found, 228.1547.

***tert*-Butyldimethyl[((*E*)-3-methyl-4-oxo-1-pentenyl)oxy]silane (2l).** 2-Butenal (83 μL, 1.00 mmol), *t*-$BuMe_2SiCl$ (151 mg, 1.00 mmol), (1-ethoxyethenyl)tributyltin (507 mL, 1.50 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) in CH_3CN (1.50 mL) were reacted for 48 h as per **2a** to afford crude *tert*-butyldimethyl[((*E*)-4-ethoxy-3-methyl-1,4-pentadienyl)oxy]silane (*E*:*Z* = 5:1; C(3):C(1) = 5:1). Chromatography (SiO_2, 35 g, gradient, 150 mL of hexane followed by 90:10 hexane/Et_2O) resulted in hydrolysis of the ethoxyvinyl group and gave pure **2l** (115 mg, 50%, *E*:*Z* = 15:1 by ^1H NMR analysis) as a clear, colorless oil. 300-MHz ^1H NMR ($CDCl_3$) δ 6.37 (1 H, dd, J = 11.7, 0.8 Hz), 4.94 (1 H, dd, J = 11.7, 9.3 Hz), 3.00 (1 H, dq, J = 9.3, 6.9 Hz), 2.13 (3 H, s), 1.13 (3 H, d, J = 6.9 Hz), 0.91 (9 H, s), 0.14 (6 H, s). 75-MHz ^{13}C ($CDCl_3$) δ 210.4, 142.7, 110.9, 46.5, 27.5, 25.6, 18.3, 16.8, −5.3. HRMS calcd for $C_{11}H_{21}O_2Si$ (M − CH_3), 213.1311; found, 213.1304. Anal. Calcd for $C_{12}H_{24}OSi$: C, 63.10; H, 10.59. Found: C, 62.90; H, 10.61.

***tert*-Butyldimethyl[((1*E*,4*E*,4*Z*)-3,5-dimethyl-1,4-pentadienyl)oxy]-silane (2m).** 2-Butenal (90.0 μL, 1.09 mmol), *t*-$BuMe_2SiCl$ (160 mg, 1.06 mmol), (*Z*,*E*)-1-propenyltributyltin (*Z*:*E* = 3:1; 670 mg, 2.02 mmol), and $Ni(COD)_2$ (55 mg, 0.20 mmol) in DMF (3.00 mL) were reacted for 96 h as per **2c** to afford, after chromatography (SiO_2, 53 g, gradient 300 mL of hexane followed by 98:2 hexane/Et_2O), an otherwise pure mixture of regio- and stereoisomers of **2m** (combined total of all isomers, 159 mg, 66%, C(3):C(1)-coupling product = 10:1, **2m** enol ether *E*:*Z* = 19:1, propenyl *E*:*Z* = 2:1 by ^1H NMR analysis; crude *E*:*Z* = 6:1, crude C(3):C(1) = 5:1) as a clear, colorless oil. (1*E*,4*E*)-**2m** 300-MHz

^{1}H NMR ($CDCl_3$) δ 6.20 (1 H, dd, J = 12.0, 1.0 Hz), 5.38 (1 H, dd, J = 16.2, 4.7 Hz), 5.40-5.18 (1 H, m), 4.93 (1 H, dd, J = 12.0, 7.9 Hz), 2.76-2.62 (1 H, m), 1.64 (3 H, d, J = 3.7 Hz), 1.03 (3 H, d, J = 6.9 Hz), 0.91 (9 H, s), 0.12 (6 H, s). (1*E*,4*Z*)-**2m** 300-MHz ^{1}H NMR ($CDCl_3$) δ 6.22 (1 H, dd, J = 12.0, 1.2 Hz), 5.40-5.18 (2 H, m), 4.95 (1 H, dd, J = 12.0, 7.1 Hz), 3.15-3.03 (1 H, m), 1.61 (3 H, dd, J = 6.7, 1.6 Hz), 1.02 (3 H, d, J = 6.8 Hz), 0.91 (9 H, s), 0.12 (6 H, s). (1*E*,4*E*)-**2m** 75-MHz ^{13}C ($CDCl_3$) δ 139.4, 136.4, 122.8, 116.6, 35.1, 25.7, 21.5, 18.3, 17.8, -5.2. (1*E*,4*Z*)-**2m** 75-MHz ^{13}C (CDCl) δ 139.3, 135.4, 122.1, 116.5, 30.1, 25.6, 22.0, 15.3, 12.8, -5.2 HRMS calcd for $C_{13}H_{26}OSi$, 226.1753; found, 226.1748.

One-Pot Procedure for the Conjugate Addition of Ethenyltributyltin to 2-Propenal with in situ Generated Ni(COD)$_2$. Preparation of *tert*-Butyldimethyl[((*E*)-1,4-pentadienyl)oxy]silane (2a). In a 25-mL Schlenk flask, equipped with a magnetic stir bar and pressure-equalizing dropping funnel, a slurry of Ni(acac)$_2$ (260 mg, 1.01 mmol), 1,5-cyclooctadiene (500 μL, 4.08 mmol), and 1.00 mL of THF was cooled to -40 °C. Through the addition funnel, diisobutylaluminum hydride (2.50 mL of a 1 M solution in THF) was added dropwise over 10 min. The temperature was maintained at -40 °C for an additional 15 min and then was allowed to increase to 0 °C. After the mixture was stirred at 0 °C for 30 min, 10 mL of Et_2O was added to assist precipitation of the Ni(COD)$_2$ and the flask was cooled to -78 °C for 12 h. The supernatent was then removed at -78 °C via a filter-tipped cannula, and the Ni(COD)$_2$ was washed with Et_2O (2 × 2.50 mL) at -78 °C. The dirty yellow or gray-green Ni(COD)$_2$ was allowed to warm to 25 °C under vacuum (0.01 mmHg) and then treated with a solution of 2-propenal (370 μL, 5.54 mmol), *t*-BuMe$_2$SiCl (830 mg, 5.51 mmol), ethenyltributyltin (1.50 mL, 5.13 mmol), and CH_2Cl_2 (7.50 mL), added via cannula. After being stirred at 25 °C for 70 h, the mixture was worked up as per the typical procedure to afford, after chromatography (SiO_2, 100 g, gradient neat hexane (500 mL) to 98:2 hexane/Et_2O) pure **2a** as a clear, colorless oil (629 mg, 62%, *E*:*Z* 10:1 by ^{1}H NMR analysis).

E. Mechanistic Studies. Kinetic Studies of the Ni(COD)$_2$-Catalyzed Reaction of Ethenyltributyltin with (*E*)-2-Butenal in DMF-d_7 To Give 2c. (a) Standard Conditions. 2-Butenal (19.5 μL, 0.235 mmol), *t*-BuMe$_2$SiCl (36 mg, 0.24 mmol), ethenyltributyltin (68.5 μL, 0.234 mmol), and Ni(COD)$_2$ (14 mg, 0.051 mmol) in DMF-d_7 (0.70 mL) were combined as per the typical procedure in a 5-mm NMR tube at time t = 0. ^{1}H NMR spectra (400-MHz) were acquired at 1, 2, 3, 5, and 6 h, and showed the fraction of product, defined as [**2c**]/{[**2c**] + [ethenyltributyltin]} and determined by cutting and weighing, to be 0.22, 0.33, 0.42, 0.56, and 0.63, respectively (each point representing the average of three experiments).

(b) Reaction with 2 equiv of *t*-BuMe$_2$SiCl. Reaction as per the standard conditions but with twice as much *t*-BuMe$_2$SiCl (72 mg, 0.48 mmol) gave 0.20, 0.40, and 0.61 fraction product at 1, 3, and 6 h, respectively.

(c) Reaction with 2 equiv of 2-Butenal. Reaction as per the standard conditions but with twice as much 2-butenal (39.0 μL, 0.470 mmol) gave 0.23, 0.48, and 0.65 fraction product of 1, 3, and 6 h, respectively.

(d) Reaction with 2 equiv of Ethenyltributyltin. Reaction as per the standard conditions but with twice as much ethenyltributyltin (137 μL, 0.468 mmol) gave 0.40, 0.48, 0.66, 0.81, and 0.92 fraction product at 1, 2, 3, 5, and 6 h, respectively, the fraction product in this case being defined as [**2c**]/{[**2c**] + [2-butenal]}.

(e) Reaction with Double the Standard Catalyst Concentration. Reaction as per the standard conditions but with twice as much Ni(COD)$_2$ (28 mg, 0.10 mmol) gave 0.38, 0.66, 0.85, and 0.87 fraction product at 1, 3, 5, and 6 h, respectively.

Crossover Experiment To Determine the Rate Constant for the Stoichiometric Coupling of 1b with Ethenyltributyltin under Catalytic Reaction Conditions. Conjugate Addition of Ethenyltributyltin to 2-Methyl-2-butenal Using 1b as the Catalyst Precursor. 2-Methyl-2-butenal (22.6 μL, 0.234 mmol), *t*-BuMe$_2$SiCl (28 mg, 0.19 mmol), ethenyltributyltin (68.5 μL, 0.234 mmol), and **1b** (14 mg, 0.050 mmol) in DMF-d_7 (0.70 mL) were combined as per the typical procedure in a 5-mm ^{1}H NMR tube. ^{1}H NMR spectra (400-MHz) were acquired at 20, 31, 45, 60, and 75 min and showed the fraction of product, defined as [**1d**]/{[**1d**] + [**1b**]}, as determined by cutting and weighing, to be 0.06, 0.18, 0.30, 0.36, and 0.46, respectively. (Calculations were based on upfield half of the upfield peak of the **1b** 3-methyl doublet at δ 0.48 ppm, which partially overlaps with the 3-methyl signal of **1d** at δ 0.46 ppm. The fraction of product at time t = 0 was set equal to zero and included in the data set.) A graph of -ln (1 - f) as a function of time gave a straight line satisfying the equation -ln (1 - f) = -0.0085 + -0.049 with R = 0.99, from which the rate constant k_{sto}, defined by the expression -d[**1b**]/dt = k_{sto}[**1b**][ethenyltributyltin], can be approximately calculated, using an average value of 0.289 M for the ethenyltributyltin concentration (which actually decreased to ca. 75% of its initial value over the interval studied), to be 0.029 min^{-1}. Although **1b** has been previously characterized, its ^{1}H NMR spectrum in DMF-d_7 had not been reported and is given below. (Poorer resolution, relative to the catalytic reaction solutions, was observed so that the couplings are not resolved). **1b** 400-MHz ^{1}H NMR (DMF-d_7) δ 5.08 (2 H, bs), 1.85 (1 H, bs), 0.80 (9 H, s), 0.48 (3 H, br s), 0.17 (3 H, s), 0.08 (3 H, s).

Attempted Conjugate Addition in the Presence of Triphenylphosphine. 2-Butenal (19.5 μL, 0.235 mmol), *t*-BuMe$_2$SiCl (36 mg, 0.24 mmol), ethenyltributyltin (68.5 μL, 0.234 mmol), triphenylphosphine (65 mg, 0.25 mmol), and Ni(COD)$_2$ (14 mg, 0.051 mmol) in DMF-d_7 (0.70 mL) were combined in an NMR tube. An ^{1}H NMR spectrum taken after 2 days showed no conjugate addition product.

Electron Spin Resonance Spectroscopy. 2-Butenal (19.5 μL, 0.235 mmol), *t*-BuMe$_2$SiCl (36 mg, 0.24 mmol), ethenyltributyltin (68.5 mL, 0.234 mmol), and Ni(COD)$_2$ (14 mg, 0.051 mmol) in DMF (0.80 mL) were combined in a 10-mL flask as per **2a** and an aliquot was removed and placed in a 3-mm quartz tube and sealed under N_2. The tube and its contents were frozen in liquid nitrogen at 77 K and a 2000-G scan spectrum, centered at g = 2.00, was obtained on a Varian E-4 spectrometer operating at 9.2 GHz. No signal was detected. Workup of the remaining solution after 72 h showed the catalytic reaction to have proceeded as usual to give **2c**.

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Unusual Coordination Number and Geometry in a Potassium 18-Crown-6 Complex

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Abstract: Crystallization of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) from $CHCl_3/CH_2Cl_2$ solution in the presence of dipotassium tartrate affords a nine-coordinate potassium complex incorporating chloride rather than tartrate as the counteranion. This complex, $[(18\text{-crown-6})K(H_2O)_3](H_3O)(H_2O)Cl_2$, displays an unusual asymmetrical conformation of the crown ether ring. The structure of the complex is discussed and compared with other reported 18-crown-6 complexes of potassium, in which the 18-crown-6 moiety always adopts a much more symmetrical conformation.

Since Pedersen's first report of the synthesis of macrocyclic polyethers and their ability to complex simple inorganic cations,[1] thousands of such "crown ether" complexes have been prepared, and hundreds have been characterized structurally by X-ray

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